

***Ab initio* study of the vanadium-based half Heusler alloys VRhZ (Z = Ge, Si, Sn) as potential thermoelectric materials**

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We embrace a high-throughput investigation strategy beginning from the electronic structure properties to examine three vanadium-based half Heusler alloys with 18 valence electrons, VRhZ (Z = Ge, Si, and Sn), for thermoelectric application. This work is inspired by expected contrasting electrical transport essentials, particularly high electrical conductivity σ and high Seebeck coefficient S for attaining enhanced figure of merit (ZT) performance. We employ the electronic fitness function (EFF), which evaluates the magnitude of decoupling σ and S for high ZT by a distinct band structure. The impact of varying the Fermi level on the power factor, electrical conductivity, and Seebeck coefficient is explored. The effects of exchange correlation are reported by use of the Perdew-Burke-Ernzerhof (PBE) functional in line with the framework of the generalized gradient approximation (GGA), as implemented in the *ab initio* density functional theory. To rigorously assess the reliability of the GGA-PBE functional, subsequent electronic structure calculations are carried out on the three compounds using the *GW* approximation. We obtain lattice constants of $a_0 = 5.79 \text{ \AA}$, $a_0 = 5.76 \text{ \AA}$, and $a_0 = 6.09 \text{ \AA}$ for VRhGe, VRhSi, and VRhSn, respectively. All materials exhibit ductility as indicated by their values of Cauchy pressure, as well as Poisson's ratio and Pugh's ratio values. The VRhSn machinability index is the highest at 2.2456. The highest hardness is realized in VRhSi, which is at 7.9957 GPa. Based on the Kleinman parameter, bond stretching is negligible in all VRhZ materials. VRhZ spatial dependence plots indicate that all investigated compounds are anisotropic. In this study, dynamic stability is observed in all compounds due to the nonexistence of phonon modes that correspond to imaginary frequencies. The derived electronic energy band structure reveals that all three alloys exhibit semiconductor properties with band gap energies of 0.50, 0.32, and 0.42 eV in VRhGe, VRhSi, and VRhSn, respectively, corresponding to indirect transitions. The maximum values realized for the EFF when $T = 1000 \text{ K}$ using *GW* are $0.69 \times 10^{-19} \text{ W}^{\frac{5}{3}} \text{ ms}^{-\frac{1}{3}} \text{ K}^{-2}$, $0.66 \times 10^{-19} \text{ W}^{\frac{5}{3}} \text{ ms}^{-\frac{1}{3}} \text{ K}^{-2}$, $0.79 \times 10^{-19} \text{ W}^{\frac{5}{3}} \text{ ms}^{-\frac{1}{3}} \text{ K}^{-2}$ for VRhGe, VRhSi, and VRhSn, respectively. The observed ZT values at 1000 K using *GW* are 0.91, 0.99, and 0.99 for VRhGe, VRhSi, and VRhSn, respectively. These results of ZT as well as EFF suggest that VRhZ (Z = Ge, Si, and Sn) compounds are promising high-temperature thermoelectric materials.

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I. INTRODUCTION

VRhZ (Z = Ge, Si, and Sn) belongs to the *ABX* category of compounds, characterized by 18 valence electrons [1]. Among all recently reported half Heusler (HH) compounds [1], these three HH compounds have not been reported. Fascinating functionalities, for example, topological characteristics of the electronic structure [2,3] and thermoelectricity [4], persist in giving this class of compounds a diverse and broad applicability. Thermoelectric (TE) materials have the capacity of converting thermal heat to electricity and they have a critical

task in optimizing energy efficiency. The energy-harvesting potentiality of TE materials has gained a lot of recognition and, also, these materials are very crucial for intelligent systems [5–7].

HH materials are intermetallic compounds comprised of three elements with general formulation, XYZ, where X as well as Y are *d*-block elements, and Z is a *p*-block or *s*-block element [8]. These materials take a crystalline form in the face centered cubic (fcc) system which possesses a *F43m* symmetry notation (International Tables of Crystallography No. 216) and its crystal structure designation is *C1_b* [9,10]. The HH materials which illustrate fcc crystal configuration and associated *F43m* (No. 216) space group possess an 18-valence electron count (VEC) [11]. These materials are identified with an acceptable Seebeck coefficient and an average electrical conductance attributed to a blend of characteristics. That is, a small energy band gap and an insignificant relocation of Fermi energy level above valence band maximum [12]. Most HH alloys with VEC = 18 are invariable in cubic structures and are promising thermoelectric compounds [11].

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HH elements occupy the Wyckoff's positions: X particles are found at (0.00 0.00 0.00) position, Y particles at (0.25 0.25 0.25) position, and Z particles at (0.50 0.50 0.50) position [13,14]. The nature of atomic configuration in XYZ is the primary determinant of all the physical characteristics of HH materials. The thermoelectric response of half Heusler systems is determined by their valence shell electron count [15,16]. HH semiconductors described by 18 valence electrons are predominantly reduced energy band gap semiconducting materials and they are promising thermoelectric candidates [17,18]. The efficiency of energy conversion in thermoelectric materials is dictated by ZT , a unitless measure of thermoelectric performance, which is determined by the properties, power factor (PF), Seebeck coefficient (S), electrical conductivity (σ), absolute temperature (T), and effective thermal conductivity (k) [7,19]. We are certain that for HH materials with a VEC of 18, optimizing them and modifying their electronic configuration provides a sure path to optimizing the high ZT for thermoelectric operations. Optimization of ZT entails high complexity, given that, σ and S are inversely proportional to each other, and the parameters σ , S , and k establishing ZT depend on each other [20–23]. The hitch in attaining high ZT is the electronic structure complexity [20], therefore, the electronic fitness function (EFF) is employed in addressing the inversely proportional correlation between σ and S [21] in attaining high ZT . We are justified in concluding that EFF considers the electronic bit of thermoelectric efficiency. EFF analyzes the complex electronic structure regarding thermoelectric performance. It is a mathematical function proportional to power factor per unit relaxation time ($\frac{PF}{\tau}$) as well as electronic states per volume (N), described by the equation

$$EFF = \frac{PF}{\tau N^{2/3}}. \quad (1)$$

In this study, EFF is determined from first principle electronic structure modelling and the semi classical Boltzmann equation model at invariable decay time [21]. EFF serves as a key element in determining the qualities of energy-conversion materials [21]. It predicts the electronic configuration detail of σ and S exhibit an inverse correlation. ZT is used to establish and estimate the capability of TE materials and is calculated as

$$ZT = \frac{S^2 \sigma}{k} T, \quad (2)$$

with σ standing for electrical conductivity, k denoting effective thermal conductivity, S symbolizing thermopower, and T indicating absolute temperature. ZT is at its optimum value at maximum power factor $PF = S^2 \sigma$ and minimum effective thermal conductivity (k). k is a function of two components. These are the lattice component (k_l), which results from vibrations, and the electronic component (k_e) from heat transferred by charge carriers. To reduce the value of k_l , atomic substitution as well as nanostructuring is employed in the crystal structure, while enhancing ZT involves variation of charge carrier density to obtain an optimal value between a maximum PF and a minimum k_e [22]. As recent as 2014, researchers primarily engaged in enhancing electron-rich semiconductors from $XNiSn$ ($X = Ti, Zr, Hf$)

