

Computational study of thermoelectric properties of two Heusler alloys and a wide gap semiconductor

**विद्या वाचस्पति की उपाधि की अपेक्षाओं की आंशिक पूर्ति
में प्रस्तुत शोध प्रबंध**

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CERTIFICATE

Certified that the work incorporated in the thesis entitled **“Computational study of thermoelectric properties of two Heusler alloys and a wide gap semiconductor”** submitted by **Vineet Kumar Pandey** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.



Date: 27-11-2023

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Declaration

I, Vineet Kumar Pandey, declare that this written submission represents my ideas in my own words and where others ideas have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.



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(Vineet Kumar Pandey)

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List of Publications

List of publications resulting from work presented in this thesis

1. Vineet Kumar Pandey, Prasenjit Ghosh, “Thermoelectric properties of Heusler-type $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ ”, (manuscript under preparation)
2. Kumar Saurabh, Vineet Kumar Pandey, Ankit Kumar, Navita Jakhar, Prasenjit Ghosh, Surjeet Singh, “Enhanced thermoelectric figure-of-merit in defective half-Heusler NbCoSb ”, *Materials Today Physics*, Volume 38, 101236, ISSN 2542-5293, (2023),
3. Gautam Sharma, Vineet Kumar Pandey, Shouvik Datta, Prasenjit Ghosh, “Effect of Electron-Phonon Coupling on Transport Properties of Monolayers of ZrS_2 , BiI_3 and PbI_2 : A thermoelectric Perspective”, *Physical Chemistry Chemical Physics*, 23, 11663-11671, (2021).

Synopsis

This thesis aims to explore and improve the thermoelectric performance of wide gap semi-conducting material and Heusler alloys using first principles calculation, focusing on the development of novel materials and design strategies. Thermoelectric materials have the unique ability to directly convert waste heat into useful electricity, offering tremendous potential for energy harvesting and waste heat recovery applications. However, their practical implementation has been hindered by the limited efficiency of existing materials. The thesis begins with an in-depth review of the fundamental principles of thermoelectricity, including the Seebeck, Peltier, and Thomson effects. It explores the key parameters that govern the thermoelectric performance of materials, such as electrical conductivity, Seebeck coefficient, and thermal conductivity. The challenges associated with simultaneously optimizing these parameters are discussed, providing a foundation for subsequent research.

The subsequent second chapter delves into the theoretical framework and computational techniques employed in first principle studies. Density functional theory (DFT) utilized to calculate electronic structures and its practical applications are briefly discussed. Further, the underlying approximations in the calculation of transport properties using semiclassical Boltzmann transport theory have been discussed. This is followed by a description of electron-phonon coupling calculations using many-body perturbation theory to improve the accuracy of the calculations. The imaginary part of electron self energy gives us the electron lifetime due to scattering by phonons, while the real part had been used to compute the renormalized band structure.

The third chapter of the thesis focuses on systematically investigating the effect of In doping on the thermoelectric properties of Fe_2VGa . We find that replacing Ga with larger sized In atoms induce local chemical pressure in the surrounding V octahedra that results in subtle changes in the band structure. While these changes help enhance the Seebeck coefficient, they are detrimental for electrical conductivity. These defects result in the scattering of phonons, which reduces the thermal conductivity in these materials.

In the fourth chapter of the thesis, I have investigated the effect of Sn doping on the electronic properties of a defect Heusler alloy $\text{Nb}_{0.8}\text{CoSb}$ to understand its thermoelectric properties. Here, we exploit the use of hole doping and alloy scattering to enhance the thermoelectric performance of defective NbCoSb .

The fifth chapter of the thesis conducts a thorough examination of the validity of certain approximations commonly employed in transport properties calculation. The accurate prediction of transport properties for novel materials necessitates the computation of carrier relaxation time. Traditionally, this is calculated using the deformation potential theory, which considers the coupling between electrons/holes and acoustic phonons. However, our research demonstrates that in the case of an ionic material (PbI_2 monolayer), the coupling between charge carriers and optical phonons is significantly substantial. Neglecting this coupling when calculating relaxation times not only leads to significant quantitative errors but also results in incorrect qualitative trends.

In the end, the summary and outlook chapter of this thesis provides a comprehensive overview of the key findings and implications of the research conducted on thermoelectric materials. It summarizes the main outcomes obtained throughout the thesis and offers a forward-looking perspective on future directions for advancing the field of thermoelectric materials research.

List of symbols

H	The Hamiltonian of a system
$\hbar$	Reduced Plank's constant
M	Mass of the nucleus
m	Mass of the electron
Z	Atomic number
e	Charge of an electron
$\mathbf{R}$	Nuclear coordinates
$\mathbf{r}$	Electronic coordinates
ϵ_n	Energy eigenvalues
$\Psi_n(\mathbf{R}, \mathbf{r})$	Eigenfunctions
$\chi_n(\mathbf{R})$	Coefficients of the electronic states
$V_{ext}(\mathbf{r})$	External potential
$E_{xc}[n]$	Exchange-correlation energy
$n(\mathbf{r})$	Charge density
$\mathbf{k}$	Wavevector
$\mathbf{G}$	Reciprocal lattice vector
r_c	Cut-off radius that separates the core and valence regions
k_B	Boltzmann's constant
T	Temperature
σ	Electrical conductivity
κ	Thermal conductivity
S	Seebeck coefficient

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Chapter 1

Introduction

A vital element of any economy in this age of technology is energy. Energy is the lifeblood of the world. The “Statistical Review of World Energy 2020” indicates that 84% of total primary energy consumption comes from coal, petroleum, and natural gas [2]. The energy consumption is expected to increase by 47% in the next 30 years. The supply of fossil fuels is limited and will be exhausted in the future. In addition, the International Energy Agency aims to achieve net-zero emission of CO₂ by 2050 [3]. Therefore, finding more efficient ways of utilizing energy and other sustainable forms, such as solar, wind power, and biofuel cells, is imperative. One of the ongoing directions regarding the production of clean energy is thermoelectric converters, which can effectively fulfill our energy demand.

1.1 Brief history of thermoelectrics

Direct conversion of heat into electricity and vice-versa is termed thermoelectricity. Thermoelectric devices have many advantages, such as requiring no moving part, not production of any harmful gases or chemical waste and safe. The term “thermoelectricity” encompasses three different effects: the Seebeck effect, the Peltier effect, and the Thomson effect. These are explained in brief in the following section.

1.1.1 Seebeck effect

In 1821, Thomas Seebeck observed that if we apply a temperature gradient (ΔT) across the ends of the material, a voltage difference (ΔV) gets generated across its ends due to the flow of carriers from the hotter side to the colder side. This phenomenon is known as the Seebeck effect. This effect is the underlying principle of thermoelectric generators.

The Seebeck coefficient is defined as the generated potential difference per unit applied temperature difference. It is given as

$$S = -\Delta V / \Delta T \quad (1.1)$$

The Seebeck coefficient's sign indicates the type of material; for example, if the Seebeck coefficient value is positive, we can infer that holes comprise the majority of the system's charge carriers, while if it is negative, electrons do.

1.1.2 Peltier effect

Jean Peltier observed this phenomenon in 1834. This is opposite to the Seebeck effect. If we apply an electric current through a junction, the heat is absorbed or emitted at the junction. This phenomenon is known as the Peltier effect. This effect is the underlying principle of thermoelectric cooling. The Peltier coefficient (Π) is defined by the rate of heat absorption or emission ($\partial Q / \partial t$) per unit applied current. It is written as

$$\frac{\partial Q}{\partial t} = \Pi I \quad (1.2)$$

The following figure 1.1 shows the schematic of the Seebeck and Peltier effect.

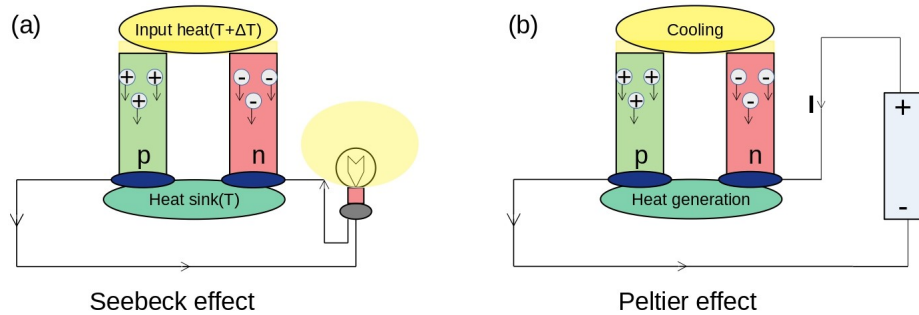


Figure 1.1: Display of (a) Seebeck effect (b) Peltier effect.

1.1.3 Thomson effect

The absorption or evolution of heat along a homogeneous sheet of material due to the flow of an electric current is known as the Thomson effect. In other terms, in the presence of a temperature gradient, the heating of the current flux in a conductor that carries current

is referred to as the Thomson effect. The gradient of the heat evolution or absorption is given by

$$\frac{\partial^2 Q}{\partial x \partial t} = \tau I \frac{\partial T}{\partial x} \quad (1.3)$$

where τ denotes the Thomson coefficient, $\frac{\partial T}{\partial x}$ is the temperature gradient across the material, and I is the current.

1.2 Mechanism of thermoelectric effects

The above-discussed thermoelectric effects involve two phenomena, i.e., charge-carrier diffusion and phonon drag. The former occurs when a material is kept in an environment with a temperature gradient. Because of the difference in carrier density at the hot end and cold end, the carriers from the hot side diffuse to the cold side to achieve a steady state. This diffusion of charge carriers at the cold end creates a net charge and generates a potential difference to counteract the chemical potential of the diffusion. As a result, it brings the system to equilibrium. The phonon drag effect is only significant at low temperatures. In this case, phonons, particularly with low frequency and longer mean free path, interact with electrons and lose their momentum. These electrons gain extra kinetic energy to overcome the generated electric field and contribute to the extra electric current and additional Seebeck coefficient. This is called as the phonon drag effect [4] because phonons traveling forward drag electrons with them to the cold side.

1.3 Efficiency and figure of merit of thermoelectric materials

The conversion ability from heat into electricity of a material is determined by a dimensionless quantity, known as the figure of merit (zT). The figure of merit is given by

$$zT = \frac{S^2 \sigma T}{\kappa} \quad (1.4)$$

where S represents the Seebeck coefficient, σ the electrical conductivity and T represents the absolute temperature. κ represents the total thermal conductivity (sum of lattice and

electronic contribution to thermal conductivity). The term “ $S^2\sigma$ ” is called the thermoelectric power factor.

Within the approximation of temperature independence of transport properties and low temperature gradient, the efficiency of thermoelectric material is related to its zT in the following manner:

$$\eta = \left(1 - \frac{T_C}{T_H}\right) \frac{\sqrt{(zT + 1)} - 1}{\sqrt{(zT + 1)} + T_C/T_H} \quad (1.5)$$

where T_H and T_C are the absolute temperature of hot and cold side and $T = \frac{T_C + T_H}{2}$. It is clear from the eqn.1.5 that high zT is needed to make an efficient thermoelectric device for cooling or electricity generation.

1.4 Governing parameters of thermoelectric performance

The performance of a thermoelectric material is determined by its zT value as given in eqn.3.11. Essentially, there are mainly two ways to augment the zT of the thermoelectric material: enhancing the thermoelectric power factor or decreasing the total thermal conductivity. The power factor of the system can be optimized by tuning the carrier concentration (n). The relationship of carrier concentration with S and σ within parabolic band and energy independent charge carrier scattering [5] is described as :

$$S = \frac{8\pi^2 k_b^2}{3eh^2} m_d T \left(\frac{\pi}{3n}\right)^{2/3} \quad (1.6)$$

$$\sigma = ne\mu = \frac{e^2 n \tau}{m_b} \quad (1.7)$$

Here e denotes the electronic charge, h denotes the Planck constant, and k_b denotes the Boltzmann constant. m_d denotes the density of states (DOS) effective mass, n denotes the carrier concentration, and T denotes the temperature. μ denotes the carrier mobility, τ denotes the carrier relaxation time, m_b denotes the band effective mass, and L denotes the Lorenz constant. The DOS effective mass is equal to the mass that provides the DOS using the DOS expression for isotropic parabolic band as given in eqn.1.8. The band effective mass is the second-order derivative of band energy in k-space as given in eqn. 1.9.

$$DOS(E) = \frac{8\pi\sqrt{2}}{h^3} m_d^{3/2} \sqrt{|E - E_m|} \quad (1.8)$$

where m_e is the electronic mass, E_m is the energy of the maxima or minima.

$$m_b = \frac{\hbar}{\frac{\partial^2 \epsilon}{\partial k^2}} \quad (1.9)$$

where ϵ is the band eigenvalue.

The total thermal conductivity is the sum of electronic thermal conductivity (κ_e) and lattice thermal conductivity (κ_l) as given in eqn. 1.10. According to Weidemann-Franz law, κ_e and σ are proportional to each other as given in eqn. 1.11, i.e., The electronic thermal conductivity increases with increase in carrier concentration.

$$\kappa = \kappa_e + \kappa_l \quad (1.10)$$

$$\kappa_e = L\sigma T = ne\mu\sigma T \quad (1.11)$$

These above equations infer that the values of the S , σ , and k_e must be chosen so that zT is optimized, as shown in the figure 1.2 [5].

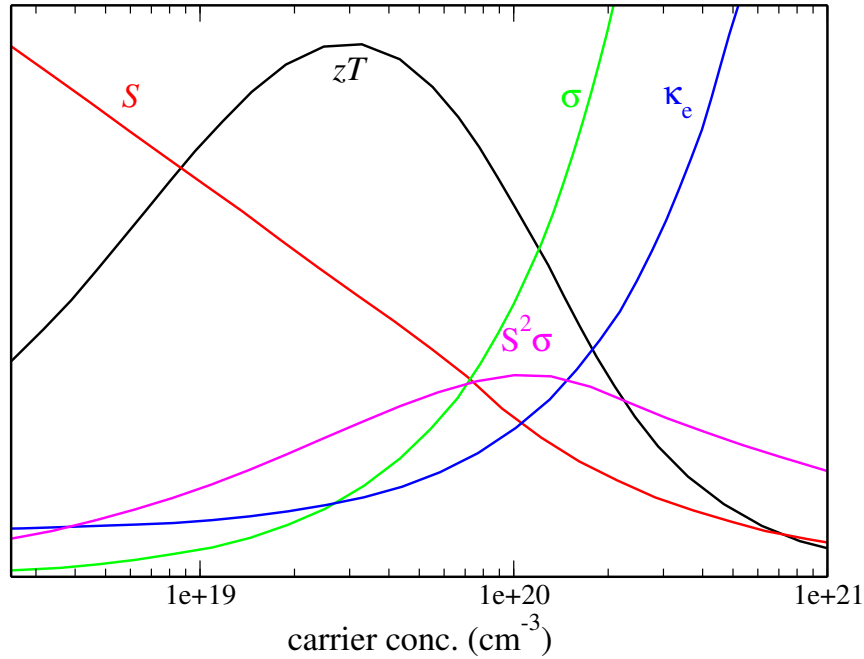


Figure 1.2: Relationship between S , κ_e , σ , $S^2\sigma$ and zT with carrier concentration

Hence to achieve a high thermoelectric power factor and zT , we need to balance be-

tween S and σ owing to the opposite behaviour of S and σ with carrier concentration, i.e., enhancing the Seebeck coefficient reduces the electrical conductivity and vice-versa. Moreover, the electronic thermal conductivity and electrical conductivity are proportional to each other. The other part of the thermal conductivity, i.e., κ_l , is independent of the carrier concentration. κ_l depends on the mass and size of the atoms, structural arrangement, defect, and vacancy in the materials. The κ_l can be reduced independently to augment the zT of the material.

1.5 Classification of thermoelectric materials

The thermoelectric materials can be divided into the following categories based on the operating range of temperature.

1.5.1 Low temperature materials

These materials are very effective for low-quality waste heat or cooling microelectronics. Their working range of temperature is around 4 K to near room temperature. Currently, Bi_2Te_3 based alloys are the best known thermoelectric material with zT around one, which dominates the industrial application till today [6–8]. However, it has low mechanical strength and a low abundance of tellurium elements. Besides this, Cu_2Se based alloys have shown zT varying between 0.4 - 0.7 [9]. However, these Cu_2Se based alloys lack chemical stability. The room temperature thermoelectric materials are very scarce in compared to high or medium temperature thermoelectric materials.

1.5.2 Medium temperature materials

These materials function effectively within 500 K-900K range of temperature. The binary and ternary chalcogenides have recently garnered more interest in thermoelectrics because of their complex structure and ultralow thermal conductivity. Currently, PbTe based alloys are mostly used for industrial applications [10–14]. Besides this, SnTe and GeTe based alloys are important in this region [15, 16].

1.5.3 High temperature materials

These materials are mainly effective for temperatures higher than 900 K. The most common material used is p-type and n-type SiGe alloys [17]. SiGe alloys have been used in space radioisotope thermoelectric generators (RTGs). Currently, many materials are being investigated; for example, a rare-earth chalcogenide $La_{3-x}Te_4$ gives a zT of 1.2 at 1300K for power generation [18] due to their high thermal stability at high temperatures. Besides, Zintl compounds, which are chemically stable at high temperatures owing to their salt-like structural environment, are also being investigated as plausible candidates for thermoelectric materials at high temperatures. Some of the intensely explored Zintl compounds are clathrates such as $Ba_8Ga_{16}Ge_{30}$ [19–21], AZn_2Sb_2 ($A=Ca, Sr, Ba$) [22–24], filled skutterudites [25–27], and $Yb_{14}MnSb_{11}$ [28–32]. Among all the Zintl phases, $Yb_{14}MnSb_{11}$ has the maximum zT of 1.3 at 1275K owing to its complex structure that causes low thermal conductivity [30].

Other than above discussed class of materials, the Heusler alloys have received great attention for thermoelectric properties. Heusler alloys are a kind of intermetallic alloys with chemical formula X_2YZ that crystalize in cubic space group $Fm\bar{3}m$ with Cu_2MnAl as prototype [33] where X and Y are transition metals and Z is the main group element. The X atoms occupy the tetrahedral sites, whereas Y and Z occupy the octahedral sites. It consists of four interpenetrating fcc sublattices. There is one more variant of the Heusler compound, Half-Heusler (HH) with chemical formula XYZ , where the other X site remains vacant. Due to their highly symmetric cubic structure, these compounds possess good electronic properties. These compounds are exceptionally stable, both chemically and mechanically at high temperatures. Many of these compounds are narrow band gap semiconductors, which makes them well suited for thermoelectric applications. The only shortcoming of Heusler alloys is their relatively high thermal conductivity. The possibility of substituting each fcc sublattice in the HH to optimize the thermoelectric performance is a great advantage. For example, one can introduce the disorder by doping at the X and Y positions to reduce the thermal conductivity and simultaneously, we can change the carrier concentration by substitution at the Z position to enhance the electronic properties. The most attractive properties of the Heusler alloys are their high Seebeck coefficient and high electrical conductivity [34–37]. Among the known Heusler alloys, $MCoSb$, $MNiSn$ ($M=Hf, Ti, Zr$) [38, 39] and Co_2TiZ ($Z=Ge, Al, Si, Sn$) [40, 41] and Fe_2VAl [42–44] have received great attention due to their unusual transport properties. It is worth noting that

Heusler alloys fulfill the industrial demand like low-cost, environment friendly, chemical and mechanical stability and raw materials availability. Heusler alloys function effectively in mid and high temperature range.

1.6 Strategies to improve zT

Though all materials show some thermoelectric effects, their efficiency is very low for practical applications. The eqn. 1.5 suggests that the efficiency of a thermoelectric material increases with increase in the figure of merit. We know that there are mainly two ways to improve the zT of thermoelectric materials: by reducing the lattice thermal conductivity or augmenting the power factor ($S^2\sigma$). In the following, we discuss the two methods to augment the thermoelectric power factor of the system and phonon glass electron crystal method to reduce the lattice thermal conductivity in brief.

1.6.1 Band engineering

From eqn. 1.6 and eqn. 1.7, we know that the Seebeck coefficient and electrical conductivity depend upon the DOS effective mass (m_d) and band effective mass (m_b). These parameters are calculated from the electronic band structure. The band effective mass is calculated as below The m_d is equal to the mass, which provides the DOS for isotropic maxima or minima under parabolic approximation as given in the eqn. 1.8.

Eqn. 1.8 suggests that m_d depends upon the variation of DOS with respect to energy. Substitution of dopants into the multi-band system can make the multiple bands align in energy, known as band convergence and modification in the band dispersion. The convergence of bands significantly modifies the DOS and, in turn, will enhance the m_d , the Seebeck coefficient. The modification in the band dispersion may decrease the band effective mass and, in turn, augment the electrical conductivity. Overall, it improves the thermoelectric power factor of the system. The pictorial representation of enhancement in thermoelectric power factor is given in the following figure 1.3. Figure 1.3 (a) shows the schematic of a band dispersion in E-k space in green color and figure 1.3 (b) shows the corresponding DOS for the band structure in green color. Figure 1.3 (c) shows the S and σ shown by solid black line corresponding to the band structure and DOS shown in green color. The effect of doping upon the band structure and DOS is shown by light green color in the figure 1.3 (a) and (b), respectively where the bands have aligned in energy near the Fermi level and band dispersion is modified as well. This modification leads to

the enhancement in both S and σ and in turn, power factor is enhanced as shown by the solid red line.

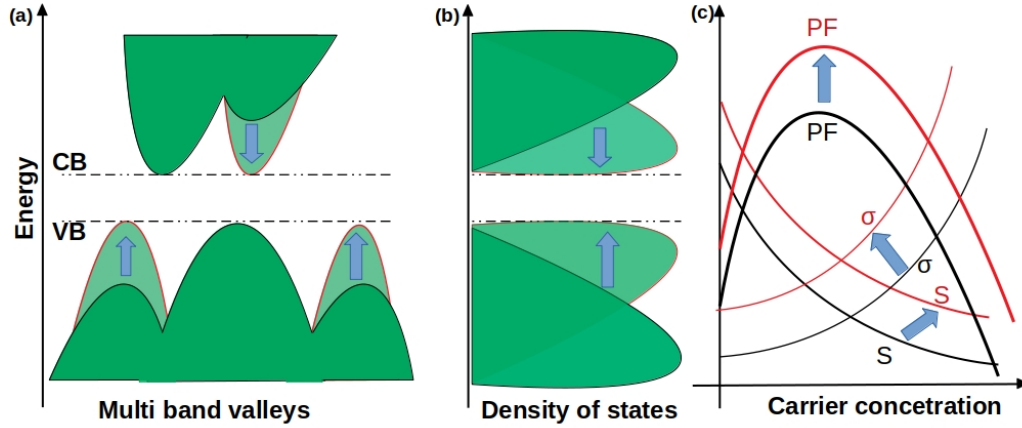


Figure 1.3: Effect of band engineering upon (a) electronic band structure (b) Density of states (c) transport properties

We have employed this band engineering technique to enhance the thermoelectric properties of In doped Fe_2VGa and Sn doped $\text{Nb}_{0.8}\text{CoSb}$.

1.6.2 Reduction of dimensionality

As we infer from the figure 1.3, the modification in DOS can significantly modify the transport properties. The DOS of the system can be enhanced by reducing the dimension of the system to approach the quantum scale. Dresselhaus et al. proposed this strategy to design new thermoelectric material with enhanced zT [45, 46]. Theoretically, the quantum well structure of Bi_2Te_3 was reported to have enhanced thermoelectric properties by augmenting the Seebeck coefficient owing to the suitable modification in DOS with dimensional reduction [45]. These predictions have given a new direction to designing novel thermoelectric materials. We have studied the thermoelectric properties of monolayer PbI_2 in chapter 5 and found that the monolayer of PbI_2 develops a Mexican hat-shaped feature in electronic band structure, which enhances the Seebeck coefficient and, in turn, thermoelectric properties.

1.6.3 Phonon glass electron crystal

Slack proposed that the lattice thermal conductivity of a system can be reduced without affecting the electronic properties known as phonon glass electron crystal approach (PGEC) [47]. Since phonons with varying mean free paths are the primary carriers for heat and glasses have the low thermal conductivity owing to the random arrangement of lattice and crystals have good electronic properties due to symmetry, i.e., a thermoelectric material should have glass like thermal conductivity and crystal like electrical conductivity. This is known as PGEC. PGEC can be achieved in thermoelectric material by alloying with different isoelectronic elements. Doping with different isoelectronic atom causes the size and mass disorder in the system and causes the reduction in the scattering of phonons and in phonon frequency without affecting the electronic properties of the system. For example, complex crystal structures show PGEC behaviour such as CsBi_4Te_6 , which is more complex than Bi_2Te_3 has lower lattice thermal conductivity and gives zT of 0.8 [48]. Other examples of PGEC are Zn_4Sb_3 [49], $\text{Yb}_{14}\text{MnSb}_{11}$ [31] and $\text{K}_2\text{Bi}_8\text{Se}_{13}$ [50].

1.7 Thesis outline

The rest of the thesis is arranged as follows.

Chapter 2 is devoted to the computational methods used to calculate the electronic and transport properties of the materials.

Further, this thesis is partitioned into two parts.

Part 1

This part is devoted to studying the effect of band engineering upon the transport properties of Fe_2VGa (full Heusler alloy) and NbCoSb (Half Heusler alloy).

Fe_2VGa is a promising thermoelectric material owing to its thermoelectric power factor. We substitute Ga with In to study the effect on the structure, electronic properties, and transport properties of Fe_2VGa . The results of our study are discussed in **Chapter 3**.

In **Chapter 4**, we study the effect of excess Nb and Sn doping upon the structural and electronic properties of $\text{Nb}_{0.8}\text{CoSb}$ to understand the experimentally measured transport

properties of $\text{Nb}_{0.83}\text{CoSb}_{0.9}\text{Sn}_{0.1}$. We found that doping of Nb significantly converges the bands near the Fermi level and, in turn, modifies the transport properties of the system. The detailed results are presented in **Chapter 4**.

Part 2

This part includes the study of transport properties of 2D PbI_2 using conventional computational methods. Additionally, we removed the constant relaxation time approximation (CRTA) using electron-phonon interaction and used the temperature-dependent band structure to understand their effect on transport properties. We found that transport properties alter significantly because of the strong coupling of electrons with polar optical phonons. The detailed study is given in **Chapter 5**.

Chapter 2

Theoretical methods

This chapter consists of details of theoretical methods used in this thesis. We calculate the material's properties from the first principles using the many-body Schrödinger equation (SE). However, due to the complicated nature of interactions, it is not realistic to do so. Thereby, some approximations are invoked. This chapter briefly describes the challenges to solving the many-body SE and describes methods, mainly density functional theory, developed to overcome the challenges. We further discuss the theory of electron-phonon interaction and semiclassical Boltzmann transport theory in solids.

