Studying the lifetime of charge and heat carriers due to intrinsic scattering mechanisms in FeVSb half-Heusler thermoelectric

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Abstract

This work presents a study of lifetime of carriers due to intrinsic scattering mechanisms viz. electron–electron interaction (EEI), electron–phonon interaction (EPI) and phonon–phonon interaction (PPI) in a promising half-Heusler thermoelectric FeVSb. Using the full-GW method, the effect of EEI and temperature on the valence and conduction band extrema and band gap are studied. The lifetime of carriers with temperature are estimated at these band extrema. At 300 K, estimated value of lifetime at VBM (CBM) is \(\sim 1.91 \times 10^{-14} \text{ s} (\sim 2.05 \times 10^{-14} \text{ s})\). The estimated ground state band gap considering EEI is \(\sim 378\) meV. Next, the effect of EPI on the lifetime of electrons and phonons with temperature are discussed. The comparison of two electron lifetimes suggests that EEI should be considered in transport calculations along with EPI. The average acoustic, optical and overall phonon lifetimes due to EPI are studied with temperature. Further, the effect of PPI is studied by computing average phonon lifetime for acoustic and optical phonon branches. The lifetime of the acoustic phonons are higher compared to optical phonons which indicates acoustic phonons contribute more to lattice thermal conductivity \(\kappa_{\text{ph}}\). The comparison of phonon lifetime due to EPI and PPI suggests that, above 500 K EPI is the dominant phonon scattering mechanism and cannot be ignored in \(\kappa_{\text{ph}}\) calculations. Lastly, a prediction of the power factor and figure of merit of n-type and p-type FeVSb is made by considering the temperature dependent carrier lifetime for the electronic transport terms. This study shows the importance of considering EEI in electronic transport calculations and EPI in phonon transport calculations in FeVSb. Our study is expected to provide results to further explore the thermoelectric transport in this material.

Keywords: carrier lifetime, transport, intrinsic carrier-scattering mechanisms

(Some figures may appear in colour only in the online journal)

1. Introduction

Thermoelectric materials are the materials in which application of temperature (electric field) gradient creates an electrical potential difference (temperature difference). This type of response to the external applied field has lead to use these materials for power generation or cooling applications utilizing the energy conversion property between heat and electricity. The efficiency of conversion from heat to electricity is connected to material specific transport coefficients via a dimensionless quantity called figure of merit \(ZT\). This quantity is useful in selecting the materials for thermoelectric application [1, 2].

The figure of merit \(ZT\) is related to transport terms as \(ZT = S^2 \sigma^{-1} T\) [3, 4]. Here, \(S\) is the Seebeck coefficient, \(\sigma\)
is electrical conductivity, $\kappa$ is total thermal conductivity and $T$ is absolute temperature. The $\kappa$ is the sum of electronic thermal conductivity $\kappa_e$ and lattice thermal conductivity $\kappa_{\text{ph}}$. Therefore, to screen a material these transport coefficients need to be theoretically calculated or experimentally measured as a function of temperature. The nature of transport coefficients are decided by the electronic and phonon spectra of the material. The dependence comes through the group velocity, specific heat, effective mass, carrier concentration (chemical potential) and relaxation time (or lifetime) of carriers. So, the theoretical or computational study of transport involves the calculation of these mentioned physical quantities [5–7].

In the first-principles study, design or in the prediction of materials for thermoelectric applications, generally density functional theory (DFT) based methods are widely employed [8–10]. From DFT based calculations the electronic dispersion and phonon spectrum are obtained. Once the dispersion is obtained, the quantities like group velocity, effective mass etc can be further derived using their relation to dispersions. Temperature dependent carrier concentration can also be obtained using the distribution functions. The semi-classical or Boltzmann transport theory is the one of the most widely used tool in this direction along with DFT [10–12]. However, in this approach the situation is hindered when it comes to the calculation of lifetime of carriers, due to the non-interacting picture considered in DFT which is used to obtain the energy spectrum. Therefore, normally a constant relaxation time approximation (CRTA) is used to obtain the transport coefficients. Under this approximation, the $\Sigma$ becomes independent of lifetime, while $\sigma$ and $\kappa_e$ are calculated in the form $\sigma/\tau$ and $\kappa_e/\tau$, where $\tau$ is lifetime [11, 13, 14]. So, to get the full transport terms, a constant value for lifetime is used in the full temperature range [15], or some model for lifetime is used [16, 17]. In some cases, by fitting the available experimental $\sigma$, lifetime is obtained. These approaches may be simple and useful only in particular cases. However, they may not capture the effect of various scattering sources or temperature properly on the transport properties. Also, these approaches make fully first-principles calculation and more certain prediction of thermoelectric properties difficult.