half Heuslers and hole-conducting compounds from $XCoSb$ ($X = Ti, Zr, Hf$). This requires alloying through material engineering in addition to electron and hole doping. The resultant donor and acceptor compounds recorded a ZT close to 1 and a ZT close to 0.7 at 773 K, respectively [23,24]. Hole-conducting materials such as $XFeSb$, given that X stands for V, Nb, and Ta, and $ZrCoBi$ recently became viable candidates in TE applications, registering ZT above 1 at 773 K [25–27]. Tobola *et al.* [28] conducted both experimental as well as computational studies on a set of intermetallic cubic half Heusler materials. Semiconducting to metallic characteristics emerged at the ground state, also, transition from Pauli paramagnetism to Curie-Weiss-type ferromagnetic ordering was witnessed at the ground state. An analysis of the stability and electronic structure was performed on the half Heusler systems expressed as $NiYSn$ where Y stands for Ti, Zr, and Hf through energy optimization conducted by Ögüt and Rabe [29]. This research identified energy gaps of the indirect type falling in a range of 0.5 eV. This category of cubic half Heusler materials, defined by narrow band gaps, was validated by Slebarski *et al.* [30]. This was done by evaluating the impact of Zr and Ti atoms substituted by Ce in the band structure of $NiYSn$ ($Y = Zr$ and Ti). Sublattice chemical disorder was observed to diminish the width of narrow band gaps [30]. Indeed, experimental studies found out that the energy gaps in these materials generally fell within a 0.1–0.5 eV range [28–30]. The thermoelectric performance of $VRhZ$ ($Z = Ge, Si, \text{ and } Sn$) HH materials is the focus of this work. The study utilizes fundamental computation to determine the energy bands and thermoelectric characteristics in $VRhZ$ ($Z = Ge, Si \text{ and } Sn$) materials. This study explores thermoelectric properties of $VRhZ$ ($Z = Ge, Si, \text{ and } Sn$) and also initial inquiry into the relationship between EFF and ZT of the investigated materials. These calculations provide vital and precise information about these materials. The traits observed in this study are anticipated to guide laboratory investigations and practical industrial use. This study is structured into the following components: Section II outlines the calculations carried out for eventual reference. Section III refers to the specifics of our results and discussions and they are presented in six divisions, that is, structural, lattice dynamics, thermo dynamics, mechanical, electronic, and transport properties. Section IV reports conclusion of our work.

II. CALCULATIONS

In the current analysis, we employ the DFT formalism [31,32] and Boltzmann transport formalism using BOLTZTRAP [33] code within the QUANTUM ESPRESSO (QE) [34] implementation. This is done through plane-wave basis based pseudopotentials [35] with the TRANSM package [21] to perform band structure calculations, electronic transport properties, EFF, and inverse effective mass of $VRhZ$ ($Z = Ge, Si, \text{ and } Sn$) cubic half Heusler materials. The entire computation work is comprised of five sequential stages: (a) energy minimization in $VRhZ$ ($Z = Ge, Si, \text{ and } Sn$) lattice constants by energy based optimization, (b) determination of $VRhZ$ ($Z = Ge, Si, \text{ and } Sn$) band structures, (c) solving the Boltzmann transport formalism to determine transport coefficients

through BOLTZTRAP code, inverse effective mass (IEM) and EFF determination of these materials by use of the TRANSM package, (d) *ab initio* molecular dynamics (AIMD) simulations, where a $2 \times 2 \times 2$ periodic supercell containing 24 atoms is created from the primitive unit cell and a $10 \times 10 \times 10$ k-point mesh is used to sample the Brillouin zone (BZ), (e) lattice thermal conductivity k_l is computed using the optimized slack model [36], and (f) strain computations performed on both the optimized lattice constant and the strained configurations to calculate the carrier relaxation time (τ) in accordance with the deformation potential theory [37]. The structural optimization, lattice dynamic stability calculations, and *ab initio* electronic simulations are carried out within density functional theory (DFT) approach as executed in QE code [34] utilizing the norm conserving pseudopotentials according to the Troullier Martins design [38]. The exchange correlation interactions are illustrated using generalized gradient approximation Perdew-Burke-Ernzerhof (GGA-PBE) [39] and were applied during the entire calculations. The numerically stable, applicable, adequate cutoff energy for plane waves at 90 Ry was utilized throughout the study. A $14 \times 14 \times 14$ Monkhorst Pack [40] k-point mesh, which ensured energy convergence to within 1 mRy/atom, was used consistently in all calculations. In representing the charge density, we use a cut off of 620 Ry in the Fourier decomposition. The valence electronic states examined for all calculations are V = [Ar]3d³4s², Rh = [Kr]4d⁸5s¹, Sn = 5s²5p², Si = 3s²3p², and Ge = 4s²4p², summing up to 18 valence electrons per half-Heusler phase investigated. Elastic constants C_{11} , C_{12} , and C_{44} were computed by use of finite difference technique within the thermo-pw framework [41]. The technique applies introduction of perturbation to the crystal using a microscopic strain, inducing both a strain tensor as well as a corresponding stress response which influences it back to stability and is calculated by use of the relation

$$\sigma_i = \sum_{j=1}^6 C_{ij} \epsilon_j, \quad (3)$$

where C_{ij} depict the elastic constants, σ_i the stress element, and ϵ_i tensor of the strain. Shear anisotropy was quantified through the elastic constants, whereas the elastic anisotropy index was derived by use of Voigt-Reuss averaged shear modulus. The laticity tensor simulation program (ELATE) [42] was applied in examining the directional dependency of elastic features, inclusive of the shear modulus (G) and the Young's modulus (E). Linear-response density functional perturbation theory (DFPT), as executed in the QE framework [43] was employed in calculating the vibrational properties of the crystal lattice. Lattice parameter optimization in VRhZ (Z = Ge, Si and Sn) half Heusler systems is crucial in determining key ground state properties. In our work, this is calculated by performing a Birch-Murnaghan third-order equation of state (EOS) [44] fit on self-consistent field total energies plotted against lattice parameter variations. The computationally determined equilibrium lattice constants $a_0 = 5.79$ Å, $a_0 = 5.76$ Å, and $a_0 = 6.09$ Å for VRhGe, VRhSi, and VRhSn, respectively (reported in Fig. 1) were employed consistently in the calculations, considering that the experimentally derived lattice parameters of VRhGe, VRhSi,

and VRhSn compounds are not available to date. Tobola and Pierre [45] experimentally worked on 15 different half Heusler alloys and obtained lattice parameters within the range of $a_0 = 5.78$ Å and $a_0 = 6.24$ Å. Solola *et al.* [46] used the GGA-PBEsol and realized a lattice constant of $a_0 = 5.73$ Å for the VRhGe half-Heusler compound. A DFT study was performed by Gautier *et al.* [1] on 23 half Heusler materials and they obtained lattice constants ranging from 5.941 Å to 6.557 Å. Our computed lattice parameters agree well with the reported values of half Heusler materials both experimentally and computationally, confirming the validity of our results. Ground-state energy evaluation at the computed lattice constants of VRhZ (Z = Ge, Si, and Sn) is carried out to determine the most stable structure. The γ state of VRhZ (Z = Ge, Si, and Sn) is most stable among the investigated structures.

III. RESULTS AND DISCUSSION

A. Structural properties

Experimentalists have worked on structural properties of these compounds extensively. Gautier *et al.* [1] used powder x-ray diffraction and transmission electron microscopy (TEM) techniques on VRhSi and VRhGe and realized the lattice constant values as $a = 6.162$ Å and $a = 6.149$ Å, respectively. They also used energy-dispersive x-ray spectroscopy to confirm the chemical composition of the materials. Gzyl *et al.* [49] employed the powder x-ray diffraction technique on VRhSn and obtained a lattice constant of $a = 6.192$ Å. While a lot has been done on structural properties, there is no theoretical or experimental work reported beyond structure. In this study, we report the electronic structure, lattice vibration, thermal, and thermoelectric properties of VRhZ (Z = Si, Ge, Sn) using DFT. These properties provide guidance to future experiments. Total energies at stable states of γ , β as well as α structures of VRhZ (Z = Ge, Si, and Sn) were computed to determine the most energetically favorable configuration among the investigated structures. Total energy values for the investigated configurations are reported in Table I. The gamma phase is the most stable. In half Heusler compounds, the heaviest transition metal will try to occupy the (0.25, 0.25, 0.25) position. The investigated compounds, VRhZ (Z = Ge, Si and Sn) have Vanadium and Rhodium as transition metals, with Rh being heavier than V. Therefore, in this study, the gamma structure of VRhZ (Z = Ge, Si, and Sn) is studied, where Rh occupies the (0.25, 0.25, 0.25) position. In the gamma structure, the V, Rh, and Z atoms are located at the crystallographic Wyckoff sites $4a$, $4b$, and $4c$, with fractional coordinates (0,0,0), (0.5,0.5,0.5), and (0.25,0.25,0.25), respectively. The bulk modulus B_0 determines the hardness of a crystal structure, and the first derivative of the bulk modulus with respect to pressure B'_0 determines the thermo-plastic characteristics in the crystal structure [50]. A large value of bulk modulus B_0 corresponds to high crystal structure rigidity as reported in this work. Bilinska and Winiarski [51] reported such high values of B_0 in TiPdGe = 132.41 GPa and TiPdPb = 104.14 GPa HH materials. Unfortunately, there are no available experimental results in the existing literature to