2.1 Many body Schrödinger equation

Condensed matter comprises n negatively charged electrons and N positively charged nuclei communicating with each other through Coulomb forces. The time-independent Schrödinger equation (T.I.S.E.) of a system is

$$H_{total}\Phi(\mathbf{r}, \mathbf{R}) = E_{total}\Phi(\mathbf{r}, \mathbf{R}) \quad (2.1)$$

$\Phi(\mathbf{r}, \mathbf{R})$ is a many-body total wavefunction dependent upon the position coordinates of all the electrons $\{\mathbf{r}\}$ and nuclei $\{\mathbf{R}\}$ in the system. The Hamiltonian (H_{total}) of the system is given as

$$\begin{aligned} H_{total} = & -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{I=1}^{N_n} \frac{\hbar^2}{2M_I} \nabla_I^2 - \frac{1}{4\pi\epsilon_0} \sum_{I=1}^{N_n} \sum_{i=1}^{n_e} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \\ & + \frac{1}{8\pi\epsilon_0} \sum_{i=1}^{n_e} \sum_{\substack{j=1 \\ i \neq j}}^{n_e} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} + \frac{1}{8\pi\epsilon_0} \sum_{I=1}^{N_n} \sum_{\substack{J=1 \\ I \neq J}}^{N_n} \frac{Z_J Z_I e^2}{|\mathbf{R}_J - \mathbf{R}_I|}, \end{aligned} \quad (2.2)$$

where e is the electronic charge and Z_I is I^{th} nuclei's atomic number, respectively. n_e and N_n represent the number of electrons and nuclei, respectively. m_e and M_I represent the masses of an electron and I^{th} nuclei, respectively. In the eq. (2.2), 1st and 2nd terms are the kinetic energy (KE) of the electrons and nuclei, respectively. The 3rd, 4th and 5th terms are the Coulombic interaction of electron-nuclei, electron-electron and nuclei-nuclei, respectively. In principle, T.I.S.E. can retrieve the system's information. However, the non-local interaction terms pose the problem while solving the eqn. (2.2). Hence, several approximations are needed to solve it further.

2.2 Born-Oppenheimer approximation

Born-Oppenheimer approximation(BO) assumes that nuclei and electronic wavefunction can be treated separately because a nucleus has a greater mass than an electron ($\frac{m_{proton}}{m_{electron}} \approx 1836$). Owing to the high mass of nuclei, nuclei move much slower than the electrons. To put it another way, compared to nuclei, the motion of electrons has a quite small time scale ($\tau_{electron} \ll \tau_{nuclei}$). Hence, it is safe to assume that the electrons will immediately respond to the nuclei movement without changing their electronic states, i.e., the electronic and nuclear motion can be separated. This is known as the Born-Oppenheimer approximation. Expanding the total wavefunction $\Phi(\mathbf{r}, \mathbf{R})$ in the complete set of electronic wavefunction ($\psi_n(\mathbf{r}; \mathbf{R})$), where the expansion coefficients are the nuclear wavefunction ($\rho_N(\mathbf{R})$) can be written as follows:

$$\Phi(\mathbf{r}, \mathbf{R}) = \sum \rho_N(\mathbf{R}) \psi_n(\mathbf{r}, \mathbf{R}) \quad (2.3)$$

Substituting eqn.2.3 to eqn.2.1 and neglecting the terms that couple the KE of the electron and the nucleus, the electronic part of the Schrödinger equation (SE) for a given $\{\mathbf{R}\}$ can be written as:

$$\left(-\frac{\hbar^2}{2m} \sum_{i=1}^{n_e} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{I=1}^{N_n} \sum_{i=1}^{n_e} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{8\pi\epsilon_0} \sum_{i=1}^{n_e} \sum_{\substack{j=1 \\ i \neq j}}^{n_e} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} \right. \\ \left. + \frac{1}{8\pi\epsilon_0} \sum_{I=1}^{N_n} \sum_{\substack{J=1 \\ I \neq J}}^{N_n} \frac{Z_I Z_J e^2}{|\mathbf{R}_J - \mathbf{R}_I|} \right) \psi_n(\mathbf{r}, \mathbf{R}) = E_n^{ele}(\mathbf{R}) \psi_n(\mathbf{r}, \mathbf{R}) \quad (2.4)$$

where the term E_n^{ele} is the electronic energy. In the above eqn, the nuclei-nuclei repulsion term is constant as the positions of the nuclei are kept fixed. Nevertheless, the non-local

electron-electron (two-body) interaction term is present in the eqn. (2.4). Thus, the analytic solution to electronic SE is not feasible, and further approximations are required.

2.3 Density functional theory

The quantum mechanics uses wavefunction as a tool to solve the SE. The wavefunction depends upon the $3N$ spatial coordinates for a given many-body system with N number of particles. In 1928, Hartree assumed that electrons are independent of each other and move independently in an average potential of all the other electrons called as the Hartree potential [51]. He approximated the all electron wavefunction with a wavefunction, which is the product of all the single electron's wavefunctions. The wavefunction in this approximation does not comply with Pauli's principle, i.e., its wavefunction is not antisymmetric with respect to the exchange of electrons.

Hartree-Fock came up with an idea to use the Slater determinant as a wavefunction instead of the Hartree product of electron's wavefunction [52]. A Slater determinant takes care of the antisymmetry of the electronic wavefunction with respect to the exchange of the coordinates, which is a consequence of the Pauli exclusion principle. This gives rise to another term in the Hartree Fock Hamiltonian, known as exchange energy. The exchange energy lowers the total energy of the system. However, it still assumes the electrons move in the Hartree potential and omits the correlation effect in energy. Moreover, The traditional wavefunction-based approaches become increasingly difficult to handle as the number of particles in a system grows due to the exponential scaling of the electronic wavefunction with the number of particles.

In 1927, Thomas and Fermi introduced charge density as the basic variable. This results in an advantage over the wavefunction based methods. Density being a scalar quantity, depends only on the position, which is a function of three coordinates. They described the kinetic energy of the system as a function of electron density [53, 54]. They assumed the electrons to be classical particles so that their potential energy could also be written in terms of electron density. The Thomas Fermi model did not include the exchange and correlation terms in energy. This model had major drawbacks; for example, it could not explain the shell structure of atoms and the stability of molecules, i.e., the binding energy of the formed molecules was positive in this model. The modern day DFT does not have this issue, which is discussed below in details.

DFT is originally based on two theorems formulated by Hohenberg and Kohn (HK) that set the foundation for the presently used theory behind electronic structure calculations. The main idea of DFT is to consider the charge density ($\rho_e(\mathbf{r})$) as the basic variable instead of the many-body electronic wavefunction. By doing so, the many-body problem can be greatly simplified with a reduction of the degree of freedom from $3n_e$ variables to 3 (n_e is the number of electrons). This theory applies to any interacting system in an external potential ($V_{ext}(\mathbf{r})$) due to ions (nuclei). In the rest of the discussion, the attractive ionic potential is considered as the external potential. The Hamiltonian for many-body interacting system is given as (within Hartree atomic units; $m=\hbar = 4\pi\epsilon_0 = e = 1$),

$$H_{in} = - \sum_i \frac{\nabla_i^2}{2} + \sum_{i \neq j} \frac{1}{2|\mathbf{r}_j - \mathbf{r}_i|} + \sum_i V_{ext}(\mathbf{r}_i). \quad (2.5)$$

where $\mathbf{r}_i$ denotes the position of the i^{th} electron.

The DFT is based on the following two theorems proposed by Hohenberg and Kohn in 1964 [55].

1st theorem: For a given external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely by the ground state (GS) density $\rho_G(\mathbf{r})$, except for a constant.

It is impossible for two different external potentials to produce the exact same GS charge density ($\rho_G(\mathbf{r})$).

$$\rho_G(\mathbf{r}) \longrightarrow V_{ext}(\mathbf{r}). \quad (2.6)$$

2nd theorem: A *universal functional* for the energy $E[\rho_e]$ can be defined as function of the density $\rho_e(\mathbf{r})$, valid for any external potential $V_{ext}(\mathbf{r})$. For any given $V_{ext}(\mathbf{r})$, the exact GS energy of the system is the global minimum value of this functional, and the density $\rho_e(\mathbf{r})$ that minimizes the functional is the exact GS density $\rho_G(\mathbf{r})$.

It implies that GS density ($\rho_G(\mathbf{r})$) minimizes the energy functional $E[\rho_e]$ and in this way can calculate the GS energy (E_{min}). In brief, if $\rho_G(\mathbf{r})$ is known, The GS properties of the system would be determined uniquely.

For a known $V_{ext}(\mathbf{r})$, the HK energy functional (E_{HK}) is given by:

$$E_{HK}[\rho_e] = F_{HK}[\rho_e] + \int V_{ext}(\mathbf{r})\rho_e(\mathbf{r})d\mathbf{r}, \quad (2.7)$$

where $F_{HK}[\rho_e]$ is sum of the electron-electron interaction energy ($E_{ee}[\rho_e]$) terms and the KE of the interacting electrons ($T[\rho_e]$). The $F_{HK}[\rho_e]$ is therefore can be written as:

$$F_{HK}[\rho_e] = E_{ee}[\rho_e] + T[\rho_e]. \quad (2.8)$$

With the HK theorem, the calculation of GS properties of an interacting system becomes much simpler via a charge density-based approach. However, the functional form of $F_{HK}[\rho_e]$ is not known. The following section briefly describes the practical way to formulate the $F_{HK}[\rho_e]$ proposed by Kohn and Sham.

2.3.1 The Kohn-Sham (KS) Ansatz

KS tackled this problem of unknown functional ($F_{HK}[\rho_e]$) [56] in 1965 by resolving it numerically by replacing interacting electrons with an auxiliary system of non-interacting electrons. Kohn and Sham proposed the following ansatz [57] :

- The GS density of the auxiliary system is likewise the actual system.
- The calculations are performed for a single electron with the KE term and an effective local potential ($V_{\text{eff}}(\mathbf{r})$) defined by Hamiltonian (H_0) (within the Hartree atomic units $m=\hbar=4\pi\epsilon_0=e=1$).

$$H_0 = -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \quad (2.9)$$

Following these two ansatz, they replaced the $F_{HK}[\rho_e]$ expression in the following manner:

$$F_{KS}[\rho_e] = T_0[\rho_e] + E_{ee}[\rho_e] = T_0[\rho_e] + E_{xc}[\rho_e] + E_H[\rho_e], \quad (2.10)$$

where E_{xc} is the sum of the exchange and correlation energy and E_H is the Hartree energy. Here $T_0[\rho_e]$ is the GS KE of the auxiliary system of non-interacting electrons and written as:

$$T_0[\rho_e] = \sum_j \int \frac{1}{2} |\nabla\psi_j(\mathbf{r})|^2 d\mathbf{r}. \quad (2.11)$$

where ψ_j is the single electron wavefunction. The term $T_0[\rho_e]$ is different than the $T[\rho_e]$ (KE of many-body interacting system) . The Hartree energy $E_H[\rho_e]$ is given as.

$$E_H[\rho_e] = \int \int \frac{1}{2} \frac{\rho_e(\mathbf{r}')\rho_e(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}d\mathbf{r}', \quad (2.12)$$

$E_{KS}[\rho_e]$ is written as:

$$E_{KS}[\rho_e] = F_{KS}[\rho_e] + \int V_{\text{ext}}(\mathbf{r})\rho_e(\mathbf{r})d\mathbf{r}. \quad (2.13)$$

KS equations (2.17) can be derived by minimizing $E_{KS}[\rho_e]$ for a system of non-interacting electrons in local effective Kohn-Sham potential ($V_{KS}(\mathbf{r})$) known as ‘‘Hohenberg-Kohn variational principle’’ and written as:

$$\frac{\delta E_{KS}[\rho_e]}{\delta \rho_e} = 0 \quad (2.14)$$

The functional form of $V_{KS}(\mathbf{r})$ is given by:

$$V_{KS}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{xc}(\mathbf{r}) + \int \frac{\rho_e(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}', \quad (2.15)$$

the second term on the R.H.S represents the exchange-correlation potential (V_{xc}) defined as in eqn.(2.16) and the 3rd term is the Hartree potential (V_H).

$$V_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta \rho_e(\mathbf{r})}, \quad (2.16)$$

With knowledge of V_{KS} , the single electron KS equation derived by minimising $E_{KS}[\rho_e]$ can be solved to obtain the GS properties of the interacting system:

$$\left(-\frac{\nabla_j^2}{2} + V_{KS}(\mathbf{r}) \right) \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}). \quad (2.17)$$

where, $\psi_j(\mathbf{r})$ is Kohn-Sham orbitals gives $\rho_e(\mathbf{r})$ as $\rho_e(\mathbf{r}) = \sum_{j=1}^{n_e} |\psi_j(\mathbf{r})|^2$.

We solve the single electron KS equation for all the non interacting n electrons and the solution of the set of n KS equations (2.17) gives the GS properties of the system.

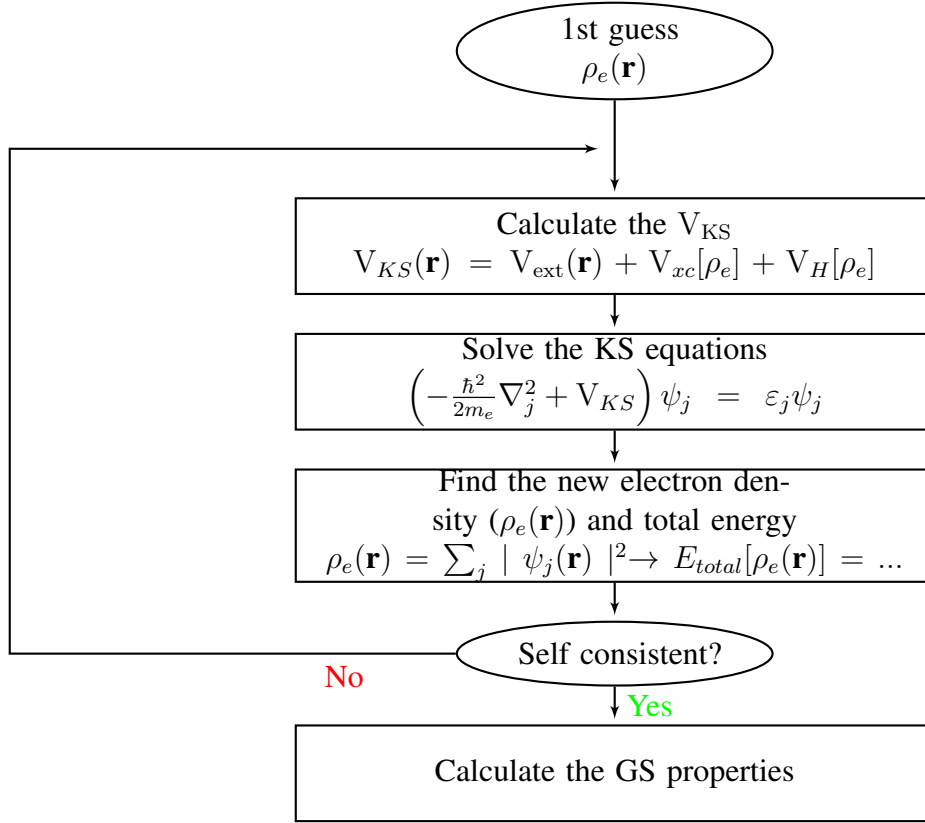


Figure 2.1: Flowchart to solve the KS equations self consistently.

The computational flowchart to find the GS of the system is given in the fig. 2.1. We first take an initial guess of electronic charge density and construct the KS potential. Then, we solve the KS equation with this constructed KS potential and find the new ground state density. This process is repeated unless a convergence criterion is met, i.e., the new ground state density is self consistent with the initial ground state density. Then, we can calculate other ground state properties. If not, we take another initial guess of density and again follow the same procedure.

2.3.2 Exchange and correlation

The exchange-correlation energy (E_{xc}) contains the exchange (E_x) and correlation (E_c) energies. The origin of the exchange interaction term comes from Pauli's exclusion principle, which spatially separates two electrons in the same quantum state with same spin,

hence reduces the Coulomb repulsion. This energy reduction is the exchange energy. The Coulomb energy of such system can be reduced further by spatially separating two electrons with opposite spins at the cost of increasing the KE of electrons. This energy reduction is correlation energy. The exchange-correlation energy is expressed as,

$$E_{xc}[\rho_e] = \int \varepsilon_{xc}([\rho_e](\mathbf{r}))\rho_e(\mathbf{r})d\mathbf{r}, \quad (2.18)$$

where, $\varepsilon_{xc}([\rho_e](\mathbf{r}))$ represent the exchange-correlation energy density at $\mathbf{r}$ dependent on the $\rho_e(\mathbf{r})$. Still, The exact form of $\varepsilon_{xc}(\rho_e(\mathbf{r}))$ is unknown and thus approximated. Following is the discussion of two most commonly used approximations.

2.3.2.1 Local density approximation (LDA)

LDA is most simple and widely used approximation. In this case, The exchange-correlation functional is approximated with the local electron density at point $\mathbf{r}$ in space in the LDA. The expression of exchange-correlation term is given as:

$$E_{xc}^{LDA} = \int \rho_e(\mathbf{r})\varepsilon_{xc}^H(\rho_e(\mathbf{r}))d^3\mathbf{r} \quad (2.19)$$

where $\varepsilon_{xc}^H(\rho_e(\mathbf{r}))$ is the exchange-correlation energy density of a homogeneous electron gas with same density($\rho_e(r)$). LDA performs well for slowly varying density systems. Hence, LDA is better in predicting properties of weakly correlated systems with reasonable accuracy.

2.3.2.2 Generalized gradient approximation (GGA)

To deal with an inhomogeneous system, GGA introduces the inhomogeneity of electron density by taking the magnitude of the gradient of the electron density ($|\nabla\rho_e(r)|$) into consideration along with local electron density($\rho_e(\mathbf{r})$). The expression for E_{xc}^{GGA} is:

$$E_{xc}^{GGA} = \int \rho_e(\mathbf{r})\varepsilon_{xc}(\rho_e(\mathbf{r}), |\nabla\rho_e(\mathbf{r})|)d^3\mathbf{r} \quad (2.20)$$

This thesis employs the GGA functional parameterized by Perdew, Burke, and Ernzerhof (PBE) as it describes many-body electronic systems better than LDA [58].

2.4 Periodic Supercells

In the previous section, it was shown that the single electron SE equation can replace the many-body interacting system with a non interacting system subject to V_{KS} . Nevertheless, there still remain problems: the first is dealing with infinite no. of electrons moving in external potential $V_{ext}(\mathbf{r})$ due to infinite nuclei, and the next is requirement of infinite large basis set to expand the wavefunction extending over the entire solid. Both these problems can be solved by making use of periodic nature of the crystals, as discussed in the following section.

2.4.1 Bloch's theorem

According to Bloch's theorem, an electronic wavefunction in a crystal can be written as

$$\psi_j(r) = e^{i\mathbf{r}\cdot\mathbf{k}} u_j(r) \quad (2.21)$$

where $u_j(r)$ is the cell-periodic part for j^{th} electron with same periodicity as that of the crystal. The periodic part of the Bloch function can be expanded as a summation of plane waves of the discrete basis set.

$$u_j(r) = \sum_{\mathbf{G}} C_{\mathbf{j},\mathbf{G}} e^{i\mathbf{r}\cdot\mathbf{G}} \quad (2.22)$$

where $\mathbf{G}$ is the reciprocal lattice vector (with $\mathbf{G}\cdot\mathbf{L} = 2\pi n$; $\mathbf{L}$ and n are the lattice vector of the crystal in real space and an integer respectively.) Using equations 2.21 and 2.22, $\psi_j(r)$ can be written as :

$$\psi_j(r) = \sum_{\mathbf{G}} \frac{1}{V} C_{\mathbf{j},\mathbf{k}+\mathbf{G}} e^{i\mathbf{r}\cdot(\mathbf{k}+\mathbf{G})} \quad (2.23)$$

The periodic nature of the Bloch function provides a solution to the first challenge encountered when dealing with infinite number of electrons in a crystal. Instead of considering the wavefunctions of infinite number of electrons throughout the crystal, we can focus on the wavefunctions of electrons confined within a primitive unit cell. This is possible because the wavefunctions of infinite number of electrons are interconnected with the wavefunctions of electrons within the primitive unit cell.

Additionally, the above equation implies that the expansion of the Bloch wavefunction needs infinite plane waves. Customarily, only the plane waves with contribution of small KE ($\frac{\hbar^2}{2m} |\mathbf{k}+\mathbf{G}|^2$) are significant. Hence, we curtail the basis set after a certain energy cutoff (E_{cut}), which is as follows:

$$\frac{\hbar^2}{2m} |\mathbf{k}+\mathbf{G}|^2 \leq \frac{\hbar^2}{2m} \mathbf{G}_{cut}^2 = E_{cut} \quad (2.24)$$

Then it becomes

$$\psi_j(r) = \sum_{|\mathbf{k}+\mathbf{G}| \leq \mathbf{G}_{cut}} \frac{1}{V} C_{\mathbf{j},\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.25)$$

Moreover, the total energy convergence decides the value of the E_{cut} .

2.4.2 k -point sampling

In order to calculate the physical quantities like total energy, numerical integration over k space is necessary. In principle, infinite number of k -points might be required to sample the irreducible Brillouin zone (IBZ). However, at close k -points, the electronic wavefunction is nearly identical. Hence, we can use only finite number of special k -points to do the numerical integration proposed by Monkhorst *et al.* [59]. In this thesis, a finite grid of k -points uniformly spaced are generated using the same procedure.

$$\mathbf{k}_n = x_{1n}\mathbf{b}_1 + x_{2n}\mathbf{b}_2 + x_{3n}\mathbf{b}_3 \quad (2.26)$$

where $\mathbf{b}_m$ is the reciprocal lattice vector, and

$$x_{mn} = \frac{(2n - r - 1)}{2r}, n = 1, 2, 3, \dots, r \quad (2.27)$$

where r is an integer.

2.4.3 Pseudopotentials

It is well known that the physical properties of the crystals are mainly dependent on the valence electrons of the atoms than on core electrons. In pseudopotential approximation, we make use of this to reduce the computational cost of the calculation by replacing potential

due to core electrons with a weaker pseudopotential that acts on a pseudo wavefunction. The pseudopotential (V_{ps}) is then used to replace V_{ext} in KS equations. Moreover, the true wavefunction, which has many wiggles in the core region caused by a strong core potential requires many plane waves to represent it. In order to resolve this issue, ψ_{ps} is used, which has smooth behavior within the core region (Fig. 2.2) [1]. This pseudo wavefunction with smooth behaviour inside core region reduces the basis set size, and therefore the computational cost.

Plane wave electronic structure calculations use mainly two types of pseudopotential: ultrasoft and norm-conserving pseudopotentials. Norm-conserving pseudopotentials follow two conditions: (1) the norm of the valence wavefunction matches with the norm of the pseudo wavefunction below r_c [60], (2) the pseudo wavefunction and valence electron wavefunction coincide after a cutoff radius (labeled as r_c). Generally, a high energy cutoff is needed for norm-conserving pseudopotential. Unlike norm-conserving pseudopotentials, ultrasoft pseudopotentials do not impose the norm conserving conditions on the pseudo wavefunction, which allows for a more flexible description of the valence electrons. This flexibility leads to a lower cutoff energy and a reduced number of basis functions required for electronic structure calculations. However, when the strict requirement for conserving the norm is relaxed, it leads to a compromise in preserving the orthonormality and norm-conservation of atomic orbitals. Nevertheless, a potential solution to the orthogonality problem can be attained by formulating a generalized eigenvalue problem that includes a generalized orthogonality constraint expressed through an overlap operator. To tackle the issue of norm-conservation, a localized augmentation charge can be introduced and combined with the system's charge.

2.5 Lattice vibrations in DFT

The energy associated with the atomic vibrations of a crystal is quantized and the associated quasiparticles are called phonons. The phonons play a very crucial role in the physical properties of crystals such as thermal conductivity and electrical conductivity through interaction with electrons.

Let's assume M nuclei or ions inside the unit cell. The position vector and cartesian coordinates of ρ^{th} nucleus's are denoted by η_ρ and $\eta_{\rho\alpha}$ ($\alpha=x,y,z$). We use Born-Von Karman (BvK) boundary conditions to describe infinitely extended crystal. The lattice vectors $\mathbf{R}_m$

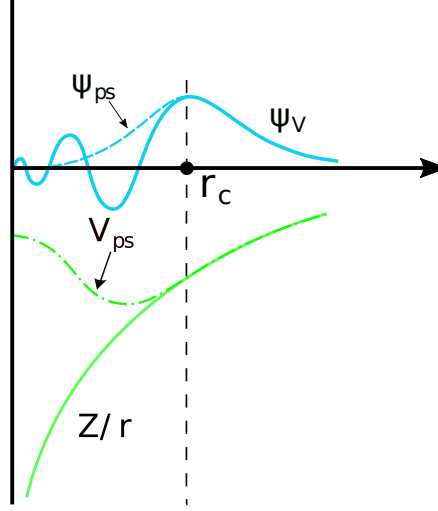


Figure 2.2: Schematic representation of pseudo-electron potential (dashed green lines) and all-electron (solid green lines) corresponding wavefunctions (cyan curves). Pseudopotential and all-electron wavefunction coincide after cutoff radius (r_c). (Reprinted with permission from ref. [1]. Copyright ©1992, American Physical Society)

(with $m = 1, \dots, N_m$) specify N_m unit cells. So, the position vector and cartesian coordinates of ρ^{th} nucleus inside m^{th} unit cell is given by $\eta_{\rho m} = \eta_{\rho} + \mathbf{R}_m$ and $\eta_{\rho\alpha m} = \eta_{\rho\alpha} + \mathbf{R}_m$ respectively.

A standard DFT code can obtain the total potential energy of the crystal. This is indicated by $U(\{\eta_{\rho}\})$; $\{\eta_{\rho}\}$ being the set of position of all nuclei.

Within harmonic approximation, the total energy of the system can be written to the second-order in terms of small amplitude $u_{\kappa p}^0$ as follows:

$$U = U_0 + \frac{1}{2} \sum_{\substack{\rho\alpha m \\ \rho'\alpha'm'}} \phi_{\rho\alpha m, \rho'\alpha'm'} \Delta\eta_{\rho\alpha m} \Delta\eta_{\rho'\alpha'm'} \quad (2.28)$$

where U_0 represents the total potential energy of the system in its equilibrium, and $\phi_{\rho\alpha m, \rho'\alpha'm'}$ represents interatomic force constants (IFC) and is written as

$$\phi_{\rho\alpha m, \rho'\alpha'm'} = \frac{\partial^2 U}{\partial \eta_{\rho\alpha m} \partial \eta_{\rho'\alpha'm'}} \quad (2.29)$$

The dynamical matrix (D^{dm}) is calculated by taking the Fourier transform of IFC given

as [61]:

$$D_{\rho\alpha,\rho'\alpha'}^{\text{dm}}(\mathbf{q}) = \sum_m \frac{1}{\sqrt{(M_\rho M_{\rho'})}} \phi_{\rho\alpha 0,\rho'\alpha' m} \exp(i\mathbf{q} \cdot \mathbf{R}_m) \quad (2.30)$$

where M_ρ denotes the mass of the ρ^{th} nucleus and $\mathbf{q}$ represents a set of phonon wavevectors in the reciprocal space.