Along with other carrier energy dispersion derived quantities, the lifetime is an important quantity in controlling the temperature dependent transport behavior. The lifetime of carriers in a material is decided by the sources of scattering (or interaction), strength of interaction and type of interaction. The impurities or defects act as a source of scattering (extrinsic) mainly in the lower temperature. In a perfect crystal the electron–electron interaction (EEI), electron–phonon interaction (EPI) and phonon–phonon interaction (PPI) mainly act as intrinsic sources of scattering mechanisms [5]. These scattering mechanisms decide the temperature dependent behavior of transport coefficients. An electron will have finite lifetime due to the interactions with other electrons and phonons. Similarly, phonon will have lifetime due to phonon–phonon and phonon–electron interactions. Quantification of these scattering mechanisms through lifetime or linewidth calculation helps to understand transport, identify dominant scattering source and fully first-principles prediction of thermoelectric properties. For such an investigation the help of beyond DFT methods becomes inevitable.

Recent advancements in the many-body theory and its implementation as computational methods are becoming useful to explore the EEI, EPI or PPI effects in solids [18–20]. These methods have enabled to see the effect of the interactions on the electronic or phonon spectrum by calculation of self-energy. The imaginary part of self-energy gives a picture of strength of interaction and lifetime of carriers. The electronic structure and strength of EPI in solids is normally studied using GW or DFT + dynamical mean field theory methods [21–23]. The electron–phonon matrix elements can be calculated under combined density functional perturbation theory (DFPT) and using Wannier functions for interpolation method [24]. Using the interpolated electron–phonon matrix elements on finer mesh, the imaginary part of self-energy and lifetime of carriers due to EPI can be obtained. This method has been found to be increasingly applied to study the EPI in materials. Study of the PPI is important in order to understand the $\kappa_{\text{ph}}$ of thermoelectric materials. This interaction is studied by calculating phonon lifetime and imaginary part of self-energy due to PPI using the anharmonic force constant under many-body perturbation theory [20].

At the present stage, the fully first-principles calculation of thermoelectric properties considering all the above interactions may be treated as computationally demanding work. However, eventually this difficulty may be overcome, considering the increased computing power and modern codes [18]. Such efforts to study carrier lifetime and thermoelectric properties on selected material classes can not only improve basic understanding of transport, but also can provide a database which can be used to create a possible lifetime model to directly apply for some material classes in the prediction or search of new thermoelectric materials thereby saving costly computations.

Using GW approximations, studies of the effect of EPI on the electronic structure of transition metal based Heuslers such as Fe$_2$VAl, Fe$_2$VGa, Co$_2$FeSi have been carried out [25–28]. A number of studies have been made in predicting or understanding few aspects of thermoelectric or transport properties on some materials considering the carrier scattering and lifetime. For instance, the thermoelectric properties studies of silicon are carried out considering the EPI and PPI by first-principles method [29–32]. The mobility of n-type Si, Al and MoS$_2$ was calculated by Li considering the EPI by ab initio method which is in in good agreement with experiments [33]. Zhou and Bernardi calculated electron mobility, and lifetime of electrons and phonons due to EPI in GaAs providing a scheme to study transport in polar materials [34]. Electronic mobility of thermoelectric material n-type PbTe is calculated as a function of temperature and carrier concentration by Cao et al considering the EPI identifying the dominant scattering source [35]. Similarly, thermoelectric parameters at 300 K in p-type PbTe is studied in reference [36] taking into account EPI. Li et al studied the electrical and thermal transport parameters, power factor (PF) and $ZT$ with change in carrier concentration at 300 K considering PPI, EPI, and phonon-dopant interaction for doped SnSe [37]. For some of
half-Heusler thermoelectric materials a study has been carried out by Samsonidze and Kozinsky [38] proposing a new electron–phonon averaged approach in calculating scattering rate treating EPI. The temperature dependent thermoelectric properties of p-type HfCoSb and n-type HfNiSn are calculated using this approach. A prediction of $ZT$ is made for number of half-Heuslers including FeVSeB at 673 K setting value of $\kappa_{\text{ph}}$ to be 2 Wm$^{-1}$ K$^{-1}$.