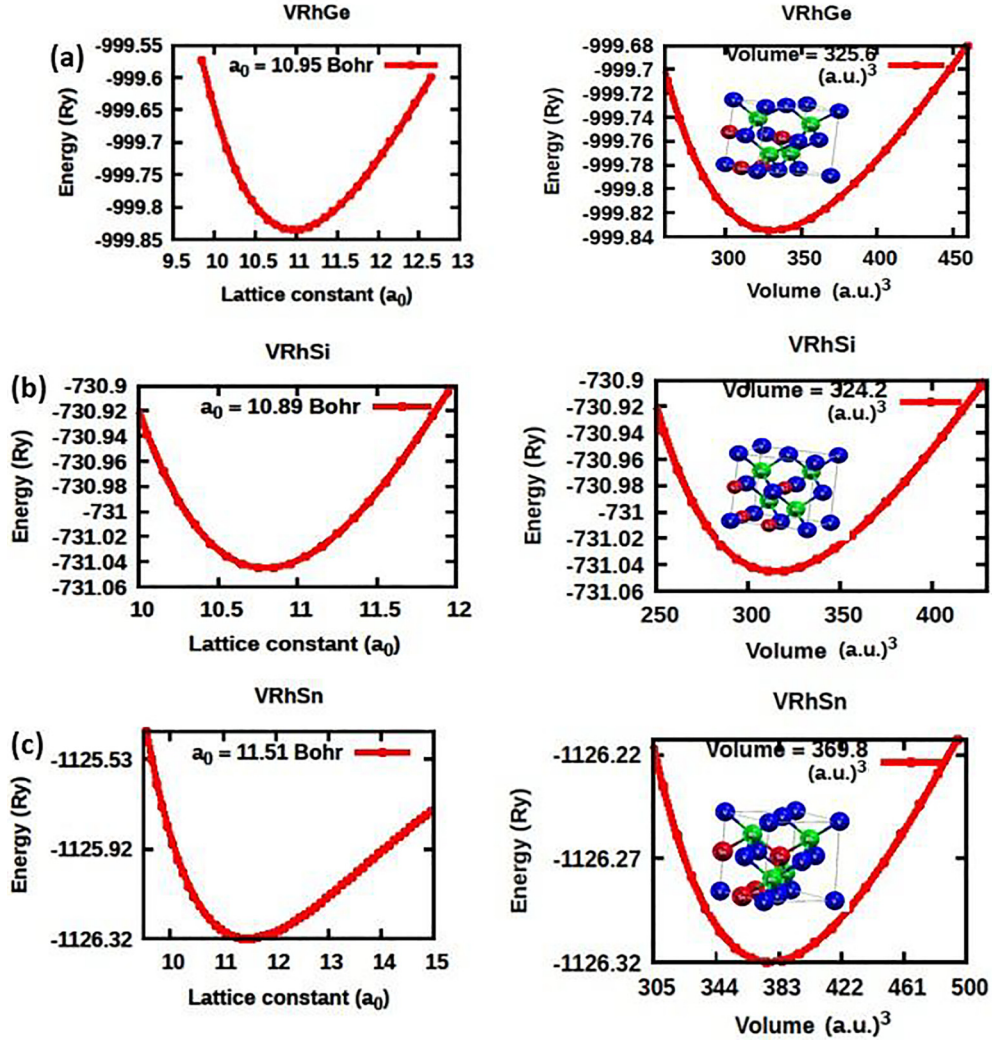


FIG. 1. Total energy vs lattice constant (left) and total energy vs volume (right) of (a) VRhGe, (b) VRhSi, (c) VRhSn. The blue, green, and red atoms represent V, Rh, and main group elements (Ge, Si, and Sn), respectively.

compare with the present bulk modulus and its first pressure derivative results.

1. Structural stability

Formation energies. With the aim of investigating stability of the material formulations, the energetics of compound formation are computed. The formation energy (E_f) represents the difference between the compound's total ground-state energy and the ground-state energies of its constituent elements in their reference bulk phases. Formation energies are used to determine thermodynamical stability and experimental synthesizability of the compound. It is estimated by using Eq. (4) [52],

$$E_{\text{form}} = E(X_m Y_n Z_t) - m \frac{E(X_a)}{a} - n \frac{E(Y_b)}{b} - t \frac{E(Z_c)}{c}, \quad (4)$$

where $E(X_m Y_n Z_t)$ represents the ground-state energy while $E(X_a)$, $E(Y_b)$ and $E(Z_c)$ are the bulk-phase total energies of X , Y , and Z with a , b , and c number of atoms for each. Our results indicate that the values of the formation energy realized in this study are negative, that is, $E_f^{\text{VRhGe}} = -1.0916$ Ry,

$E_f^{\text{VRhSi}} = -1.16389$ Ry and $E_f^{\text{VRhSn}} = -0.9901$ Ry ensuring that the materials VRhGe, VRhSi, and VRhSn can be synthesized experimentally [53].

Cohesive energy (E_c). The structural stability of VRhZ ($Z = \text{Ge, Si, and Sn}$) alloys was anticipated by computing the binding energy (E_c). E_c denotes variation between crystal energy $E_{\text{tot}}^{\text{VRhZ}}$ and the sum of the energies of the constituent noninteracting atoms. This binding energy establishes stability of the alloys with respect to total energy, and this stability is obtained from Ref. [54]. These enthalpies are achieved by employing Eqs. (5)–(7):

$$E_{\text{Coh}}^{\text{VRhGe}} = E_{\text{tot}}^{\text{VRhGe}} - (E_{\text{V}}^{\text{atom}} + E_{\text{Rh}}^{\text{atom}} + E_{\text{Ge}}^{\text{atom}}), \quad (5)$$

$$E_{\text{Coh}}^{\text{VRhSi}} = E_{\text{tot}}^{\text{VRhSi}} - (E_{\text{V}}^{\text{atom}} + E_{\text{Rh}}^{\text{atom}} + E_{\text{Si}}^{\text{atom}}), \quad (6)$$

$$E_{\text{Coh}}^{\text{VRhSn}} = E_{\text{tot}}^{\text{VRhSn}} - (E_{\text{V}}^{\text{atom}} + E_{\text{Rh}}^{\text{atom}} + E_{\text{Sn}}^{\text{atom}}). \quad (7)$$

The cohesive energies obtained in this study are -1.2019 Ry, -1.1382 Ry, and -1.1064 Ry for VRhGe, VRhSi, and VRhSn compounds, respectively. To obtain these results, a

TABLE I. Structures, ground state energy, equilibrium lattice constants (a_0), unit cell volume (V_0), bulk modulus (B_0), rate of change of bulk modulus with pressure (B'_0), and band gap energy of VRhZ ($Z = \text{Ge, Si, and Sn}$).

		VRhGe	VRhSi	VRhSn
Wyckoff positions	γ	V(4a)Rh(4c)Ge(4b)	V(4a)Rh(4c)Si(4b)	V(4a)Rh(4c)Sn(4b)
	β	V(4b)Rh(4a)Ge(4c)	V(4b)Rh(4a)Si(4c)	V(4b)Rh(4a)Sn(4c)
	α	V(4c)Rh(4b)Ge(4a)	V(4c)Rh(4b)Si(4a)	V(4c)Rh(4b)Sn(4c)
E_{total} (Ry)	γ	−999.73527629	−730.90411455	−1126.29566341
	β	−940.68223672	−671.87964566	−1067.42532183
	α	−960.51378624	−691.86532411	−1087.94583526
Gamma phase of VRhZ ($Z = \text{Ge, Si, and Sn}$)				
a_0 (Å)	This work	5.79	5.76	6.09
	Other DFT	5.73 [48]	5.71 [46]	6.06 [47]
	Experiment	6.149 ⁵¹	6.162 [1]	6.192 [49]
V_0 (a.u.) ³		325.6	324.2	349.8
B_0 (GPa)	This work	165.00	186.52	185.53
	Other DFT	172.5 [47]		149.6 [47]
B'_0	This work	4.82	5.05	4.98
	Other DFT	4.66 [48]		
E_g (eV)	This work	0.50	0.32	0.42
	Other DFT	0.34 [48]	0.59 [46]	0.391
Nature of band gap		Indirect	Indirect	Indirect

large cell was used to avoid the atom-atom interaction. With these negative cohesive energies, the chemical stability of the investigated compounds is guaranteed.

