

INVESTIGATION OF THERMOELECTRIC PROPERTIES OF 2D β -SILICON MONOTELLURIDE (SITE)

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Investigation of Thermoelectric properties of 2D β -Silicon monotel-
luride (SiTe)

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September 2018

We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.



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ABSTRACT

INVESTIGATION OF THERMOELECTRIC PROPERTIES OF 2D β -SILICON MONOTELLURIDE (SITE)

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Thermoelectric properties of novel 2D silicon monotelluride (SiTe) are studied using first principles calculations. The plane wave method based on density functional theory as implemented in Vienna ab *initio* simulation package (VASP) is used to calculate the electronic structure. For the exchange correlation functionals, the generalized gradient approximation developed by Perdew-Burke-Ernzerhof (PBE-GGA) is taken into account. The calculated band gap for β -SiTe is 1.83 eV which is in consistence with the previous theoretical data.

The electronic and lattice transport properties are investigated using the Boltzmann transport equation. For the electronic transport properties, BoltzTraP code is used which relies on the Fourier interpolation of electronic band structure and thus requires a large k-sampling to optimize the interpolation and produce better results. The Seebeck coefficient obtained at room temperature is $290 \mu V/K$ and the figure of merit with $\kappa_\ell = 0$ is 0.98.

The density functional perturbation theory (DFPT) is used to calculate the 2nd order harmonic and 3rd order anharmonic force constants. The phonon dispersion and density of states are computed from the 2nd order harmonic force constants using Phonopy code. The lattice thermal conductivity and other lattice dependent transport properties are calculated using both the harmonic and anharmonic force constants via ShengBTE program. The specific heat and lattice thermal conductivity at room temperature is $305.5 J/mol K$ and $1.35 \times 10^{-3} W/m K$, respectively. The figure of merit ZT for β -SiTe at room temperature using the κ_ℓ obtained from ShengBTE is 0.78 at 800k.

Keywords: 2D material, Density fuctional theory (DFT), Boltzmann transport equation (BTE), Density fuctional perturbation theory (DFPT), Seebeck coefficient, lattice thermal conductivity, Figure of merit (ZT).

ÖZET

TÜRKÇE BAŞLIK

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Özgün 2 boyutlu silikon monotellür (SiTe) moleküllerinin termoelektrik özellikleri temel ilke hesaplar ile araştırıldı. Elektronik yapının hesaplanması için yoğunluk fonksiyonel teorisine dayalı artırılmış düzlemsel dalga metodu “Vienna Ab Initio Simulation Package” (VASP) kullanılarak uygulandı. Değişim bağıntı fonksiyoneli için, Perdew-Burke-Ernzerhof (PBE-GGA) tarafından geliştirilen genelleştirilmiş gradyan yakınsaması hesaba katıldı. Beta-SiTe için hesaplanan bant genişliği 1.83eV , teorik veri ile uyum içinde bulunmuştur.

Elektronik ve kafes taşıma özellikleri Boltzmann taşıma denklemi kullanılarak araştırıldı. Elektronik taşıma özellikleri için elektronik bant yapısının Fourier interpolasyonunu kullanan Boltz-TraP kodu kullanıldı, bu sebeple interpolasyon küçültmek ve daha iyi sonuçlar elde etmek için büyük bir k örneğine ihtiyaç duyuldu. Oda sıcaklığında Seebeck sabiti $290\text{ }\mu\text{V/K}$ ve $\kappa_l = 0$ için liyakat figürü 0.98 olarak bulundu.

İkinci mertebeden harmonik ve üçüncü mertebeden anharmonik kuvvet sabitleri VASP yardımı ile yoğunluk fonksiyoneli tedirginlik teorisi kullanılarak hesaplandı. Fonon dağılımı ve durum yoğunluğu, Phonopy kodu kullanılarak ikinci mertebeden kuvvet sabitleri ile bulundu. Kafes termal iletkenliği ve diğer kafese bağlı taşıma özellikleri ShengBTE programı yardımıyla, harmonik ve anharmonik kuvvet sabitleri ile hesaplandı. Oda sıcaklığında özısı 305.5 J/molK olarak ve kafes termal iletkenliği $1.35 \times 10^{-3}\text{ W/mK}$ olarak bulundu. Beta-SiTe için ZT liyakat figürü, ShengBTE’den elde edilen κ_l kullanılarak, oda sıcaklığında 0.78 olarak bulunmuştur.

Anahtar sözcükler: 2B malzeme, Yoğunluk fonksiyoneli teorisi (YFT) Boltzman taşınım denklemi (BTE), Yoğunluk fonksiyoneli tedirginlik teorisi (YFTT), Seebeck sabiti, örgü ısı iletkenliği, Liyakat figürü (ZT).

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Chapter 1

Introduction

Thermoelectric materials have drawn vast attention due to their key role as alternate source of power generation and refrigeration, where waste heat from internal combustion engines and other electrical appliance is converted directly and reversibly into useful electrical energy . Since there are no moving parts or any greenhouse emissions, these thermoelectric devices can be characterized as environmental friendly clean energy sources [1, 2].

Thus, the development of highly efficient thermoelectric materials has become more significant during the last few decades [3, 4]. Currently the investigation of energy harvesting technologies is carried out by automotive industry in order to generate electrical power from the engine's waste heat, which can be used in next-generation vehicles [5, 6, 7]. NASA's deep space exploration missions such as Voyager and Cassini missions utilizes the radioisotope thermoelectric generators (RTGs) [8, 9, 10, 11]. Thermoelectric refrigeration on the other hand also has vast applications such as electronic component cooling that prevents any damage to the electronic components caused by high temperature. Additionally the performance of computer processors can also be enhanced significantly using these economical thermoelectric refrigerators as the rise in temperature greatly effect the performance of these computer processors [12, 13].

However, the most challenging hurdle is the low efficiency of thermoelectric

materials, which is determined by a dimensionless quantity called figure of merit ZT. The figure of merit ZT can be expressed as

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_\ell} \quad (1.1)$$

Where σ is the electrical conductivity, S is the Seebeck coefficient, κ_e and κ_ℓ is electronic and lattice thermal conductivity, respectively and T is the absolute temperature [14, 15, 16, 17]. Currently the highest achieved value for ZT is between 1.5 and 2 [18, 19] and in order to compete with the existing technologies, a well above 3 value is required for ZT.

From the figure of merit expression, it can be easily deduced that the two main factors affecting the performance of thermoelectric materials are the power factor ($PF = S^2 \sigma$) and thermal conductivity (both electronic and lattice). To enhance the power factor either Seebeck coefficient or electrical conductivity must be increased. Different techniques can be used to raise the electrical conductivity such as varying the doping concentration, decreasing the band gap or by the introduction of new resonating bands [20]. Whereas, the Seebeck coefficient can be enhanced by either varying the material's composition or by searching new materials with high Seebeck coefficient [21, 12, 22, 23]. The electronic thermal conductivity can not be controlled since it is directly proportional to electrical conductivity and any attempt on decreasing the electronic thermal conductivity will results in the reduction of σ . However, lattice thermal conductivity can be reduced by different techniques such as the introduction of various defects [21, 17, 22].

1.1 Context and Background

Investigation of novel materials for enhanced thermoelectric properties is critical in order to expedite the process. Properties of novel 2D group IV-VI materials have been studied recently for their potential applications in flexible

electronics, battery electrodes devices, optoelectronic and thermoelectric devices [24, 25, 26, 27, 28]. Silicone based binary sheets have finite band gap which make them potential candidates for switching devices and other electronic applications but a very limited study is available on these materials. 2D silicon monotelluride (SiTe) falls in this group but despite of it's compatibility with the existing silicon-based technology not much attention has been given to this material. For a long time Si_2Te_3 was considered to be the only stable crystal in silicone-telluride series [29]. Only recently Yu Chen *et al* theoretically prove the structural stability of two different lattice arrangements of silicon monotelluride i.e. α -SiTe and β -SiTe and calculate its electronic and mechanical properties using first principle calculations [30]. Wang *et al* on the other hand investigate the thermoelectric properties of QL-, α - and β -Site [84].

In this work, thermoelectric properties of β -SiTe has been studied using first principle calculations. Density functional theory (DFT) among others is a well tested technique used to calculate the ground state electronic properties of materials. In this approach, a ground state density is obtained using variational principle, which is then used to compute all the electronic properties of a material such as electronic density of states, molecular spectra, band structure etc. The electronic and lattice transport properties are then calculated using Boltzmann transport equation.

1.2 Thesis Organization

This thesis includes three chapters. The first chapter provides a detail description of density functional theory, its back ground and different approximations used in electronic structure calculation.

In the second chapter, Boltzmann transport theory is discussed in detail. The electronic and lattice transport are addressed in separate sections.

In third chapter all the results obtained using the density functional theory and Boltzmann transport equation are presented. Since β -SiTe is a novel material there is no such experimental data to compare our results with. The last chapter conclude this research work and provide some major findings of this project.

Chapter 2

Density Functional Theory

2.1 First-principles study

First-principles study includes pure quantum mechanics calculations and is considered a powerful tool for the prediction of a vast set of materials properties. Major advancements have been made in this field during the last few decades. The recent development in computational power led to the formulation of highly efficient predictive methods which can be used both to investigate the unknown properties of new materials and to get insight into the existing materials properties. This chapter gives a comprehensive analysis of these methods.

2.1.1 Wave Function (Ψ)

At quantum level a system is represented by a wave function ψ . Wave function plays a very significant role in quantum mechanics since it contains all the required information about a system [31, 32, 33]. The amplitude square of wave function $|\psi|^2$ also known as probability density gives the particle's position at some point

in a system [31, 34]. Max Born provided this interpretation in 1926 [35] as

$$\int |\psi|^2 dx = \int \psi^* \psi dx = 1 \quad (2.1)$$

Thus for a wave function ψ , that represents a particle somewhere in space, the integral over $|\psi|^2$ should be equal to 1 [36].

2.1.2 Schrödinger Wave Equation

An appropriate wave equation is required to obtain the wave function for a system [31, ?]. Erwin Schrödinger developed a partial differential wave equation in 1926 [37] known as the Schrödinger wave equation to describe the time evolution of a physical system's quantum state.

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = i\hbar \frac{\partial^2 \Psi}{\partial t^2} \quad (2.2)$$

Eq. 2.2 is time-dependent Schrödinger equation in one dimension applied to a particle of mass m moving in x direction in a potential $V(x, t)$. The presence of imaginary number (i) indicates that the time dependent Schrödinger equation has complex solution [31, ?]. Solving the time-dependent Schrödinger equation is a very difficult job and we need to separate the time dependent term in order to achieve a much simpler time-independent Schrödinger equation.

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\Psi = E\psi \quad (2.3)$$

Eq. 2.3 is time-independent Schrödinger Equation in one dimension. More generally we can write the three dimensional time-independent Schrödinger Wave Equation as:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + V\Psi = E\psi \quad (2.4)$$

where ∇^2 in cartesian coordinates is written as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (2.5)$$

From the solution of the Schrödinger wave equation we get the **Hamiltonian**, which represents the states with definite total energy

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V \quad (2.6)$$

Thus we can write the Schrödinger equation more compactly as

$$\hat{H}\Psi = E\Psi \quad (2.7)$$

solving Eq. 2.4 for a single particle system with three spatial variables is an easy task but things get much more complicated when we try to solve the same equation for a many body system.

Reduce Mass

A combine effect of two masses in a system is known as reduced mass system which reduces an interactive two body problem to a one body problem [34, 38].

$$m = \frac{m_1 m_2}{m_1 + m_2} \quad (2.8)$$

and the center of mass where the reduced mass is observed is written as

$$r_{cm} = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \quad (2.9)$$

Using reduced mass system one can easily solve the time-independent Schrödinger equation for two body problem.

2.1.3 Many Body Problem

At quantum level a smallest physical system under observation consists of billions of interacting particles. For a system of N number of particles the number of spatial variables goes up to $3N$ which makes it nearly impossible to solve the

Schrödinger equation for such a system. The wave function to such system contain a large amount of information and thus is too complicated. Finding ground state wave function for interacting electrons in an external local potential is the main problem in such systems. To solve this problem many approaches and approximations have been introduced over the last few decades. So far Density Functional Theory is the most convenient approach among all.

2.2 Density Functional Theory (DFT)

Density functional Theory (DFT) is a useful technique to investigate the ground state properties of materials. DFT is not only successful for ordinary bulk materials but is also found useful in determining the properties of complex materials like proteins and nanotubes. The basic idea behind DFT is to investigate a system of interacting fermions using its charge density instead of its wave function. The number of independent variables reduced to 3 rather than $3N$ if density is used as a basic variable for an N electron system in a coulombic potential obeying Pauli Exclusion principle, since many body wave function depends on $3N$ variable while density only depend on 3 spatial variables. Additionally, using $E(\rho)$ instead of $E(\Psi)$ significantly reduces the computational power required to investigate the ground state properties. Results obtained using DFT calculations are very close to the data achieved experimentally.

2.3 Derivation and Formalism

To determine a system's ground state containing N interacting electrons under a nuclear potential, the Schrödinger equation can be written as

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad (2.10)$$

where $\hat{H}$ is the Hamiltonian operator corresponds to the system's total energy. Here the Hamiltonian is equal to the total kinetic energy of electrons $\hat{T}$, the

electrons coulombic interaction with each other $\hat{V}_{ee}$, and the external potential i.e. interaction between nuclei and electrons $\hat{V}_{ext}$. The kinetic energy of nuclei is neglected here as we apply Born Oppenheimer approximation where nuclei are consider stationary relative to the motion of electrons. So the Hamiltonian is written as:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} \quad (2.11)$$

or

$$\hat{H} = \sum_i^N \left(\frac{-\hbar}{2m_i} \nabla_i^2 \right) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j) + \sum_i^N V(\vec{r}_i) \quad (2.12)$$

putting in Eq. 2.10 we get

$$\hat{H}|\psi\rangle = \left(\sum_i^N \left(\frac{-\hbar}{2m_i} \nabla_i^2 \right) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j) + \sum_i^N V(\vec{r}_i) \right) |\psi\rangle = E|\psi\rangle \quad (2.13)$$

Eq. 2.13 is a second order differential equation and is extremely difficult to deal with since it contain $3N$ independent variables.

2.4 Ritz Variational Principle

Ritz variational principle is a very useful tool to investigate the ground state of a system by solving the second order differential equation consist of $3N$ independent variables [39]. The system's ground state energy is minimized using this technique.

$$E_0 = \text{Min}_{\psi \rightarrow N} \langle \psi | \hat{H} | \psi \rangle \quad (2.14)$$

In the first step a Hamiltonian is set up for the system under observation. Eq. 2.11 shows that the only information we obtain from the molecule is the number of electrons N in the system and external potential $\hat{V}_{ext}$. $\hat{V}_{ext}$ gives complete information about the positions and charges of all the nuclei in the particular molecule. The electron-electron repulsion and total kinetic energy

(of electrons) terms are independent of the molecule. In the following step the eigen function ψ and the corresponding eigen values of the Hamiltonian $\hat{H}$ are determined. Variational principle is the recipe for systematically calculating the wave function of a ground state which in turns gives the lowest energy state. The expectation value of any observable, as is known from the standard quantum mechanics, is represented by an operator $\hat{O}$, using a trial wave function.

$$\langle \hat{O} \rangle = \langle \psi_{trial} | \hat{O} | \psi_{trial} \rangle \quad (2.15)$$

Variational principle states that the energy obtained via Eq. 2.15 as an expectation value of Hamiltonian operator $\hat{H}$ using any guessed wave function ψ_{trial} is an upper bound to the true ground state energy.

$$\langle \psi_{trial} | \hat{O} | \psi_{trial} \rangle = E_{trial} \geq E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle \quad (2.16)$$

The equality holds only if ψ_{trial} is the actual ground state wave function ψ_0 . In this way the minimized ground state is obtained.

2.5 Density as a Basic Variable

Up till now, wave function of a system with N number of particles is considered that depends on $3N$ spatial coordinates and is nearly impossible to solve. In order to simplify the problem, density as a basic variable is introduced which can be expressed as

$$\rho(r) = N \sum_{S_1} \dots \sum_{S_2} \int \dots \int (|\Psi(r_1, S_1, \dots r_N, S_N)|^2) dr_1 dr_2 \dots dr_N \quad (2.17)$$

$$\rho(r) = \langle \psi | \hat{\rho} | \psi \rangle \quad (2.18)$$

where the density operator is given as

$$\rho(r) = \sum_i^N \sum_{S_i} \delta(r - r_i) \quad (2.19)$$

Previously it is concluded about the Hamiltonian operator that it is uniquely characterized by the nuclei's positions R_A and charges Z_A and the number of electrons N in a system. Once the Hamiltonian of the system is known the Schrödinger equation can be solved in principle.