The application potential in spintronics or thermoelectric generators attracts study of the Heusler compounds [39–47]. Many of compounds of Heusler family have drawn attention as promising thermoelectric materials for high temperature applications due to many desirable material features [48–51]. Therefore, it is important to study the different carrier scattering mechanism in this class of materials in order to further understand and predict thermoelectric properties. Recently, the FeVSeB is found to show high $S$, moderate $\sigma$ and promising p-type thermoelectric property with suitable substitution [48, 49, 52, 53]. Considering this aspect, in our work we focus on the charge and heat carrier lifetimes due to intrinsic scattering mechanisms in the promising half-Heusler thermoelectric FeVSeB. In FeVSeB, the transition metal atoms with 3d bands are present so it is interesting to study the electronic structure using GW method. So, firstly the effect of EEI with temperature on the valence band maximum (VBM) and conduction band minimum (CBM) is studied under full-GW method. The carrier lifetime at VBM and CBM with temperature are estimated. The change in band gap due to EEI with temperature is also discussed. Next, the effect of EPI is studied by calculating linewidth of electrons and phonons using the EPW method. The temperature dependent variation of electron and phonon lifetimes due to EPI is calculated. The variation of phonon lifetime with temperature is discussed for different branches. Similarly, the effect of PFI on the lifetime of phonons are studied by calculating branch wise lifetime. By comparing the electron and phonon lifetime due to different scattering mechanisms, major sources of carrier scattering are identified in FeVSeB. Then, the PF and ZT are estimated for p-type and n-type FeVSeB using the temperature dependent carrier lifetime.

2. Brief description of the calculation methods

In our work mainly three different computational tools are used to study the lifetime of carriers due to intrinsic scattering mechanisms. The methods used to study different interactions and calculate imaginary part of carrier self-energy are briefly described in this section.

In the full-GW method, the spectral function $A(k, \omega)$ for single band is given by [54]:

$$A(k, \omega) = \frac{1}{\pi} \frac{|\text{Im } \Sigma(k, \omega)|}{[\omega - \varepsilon_k(k) - \text{Re } \Sigma(k, \omega)]^2 + [\text{Im } \Sigma(k, \omega)]^2},$$

where, $\omega$ is real frequency, $\varepsilon_k(k)$ is energy of a single electronic state in the non-interacting system with crystal momentum $k$. The chemical potential is taken to be zero in the above expression. The terms $\text{Re } \Sigma(k, \omega)$ and $\text{Im } \Sigma(k, \omega)$ are the real and imaginary part of the self-energy $\Sigma(k, \omega)$, respectively.

The $\text{Im } \Sigma(k, \omega)$ gives broadening due to EEI while, $\text{Re } \Sigma(k, \omega)$ gives energy shift due to interaction from $\varepsilon_{k}^{0}(k)$. The temperature dependent electronic structure is studied by using Green’s function $G$ defined in Matsubara-time domain which is called temperature Green’s function method. Another approach is by using conventional statistical mechanical approach to calculate $G$. In the temperature Green’s function method, the concept of temperature is introduced through Matsubara-time. This method is easy to adopt in self-consistent calculations [55–58].

The imaginary part of electron and phonon self-energy due to the EPI is obtained in the EPW as below [59]:

$$\text{Im } \Sigma'(\omega, T) = \frac{\pi}{2} \sum_{nm} \int_{BZ} \frac{d \mathbf{q}}{\Omega_{BZ}} |g_{nm,\nu}(\mathbf{k}, \mathbf{q})|^2$$

$$\times \left\{ \int_0^{\pi} \int_0^{2\pi} \frac{d \mathbf{k}}{\Omega_{BZ}} |g_{nm,\nu}(\mathbf{k}, \mathbf{q})|^2$$

$$\times \left[ f_{nk}(T) - f_{nk+q}(T) \right] \delta(\omega - \varepsilon_{nk+q} + \varepsilon_{F})$$

$$+ \omega_{\mathbf{q}} \right\}.$$

(2)