2. Total energy and phase stability

In determining stability of investigated phases from an energetic perspective, we computed the stable-state total energy of the half-Heusler materials under consideration. Given that the lowest energy phase is deemed the most stable, we determine the energetically favored phase amongst VRhGe, VRhSi, and VRhSn. In this study, this is done by fitting the total energies of the primitive unit cells at equilibrium with respect to lattice constants into third-order Birch-Murnaghan EOS. The data is illustrated in Fig. 1. The energy values are −999.73527629 Ry at a lattice constant of 5.79 Å, −730.90411455 Ry at a lattice constant of 5.76 Å and −1126.29566341 at a lattice constant of 6.09 Å for VRhGe, VRhSi, and VRhSn, respectively. For each structure, the equilibrium unit cell volume, in response to the stable state energy at the equilibrium lattice constant, is applied to Birch-Murnaghan's EOS to derive the bulk modulus and its pressure dependence and Table I provides a summary of the findings. These results are consistent with other computational findings from half Heusler compounds as reported in Table I. The gamma phase of VRhSn is considered the most energetically favorable among the investigated materials, given that it has the lowest energy. The atomic configurations of the stable phases of VRhZ ($Z = \text{Ge, Si, and Sn}$) generated by Xcrysden [55] are depicted in Fig. 1, which displays the $C1_b$ structures [56]. In these structures, the blue atoms represent vanadium, green atoms display rhodium, and red represents the main group elements, Ge, Si, and Sn.

B. Lattice dynamical characteristics

Phonon energy spectrum and phonon density of states (PDOS) for VRhZ ($Z = \text{Ge, Si, Sn}$) materials in the $C1_b$ phase, along the $K-\Gamma-L-U-\Gamma-W-X-\Gamma$ points of high symmetry, are depicted in Fig. 2. These phonon frequencies are computed by use of the PHONOPY code [57] using the interatomic force constants obtained from QE, and uses the linear response approach as described by DFPT [58]. PHONOPY code is dependent on real space supercells and computes phonon dispersion from the dynamical matrix. The phonon frequencies in Fig. 2 were calculated in high symmetry directions using a $2 \times 2 \times 2$ supercell approach. The primitive unit cell of the investigated materials consists of three atoms, therefore nine lattice vibrational eigenmodes are observed at every wave vector (q point) in the Brillouin zone. Two distinct branches appear in the dispersion curve, that is, the optical and acoustic modes. In the acoustic phonon spectrum, the transverse modes (TA) are two while the longitudinal mode (LA) is one. In the case of optical modes, the longitudinal optical phonon modes (LO) are three while the transverse optical phonon modes (TO) are also three [59]. Dynamical stability of a material, within the harmonic approximation, requires real and positive phonon frequencies, otherwise the perturbative approach breaks down [60]. Figure 2 does not report any imaginary frequency in all dispersion curves, which implies investigated materials exhibit dynamical stability in the $C1_b$ structure. A fascinating property realized from the phonon band structures is that the high-frequency optical modes of VRhSn exhibit coupling. This impact is less noticeable in VRhGe and undetected in VRhSi, where the three high energy optical phonon modes are energetically well separated from the three lower-energy optical phonon modes, that is, no coupling. This behavior indicates the inverse relationship between

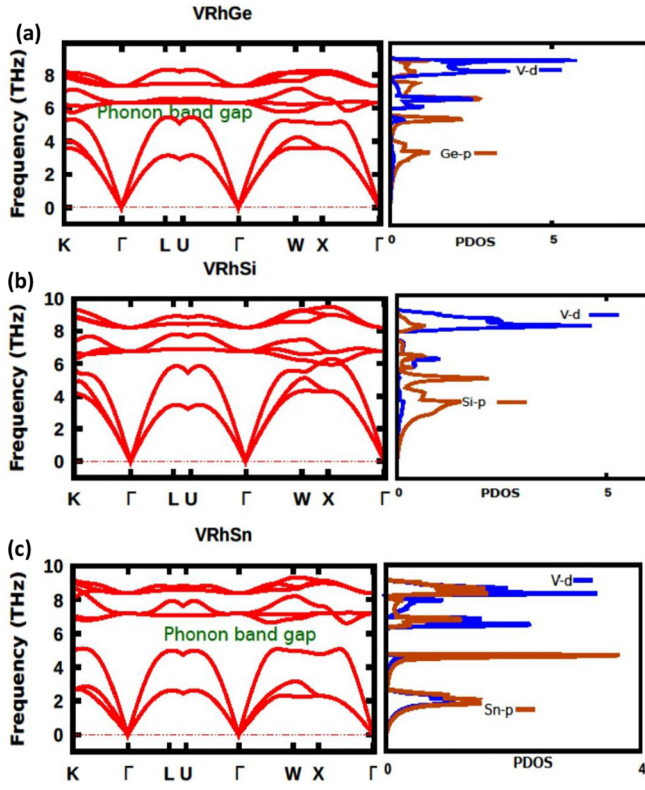


FIG. 2. Phonon dispersion curves and phonon density of states for (a) VRhGe, (b) VRhSi, (c) VRhSn.

atomic mass and vibrational amplitude in phonon spectra. Given that, in the lattice vibration spectrum, the atoms' vibrational amplitudes exhibit an inverse relationship with their atomic masses. Mass of the tin (Sn) atom is greater than that of germanium (Ge) which in turn is greater than the mass of silicon (Si) atom. The low Si atomic mass causes a distinct energy separation between the two sets of optical phonon modes. This suggests that the Si atom contributes most significantly to the vibrational amplitude of VRhSi owing to its lower mass. The energy gap between the acoustic and optical phonon branches is referred to as a phonon band gap and the dispersion relation does not exist inside this gap [61]. Figure 2(b) presents the overlapping of optical and acoustic modes and nonexistence of a phonon band gap as depicted in VRhSi. VRhGe illustrated a narrow phononic band gap in Fig. 2(a) and VRhSn displayed a significant phonon band gap in Fig. 2(c). In Fig. 2, the acoustic phonon modes exhibit double degeneracy along the $X-\Gamma$ path. In ionic materials, extended macroscopic electric fields emerge. Electric fields are generated due to the long-wavelength longitudinal optical vibrations and are responsible for the longitudinal-transverse optical mode (LO and TO) splitting. This splitting refers to the frequency difference between LO and TO phonon modes at the center of the Brillouin zone (at Γ). In fact, at Γ point of the BZ, the Born effective charges generate macroscopic electric fields that decouple the LO mode from its degenerate TO counterpart. The reported phonon mode splitting at the Brillouin zone center (Γ) is a critical parameter for evaluating ionicity within the investigated materials [62]. There isn't any LO-TO splitting, demonstrating weak ionic contribution

of the investigated half Heusler materials. A linear phonon dispersion is observed in the acoustic branches approaching the Γ point. The right-hand sides of Fig. 2 depict the PDOS. For PDOS plots, the contribution from d and p orbitals is certainly dominant.

C. Thermodynamical properties

These properties provide important information on the efficiency, stability, and thermal regulation of the investigated materials over a wide range of temperature. The properties investigated here are free energy, entropy, and heat capacity, as shown in Fig. 3. For all the materials investigated, heat capacity remained constant at approximately 500 K. At low temperatures, the free energy (F) is dominated by the internal energy (U), signifying the stability and ordered phase transformations of the materials. With increase in temperature, the entropy term ($-TS$) becomes more prominent, resulting in a reduced free energy. Among the investigated materials, VRhSi exhibits the highest decrease which means VRhSi encounters the highest entropy-induced instability at elevated temperatures. This property is important while identifying thermoelectric materials which must sustain significant thermal gradients. The free energy curves as well as the entropy plots present the expected trend at a considerable temperature range. The Debye temperature (θ_D) is an important thermophysical factors that describe all phonon modes excitation temperature. Because of these property θ_D relates closely to thermophysical properties such as; heat capacity, entropy and free energy. θ_D is evaluated by use of the average sound wave velocities as described in Eqs. (8)–(10).