From the knowledge of electron density properties the following conclusions are made:

1. By integrating density the number of e^- in a system is obtained i.e.

$$\int \rho(r) dr = N$$
2. The density maxima occurs at the positions of nuclei R_A .
3. the density contain information regarding the nuclear charge Z_A at the positions of nuclei.

Thus all the necessary information about the system is provided by the electron density and all the molecular properties can be determined using electron density as a basic variable.

2.6 Thomas Fermi Model

Thomas and Fermi developed a theory known as Thomas and Fermi theory for many body system using density as a basic variable for the first time[40, 41]. Their approach is valid only for the case of infinite nuclear charge. It only deals with the kinetic energy quantum mechanically where as $\hat{V}_{ee}$ and $\hat{V}_{ext}$ are treated classically. Using uniform electron density, Thomas and Fermi expressed the kinetic energy as

$$T_{TF}(\rho(r)) = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(r)^{5/3} dr \quad (2.20)$$

combining Eq. 2.20 with electron-electron interaction and nuclear-electron potential the well known Thomas-Fermi expression for the atom's energy is obtained

$$E_{TF}(\rho(r)) = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(r)^{5/3} dr - Z \int \frac{\rho(r)}{r} dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 \quad (2.21)$$

This expression fails to yield good quantitative prediction but can give a good description of an atom's energy and shows that the density of electrons can be used as a basic variable to obtain the energy of an atom [42]. TF model gives a perception of how to get energy from density without using any additional information by expressing energy in terms of density. The ground state is achieved by using the variational principle and is assumed to be associated with electron density, that yields the lowest energy.

2.7 Hohenberg and Kohn Theorems

Thomas and Fermi did not have any actual physical basis to support their model. The justification of expressing energy as a functional of density was not possible at that time. Density Functional theory replaced TF model when Hohenberg and Kohn [42] published their landmark work based on 2 fundamental theorems in physics review. These two theorems lay the foundation for DFT. A brief insight of HK-theorems is given:

2.7.1 Theorem 1

The first HK theorem states that ***“the external potential $V(r)$ is determined by electronic ground state density $\rho(r)$ of the system . The electronic density thus uniquely determine the systems Hamiltonian, its ground state wave function and all its electronic properties.”*** This theorem provide justification for the wave function with physical meaning to be associated uniquely with certain density. Thus the total energy of many electrons system in

external potential is given as

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{Ne}[\rho] \quad (2.22)$$

where the external potential is given as

$$V_{Ne} = \int V(r)\rho(r)dr \quad (2.23)$$

and the electron-electron repulsive interaction can be expressed as

$$V_{ee}[\rho] = U[\rho] + E_{xc}[\rho] \quad (2.24)$$

where $U(\rho)$ is the classical coulombic part and can be expressed as

$$U[\rho] = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{r-r'} d^3r d^3r' \quad (2.25)$$

while $E_{xc}(\rho)$ is the non-classical part of electron-electron repulsive potential including all the effects of coulombic corelation and self interaction correction. The kinetic energy term $T(\rho)$ and the electron-electron repulsive potential $V_{ee}(\rho)$ do not depend on the system. The only term that depends on the actual system is the external potential $V_{Ne}(\rho)$. So Eq. 2.22 can be expressed as

$$E[\rho] = F_{HK}[\rho] + \int V(r)\rho(r)dr \quad (2.26)$$

where $F_{HK}(\rho)$ is called the HK-functional and can be expresses as

$$F_{HK}[\rho] = Min_{\psi \rightarrow \rho(r)} \langle \psi[\rho] | \hat{T} + \hat{V}_{ee} | \psi[\rho] \rangle \quad (2.27)$$

The Schrödinger equation can be solved exactly and not approximately if the $F_{HK}(\rho)$ is known. The HK-functional absorbs all the information about the

intrinsic properties of an electronic system. It is independent of the system and can be applied well from a single H-atom to a gigantic molecules such as DNA. Information of positions and charges of nuclei are associated only with the electron density in ground state and the excited state electron density can not be used.

2.7.2 Theorem 2

The 2nd HK-theorem states that *“The electron density yields the ground state energy satisfying variational principle. The electron density, that gives the minimum ground state energy is the true ground state density.”*

The ground state energy can be determined using the Ritz variational principle as

$$E_{v,0} = \text{Min}_{\psi' \rightarrow N} \langle \psi' | \hat{H} | \psi' \rangle \quad (2.28)$$

A trial density $n'(r)$ is associated with every trial wave function since the electron density uniquely determines a quantum state of a system with many electrons. The minimization of energy is performed in two steps. At first, a trial electron density $n'(r)$ and the corresponding class of wave functions $\psi_{n'}'^\alpha$ are considered. Then the energy minimum is expressed as

$$E_v(n'(\vec{r})) = \text{Min}_\alpha \langle \psi_{n'}'^\alpha | \hat{H} | \psi_{n'}'^\alpha \rangle = \int v(\vec{r}) n'(\vec{r}) d\vec{r} + F[n'(\vec{r})] \quad (2.29)$$

where F_{HK} is the Hohenberg-Kohn functional given as

$$F_{HK} \equiv \text{Min}_\alpha \langle \psi_{n'}'^\alpha | \hat{T} + \hat{U} | \psi_{n'}'^\alpha \rangle \quad (2.30)$$

Here it is important to note that any explicit knowledge of external potential $V(\vec{r})$ is not required for the HK functional. In the next step, the energy minimization is evaluated for all trial densities $n'(\vec{r})$ using variational principle. The functional

delivers the lowest energy if the trial density is the actual ground state electron density.

2.8 Kohn-Sham Equation

To deal with the N interacting electrons is a very difficult job and a feasible scheme is needed to treat the system. Kohn and Sham solve this problem by developing a method of mapping the system of interacting electrons to a fictional non-interacting electrons system, which yields the exact density of electrons in the ground state and thus the exact energy of ground state as produced by the interacting electrons system. In such systems the electrons do not interact with one another but the combine effect of all these electrons is felt by every single electron in the system. The wave function $\Phi[\rho]$ of Kohn-Sham system minimizes the constrained search minimization. The kinetic energy functional $T_s[\rho]$ of such non-interacting system is expressed as

$$T_s[\rho] = \min_{\psi \rightarrow \rho(r)} \langle \psi | \hat{T} | \psi \rangle \quad (2.31)$$

the exchange energy is expressed as

$$T_x[\rho] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle - U[\rho_0] \quad (2.32)$$

and the correlation energy is written as

$$E_c[\rho] = \langle \psi[\rho] | \hat{T} + \hat{V}_{ee} | \phi[\rho] \rangle - \langle \Phi[\rho] | \hat{T} + \hat{V}_{ee} | \Phi[\rho] \rangle \quad (2.33)$$

the total energy is then expressed as

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int V(r)\rho(r)dr \quad (2.34)$$

$$E[\rho] \equiv T_s[\rho] + U[\rho] + E_{xc} + \int V(r)\rho(r)dr \quad (2.35)$$

where the exchange-correlation functional $E_{xc}(\rho)$ is given as

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \quad (2.36)$$

which can also be expressed as

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - U[\rho] \quad (2.37)$$

All the unknown contribution is absorbed by the exchange-correlation functional E_{xc} , and now the main problem is to find an expression that can determine the exchange-correlation functional E_{xc} in a more exact manner. The constraint on the variational problem, introduced in the second HK-theorem that the number of electrons must remain conserved leads to

$$\delta \left[E[\rho] - \mu \left(\int \rho(r) dr - N \right) \right] \quad (2.38)$$

The Euler-Lagrange expression of Kohn-Sham theory is obtained by varying the total energy w.r.t density

$$\mu = \frac{\delta E[\rho]}{\delta \rho} = \frac{\delta T_s[\rho]}{\delta \rho} + \frac{\delta U[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} + V(r) \quad (2.39)$$

the potential of KS theory is defined as

$$V_s(r) = V(r) + \frac{\delta U[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (2.40)$$

$$V_s(r) = V(r) + V_H(r) + V_{xc}(r) \quad (2.41)$$

thus the Lagrange multiplier becomes

$$\mu = \frac{\delta T_s[\rho]}{\delta \rho} + V_s[\rho] \quad (2.42)$$

the Hartree potential $V_H(r)$ in Eq. 2.41 is expressed as

$$V_H(r) = \int \frac{\rho(r')}{r - r'} dr \quad (2.43)$$

and the exchange correlation potential in Eq. 2.41 is given as

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (2.44)$$

Kohn and Sham originally introduced the concept of orbitals $\phi_i(r)$ replacing the wave-function ψ for a non-interacting fictitious system. The Hamiltonian applied to KS orbitals characterizes a non-interacting many electrons system. The Slater's determinant is used to determine the ground state of such non-degenerate systems

$$|\Phi\rangle = \frac{1}{N!} \det[\phi_1(r), \phi_2(r), \dots, \phi_n(r)] \quad (2.45)$$

using Slater determinant to express the ground state, density $\rho(r)$ is determined from the KS orbitals which is equivalent to interacting systems ground-state density ρ_0

$$\rho(r) = \sum_{i=1}^N |\phi_i(r)|^2 \quad (2.46)$$

there is no simple method for the construction of energy functional but separation of exchange and correlation parts is certainly possible. The same is true for the exchange-correlation potentials, the derivatives of energy functionals w.r.t density

$$V_x(r) = \frac{\delta E_x[\rho]}{\delta \rho} \quad V_c(r) = \frac{\delta E_c[\rho]}{\delta \rho} \quad (2.47)$$

the exchange energy functional in DFT is defined by the expression

$$E_x^{DFT} \equiv E_x[\rho] \equiv \langle \Phi[\rho] | \hat{V}_{ee} | \Phi[\rho] \rangle - U[\rho] \quad (2.48)$$

where the term $\langle \Phi(\rho) | \hat{V}_{ee} | \Phi(\rho) \rangle$ is not the true electron-electron repulsive potential energy but is the repulsive interaction between electrons of KS state. The correlation energy absorb the difference between the actual electron-electron interaction and the expectation value $\langle \Phi(\rho) | \hat{V}_{ee} | \Phi(\rho) \rangle$ and it also contained the difference between the *K.E* of actual system and KS non-interaction electrons

system. Now to derive the correlation energy, the exchange-correlation energy expression is given as

$$E_{xc}(\rho) = T(\rho) - T_s(\rho) + V_{ee}(\rho) - U(\rho) \quad (2.49)$$

and we know that

$$E_{xc}(\rho) = E_x(\rho) + E_c(\rho) \quad (2.50)$$

so

$$E_x(\rho) + E_c(\rho) = T(\rho) - T_s(\rho) + V_{ee}(\rho) - U(\rho) \quad (2.51)$$

putting the values of $E_x(\rho)$ we get

$$\langle \Phi(\rho) | \hat{V}_{ee} | \Phi(\rho) \rangle - U(\rho) + E_c(\rho) = T(\rho) - T_s(\rho) + V_{ee}(\rho) - U(\rho) \quad (2.52)$$

and finally we get

$$E_c(\rho) = T(\rho) - T_s(\rho) + V_{ee}(\rho) - \langle \Phi(\rho) | \hat{V}_{ee} | \Phi(\rho) \rangle \quad (2.53)$$

so we can determine the correlation function if the four terms on the right hand side are known.

2.9 Approximate Exchange Correlation Functionals

To calculate the exchange-correlation functional we need to solve their integrals

$$E_{xc} = E_x + E_c \quad (2.54)$$

$$E_x = \int \rho(r) \epsilon_x(\rho(r)) dr \quad E_c = \int \rho(r) \epsilon_c(\rho(r)) dr \quad (2.55)$$

different approximations are used to calculate the exchange correlation functional. Some important approximations used to solve these functionals are local density approximation (LDA), local spin density approximation (LSDA) and generalized gradient approximation (GGA).

2.9.1 Local Density Approximation (LDA)

Kohn-Sham formalism treats exactly most parts of the system's total energy including a major portion of the kinetic energy. However, the remaining unknown contributions are absorbed in the exchange-correlation functional $E_{xc}(\rho)$, which includes the electron-electron (non-classical) interaction as well as the self-interaction correction. The K.E component which is not included in the fictitious non-interacting system is also absorbed in the exchange-correlation functional. LDA developed by Kohn and Sham is one of the most well-known technique used to calculate exchange correlation functional. Kohn and Sham considered an electrically neutral homogeneous electron gas system under the influence of positive charge. The density of electrons ρ approaches to a constant value as volume of gas V and number of electrons N reaches infinity. Thus for every point in the space the density of electrons $\rho(r)$ remains the same. The exchange-correlation energy E_{xc} of a homogeneous system is used for the non-homogeneous system such as atom, molecules and solids. LDA approximation is more suitable for systems with slowly varying densities. Thus for those systems where the density varies rapidly, LDA has no comparable impact. In LDA approximation, the exchange-correlation energy of a system is obtained by integrating over the parameter $\epsilon_{xc}^{LDA}(\rho(r))$ times the local density $\rho(r)$ at every point in space.

$$E_{xc}^{LDA} = \int \rho(r) \epsilon_{xc}^{LDA}(\rho(r)) dr \quad (2.56)$$

Separating the exchange and correlation terms

$$E_x^{LDA} = \int \rho(r) \epsilon_x^{LDA}(\rho(r)) dr \quad E_c^{LDA} = \int \rho(r) \epsilon_c^{LDA}(\rho(r)) dr \quad (2.57)$$

and the functional derivatives of these energies gives the exchange and correlation potential

$$V_{xc}^{LDA}(r) = \frac{\delta E_{xc}^{LDA}[\rho]}{\delta \rho} = \epsilon_{xc}^{LDA}(\rho(r)) + \frac{\delta \epsilon_{xc}^{LDA}(\rho(r))}{\delta \rho} \quad (2.58)$$

Dirac originally derived the exchange energy part, however an explicit expression for correlation energy does not exist. Ceperley and Alder used the Monte Carlo scheme to calculate the total energy of a homogeneous system and determined the correlation part by subtracting the exchange and $K.E$ terms[43]. The LDA developed by Vosko et al in 1980 is widely used [44]. However, LDA scheme developed by Perdew and Wang yield much better results [45].

2.9.2 Local Spin Density Approximation (LSDA)

LSDA is a small modification to the LDA scheme. In this case the spin polarization of electrons is taken into account for more accuracy. Here the electron density is divided into two segments i.e. spin-up density denoted by $\rho_{\alpha}(r)$ and spin-down density denoted by $\rho_{\beta}(r)$ [46].

$$E_{xc}^{LDA} = \int \rho_{\alpha}(r) \epsilon_{xc}^{LDA} dr \quad E_{xc}^{LDA} = \int \rho_{\beta}(r) \epsilon_{xc}^{LDA} dr \quad (2.59)$$

2.9.3 Generalized Gradient Approximation (GGA)

Since the basis for LDA and LSDA is a homogeneous gas model with uniform density, the exchange correlation potential obtained using these approximation may not be accurate enough. A more realistic approach was proposed in early 1980s considering electrons not distributed uniformly but actually spread in a gradient over a system. In this method, the non-homogeneous behavior of rapidly varying electron density is mimicked using the electron density $\rho(r)$ at some point r and the gradient of this electron density $\nabla \rho(r)$ [47]. The exchange correlation term now become

$$E_{xc}^{GGA}[\rho] = \int f_{xc}^{GGA}(\rho(r), \nabla \rho(r)) dr \quad (2.60)$$

this approach is called generalized gradient approximation and is expressed with a functional which includes the gradient of density $\nabla\rho(r)$, explicitly. The exchange and correlation terms are dealt with individually in this case as well

$$E_{xc}^{GGA}[\rho] = E_x^{GGA}[\rho] + E_c^{GGA}[\rho] \quad (2.61)$$

the exchange part is given as

$$E_x^{GGA}[\rho] = \int \rho(r) \epsilon_x^{GGA}[\rho] F(s) dr \quad (2.62)$$

where $F(s)$ is a scaling function and can have a very complicated form depending on the type of approximation. From the derivative of GGA exchange-correlation functional, the exchange-correlation potential is derived as [47]

$$V_{xc}^{GGA} = \left[\frac{\delta f_{xc}}{\delta \rho} - \nabla \left(\frac{\delta f_{xc}}{\delta \nabla \rho} \right) \right] \quad (2.63)$$

GGA functional often give better results compared to LDA. However, some of these functionals consist of fitting parameters which are used solely for specific boundary conditions and yield better results in appropriate computing time. Some significant and most widespread GGAs are

- Becke's exchange functional (B88) [48, 49].
- Perdew, Burke and Ernzerhofs exchange-correlation functional (PBE) [50, 51].
- Lee, Yang and Parrs correlation functional (LYP) [52, 53].
- Perdews 1986 correlation functional (P86) [54, 55, 56, 57].
- Perdew and Wangs correlation functional (PW91) [58, 59].
- Engel and Voskos (EV) correlation functional [85][60].
- Wu and Cohen density gradient functional (WC) [86][61].