The imaginary part of phonon self-energy:

$$\text{Im } \Sigma''(\omega, T) = \frac{\pi}{2} \sum_{nm} \int_{BZ} \frac{d \mathbf{q}}{\Omega_{BZ}} |g_{nm,\nu}(\mathbf{k}, \mathbf{q})|^2$$

$$\times \left\{ \int_0^{\pi} \int_0^{2\pi} \frac{d \mathbf{k}}{\Omega_{BZ}} |g_{nm,\nu}(\mathbf{k}, \mathbf{q})|^2$$

$$\times \left[ f_{nk}(T) - f_{nk+q}(T) \right] \delta(\varepsilon_{nk+q} - \varepsilon_{nk} - \omega) \right\}.$$

(3)

In the above expressions $g_{nm,\nu}(\mathbf{k}, \mathbf{q})$ is the first-order electron–phonon matrix elements from DFPT calculations. This gives a quantification of the scattering process between Kohn–Sham states $\mathbf{m}k + \mathbf{q}$ and $\mathbf{n}k$ connected with a phonon of wave vector $\mathbf{q}$, $\omega_{\mathbf{q}}$, is phonon frequency of branch index $\nu$. $\varepsilon_{nk}$ is the eigenvalue of electron with band index $n$ and wave vector $\mathbf{k}$. $\varepsilon_{F}$ is the Fermi energy. The Bose–Einstein and Fermi–Dirac distributions are denoted by $n_{q}(T)$ and $f_{nk}(T)$, respectively. A carrier lifetime (or relaxation time) due to EEI or EPI is obtained in $h$/linewidth [60]. Here linewidth is obtained as the twice of the imaginary part of electron or phonon self-energy.

The lifetime of phonons due to PFI is obtained from the imaginary part of phonon self-energy. The imaginary part of phonon self-energy of a mode, $\Gamma_{\nu}(\omega) (\lambda = \mathbf{q}, \nu)$ can be obtained using the third order anharmonic force constants under many-body perturbation theory as [20]:

$$\Gamma_{\nu}(\omega) = \frac{18\pi}{h^2} \sum_{\lambda\lambda'} |\Phi_{\lambda-\lambda',\nu}|^2 \left\{ \langle n_{\lambda'} + n_{\lambda'} + 1 \rangle$$

$$\times \delta(\omega - \omega_{\lambda} - \omega_{\lambda'}) + \langle n_{\lambda'} - n_{\lambda'} \rangle$$

$$\times \delta(\omega + \omega_{\lambda} - \omega_{\lambda'}) - \delta(\omega - \omega_{\lambda} + \omega_{\lambda'}) \right\}.$$
Then, the lifetime (or relaxation time) of a mode $\lambda$ is obtained as $\tau_\lambda = 1/2\Gamma_{\lambda}(\omega)$ [20]. Here, $2\Gamma_{\lambda}(\omega)$ is called linewidth of a phonon mode $\lambda$.

4. Results and discussion

4.1. Electron–electron interaction (EEI)

The study of EEI and temperature effects on the electronic structure is important to understand the transport properties. Therefore, to see the effect of EEI and temperature on the electronic energy states of FeVSb, the spectral function $A_j(k, \omega)$ (here, $j$ is band index) is calculated at different electronic temperatures using the full-GW method. The obtained excited state electronic structure, $A_j(k, \omega)$ at the VBM at $k$-point ($L_V$) and conduction band bottom (CBM) at $X$-point ($C_X$) for four temperatures are shown in figure 2(a). Since, the chemical potential in this $GW$ spectral function calculation is not determined, it is taken to be the middle of center of VBM peak P2 and CBM peak at 300 K for the reference purpose. In figure 2(a), the energy of $A_j(k, \omega)$ is shown with respect to the chemical potential (dotted line). Here, the effect of EEI and temperature on $A_j(k, \omega)$ at the VBM and CBM are focused since, the major contribution to transport comes from the carriers in the neighborhood of these points. To see the changes in the electronic structure with the inclusion of EEI and temperature, the ground state electronic structure calculated using DFT is also shown in figure 2(b) for a reference purpose. It is known that in DFT, the interacting many particles are treated as non-interacting particles, but in an effective potential. As one can see from figure 2(b), the VBM in the calculated DFT dispersion in FeVSb is doubly degenerate. But, as can be seen from figure 2(a), this degeneracy is lifted and two well separated peaks (marked P1 and P2, in the order of energy) corresponding to VBM can be seen at 300 K. The energy difference between these two peaks is $\sim 91$ meV. With the increase in temperature (300 K to 1000 K), the height of the peaks are observed to be reducing and simultaneously the broadening (width of peaks) is also increasing due to electronic excitations. At 1000 K, the separation between center of two peaks are very much reduced forming a hump-like shape. On observing the peaks’ behavior, it suggests that at still lower temperatures the separation between them becomes more prominent indicating a non-degeneracy at the VBM in FeVSb. Therefore, this result shows and suggests the importance of EEI in...
from SCAN (value of band gap is slightly higher than the band gap obtained from DFT calculations. We could not come across any band gap dispersion around the Fermi level. (c) The estimated variation of band gap from the temperature dependent spectral function.