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m, \quad (8)$$

where v_m is the directional averaged phonon velocity, k_B stands for Boltzmann's constant, N_A indicates the Avogadro's number, ρ represents density, M means molecular weight, n signifies number of atoms present in a single molecule, and h is the Planck's constant,

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}}, \quad (9)$$

where v_l stands for longitudinal sound velocity while v_t implies transverse sound velocity. Both v_t and v_l are derived from the bulk and shear moduli by the use of Navier's equation:

$$v_t = \left(\frac{B + \frac{4G}{3}}{\rho} \right)^{\frac{1}{2}}, \quad (10)$$

$$v_l = \left(\frac{G}{\rho} \right)^{\frac{1}{2}}. \quad (11)$$

High Debye temperature means high thermal conductivity while lowest thermal conductivity ($k_{\min}$) is proportional to v_m , that is,

$$k_{\min} = k_B v_m \frac{n N_A \rho}{M}. \quad (12)$$

The entropy (S) shown in Fig. 3(a) measures the disorder in the systems. Inline with the third law of thermodynamics,

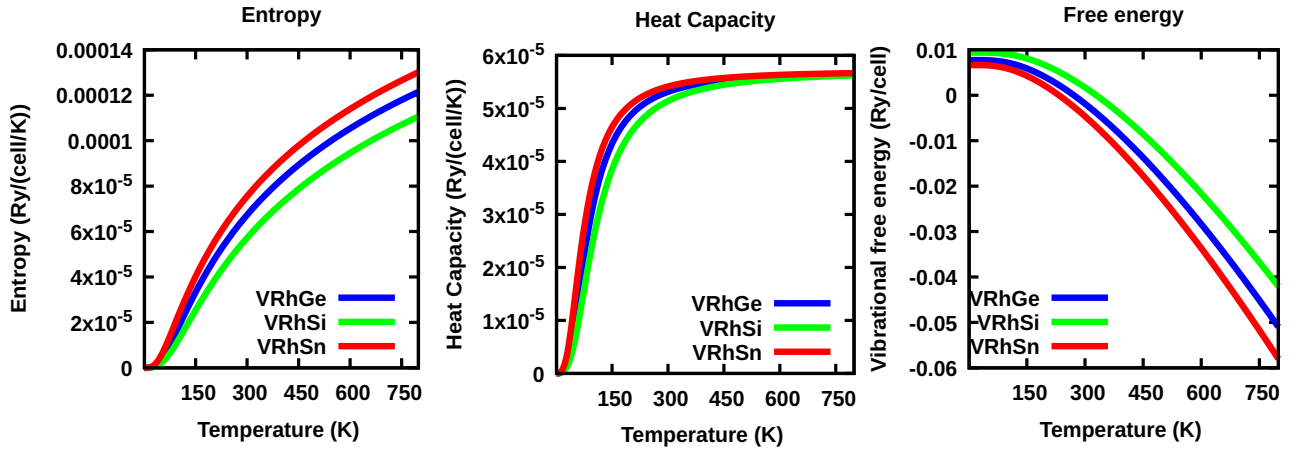


FIG. 3. Thermal properties of VRhZ ($Z = \text{Ge, Si, Sn}$): (a) Entropy as a function of temperature. (b) Heat capacity as a function of temperature. (c) Free energy as a function of temperature.

Fig. 3(a) presents zero entropy at absolute zero, given that the materials are at their ordered ground state. As the temperature increased, S also increased due to excitation of the phonons. Among the studied materials, VRhSi has the highest entropy within the studied temperature range, followed by VRhGe and VRhSn. This suggests intensified vibrational modes and escalated thermal instability in VRhSi. The intensified disorder enhances thermal stability, in favor of materials subjected to periodic temperature patterns in thermoelectric components. Figure 3(b) presents heat capacity, describing the mechanisms by which these compounds store and release thermal energy. Considering phonon vibration in the solid lattice, at constant volume and low temperatures, the heat capacity is proportional to T^3 obeying the Debye model. At high temperature, this T^3 dependence raises swiftly due to phonon stimulation. As shown in Fig. 3(b), at average temperatures (100 K to 500 K), heat capacity continues rising, suggesting thermal stimulation of supplementary vibrational modes. Figure 3(b) again tells us that, above 500 K, heat capacity approaches the Dulong–Petit limit, which is a sign of saturation in the accessible vibrational modes. The trend of the heat capacity values, that is, $\text{VRhSi} > \text{VRhGe} > \text{VRhSn}$, relate to the trend of entropy values and they predict that, among the investigated materials, VRhSi is most effective in absorption and dissipation of thermal energy, and therefore a good candidate for thermoelectrics.

1. High-temperature stability

High-temperature stability of VRhSi, VRhSn, and VRhGe was examined by use of AIMD simulations [63] as implemented in QE code, where, a $2 \times 2 \times 2$ supercell was utilized. The AIMD simulations were carried out under canonical ensemble (NVT) conditions, performing time integration of the equations of motion at discrete time steps of 1 fs. The system was maintained in thermal equilibrium at 900 K by use of a Nosé thermostat, which allowed effective equilibration [64] of energy fluctuations as a function of time. The investigated alloys reached energy equilibrium over one picosecond (ps), as shown in Fig. 4. Similar energy fluctuations were realized

by Mahakal *et al.* [65] where the investigated half Heusler alloy gained stability over 8 ps. The slight deviation in the energy fluctuation amplitudes is attributed to the difference in masses of the respective half Heusler alloys. In Fig. 4(a), for VRhSi and VRhGe, there was minimal total energy fluctuation around the mean energy value throughout the simulation. For VRhSn, there was significant total energy fluctuation upto 0.3 ps, followed by minimal fluctuations around the mean energy value upto 0.65 ps, then stability at a constant energy value was achieved. During AIMD, the structure may collapse, therefore, visualization of the atomic positions was carried out after the AIMD simulations. Figures 4(b)–4(d) show that even at high temperatures of 900 K and after 1 ps, there was negligible distortions. Similar crystal structures were realized by Uto *et al.* [66] These results demonstrate the thermal stability for the compounds VRhSi, VRhSn, and VRhGe at 900 K.

D. Mechanical properties

The materials VRhGe, VRhSi, and VRhSn are described by cubic configurations where the independent elastic constants are C_{11} , C_{12} , and C_{44} . As presented in Table II, for the stability of the lattice, the Born's stability criterion is satisfied. The calculations are such that G_R represents Reuss shear modulus and G_V represents the Voigt shear modulus. In the Voigt-Reuss-Hill relation for the cubic configurations, G denotes the shear modulus and B the bulk modulus of VRhZ ($Z = \text{Ge, Si, Sn}$). The approximations are computed as follows:

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (13)$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}), \quad (14)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}, \quad (15)$$