2.9.4 Hybrid Functionals

The Hartree-Fock theory, a predecessor of DFT, is a well known formalism used widely to calculate the electronic structure of materials. Their model only account for the exact exchange energy leaving the correlation effect completely untreated. Post HF methods are introduced in DFT in order to explicitly determine the exchange correlation parameters. Previously discussed, DFT based first-principles methods such as LDA, LSDA and GGA etc give fine results with some limitations. These approximations usually underestimate or overestimate the band gap of materials.

Becke proposed the use of a portion of exact Hartree-Fock exchange energy along with conventional GGA correlation [62, 63]

$$E_{xc}^{Hyb} = E_{xc}^{GGA}[\rho] + \alpha[E_x^{HF}[\phi_{sel}] + E_x^{GGA}[\rho_{sel}]] \quad (2.64)$$

where α is a semi-empirical parameter obtained from the fitting of experimental data, ϕ_{sel} are the orbitals selected (correlated d-electrons) for the exact exchange and ρ is the density of these selected electrons. Applying the exact exchange to these localized electrons has the same effect as PBE+U. Hybrid functionals have benefit over the PBE+U scheme as they do not rely on any system dependent parameters.

2.9.5 Heyd-Scuseria-Ernzerhof (HSE)

The exact Hartree-Fock exchange interaction is essentially long range and is highly dependent on the system. This exact HF exchange can be implemented to the selected orbitals by Hybrid functions, discussed in the previous section, relatively efficiently. However, it's implementation to the entire system can make the calculation difficult to handle. Generally, to deal with such problem the HF exchange is screened. The HSE functional divide the full ($\frac{1}{r}$) Coulomb potential into two partitions i.e. short range (SR) and long range (LR) Coulombic

potential. The HSE functional is expressed as:

$$E_{xc}^{HSE} = E_x^{HSE,SR} + E_x^{PBE,LR}(\omega) + E_c^{PBE} \quad (2.65)$$

where

$$E_x^{HSE,SR} = \frac{1}{4}E_x^{FOCK,SR}(\omega) + \frac{3}{4}E_x^{PBE,SR}(\omega) \quad (2.66)$$

Where ω is the screening parameter that determines the partition into short range (SR) and long range (LR) terms [63]. In the short range, the HSE exchange includes a fraction ($\alpha = \frac{1}{4}$) of exact Fock exchange and a portion ($1-\alpha$) of PBE functional while the long range exchange is given solely by PBE functional. The HSE functional produce much better results for the structural properties band gaps of many metallic and semi-conducting materials compare to the traditional PBE techniques [63, 64].

2.10 The Full Potential LAPW Basis

The linearized augmented plane wave (LAPW) method is a very accurate technique to calculate the electronic structure. This technique is basically derived from the APW scheme. APW scheme suggest that the behavior of wave-functions are nearly spherical and hugely varying close to the nuclear potential and are much smoother between the atoms. Thus the whole unit cell splits in two parts i.e. atomic spheres and interstitial regions. The solution to the Schrödinger equation is radial for the atomic sphere while that for the interstitial region is plan wave.

$$\phi(r) = \sum_{lm} A_{lm} u_l(r) Y_{lm}(r) \dots r \in \text{spherical region} \quad (2.67)$$

$$\phi(r) = \frac{1}{V^{1/3}} \sum_G C_G e^{i(G+k)r} \dots r \in \text{interstitial region} \quad (2.68)$$

where the quantities A_{lm} and C_G are the expansion coefficients and V is the unit cell volume. Thus we obtain

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] r u_l = 0 \quad (2.69)$$

where E_l is the band energy and u_l is the regular solution. This scheme is known as Muffin-Tin approximation, it gives good results for closed pack materials. A linear combinations of radial functions are used as the basis function in the LAPW method. These basis functions are matched with values of plane waves on the sphere boundaries in the non-relativistic approach.

2.11 Pseudopotentials

Contrary to the valence electrons which interact strongly with the nearby atoms and thus greatly effect the ground state properties, the core electrons interact only weakly with the neighboring atoms and have a very small effect on the ground state properties. These core electrons tend to be more localized and have much deeper energy levels in the respective host atomic potential compare to the valence electrons. Thus the interaction between core and valence orbital wave functions have a very small effect on each other.

Pseudopotentials are introduced in DFT to justify these considerations and compute the ground state properties where instead of modeling the full atomic potential and taking all the electrons in each atom into account, only valence electrons are considered which are important to determine the material properties. This significantly reduces the system's complexity without compromising the predictive power.

A fictitious pseudo potential is constructed, which when act on the electrons placed in a potential, produces the orbital wave functions which replicate the characteristics of exact valence orbital wave functions. Beyond a specific cutoff radius, these pseudo wave functions match the exact wave functions. The accuracy of the system might be increased by selecting a small radius cutoff but this makes the DFT calculation more expensive. A long cutoff radius on the

other hand decrease the computational cost but effect the predictive power of the material model. In some cases, certain core electrons strongly interact with the valance electron and affect the ground state properties, these core electrons must also be treated in the same way as valance electrons while constructing the pseudo-atom.



Chapter 3

Boltzmann Transport Equation

Heat transport in 2-D materials is of great significance in several applications, including thermoelectric materials, thermal management materials and emerging micro electronics [24, 25, 26, 27, 28]. At such small scales, the classical transport theories like Fourier's law are not plausible and therefore the phonon transport is more efficiently described by Boltzmann transport equation. In the following chapter a brief review of the semi-classical Boltzmann transport theory is presented.

3.1 Boltzmann transport equation (BTE)

Boltzmann transport equation, a semi-classical approach, is a useful tool to gain insight into material's transport [65, 66, 67]. However solution to the BTE is far from trivial. There are several different models to solve the BTE. These models are classified into two different classes. The first class of models are of semi-empirical nature, as they include parameters obtained experimentally such as effective masses of electrons or holes, dielectric constant, phonon frequencies and band gaps. Using these adjustable parameters the calculated results are fitted to the experimental measurements. These models give impressive results for

the variation in material properties with temperature but they have no prediction power and are restricted to only those materials whose experimental data is available. In such models, the relaxation time approximation (RTA), which is expressed as energy's power law function, is usually used to treat the scattering processes. Thus the characteristics of elastic and inelastic scattering determined by the band structure obtained using *ab initio* techniques are ignored in these models since the scattering rates specially the inelastic ones do not follow the power law distribution functions[68, 69].

The second class, include models that depend on the *ab initio* band structure of materials instead of relying on the experimentally determined parameters. Usually for simplification most of these models also rely on relaxation time approximation RTA for the solution of BTE. Restrepo et al used the BTE-RTA to determined silicon's mobility for various carrier concentrations while considering the electron-phonon interactions to be elastic and the electron distribution at equilibrium [70].

Constant relaxation time approximation CRTA allows the closed-form expression for electronic transport such as Seebeck coefficient and conductivity which simplifies the problem even more. These models give good results for materials where the relaxation time is constant or nearly constant [71]. These models have good predictive power and can predict the properties of novel materials. However, the inclusion of inelastic scattering processes alter the energy of electrons and therefore greatly influence the prediction power of these models.

To investigate the transport properties (both electronic and lattice) using Boltzmann transport theory, an appropriate treatment of scattering mechanisms, elastic and inelastic, should be combined with the *ab initio* band structure calculation.

3.2 Electronic Transport

The function $f(r, k, t)$, which describes the occupation probability of an electron state, describes the dynamics of charge carriers. This distribution function can be determined using Boltzmann transport equation (BTE)

$$\frac{\partial f(r, k, t)}{\partial t}|_{fields} + \frac{\partial f(r, k, t)}{\partial t}|_{scattering} + \frac{\partial f(r, k, t)}{\partial t}|_{diffusion} = 0 \quad (3.1)$$

where the external fields, carrier diffusion and scattering among the charge carriers are assumed to be the only factors affecting the charge carriers behavior described by the distribution function. Here the time derivative term $\frac{df(r, k, t)}{dt}$ is not included since the thermoelectric properties are calculated in principles for quasi-static systems near equilibrium. The linearized BTE is expressed as

$$\frac{\partial f_0(r, k, t)}{\partial \varepsilon_i(k)} + \left(\frac{\varepsilon_i(k) - \mu}{T} \nabla T + \nabla \mu \right) \cdot v_i(k) = \frac{f_1(r, k, t)}{\tau} \quad (3.2)$$

where $f_0(r, k, t)$ is the Fermi-Dirac distribution function that gives the distribution of electrons or holes at thermodynamic equilibrium. The Fermi-Dirac distribution function is given as

$$f_0(r, k, t) = \frac{1}{e^{\frac{\varepsilon_i(k) - \mu}{k_b T}} + 1} \quad (3.3)$$

$f_1(r, k, t)$ in Eq. 3.2 give the charge carriers distribution in a system where the external forces are applied. μ is the electrochemical potential while $\nabla \mu$ is the change in chemical potential due to external forces. $v_i(k)$ and $E_i(k)$ are the group velocity and corresponding eigenenergies of the charge carriers. The term $\frac{f_1(r, k, t)}{\tau}$ on the R.H.S describes the scattering of charge carriers using the relaxation time approximation

$$\frac{\partial f(r, k, t)}{\partial t}|_{scattering} = \frac{f_1(r, k, t)}{\tau(\varepsilon_n(k))} = \frac{f(r, k, t) - f_0(r, k, t)}{\tau(\varepsilon_n(k))} \quad (3.4)$$

where $\tau(\varepsilon_n(k))$ is the relaxation time, which represents the average meantime between scattering encounters for charge carriers of specific energy E with band

index n and momentum k . The relaxation time is considered to be energy dependent and can be determined from first principles or obtained experimentally. Various components of relaxation time can be obtained using Matthiessens rule

$$\frac{1}{\tau} = \frac{1}{\tau_{cr}} + \frac{1}{\tau_{im}} + \frac{1}{\tau_p} + \frac{1}{\tau_b} \quad (3.5)$$

where τ_{cr} is the contribution of crystallographic defects to the relaxation time, τ_{im} represents the scattering from charge impurities, τ_p is the contribution from electron-phonon interactions and τ_b is due to the boundary or edge states. The group velocity $v_i(k)$ is from the band structure data as

$$\vec{v}(n, \vec{k}) = \frac{1}{\hbar} \left(\frac{\partial \varepsilon(n, \vec{k})}{\partial \vec{k}} \right) \quad (3.6)$$

once the non-equilibrium distribution function $f_1(r, k, t)$ in Eq. 3.2 is known, the thermodynamic transport properties can be obtained using the electrical and heat current densities.

$$J_e = -\frac{16\pi e\sqrt{2m}}{3h^3} \int E^{\frac{3}{2}} \tau(\varepsilon) \frac{\partial f_0}{\partial E} \left(\frac{E - \mu}{T} \nabla T + \nabla \mu + eE_0 \right) dE \quad (3.7)$$

and

$$J_Q = -\frac{16\pi\sqrt{2m}}{3h^3} \int E^{\frac{3}{2}} (E - \mu) \tau(E) \frac{\partial f_0}{\partial E} \left(\frac{E - \mu}{T} \nabla T + \nabla \mu + eE_0 \right) dE \quad (3.8)$$

which leads to the Onsager reciprocal relations expressed as

$$\vec{j} = \sigma E_0 - \sigma S \nabla T \quad (3.9)$$

and

$$\vec{j} = \sigma S T E_0 - \kappa' \nabla T \quad (3.10)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, E_0 is the external electric field and ∇T is the temperature gradient. The κ' term represents the electronic thermal conductivity which is obtained from electrical conductivity using Wiedmann-Franz law and is in principles an approximation to the true thermal conductivity. Now in order to calculate the electrical and heat current densities, we need to determine these thermoelectric coefficients.

3.2.1 Electrical Conductivity

One of the most important components in the current density equations is the electrical conductivity, which is the ability of a material to conduct electric current. The electrical conductivity can be expressed as

$$\sigma = \frac{ne^2\tau(E_f)}{m} \quad (3.11)$$

where n is the carriers concentration, e is the electronic charge, m represent the effective mass of charge carriers and $\tau(\varepsilon_f)$ stands for relaxation time.

3.2.2 Seebeck Coefficient

Another important constituent of the current density expressions is the Seebeck coefficient also called the thermopower. It gives the magnitude of thermoelectric voltage generated by the temperature gradient in a material. The Seebeck coefficient is calculated using Boltzmann transport equation as

$$S = -\frac{\pi^2 k_B^2}{3e} \frac{\partial}{\partial E} \ln[E^{\frac{1}{2}} \tau(E)]_{E=\mu} \quad (3.12)$$

where the sign of Seebeck coefficient depends on the nature of charge carriers. The Seebeck coefficient is positive for p-type thermoelectric material where holes are the majority charge carriers, while for n-type where electrons are the majority charge carriers, the Seebeck coefficient is negative.

3.2.3 Electronic Thermal conductivity

Thermal conductivity is the material's ability to conduct heat. The thermal conductivity in metals is in accordance with the electrical conductivity as the free valance electrons transfer both electric and heat current. However, in non metals there is also contribution from lattice vibrations. Thus for such materials the electrical and thermal conductivities do not have a direct correlation. However, the Wiedmann-Franz law [72] can be used to obtain the electronic thermal conductivity. The Wiedmann-Franz law is based on the premise that both electrical and thermal transport involve free electrons in the system and can be expressed as

$$\kappa'_e = L\sigma T \quad (3.13)$$

where L represents the Lorentz number for free electrons which can be expressed as

$$L = \frac{\pi^2 k_B^2}{3e^2} = 2.44 \times 10^{-8} W\Omega K^{-2} \quad (3.14)$$

By increasing the average velocity of charge particles, the forward transport of energy increases which in turns increase the thermal conductivity. However, the electrical conductivity reduces as particle velocity increases since the electrons divert from the forward transport due to collisions.

3.2.4 BoltzTraP

BoltzTraP code was developed by Georg Madsen and David Singh in 2006 which can be used calculate all the thermoelectric properties except the lattice thermal conductivity [71]. The electric current j in the presence of an external electric and magnetic field and a temperature gradient can be expressed as

$$j_i = \sigma_{ij}E_j + \sigma_{ijk}E_jB_k + v_{ij}\nabla_j T \quad (3.15)$$

where σ_{ij} and σ_{ijk} are the conductivity tensors, and v_{ij} is the group velocity. The group velocity and inverse mass tensor are the two components of conductivity tensor that directly exploit the band structure data obtained from DFT calculation. The group velocity is obtained from the slope of energy bands as

$$v_\alpha(i, \vec{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon(i, \vec{k})}{\partial k_\alpha} \quad (3.16)$$

and the inverse mass tensor is determined from the energy band dispersion as

$$M_{\beta\mu}^{-1}(i, \vec{k}) = \frac{1}{\hbar} \frac{\partial^2 \varepsilon(i, \vec{k})}{\partial k_\beta \partial k_\mu} \quad (3.17)$$

the conductivity tensors can be expressed as

$$\sigma_{\alpha\beta}(i, \vec{k}) = e^2 \tau v_\alpha(i, \vec{k}) v_\beta(i, \vec{k}) \quad (3.18)$$

and

$$\sigma_{\alpha\beta\gamma}(i, \vec{k}) = e^3 \tau^2 \zeta_{\gamma uv} v_\alpha(i, \vec{k}) v_\beta(i, \vec{k}) M_{\beta u}^{-1} \quad (3.19)$$

where $\zeta_{\omega uv}$ is the Levi-Civita symbol, which is equal to zero if any of the indexes

are equal and is ± 1 depends on the direction of permutation. The transport tensors can then be computed from the conductivity distributions.

$$\sigma_{\alpha\beta}(T; \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (3.20)$$

$$v_{\alpha\beta}(T; \mu) = \frac{1}{eT\Omega} \int \sigma_{\alpha\beta}(\varepsilon)(e - \mu) \left[-\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (3.21)$$

$$k_{\alpha\beta}^{elec}(T; \mu) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta}(\varepsilon)(e - \mu)^2 \left[-\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (3.22)$$

$$\sigma_{\alpha\beta\gamma}(T; \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta\gamma}(\varepsilon) \left[-\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (3.23)$$

where k_e is the electronic part of thermal conductivity, Ω is the unit cell volume, μ is the chemical potential and $f_{\mu}(T; \varepsilon)$ is the distribution function. Once these values are calculated the Hall and Seebeck coefficients can be obtained;

$$S_{ij} = E_i (\nabla_j T)^{-1} = (\sigma^{-1})_{\sigma i} v_{\alpha j} \quad (3.24)$$

$$R_{ijk} = \frac{E_j^{ind}}{j_i^{appl} B_k^{appl}} = (\sigma^{-1})_{\alpha j} \sigma_{\alpha\beta k} (\sigma^{-1})_{i\beta} \quad (3.25)$$

Thus by choosing the relaxation time and calculating the conductivity tensors all the components of figure of merit can be obtained except k_l which can be obtained from molecular dynamics calculations.