The dynamical matrix is hermitian. Hence, its eigenvalues are real ($\omega_{\mathbf{q}\nu}^2$).

$$\sum_{\rho'\alpha'} D_{\rho\alpha,\rho'\alpha'}^{\text{dm}}(\mathbf{q}) e_{\rho'\alpha',\nu}(\mathbf{q}) = \omega_{\mathbf{q}\nu}^2 e_{\rho\alpha,\nu}(\mathbf{q}) \quad (2.31)$$

where ν runs from 1 to $3M$. $\omega_{\mathbf{q}\nu}$ indicates the phonon frequency of wavevector $\mathbf{q}$ in branch ν and $e_{\rho\alpha,\nu}(\mathbf{q})$ is the normal modes of vibration. The DFPT or frozen-phonon method is used to compute the dynamical matrix [62].

The Hamiltonian for the nuclei within harmonic potential given in the eqn. 2.28 is written as follows:

$$H_m = -\frac{\hbar^2}{2M_\rho} \sum_{\rho\alpha m} \frac{\partial^2}{\partial \eta_{\rho\alpha m}^2} + \sum_{\substack{\rho\alpha m \\ \rho'\alpha' m'}} \frac{1}{2} \phi_{\rho\alpha m,\rho'\alpha' m'} \Delta \eta_{\rho\alpha m} \Delta \eta_{\rho'\alpha' m'} \quad (2.32)$$

Where the constant term U_0 is omitted. The above equation relies on the following approximations:

- Harmonic approximation, which considers only up to the second-order terms in the Taylor expansion of U . Omitted higher-order terms are known as anharmonic terms and only important at higher temperatures [63].
- The Born-Oppenheimer (adiabatic) approximation for the calculation of IFC.

The above given Hamiltonian for nuclei can be written within the formalism of second quantization as follows [64] :

$$H_m = \hbar \sum_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu} \left(\frac{1}{2} + \hat{a}_{\mathbf{q}\nu}^\dagger \hat{a}_{\mathbf{q}\nu} \right) \quad (2.33)$$

2.6 Electron-phonon interactions (EPIs)

The electron-phonon interactions are responsible for many physical phenomena such as superconductivity, temperature-dependence of electrical conductivity of materials, carrier mobility of semiconductors, etc. In this section, we describe in brief the Hamiltonian of a crystal system, how they are computed for from different approximations and its computation from the first principles. In addition, we discuss the electron self-energy useful for renormalization of band structure and computing the carriers' relaxation time. The Hamiltonian of the electron-phonon coupled system is given as [65]:

$$H = H_e + H_p + H_{ep} + H_{ep}^{(2)} \quad (2.34)$$

where

$$H_e = \sum_{m\mathbf{k}} \varepsilon_{m\mathbf{k}} \hat{c}_{m\mathbf{k}}^\dagger \hat{c}_{m\mathbf{k}} \quad (2.35)$$

$$H_p = \hbar \sum_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu} \left(\frac{1}{2} + \hat{a}_{\mathbf{q}\nu}^\dagger \hat{a}_{\mathbf{q}\nu} \right) \quad (2.36)$$

$$H_{ep} = N_r^{-1/2} \sum_{\substack{mn\nu \\ \mathbf{k}, \mathbf{q}}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} (\hat{a}_{-\mathbf{q}\nu}^\dagger + \hat{a}_{\mathbf{q}\nu}) \quad (2.37)$$

$$H_{ep}^{(2)} = N_r^{-1} \sum_{\substack{mn\nu\nu' \\ \mathbf{k}, \mathbf{q}, \mathbf{q}'}} g_{mn\nu\nu'}^{2\text{nd}}(\mathbf{k}, \mathbf{q}, \mathbf{q}') \hat{c}_{m\mathbf{k}+\mathbf{q}+\mathbf{q}'}^\dagger \hat{c}_{n\mathbf{k}} (\hat{a}_{-\mathbf{q}\nu}^\dagger + \hat{a}_{\mathbf{q}\nu}) (\hat{a}_{-\mathbf{q}'\nu'}^\dagger + \hat{a}_{\mathbf{q}'\nu'}) \quad (2.38)$$

The eqn.2.35 and eqn.2.36 correspond to the electron and phonon Hamiltonian expressed within the second quantization formalism. The eqn.2.37 and eqn.2.38 represent the EPIs of the first and second-order in atomic displacement, respectively. Here $\varepsilon_{m\mathbf{k}}$ is the single particle eigenvalue of an electron in band m with crystal momentum $\mathbf{k}$. $\omega_{\mathbf{q}\nu}$ is the frequency of lattice vibration in branch ν with crystal momentum $\mathbf{q}$. $\hat{a}_{\mathbf{q}\nu}^\dagger$ and $\hat{a}_{\mathbf{q}\nu}$ ($\hat{c}_{n\mathbf{k}}^\dagger$ and $\hat{c}_{n\mathbf{k}}$) denote the bosonic (fermionic) creation and annihilation operators, respectively. N_r is the number of unit cells in a periodic supercell. The terms $g_{mn\nu}(\mathbf{k}, \mathbf{q})$ and $g_{mn\nu\nu'}^{2\text{nd}}(\mathbf{k}, \mathbf{q}, \mathbf{q}')$ denote the strength of the coupling between electron and phonon.

The following portions describe some approaches to estimate the strength of the electron-phonon interactions in different type of solids.

2.6.1 Metals

In early studies, the quest for quantum theory of electrical resistivity in metals motivated the study of EPIs. Earlier electronic excitation was described by the free electron gas theory ($\varepsilon_{n,\mathbf{k}} = \frac{1}{2m_e}\hbar^2 k^2 - \varepsilon_f$, where ε_f denotes the Fermi energy) in eqn 2.34 and the phonon vibration was described by the Debye theory ($\omega_{\mathbf{q}\nu} = \mathcal{V}_s|\mathbf{q}|$, $\mathcal{V}_s$ represents the sound's speed inside the medium). These approximations worked reasonably well, provided the system is noble, elemental, and monovalent alkali metals. However, estimation of the electron-phonon (EP) matrix elements using these approximations was more challenging. In 1929, Bloch wrote the very first expression for the EP matrix element that describes the scattering of the particle from the initial electronic state with wavevector $|\mathbf{k}\rangle$ to final state with wavevector $|\mathbf{k}+\mathbf{q}\rangle$ by an acoustic phonon (with frequency $\omega_{\mathbf{q}\nu}$) and is given by [64]

$$g_{mn,\nu}(\mathbf{k}, \mathbf{q}) = -i\sqrt{\frac{1}{2M_\rho\omega_{\mathbf{q}\nu}N_r}}\hbar\mathbf{q}\cdot\mathbf{e}_{\rho\nu}(\mathbf{q})V_0 \quad (2.39)$$

where M_ρ is the mass of the ρ^{th} nucleus, and $\mathbf{e}_{\rho\nu}(\mathbf{q})$ is the polarization vector of the acoustic wave associated with the wavevector $\mathbf{q}$ and branch ν . N_r is the number of unit cells in the Born-van Karman boundary condition. V_0 represent the effective potential, averaged over a unit cell, felt by the electron inside the crystal [64].

2.6.2 Semiconductors

In 1950, Bardeen and Shockley laid the foundation of the “deformation-potential” theory to study the EPIs in covalently bonded semiconductors [66]. It assumes that the atomic displacement pattern of long wavelength acoustic phonons is similar to deformation in the homogeneous solid. In semiconductors, since the carriers are mainly concentrated near the band extrema in a narrow energy window. Hence, the low energy phonons near the Brillouin zone center will significantly contribute to EPIs. Moreover, acoustic phonons are associated with elastic strain in a system.

Bardeen and Shockley assumed that the elastic strain in the crystal can be described by the displacement pattern associated with the long wavelength acoustic mode. Using the effective mass approximation, they showed that the effective potential (V_0) in eqn. 2.39

can be replaced with a “deformation potential” (E_{dp}) which is given as:

$$V_0 \rightarrow E_{dp} = \Omega \frac{\partial \varepsilon_{n,\mathbf{k}}}{\partial \Omega} \quad (2.40)$$

Where $\varepsilon_{n,\mathbf{k}}$ is the conduction (valence) band minima(maxima) energy and Ω denotes the volume of the unit cell. The original paper of Bardeen and Shockley [66] contains this theory in detail.

2.6.3 Polar materials

Polar materials have a crucial role in development of the theory of EPIs. The main difference between semiconductors and polar materials is that the atomic displacement in polar materials generates the long ranged electric fields, which provide an additional scattering channel to the carriers. Hence, EPIs are very strong in polar materials.

In 1950, a work by Frohlich *et al.* considered the screening effects resulting from dielectric polarization in insulating media and modeled the effective potential (V_0) inside isotropic ionic systems. This effective potential is given by

$$V_0 \rightarrow -\frac{1}{|\mathbf{q}^2|} \sqrt{\left[\frac{e^2 \omega_{\mathbf{q}\nu}^2 M_\rho}{\Omega \varepsilon_0} \left(\frac{\varepsilon^0 - \varepsilon^\infty}{\varepsilon^0 \varepsilon^\infty} \right) \right]} \quad (2.41)$$

where ε_0 denotes the free space permittivity. ε^∞ and ε^0 are the high-frequency and static relative permittivities, respectively. Ω is the unit cell volume. For $\varepsilon^\infty < \varepsilon^0$ case, EP matrix elements are calculated by 2.39 and 2.41. It is to be noted that EP matrix elements ($g_{mn,\nu}(\mathbf{k}, \mathbf{q})$) diverge as $|\mathbf{q}|^{-1}$ at long-wavelengths and generate very strong EPIs.

2.6.4 Electron-phonon interactions in DFT

This section discusses the basic formalism underlying the EPIs calculations using DFT. First, we start by introducing the EP coupling Hamiltonian. Then, we briefly discuss the procedure to calculate EP matrix elements using the density functional perturbation theory (DFPT).

2.6.4.1 EP coupling from DFT

In this portion, we describe how the electron-phonon interaction terms are calculated. The electronic Hamiltonian (H_e) given in the eqn. 2.34 is solved using DFT. We can write the KS Hamiltonian within the second quantization formalism as follows:

$$H_e = \sum_{n\mathbf{k}, n'\mathbf{k}'} \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n'\mathbf{k}'} \langle \psi_{n\mathbf{k}} | H_{KS} | \psi_{n'\mathbf{k}'} \rangle = \sum_{n\mathbf{k}} \varepsilon_{n\mathbf{k}} \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n\mathbf{k}} \quad (2.42)$$

The phonons are solved using the DFPT in DFT as described in the section 2.5. Here we briefly discuss the formalism to calculate EP matrix elements $g_{mn\nu}(\mathbf{k}, \mathbf{q})$ and $g_{mn\nu\nu'}^{2\text{nd}}(\mathbf{k}, \mathbf{q}, \mathbf{q}')$ mentioned in the eqn. 2.37 and eqn. 2.38. To do this, we expand the KS potential (V_{KS}) in terms of atomic displacements.

$$V_{KS}(\{\eta_{\rho m}\}) = V_{KS}(\{\eta_{\rho m}^0\}) + \sum_{\rho\alpha m} \frac{\partial V_{KS}}{\partial \eta_{\rho\alpha m}} \Delta\eta_{\rho\alpha m} \quad (2.43)$$

where

$$\Delta\eta_{\rho\alpha m} = \left(\frac{m_p}{N_m M_\rho} \right)^{1/2} \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p} e_{\rho\alpha, \nu}(\mathbf{q}) Z_{\mathbf{q}\nu} (\hat{a}_{-\mathbf{q}\nu}^\dagger + \hat{a}_{\mathbf{q}\nu}) \quad ; \quad Z_{\mathbf{q}\nu} = \sqrt{\frac{\hbar/2}{\omega_{\mathbf{q}\nu} m_p}} \quad (2.44)$$

where m_p is arbitrary reference mass introduced to ensure that $Z_{\mathbf{q}\nu}$ has dimension of length and M_ρ is the mass of ρ th ion. The $Z_{\mathbf{q}\nu}$ is “zero-point” amplitude.

The eqn. 2.43 can also be rewritten in terms of normal modes coordinates.

$$V_{KS}(\{\eta_{\rho m}\}) = V_{KS}(\{\eta_{\rho\alpha m}^0\}) + N_m^{-1/2} \sum_{\mathbf{q}\nu} \Delta_{\mathbf{q}\nu} V_{KS}(\hat{a}_{-\mathbf{q}\nu}^\dagger + \hat{a}_{\mathbf{q}\nu}) \quad (2.45)$$

where

$$\Delta_{\mathbf{q}\nu} V_{KS} = e^{i\mathbf{q}\cdot\mathbf{r}} \Delta_{\mathbf{q}\nu} v_{KS} \quad ; \quad \Delta_{\mathbf{q}\nu} v_{KS} = Z_{\mathbf{q}\nu} \sum_{\rho\alpha} \sqrt{\frac{m_p}{M_\rho}} e_{\rho\alpha, \nu}(\mathbf{q}) \partial_{\rho\alpha, \mathbf{q}} v_{KS} \quad (2.46)$$

$$\partial_{\rho\alpha, \mathbf{q}} v_{KS} = \sum_m e^{-i(\mathbf{r}-\mathbf{R}_m)\cdot\mathbf{q}} \left. \frac{\partial V_{KS}}{\partial \eta_{\rho\alpha}} \right|_{\mathbf{r}-\mathbf{R}_m} \quad (2.47)$$

In the eqn. 2.46 and 2.47, $\partial_{\rho\alpha, \mathbf{q}} v_{KS}$ and $\Delta_{\mathbf{q}\nu} v_{KS}$ are lattice-periodic functions.

The above expression is related to first-order EPIs within the formalism of second quanti-

zation as follows:

$$H_{ep} = \sum_{n\mathbf{k}, n'\mathbf{k}'} \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n'\mathbf{k}'} \langle \psi_{n\mathbf{k}} | V_{KS}(\{\eta_{\rho m}\}) - V_{KS}(\{\eta_{\rho\alpha m}^0\}) | \psi_{n'\mathbf{k}'} \rangle \quad (2.48)$$

With the eqn. 2.46, 2.47 and $\psi_{n\mathbf{k}}(\mathbf{r}) = N_m^{-1/2} \eta_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$, H_{ep} can be given as:

$$H_{ep} = N_m^{-1/2} \sum_{\substack{\mathbf{k}, \mathbf{q} \\ mn\nu}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} (\hat{a}_{-\mathbf{q}\nu}^\dagger + \hat{a}_{\mathbf{q}\nu}) \quad (2.49)$$

where the EP matrix element is

$$g_{mn\nu}(\mathbf{k}, \mathbf{q}) = \langle \eta_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} v_{KS} | \eta_{n\mathbf{k}} \rangle_{uc} \quad (2.50)$$

where the subscript “uc” indicates that the integration is carried over one unit cell of crystal. Following the similar method as above, we can write the second-order EP coupling Hamiltonian as follows:

$$H_{ep}^{(2)} = N_m^{-1} \sum_{\substack{\mathbf{k}, \mathbf{q}, \mathbf{q}' \\ mn\nu\nu'}} g_{mn\nu\nu'}^{2nd}(\mathbf{k}, \mathbf{q}, \mathbf{q}') \hat{c}_{m\mathbf{k}+\mathbf{q}+\mathbf{q}'}^\dagger \hat{c}_{n\mathbf{k}} (\hat{a}_{-\mathbf{q}\nu}^\dagger + \hat{a}_{\mathbf{q}\nu}) (\hat{a}_{-\mathbf{q}'\nu'}^\dagger + \hat{a}_{\mathbf{q}'\nu'}) \quad (2.51)$$

here $g_{mn\nu\nu'}^{2nd}(\mathbf{k}, \mathbf{q}, \mathbf{q}') = (1/2) \langle \eta_{m\mathbf{k}+\mathbf{q}+\mathbf{q}'} | \Delta_{\mathbf{q}\nu} \Delta_{\mathbf{q}'\nu'} v_{KS} | \eta_{n\mathbf{k}} \rangle_{uc}$.

2.6.4.2 Calculation of EP matrix elements

Calculation of the EP matrix elements ($g_{mn\nu}(\mathbf{k}, \mathbf{q})$) are performed using one of the three approaches namely, frozen-phonon method, DFPT and the dielectric approach. Here we discuss the frozen-phonon and DFPT approach to find the EP matrix elements. The dielectric approach can be found elsewhere [64].

The frozen-phonon method makes use of finite difference method to evaluate the potential derivative as given below:

$$\left. \frac{\partial V_{KS}}{\partial \eta_{\rho\alpha m}} \right|_{\eta_{\rho m}^0} \simeq \frac{1}{2x} \left[V_{KS}(\mathbf{r}; \eta_{\rho\alpha m}^0 + x) - V_{KS}(\mathbf{r}; \eta_{\rho\alpha m}^0 - x) \right] \quad (2.52)$$

Where x is a small atomic displacement of the ρ^{th} nucleus in m^{th} unit cell along the α -direction. x is of the order of 0.1 Å, i.e., zero-point amplitude. In this method, a big supercell is needed to compute the EP matrix elements corresponding to long-wavelength phonons, thereby making it prohibitively expensive.

Baroni *et al.* came up with a new method DFPT [62] to calculate the scattering potential. In this method, the lattice-period scattering potential ($\partial_{\rho\alpha,\mathbf{q}}v_{KS}$) is computed by differentiating V_{KS} using 2.47. Hence, it is less time consuming than the frozen-phonon method. the lattice-period scattering potential ($\partial_{\rho\alpha,\mathbf{q}}v_{KS}$) is given by

$$\partial_{\rho\alpha,\mathbf{q}}v_{KS} = \partial_{\rho\alpha,\mathbf{q}}v_{ext} + \partial_{\rho\alpha,\mathbf{q}}v_{xc} + \partial_{\rho\alpha,\mathbf{q}}v_H \quad (2.53)$$

The partial derivative of these potentials are computed using V_{ext} , V_{xc} and V_H and expressed in reciprocal space using Fourier transform as follows” $f(G) = \frac{1}{\Omega} \int d\mathbf{r} e^{-i\mathbf{G}\cdot\mathbf{r}} f(\mathbf{r})$

$$\partial_{\rho\alpha,\mathbf{q}}v_{ext}(\mathbf{G}) = -i(\mathbf{G}+\mathbf{q})_\alpha V_\rho(\mathbf{G}+\mathbf{q}) e^{-i(\mathbf{G}+\mathbf{q})\cdot\eta_\rho} \quad (2.54)$$

$$\partial_{\rho\alpha,\mathbf{q}}v_{xc}(\mathbf{G}) = \Omega \sum_{\mathbf{G}'} f_{xc}(\mathbf{G}+\mathbf{q}, \mathbf{G}+\mathbf{q}') \partial_{\rho\alpha,\mathbf{q}}\rho_e(\mathbf{G}') \quad (2.55)$$

here $f_{xc}(\mathbf{r}, \mathbf{r}')$ is given as the double derivative of the electronic density($\rho_e(\mathbf{r})$)

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 E_{xc}[\rho_e]}{\delta \rho_e(\mathbf{r}) \delta \rho_e(\mathbf{r}')} \right|_{\rho_e(\mathbf{r}; \{u_{\kappa\alpha p}^0\})} \quad (2.56)$$

$$\partial_{\rho\alpha,\mathbf{q}}v_H(\mathbf{G}) = \Omega v_C(\mathbf{G}+\mathbf{q}) \partial_{\rho\alpha,\mathbf{q}}\rho_e(\mathbf{G}) \quad ; \text{ where } v_C(\mathbf{q}) = \frac{e^2}{\Omega 4\pi\epsilon_0} \int d\mathbf{r} e^{-i\mathbf{r}\cdot\mathbf{q}} (|\mathbf{r}|)^{-1} \quad (2.57)$$

The above equations 2.55 and 2.57 include the variation in the charge density. This variation is obtained by the first-order correction to KS wavefunctions by the perturbation theory. Further details are given elsewhere [62, 64].

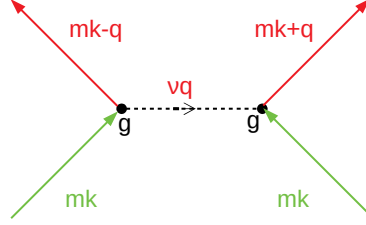


Figure 2.3: Feynman diagram for first-order EPIs. This diagram is comprised of two diagrams depicting the phonon absorption (right half) and emission (left half). The solid lines show the electron and dotted line shows the phonon

2.7 Electron self energy

The many-body interactions modify the state of the electron due to other electrons and phonons inside the crystal. This modification leads to electron becoming a quasiparticle whose energy is known as electron self energy. The imaginary part of this energy determines the relaxation time of the electron. The electron self-energy is explained with help of infinite Feynman diagrams. Notably, Migdal proved that the first-order Feynmann diagram is sufficient in order to calculate electron self-energy [67]. Under the Migdal approximation, Feynman diagram of first-order EPIs is shown in Fig. 2.3. The expression for electron-self energy within the Migdal approximation can be given as :

$$\sum_{n\mathbf{k}}^{elph} = \sum_{\mathbf{q}, m} w_{\mathbf{q}} |g_{mn, \nu}(\mathbf{k}, \mathbf{q})|^2 \left[\frac{n_{\mathbf{q}\nu} - f_{m\mathbf{k}+\mathbf{q}} + 1}{\varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - i\delta} + \frac{f_{m\mathbf{k}+\mathbf{q}} + n_{\mathbf{q}\nu}}{\varepsilon_{n\mathbf{k}} + \hbar\omega_{\mathbf{q}\nu} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - i\delta} \right] \quad (2.58)$$

where $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$ is given as:

$$g_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \left(\sqrt{\frac{\hbar}{2\omega_{\mathbf{q}\nu}m_0}} \right) \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V_{KS} | \psi_{n\mathbf{k}} \rangle \quad (2.59)$$

here $w_{\mathbf{q}}$ is the weight related to the phonon wavevector $\mathbf{q}$ in the Brillouin zone, $\partial_{\mathbf{q}\nu} V_{KS}$ represent the KS potential derivative related to a phonon wavevector $\mathbf{q}$, frequency $\omega_{\mathbf{q}\nu}$ and mode ν . The temperature dependence of electron self-energy stems from the Bose-Einstein occupations ($n_{\mathbf{q}\nu}$) and Fermi-Dirac occupation ($f_{m\mathbf{k}+\mathbf{q}}$). In 2.58, the first and second term refer to process of phonon emission and absorption, respectively. More details on this are given elsewhere [64, 68].

The real part of electron self-energy can be added into the KS eigenvalues to get the temperature-dependent band structure as follows:

$$E_{n,k} = \text{Re} \sum_{n\mathbf{k}}^{elph} + \varepsilon_{n,k} \quad (2.60)$$

In addition, The relaxation time of the electrons associated with electronic state $n\mathbf{k}$ is related to imaginary part of the electron self-energy as follows:

$$\tau_{n,\mathbf{k}} = \frac{\hbar}{2} \left(\text{Im} \sum_{n\mathbf{k}}^{elph} \right)^{-1} \quad (2.61)$$

The electronic transport properties of a material, like conductivity and mobility, etc., depend on the relaxation time $\tau_{n,\mathbf{k}}$, which depends on the strength of EPIs in the system. Ignoring the scattering contribution due to various phonon modes possibly results in the wrong estimation of $\tau_{n,\mathbf{k}}$, and in turn, it might overestimate the transport properties. Thus the calculation of $\tau_{n,\mathbf{k}}$ to a reasonable accuracy is important for *in silico* search of new thermoelectric materials. This becomes more significant at high temperatures.

2.8 Boltzmann Transport theory

In this section, we first discuss the Boltzmann transport theory, charge carrier transport and then Boltztrap to solve the semiclassical Boltzmann transport equation.

The transport properties of charge carriers are described by a distribution function. In

general, a distribution function of a system describes the probability density of finding a particle with a given position r , momentum k , and at any given time t . For example, the distribution function for electrons in equilibrium [69, 70] is given as

$$f(\epsilon(k)) = \frac{1}{\exp(\frac{\epsilon(k) - \epsilon_f}{k_b T}) + 1} \quad (2.62)$$

here $\epsilon(k)$ is the energy of the electron in state k . ϵ_f is the Fermi energy of the electron at temperature T . The distribution function $f(\epsilon(k))$ describes the equilibrium of an electronic system and is independent of any collisions. Though the internal collision will continuously remove electrons from one k state to another, this will not disturb the net distribution of electrons unless there is any external force applied. To deal with the cases where external fields are present, we use the Boltzmann transport equation. Let's assume a distribution function $f(r, k, t)$ represents the probability density of particles in neighbourhood of point r , in momentum state k , and at a time t . The Boltzmann transport equation determines the time evolution of the distribution function $f(r, k, t)$. There are mainly three ways that leads the time evolution of this distribution function namely, diffusion, scattering and external field. The time evolution of this distribution function [71] can be written mathematically as

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{diffusion} + \left(\frac{\partial f}{\partial t}\right)_{scattering} + \left(\frac{\partial f}{\partial t}\right)_{externalfield} \quad (2.63)$$

where the first term of the right hand side (R.H.S) represents the diffusion term, which takes care of the carriers coming in and out of the space r . If the velocity of the carrier is v_k at any given time t in state k , then the number of carriers at space r at time t would be equal to the number of particles at space $r - v\partial t$ at time $t - \partial t$. Hence, the time evolution of the distribution function owing to the diffusion term can be written as

$$\left(\frac{\partial f}{\partial t}\right)_{diffusion} = -v_k \frac{\partial f}{\partial r} \quad (2.64)$$

The second term of the R.H.S represents the time evolution of the distribution function due to scattering. This term is given as follows

$$\left(\frac{\partial f}{\partial t}\right)_{scattering} = -\frac{f - f^0}{\tau_k} \quad (2.65)$$

here f^0 is the equilibrium distribution function and τ_k is the relaxation time of carrier in state k . The third term of the R.H.S represents the time evolution of the distribution function due to the external field. This term is given as

$$\left(\frac{\partial f}{\partial t}\right)_{external\ field} = -\left(\frac{\partial k}{\partial t}\right)\frac{\partial f}{\partial k} \quad (2.66)$$

The term $\frac{\partial k}{\partial t}$ shows the time evolution of the carrier's momentum from state k to another state under external force (F_{ext}) according to $\hbar\frac{\partial k}{\partial t} = F_{ext}$. Substituting the eqn. 2.64, 2.65 and 2.66 into the eqn. 2.63, we write the Boltzmann transport equation [70] as follows

$$\frac{\partial f}{\partial t} = -v_k \frac{\partial f}{\partial r} - \frac{(f - f^0)}{\tau_k} - \left(\frac{\partial k}{\partial t}\right)\frac{\partial f}{\partial k} \quad (2.67)$$

For a steady state, the Boltzmann transport equation can be written as

$$-v_k \frac{\partial f}{\partial r} - \frac{(f - f^0)}{\tau_k} - \left(\frac{\partial k}{\partial t}\right)\frac{\partial f}{\partial k} = 0 \quad (2.68)$$

We solve the Boltzmann transport equation mainly using two approximations: The first approximation is to assume that the perturbation due to the external force is so small that it can be written as :

$$f(r, k, t) = f^0(r, k, t) + f^1(r, k, t) \quad (2.69)$$

where $f^1(r, k, t)$ is the perturbation term for departure from equilibrium.