Figure 2. (a) The spectral function at the L-point (VBM \( L_x \)) and X-point (CBM \( X_e \)) at different temperatures. (b) The ground state dispersion around the Fermi level. (c) The estimated variation of band gap from the temperature dependent spectral function.

FeVSb. Similarly, the height of the peak at CBM is found to be reducing and simultaneously broadening is increasing with the rise in temperature. Also, one can observe the effect of reduction in the energy separation between the VBM and CBM with the increase in temperature. Thus, to see this effect quantitatively we move on to estimate the temperature dependent band gap.

To see the effect of EEI and temperature on the electronic band gap (or more precisely quasi-particle gap), the energy separation between VBM and CBM is estimated from the \( GW \) spectral function. Here, the indirect electronic gap is defined as the energy difference between the center of the peak P2 of VBM and the center of the peak of CBM at a given temperature. The calculated band gap with temperature is presented in figure 2(c). The value of band gap at 300 K is \( \sim 367 \) meV and it reaches a lower value of \( \sim 341 \) meV at 1000 K. The calculated band gap data is fitted with linear equation and it is found to obey a linear decreasing trend with rise in temperature. In order to estimate ground state band gap considering the effect of EEI, the linear fit is extrapolated to 0 K. The obtained value of ground state band gap at 0 K is \( \sim 378 \) meV. This ground state value of band gap is slightly higher than the band gap obtained from SCAN (\( \sim 330 \) meV) \cite{65} and GGA-PBE (\( \sim 320 \) meV) \cite{8} DFT calculations. We could not come across any band gap from optical measurements in the literature for this compound. However, the thermal band gap estimated from Goldsmid and Sharp formula is \( 0.27 \) eV \cite{52}. This band gap is lower than the theoretically calculated band gaps which may be due to the defects or impurities present in the sample. The 300 K band gap is \( \sim 3\% \) reduced with respect to ground state band gap. Thus, the calculated spectral function shows the effect of temperature along with EEI on the electronic structure and band gap of FeVSb.

The width of the quasiparticle (QP) peak gives information about the imaginary part of electron self-energy \( \text{Im} \Sigma(k, \omega) \), This \( \text{Im} \Sigma(k, \omega) \) is related to the QP–QP interaction. Using the \( \text{Im} \Sigma(k, \omega) \) one can estimate the lifetime of carriers as mentioned in section 2. So, here the effect of EEI on the lifetime of particles at the band extrema are estimated from the \( GW \)-spectral function peaks. We calculated \( \text{Im} \Sigma(k, \omega) \) as the half-width at half maximum (HWHM) of the Lorentzian fit to the peaks at VBM and CBM. Then, the lifetime of carriers \( (\tau_{e-e}) \) due EEI is calculated as \( \hbar/(2 \times \text{HWHM}) \). The obtained \( \tau_{e-e} \) at the VBM and CBM of FeVSb for 300 K to 1000 K is shown in figure 3. The peaks P1 and P2 have the same width therefore same lifetimes are estimated for the particles. The \( \tau_{e-e} \) decreases with the rise in temperature. Also, the particle lifetime at VBM is found to be slightly lower than that of CBM. At 300 K, the \( \tau_{e-e} \) of particles at VBM (CBM) is \( \sim 1.91 \times 10^{-14} \) s \( (\sim 2.05 \times 10^{-14} \) s). With the rise in temperature, the scattering increases and at 1000 K, the \( \tau_{e-e} \) reaches a value of \( \sim 0.55 \times 10^{-14} \) s and \( \sim 0.61 \times 10^{-14} \) s at VBM and CBM, respectively. These calculated values of lifetime due to EEI suggests a high scattering of electrons in FeVSb at the band extrema. Also, the order of magnitude of lifetime suggests EEI is a major source of scattering in FeVSb and cannot be neglected in transport properties calculation. These estimated lifetime are due to the EEI but, the thermal vibration of lattice acts as another intrinsic source of scattering of electrons in crystalline solids. This interaction between electron and phonons plays important role in the transport mechanism which is studied for FeVSb in the next section.