3.3 Lattice Transport

Lattice thermal conductivity k_l plays a significant role in various applications which require materials with tuned thermal conductivities. In order to investigate k_l a parameter free model with great prediction power is required. Similar to the electronic part, k_l can also be obtained from the Boltzmann transport equation.

3.3.1 Heat Transport

Heat is transfer in materials by both electrons and lattice vibrations (Phonon) due to the temperature gradient ∇T . In semi conducting materials, the heat transfer by electrons is smaller compare to that transfer by phonons. The heat current J induced by the temperature gradient ∇T can be obtained as

$$J = \sum_p \int f_\lambda \hbar \omega_\lambda v_\lambda \frac{dq}{(2\pi)^3} \quad (3.26)$$

where λ contain both the phonon branch index p and wave vector q , f_λ is the distribution function of phonons, ω_λ and v_λ are the angular frequency and group velocity of phonon mode λ , respectively. The Bose-Einstein distribution function gives the phonon distribution at thermal equilibrium as

$$f_0(\omega_\lambda) = \frac{1}{e^{\frac{\hbar\omega_\lambda - \mu}{k_b T}} - 1} \quad (3.27)$$

The phonon distribution function f_λ deviates from f_0 under the influence of a temperature gradient ∇T . BTE is used to determine such deviation. The main factors affecting the phonon distribution includes the diffusion caused by temperature gradient ∇T and scattering. The change in phonon distribution w.r.t time vanishes under steady state conditions, which is expressed by BTE as [73, 74]:

$$\frac{df_\lambda}{dt} = \left. \frac{\partial f_\lambda}{\partial t} \right|_{diffusion} + \left. \frac{\partial f_\lambda}{\partial t} \right|_{scattering} = 0 \quad (3.28)$$

where the change in the distribution function in time caused by diffusion is obtained as

$$\left. \frac{\partial f_\lambda}{\partial t} \right|_{diffusion} = -\nabla T \cdot v_\lambda \frac{\partial f_\lambda}{\partial T} \quad (3.29)$$

The rate of change due to scattering $\left. \frac{\partial f_\lambda}{\partial t} \right|_{scattering}$ depends on particular scattering processes, that can be analyzed by perturbation theory. In single crystal systems, the phonon scattering is mainly caused by phonon-phonon collision and impurities such as isotopes. Boundary scattering play an important role at very low temperature as the real bulk samples have finite sizes, but its treatment is not covered in this study.

3.3.2 Linearized Boltzmann Transport Equation

Generally, the temperature gradient ∇T has a small norm which enable us to expand the distribution function f_λ up to first order in ∇T

$$f_\lambda = f_0(\omega_\lambda) + g_\lambda \quad (3.30)$$

where g_λ is linearly dependent on temperature and can be expressed as

$$g_\lambda = -F_\lambda \cdot \nabla T \frac{df_0}{dT} \quad (3.31)$$

When the only scattering sources are the two and three phonon processes, the resulting linearized BTE are expressed as [75, 76, 77, 78]:

$$F_\lambda = \tau_\lambda^0(v_\lambda + \Delta_\lambda) \quad (3.32)$$

where the relaxation time τ_λ^0 can be determined using the perturbation theory which is generally used in RTA. The term Δ_λ has the dimensions of velocity and it gives the deviation of specific phonon mode population and the corresponding heat current from the results obtained using RTA. Thus taking Δ_λ equals zero is similar to operating in RTA. More explicitly, the relaxation time τ_λ^0 and Δ_λ are obtained as

$$\frac{1}{\tau_\lambda^0} = \frac{1}{N} \left(\sum_{\lambda'\lambda''}^+ \Gamma_{\lambda\lambda'\lambda''}^+ + \sum_{\lambda'\lambda''}^- \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''}^- \sum_{\lambda'} \Gamma_{\lambda\lambda'} \right) \quad (3.33)$$

and

$$\begin{aligned} \Delta_\lambda = & \frac{1}{N} \sum_{\lambda'\lambda''}^+ \Gamma_{\lambda\lambda'\lambda''}^+ (\xi_{\lambda\lambda''} F_{\lambda''} - \xi_{\lambda\lambda'} F_{\lambda'}) + \frac{1}{N} \sum_{\lambda'\lambda''}^- \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''}^- (\xi_{\lambda\lambda''} F_{\lambda''} + \xi_{\lambda\lambda'} F_{\lambda'}) + \\ & \frac{1}{N} \sum_{\lambda'} \Gamma_{\lambda\lambda'} \xi_{\lambda\lambda'} F_{\lambda'} \end{aligned} \quad (3.34)$$

where the Brillouin zone is discretized into Γ -centered grid with $N = N_1 \times N_2 \times N_3$ $\mathbf{q}$ points. The term $\xi_{\lambda\lambda'}$ is the ratio of angular frequencies given as

$$\xi_{\lambda\lambda'} = \frac{\omega_{\lambda'}}{\omega_\lambda} \quad (3.35)$$

The quasimomentum is conserved if the relation $q'' = q \pm q' + Q$ is satisfied where Q is some reciprocal lattice vector for which the vectors q , q' and q'' lies in the same Brillouin zone.

3.3.3 Interatomic Lattice Potential

In order to go beyond the framework of RTA and directly calculates the three-phonon scattering rates, investigation of the inter atomic lattice potential Φ which describes the inter atomic forces is required. Using Taylor series this potential can be expressed as

$$\begin{aligned} \Phi = & \Phi_0 + \sum_{lk\alpha} \Phi_{\alpha}(lk)u_{\alpha}(lk) + \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \Phi_{\alpha\beta}(lk;l'k')u_{\alpha}(lk)u_{\beta}(l'k') + \\ & \frac{1}{3!} \sum_{lk\alpha} \sum_{l'k'\beta} \sum_{l''k''\gamma} \Phi_{\alpha\beta\gamma}(lk;l'k';l''k'')u_{\alpha}(lk)u_{\beta}(l'k')u_{\gamma}(l''k'') + \dots \end{aligned} \quad (3.36)$$

where l represents the unit cell and k refers to an atom in that unit cell. μ_{α} describe the deviation of atoms from their original positions at equilibrium and α , β and γ are the Cartesian coordinates. The first term on R.H.S is constant and can be ignored while the second term is the measure of force on each atom due to all the other atoms in the system. In equilibrium conditions, this force should be equal to zero and can be ignored as well. The only terms of interest in Eq. 3.36 are those which include the harmonic and third order anharmonic interatomic force constants (IFCs) represented by $\Phi_{\alpha\beta}$ and $\Phi_{\alpha\beta\gamma}$ respectively. These IFCs can be written as

$$\Phi_{\alpha\beta}(lk;l'k') = \left. \frac{\partial^2 \Phi}{\partial u_{\alpha}(lk) \partial u_{\beta}(l'k')} \right|_{\vec{u}=0} \quad (3.37)$$

and

$$\Phi_{\alpha\beta\gamma}(lk;l'k';l''k'') = \left. \frac{\partial^3 \Phi}{\partial u_{\alpha}(lk) \partial u_{\beta}(l'k') \partial u_{\gamma}(l''k'')} \right|_{\vec{u}=0} \quad (3.38)$$

The phonon frequencies and eigenvectors can be determined from harmonic IFCs. Phonons do not interact with each other in the harmonic approximation.

The interaction term is embedded into Eq. 3.38 and is considered to be the perturbation in the harmonic approximation. The calculation of harmonic IFCs has been carried out extensively and extremely good agreement has been found with experimental measurements. Calculation of the anharmonic IFCs on the other hand is more complex job and only now the parameters obtained from them begins to yield good results.

3.3.4 Harmonic interatomic force constants

The third term in the interatomic potential equation represents the harmonic part of interatomic potential, which gives the phonon eigenvectors and the corresponding eigenvalues. In harmonic approximation, the equation of motion for atoms is given as

$$M_k \ddot{u}_\alpha(lk) = - \sum_{l'k'\beta} \Phi_{\alpha\beta}(0k; l'k') u_\beta(l'k') \quad (3.39)$$

where M_k represents the mass of k^{th} atom. To solve Eq. 3.39, the atomic displacement is assumed to have the formalism

$$u_\alpha(lk) = \frac{1}{\sqrt{M_k}} \sum_{\vec{q}} U_\alpha(\vec{q}; k) \exp[i(\vec{q} \cdot \vec{x}(l) - \omega t)] \quad (3.40)$$

where $\vec{x}(l)$ represents the l^{th} unit cell equilibrium position. Putting Eq. 3.40 into Eq. 3.39 yields

$$\omega^2 U_\alpha(\vec{q}; k) = \sum_{k'\beta} D_{\alpha\beta}(kk'; \vec{q}) U_\beta(\vec{q}; k') \quad (3.41)$$

A non-trivial solution is obtained from Eq. 3.41 using the form

$$|D_{\alpha\beta}(kk'; \vec{q}) - \omega^2 \delta_{\alpha\beta} \delta_{kk'}| = 0 \quad (3.42)$$

The dynamical matrix, $D_{\alpha\beta}(kk'; \vec{q})$, can be expressed as the Fourier transform of $\Phi_{\alpha\beta}$

$$D_{\alpha\beta}(kk'; \vec{q}) = \frac{1}{\sqrt{M_k M'_k}} \sum_{l'} \Phi_{\alpha\beta}(0k; l'k') \exp[i\vec{q} \cdot \vec{x}(l')] \quad (3.43)$$

if the harmonic IFCs are known, the dynamical matrix can be constructed for any arbitrary $\vec{q}$ and thus all eigenvector and phonon frequencies can be calculated.

3.3.5 Third-order anharmonic interatomic force constants

Eq. 3.38 gives the third order anharmonic IFCs. Here, it is convenient to give an expression for the displacement of atoms in terms of raising and lowering operators

$$u_\alpha(lk) = \left(\frac{\hbar}{2NM_k} \right)^{\frac{1}{2}} \sum_{j, \vec{q}} \omega_j^{-\frac{1}{2}}(\vec{q}) e_\alpha(k|j\vec{q}) e^{i\vec{q} \cdot \vec{R}_l} (a_{j\vec{q}} + a_{-j\vec{q}}^+) \quad (3.44)$$

where $e_\alpha(k|j\vec{q})$ is the α^{th} component of eigenvector. Substituting the atomic displacement into the fourth term of Eq. 3.36, the third-order part of interatomic potential is obtained

$$\begin{aligned} \Phi_3 = & \frac{1}{3!} \sum_{lk} \sum_{l'k'} \sum_{l''k''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma} \left(\frac{\hbar}{2N} \right)^{\frac{3}{2}} \frac{1}{\sqrt{M_k M'_k M''_k}} \sum_{\lambda_1 \lambda_2 \lambda_3} \frac{e_{\alpha k}^{\lambda_1} e_{\beta k}^{\lambda_2} e_{\gamma k}^{\lambda_3}}{\sqrt{\omega_{\lambda_1} \omega_{\lambda_2} \omega_{\lambda_3}}} \\ & e^{i\vec{q}_1 \cdot \vec{R}_l} e^{i\vec{q}_2 \cdot \vec{R}'_l} e^{i\vec{q}_3 \cdot \vec{R}''_l} \times (a_{\lambda_1} + a_{-\lambda_1}^+)(a_{\lambda_2} + a_{-\lambda_2}^+)(a_{\lambda_3} + a_{-\lambda_3}^+) \end{aligned} \quad (3.45)$$

where λ contain both the wave vector $\vec{q}$ and branch index j . Similarly, $-\lambda$ is used to designate j and $-\vec{q}$. The addition of lattice vector, R to R_l , R_l or R_l

should not alter ϕ_3 since the interatomic potential obeys translational invariance. Hence the addition of $\vec{R}$ leads to the condition

$$e^{i(\vec{q}_1 + \vec{q}_2 + \vec{q}_3) \cdot \vec{R}} = 1 \quad (3.46)$$

$$\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = \vec{K} \quad (3.47)$$

The sum over l can be eliminated in Eq. 3.45 as the third-order IFCs do not depend on the absolute positions of ions but only on their relative positions. Therefore

$$\Phi_{\alpha\beta\gamma}(lk; l'k'; l''k'') = \Phi_{\alpha\beta\gamma}(0k; l' - lk'; l'' - lk'') \quad (3.48)$$

By redefining l' to $l' - l$ and l to $l'' - l$, ϕ_3 can be expressed as

$$\begin{aligned} \Phi_3 = & \frac{1}{6} \left(\frac{\hbar}{2N} \right)^{\frac{3}{2}} N \sum_k \sum_{l'k'} \sum_{l''k''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma} \frac{1}{\sqrt{M_k M'_k M''_k}} \sum_{\lambda_1 \lambda_2 \lambda_3} \\ & \frac{e^{\lambda_1}_{\alpha k} e^{\lambda_2}_{\beta k} e^{\lambda_3}_{\gamma k}}{\sqrt{\omega_{\lambda_1} \omega_{\lambda_2} \omega_{\lambda_3}}} e^{i\vec{q}_2 \cdot \vec{R}'_l} e^{i\vec{q}_3 \cdot \vec{R}''_l} \times (a_{\lambda_1} + a_{-\lambda_1}^+)(a_{\lambda_2} + a_{-\lambda_2}^+)(a_{\lambda_3} + a_{-\lambda_3}^+) \quad (3.49) \end{aligned}$$

The extra term N comes from the redefinition of l and the evaluation of sum over l . It is clear from the expansion of parentheses containing the raising and lowering operators that Eq. 3.49 describes processes where each phonon is either created or destroyed. Since the energy should remain conserved therefore all the three phonon scattering processes are energetically not possible and the terms in Eq. 3.49 corresponding to these processes should be disregarded.

3.3.6 Three-phonon scattering processes

The terms, $\Gamma_{\lambda\lambda'\lambda''}^{\pm}$ in Eq. 3.33 and Eq. 3.34 are the three-phonon scattering rates, which can be obtained as

$$\Gamma_{\lambda\lambda'\lambda''}^+ = \frac{\hbar\pi}{4} \frac{f_0' - f_0''}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} |V_{\lambda\lambda'\lambda''}^+|^2 \delta(\omega_{\lambda} + \omega_{\lambda'} - \omega_{\lambda''}) \quad (3.50)$$

and

$$\Gamma_{\lambda\lambda'\lambda''}^- = \frac{\hbar\pi}{4} \frac{f_0' + f_0'' + 1}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} |V_{\lambda\lambda'\lambda''}^-|^2 \delta(\omega_{\lambda} - \omega_{\lambda'} - \omega_{\lambda''}) \quad (3.51)$$

The quantity, $\Gamma_{\lambda\lambda'\lambda''}^+$ represents the absorption processes, where the two incident phonons combine to produce a single resultant phonon with energy equal to the sum of individual incident phonon energy.

$$\omega_{\lambda} + \omega_{\lambda'} = \omega_{\lambda''} \quad (3.52)$$

Whereas the quantity, $\Gamma_{\lambda\lambda'\lambda''}^-$ corresponds to the emission process, where energy of a single incident phonon splits into two phonons.

$$\omega_{\lambda} = \omega_{\lambda'} + \omega_{\lambda''} \quad (3.53)$$

The Dirac delta distribution in Eq. 3.50 and Eq. 3.51 enforces the energy conservation in both the absorption and emission processes. To successfully calculate the quantities, $\Gamma_{\lambda\lambda'\lambda''}^{\pm}$, elements of the scattering matrix, $V_{\lambda\lambda'\lambda''}^{\pm}$ are required, which can be obtained as

$$V_{\lambda\lambda'\lambda''}^{\pm} = \sum_{i \in u.c.} \sum_{j,k} \sum_{\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} \frac{e_{\lambda}^{\alpha}(i) e_{p', \pm q'}^{\beta}(j) e_{p'', -q''(k)}^{\gamma}}{\sqrt{M_i M_j M_k}} \quad (3.54)$$

which in turn depend on the anharmonic IFCs $\Phi_{ijk}^{\alpha\beta\gamma} = \frac{\partial^3 E}{\partial r_i^\alpha \partial r_j^\beta \partial r_k^\gamma}$ and the normalized eigenfunctions $e_{p,q}$ of phonons involved such processes. The indexes i, j and k in these expressions are the atomic indices whereas α, β and γ represent the Cartesian coordinates. M_i & r_i^α represents the mass of the i^{th} atom and its displacement from equilibrium, respectively. Lastly, $e_\lambda^\alpha(i)$ denotes the α component of the i^{th} atoms eigenfunction of phonon mode λ .