The second approximation is to consider the scattering term τ_k is equal to a constant τ . Using above two approximations, we can solve the Boltzmann transport equation to find out the distribution function. Further we can calculate the number density ($n(r, t)$), current density ($j(r, t)$) and thermal current density ($j_Q(r, t)$) [70] as follows:

$$n(r, t) = \frac{1}{4\pi^3} \int f(r, k, t) d^3k \quad (2.70)$$

$$j(r, t) = \frac{e}{4\pi^3} \int v_k f(r, k, t) d^3k \quad (2.71)$$

$$j_Q(r, t) = \frac{1}{4\pi^3} \int v_k (\epsilon - \mu) f(r, k, t) d^3k \quad (2.72)$$

where v_k is the velocity of electron in state k . ϵ is the energy of the electron and μ is the chemical potential.

Solving the above eqn. 2.70, 2.71 and 2.72 using the distribution function leads to the

Onsager relations [70, 72].

$$j = \sigma E - \sigma S \Delta T \quad (2.73)$$

$$j_Q = \sigma S T E - \kappa \Delta T \quad (2.74)$$

here σ is the electrical conductivity. S is the Seebeck coefficient, ΔT is the temperature gradient, E is the external electric field and κ is the thermal conductivity.

The BoltzTraP code [73] calculates the electronic transport properties such as electrical conductivity, electronic thermal conductivity and Seebeck coefficient using the Boltzmann transport equation semiclassically. It uses Fourier expansion of the band energy from DFT calculations to calculate the transport properties. In general, The electric current expression in the presence of temperature gradient and external electric field is given below:

$$j_i = E_j \sigma_{ij} + \nabla_j T \nu_{ij} + \dots \quad (2.75)$$

The conductivity tensor in terms of relaxation time (τ) and group velocity (v) is :

$$\sigma_{\alpha\beta}(m, \mathbf{k}) = \tau_{m,\mathbf{k}} e^2 v_\alpha(m, \mathbf{k}) v_\beta(m, \mathbf{k}) \quad (2.76)$$

where $\tau_{m,\mathbf{k}}$ is the relaxation time of electrons with band index m and state k . The group velocity of electron with band index m and state k along α -direction is obtained as:

$$v_\alpha(m, \mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_{m,\mathbf{k}}}{\partial k_\alpha} \quad (2.77)$$

$\tau_{m,\mathbf{k}}$ depends on several factors like scattering by defects, disorders and electron-phonon interactions, etc. Dependence of $\tau_{m,\mathbf{k}}$ on scattering from phonons can be theoretically obtained from electron-phonon coupling as described in the previous sections. The BoltzTraP assumes that $\tau_{m,\mathbf{k}}$ is independent of the electron's energy and wave vector. This approximation is known as the constant relaxation time approximation (CRTA). Moreover, the conductivity tensor can be expressed as function of energy tensor as follows.

$$\sigma_{\alpha\beta}(\varepsilon) = N^{-1} \sum_{m,\mathbf{k}} \sigma_{\alpha\beta}(m, \mathbf{k}) \frac{\delta(\varepsilon - \varepsilon_{m,\mathbf{k}})}{d\varepsilon} \quad (2.78)$$

In addition, the BoltztraP uses the following equations to calculate the transport coefficients as a function of temperature (T) and chemical potential (μ) [73]:

$$\sigma_{\alpha\beta}(\mu; T) = V^{-1} \int \sigma_{\alpha\beta}(\varepsilon) \left[\frac{-\partial f_d(\mu, T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (2.79)$$

$$\nu_{\alpha\beta}(\mu; T) = \frac{1}{TVe} \int \sigma_{\alpha\beta}(\varepsilon) \left[\frac{-\partial f_d(\mu, T, \varepsilon)}{\partial \varepsilon} \right] (\varepsilon - \mu) d\varepsilon \quad (2.80)$$

$$\kappa_{\alpha\beta}(\mu; T) = \frac{1}{TVe^2} \int \sigma_{\alpha\beta}(\varepsilon) \left[\frac{-\partial f_d(\mu, T, \varepsilon)}{\partial \varepsilon} \right] (\varepsilon - \mu)^2 d\varepsilon \quad (2.81)$$

$$S_{\alpha\beta}(\mu; T) = \frac{1}{T\sigma_{\alpha\beta}(\mu; T)e} \int \sigma_{\alpha\beta}(\varepsilon) \left[\frac{-\partial f_d(\mu, T, \varepsilon)}{\partial \varepsilon} \right] (\varepsilon - \mu) d\varepsilon \quad (2.82)$$

where V is the unit cell volume, f_d is the Fermi Dirac distribution function.

Chapter 3

Thermoelectric properties of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ full Heusler alloy

3.1 Introduction

As mentioned in the introduction of the thesis, Heusler alloys are currently being explored as probable candidates for high temperature thermoelectrics. Amongst these, full Heusler alloys are intermetallic compounds with the chemical composition of X_2YZ , where X and Y are early and late transition metals, respectively, and Z is a main group element. The X, Y and Z atoms occupy the 8c(0.25, 0.25, 0.25), 4a(0, 0, 0) and 4b(0.50, 0.50, 0.50) Wyckoff positions, respectively. They crystallize into the cubic structure with space group $Fm\bar{3}m$. The structure of full Heusler alloys can be understood as a zinc blende structure formed of X and Z atoms, where the tetrahedral and octahedral holes are occupied by X and Z atoms, respectively. Cu_2MnAl is the first ever discovered Heusler alloy, which was found to be a magnetic material, even though its individual components are not magnetic. Since then, researchers have shown great interest in their physical properties for electronic applications such as spintronics [74, 75], superconductivity [76], half-metallicity [77], shape memory materials [78] and thermoelectricity [79, 80]. Generally, the properties of Heusler alloys are governed by the number of valence electrons of the system [81].

Full-Heusler alloys have got less attention as thermoelectric materials since they typically display metallic behaviour that results in a low power factor and subpar thermoelectric properties. However, for some full Heusler alloys, there are controversies as to whether they are metal, semimetal or semiconductor. For example, Nishino et al. have shown that Fe_2VAl has semiconductor-like temperature dependence of electrical conductivity up to

1200 K [82]. However, the experimental results of nuclear magnetic resonance by Lue et al. and photoemission measurement by Soda et al. indicate it to be a low carrier density semimetal [83, 84]. Furthermore, Nishino demonstrated that doping at the place of Al causes a systematic change in the Seebeck coefficient at 300 K, exhibiting rigid band like behaviour for any type of doping element [85]. This rigid band like behaviour of Fe_2VAl also aids in the enhancement of its thermoelectric properties. In addition to this, n type doping in Fe_2VAl has been carried out at sites of Fe, V and Al, and p type doping was carried out at V and Al sites [42, 86–89]. Recently, it was reported that 10% Si doping in Fe_2VAl at the Al site significantly improves the thermoelectric power factor more than Bi_2Te_3 [42], which is a commercially available thermoelectric material. Despite having a high thermopower of $5.59 \times 10^3 \text{W/mK}^2$ in the 300 - 400 K temperature range, this alloy's performance is poor with zT varying between 0.1 – 0.3 because of its high thermal conductivity, which exceeds 20W/mK at 300 K.

Fe_2VGa , isostructural and isoelectronic to Fe_2VAl , exhibits similar electronic properties: NMR study shows that it has a small density of states at the Fermi level [90] and semiconductor like electrical conductivity [91]. Fe_2VGa has lower thermal conductivity and high electrical conductivity [92] compared to Fe_2VAl . In addition, temperature dependent specific heat measurement for Fe_2VGa revealed it to have high effective mass that is beneficial for high Seebeck coefficient [93]. A study of the transport properties on $\text{Fe}_2\text{VGa}_{1+x}$ showed that increasing the Ga content up to 4% increased the electrical conductivity and reduced the Seebeck coefficient, while reduction of the Ga content increased the Seebeck coefficient and decreased the electrical conductivity, suggesting that transport properties of Fe_2VGa are very sensitive to the off-stoichiometric effect [94]. Furthermore, 20% Ti doping in Fe_2VGa at the V site had shown significant improvement in thermoelectric power factor, which led to a zT of 0.07 at 400 K. To the best of our knowledge, this is the maximum reported value of zT for Fe_2VGa [95].

Motivated by these results, we have studied the effect of Indium (In) doping on the structural, electronic and thermoelectric properties of Fe_2VGa . 25 % to 100 % Ga atoms are substituted with In. We expect that the substitution of Ga with In can significantly reduce the lattice thermal conductivity due to its higher atomic mass and alloy scattering, keeping the electronic properties relatively unchanged.

The rest of the paper is divided as follows: Section 3.2 contains the computational methods of the calculation. In the section 3.3, we discuss the structural properties, electronic

properties and then thermoelectric properties of the system. We summarize and conclude the work in the section 3.4.

3.2 Computational details

Our first principles calculations are based on density functional theory as implemented in Quantum ESPRESSO [96]. Ultrasoft pseudopotentials were used to account for the interaction between valence electrons and ionic cores. The exchange-correlation potential of electrons was described by using the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) [58]. The wavefunctions were expanded using a plane wave basis. We used an energy cutoff of 60 Ry and a charge density cutoff of 500 Ry to truncate the plane wave basis used in the Kohn-Sham wave function. The valence electronic configuration for Fe, V, Ga, and In are $3s^23p^63d^{5.50}4s^{0.40}4p^{0.10}$, $3s^23p^63d^34s^2$, $3d^{10}4s^24p^1$, and $4d^{10}5s^25p^1$, respectively. Structural relaxation was done until the Hellman Feynman force on each atom was less than 0.03 eV/Å. A Monkhorst-Pack kmesh of $6 \times 6 \times 6$ (shifted) was used for Brillouin zone integration. Marzari-Vanderbilt smearing [97] with a smearing width of 0.01 Ry was used to expedite the convergence of electronic energy. To check the dynamical stability of the systems, we have computed the phonon dispersion using DFPT [62]. We used q-mesh of $2 \times 2 \times 2$ qmesh for all the systems. To obtain the thermoelectric properties, we have used semi-classical Boltzmann transport theory within the rigid band approximation and constant relaxation time approximation (CRTA) as implemented in BoltzTraP code [98] where it uses a Fourier expansion scheme to fit the band structure for transport properties calculation. We used a dense k-mesh of $36 \times 36 \times 36$ (shifted) to calculate the transport properties of Fe_2VGa and Fe_2VIn and $24 \times 24 \times 24$ (shifted) for $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0.25, 0.50$ and 0.75 . We used electron-phonon averaged (EPA) approximation to calculate the electronic relaxation time(τ). The details of EPA can be found in the ref. [99]. In particular, τ is defined in EPA method as follows:

$$\tau^{-1}(\epsilon, \mu, T) = \frac{2\pi\Omega}{g_s\hbar} \sum_{\nu} \{g_{\nu}^2(\epsilon, \epsilon + \bar{\omega}_{\nu})[n(\bar{\omega}_{\nu}, T) + f(\epsilon + \bar{\omega}_{\nu}, \mu, T)]\rho(\epsilon + \bar{\omega}_{\nu}) + g_{\nu}^2(\epsilon, \epsilon - \bar{\omega}_{\nu})[n(\bar{\omega}_{\nu}, T) + 1 + f(\epsilon - \bar{\omega}_{\nu}, \mu, T)]\rho(\epsilon - \bar{\omega}_{\nu})\} \quad (3.1)$$

where Ω is primitive cell volume, g_s is the spin degeneracy, $\overline{\omega}_\nu$ is average phonon energy, g_v is average electron-phonon matrix element, $\rho(\epsilon)$ is electron density of states and T is the absolute temperature. $f(\epsilon + \overline{\omega}_\nu, \mu, T)$ and $n(\overline{\omega}_\nu, T)$ represent the Fermi Dirac and Bose Einstein distribution. We used the optimized Slack model to calculate the lattice thermal conductivity of the system $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0, 0.25, 0.50, 0.75$ and 1.00 . The lattice thermal conductivity(κ_l) using the optimized Slack model is calculated as follows [100]:

$$\kappa_l = A \frac{\theta_D^3 V_a^{1/3} m_{av}}{\gamma^2 n^{2/3} T} \quad (3.2)$$

where θ_D is the Debye temperature, V_a is the volume of unit cell per atom, m_{av} is the mass of the unit cell per atom, γ is the Grüneisen parameter, n is the number of atoms in the unit cell and T is the absolute temperature. The constant A is calculated as $A = \frac{1}{1 + \frac{1}{\gamma} + \frac{8.3 \times 10^5}{\gamma^{2.4}}}$ [100]. The average Debye velocity (v_{av}) is calculated as:

$$\frac{1}{v_{av}^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3} \quad (3.3)$$

where v_L and v_T is longitudinal and transverse acoustic velocity. The Grüneisen parameter (γ) is related to the Debye velocity. It is calculated as:

$$\gamma = \frac{3}{2} \left(\frac{1 + \nu}{2 - 3\nu} \right), \nu = \frac{1 - 2(v_T/v_L)^2}{2 - 2(v_T/v_L)^2} \quad (3.4)$$

3.3 Results

3.3.1 Structure optimization and dynamical stability

Fe_2VGa and Fe_2VIn possess face-centered cubic (fcc) crystal structure having space group $\text{Fm}\bar{3}\text{m}$ as shown in fig.3.1 (a) and (e) respectively. Fe is tetrahedrally coordinated to V and Ga/In and vice-versa. V is octahedrally coordinated to Ga/In. The conventional cubic unit cell of Fe_2VGa contains four formula units of Fe_2VGa . We optimized the structure of Fe_2VGa and Fe_2VIn and found the lattice constant to be $5.71 \text{ \AA}$ and $5.96 \text{ \AA}$, respectively. Our computed lattice parameters are in reasonably good agreement with the experimentally reported lattice constant of $5.77 \text{ \AA}$ [101] and computational value of $5.72 \text{ \AA}$ [102] for Fe_2VGa . However, to the best of our knowledge, there is not any report on the lattice parameter of Fe_2VIn .

To investigate the effect of In doping, we chose the conventional cubic unit cell of Fe_2VGa ($\text{Fe}_8\text{V}_4\text{Ga}_4$) as we know from the literature that such substitutions or doping have not caused any change in the crystal structure [42, 86, 87, 89, 103]. We relaxed the cubic structure by substituting Ga with In into Fe_2VGa from 25% to 100%. The crystal structure of the In doped Fe_2VGa is shown in fig:3.1 (b),(c) and (d). Doping of In linearly increases the lattice parameter of the system owing to the higher atomic radii of the In following the Vegard's law as shown in the fig:3.2. The presence of both Ga and In distorted the local Fe-V and Fe-Ga/In tetrahedral environment, which in turn causes the absence of cubic symmetry in the In doped Fe_2VGa system.

The structural details of the Fe_2VIn , Fe_2VGa , and $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ is given in the table:4.1.

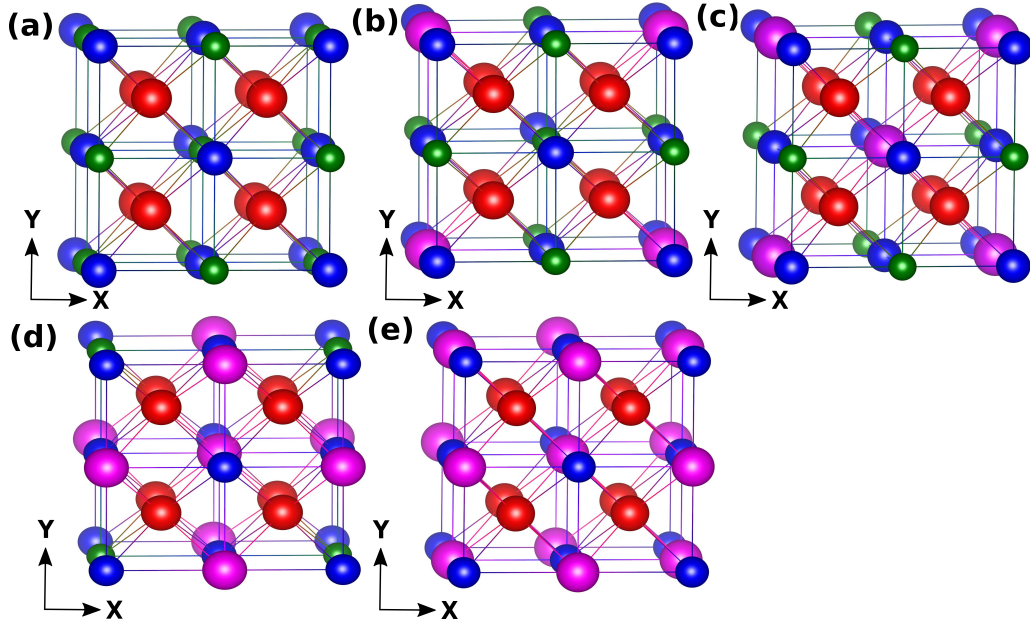


Figure 3.1: Crystal structure of $\text{Fe}_2\text{VIn}_{1-x}\text{Ga}_x$ system in X-Y plane (a) Fe_2VGa (b) $\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$ (c) $\text{Fe}_2\text{VGa}_{0.5}\text{In}_{0.5}$ (d) $\text{Fe}_2\text{VGa}_{0.25}\text{In}_{0.75}$ (e) Fe_2VIn . Here, red, blue, green, and magenta colour shows Fe, V, Ga, and In atoms, respectively.

In addition, we calculated the cohesive energy for the In doped Fe_2VGa using the eqn:3.5. We find the cohesive energy to be negative for all the doped systems, which means the doped products are stable. The cohesive energy of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0, 0.25, 0.50, 0.75$, and 1.00 are $-2.01, -1.54, -1.12, -0.74$, and -0.36 eV, respectively. However, the cohesive energy of doped products is lower than the parent Fe_2VGa .

$$E_c = E_{\text{Fe}_2\text{VGa}_{1-x}\text{In}_x} - (2 * E_{\text{Fe}} - E_{\text{V}} - (1 - x)E_{\text{Ga}} - xE_{\text{In}}) \quad (3.5)$$

Table 3.1: Calculated lattice parameter(a), Fe-V bond distance(d_{Fe-V}), Fe-Ga/In bond distance($d_{Fe-Ga/In}$), V-Ga/In bond distance($d_{V-Ga/In}$), and Fe-Fe bond distance(d_{Fe-Fe}) for $Fe_2VGa_{1-x}In_x$ with $x=0, 0.25, 0.50, 0.75$, and 1.00 . All the distances are in Å unit.

Systems	a	d_{Fe-V}	$d_{Fe-Ga/In}$	$d_{V-Ga/In}$	d_{Fe-Fe}
Fe_2VGa	5.71	2.47	2.47/2.47	2.85/2.85	2.85
$Fe_2VIn_{0.25}Ga_{0.75}$	5.77	2.45-2.52	2.48/2.56	2.95/2.95	2.82-2.95
$Fe_2VIn_{0.5}Ga_{0.5}$	5.84	2.49-2.57	2.49/2.57	2.95/2.95	2.78-3.06
$Fe_2VIn_{0.75}Ga_{0.25}$	5.90	2.53-2.62	2.49/2.58	2.95/2.95	2.87-3.03
Fe_2VIn	5.96	2.58	2.58/2.58	2.98/2.98	2.98

where the E_c is the cohesive energy. $E_{Fe_2VGa_{1-x}In_x}$ is the total energy of the system $Fe_2VGa_{1-x}In_x$. E_{Fe} , E_V , E_{Ga} , and E_{In} are the total energies of bulk Fe, bulk V, bulk Ga, and bulk In per atom, respectively. Further, to determine the stability of In doped phases, we calculated the formation energy (ΔE) of $Fe_2VGa_{1-x}In_x$ with respect to undoped Fe_2VGa and Fe_2VIn using the following equation:

$$\Delta E = E_{Fe_2VGa_{1-x}In_x} - (1-x)E_{Fe_2VGa} - xE_{Fe_2VIn} \quad (3.6)$$

$E_{Fe_2VGa_{1-x}In_x}$, E_{Fe_2VGa} , and E_{Fe_2VIn} denote the total energy of $Fe_2VGa_{1-x}In_x$, Fe_2VGa , and Fe_2VIn respectively. ΔE provides us with information about the thermodynamic stability of the doped phases. A -ve value of ΔE implies that the doped phase is more stable than the parent phase. The fig:3.2(a) and (b) show the lattice parameter and formation energy of $Fe_2VGa_{1-x}In_x$ with $x=0, 0.25, 0.50, 0.75$, and 1.00 . All the doped cases have positive values of formation energy suggesting that on doping Fe_2VGa (Fe_2VIn) with In (Ga) will result in phase segregation. However, these calculations are done at 0 K while these are synthesized at high temperatures. We expect that at higher temperatures, they might be stabilized due to enhanced mixing entropy. Among all the In doped systems, we find that the $Fe_2VGa_{0.50}In_{0.50}$ has higher formation energy than the $Fe_2VGa_{0.25}In_{0.75}$ and $Fe_2VGa_{0.75}In_{0.25}$ as the $Fe_2VGa_{0.50}In_{0.50}$ has accommodated more defect atoms. To understand the trend of formation energy, we calculated the standard deviation of bonds and angles for $Fe-V$ tetrahedra. The table:3.2 shows the mean and standard deviation for bond length and angles of Fe-V tetrahedra. The mean of bond length (angle) is calculated as the sum of all Fe-V bond lengths divided by the number of Fe-V bond length (angle). The standard deviation of bond length (angle) is calculated as the square root of variance, where the variance is the sum of the mod of the difference of bond length (angle) and mean bond length (angle) divided by the number of Fe-V bond length (angle). The

maximum value of formation energy in case of $\text{Fe}_2\text{VGa}_{0.50}\text{In}_{0.50}$ is attributed to the maximum distortion of $Fe - V$ tetrahedra due to the maximum standard deviation of $Fe - V$ tetrahedral angles.

The formation energies computed tell us that thermodynamically, these doped phases are unstable with respect to their parent compounds. However, these compounds are usually synthesized at high temperatures where the entropic contributions to free energy are important. In particular these compounds are stabilized by their mixing entropy contributions ($-TS_{mix}$). Hence to predict the synthesis temperature of these compounds at which the doped phases will be stable, we have included the contribution of the mixing entropy, which is given by:

$$S_{mix} = -R \sum_{x=1}^x a^x \sum_{i=1}^N f_i^x \ln(f_i^x) \quad (3.7)$$

where S_{mix} is the mixing entropy of the doped system per mole. a^x is the number of sites on the x sublattice and f_i^x is the fraction of element species i randomly distributed on the x sublattice, where the total number of species is N . The correction energy term because of mixing entropy at 300 K comes out to be 14.56, 17.94, and 14.56 meV for $\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$, $\text{Fe}_2\text{VGa}_{0.50}\text{In}_{0.50}$ and $\text{Fe}_2\text{VGa}_{0.25}\text{In}_{0.75}$ respectively. These compounds will be stable if the contribution (TS_{mix}) is larger than the ΔE . Based on these, we predict that $\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$, $\text{Fe}_2\text{VGa}_{0.50}\text{In}_{0.50}$, and $\text{Fe}_2\text{VGa}_{0.25}\text{In}_{0.75}$ can be synthesized at 822 K, 1003 K, and 1029 K, respectively.

Table 3.2: Mean bond distance (μ_d), standard bond distance deviation(σ_d), mean bond angle (μ_θ) and standard bond angle deviation(σ_θ) for $Fe - V$ tetrahedra for $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0, 0.25, 0.50, 0.75$, and 1.00 .

Systems	μ_d (Å)	σ_d (Å)	μ_θ (°)	σ_θ (°)
Fe_2VGa	2.47	0.00	109.471	0.00
$\text{Fe}_2\text{VIn}_{0.25}\text{Ga}_{0.75}$	2.50	0.03	109.459	1.19
$\text{Fe}_2\text{VIn}_{0.5}\text{Ga}_{0.5}$	2.53	0.04	109.449	1.56
$\text{Fe}_2\text{VIn}_{0.75}\text{Ga}_{0.25}$	2.55	0.04	109.452	1.43
Fe_2VIn	2.58	0.00	109.471	0.00

The calculated phonon dispersions of the parent compounds and In doped ones along the high symmetry points of the Brillouin zone (BZ) along with their partial phonon density of states (DOS) are shown in the fig.3.3. All the systems are dynamically stable. This is evident from the absence of imaginary frequencies throughout the Brillouin zone.

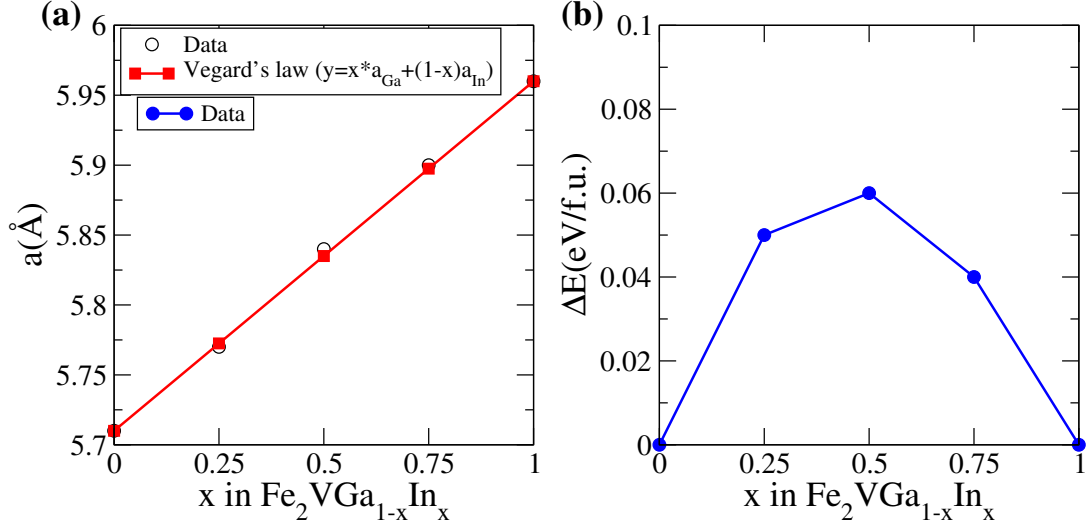


Figure 3.2: (a) Lattice parameter and (b) formation energy of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0, 0.25, 0.50, 0.75$, and 1.00 .

The partial phonon DOS reveals that Fe and V have significantly contributed in the high optical frequency zone ($> 100 \text{ cm}^{-1}$) and Ga/In has mainly contributed near the low frequency zone ($< 100 \text{ cm}^{-1}$). Doping of In in Fe_2VGa leads to phonon softening in the $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ system following the mass increment and increasing trend of the bond distance of Fe-V ($d_{\text{Fe-V}}$).