$$G = \frac{1}{2}(G_V + G_R). \quad (16)$$

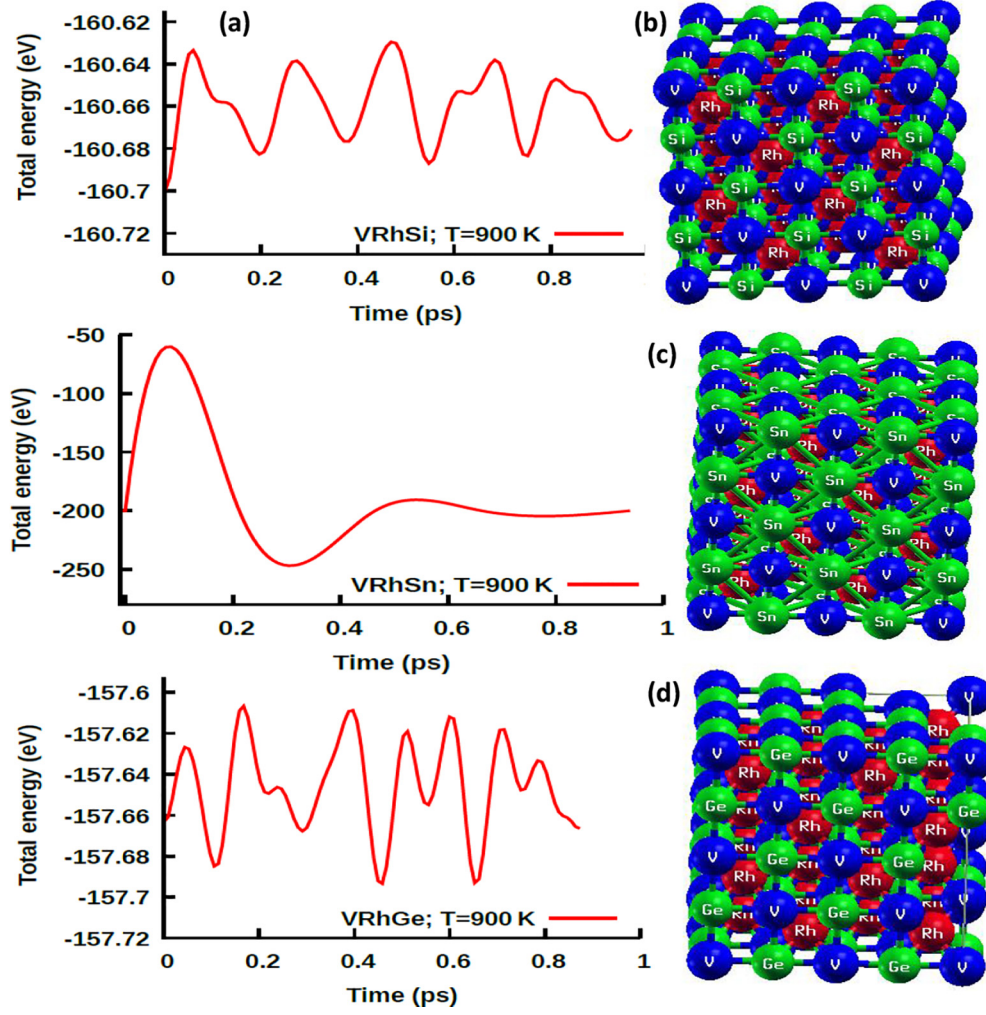


FIG. 4. (a) Energy fluctuations as a function of time from the AIMD calculations of VRhZ ($Z = \text{Si, Sn, Ge}$) at 900 K. Final stable supercells at 900 K for (b) VRhSi, (c) VRhSn, (d) VRhGe.

Mechanical stability for a cubic structure is at pressure (P) = 0 GPa defined by the criteria [67]

$$C_{11} - C_{12} > 0, \quad (17)$$

$$C_{11} - C_{12} > 0, \quad (18)$$

$$C_{44} > 0. \quad (19)$$

In this work, Pugh's ratio (B/G) was utilized in determining the ductility or brittle classification of the materials. For

$B/G > 1.75$, the material is ductile, while for $B/G < 1.75$ the material is brittle [68]. In terms of Poisson's ratio (ν), for $\nu > 0.26$.

the material displays mechanical ductility and when $\nu < 0.26$, the material displays a brittle mechanical response [69]. Table II confirms that all the investigated materials are ductile. Considering the Cauchy pressure, ($C_{12} - C_{44}$), where positive values of Cauchy pressure are indicative of metallic bonding, reflecting ductile behavior, whereas a negative Cauchy pressure implies strong resistance to angular deformation.

TABLE II. Bulk modulus (B) in GPa, elastic constants (C_{11} , C_{12} , C_{44}), Young modulus (E), Cauchy pressure ($C_{12} - C_{44}$), shear modulus (G) in GPa, Pugh's ratio (B/G), Debye temperature θ_D (K), and Poisson's ratio (ν) for VRhZ ($Z = \text{Ge, Si, Sn}$).

	C_{11}	C_{12}	C_{44}	$C_{12} - C_{44}$	E	B	G	B/G	θ_D	ν	Reference
VRhGe	219.57	137.72	74.78	62.94	157.43	165.00 172.5 [46]	58.71	2.81	364.24	0.3407	This work Other DFT
VRhSi	249.89	154.83	92.77	62.06	188.79	186.52	70.93	2.63	442.50 313.41 [74]	0.3309	This work Other DFT
VRhSn	252.3	152.14	82.62	69.52	156.34	185.53 149.6 [46]	67.80	2.74 3.22 [73]	360.95	0.3275 0.35 [73]	This work Other DFT

TABLE III. Kleinman parameter (ξ), machinability index (μ_M), and Vickers hardness (H_V) in GPa for VRhZ ($Z = \text{Ge, Si, Sn}$).

	μ_M	H_V	ξ
VRhGe	2.2064	6.2343	0.7290
VRhSi	2.0106	7.9957	0.7230
VRhSn	2.2456	6.7718	0.7097

tion, characteristic of covalently bonded materials [70]. The presence of positive Cauchy pressure indicates that all the investigated materials are ductile, as presented in Table II. The shaping of a material in the industry, that is, machinability, is crucial because it addresses the cost effectiveness and high quality of the product. The machinability index value, given by [71]

$$\mu_M = B/C_{44}, \quad (20)$$

determines the lubricating ability and plasticity of the material. A material of high machinability has perfect lubricating ability and a comparatively low friction. Table III presents the machinability indices of the investigated compounds. Sattar *et al.* [72] reported on the machinability index of other vanadium-based half Heusler materials as VFeTe (1.39) and VCoTe (1.62). In this study, VRhSn has the highest machinability index, which is at 2.2456, whereas VRhSi is lowest in machinability, with an index value of 2.0106. The potentiality of materials to resist deformation, that is, estimation of the hardness of the investigated materials (Vickers hardness) is still a challenge. Experimentally, El-Khouly *et al.* [73] investigated the Vickers hardness (H_V) of vanadium-based materials and realized a value of 6.87 in FeVSb-based half Heusler alloys. In DFT, Vickers hardness is investigated by the use of Young's modulus as well as Poisson's ratio [70],

$$H_V = \frac{(1 - 2\nu)E}{1 + \nu}, \quad (21)$$

where ν and E indicate the Poisson's ratio and the Young's modulus, respectively. As shown in Table III, the materials' hardness ranges from 6.2343 to 7.9957 GPa, where VRhSi has the highest hardness at 7.9957 GPa. Poisson's ratio ν also illustrates the bonding nature of material by the relation

$$\nu = \frac{3B - E}{6B}. \quad (22)$$

The Poisson's ratio for a standard covalently bound material is less than 0.25. For a standard ionic material, it is almost 0.25 or greater. The obtained values of ν are 0.34072, 0.3309, and 0.3275 for VRhGe, VRhSi, and VRhSn, respectively, suggesting that ionic bonding is dominant. Klein introduced a significant parameter in materials, which is used to determine the internal strain. This Kleinman parameter (ξ) is computed from elastic constants. In solid materials, this parameter describes the bending and stretching of a bond. Shortened bond bending in a material shows $\xi = 0$, while escalated bond stretching suggests $\xi = 1$. The Kleinman parameter is established by the relation

$$\xi = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}}. \quad (23)$$

In this work, the realized Kleinman parameters are 0.729, 0.723, and 0.7097 for VRhGe, VRhSi, and VRhSn, respectively. Therefore, VRhGe exhibits slightly enhanced resistance to bond bending compared to VRhSi and VRhSn. Brito *et al.* [74] used DFT on vanadium-based half Heusler alloys and realized the Kleinman parameters of VPtSi, VPtGe, and VPtSn to be 1.163, 1.174, and 1.312, respectively. Sattar *et al.* [72] worked on vanadium-based half Heuslers and realized the Kleinman parameters of 0.6664 and 0.9456 for VCrTe and VCoTe, respectively.

The anisotropic behavior of VRhZ ($Z = \text{Ge, Si, Sn}$) is discussed in the Supplemental Material [75].

E. Electronic properties

The electronic band structures of VRhZ ($Z = \text{Ge, Si, and Sn}$) obtained with and without GW are given in Fig. 5. The electronic structures reflect the expected behavior of half Heusler materials with an 18-electron configuration. Energy band gaps of the three investigated compounds, VRhGe, VRhSi, and VRhSn computed with GW, occurs at $U-W$ points of high symmetry. The three half Heusler compounds computed without GW displayed metallic features. The energy gap values are tabulated in Table I and evaluated against existing literature findings. Yang *et al.* [76] used GGA-PBE functionals on VRhSn and obtained a band gap of 0.391 eV. The band gap values are in strong agreement with those computed using the GGA-PBE approximation. The existence of energy gaps in the investigated structures indicates that VRhZ ($Z = \text{Ge, Si, and Sn}$) are semiconducting half Heusler systems. The valence bands become degenerate at the X and Y points, giving rise to both flat and parabolic band characteristics. Flattened bands enhance the Seebeck coefficient's size, whereas the parabola bands are in favor of electrical conductivity, implying that these materials are viable thermoelectric candidates. The computed energy gap values and their characteristics, as determined from electronic structure calculations, classify VRhZ ($Z = \text{Ge, Si, and Sn}$) semi-Heusler materials as narrow-gap indirect semiconductors. The energy band gaps determined here are in good agreement with existing literature on comparable half-Heusler systems.