4.2. Electron–phonon interaction (EPI)

The thermal vibrations causes the ions/nuclei to undergo oscillatory motion from the equilibrium positions. This motion of nuclei affects the motion of electrons and vice-versa coupling to each other which is called EPI. This effect of EPI on the lifetime of electrons and phonons is studied by calculating the electron and phonon linewidth in FeVSb. In figure 4(a), the linewidth of electrons due to EPI at 300 K (300 K) along the high symmetric \( k \)-directions in the BZ are shown. The electron linewidths are calculated for the three bands (denoted as B1, B2 and B3 in figure 2(b)) close to the valence band edge. The value of electron linewidth at the doubly degenerate VBM at \( L \)-point is \( \sim 3.4 \) meV and lower compared to that of other high symmetric \( k \)-points. At the \( X \)-point electron linewidth is \( \sim 244 \)
meV for band B3 which is higher compared to other k-points shown. This indicates that the electrons in the neighborhood of VBM at L-point is less affected by the EPI and have lesser scattering (or more lifetime) relative to other k-points at the valence band edge.

In order to study the effect EPI on the phonons, linewidth and lifetime are calculated for FeVSb half-Heusler. In our earlier work, we have calculated the phonon properties of FeVSb [65]. The phonon dispersion in FeVSb has six optical and three acoustic branches. For these phonon branches the linewidth and lifetime are calculated. The calculated room temperature linewidth of optical phonon branches (b4–b9) and acoustic phonon branches (b1–b3) along high symmetric q-directions are shown in figures 4(b) and (c), respectively to see the main scattering regions in the BZ. From the energy scale of acoustic and optical phonon linewidths, one can see that acoustic phonons have overall lower interactions with the valence band electrons compared to the optical phonons. This also suggests that the lifetime due to interactions with electrons for acoustic phonons is higher compared to optical phonons. The optical phonons are mainly scattered after interacting with electrons in FeVSb. From figure 3(b) one can see that the optical phonons close to Γ-point have higher linewidth relative to that of other high symmetric points. Also, one can observe that the highest energy branch (b9) optical phonons experience more scattering around the Γ-point with linewidth of ∼2.1 meV. The acoustic phonons have higher scattering around the X-point relative to other points as can be observed from figure 4(c) which is suggested by a linewidth of ∼0.05 meV for b1, b2 and ∼0.03 meV for b3.

Further, to see the effect of temperature on the EPI and carrier scattering, the lifetimes of electrons and phonons are calculated at higher temperatures. The calculated electron lifetime τ_e–ph due to EPI, at the VBM at L-point in the temperature range 300 to 1200 K is shown in figure 5(a) for FeVSb. At a given temperature, the value of τ_e–ph is obtained from the calculated imaginary part of electron self-energy due to EPI, using the formula mentioned before. The τ_e–ph has decreasing trend in the temperature range shown. The room temperature τ_e–ph is ∼19.3 × 10^{-14} s and it decrease to a value of ∼3.7 × 10^{-14} s at 1200 K. The values of τ_e–e is slightly lower compared to τ_e–ph indicating that effect of EPI is comparable to EPI at the VBM. This suggests that EPI is not ignorable in computing transport coefficients. We could not come across any reported value of electron lifetime due to EPI in literature for FeVSb. However, Samsonidze and Kozinsky have studied p-type HfCoSb and n-type HfNiSn Heuslers with EPI [38]. The reported value of electron lifetime at 673 K, for p-type HfCoSb at VBM is ∼20 × 10^{-13} s and for n-type HfNiSn at CBM is ∼80 × 10^{-15} s.

The phonons in the solid also interact with electrons and have finite lifetime due to this interaction which is important in deciding the heat transport through them. Thus, to see the EPI effect on phonons, linewidth and lifetime at different temperatures are calculated for all points in irreducible part of BZ. The phonon mode lifetime due to EPI is obtained as inverse of phonon mode linewidth using the formula mentioned earlier. The overall phonon mode linewidth using the formula mentioned earlier.