3.3.2 Electronic properties of Fe_2VGa and Fe_2VIn

The fig:3.4 shows the electronic band structure of Fe_2VGa and Fe_2VIn along with their partial DOS. Fe_2VGa is a semimetal due to electronic states present at the Fermi level, which is in good agreement with other DFT studies [102] and experimental studies [90]. Partial DOS analysis of Fe_2VGa reveals that states below the Fermi level are mainly from Fe-d orbitals while states above the Fermi level are due to the hybridization between V and Fe-d states with the latter having a dominating contribution. Like Fe_2VGa , Fe_2VIn is predicted to be a semimetal with a similar contribution of atomic orbitals around the Fermi energy. At the Fermi level, we observe band crossing in both the systems Fe_2VGa and Fe_2VIn about the $\Gamma \rightarrow M$ and $\Gamma \rightarrow R$ direction of the BZ as shown in fig:3.4 (a) and (b), respectively. At Γ point, the conduction band is triply degenerate at 0.12 eV and 0.13 eV above the Fermi level for Fe_2VGa and Fe_2VIn , respectively. Similarly, the valence band is also triply degenerate exactly 0.13 eV and 0.06 eV below the Fermi level for Fe_2VGa and Fe_2VIn , respectively. These conduction and valence bands at Γ point

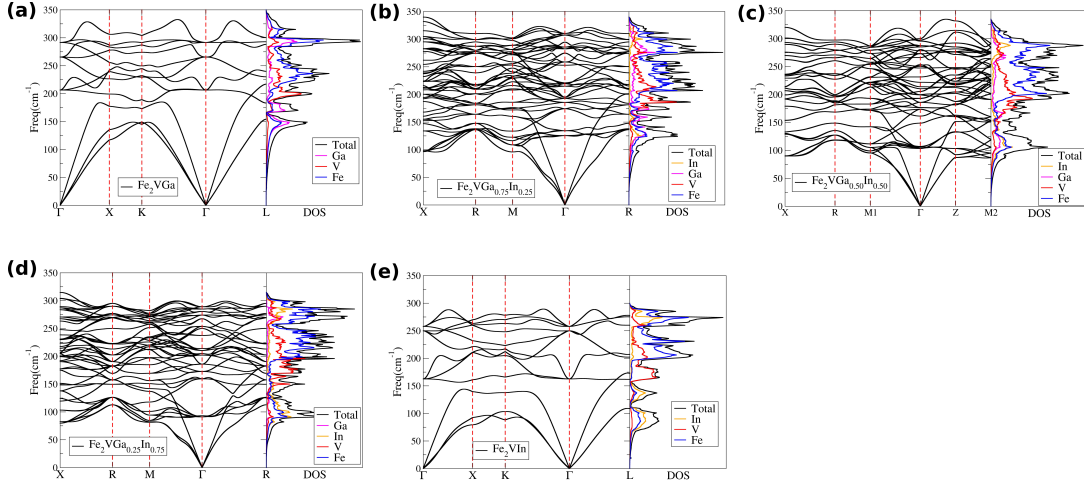


Figure 3.3: Phonon band dispersions of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with (a) $x=0$, (b) $x=0.25$, (c) $x=0.50$, (d) $x=0.75$, and (e) $x=1.00$.

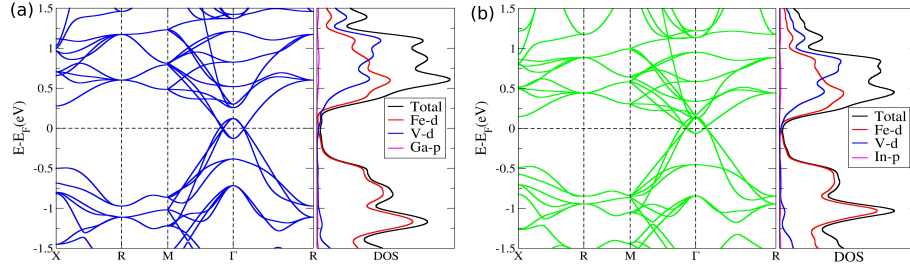


Figure 3.4: Electronic band structure along with partial DOS of (a) Fe_2VGa (b) Fe_2VIn .

are separated by 0.25 eV and 0.19 eV in Fe_2VGa and Fe_2VIn , respectively. In addition, The conduction bands of Fe_2VIn have come closer to the Fermi level mainly at the Γ point compared to the conduction bands of Fe_2VGa . This availability of bands in case of Fe_2VIn at lower value of band energy leads to carrier optimization. This carrier optimization affects the transport properties significantly, which we will see in the transport properties.

Fig.3.5 shows the electronic band structure along with partial DOS of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0.25, 0.50$, and 0.75 . Similar to the parent compounds, all the intermediate systems are semimetallic, comprising Fe and V d hybridized states near the Fermi level. The effect of In doping upon the electronic band structure is prominent in the conduction bands, mainly at R and Γ high symmetry points. The conduction band degeneracy at the R point is broken, leading to band flattening. This behavior becomes prominent in the 50 % In doping case. At the Γ point, the conduction band comes closer to the Fermi level with an increased doping concentration of In. The band flattening in the conduction band enhances the effective mass of the electrons and affects the transport properties of

$\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$.

3.3.3 Computation of relaxation time

The fig:3.6 depicts the electronic relaxation time for $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0, 0.25, 0.5, 0.75$, and 1.0 as a function of temperature. The decrease in relaxation time with increase in temperature for all systems is attributed to the increment in phonon population. Further, the parent systems Fe_2VGa and Fe_2VIn have high relaxation time compared to the doped systems at any given temperature. The presence of alloy disorder scattering in doped systems causes low relaxation time in these systems of carriers as compared to the parent ones.

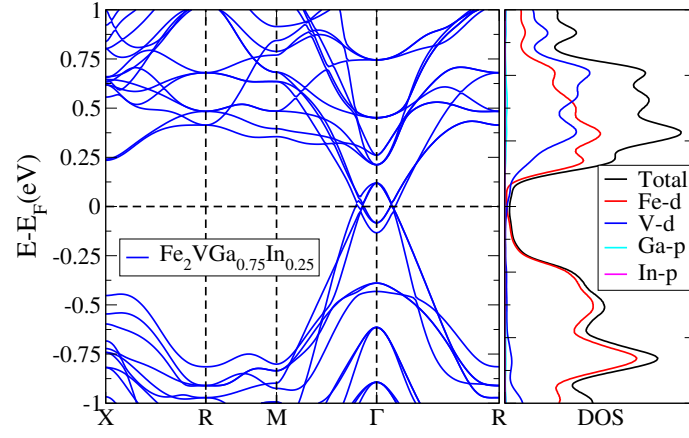
3.3.4 Thermoelectric properties of In doped Fe_2VGa

To characterize the thermoelectric performance of In doped Fe_2VGa , we calculated the transport properties such as, Seebeck coefficient, electrical conductivity, electronic thermal conductivity and lattice thermal conductivity. The discussion of transport properties is as follows:

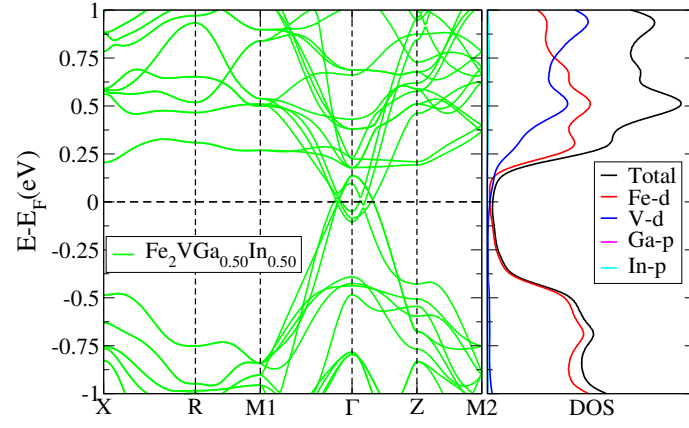
3.3.4.1 Seebeck coefficient

Fig:3.7(a) shows the Seebeck coefficient as a function of chemical potential (μ), for the undoped and doped systems at 300 K. At low concentration of hole doping, the Seebeck coefficient of Fe_2VIn is more than Fe_2VGa . Further, the maximum value of the Seebeck coefficient of In doped systems for hole doping is significantly higher than the parent systems, i.e., it improved from $\sim 35 \mu\text{V}/\text{K}$ for Fe_2VGa to $\sim 65 \mu\text{V}/\text{K}$ for hole doping at $\mu = -0.03 \text{ eV} \sim 2.21 \times 10^{20} \text{ cm}^{-3}$ for $\text{Fe}_2\text{VGa}_{0.5}\text{In}_{0.5}$. Moreover, the maximum value of the Seebeck coefficient of In doped systems are independent of carrier concentration for hole doping.

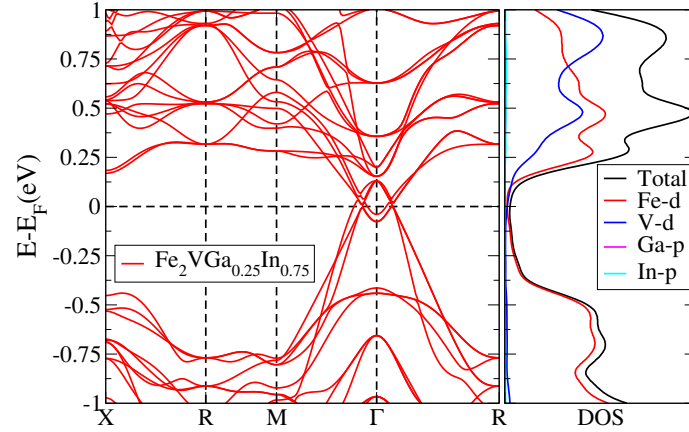
For electron doping, the maximum value of the Seebeck coefficient increases as the In concentration increases. For example, for Fe_2VGa , the Seebeck coefficient is $\sim 69 \mu\text{V}/\text{K}$ while for Fe_2VIn , it is $90.5 \mu\text{V}/\text{K}$ at $9.47 \times 10^{20} \text{ cm}^{-3}$. The table:3.3 contains the maximum Seebeck coefficient of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ for $x=0, 0.25, 0.50, 0.75, 1.00$ at corresponding values of chemical potential and carrier concentration.



(a)



(b)



(c)

Figure 3.5: Electronic band structure along with partial DOS of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with (a) $x=0.25$ (b) $x=0.50$ (c) $x=0.75$.

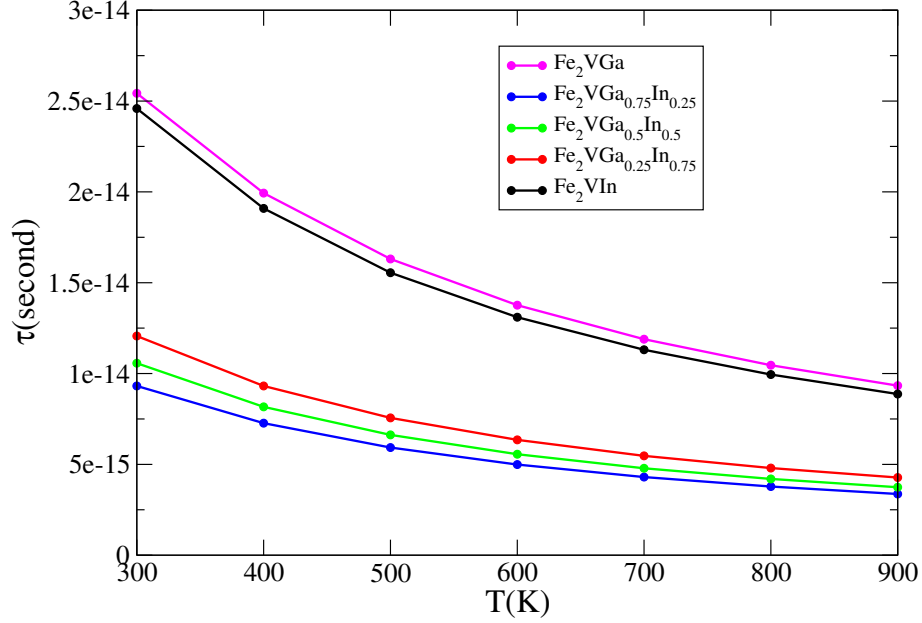


Figure 3.6: Electronic relaxation time for $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0, 0.25, 0.5, 0.75$, and 1.0 .

In table:3.4, we have compared the Seebeck coefficient of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with those of Heulser compounds and efficient thermoelectric materials. We observe that the Seebeck coefficient for holes in the In doped Fe_2VGa are higher than the other compounds, except for Bi_2Te_3 and Sb_2Te_3 . Similarly, when electrons are majority carriers, the Seebeck coefficient for the doped systems are either larger or comparable to the doped Fe_2VAl (champion material in this family of compounds), except for Ce or Ge doping. Moreover, electrons in Fe_2VIn show large values of Seebeck coefficient, which is comparable to that observed in Bi_2Te_3 . Thus, this comparison shows that In doping can be an effective strategy to enhance the Seebeck coefficient in Fe_2VGa .

To understand the trend of the Seebeck coefficient of In doped Fe_2VGa , we use the Seebeck coefficient formula of a metallic system within a parabolic band and energy independent scattering approximation, which is governed by the following law [5] :

$$S = \frac{8\pi^2 k_b^2}{3eh^2} m_d^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (3.8)$$

where k_b is the Boltzmann constant, e is electronic charge, h is Planck's constant, T is temperature, m_d^* is DOS effective mass and n is carrier concentration. The Seebeck coefficient is mainly governed by the ratio of m_d^* and carrier concentration. We calculated the

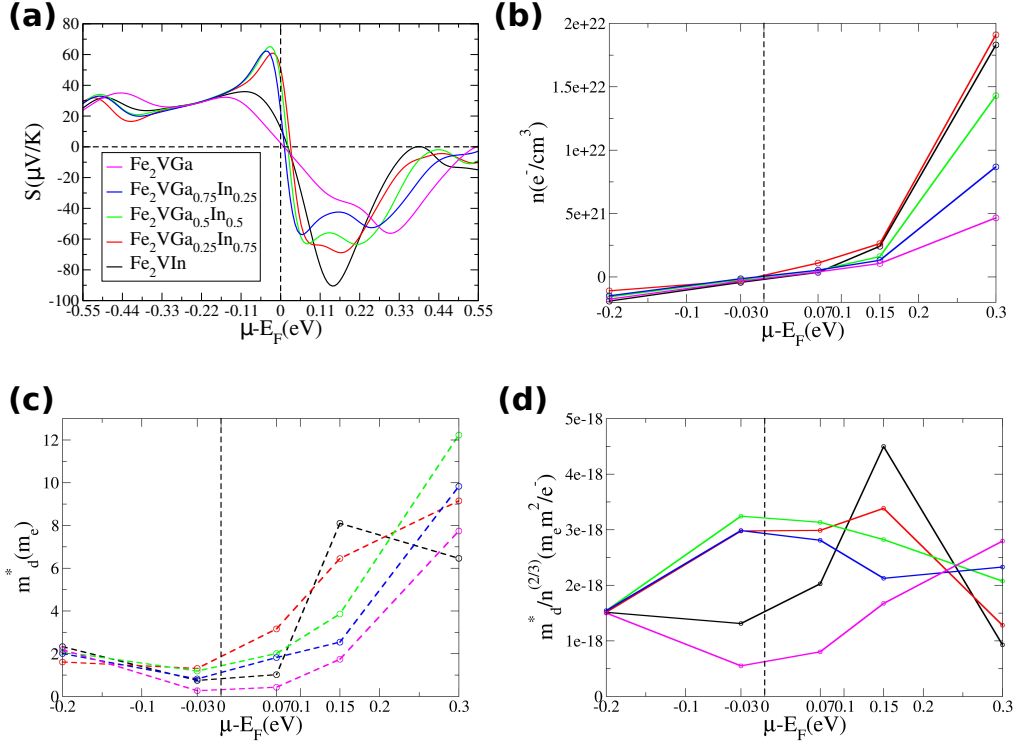


Figure 3.7: (a) Seebeck coefficient of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$) (b) chemical potential of In doped Fe_2VGa (c) DOS effective mass of In doped Fe_2VGa (d) ratio ($m_d^*/n^{2/3}$) of In doped Fe_2VGa .

carrier concentration (fig:3.7(b)), m_d^* (fig:3.7(c)) and their ratio (fig:3.7(d)). We inserted the value of the Seebeck coefficient and carrier concentration at a given chemical potential in the above eqn:3.8 to calculate the m_d^* . The increased value of DOS effective mass (m_d^*) of Fe_2VIn causes it to have higher Seebeck coefficient than Fe_2VGa (Fig:3.7(c)). In the same manner, for electron doping, the increase in In concentration leads to increase in the ratio of ($m_d^*/n^{2/3}$) as shown in the fig:3.7(d) and in turn, the Seebeck coefficient increases for In doped Fe_2VGa .

3.3.4.2 Electrical conductivity

Fig:3.8(a) depicts the electrical conductivity of the system $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$) as a function of chemical potential at 300 K. Unlike the Seebeck coefficient, the electrical conductivity of all the systems increases as the chemical potential move away from the Fermi level due to the increase in the carrier concentration. The

Table 3.3: Maximum Seebeck coefficient ($S(\mu V/K)$) of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with $x=0.0, 0.25, 0.50, 0.75$, and 1.00 .

hole doping					
Systems	Fe_2VGa	$\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$	$\text{Fe}_2\text{VGa}_{0.50}\text{In}_{0.50}$	$\text{Fe}_2\text{VGa}_{0.25}\text{In}_{0.75}$	Fe_2VIn
$S_{\max} (\mu V/K)$	35	62.3	65.1	60.9	35.9
chemical potential (eV)	-0.45	-0.04	-0.03	-0.02	-0.10
carrier conc. ($e^- \text{cm}^{-3}$) $\times 10^{21}$	8.53	0.235	0.221	0.337	0.947
electron doping					
$S_{\max} (\mu V/K)$	56	57.1	63.5	68.9	90.5
chemical potential (eV)	0.30	0.06	0.21	0.17	0.14
carrier conc. ($e^- \text{cm}^{-3}$) $\times 10^{21}$	4.61	0.474	0.414	3.18	2.11

Table 3.4: Comparison of maximum achieved Seebeck coefficient ($S(\mu V/K)$) at 300 K in $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ with other thermoelectric materials reported in literature. Our results are highlighted in bold fonts.

Systems	$S(\mu V/K)$ (hole doping)	$S(\mu V/K)$ (electron doping)
Fe_2VGa	13,22 [95]	-25
Fe_2VIn	36	-91
Fe_2VAl	25 [104]	
$\text{Fe}_2\text{VGa}_{0.25}\text{In}_{0.75}$	61	-69
$\text{Fe}_2\text{VGa}_{0.5}\text{In}_{0.5}$	65.1	-63.5
$\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$	62.3	-57.1
$\text{Fe}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{Ga}$	58 [95]	
$\text{Fe}_2\text{VGa}_{0.9}\text{Ge}_{0.1}$		-50 [105]
$\text{Fe}_2\text{VAl}_{0.97}\text{Ce}_{0.03}$		-160 [106]
$\text{Fe}_2\text{VAl}_{0.8}\text{B}_{0.2}$		-10 [107]
$\text{Fe}_2\text{VAl}_{0.8}\text{Si}_{0.2}$		-70 [107]
$\text{Fe}_2\text{VAl}_{0.8}\text{In}_{0.2}$		-60 [107]
$\text{Fe}_2\text{VAl}_{0.8}\text{Ge}_{0.2}$		~ -110 [108]
$\text{Ru}_2\text{VAl}_{0.25}\text{Ga}_{0.75}$		-18 [103]
Ru_2VGa	8 [103]	
Bi_2Te_3	166 [109]	107 [109]
Sb_2Te_3	~ 100 [110]	
$\text{Yb}_{14}\text{MnSb}_{11}$	60 [111]	
$\text{CeFe}_4\text{Sb}_{12}$	50 [106]	

electrical conductivity of In doped Fe_2VGa has been reduced compared to the undoped parent systems owing to the decreased relaxation time. Fe_2VIn and Fe_2VGa have almost similar electrical conductivity near the Fermi level for hole doping case. However, for

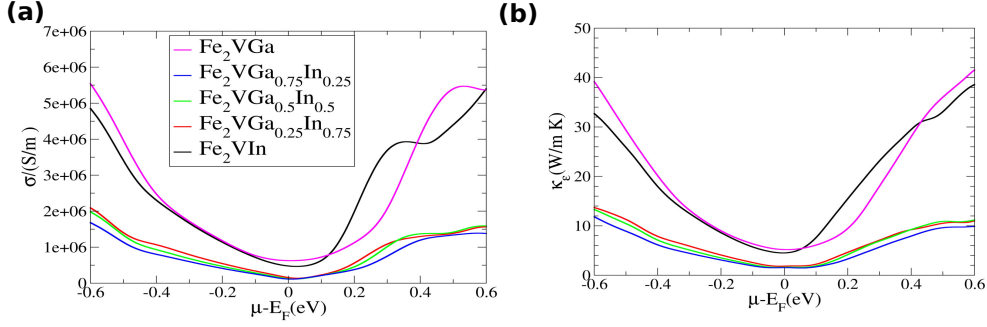


Figure 3.8: (a) Electrical conductivity and (b) Electronic thermal conductivity of Fe₂VGa_{1-x}In_x (x=0.0, 0.25, 0.50, 0.75, 1.00).

electron doping, Fe₂VIn has higher electrical conductivity compared to Fe₂VGa. We find the electrical conductivity of Fe₂VGa to be 6.02×10^5 S/m at the Fermi level, which matches well with the experimental value of 3.6×10^5 S/m at 300 K [94]. Among the In doped Fe₂VGa systems, Fe₂VGa_{0.25}In_{0.75} has slightly higher electrical conductivity near the Fermi level owing to its high value of electronic relaxation time. The electronic thermal conductivity of these systems as a function of chemical potential at 300 K is shown in the fig:3.8(b). The electronic thermal conductivity increases as chemical potential moves away from the Fermi level due to the increase in carrier concentration. The electronic thermal conductivity follows the trend of electrical conductivity for all the systems following the Weidemann-Franz law, which is given by

$$\kappa_e / \sigma = LT \quad (3.9)$$

where κ_e is electronic thermal conductivity, L is Lorentz number, and T is temperature.

3.3.4.3 Lattice thermal conductivity

Knowing that acoustic phonons have dominant contribution in lattice thermal conductivity, we used the optimized Slack model [100] to calculate the lattice thermal conductivity of Fe₂VGa_{1-x}In_x (x=0.0, 0.25, 0.50, 0.75, 1.00) as a function of temperature. The table:3.5 shows all the parameters used in the calculation of lattice thermal conductivity. It is depicted as a function of temperature in the fig:3.9. We find the lattice thermal conductivity of Fe₂VGa to be ~ 32 (W/m K). However, it is experimentally reported to be ~ 15 (W/m K) at 300 K [112]. This difference might be attributed to the defect disorder that is not considered in our calculation. The lattice thermal conductivity gradually decreases

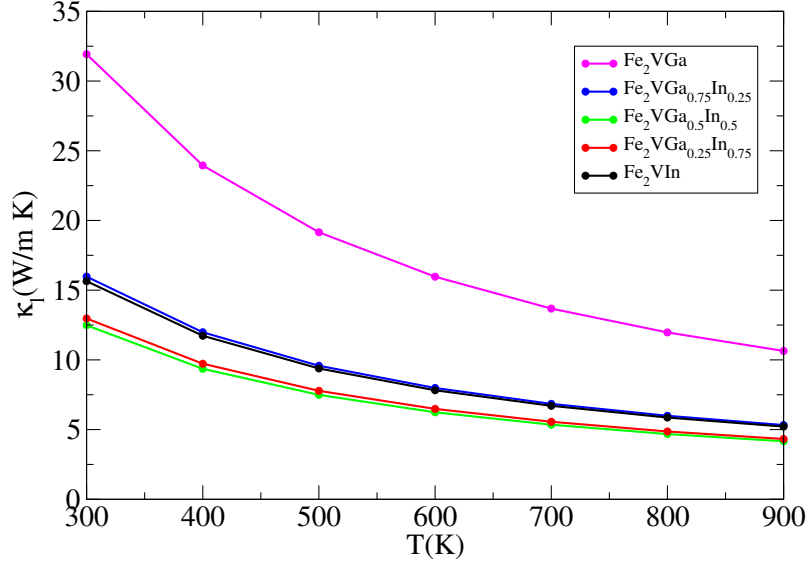


Figure 3.9: Lattice thermal conductivity of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$).

with increase in temperature for all the systems owing to the enhanced phonon population. Fe_2VGa has the maximum lattice thermal conductivity among all the systems owing to its high value of debye velocity and relatively low value of Grüneisen parameter. Doping of In causes the significant decrease in the lattice thermal conductivity that indicates the enhanced phonon scattering because of alloying effect. However, the lattice thermal conductivity of Fe_2VIn is lower than that of $\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$ owing to very low Debye velocity and relatively high value of the Grüneisen parameter of Fe_2VIn . The high value of the Grüneisen parameter of Fe_2VIn is attributed to the large difference in transverse and acoustic velocities. We further notice that $\text{Fe}_2\text{VGa}_{0.5}\text{In}_{0.5}$ has lowest lattice thermal conductivity among all the systems.

Table 3.5: Parameters used in the calculation of lattice thermal conductivity using optimized Slack model. Here, v_d , v_{la} , v_{ta1} , and v_{ta2} denote Debye velocity, longitudinal acoustic velocity, first transverse velocity and second transverse velocity.

Systems	Group velocity (m/s)				Grüneisen parameter	Average mass (u)	Debye temp. (K)
	v_d	v_{la}	v_{ta1}	v_{ta2}			
Fe_2VGa	4011	5676	3654	3654	1.10	58.09	527
$\text{Fe}_2\text{VGa}_{0.75}\text{In}_{0.25}$	4400	5971	4032	4032	0.92	60.91	571
$\text{Fe}_2\text{VGa}_{0.5}\text{In}_{0.5}$	3831	6037	3448	3448	1.54	63.73	492
$\text{Fe}_2\text{VGa}_{0.25}\text{In}_{0.75}$	3920	5629	3564	3564	1.16	66.54	498
Fe_2VIn	2811	5186	2501	2501	2.12	69.36	353

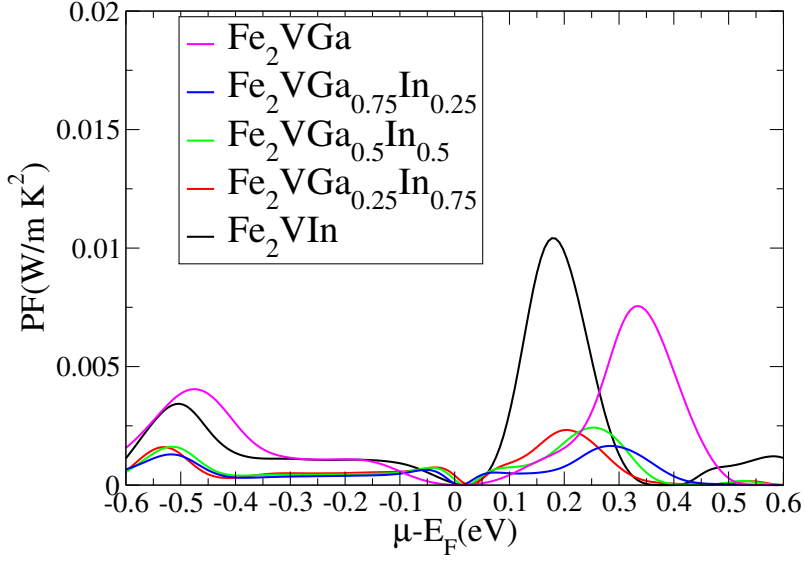


Figure 3.10: Thermoelectric power factor of $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$).