F. Transport properties

The ability of a material to efficiently convert heat to thermoelectric power is referred to as ZT and is determined by Eq. (2). To approximate ZT , for any thermoelectric material, we have to solve Eqs. (26)–(28) within a certain temperature range. Electronic structure calculations act as inputs in determining all transport coefficients as implemented in BOLTZTRAP code [34]. The system information is derived from the conductivity tensor and the projected energy distribution tensor, presented as

$$\sigma_{\alpha\beta}(T, \mu) = \frac{e^2}{N} \sum_{i,k} \tau_{i,k} V_{\alpha}(i, k) V_{\beta}(i, k) \left(\frac{\delta(\mathcal{E} - \mathcal{E}_{i,k})}{d\mathcal{E}} \right), \quad (24)$$

where α and β represent the Cartesian tensors. N depicts the k -point mesh density. i is the band index, k stands for the

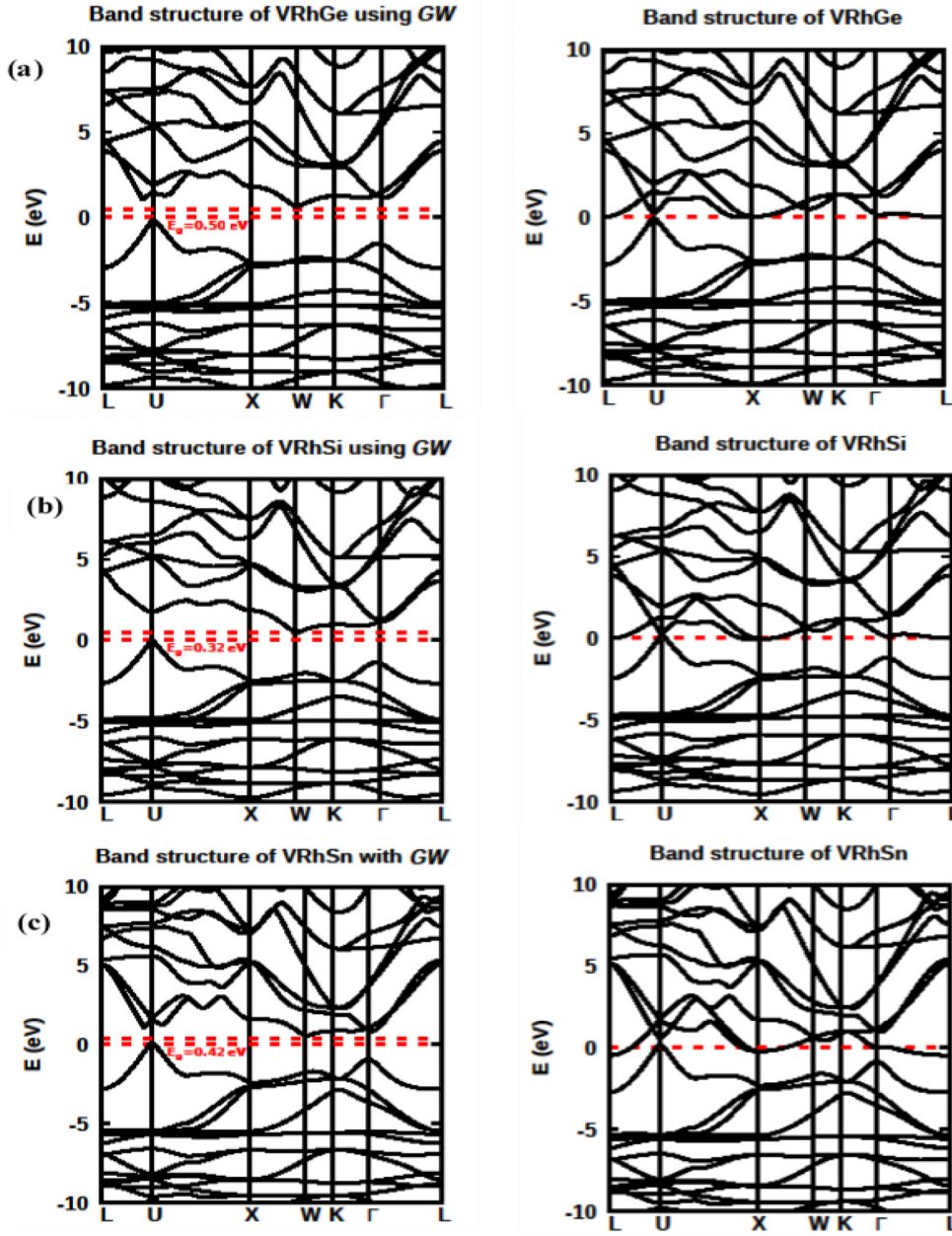


FIG. 5. Electronic band structures of (a) VRhGe (b) VRhSi, and (c) VRhSn with GW (left) and without GW (right). The Fermi energy is set to zero.

wave vector, and $V_\alpha(i, k)$ illustrates the group velocity, which is determined from electronic band structure calculations by use of

$$V_\alpha(i, k) = \frac{1}{\hbar} \frac{\partial \mathcal{E}_{i,k}}{\partial k_\alpha}, \quad (25)$$

where $\hbar$ is the Dirac constant.

The relaxation time ($\tau_{i,k}$) shown in Eq. (24) is dependent on wave vector and it is difficult to obtain it using *ab initio* calculations—therefore, the use of constant relaxation time approximation [77] in solving Eq. (24). Variation of transport tensors with chemical potential and temperature can be calculated using the conductivity tensor as shown

in Eqs. (26)–(28):

$$\sigma_{\alpha\beta}(T, \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\mathcal{E}) \left\{ -\frac{\partial f_\mu(T, \mathcal{E})}{\partial \mathcal{E}} \right\} d\mathcal{E}, \quad (26)$$

$$S_{\alpha\beta}(T, \mu) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T, \mu)} \int \sigma_{\alpha\beta}(\mathcal{E})(\mathcal{E} - \mu) \times \left\{ -\frac{\partial f_\mu(T, \mathcal{E})}{\partial \mathcal{E}} \right\} d\mathcal{E}, \quad (27)$$

$$k_{e(\alpha\beta)}(T, \mu) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta}(\mathcal{E})(\mathcal{E} - \mu)^2 \left\{ -\frac{\partial f_\mu(T, \mathcal{E})}{\partial \mathcal{E}} \right\} d\mathcal{E}, \quad (28)$$

where k_e is the electronic component of the thermal conductivity, f_μ denotes Fermi–Dirac distribution function, Ω indicates volume of the unit cell, and e stands for the electronic charge as effected in the BOLTZTRAP code [34].