3.3.7 Isotopic impurity scattering

In BTE framework the crystals are considered to be isotopically pure and thus only three-phonon scattering is included but actual physical samples under experimental study are not infinite or isotopically pure. While various pure samples have been artificially synthesized and measured, still a small concentration of isotopic impurities exist in these samples. The presence of such impurities modifies the thermal conductivity k_L through different isotopic masses. The elastic scattering effect between isotopic impurities and phonons is introduced to the BTE formalism and its rate is expressed as

$$\Gamma_{\lambda\lambda'} = \frac{\pi\omega^2}{2} \sum_{i \in u.c.} g(i) |e_\lambda^*(i) \cdot e_{\lambda'}(i)|^2 \delta(\omega_\lambda - \omega_{\lambda'}) \quad (3.55)$$

where $g(i)$ is the Pearson deviation coefficient and is given as

$$g(i) = \sum_s f_s(i) [1 - M_s(i)/\bar{M}]^2 \quad (3.56)$$

where $M_s(i)$ is the mass of s isotope of i^{th} atom, obtained using relative frequency $0 < f_s(i) \leq 1$ and their average $\bar{M}(i) = \sum_s f_s(i) M_s(i)$.

3.3.8 Lattice thermal conductivity

The lattice thermal conductivity can be expressed in terms of $\mathbf{F}$ as

$$\kappa_\ell^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_\lambda f_0(f_0 + 1) (\hbar\omega_\lambda)^2 v_\lambda^\alpha F_\lambda^\beta \quad (3.57)$$

where Ω represents volume of the unit cell. The lattice thermal conductivity and other related properties are calculated using the ShengBTE code. In this approach the linearized BTE can be solved iteratively for $\mathbf{F}_\lambda$ beginning from a zero-order approximation $F_\lambda^0 = \tau_\lambda^0 v_\lambda$. The iterative process ends when the relative variation in conductivity tensor calculated using Eq. 3.57 is less than a default value of 10^{-5} . The iterative process may greatly affect the calculations while investigating materials with high k_ℓ values such as diamond where the three-phonon processes are of great importance, since the normal processes are considered resistive in the RTA [79]. However, in systems with strong umklapp scattering such as Si and Ge, the iterative process usually add only 10% to k_ℓ at 300 k as compare to the results obtained with RTA [80]. It may take a huge amount of time to calculate the phonon scattering rates $\Gamma_{\lambda\lambda'\lambda''}^\pm$. Therefore, only $\mathbf{q}$ points lying inside the BZ must be selected from the grid. The effect of such reduction can be maximized by choosing N_1 , N_2 and N_3 in such manner that the crystal symmetry of the sample remain unchanged. A particular choice that guarantee the preservation of symmetry is $N_1 = N_2 = N_3$.

3.3.9 Specific Heat

Although the main results obtained from ShengBTE program is the thermal conductivity, k_ℓ , for bulk and nanowires but other important quantities might also be calculated to gain additional information about the thermodynamics of materials. The specific heat per unit volume C_v is an important quantity calculated using harmonic approximations. The specific heat per unit volume can be expressed as

$$C_v = \frac{k_B}{\Omega N} \sum_{\lambda} \left(\frac{\hbar \omega}{k_B T} \right)^2 f_0(f_0 + 1) \quad (3.58)$$

$$= \frac{k_B}{(2\pi)^3} \int_{BZ} \left(\frac{\hbar \omega}{k_B T} \right)^2 f_0(f_0 + 1) d^3 \mathbf{q} \quad (3.59)$$

3.3.10 Small grain limit reduced thermal conductivity

Another significant quantity calculated by ShengBTE is the small-grain-limit reduced thermal conductivity $\tilde{\kappa}_{SG}$. A new kind of contribution arise from the introduction of nanostructuring in the bulk material to the scattering rate of phonons. This contribution become dominant by making the size small and therefore the mean free path is limited to a constant value Λ . Thus by substituting $F_{\lambda}^{\beta} = \Lambda v_{\lambda}^{\beta} / |\mathbf{v}_{\lambda}|$ into Eq. 3.57 κ_{ℓ} becomes proportional to Λ . $\tilde{\kappa}_{SG}$ can be expressed as the proportionality tensor

$$\tilde{\kappa}_{SG}^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0(f_0 + 1) \frac{v_{\lambda}^{\alpha} v_{\lambda}^{\beta}}{|\mathbf{v}_{\lambda}|} \hbar^2 \omega_{\lambda}^2 \quad (3.60)$$

This quantity shows how the conductivity of materials is influenced by their harmonic properties. Sometimes, it is useful to calculate the phonons mean free path which are most relevant to the thermal conductivity. For which ShengBTE also gives the cumulative thermal conductivity, where only those phonons are considered which has mean free path smaller than certain threshold length.

3.3.11 Phase space

Another important factor that affects the thermal properties is the portion of three-phonon processes allowed by energy conservation. This factor is called phase space and can be studied individually by removing other probabilities from the picture. The phase space is expressed as

$$P_3 = \frac{\Omega}{(6\pi n)^3} \sum_{p,p',p''} \int \int_{BZ} \delta[\omega_p(\mathbf{q}) + \omega_{p'}(\mathbf{q}') - \omega_{p''}(\mathbf{q} + \mathbf{q}' - \mathbf{Q})] d^3\mathbf{q}' d^3\mathbf{q} \quad (3.61)$$

it can be easily seen that $0 \leq P_3 \leq 1$. The actual values of phase space are strongly correlated with thermal conductivity k_ℓ and are much lower than the upper limit⁵. ShengBTE give both the global value of P_3 and individual contributions from modes and q points. Finally, the total and partial phonon density of states (DOS) and (PDOS) is also from ShengBTE.

3.3.12 Mode Grüneisen parameter

Mode Grüneisen Parameter is of great significance as it provide the measure of anharmonicity of the crystal. The term is generally used to describe a single thermodynamic property γ , which is an average of many individual parameters γ_i included in the original Grüneisens expression in terms of phonon nonlinearities. The mode Grüneisen Parameter can be calculated using two different schemes. The first scheme requires only the harmonic IFCs while the second method involve both the harmonic and anharmonic IFCs.

3.3.13 Second-order IFC method

The mode Grüneisen Parameter can be defined as the variation in phonon mode frequency with a small variation in crystal volume

$$\gamma_j(\vec{q}) = -\frac{V}{\omega_j(\vec{q})} \frac{\partial \omega_j(\vec{q})}{\partial V} \quad (3.62)$$

In order to determine the Grüneisen Parameter numerically, the phonon frequencies are calculated at the lattice constants slightly different from those at equilibrium and evaluating the following expression

$$\gamma_j(q) = -\frac{V^0}{\omega_j^0(\vec{q})} \frac{\omega_j(a + \delta a) - \omega_j(a - \delta a)}{V(a + \delta a) - V(a - \delta a)} \quad (3.63)$$

where $\omega_j^0(\vec{q})$ represent the phonon frequency, V^0 is the unit cell volume at equilibrium lattice constant and $V(a \pm \delta a)$ is the unit cell volume at the lattice constant slightly different from the equilibrium value. The Grüneisen Parameter obtained from the above equation is dependent on δa . In order to get rid of any possible dependence, phonon frequencies are computed for a set of lattice constants which includes the equilibrium lattice constant, where each calculation requires a new set of harmonic IFCs for a given lattice constant. Linear regression techniques are then used to calculate the gradient $\partial\omega_j(\vec{q})/\partial V$ and the Grüneisen Parameter is computed for the considered $j, \vec{q}$ pair.

3.3.14 Third-order anharmonic IFC method

Since the Grüneisen Parameter is the measure of anharmonicity in the crystal, it is only logical to use anharmonic IFCs to calculate the Grüneisen Parameter. The expression for Grüneisen Parameter in terms anharmonic IFCs is given as

$$\gamma_j(\vec{q}) = -\frac{1}{6\omega_j^2(\vec{q})} \sum_k \sum_{l'k'} \sum_{l''k''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(0k, l'k', l''k'') \frac{e_{\alpha k}^{j*}(\vec{q}) e_{\beta k'}^j(\vec{q})}{\sqrt{M_k M_{k'}}} e^{iq \cdot \vec{R}_l} \vec{r}_{l''k''\gamma} \quad (3.64)$$

The harmonic IFCs are still needed to calculate the eigenvectors, $e_{\alpha k}^j(\vec{q})$ and phonon frequencies. The Grüneisen Parameter obtained from both methods can be compared to check the accuracy of anharmonic IFCs.

3.3.15 Sum rules for anharmonic IFCs

For any global displacement the invariance in the lattice potential requires that

$$\sum_k \Phi_{ijk}^{\alpha\beta\gamma} = 0 \quad (3.65)$$

which is also valid for summation over i or j because of permutation symmetries. Eq. 3.65 is very crucial for the calculation of low frequency scattering rates. In principles, no *ab initio* package exactly satisfies these sum rules while calculating the force constants, and some sort of manipulation is required to enforce them while simultaneously varying the IFCs. The main goal is to compensate every non-zero IFC in order to satisfy these conditions. A reasonable choice is the minimization of the sum of squares of these minor compensations, that results into a well-posed minimization problem [81]. However, enforcing all the sum rules is not necessary since the partially symmetrized third-order IFCs satisfy some of them. Imposing the sum rules on a minimal set of anharmonic IFCs ϕ_j results in minimizing $\frac{1}{2} \sum_J \phi_J^2$ where ϕ_J is the small compensation to Φ_J , under the influence of a set of linear constraints

$$\sum_J A_{IJ}(\Phi_J + \phi_J) = 0 \quad (3.66)$$

where all the subscripts and superscripts are summarized in the index J . To solve this a Lagrange multiplier λ_l is introduced for each constraint which leads to

$$\sum_J \left[\sum_M A_{IM} A_{IM} \right] \lambda_J = - \sum_J A_{IJ} \Phi_J \quad (3.67)$$

the values of ϕ_j can be obtained from its solution as

$$\phi_J = \sum_I \lambda_I A_{IJ} \quad (3.68)$$

Chapter 4

Results and Discussion

The aim of this chapter is to provide a detailed description of different computational parameters used to study the thermoelectric properties of novel 2D Silicon Telluride. The results obtained using these parameters are reported in this chapter. The comparison of the phonon dispersion with previous theoretical data is also presented here.

4.1 Computational detail

β -SiTe monolayer has an isotropic puckered structure where each silicon atom makes covalent bond with 3 telluride atoms, which results in a hexagonal unit cell. The space group of β -SiTe is $P3m1$. The optimized lattice constants for β -SiTe are $a = b = 3.83\text{\AA}$. Buckling appears at various sites in the unit cell. The buckling parameter Δz that gives the vertical distance between two adjacent atomic planes is $1.53\text{\AA}$ [30]. The geometrical structure of 2D β -SiTe is given in fig. 4.1.

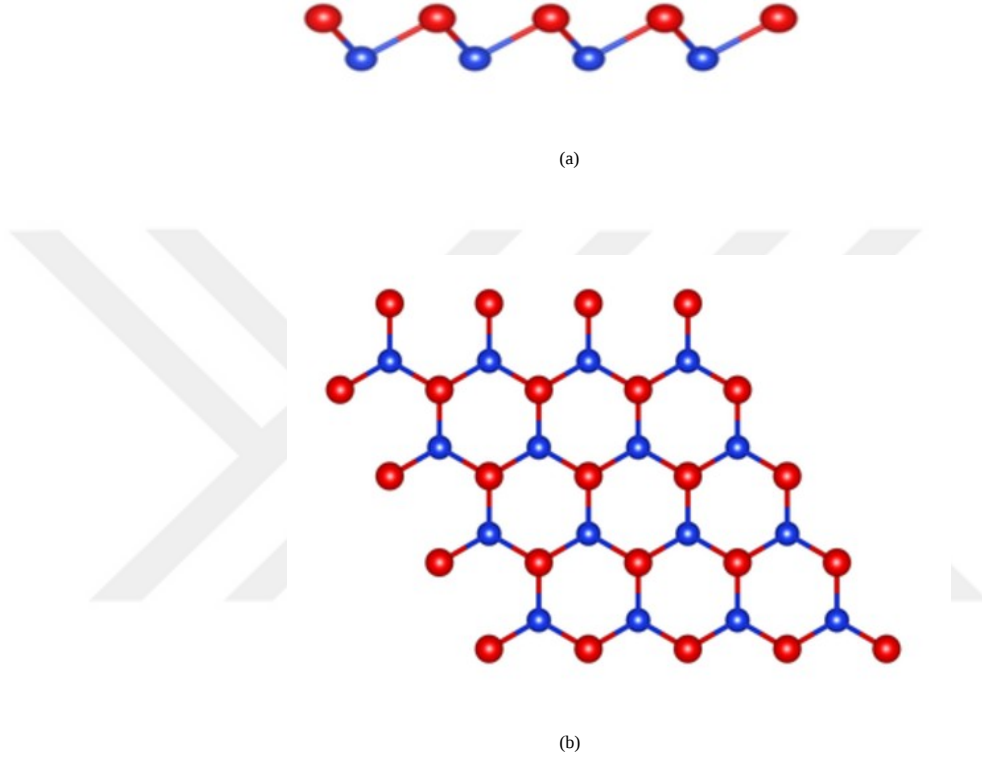


Figure 4.1: Geometric structure of 2D β -SiTe. (a) side view (b) real space lattice for β -SiTe

The energy cutoff is taken as high as 520 eV and the convergence of total energy and force is achieved at $1 \times 10^{-7} \text{ eV}$ and $1 \times 10^{-5} \text{ eV \AA}^{-1}$, respectively. For the band energy calculation a K mesh of $(19 \times 19 \times 1)$ is used in the irreducible Brillouin Zone. A $\sim 20 \text{ \AA}$ vacuum space is introduced along the $\hat{z}$ direction for 2 dimensional calculations in order to avoid any interaction between neighbor images. The structure is relaxed fully using the conjugate gradient method with no symmetric constraints.

The density functional perturbation theory (DFPT) is used to calculate the necessary force constants in order to verify the dynamic stability and estimate the

thermodynamic properties of β -SiTe. The phonon dispersion and density of states are then computed using PHONOPY code [82]. The energy cutoff for the force constant calculations is set to 520 eV. To calculate the 2nd order force constants, a $10 \times 10 \times 1$ supercell is used along with a K mesh of $3 \times 3 \times 1$. For 3rd order force constant calculation, a $5 \times 5 \times 1$ super cell is used along with $7 \times 7 \times 1$ special k-points. A minimum set of displacements are generated for the calculation of 3rd order force constant using Third order.py code, which is far more efficient and computationally economic compare to phono3py program which generates almost three times more displaced supercell configurations. The lattice thermal conductivity and other important lattice dependent properties are calculated using ShengBTE program [83] the 2nd and 3rd order force constants are taken into account. A mesh of $16 \times 16 \times 1$ special q -points is used for these thermodynamic calculations.

4.2 Electronic Density of States (DOS)

To determine the band energies and structural properties of β -SiTe the electron density of states are computed, which shows the electronic states distribution in various energy levels. The total and partial density of states are given in fig. 4.2 where a forbidden energy gap can be seen between the valance and conduction band. The Fermi level E_f lies between the conduction and valance band at 0 eV. From the partial density of state (PDOS), the contribution of each individual atomic states can be observed. The p -state of Te atom has main contribution to the valance band while Si-s and Si-p states also have considerable contributions. The conduction band has almost equal contribution from Si-p and Te-p states while the contribution from Si-s and Te-s is relatively much smaller. The high peak near Fermi-level indicates a flat valance band maxima.