The acoustic branch (b9) has the lowest lifetime indicating large scattering. τ_e–ph, for a particular phonon branch is obtained as the weighted average over the q-points in the BZ which is shown in figure 4(a) for 300–1200 K. The branches b1–b3 are acoustic phonon branches and b4–b9 are optical branches. Further, acoustic, optical and overall phonon lifetimes are obtained by averaging over respective number of phonon branches. This is presented in figure 5(c) as a function of temperature for FeVSb. From figure 5(b), the range in values of lifetime for different phonon branches at a particular temperature can be observed. The figure also indicates order of magnitude changes in the τ_e–ph with temperature. The lifetime of acoustic phonons shown in figure 5(c), indicates that the optical phonons strongly interact with the electrons and thus have lower lifetime compared to acoustic phonons. This analysis suggests acoustic phonons mainly transport heat in FeVSb while optical phonons experience more scattering. The value of τ_e–ph in FeVSb is reducing drastically (by 3 order of magnitude) from room temperature to 1200 K. The overall τ_e–ph at 300 K is ∼5.8 × 10^{-11} s and reaches a value of ∼4.2 × 10^{-14} s at 1200 K. This large reduction in lifetime indicates that, EPI plays the major role in deciding the lattice thermal conductivity behavior.

### 4.3. Phonon–phonon interaction (PPI)

The phonons interact with other phonons in the solid. This PPI acts as another intrinsic source of phonon scattering leading to finite lifetime of phonons. In this section, the average phonon lifetime due to the PPI with temperature is calculated to understand κ_{ph} behavior. The lifetime for each of phonon modes is calculated from phonon mode linewidth using the relation mentioned in section 2. Then for each of the nine phonon branches, the branch phonon lifetime τ_{ph–ph} is calculated as the weighted average over the q-points in the BZ. Further, acoustic, optical and overall phonon lifetimes τ_{ph–ph} are obtained by averaging the branch lifetime over respective number of phonon branches at each temperature. These results calculated for the temperature range 300 K to 1200 K are shown in figures 6(a) and (b), respectively.

From figure 6(a), one can observe that highest energy optical branch (b9) has the lowest lifetime indicating large scattering due to PPI. The acoustic branch phonons (b1 and b2)
have higher lifetime and experience relatively lesser scattering. In figure 6(b), the lifetimes of acoustic and optical phonons along with overall phonon lifetime as a function of temperature in FeVSb is presented. As can be seen from the figure, the nature of the phonon lifetime curve with temperature is similar to that of $\kappa_{ph}$ calculated in our previous work for FeVSb [65]. The group velocity is a temperature independent quantity in the method of calculation of $\kappa_{ph}$ used in reference [65] and specific heat is almost constant above $\sim 400$ K. Therefore, the nature of phonon lifetime curve with temperature suggests that the lattice part of thermal conductivity due to PPI is mainly decided by the phonon lifetime. The value of overall $\tau_{ph-ph}$ at room temperature is $\sim 5.3 \times 10^{-12}$ s and it reaches to a value of $\sim 1.2 \times 10^{-12}$ s at 1200 K. Also, it can be observed that the optical phonons have shorter lifetime compared acoustic phonons. Similar trend for lifetime of optical and acoustic phonons due to EPI can also be observed in figure 5(c). This suggests that acoustic phonons undergo lesser scattering and carry more heat energy compared to optical phonons in FeVSb. The cumulative lattice thermal conductivity analysis carried out in our previous work also suggested that larger contribution to $\kappa_{ph}$ comes from acoustic phonons. The lifetime analysis in this work further supports this finding in FeVSb thermoelectric half-Heusler. Here, it is interesting to notice by
4.4. Thermoelectric properties

In this section, a prediction of PF $S^2\sigma$ and figure of merit $ZT$ for p-type and n-type FeVSb using the first-principles carrier lifetimes is presented. In the BoltzTraP program which is normally used to calculate thermoelectric properties, the transport coefficients are obtained under CRTA. But, the variation of carrier lifetime with temperature is one of the important quantities in deciding the transport behavior which is not captured in such calculations. Therefore, here a prediction of thermoelectric properties is made by using the temperature dependent carrier lifetime estimated from first-principles, in the electronic transport coefficients calculated from BoltzTraP calculations in our last work [65].