3.3.4.4 Thermoelectric power factor

The fig:3.10 shows the power factor of the system $\text{Fe}_2\text{VGa}_{1-x}\text{In}_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$) as a function of chemical potential at 300 K. We find that doping of In has not caused any significant improvement in the thermoelectric power factor compared to the parent systems Fe_2VIn and Fe_2VGa . Further, the power factor is nearly constant for the In doped systems in the hole doping region of upto $\mu = -0.2 \sim -0.3$ eV. In addition, hole doping at $\mu = -0.47$ eV Fe_2VGa has higher thermoelectric power factor owing to the enhanced Seebeck coefficient in this region. For the electron doping case, Fe_2VIn has the highest value of thermoelectric power factor at $\mu = 0.18$ eV $\sim 4.01 \times 10^{21} \text{ cm}^{-3}$ because of the high Seebeck coefficient and high electrical conductivity. Generally, it is expected that an increase in the Seebeck coefficient is followed by a decrease in electrical conductivity. However, here we see that both are increasing for Fe_2VIn for the electron doping case. The high value of electrical conductivity is caused by the optimization of carrier concentration owing to the increased DOS of Fe_2VIn following the collapse of bands above the Fermi level near the Γ point (Fig:3.4(b)). The high value of the Seebeck coefficient is led by the relatively more increment in the DOS effective mass compared to the carrier concentration of Fe_2VIn .

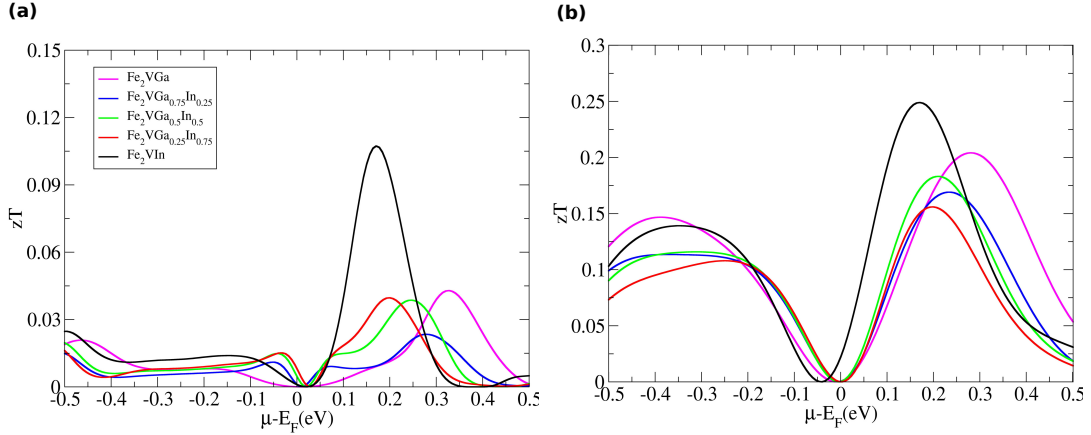


Figure 3.11: Thermoelectric figure of merit of $Fe_2VGa_{1-x}In_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$) (a) 300 K (b) 900 K.

3.3.4.5 Figure of merit

Based on the electronic transport properties discussed above, we calculate the zT of our In doped systems. In fig:3.11(a) and (b), we plot the thermoelectric figure of merit of our system $Fe_2VGa_{1-x}In_x$ ($x=0.0, 0.25, 0.50, 0.75, 1.00$) at 300 K and 900 K, respectively, as a function of chemical potential. For the hole doping case, we see that doping of In has not caused any significant improvement in the figure of merit of Fe_2VGa . For hole doping, the parent system Fe_2VIn has the maximum zT of 0.03 at chemical potential $\mu = -0.49$ eV at 300 K. Whereas for electron doping, Fe_2VIn has highest zT of 0.1 at chemical potential $\mu = 0.17$ eV at 300 K. Though $Fe_2VGa_{0.5}In_{0.5}$ and $Fe_2VGa_{0.25}In_{0.75}$ show similar zT compared to Fe_2VGa , the doping of In has led to optimization of carrier concentration. However, it remains lower than the zT of Fe_2VIn for electron doping. With increase in the temperature, we find that the zT has increased significantly for the In doped systems and Fe_2VIn has maximum zT of 0.25 at 900 K for electron doping.

3.4 Conclusions

In summary, we have systematically investigated the electronic and thermoelectric properties of $Fe_2VGa_{1-x}In_x$ with $x=0, 0.25, 0.50, 0.75, 1.00$. The results show that doping of In significantly affects the conduction bands of In doped Fe_2VGa and leads to flattening of bands. Moreover, conduction bands come closer to the Fermi level with In inclusion, which helps optimize carriers and leads to enhanced thermoelectric properties of Fe_2VIn

for electron doping case. Though the In doping in Fe_2VGa has caused significant improvement in the Seebeck coefficient for hole doping, it has reduced the electrical conductivity compared to the Fe_2VGa and in turn, there is no significant improvement in the zT . However, the parent system Fe_2VIn has the highest zT of 0.1 for the electron doping at 300 K, which further increases to 0.25 at 900 K.

Chapter 4

Implications of Nb and Sn co-doping on thermoelectric properties of defective half Heusler $\text{Nb}_{0.8}\text{CoSb}$

4.1 Introduction

Small band gap semiconducting half Heuslers (HH) are being actively investigated for high temperature thermoelectric applications. HH compounds are ternary intermetallics with the general formula XYZ, where X (Z) is typically the most electropositive (electronegative) transition metal (main group element), and Y is transition metal with electronegativity between X and Z. Similar to full Heuslers, HH crystal structure consists of 4 face-centered cubic (fcc) sublattices. However, in contrast with full Heuslers, one of these sublattices is empty. Their crystal structure can be understood as a combination of a Zinc blende type of structure between X and Y atoms and a NaCl type of structure between Y and Z atoms. X and Y are bonded with covalent type of interactions, while the Y and Z are bonded with strong ionic interactions.

The stability and electronic properties of half Heusler alloys are governed by the number of valence electron counts (VEC) [113]. HHs with VEC-18 are found to be a stable semiconductor. Many HH alloys have received great attention as a potential thermoelectric material due to their low toxicity, semiconducting nature, and large power factor [6–8, 114–121]. However, like the full Heuslers, they also have high thermal conductivity, which is detrimental to their overall performance as a thermoelectric material. Currently, there have been many reports on the reduction of their intrinsic high thermal conductivity [122–127] and optimization of carrier concentration [9, 128–130]. Due to its small band gap and steep slope of the density of states towards the Fermi level, HH compounds with a VEC = 18 have been thoroughly explored as prospective high temperature

thermoelectric materials. For example, MNiSn and MCoSb (M = Hf, Zr, and Ti) compounds with VEC of 18 have been extensively investigated because of their high Seebeck coefficients and high electrical conductivities [131, 132] as high Seebeck coefficient and high electrical conductivity favors high thermopower and in turn high zT . Sb doping into the Sn site in the n-types or Sn doping into the Sb site in the p-types are often investigated in order to maximize the carrier concentration. Isoelectronic alloying on the M sublattice in the HH compounds MNiSn and MCoSb (M = Hf, Zr, and Ti) has been proven to lower the lattice thermal conductivity κ_l [133, 134]. Point defect disorder, owing to the strain and mass differences between alloying atoms and host atoms, scatters the phonons effectively and lowers κ_l . A highest zT of 0.8 has been obtained for ZrNiSn_{0.99}Sb_{0.01} for $x=0.01$ at 875 K [135].

While, semiconductors exhibit good thermoelectric properties generally, the HHs with metallic properties such as VCoSb, NbCoSb, and TiNiSb (VEC-19) have also shown reasonably good thermoelectric performance [136–138]. These materials with one extra electron are better described as heavily doped semiconductors. Lihong et al. recently showed that NbCoSb (VEC-19) is a thermoelectric material with zT of 0.4 at 973 K [137]. Such a high zT in a metallic system NbCoSb was attributed to its high electrical conductivity and Seebeck coefficient. Although the zT peak of 0.4 is impractical for real-world applications, it's intriguing to note that a valence electron count traditionally thought to be 18 is not necessary. They further reported that NbCoSb has a very high carrier concentration ($\sim 10^{21} \text{cm}^{-3}$) at room temperature. In addition to this work, Lihong et al. further doped Sn into the NbCoSb system (NbCoSb_{1-x}Sn_x) up to 25 % and found that with Sn doping, carrier concentration decreased and led to enhancement in the Seebeck coefficient. 20 % Sn doping led to increase zT by 40 % to be 0.60 at 973 K [139]. Later Zeier et al. showed that Nb_{0.8}CoSb is a stable phase with 18 valence electrons [140]. Further, using cluster expansion and DFT based calculations, Zeier et al. showed that Nb_{0.8}CoSb acquires a tetragonal phase with space group $I\bar{4}$. Furthermore, Zeier et al. showed that Nb_{0.8}CoSb is semiconducting with a bandgap of 1.0 eV. Later, Xia et al. showed that NbCoSb is a composite of Nb_{0.8}CoSb and impurity phases [141]. In addition, Xia et al. reported that Nb_{0.8+ δ} CoSb ($0 \leq \delta < 0.05$) is a thermoelectric material with zT of 0.9 at 1123 K. Xie et al. further showed that, compared to NbCoSb, Nb_{0.8}CoSb has lower electrical conductivity and high Seebeck coefficient due to low carrier concentration that led to its high zT . They also demonstrated that as the contribution of Nb increases, the peak value of the

Seebeck coefficient, influenced by bipolarity effects, shifts towards higher temperatures. At a doping level of $\delta = 0.03$, this bipolarity effect disappears as carrier concentration increases due to the introduction of Nb, leading to a rapid decline in the Seebeck coefficient.

Motivated by the improved performance of thermoelectric properties in NbCoSb by Sn doping as discussed above, our collaborators (Saurabh kumar under the supervision of Dr. Surjeet Singh) doped Sn into Nb_{0.8}CoSb to improve the thermoelectric performance of Nb_{0.8+ δ} CoSb. They doped Sn in Nb_{0.8+ δ} CoSb gradually from 1% to 10 % and prepared the samples with composition of Nb_{0.8+ δ} CoSb_{1- x} Sn _{x} where $\delta \leq 0.05$ and $x \leq 0.10$ and measured the transport properties of the sample. They measured the zT of 1 at 1100 K for Nb_{0.84}CoSb_{0.95}Sn_{0.05}. Though with Sn doping, the thermoelectric performance of the sample was enhanced greatly, the role of Sn and Nb in the transport properties of Nb_{0.8+ δ} CoSb_{1- x} Sn _{x} is not very clear. In addition to the transport properties measurement study of Nb_{0.8+ δ} CoSb_{1- x} Sn _{x} from 1% to 10 %, we have studied the role of Sn doping and excess Nb upon structural and electronic properties of Nb_{0.8}CoSb to understand the reason behind the improved thermoelectric performance using first principles.

The rest of the chapter is as follows: Section 4.2 contains the computational details. The results are summarized in Section 4.3. Finally, we conclude in Section 4.4.

4.2 Computational details

The calculations in the present chapter are performed using the Quantum ESPRESSO software, which is a plane-wave based implementation of density functional theory [96, 142]. The electronic exchange and correlation potential were described by the generalized gradient approximation (GGA) as parametrized by Perdew, Burke, and Ernzerhof (PBE) [58]. The valence electronic configuration of Nb, Co, and Sb, considered in our calculations are $4s^2 4p^6 4d^3 5s^2$, $4s^1 3d^8$, and $4d^{10} 5s^2 5p^3$, respectively. We have used ultrasoft pseudopotentials to account for the electron-ion interactions [143]. We used a kinetic energy cutoff of 110 Ry and a charge density cutoff of 880 Ry to truncate the plane wave basis used in the Kohn-Sham wave function. The structure was relaxed until the Hellman-Feynman force on each atom became less than 0.025 eV/Å. An unshifted Monkhorst-Pack k-mesh of $5 \times 5 \times 8$ was used for Nb_{0.8}CoSb, Nb_{0.8}CoSb_{0.9}Sn_{0.1} and Nb_{0.9}CoSb_{0.9}Sn_{0.1} for the

Brillouin zone integration [59]. Marzari-Vanderbilt smearing with a smearing width of 0.005 Ry was used to expedite the convergence of electronic energy [144].

4.3 Results and discussion

4.3.1 Structural details

NbCoSb possesses fcc crystal structure with space group (F-43m) as shown in the fig:4.1(a). Nb, Co, and Sb atoms occupy the 4a (0,0,0), 4c (0.25, 0.25, 0.25), and 4b (0.50, 0.50, 0.50) positions, respectively. Nb is octahedrally coordinated to Sb, tetrahedrally coordinated to Co, and vice versa. Co is tetrahedrally coordinated to Nb and Sb. We obtained an optimized lattice parameter of 5.97 Å. This is in reasonably good agreement with the experimental lattice parameter of 5.90 Å [137]. The Nb-Co, Nb-Sb, and Co-Sb bond distances are 2.59 Å, 2.99 Å, and 2.59 Å, respectively.

Recently, Zeier et al. [140] studied the diffraction data of the “NbCoSb” and revealed that “it exist in two phases, Nb defective half-Heusler phase $\text{Nb}_{0.84}\text{CoSb}$ and Nb_3Sb . Further, they studied the formation enthalpy of $\text{Nb}_{1-x}\text{O}_x\text{CoSb}$ with $x=0.111, 0.166, 0.2$, and 0.9 (O denotes the vacancy). They reported that among all the ordered vacancy structures, $\text{Nb}_{0.8}\text{CoSb}$ (20 % Nb vacancies) has the lowest formation enthalpy that corresponds to valence electron count 18. They found that among all the vacancy ordered structures, only $\text{Nb}_{0.8}\text{CoSb}$ breaks the Nb-Co-Sb ternary convex hull as described in [140] and emerges as ground state configuration. The crystal structure of the most stable configuration of $\text{Nb}_{0.8}\text{CoSb}$ belongs to the tetragonal $I\bar{4}$ space group with lattice parameter of 9.34 Å along a axis and 5.96 Å along the c axis. The local structural environment of the $\text{Nb}_{0.8}\text{CoSb}$ is distorted, i.e., in tetragonal $\text{Nb}_{0.8}\text{CoSb}$, the Sb atoms have two different arrangements with respect to the Nb atoms, as opposed to NbCoSb where Sb atoms occupy the Nb octahedra. Out of the ten Sb atoms in a single unit cell, two of them form a square planar shape around the Nb atoms with a bond length of about 2.95 Å, while the remaining eight Sb atoms are positioned in a distorted octagonal arrangement with Nb vacancies within each octahedron. The bond length between Nb and Sb in this environment varies from 2.94 Å to 3.10 Å. Since $\text{Nb}_{0.8}\text{CoSb}$ was found to have cubic symmetry in experiments, he generated many special quasirandom structures for $\text{Nb}_{0.8}\text{CoSb}$, and found that the disordered phase of $\text{Nb}_{0.8}\text{CoSb}$ is 50 meV/atom higher in energy than the ordered phase at this same

composition and thermal energy alone can overcome this energy and lead to an order-disorder phase transition as $\text{Nb}_{0.8}\text{CoSb}$ was prepared at very high temperature. Hence, we chose tetragonal $\text{Nb}_{0.8}\text{CoSb}$ for further study. The crystal structure of $\text{Nb}_{0.8}\text{CoSb}$ is shown in the fig:4.1(b)

To study the role of Sn and Nb in the transport properties of $\text{Nb}_{0.8+\delta}\text{CoSb}_{0.9}\text{Sn}_{0.1}$, we first study the role of the 10% Sn doping into $\text{Nb}_{0.8}\text{CoSb}$ ($\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$) as it is computationally inexpensive to accommodate 10% Sn doping in the system. The crystal structure of $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ is shown in the fig:4.1(c). Since, Sb and Sn have almost similar atomic radii, we only relaxed the atomic position of $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ to minimize the forces. In the tetragonal $\text{Nb}_{0.8}\text{CoSb}$, as discussed above, there are two different types of Sb: one in the square planar environment with Nb and other in distorted octagonal arrangement. We notice that doped Sn prefers to substitute the Sb in the square planar environment compared to the distorted octagonal environment by 1.2 meV in energy. Doping of Sn has not led to any significant change in bond distances as shown in the table:4.1. This substitution of Sn results in a bond length of 2.95 Å between Sn and Nb.

In addition to the doped Sn, we included excess Nb into the system ($\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$) to understand the role of excess Nb into the transport properties because experimentally, it has been found that Sn doping results in incorporation of Nb in the sample. Since it is computationally expensive to consider the small concentration of Nb as found in $\text{Nb}_{0.83}\text{CoSb}_{0.9}\text{Sn}_{0.1}$, we have included 10 % Nb and relaxed the atomic positions of the system $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$. We notice that the excess Nb prefers to occupy the vacant position where the Sn is in square planar environment than to the vacant position where Sb is in the square planar environment by 0.32 eV. The excess Nb is bonded with Sn with bond distance of 2.98 Å. The crystal structure of $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ is shown in the fig:4.1(d).

The table:4.1 contains all the relevant bond distances of the systems $\text{Nb}_{0.8}\text{CoSb}$, $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ and $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$.

4.3.2 Electronic properties

4.3.2.1 NbCoSb and $\text{Nb}_{0.8}\text{CoSb}$

The electronic band structure of NbCoSb and its partial DOS is shown in the fig:4.2 (a) and (b), respectively. NbCoSb is a metal with states present at the Fermi level. The

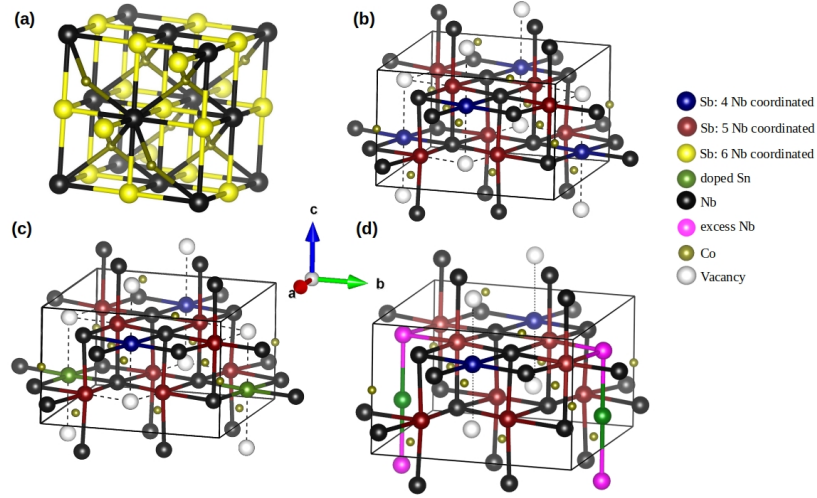


Figure 4.1: Crystal structure (a) fcc NbCoSb, (b) tetragonal Nb_{0.8}CoSb, (c) tetragonal Nb_{0.8}CoSb_{0.9}Sn_{0.1}, and (d) tetragonal Nb_{0.9}CoSb_{0.9}Sn_{0.1}.

Table 4.1: Calculated Nb-Co bond distance (d_{Nb-Co}), Nb-Sb bond distance (d_{Nb-Sb}), Co-Sb bond distance (d_{Co-Sb}), Nb-Sn bond distance (d_{Nb-Sn}), and Co-Sn bond distance (d_{Co-Sn}) for Nb_{0.8}CoSb, Nb_{0.8}CoSb_{0.9}Sn_{0.1}, and Nb_{0.9}CoSb_{0.9}Sn_{0.1}.

Bond distances (Å)	Nb _{0.8} CoSb	Nb _{0.8} CoSb _{0.9} Sn _{0.1}		Nb _{0.9} CoSb _{0.9} Sn _{0.1}		
		Sn unattached	Sn attached	Sn unattached	Sn attached	attached excess Nb
d_{Nb-Co}	2.52, 2.46, 2.56, 2.54	2.50, 2.53, 2.45, 2.56	2.53, 2.47, 2.56, 2.53	2.53, 2.61, 2.53, 2.61	2.60, 2.53, 2.53, 2.51	2.53, 2.63, 2.60, 2.51
d_{Nb-Sb}	2.99, 3.02, 2.95, 2.94, 2.98, 3.10	2.94, 3.03, 2.95, 3.00, 2.97, 3.11	3.03, 2.99, 2.98, 2.93, 3.11	2.98, 2.93, 2.99, 2.92, 2.99, 3.00	2.99, 2.97, 2.99, 2.97, 3.08	2.92, 2.92, 2.92, 2.92
d_{Co-Sb}	2.61, 2.54, 2.57, 2.52	2.53, 2.54, 2.61, 2.57	2.50, 2.56, 2.54	2.56, 2.56, 2.63, 2.63	2.58, 2.59, 2.54	
d_{Nb-Sn}			2.96		2.95	2.98
d_{Co-Sn}			2.65		2.62	

states at the Fermi level are mainly comprised of the d states of Nb and Co with a small admixture of Sb p states where Nb has most dominant contribution. Although the band structure of NbCoSb has an energy gap of 0.9 eV, the excess e^- pushes the Fermi level into the conduction band, making it metallic. This suggests that an appropriate amount of hole doping can bring the Fermi level down in this gap region to make it semiconducting. Hence, 20 % Nb removal from NbCoSb makes it a semiconductor and the system Nb_{0.8}CoSb stabilizes further this system by fulfilling the valence bal-

anced condition [Net valence= $+4(Nb_{0.8}^{+5}) - 1(Co^{-1}) - 1(Sb^{-3}) = 0$] as it attains VEC-18 [VEC= $0.8 \times 5 + 1 \times 9 + 1 \times 5 = 18$] configuration. Fig.4.3(a) and (b) depict the electronic band structure and its DOS projected onto the atomic orbitals, respectively. We find $Nb_{0.8}CoSb$ to be an indirect semiconductor with a bandgap of 1.01 eV with conduction band minima (CBM) and valence band maxima (VBM) at Γ and R point of the Brillouin zone, respectively. Interestingly, we observe that there are 4 electron pockets at the M point, which are almost degenerate with CBM (0.02 eV above CBM). The partial In addition to this, Zeier et al. considered all the possible configurations of $Nb_{0.8}CoSb$ up to 5 formula units of $NbCoSb$ to find the structure of $Nb_{0.8}CoSb$ as any other low energy structure for this composition was not found above this formula unit DOS analysis of $Nb_{0.8}CoSb$ reveals that Nb d states have a dominant contribution in the conduction band, However, the valence bands have significant contribution from Co d states with minor contribution from Sb p states.

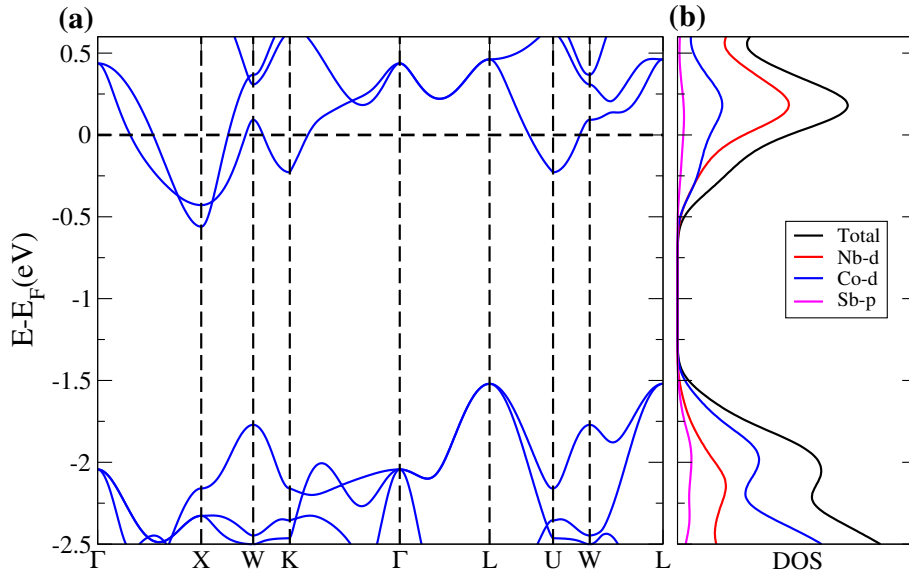


Figure 4.2: (a) Band structure and (b) density of states of $NbCoSb$.

4.3.2.2 Effect of Sn doping upon electronic properties of $Nb_{0.8}CoSb$

Fig.4.4(a) and (b) depict the electronic band structure and partial DOS of $Nb_{0.8}CoSb_{0.9}Sn_{0.1}$. Since Sn lies ahead of Sb in the periodic table, substituting Sb by 10% Sn induces hole doping, which shifts the Fermi level into the valence band. The partial DOS analysis reveals that p orbitals of Sn has mostly contributed near the Fermi level. In addition to

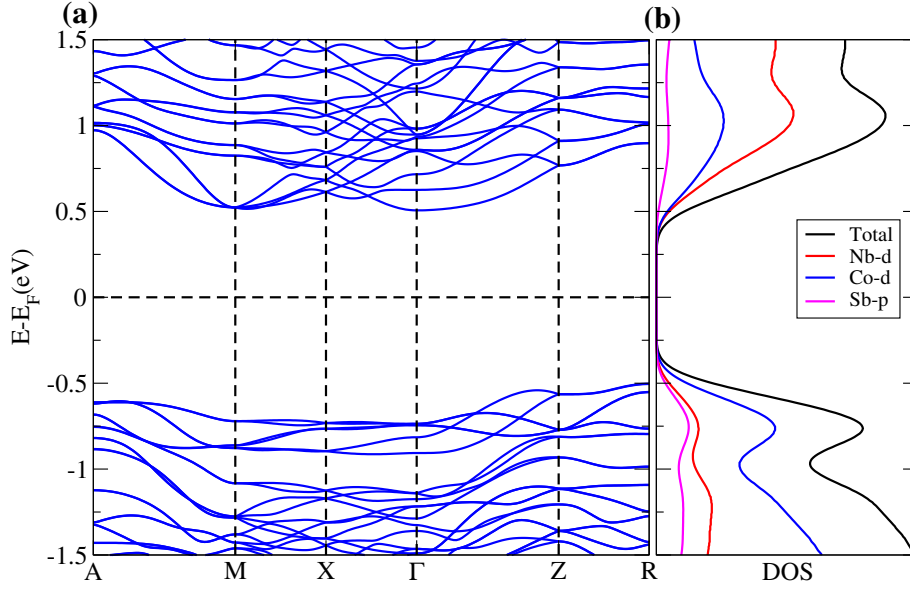


Figure 4.3: (a) Band structure and (b) density of states of $\text{Nb}_{0.8}\text{CoSb}$.

this, Sn doping has very minimal effect on the band curvature of both the valence and conduction bands, as the contribution of Sn orbitals is negligible. To confirm this, we calculated the effective masses for $\text{Nb}_{0.8}\text{CoSb}$ and $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ along different high symmetry paths as shown in the table:4.2. We notice that both the systems have almost similar values of effective masses along the different high symmetry paths near the Fermi level. Apart from this, Sn doping results in the breaking of degeneracy at certain points in the band structure, such as the M point in the conduction band, and the A, Z, and R points in the valence band. Upon analyzing the density of states (DOS), we observe that there is very small difference between the partial DOS of $\text{Nb}_{0.8}\text{CoSb}$ and $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$, as the contribution of Sn p orbitals near the Fermi energy is minimal.