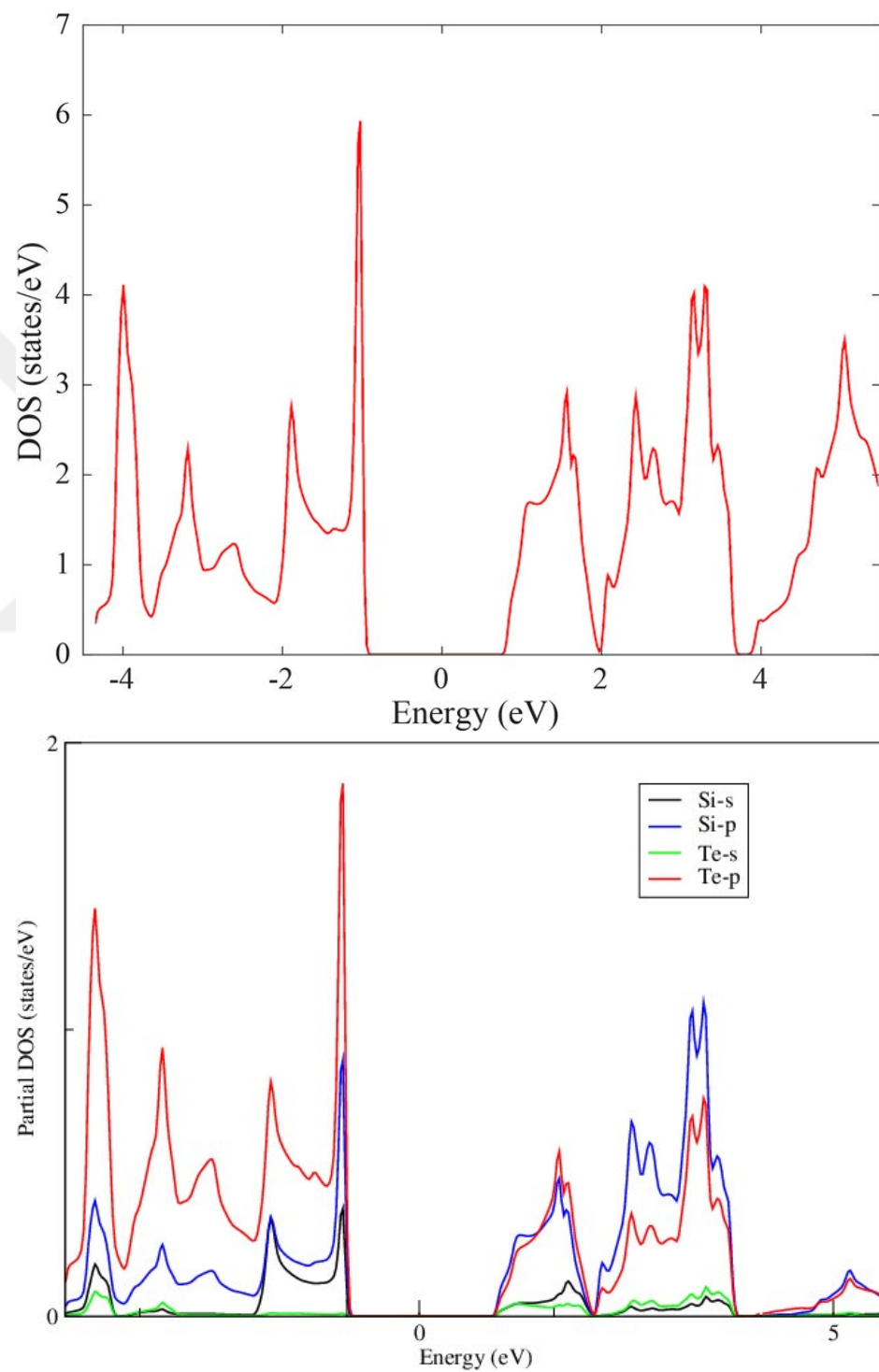


Figure 4.2: Total and Partial density of states of β -SiTe

4.3 Band structure

The electronic band structure of β -SiTe calculated using PBE-GGA is given in fig. 4.3 which indicates that β -SiTe has an indirect band gap. The band gap of β -SiTe is 1.823 eV where the valance band maximum (VBM) occurs at Γ point while the conduction band minimum (CBM) occurs at M' point in the Brillouin Zone. The flatness of valance band top results in large density of states and heavy holes.

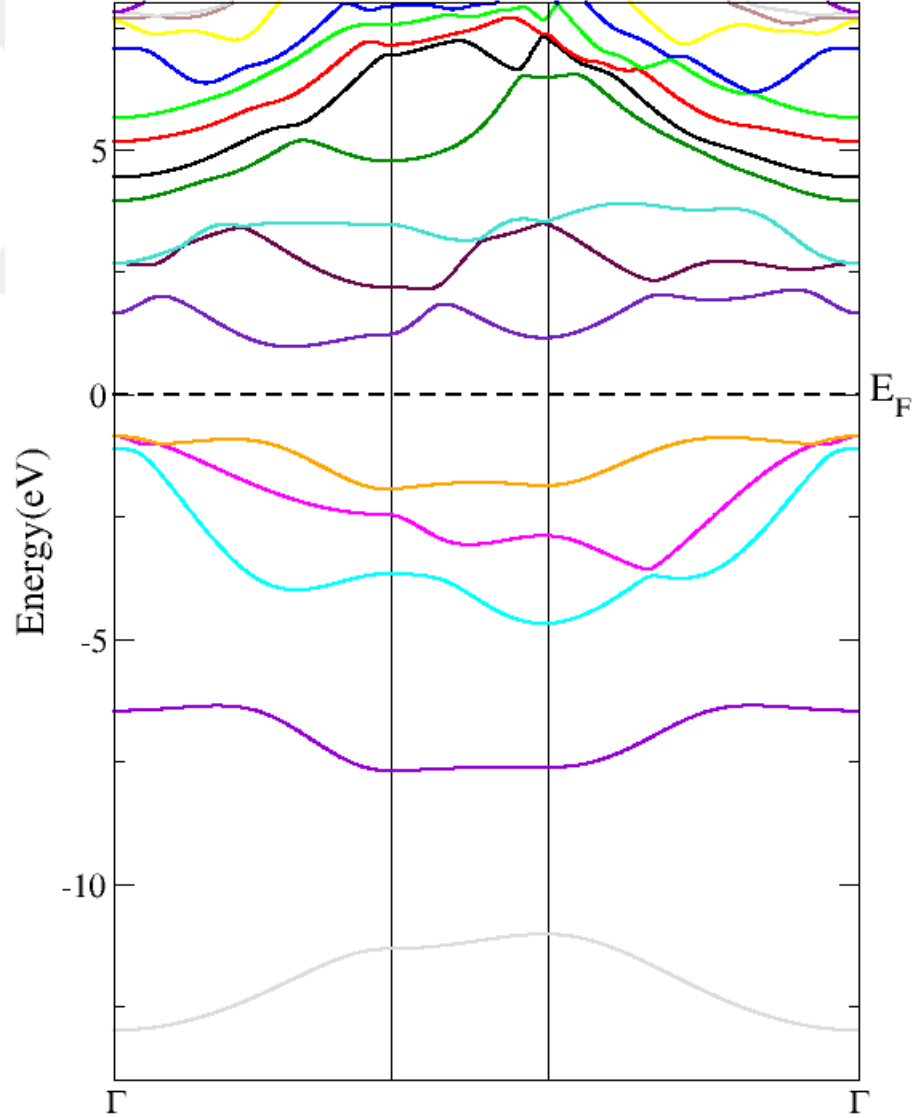
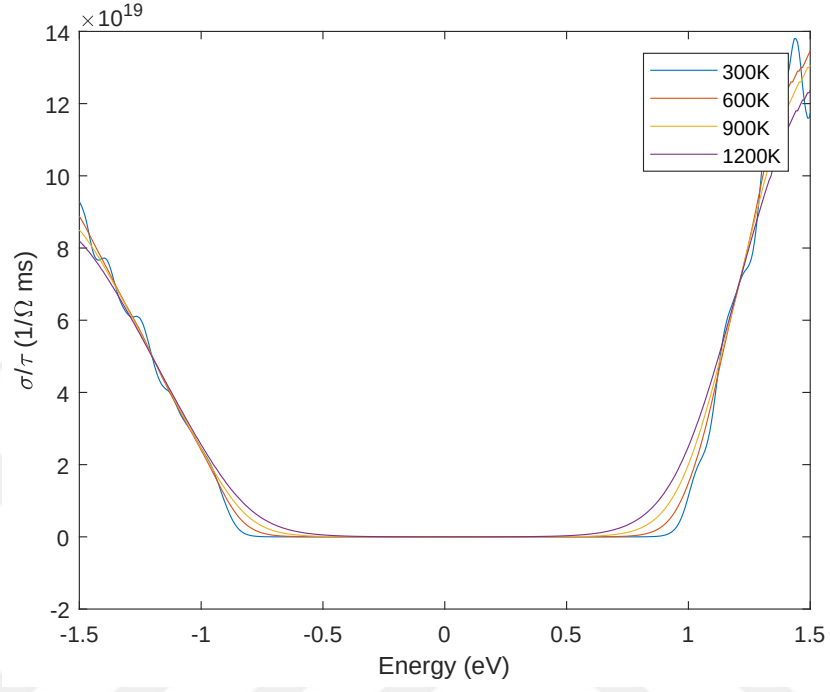


Figure 4.3: Electronic band structure of β -SiTe

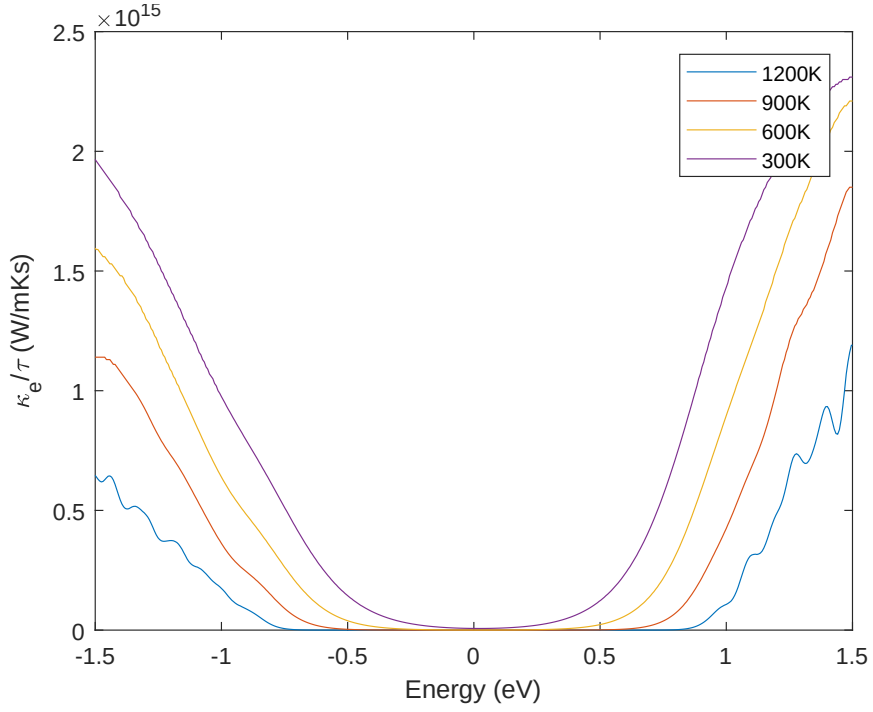
4.4 Electronic Transport properties

In this work, the electronic transport properties are computed using Boltzmann transport equation implemented in BoltzTraP code. The necessary transport coefficients are determined using a well-tested Fourier interpolation of electronic band structure. The results obtained using this approach are very close to the data obtained experimentally and can be used to gain insight into the thermoelectric properties of novel materials.

To derive the carrier concentrations from chemical potentials for p or n-type doping the Fermi level is lifted up and down. Thus for any material only the electronic band structure calculation is required. The transport coefficients are computed using a constant relaxation time. The Seebeck coefficient is determined free of relaxation time. However, the electrical conductivity and electronic thermal conductivity can only be computed with respect to the relaxation time. The electrical conductivity and electronic thermal conductivity of β -SiTe computed using BoltzTraP code w.r.t relaxation time σ/τ and κ/τ are plotted against chemical potential for different temperatures in fig. 4.4a and fig. 4.4b, respectively. It can be observed from the fig. 4.4b that electrons dominate the thermal conductivity unless μ is inside the band gap.



(a)



(b)

Figure 4.4: Electrical conductivity and electronic thermal conductivity versus chemical potential for different Temperatures

To obtain a high value for figure of merit (ZT), the thermal conductivity must decreased while keeping the electrical conductivity maximum. Since the thermal conductivity has contribution from both electronic and lattice conductivities, therefore reducing lattice thermal conductivity can greatly improve the thermoelectric performance of materials.

The performance of thermoelectric materials directly depends on the Seebeck coefficient, which measures the thermoelectric voltage induced by the temperature gradient across the material. The Seebeck coefficient for β -SiTe is plotted against chemical potential at different temperatures in fig. 4.5. The maximum value of Seebeck coefficient at room temperature is $290 \mu V/K$.

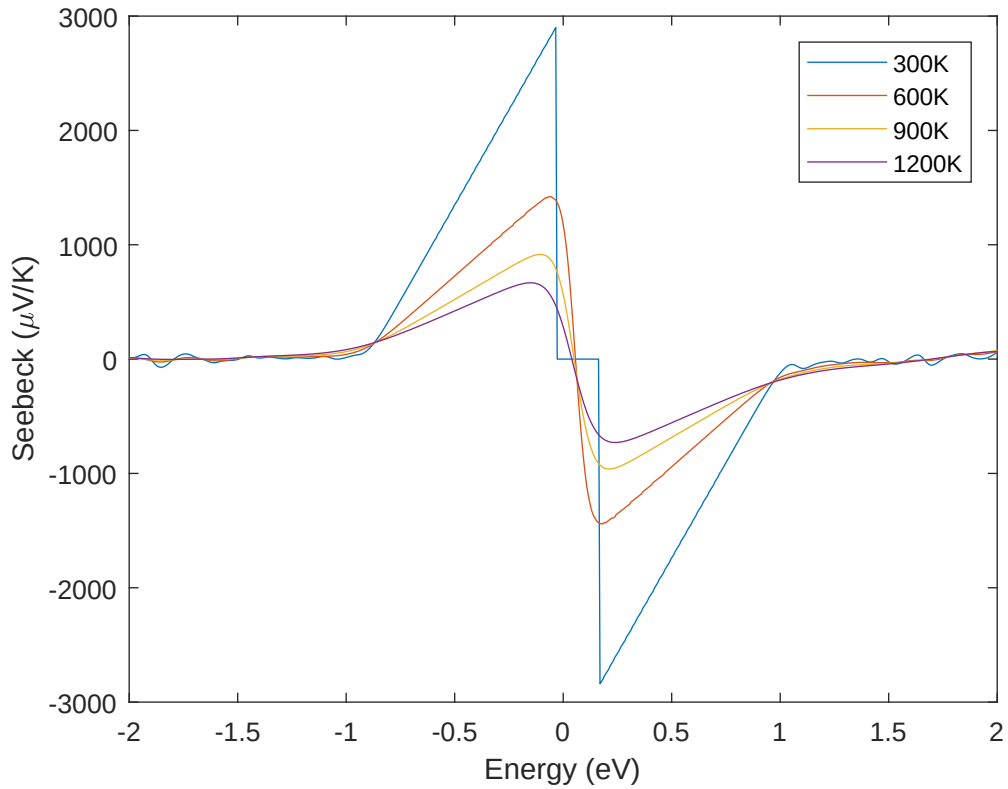


Figure 4.5: Seebeck versus chemical potential of β -SiTe

The thermoelectric efficiency of materials is centered on a dimensionless parameter known as the figure of merit, which can be expressed as

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_\ell} \quad (4.1)$$

Up till now we use only BoltzTrap code for the investigation of thermoelectric properties which does not calculate the lattice thermal conductivity. So the figure of merit obtained using BoltzTraP code does not contain κ_ℓ . The figure of merit (ZT) for β -SiTe obtained using BoltzTraP code versus chemical potential is plotted for different temperatures in fig. 4.6. The difference in ZT can be observed for different temperatures. The figure of merit value for β -SiTe at room temperature is 0.96. The relaxation time canceled out since σ and κ_e are both calculated with respect to relaxation time and thus we get a figure of merit free of τ .