The calculated PF and $ZT$ for the p-type and n-type FeVSb as a function of temperature are shown in figures 7(a) and (b), respectively. Here, the electronic transport coefficients appearing in $ZT$ are calculated by using temperature dependent carrier lifetimes ($\tau_{\text{e-ph}}$) obtained in this work. The carrier lifetime $\tau_{\text{e-c}}$ due to EEI at VBM and CBM are fitted with a function of the form $y = a \times x^b$ and extrapolated up to 1200 K. Using this fit, the values of $\tau_{\text{e-c}}$ at the intermediate temperature are obtained. The value of coefficient $a$ and $b$ for VBM (CBM) is 701.81 (631.96) and $-1.0367 (-1.0038)$, respectively. The overall carrier lifetime at each temperature $\tau_{\text{e}}(T)$ is obtained from the $\tau_{\text{e-c}}(T)$ and $\tau_{\text{e-ph}}(T)$ using Matthiessen’s rule. From figure 7, one can see that the PF and $ZT$ are higher for the p-type FeVSb compared to that of n-type FeVSb. The value of PF for p-type (n-type) FeVSb is $\sim 6 \times 10^{-3}$ (1.3 $\times 10^{-3}$) at 300 K and reaches a value of $\sim 8 \times 10^{-3}$ (5 $\times 10^{-3}$) at 1200 K. The PF for p-type FeVSb is increasing up to $\sim 800$ K and above this temperature there is slow reduction in the value. Similarly, the PF for n-type FeVSb is increasing up to $\sim 900$ K and then it is almost constant. The $ZT$ for the p-type (n-type) FeVSb at 300 K is 0.07 (0.01) and it reaches the maximum $ZT$ of 0.51 (0.34) at 1200 K. The predicted $ZT$ values suggest that the FeVSb can be used for thermoelectric application in the high temperature region. Also, this predicted values of $ZT$ give a more realistic result for FeVSb half-Heusler. In the calculation of $ZT$, the values are used from our previous work [65]. Here, the carrier lifetime due to EEI is not considered in the calculation of $ZT$, which if considered, can lead to further improvement in $ZT$. In this direction, a more detailed and careful study is needed to take into account mode wise phonon lifetime and band index, k-point dependent electron lifetime in transport coefficient calculations.

5. Conclusions

In summary, the lifetime of charge and heat carriers due to intrinsic scattering mechanisms, viz. EEI, EPI and PPI are studied from first-principles in FeVSb. The temperature dependent electronic structure at the VBM and CBM are studied by calculating the spectral function from the full-GW method considering EEI. The results show a lift of degeneracy due to EEI at the VBM compared to DFT dispersion. The electronic band gap in FeVSb is found to decrease linearly with increase in temperature from this calculations. The obtained room temperature band gap with EEI is $\sim 367$ meV and it reaches a lower value of $\sim 341$ meV at 1000 K. The lifetime of carriers at VBM and CBM are estimated considering EEI with temperature. The room temperature value of lifetime at VBM (CBM) is $\sim 1.91 \times 10^{-14}$ s ($\sim 2.05 \times 10^{-14}$ s). The values obtained suggest in fact, the scattering due to EEI is of considerable importance in electronic lifetime calculations in this compound. The effect of EEI is discussed by calculating temperature dependent lifetime of electrons and phonons. A branch wise analysis of lifetime of phonons due to EEI is carried out. The calculated values of electron lifetime suggest, both EEI and PPI should be taken into account in estimating the electronic transport parameters in FeVSb. Further, the effect of PPI on phonon lifetime is analyzed by computing the lifetime for acoustic and optical phonon branches. This analysis suggest, the acoustic phonons experience lesser scattering due to PPI and EPI compared to optical phonons playing a role...
of major heat carriers. Also, the comparison of phonon life-
time due to EPI (~8.9 × 10^{-13} s at 550 K) and PPI (~2.8 × 10^{-13} s at 550 K) suggested, the EPI is the dominant scatter-
ing mechanism above 500 K for phonons and hence cannot be
ignored in ρ_{Nf} calculation and ZT predictions. Lastly, a prediction of
ZT of p-type and n-type FeVSb made by considering
the temperature dependent phonon lifetime calculated for the
electronic transport terms.

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Data availability statement

The data that support the findings of this study are available
upon reasonable request from the authors.

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