4.3.2.3 Effect of excess Nb on the electronic properties of $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$

Fig:4.5(a) and (b) display the electronic band structure of $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ and partial DOS of its constituent atoms, respectively, where the contribution of excess Nb is highlighted in the fig:4.5(a). The doping of an extra Nb pushes the Fermi level into the conduction band, as Nb is a strong electron donor. In addition, it has caused significant modification to the band dispersion near the Fermi level and has led to the band convergence at Γ point. Specifically, the first and second conduction bands at Γ point have come

Table 4.2: Effective masses of $\text{Nb}_{0.8}\text{CoSb}$ and $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ (All the masses are given in units of m_e). VB and CB stand for valence band and conduction band. $A \rightarrow M$, $Z \rightarrow \Gamma$, $R \rightarrow Z$, $M \rightarrow A$, $M \rightarrow X$, $\Gamma \rightarrow Z$ and $Z \rightarrow R$ represent the path along high symmetry point A to M, Z to Γ , R to Z, M to A, M to X, Γ to Z, Z to R, respectively. @R, @M, @ Γ and @Z indicate that extrema is at R, M, Γ and Z, respectively.

Path	Effective masses(m_e)	
	$\text{Nb}_{0.8}\text{CoSb}$	$\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$
VB($A \rightarrow M$)	0.14	0.15
VB($Z \rightarrow \Gamma$)	0.15	0.14
VB@R($R \rightarrow Z$)	0.27	0.39
CB@M($M \rightarrow A$)	0.21, 0.09	0.21, 0.08
CB(M $\rightarrow X$)	0.13, 0.40	0.20, 0.33
CB@M (M $\rightarrow X$)	0.30, 0.12	0.33, 0.07
CB@ Γ ($\Gamma \rightarrow Z$)	0.61	0.55
CB@Z($Z \rightarrow R$)	0.14	0.14

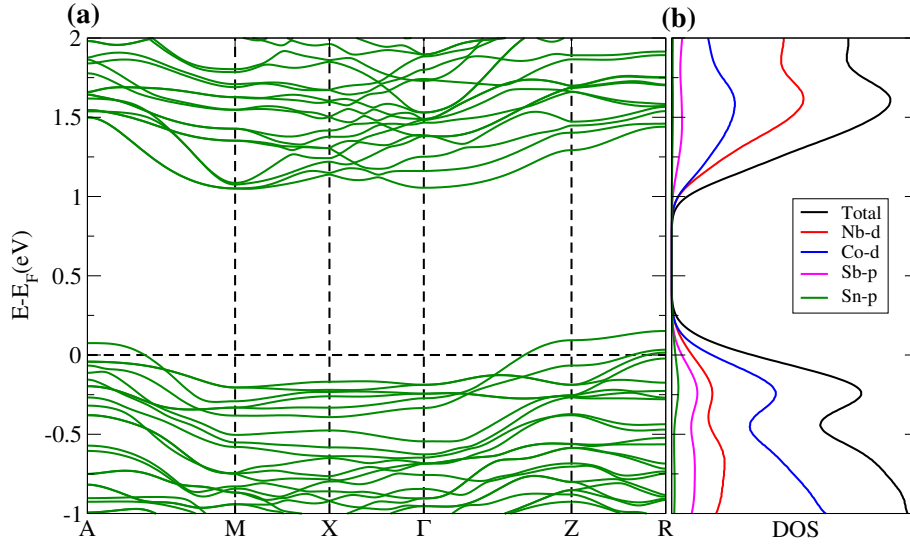


Figure 4.4: (a) Band structure and (b) partial DOS of $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$.

closer in energy, from 0.12 eV apart in case of $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ to 0.03 eV in case of $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$. We further notice that excess Nb d state has more contribution at the Fermi level and has led to a new flat band at 0.03 eV below the Fermi level with relatively weak dispersion along $M \rightarrow X$ and $X \rightarrow \Gamma$, as shown by thick band in color in the fig:4.5(a).

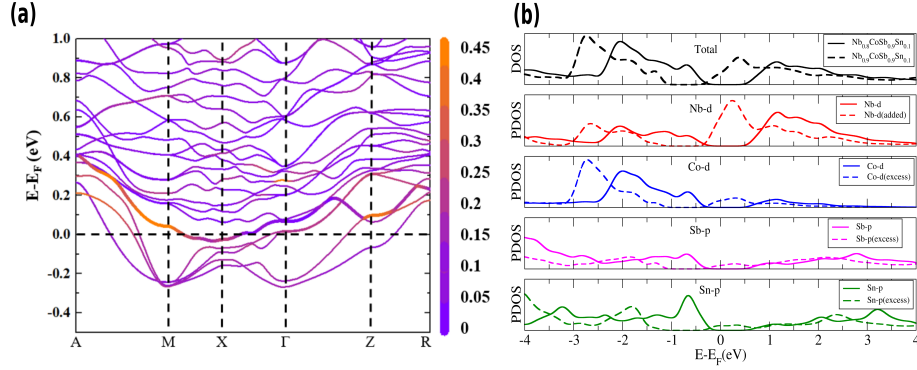


Figure 4.5: (a) Dispersion of the conduction band of $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ showing the contribution from excess Nb atoms. (b) Partial DOS of each constituent atoms.

4.3.3 Transport properties

The transport properties of the sample $\text{Nb}_{0.83}\text{CoSb}_{1-x}\text{Sn}_x$ ($x=0.0, 0.01, 0.05, 0.10$) were measured experimentally (Dr. Saurabh Kumar under supervision of Dr. Surjeet Singh). The electrical conductivity of the sample is shown in the fig:4.6 (a). The electrical conductivity of the undoped sample decreases from its value of 500 S cm^{-1} at 300 K to 400 S cm^{-1} at 1100 K with the increase in temperature. There is a significant enhancement in electrical conductivity with 1% Sn doping. With a further increase in Sn doping, the electrical conductivity decreases but remains more than that of the undoped sample. The increase in the electrical conductivity for Sn doped samples is owing to the excess Nb that gives free carriers as Nb has a significant contribution at the Fermi level as shown in the fig:4.5 (b). We notice that electrical conductivity varies with temperature as $T^{-0.5}$ for the samples $\text{Nb}_{0.83}\text{CoSb}_{1-x}\text{Sn}_x$ ($x=0.0, 0.01, 0.05, 0.10$). This temperature variation of electrical conductivity can be attributed to the alloy scattering. The slight upturn in the electrical conductivity for the undoped sample at 800 K is due to the thermal excitation of minority carriers around this temperature. The absence of such behavior in electrical conductivity for 1 % Sn doped samples is because of the presence of Sn and excess Nb that pushes the Fermi level deep inside the conduction band. However, this upturn reappears again with a higher Sn doping percentage(5% and 10 %).

The Seebeck coefficient of the sample $\text{Nb}_{0.83}\text{CoSb}_{1-x}\text{Sn}_x$ ($x=0.0, 0.01, 0.05, 0.10$) is shown in the fig:4.6 (b). All the samples have a negative Seebeck coefficient, i.e., electrons are the majority carriers. The Seebeck coefficient of the undoped sample increases from $-120 \mu\text{V/K}$ at 300 K to $-200 \mu\text{V/K}$ at 800 K and reaches a downturn around 900 K

owing to the excitation of minority carriers. Further, the Seebeck coefficient decreases to $-100 \mu V/K$ at 300 K upon 1 % Sn doping owing to the increase of carrier concentration. The Seebeck coefficient of 1% Sn doped decreases for the entire range of temperature and does not attain maxima, unlike the undoped sample. The Seebeck coefficient of the 5% and 10% Sn doped samples show some increment compared to the 1% Sn doped sample. However, it remains less than the Seebeck coefficient of the undoped sample.

In order to understand the behavior of electrical conductivity and Seebeck coefficient for the doped sample, particularly 10 % Sn doped sample, we refer to the zoomed view of the electronic band structure of $Nb_{0.8}CoSb$ and $Nb_{0.9}CoSb_{0.9}Sn_{0.1}$. Fig:4.7 (a) shows the conduction bands of $Nb_{0.8}CoSb$ and $Nb_{0.9}CoSb_{0.9}Sn_{0.1}$ near the Fermi energy. The energy eigenvalues are scaled with respect to those at M point of the Brillouin zone. $Nb_{0.8}CoSb$ has six nearly degenerate bands that include 4 at M point, one between X and Γ point, and one at Γ point (Fig:4.3). Additionally, there is a flat band at Γ point at around 0.12 eV above the conduction band at Γ point. The incorporation of excess Nb and Sn into the system has significantly lowered this band's energy with suitable modification in band dispersion and converged to the Γ point. Moreover, the band degeneracy at M point of the Brillouin zone is broken. In addition to this, the excess Nb, along with other Nb and Co atoms, give rise to a flat band centered at X point nearly 0.24 eV above the conduction band minima (CBM) (Fig:4.5(a)). This flat band, which is away from the Fermi energy, shown schematically in the fig:4.7(b), will have no contribution to electrical conductivity and Seebeck coefficient. However, at high temperatures, this flat band can contribute to the transport properties, i.e., it can increase the Seebeck coefficient owing to heavy electrons and increase electrical conductivity by providing another channel for conduction, as we see in the transport properties at high temperatures in the fig:4.6.

4.4 Summary

We have systematically studied the role of excess Nb and Sn doping upon the structure and electronic properties of $Nb_{0.8}CoSb$ to understand the experimentally observed changes in its transport properties upon Sn doping. We find that doping of Nb, not only gives free electrons to the system, but also suitably modifies the band structure near the Fermi level. Specifically, doping of Nb causes the band convergence at Γ point of the Brillouin zone near the Fermi level and gives rise to a flat band above the Fermi level. The convergence

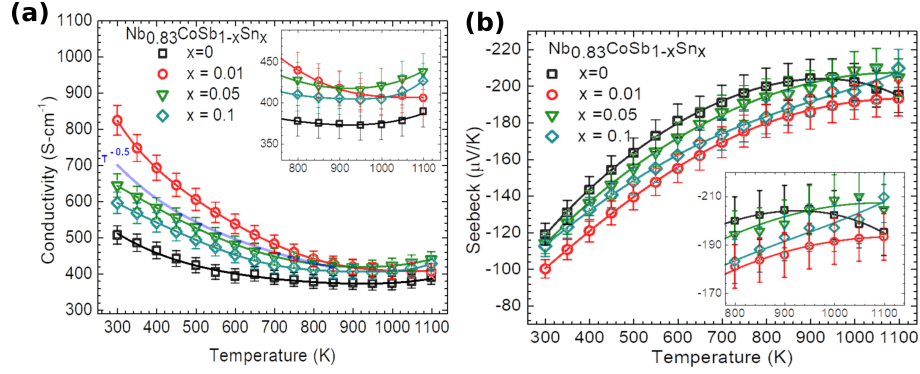


Figure 4.6: (a) Electrical conductivity and (b) Seebeck coefficient of $\text{Nb}_{0.83}\text{CoSb}_{1-x}\text{Sn}_x$ ($x=0.0, 0.01, 0.05, 0.10$) as function of temperature. (These measurements were done by Dr. Saurabh Kumar under the supervision of Dr. Surjeet Singh.)

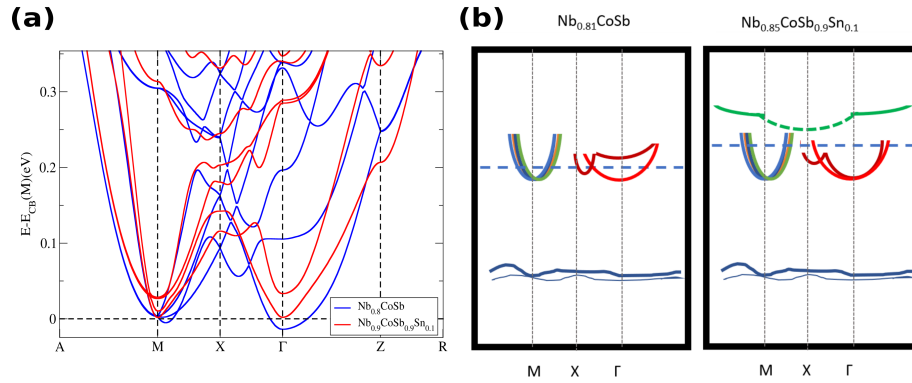


Figure 4.7: (a) Conduction bands, scaled with respect to the conduction band energy at M point of the BZ, $\text{Nb}_{0.8}\text{CoSb}$ and $\text{Nb}_{0.9}\text{CoSb}_{0.9}\text{Sn}_{0.1}$. (b) Schematic of the band structure for the actual composition of $\text{Nb}_{0.8}\text{CoSb}$ and $\text{Nb}_{0.85}\text{CoSb}_{0.9}\text{Sn}_{0.1}$ explaining the effect of Sn and Nb doping (The Fermi level is positioned at the experimentally measured carrier concentration using Hall measurements done by Dr. Saurabh kumar and Dr. Surjeet Singh).

of bands leads to the increased electrical conductivity. In addition, the appearance of flat band affects the Seebeck coefficient significantly, at high temperatures, improving the transport properties. Doping of Sn controls the electron concentration by giving holes, which helps in the improvement of the Seebeck coefficient and does not modify the band structure significantly.

Chapter 5

Effect of Electron-Phonon Coupling on Transport Properties of Monolayer of PbI_2 : A thermoelectric Perspective

5.1 Introduction

Research activities focused on developing alternative technologies that can harness renewable sources of energy for mankind, have grown tremendously due to the decline in fossil fuel availability and the increase in environmental pollution caused by their use as a primary source of energy. Among these alternative technologies, thermoelectric (TE) materials have gained significant attention because they can directly convert waste heat from various sources, such as industries, automobile engines, microprocessors, and mobile phones, into electrical energy through the thermoelectric effects, such as the Seebeck effect. The efficiency of a TE material is quantified by a dimensionless figure of merit, $zT = S^2 \sigma T / \kappa$, where S represents the Seebeck coefficient, σ denotes the electrical conductivity, T stands for the absolute temperature, and κ denotes the total thermal conductivity, which is the sum of the contributions from the carrier (κ_e) and lattice (κ_L) thermal conductivities. A higher value of zT indicates better performance of a TE material. However, optimizing zT is challenging because the different material parameters, including S , σ , and κ_e , have complex interrelationships. For example, increasing the doping concentration leads to an increase in σ but a decrease in S . Additionally, a material with high zT should have high electrical conductivity and low thermal conductivity, but materials with high electrical conductivity typically exhibit high electronic thermal conductivity as well. Therefore, controlling these material parameters independently is a challenging task. Increasing the power factor ($\text{PF} = S^2 \sigma$) and reducing the thermal conductivity, specifically

κ_l , which is independent of S , σ , and κ_e , can boost the value of zT . Various strategies have been proposed to enhance the power factor, including reducing dimensionality, as predicted by Dresselhaus *et al.* [45, 46], and adopting novel routes like nanostructuring [145–150], band structure engineering [151], etc. These efforts have resulted in the development of a large family of thermoelectric materials based on metal chalcogenides (Bi_2Te_3 , Sb_2Te_3 , and PbTe), superionic conductors, metal oxides, SiGe alloys, and more. [152]

In the realm of computational analysis, transport properties such as Seebeck coefficient (S), electrical conductivity (σ), and electronic thermal conductivity (κ_e) are typically evaluated using BoltzTraP software [153]. This software solves the semiclassical Boltzmann transport equation (BTE) through two approximations, namely, the rigid band approximation (RBA) and constant relaxation time approximation (CRTA). Under RBA, it is assumed that doping and changes in temperature do not impact the electronic band structure, and instead, the chemical potential (μ) is shifted with doping. As a result, the energy eigenvalues computed at 0K are utilized as an input to compute transport coefficients. The temperature dependence of transport coefficients is accounted for by the Fermi-Dirac (FD) occupation while computing the Onsager coefficients based on FD integrals. The present study aims to investigate the influence of temperature-dependent energy eigenvalues on transport properties.

CRTA assumes that relaxation time is independent of energy eigenvalues and wave vector, and BoltzTraP calculates electrical conductivity and electronic thermal conductivity in terms of relaxation time as a function of chemical potential and temperature. To determine the absolute value of electrical and electronic transport properties, determining the relaxation time explicitly is necessary. To estimate the relaxation time of charge carriers in semiconductors, the Deformation Potential (DP) theory was proposed. It has been applied to both non-polar and polar semiconductors, but it has several limitations. DP theory only considers interactions between charge carriers and acoustic phonon modes, neglecting scattering due to the optical phonon modes. As a result, DP theory fails to provide reasonable estimates of the relaxation time, especially in polar semiconductors where the contribution of optical modes is significant. Hence, BTE provides inaccurate thermoelectric coefficients for polar semiconductors when the relaxation time (τ) is estimated using the DP theory.

The objective of this study is to investigate the electron-phonon interactions (EPI) present

in the PbI_2 monolayer (ML- PbI_2), a polar semiconductor, by utilizing the Electron-Phonon Wannier (EPW) package. The EPW package provides information about the scattering due to both acoustic and optical vibrational modes, allowing for accurate estimation of relaxation times. These relaxation times can then be used to obtain absolute transport coefficients (such as σ and κ_e) for any material. Additionally, we computed the renormalized energy eigenvalues of electrons and holes due to EPI at finite temperature by adding the real part of the self energies of electrons and holes to Kohn-Sham energy eigenvalues ($\epsilon'_{nk} = \epsilon_{nk} + \text{Re}\Sigma_{nk}$), as described in [154]. Finally, we solved the BTE using BoltzTraP based on the renormalized energy eigenvalues to study the effects of EPI on transport properties.

5.2 Computational details

DFT calculations: Our first principles calculations are based on density functional theory as implemented in the Quantum ESPRESSO software [96, 142]. Norm-conserving pseudopotentials [60] have been used to account for interactions between the valence electrons and ionic cores. Moreover, Pb and I being heavy atoms, spin orbit interactions (SOI) are important. To correctly account for the SOI, relativistic Kohn-Sham equations have been solved self consistently using fully relativistic norm conserving pseudopotentials [155]. The valence electronic configuration considered in our calculations for Pb and I are $4f^{14}5d^{10}6s^26p^2$ and $4d^{10}5s^25p^5$, respectively. The exchange-correlation potential of electrons was described by using the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) [58]. We use an energy cutoff of 90 Ry to truncate the plane wave basis used in calculating the Kohn-Sham wave-function for ML- PbI_2 . Previous computational study of this monolayer indicated that van der Waals (vdW) interactions are important [156]. Since PBE-GGA does not include the vdW interactions, so it was included in our calculations using the semi-empirical approach of Tkatchenko-Scheffler for ML- PbI_2 [157], in which the C_6 coefficients are obtained from ground state electron density. Brillouin zone integrations are done using a $15 \times 15 \times 1$ Monkhorst-Pack [59] k -point grid. To avoid the spurious interactions between periodic images in the direction perpendicular to the plane of the ML- PbI_2 (along z -direction in this case), we have used a vacuum of 13 Å along the z -direction. In order to check the dynamical stability of the ML- PbI_2 and to calculate the vibrational properties and electron-phonon coupling, we used density functional perturbation theory [62]. The calculations have been

carried out using a $11 \times 11 \times 1$ q -mesh.

Electronic transport properties: To obtain the transport properties, we have solved the semiclassical Boltzmann transport equations within the rigid band approximation as implemented in the BoltzTraP code [73], where it uses a Fourier expansion scheme to fit the band structure for the calculation of transport properties. A Γ -centred $15 \times 15 \times 1$ grid is introduced for the ML-PbI₂ to enable accurate Fourier interpolation of Kohn-Sham eigenvalues.

BoltzTraP has two options for computing transport properties: it can either calculate σ/τ and κ_e/τ using the constant relaxation approximation (CRTA), or it can use relaxation times for each state and compute transport properties through the beyond CRTA method. To obtain the absolute values of transport coefficients, it is necessary to know the values of τ/τ_{nk} . However, calculating τ can be challenging as it depends on factors such as electron-phonon interactions (EPIs), defects, impurities, etc. While computing contributions to τ from first principles for all factors is difficult, the contribution to τ from EPIs can be computed in two ways. The average value of τ can be obtained through the deformation potential theory and the effective mass approximation. Using these, it can be shown that τ is given by:

$$\tau = \frac{\hbar^3 C}{k_B T m_d E_{dp}^2} \quad (5.1)$$

where C is the 2D elastic constant, m_d is the average effective mass, E_{dp} is the deformation potential, T is the temperature and k_B is the Boltzmann constant. $\hbar = h/2\pi$, h being the Planck's constant.

The computation of τ using Eqn. 5.1 has two limitations: it only estimates an average value of τ , and it only considers the contributions from acoustic modes, neglecting the importance of scattering from optical modes, which can result in an overestimation of τ for certain systems. To move beyond the CRTA, it is necessary to calculate τ_{nk} for each n and k . Therefore, we have computed τ_{nk} explicitly from the imaginary part of the electron self energy. In addition to providing the relaxation time, the electron-phonon coupling also affects the band structure, which in turn modifies the band gap and transport properties of the system. The real part of the electron self energy can be used to obtain information about this band structure renormalization. The electron self energy within the

Migdal approximation is given by

$$\sum_{n\mathbf{k}}^{EP} = \sum_{\mathbf{q}\nu, m} w_{\mathbf{q}} |g_{mn, \nu}^{SE}(\mathbf{k}, \mathbf{q})|^2 \left[\frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu} - i\delta} + \frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu} - i\delta} \right] \quad (5.2)$$

where $g_{mn, \nu}^{SE}(\mathbf{k}, \mathbf{q}) = (\frac{\hbar}{2m_0\omega_{\mathbf{q}\nu}})^{1/2} \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V | \psi_{n\mathbf{k}} \rangle$. $w_{\mathbf{q}}$ is the weight associated with phonon wavevector $\mathbf{q}$ in the BZ, $\psi_{m\mathbf{k}}$ represents the electronic wavefunction for band m , wavevector $\mathbf{k}$, and eigenvalue $\epsilon_{m\mathbf{k}}$. $\partial_{\mathbf{q}\nu} V$ is the derivative of self consistent potential associated with a phonon of wavevector $\mathbf{q}$, branch index ν and frequency $\omega_{\mathbf{q}\nu}$. $f_{m\mathbf{k}+\mathbf{q}}$ ($n_{\mathbf{q}\nu}$) is the occupation of the electronic (vibrational) state and is given by the Fermi-Dirac (Bose-Einstein) distribution. The electron self energies were calculated using the EPW software [68]. To compute the electron-phonon matrix elements, we first use a coarse grid of k and q values, as described earlier. These matrix elements are then interpolated to a denser $300 \times 300 \times 1$ q -mesh for ML-PbI₂. A 25 meV Gaussian broadening is applied to the Dirac delta function in Eqn. 5.2 to account for the finite lifetime of the electron. We take into account the scattering rates due to all possible vibrational modes in our calculations. Using the imaginary part of the electron self energy ($\sum_{n\mathbf{k}}^{EP}$), we calculate the relaxation time for each state using the formula $\tau_{n\mathbf{k}} = \frac{\hbar}{2(\text{Im} \sum_{n\mathbf{k}}^{EP})}$, where $\hbar$ is the reduced Planck constant. The renormalized electronic eigenvalues ($\epsilon_{n\mathbf{k}}^{RG}$) is given by [64]:

$$\epsilon_{n\mathbf{k}}^{RG} = \epsilon_{n\mathbf{k}} + \text{Re} \sum_{n\mathbf{k}}^{EP} \quad (5.3)$$

5.3 Results and discussion

5.3.1 Crystal structure and lattice vibrations.

PbI₂ adopts a hexagonal crystal system and crystallizes in a layered structure in the most stable polytype 2H. PbI₂ is known to possess $P\bar{3}m1$ symmetry. The top and side view of the crystal structure of the ML-PbI₂ are shown in the fig.5.1(a) and (b), respectively. A single layer of PbI₂ comprises of three atomic sublayers. The layer of Pb atom is sandwiched between two atomic layers of I. These subatomic layers are stacked in ABC form along the z -axis. The building block of PbI₂ is composed of one Pb atom octahedrally coordinated to its six nearest I atoms. Further, interlayers I-Pb-I are held by the weak van

der Waals (vdW) interactions.

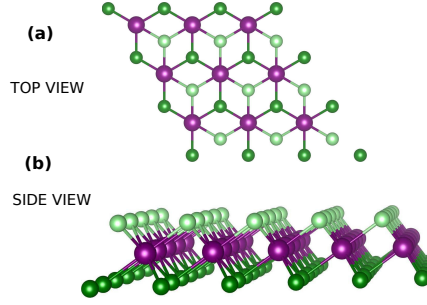


Figure 5.1: The top and the side view of ML-PbI₂, where Iodine is represented by light green and dark green colored balls belonging to two different sublayers. Pb atoms are shown by violet color.

The optimized lattice parameter of ML-PbI₂ is found to be 4.55 Å, at PBE level including vdW correction Tkatchenko-Scheffler [157], which matches well with experimentally reported lattice parameter of single crystal PbI₂, i.e, 4.56 Å [158]. However, computational studies within PBE and Grimme’s vdW interaction report it to be 4.32 Å [159]. We observe the Pb-I bond distance to be 3.25 Å in ML-PbI₂. We find the thickness of monolayer to be 6.88 Å, which matches with experimentally reported thickness 7.00 Å [160].

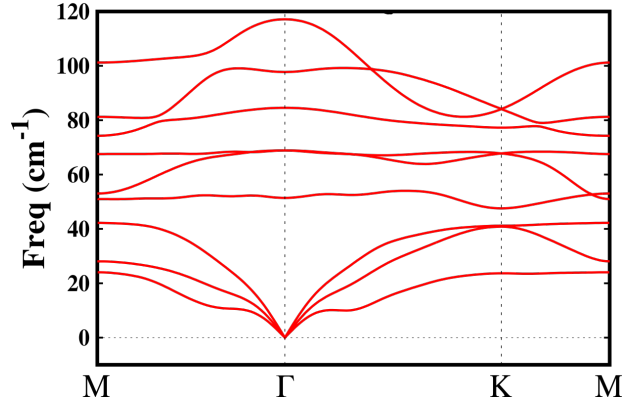


Figure 5.2: The phonon band structures of ML-PbI₂.