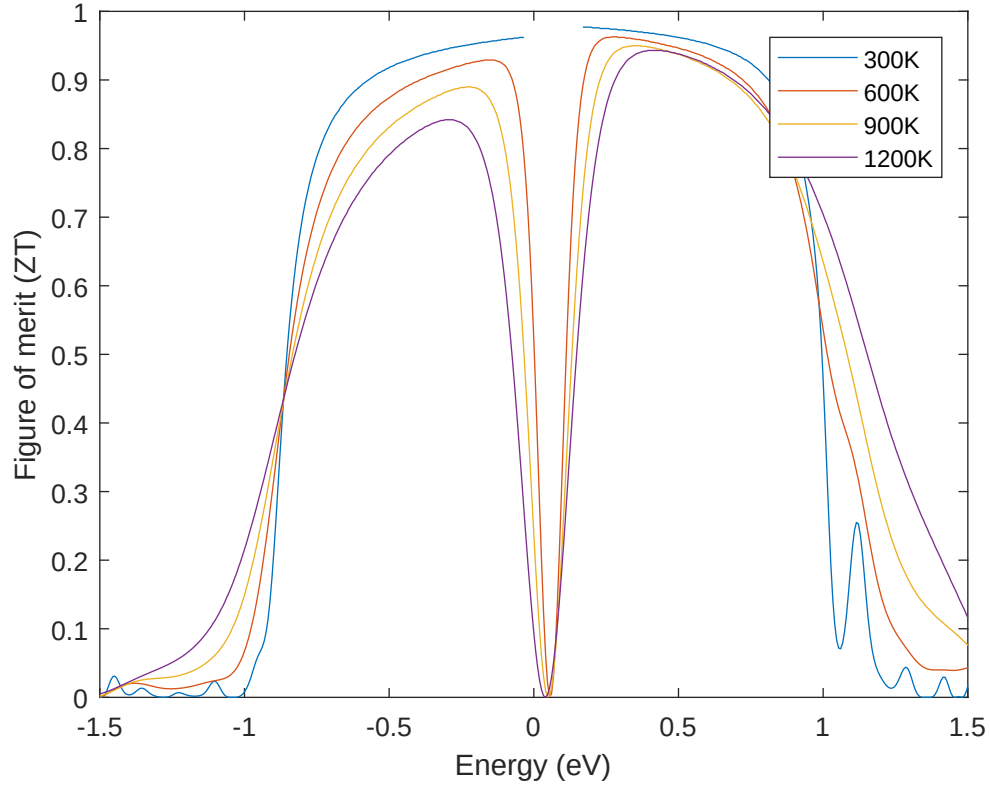
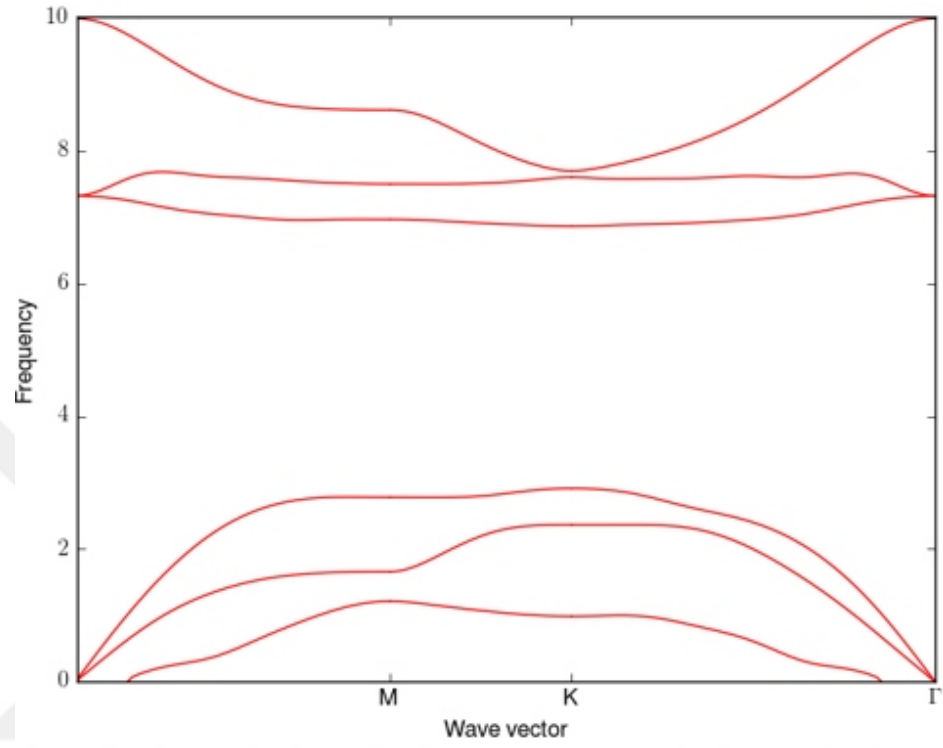


Figure 4.6: ZT versus chemical potential of β -SiTe

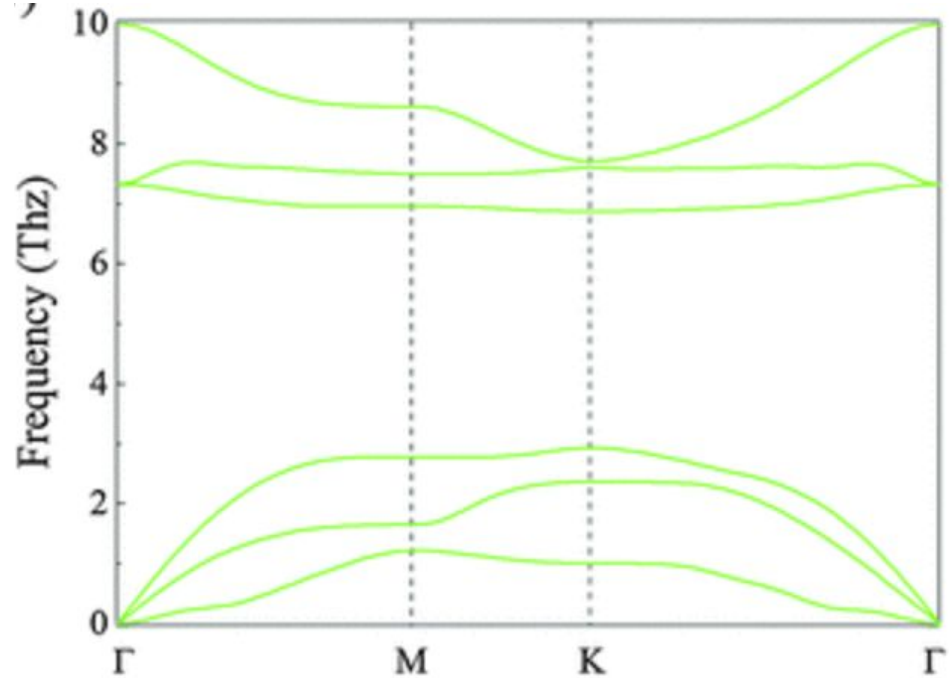
The relaxation time canceled out since σ and κ_e are both calculated with respect to relaxation time and thus we get a figure of merit free of τ .

4.5 Phonon Dispersions

The Phonon dispersions curves show the dependence of phonon energies on q vector along various high symmetry directions within the Brillouin Zone. For 2D β -SiTe the phonon dispersions are calculated using density functional perturbation theory (DFPT). PHONOPY package is used to get these dispersions from the 2^{nd} order force constants. Fig. 4.7a shows the phonon dispersions obtained in this work while fig. 4.7b shows the phonon spectra obtained by YU Chen *et al.* Our computed results are in excellent agreement with their data except for the negative frequencies near Γ point, which can be achieved by using a huge supercell but those calculations will be computationally much more expensive.



(a)



(b)

Figure 4.7: Phonon dispersions curves of β -SiTe

4.6 Phonon Density of States

To investigate the thermodynamic properties, the phonon density of states are required. Fig. 4.8 shows the total and partial phonon density of states versus frequency for β -SiTe. The contribution of atomic vibrations to the particular frequency range can be seen from the partial Phonon DOS, Where the heavy Te atom mainly contribute to the lower phonon branches while the light Si atom has great contribution to the upper phonon branches.

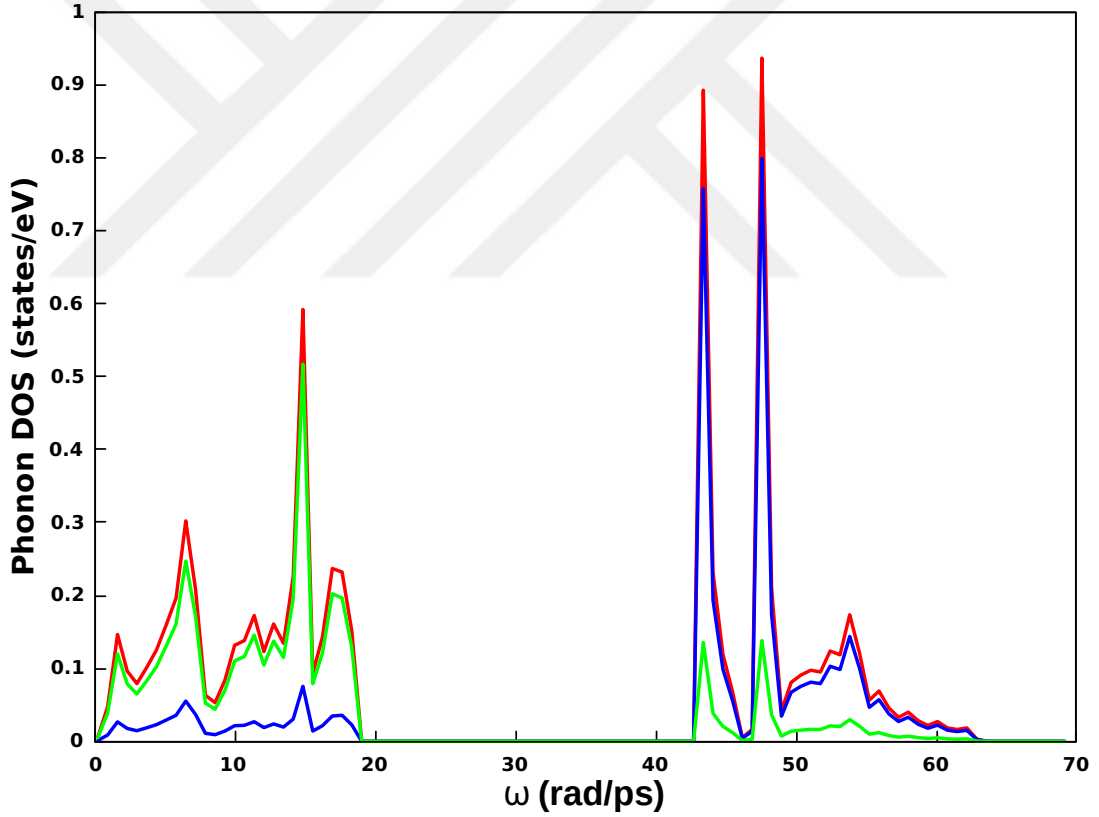


Figure 4.8: Total and partial phonon density of states of β -SiTe.

4.7 Lattice Thermal conductivity

The lattice thermal conductivity of β -SiTe is calculated from the harmonic and third-order anharmonic force constants determined using density functional perturbation theory (DFPT). A mesh of $16 \times 16 \times 1$ q -points with the default scale-broad value of 1.0 is used. The lattice thermal conductivity of β -SiTe versus temperature is given in fig. 4.9, where one can see the decreasing behaviour of thermal conductivity with temperature. At room temperature the lattice thermal conductivity is $0.13525 \times 10^{-2} \text{W/mK}$, which is 3 order of magnitude smaller than the value obtained by wang *et al* [84]. The very low value of lattice thermal conductivity is due to the negative phonon frequencies.

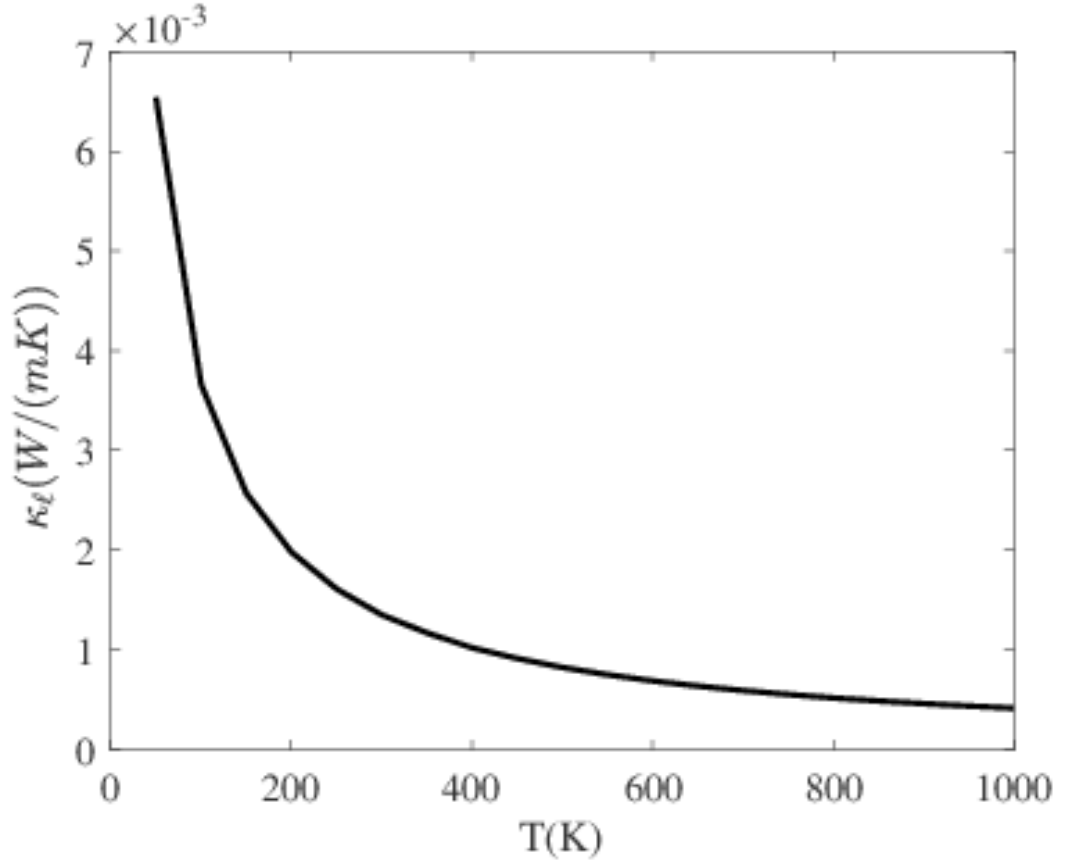


Figure 4.9: Lattice thermal conductivity versus temperature of β -SiTe

4.8 Lattice thermal conductivity (RTA)

The lattice thermal conductivity in relaxation time approximation is given in fig. 4.10, where the quantity Δ_λ in the expression $F_\lambda = \tau_\lambda^0(v_\lambda + \Delta_\lambda)$ is taken as zero, which gives the deviation of phonon mode and corresponding heat current from RTA prediction. One can see the effect of this deviation on thermal conductivity by comparing fig. 4.9 and fig. 4.10

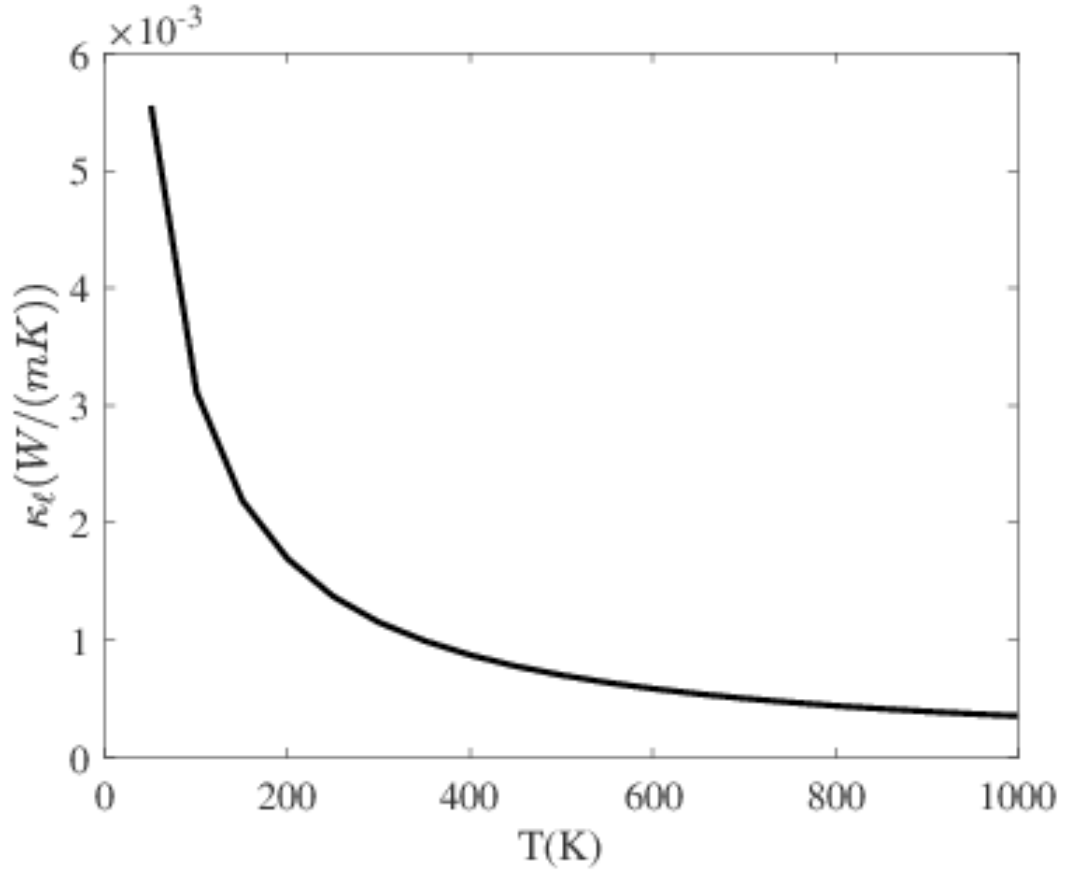


Figure 4.10: Lattice thermal conductivity versus temperature of β -SiTe within RTA

4.9 Cumulative Thermal conductivity

The cumulative lattice thermal conductivity versus maximum mean free path (MFP) at room temperature is given in fig. 4.11, where only phonons below a threshold mean free path are considered as these phonons are more relevant to the thermal conductivity. These quantities play a significant role since they predict the effects that the size of materials has on lattice thermal conductivity. It can be observed from the plot that with the increase of MFP, the cumulative lattice thermal conductivity increases until the MFP reaches a threshold value. The cumulative thermal conductivity reaches it's maximum value at of $0.135 \times 10^{-2} \text{W/mK}$ at maximum mean free path of 14.17 nm .

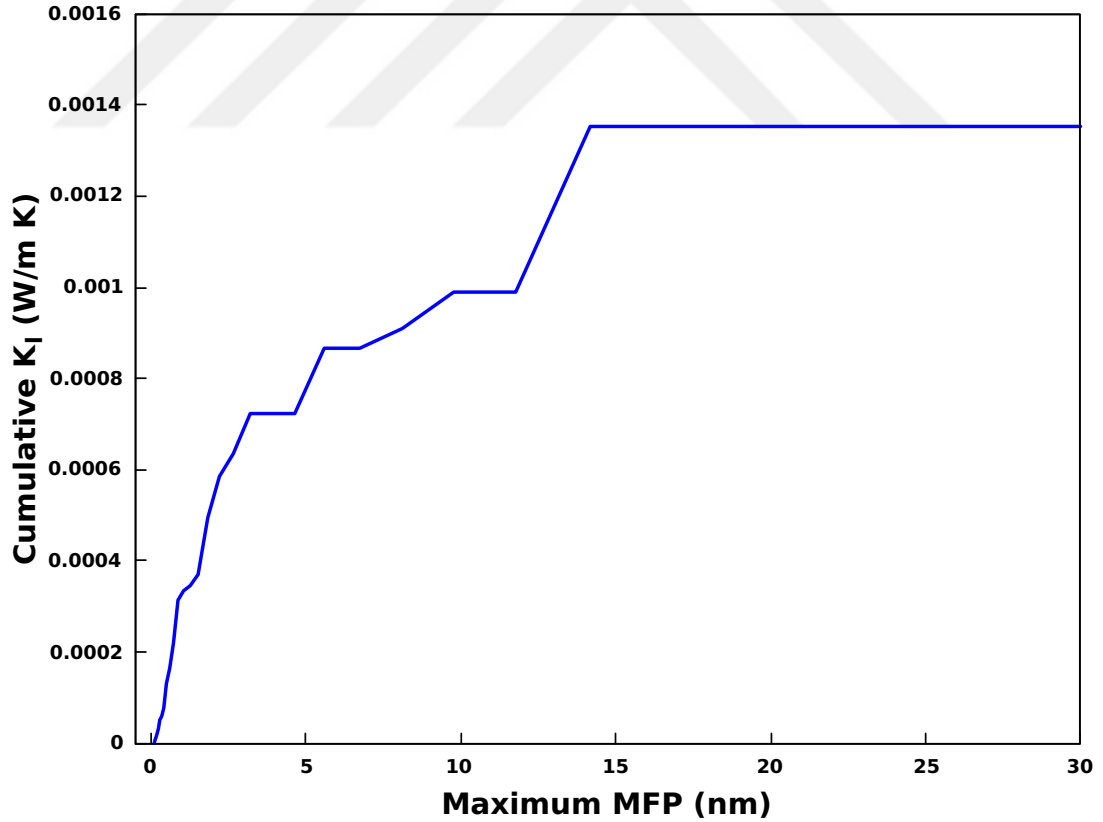


Figure 4.11: Cumulative lattice thermal conductivity versus maximum MFP of β -SiTe

4.10 Specific Heat

Heat capacity C_v is of great importance in condensed matter physics since it provide essential information about the vibrational properties of the system. The heat capacity C_v of β -SiTe is plotted against the temperature in fig. 4.12. The rapid increase in the C_v with the rise in temperature below $300K$ can be seen from the plot. The C_v is nearly propertional to T^3 which results from the anharmonic approximation. As the temperature increases this anharmonic effect on heat capacity reduces and thus above the room temperature, C_v approaches to a constant value [$C_v(T) = 3R$], obeying the Dulong-petit law. Additionally, it can also be inferred from the strong dependence of C_v on temperature below $300K$ that the atomic interaction favorably occur at low temperatures.

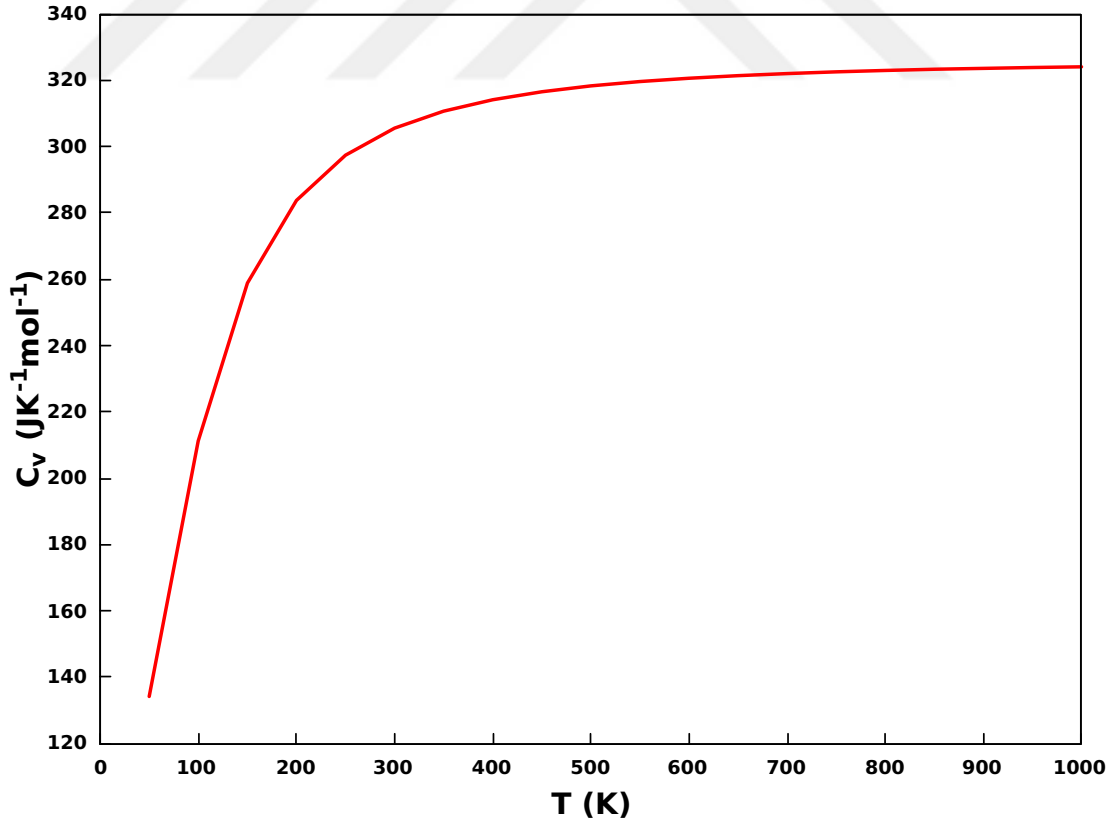


Figure 4.12: Heat capacity of β -SiTe versus temperature

4.11 Scattering Rates

The room temperature frequency dependent scattering rates of β -SiTe are presented in fig. 4.13 where the rates below 20 THz corresponds to the acoustic modes while those above 40 THz corresponds to the optical phonon modes. The total thermal conductivity has higher contribution from acoustic branches compare to that from the optical modes. Such high scattering rates greatly reduces the lattice thermal conductivity.

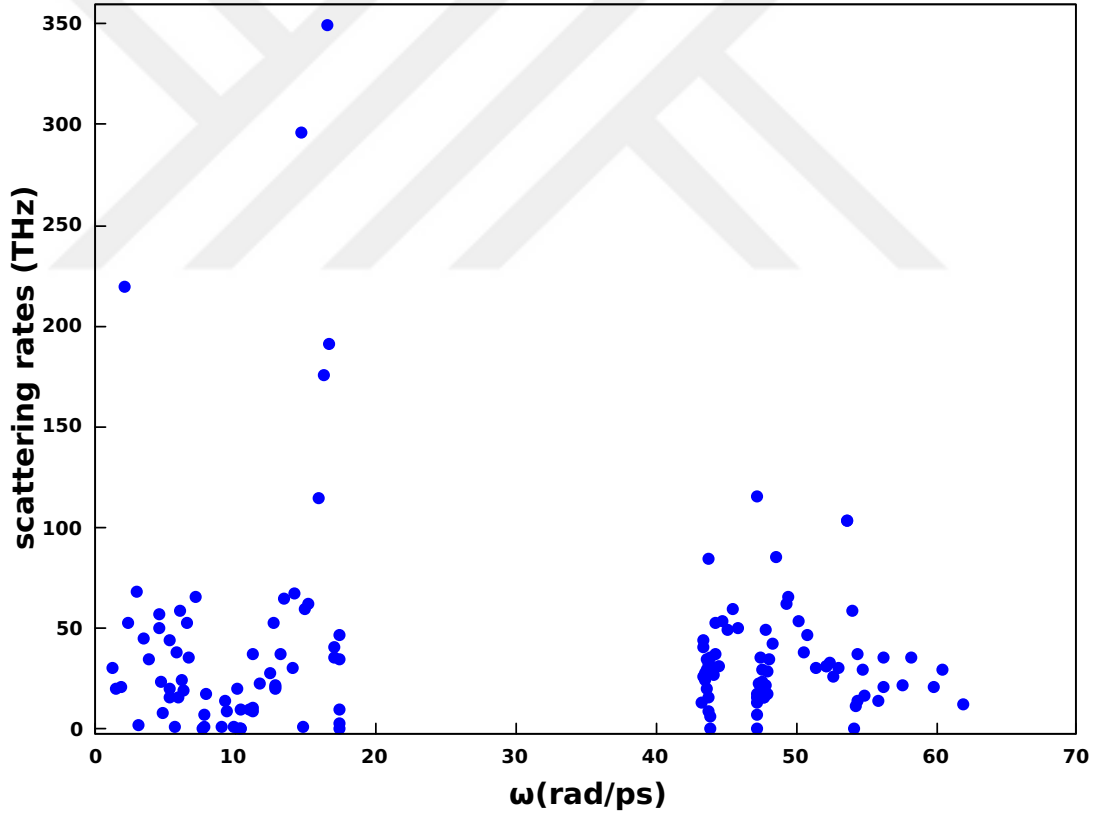


Figure 4.13: Phonon scattering rates in β -SiTe at room temperature calculated using $16 \times 16 \times 1$ q-point grid.

4.12 Figure of Merit

Finally the total figure of merit for β -SiTe is obtained after calculating the lattice thermal conductivity and is expressed as

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_\ell} \quad (4.2)$$

The constant relaxation time as obtained by Wang *et al* for β -SiTe is $31fs$ and $81fs$ for electrons and holes, respectively [84]. The figure of merit (ZT) is plotted versus temperature in fig. 4.14. An increasing behaviour of figure of merit With the addition of κ_ℓ can be observed.

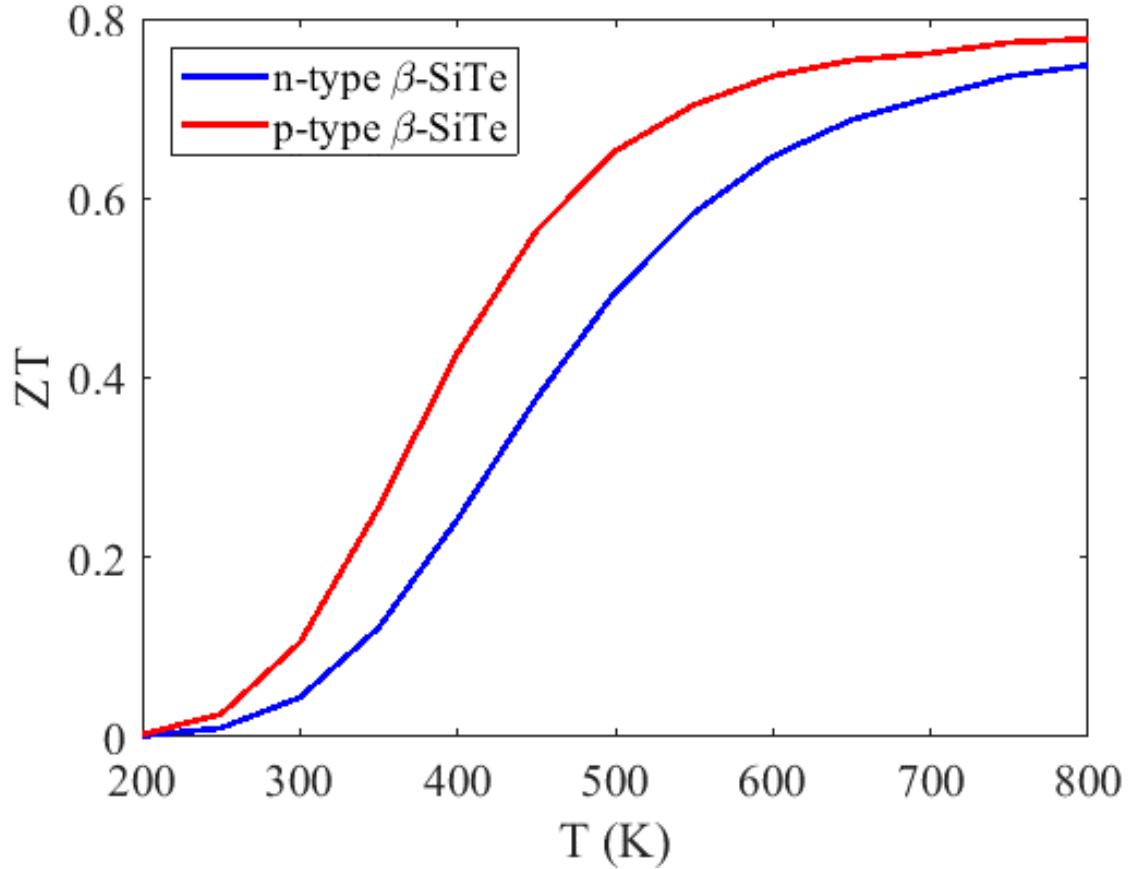


Figure 4.14: Figure of merit versus temperature of β -SiTe

At room temperature, the ZT has a value of 0.831 for a chemical potential of $\mu - \mu_0 = 1.7091(eV)$. The room temperature results for thermodynamic properties are given in table 4.1

Table 4.1: The room temperature results for thermoelectric coefficients and figure of merit ZT of β -SiTe

Seebeck Coefficient	ZT($\kappa_\ell = 0$)	κ_ℓ	Specific Heat (C_v)	ZT ($\kappa_\ell \neq 0$)
290 $\mu V/K$	0.96 (300k)	$0.13 \times 10^{-2} W/mK$	305.5 $J/mol K$	0.78 (800k)

Chapter 5

Conclusions

In this work the thermoelectric properties of novel 2 dimensional β -SiTe are investigated. Density functional theory was used along with Boltzmann transport equation to describe these thermoelectric properties. Firstly, to examine the electronic structure, the generalized gradient approximation developed by Perdew, Burke and Ernzerhof (PBE-GGA) was used. The electronic band structure and density of states were found in consistence with the previous theoretical data. Then the BoltzTraP code was used to calculate the electronic transport coefficients such as the conductivities and Seebeck coefficient. The figure of merit ZT was calculated using these transport coefficients while keeping the lattice thermal conductivity equals to 0 in the first part.

The second-order harmonic and third-order anharmonic force constants were calculated using Phonopy code and thirdorder.py respectively. Using these harmonic and anharmonic force constants the lattice thermal conductivity and all the lattice dependent transport properties were computed using Boltzmann transport equation implemented in ShengBTE code. Finally the calculated lattice thermal conductivity was added to the figure of merit ZT equation which characterizes the efficiency of thermoelectric materials.

Some major findings of this work are as follows:

- The maximum value of Seebeck coefficient of β -SiTe at room temperature is $290 \mu V/K$.
- The room temperature figure of merit of β -SiTe for $\kappa_\ell = 0$ as obtained from the BoltzTraP code is equal to 0.98
- The Specific heat C_v and lattice thermal conductivity κ_ℓ at room temperature is $305.5 J/mol K$ and $1.35 \times 10^{-3} W/m K$, respectively.
- The figure of merit obtained after adding the lattice thermal conductivity to the equation is $ZT = 0.78$, at 800k.
- β -SiTe is a potential candidate as thermoelectric material at high temperatures.

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