To check the dynamical stability, we have calculated the phonon dispersion of the ML-PbI₂. The result is shown in the fig. 5.2. We have not found any imaginary modes for ML-PbI₂, which confirms that the system is dynamically stable at 0 K. We notice that the phonon frequencies extend up to 120 cm⁻¹. Interestingly, for ML-PbI₂, we do not observe mixing of the optical and acoustic modes over the complete BZ. Quantitatively, there is a phonon gap of about 5.30 cm⁻¹.

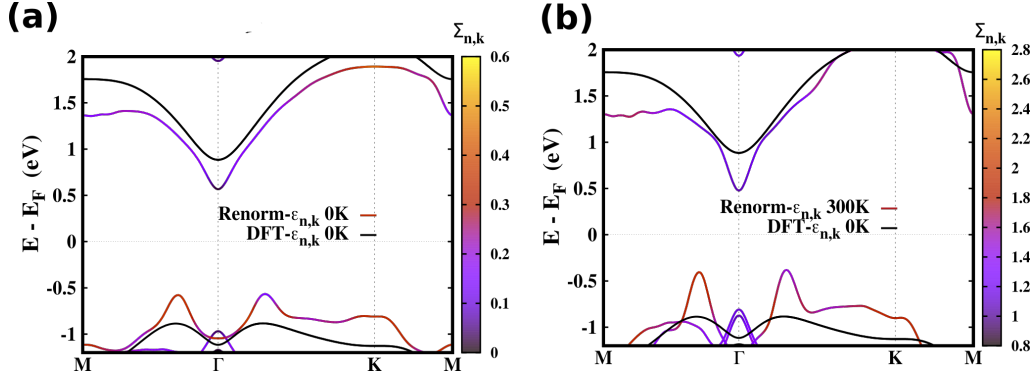


Figure 5.3: The DFT band structure (black) and the renormalized ones (a) at 0K (colored lines) and (b) at 300 K for ML-PbI₂). For the renormalized band structure, the magnitude of the imaginary part of electron-phonon self energy is also shown. The energy eigenvalues are shifted with respect to the Fermi energy. The middle of the band gap is taken to be the Fermi energy.

5.3.2 Temperature dependent renormalization of the band structure

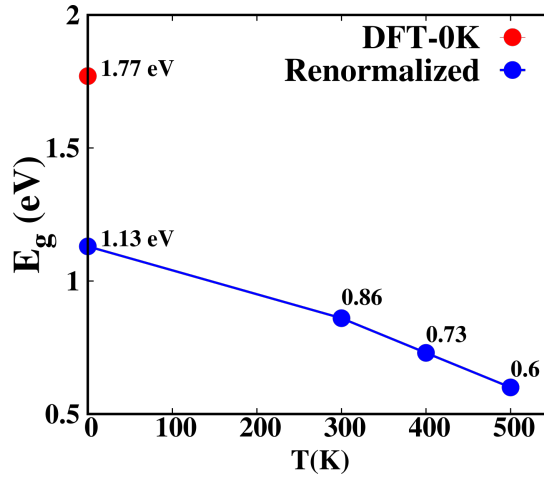


Figure 5.4: The variation of renormalized band gap as a function of temperature for ML-PbI₂.

Fig. 5.3 shows the DFT and renormalized band structure of the ML-PbI₂. We observe an indirect band gap for ML-PbI₂ where the valence band maxima (VBM) is along the $\Gamma \rightarrow K$ direction (closer to the Γ point) and conduction band minima (CBM) is at Γ point of the Brillouin zone. In addition to the DFT band structure, the renormalized band structure at 0K (Fig. 5.3(a)) and 300 K (Fig. 5.3(b)). The 0K renormalized band structure corresponds to zero-point energy (ZPE) corrections to the band structure due to the lattice vibrations. While the positions of VBM and CBM in the BZ are unaffected by the band structure renormalization, we observe significant shifts in the renormalized

energy eigenvalues with the VBM (CBM) moving up (down) in energy. This results in significant reduction in the band gap of PbI₂ by 0.64 eV. Fig. 5.4 shows the temperature dependence of the band gap. We find that as the temperature is increased from 0K to 500K, the band gap reduces by 0.53 eV. A comparison of the changes in band gap due to ZPE corrections and temperature renormalization shows that the modification in the band structure becomes more prominent as the temperature increases. The temperature renormalization of the band structure causes the shift in the band edges of ML-PbI₂ (Fig. 5.3(a) vs. Fig. 5.3(b)). To quantify the effect of band curvature modification, we have computed the effective masses of the electrons and holes along certain high symmetry directions for ML-PbI₂ using the DFT band structure and the renormalized band structure. The same is listed in Table 5.1. We find that the effective masses of both holes and electrons are significantly reduced due to the renormalization of the band structure. For the renormalized

Table 5.1: Comparison of effective masses of electrons and holes in these monolayers between DFT-band structure and the renormalized band structure.

Carrier type	PBE band		Renormalized band structure @ 300 K	
	m^* (zigzag) (m_e)	m^* (armchair) (m_e)	m^* (zigzag) (m_e)	m^* (armchair) (m_e)
electron	0.48	0.34	0.05	0.07
hole	5.68	0.64	0.17	0.04

band structure, we have also plotted the $\text{Im} \sum_{nk}^{EP}$ in the colour scale for ML-PbI₂ in the fig:5.3(a) and (b). The inverse of $\text{Im} \sum_{nk}^{EP}$ is related to the lifetime of carriers in that state. At 0K, we find that $\text{Im} \sum_{nk}^{EP}$ are larger for holes than electrons, suggesting that electrons have higher lifetime than holes. As the temperature is increased to 300 K, we observe significant change in the electron lifetime of ML-PbI₂ ((Fig:5.3(b)).

5.3.3 Computation of τ .

5.3.3.1 τ from electron-phonon coupling.

The temperature dependency of the imaginary part of the self energy ($\text{Im}\Sigma$) for the valence and conduction bands along high symmetry directions of the BZ are shown in the fig. 5.5. The values of $\text{Im} \sum_{nk}^{EP}$ for ML-PbI₂ increases with rise in temperature owing to the increase in phonon population with temperature. Increase in the $\text{Im} \sum_{nk}^{EP}$ suggests the enhanced scattering of electrons at high temperatures. Further, by plotting the mode

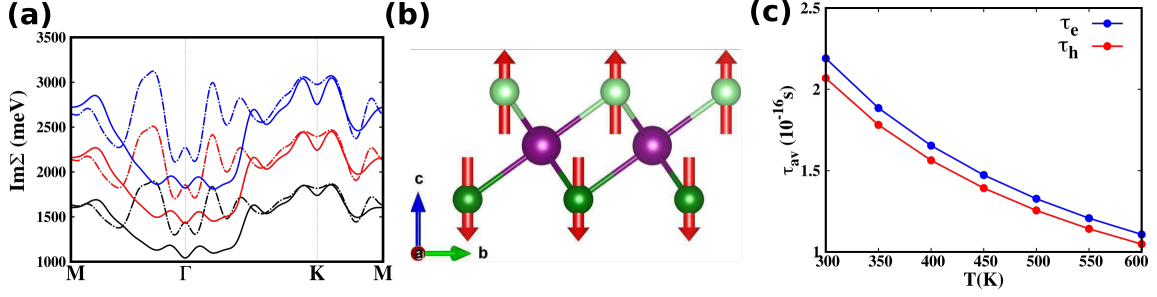


Figure 5.5: (a) The imaginary part of the electron self energy for the conduction (solid lines) and valence band (dashed lines) for ML-PbI₂ at 300 K (black), 400 K (red) and 500 K (blue). (b) The vibrational patterns of optical modes at Γ point, which has the largest contribution to $\text{Im}\Sigma_{nk}$. (c) The average relaxation times for electrons (blue) and holes (red) as a function of temperature for the ML-PbI₂.

resolved $\text{Im} \sum_{nk}^{EP}$, we find that only one particular optical mode has a dominant contribution. The displacement pattern of the dominant optical mode is shown in the fig. 5.5(b). This optical mode corresponds to compression and expansion of the monolayer along the direction normal to the plane of monolayer. This result clearly shows that computing τ by ignoring the contribution of the optical modes will clearly give erroneous results. The τ_{av} for the electrons and holes in the system as a function of temperature is shown in fig. 5.5(c). We find that for both the valence and conduction bands τ_{av} decreases with increase in the temperature following the increase in the $\text{Im} \sum_{nk}^{EP}$. In addition, we find that electrons have higher relaxation time compared to holes due to the higher effective mass of holes.

5.3.3.2 τ from deformation potential theory.

In this section, we compute the average relaxation time for the electrons and holes for PbI₂ monolayer from the deformation potential theory. We note that the major difference between the two methods is that in the latter the contributions to τ_{av} from the optical phonon modes are neglected.

Table 5.2: C , E_{dp} and τ for the electrons and holes in PbI₂ monolayer.

	C (eV/Å ²)	E_{dp} (eV)	τ (10 ⁻¹⁴ s)		
			$T = 300$ K	$T = 400$ K	$T = 500$ K
electron	1.01	-7.73	0.80	0.60	0.48
hole		-6.58	0.23	0.18	0.14

The values of C , E_{dp} and τ are computed from the deformation potential theory is

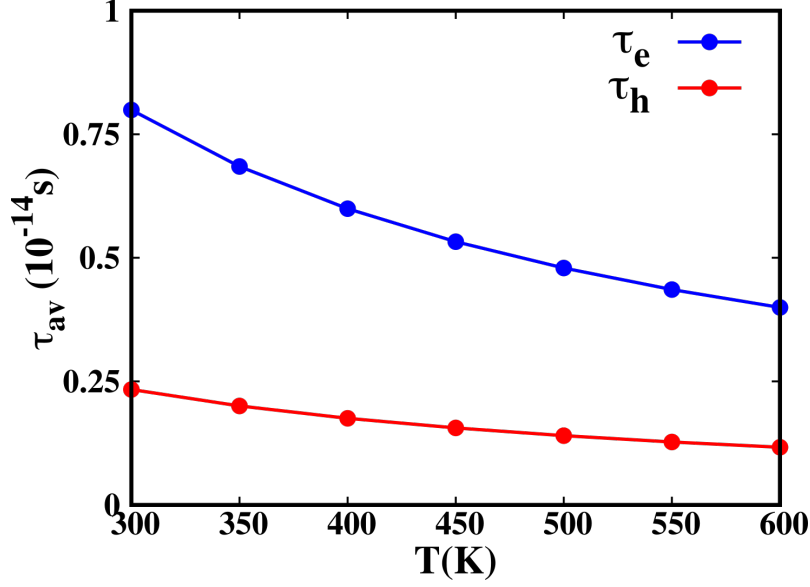


Figure 5.6: The average relaxation time estimated using the deformation potential theory for electrons (blue) and holes (red) as a function of temperature for PbI₂ monolayer.

given in Table 5.2. The coupling strength between the electrons/holes and the acoustic phonons are indicated by $|E_{dp}|$. We find that $|E_{dp}|$ is larger for the electrons than for the holes suggesting that electrons couple more strongly to acoustic phonons than holes. The anisotropy in the transport properties is reflected in the anisotropy of the effective masses of the charge carriers along the armchair and zigzag directions of the monolayer as shown in the table:5.1. Along the zigzag direction, m^* for electrons and holes are larger compared to the armchair direction. The τ for the electrons and holes in ML-PbI₂, as a function of temperature, is shown in the fig:5.6 and also listed in Table 5.2 for some temperatures. Over the complete temperature range considered in this study, τ for electrons are larger than that observed for holes. A comparison of τ computed using EPI (Fig:5.5) and deformation potential theory (Fig:5.6) shows stark differences, not only quantitatively but also qualitatively. On the quantitative side, the values of τ computed using the deformation potential theory are overestimated by about two orders of magnitude compared to those obtained from EPI. Moreover, the qualitative picture is also different as we find that the difference in the relaxation time between holes and electrons obtained from the deformation potential theory is larger compared to EPI calculated relaxation time. This difference can be understood from the fact that in the case of deformation potential theory we consider the coupling of the acoustic phonons only (which has negligible contributions), while the coupling with the optical phonons is much stronger for this system as

captured from the EPW calculations.

5.3.4 Transport properties

5.3.4.1 Effect of CRTA and EPIs on transport properties.

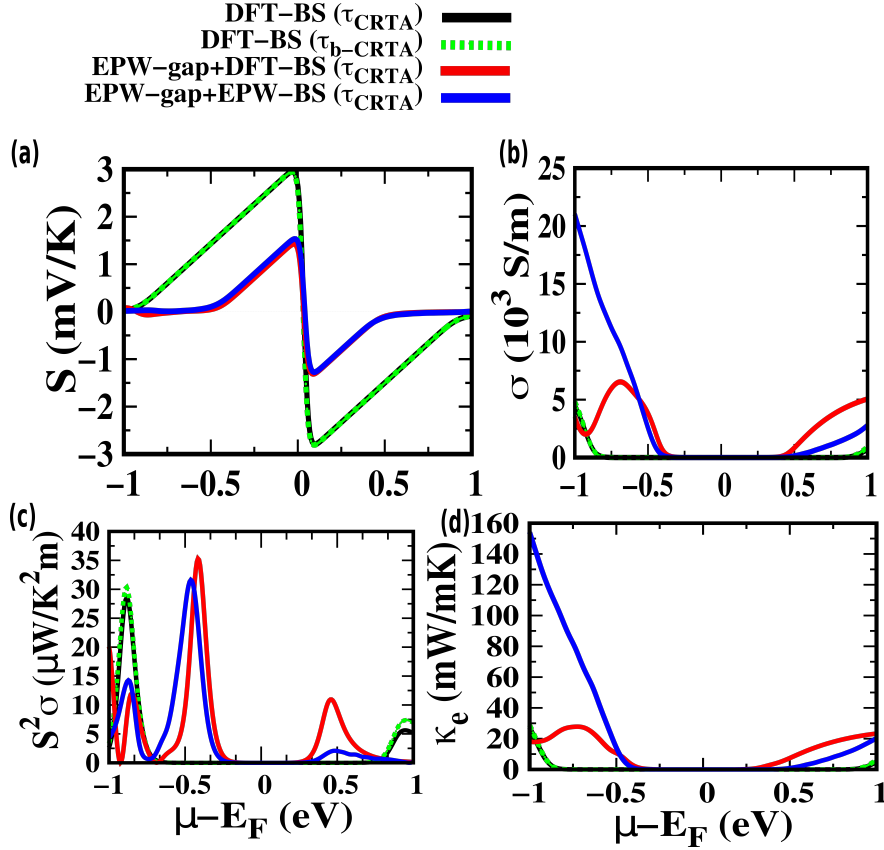


Figure 5.7: The transport properties as a function of chemical potential (μ) based on DFT-BS and CRTA [DFT-BS (τ_{CRTA})] (black solid lines), DFT-BS and with explicit values of τ_{nk} for each state [DFT-BS (τ_{b-CRTA})] (black dashed-dot lines), DFT-BS and renormalized band gap within CRTA [EPW-gap+DFT-BS (τ_{CRTA})] (red solid line) and renormalized band structure and band gap within CRTA [EPW-gap+EPW-BS (τ_{CRTA})] (blue). The transport coefficient S , σ , power factor ($S^2\sigma$) and κ_e are shown in (a), (b), (c), and (d), respectively.

In order to understand the effectiveness of the CRTA and the effect of the band structure renormalization on the transport properties, we have computed S , σ and the power factor ($S^2\sigma$) at room temperature. For this system, the transport coefficients have been computed in four different ways: (1) using DFT band structure and band gap within CRTA [DFT-BS (τ_{CRTA})], (2) using DFT band structure and band gap with τ_{nk} for each band

[DFT-BS (τ_{b-CRTA})], (3) using DFT band structure and renormalized band gap within the CRTA [EPW-gap+DFT-BS (τ_{CRTA})], (4) using renormalized band structure and band gap within the CRTA [EPW-gap+EPW-BS (τ_{CRTA})]. For all these cases we have used the values of τ obtained from the EPW calculations. A comparison between (1) and (2) enables us to understand the effectiveness of the CRTA while that between (1) and (3) highlights the effect of the band gap on the transport properties. Comparing (3) and (4) will help us in understanding the importance and influence of the changes in the transport properties due to changes in the band structure because of the finite temperature effects. The results as a function of chemical potential (μ) at 300K are plotted in the fig. 5.7. Negative (positive) values of μ implies hole (electron) doping.

Going beyond the CRTA and using explicit values of τ yield values of S that are similar to that obtained within CRTA, at least for the range of chemical potential considered in this study (black and green dashed lines in the fig. 5.7(a)). However, for σ , we observe small changes as one goes beyond CRTA. Specifically, we observe that the changes are more for electrons compared to holes. While at low hole doping concentration, we do not observe significant changes in the values of σ obtained within CRTA and using explicit values of τ for each electronic state, at higher doping concentration small changes are observed in the magnitude of σ (black and green-dashed lines for negative values of μ in the fig. 5.7(b)). In contrast, for electrons, there are differences in the values of σ obtained using the two methods. This difference increases with the increase in the doping concentration. Consistent with the changes in the values of S and σ , we observe small changes in the values of power factor (PF) as one goes beyond the CRTA (Fig. 5.7(c)). Similar to that observed in the case of conductivity, we note that the changes in PF for the electrons is larger than that observed for holes. Additionally, we have also studied the effect of the two methods on estimates of electronic contribution to thermal conductivity (κ_e) (Fig. 5.7(d)). We find that the changes in κ_e follows the changes in σ .

In contrast with the choice of τ , i.e. CRTA or beyond CRTA, used to compute S , the magnitude of the band gap significantly alters the values of Seebeck coefficient observed for this system. As observed in the fig. 5.7(a) (black vs. red plot) we find that the maximum value of Seebeck coefficient is significantly reduced with the decrease in the band gap. In case of σ and PF, the band gap results in shift of the σ plots (black vs. red lines in the fig. 5.7(a)). This implies that with the decrease in the band gap, it is possible to achieve the same value of conductivity and PF at smaller doping concentration.

A comparison of the red and blue plots in the fig. 5.7 highlights the effect of the band

structure renormalization on the transport properties. The modified band structure slightly enhances the maximum value of Seebeck coefficient. However, the effect is stronger for σ . Specifically, the effect is stronger in the holes compared to that in electrons (Fig. 5.7(b)). While for the electrons the overall shape of the conductivity plots are similar, for the holes we not only observe changes in their magnitude but also changes in their shape. As observed in the previous cases, the changes in κ_e follows the changes in σ .

5.4 Summary

In conclusion, we have studied the effect of electron-phonon interactions on the transport properties of the PbI_2 monolayer. Further, we also evaluated the validity of the constant relaxation time approximation. EPI affects the transport properties in two ways: (1) the relaxation time of the carriers and (2) the renormalization of the band structure. Our calculations show that for ionic systems it is crucial to incorporate the effect of scattering of electrons by optical phonons because this is the dominant scattering channel for the carriers in these systems. Neglecting the contributions of the scattering of charge carriers by optical phonons results in overestimation of relaxation times by two orders of magnitude. Comparison of the computed values of τ obtained within CRTA and beyond CRTA shows that for heavy doping it might be important to go beyond CRTA to make reasonable estimates of the transport coefficients. Additionally, our results also show that, since the EPI results in significant changes in the band gap and the band structure, it is important to consider these effects in order to predict or understand the transport properties of ionic solids. We hope that our results will motivate further investigations on electron-phonon interactions in thermoelectric materials.

Chapter 6

Summary and Outlook

To summarize, **chapters 3 and 4** of this thesis focus on performing first principles DFT based calculations, along with solving semiclassical Boltzmann transport equation within the constant relaxation time approximation, to understand the thermoelectric properties of two Heusler alloys Fe_2VGa and NbCoSb . For Fe_2VGa , the relaxation times of the charge carriers were computed within electron-phonon averaged approximation. **Chapter 3** presents our utilization of the alloy disorder scattering technique to enhance the figure of merit of Fe_2VGa using In dopant at Ga site, while **Chapter 4** explores the effect of co-doping of Nb and Sn in $\text{Nb}_{0.8}\text{CoSb}$ to improve its thermoelectric performance. The **chapter 5** of the thesis critically evaluates the implications of the commonly employed approximations used in predicting transport coefficients in ionic low dimensional materials, that are used in the rational design of novel thermoelectric materials.

In **Chapter 3**, we investigate the thermoelectric properties of In doped Fe_2VGa using first principles calculations. Fe_2VGa is known to exhibit high power factor, however, its thermoelectric performance is poor due to high lattice thermal conductivity of 15 W/m K at 300 K. To address this, we introduced In doping at the Ga site to reduce the lattice thermal conductivity, while aiming to maintain the electronic transport properties. We observe that though In doping significantly decreases the lattice thermal conductivity, it also reduces the thermoelectric power factor by negatively impacting the electrical conductivity. This decrease in electrical conductivity is attributed to the reduced relaxation time caused by size disorder scattering in In-doped Fe_2VGa . Although In doping in Fe_2VGa does not greatly enhance the zT of Fe_2VGa , we predict a novel system Fe_2VIn , which exhibits better thermoelectric performance compared to Fe_2VGa . The enhanced performance of Fe_2VIn can be attributed to reduced phonon group velocities and improved electrical con-

ductivity achieved through carrier optimization. To extend this project further, we can explore the effects of other alloying elements on the thermoelectric properties of Fe_2VIn . In addition to this, we can study the role of defects such as point defects or vacancies in influencing the thermoelectric properties and fine-tuning the material's behaviour. While calculating the transport properties, we have not incorporated the temperature effect in the band structure. It might be interesting to study the effect of temperature on the band structure and transport properties.

In **Chapter 4** of our study, we investigate the role of co-doping of Nb and Sn in $\text{Nb}_{0.8}\text{CoSb}$ in the enhancement of thermoelectric performance. Experimentally, the thermoelectric properties of $\text{Nb}_{0.8+\delta}\text{CoSb}_{1-x}\text{Sn}_x$ where $\delta \leq 0.05$ and $x \leq 0.10$ was measured and $\text{Nb}_{0.84}\text{CoSb}_{0.95}\text{Sn}_{0.05}$ was found to have zT of 1. Specifically, the doped sample exhibited an enhancement in electrical conductivity, but this improvement declined with higher Sn concentration. Simultaneously, the Seebeck coefficient showed an increase, in contrast to the trend observed in electrical conductivity, although it still remained lower than the Seebeck coefficient of the undoped sample. As the temperature rose to 800 K, the undoped sample initially reached a minimum in electrical conductivity before showing an upward trend. Conversely, the Seebeck coefficient exhibited a consistent increase with temperature and reached a peak at higher temperatures in the undoped sample. With increasing Sn concentration, the upward trend in electrical conductivity continued, but the downturn in the Seebeck coefficient was no longer observed. Although Sn doping, especially in the presence of excess Nb, significantly enhanced the thermoelectric performance, the precise contributions of the additional Nb and Sn to the sample remained unclear. To gain insight into this, we initially doped 10 % Sn at the Sb site in $\text{Nb}_{0.8}\text{CoSb}$, doping of Sn breaks the band degeneracy at conduction band minima (CBM) at M point of the BZ, enhances the band convergence between M and Γ point of the BZ and provides holes. We further doped 10% Nb into $\text{Nb}_{0.8}\text{CoSb}_{0.9}\text{Sn}_{0.1}$. Nb doping not only provides electrons as charge carriers but also suitably modifies the electronic band structure that leads to convergence of bands at the Fermi level and gives rise to a relatively flat band above the Fermi level. The electrical conductivity varies with temperature as $T^{-0.5}$. This is attributed to the alloy scattering. The upturn (downturn) in electrical conductivity (Seebeck coefficient) at high temperature for the undoped sample is because of the excitation of minority carriers. With Sn doping in the presence of excess Nb, the downturn present in the Seebeck coefficient at high temperature disappear owing to the presence of a flat band that contributes heavy

electrons, which helps in further increase in the Seebeck coefficient that was inaccessible at low temperature as the flat band is slightly above the Fermi level. In addition, this flat band provides another channel for conduction that causes the electrical conductivity to increase at high temperature. In short, while the introduction of Sn doping alters the conduction band dispersion, thereby enhancing the Seebeck coefficient, the presence of excess Nb, apart from increasing the carrier concentration, leads to appropriate band modifications that result in improved electrical conductivity at high temperature. The defective Heusler alloys have shown low lattice thermal conductivity. Further research may focus on exploring the effect of other dopants in addition to Nb and Sn to have a broader understanding of material's behaviour towards thermoelectric properties.

In **Chapter 5** we investigate the electron-phonon interactions (EPIs) and their profound effects on the electronic structure and transport properties of monolayer PbI_2 . To calculate the properties of the electronic system, we use a numerical scheme based on density functional theory. Our calculation of transport coefficients involves calculating the Onsager coefficient within constant relaxation time approximation (CRTA). To find accurate transport coefficients, we must explicitly ascertain the relaxation times (τ) that govern the behavior of the charge carriers. Traditionally, the deformation potential approximation (DPA) has been the conventional method for estimating τ . However, the DPA has limitations as it is based solely on the consideration of interactions between charge carriers and acoustic phonons, thus ignoring the crucial role of optical phonons in the scattering process. This exclusion can lead to a significant overestimation of τ , especially in ionic solids where optical phonons strongly influence the scattering rate by generating strong electric fields. With advancements in computational materials science, we can now explore the contributions of all phonon modes to scattering rate using first-principles methods. However, this computation can be complex and time-consuming in most cases. Our study highlights the critical importance of accurately predicting relaxation times in computational material prediction, especially in the development of new thermoelectric materials. Our results reveal that the computation of τ based on DPA leads to an unexpected overestimation by two orders of magnitude since it ignores optical phonon contributions. In the same manner, this overestimation goes further to the material's electrical conductivity and electronic thermal conductivity. This highlights the critical importance of relaxation time and emphasizes the necessity for accurate computation of scattering rate, as we show in our work by the rigorous calculation of electron self-energies for charge carriers. We also

investigate how EPIs affect the electronic band structure, causing band structure renormalization and its subsequent impact on the transport properties. Our analysis reveals significant changes in monolayer PbI_2 's band gap and band dispersion, which have an impact on the transport properties based on this renormalized band structure. In addition, we go beyond the limitations of CRTA and investigate transport properties by explicitly adding τ for each electronic state. We notice significant changes in the transport properties, particularly in highly doped regions. Further, we can extend this work by including the calculation of the phonon self-energy, which can give intriguing and insightful results regarding the effect of EPIs on phonon transport properties.

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hole concentration (p) and electrical conductivity (σ) decreased. While Ba filling fraction was about 0.4, the lattice thermal conductivity (κ_L) reached the minimum value. The results show that effect of Ba rattling on phonon scattering is the strongest as Sb-icosahedron partial voids are filled by Ba. A maximum dimensionless thermoelectric figure of merit (ZT) value of 0.7 was obtained for $\text{Ba}_{0.38}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ at 750 K., issn=1993-0437, doi=10.1007/BF02838529, url=https://doi.org/10.1007/BF02838529. 7

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