1. Carrier relaxation time (τ)

In this study, the obtained electronic band structure calculations and the effective masses of electrons and holes were determined at the valence band maximum and conduction band minimum. Using the obtained anisotropic elastic constants, effective masses and deformation potentials, the thermally dependent carrier relaxation time (τ) was computed by use of the deformation potential theory [37]. In this theory, the effective mass m^* technique, adapted for use in gradual shifting of energy bands which results from deformation of the crystal lattice, is utilized in estimation of correlation between thermal electrons and acoustic phonons. Charge carrier mobilities are therefore associated with shifting of the conduction band and the fully occupied valence band. That is,

$$\tau = \left(\frac{2}{m_{eh}^* K_B T} \right)^{3/2} \frac{\pi^{1/2} \hbar^4 C_{ii}}{3(D_p^{v,b})^2}, \quad (29)$$

where $D_p^{v,b}$ is the band edge deformation potential constant, m_{eh}^* denotes effective mass of hole and electron, and C_{ii} indicates anisotropic elastic constants. Mathematically,

$$D_p^{v,b} = \frac{\delta E_{\text{edge}}}{\delta \left(\frac{\Delta a}{a_0} \right)}. \quad (30)$$

$\Delta a = a - a_0$, given that a_0 is the optimized lattice constant, while a is the lattice constant under strain. δE_{edge} is computed from the minimum conduction band shift in energy and energy of the maximum valence band as a result of the applied strain. The anisotropic elastic constants are formulated as

$$C_{ii} = C_{11} \text{ for (100)}, \quad (31)$$

$$C_{ii} = \frac{1}{2} (C_{11} + C_{12} + 2C_{44}) \text{ for (110)}, \quad (32)$$

$$C_{ii} = \frac{1}{3} (C_{11} + 2C_{12} + 4C_{44}) \text{ for (111)}. \quad (33)$$

Effective mass $m_{(e,h)}^* = \hbar^2 \left[\frac{\partial(E(k))}{\partial(k^2)} \right]^{-1}$ is estimated by carrying out a quadratic approximation of the energy as a function of Brillouin zone sampling points at the minimum of the conduction band for electrons and maximum of valence band for holes. Our evaluated alloys possess significantly high elastic constants, enabling their use in structural stability applications. The applied strain causes the deformation potential constants for both electrons and holes to undergo a sign reversal—this was also reported by Saini *et al.* [78]. Consequently, it resists deformation and is mechanically stable. A comparative analysis of charge carrier effective masses, carrier relaxation time (τ), elastic moduli, and deformation potential values of VRhZ ($Z = \text{Si, Ge, and Sn}$) alloys are reported in this study. We realized that, compared to electrons, holes exhibit substantially higher effective masses, which means holes present lower thermal conductivity than electrons in the investigated alloys. Mahakal *et al.* [65]

TABLE IV. Maximum values of transport coefficients of VRhZ ($Z = \text{Ge, Si, and Sn}$) at 1000 K.

	VRhGe	VRhSi	VRhSn
ZT with GW	0.91	0.99	0.99
Without GW	0.81	0.81	0.82
EFF ($10^{-19} \text{W}^{\frac{5}{3}} \text{ms}^{-\frac{1}{3}} \text{K}^{-2}$) with GW	0.69	0.66	0.79
Without GW	0.41	0.36	0.45
PF ($^{\circ}\text{W}/\text{msK}^2$) with GW	15.63	14.22	15.99
Without GW	13.82	13.05	13.99
σ ($^{\circ}\text{S}/\text{ms}$) with GW	22.5	22.5	26
Without GW	21.91	21.91	25
S (μ^{V}/K) with GW	300.42	500.12	400.25
Without GW	289.4	289.4	290.2
K_e ($10^{-16} \text{W}/\text{mK s}$) with GW	0.42	0.41	0.45
Without GW	0.36	0.38	0.42

worked on ZrCoBi half-Heusler alloy and realized a similar trend.

2. Seebeck coefficient and electrical conductivity

This study focuses on evaluating thermoelectric characteristics of VRhZ ($Z = \text{Ge, Si, and Sn}$), namely, the power factor, electrical conductivity, and Seebeck coefficient. Although τ does not influence the Seebeck coefficient in the context of constant scattering time approximation, the coefficient is still governed by carrier concentration and temperature, and the BoltzTrap output provides electrical conductivity values in the form of σ/τ , that is, conductivity per relaxation time rather than as an absolute value. This implies that the precise determination of electrical conductivity and power factor can only be done when the relaxation time (τ) is specified. This work focuses on the evaluation of electrical conductivity and power factor per relaxation time, as experimental data required to determine τ for the examined half Heusler compounds are currently unavailable. Electrical transport coefficient per relaxation time σ/τ , effective power factor divided by relaxation time PF/τ , and also Seebeck coefficient (S), for VRhZ ($Z = \text{Ge, Si, and Sn}$) half Heusler materials are discussed: The Seebeck coefficient (S) quantifies the entropy transmitted by an electric current per unit charge. There is a strong correlation between the S and the type and concentration of charge carriers within the material. The reliance of the Seebeck coefficient on charge carrier density is presented in Figs. 6 and 7. A consistent decline in the Seebeck coefficient was noted with increasing hole carrier density over the entire temperature range studied. The Seebeck coefficient values obtained over the studied temperature range fall within the optimal range expected for high-performance thermoelectric materials. The optimal transport coefficient values at 1000 K are presented in Table IV. At maximum temperature, which is 1000 K in this case, the Seebeck coefficient values obtained with GW corrections are higher than those without GW , which aligns well with previous studies on the thermoelectric characteristics of half Heusler materials. As reported in Tables IV and V and presented in Figs. 6 and 7, the Seebeck coefficients of the analyzed materials are greater than 200 $\mu\text{V}/\text{K}$. Literature

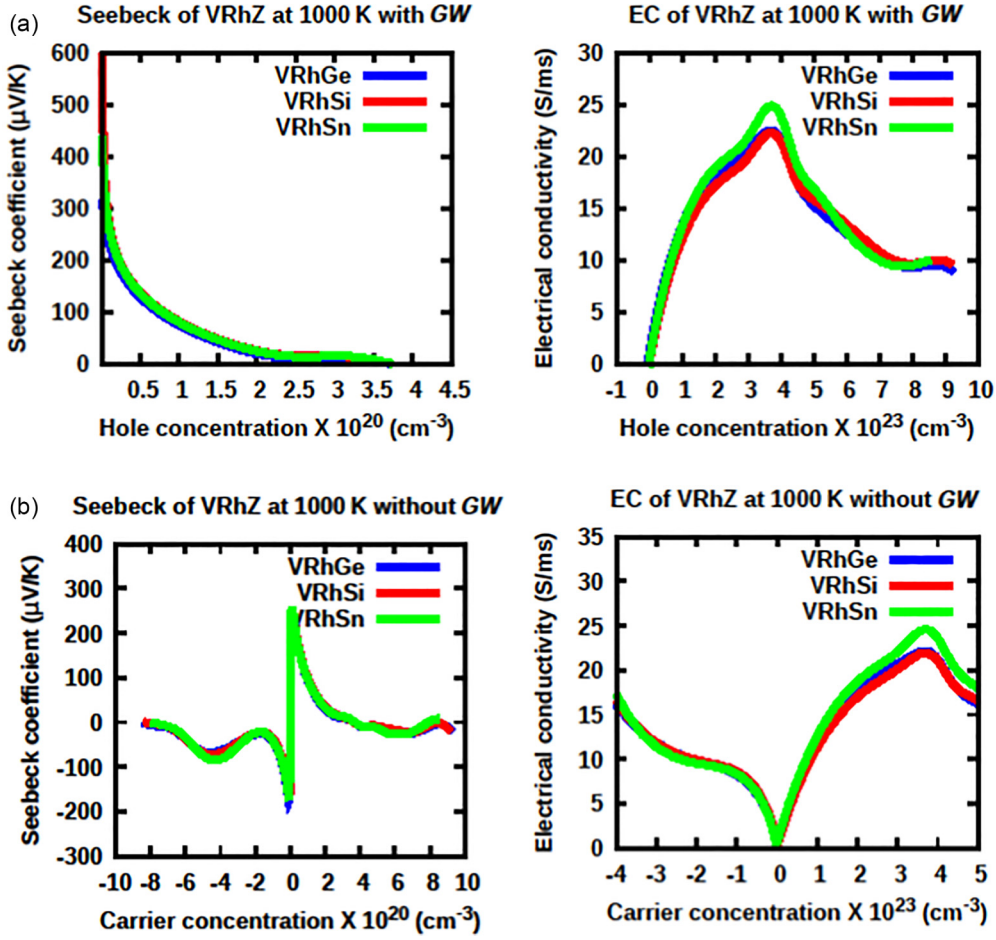


FIG. 6. Seebeck coefficient (left) and electrical conductivity (right) of VRhZ ($Z = \text{Ge}, \text{Si}, \text{and Sn}$) at 1000 K: (a) with GW and (b) without GW.

reports that, from previous research, alloys characterized by a high Seebeck coefficient exceeding 200 $\mu\text{V/K}$, are high-efficiency thermoelectric materials [79]. At 1000 K within the GW framework, VRhSi presents the highest Seebeck coefficient at 500.12 $\mu\text{V/K}$ while the Seebeck coefficients of VRhSn and VRhGe are 400.25 $\mu\text{V/K}$ and 300.42 $\mu\text{V/K}$, respectively.

In Tables IV and V, the Seebeck coefficient at 300 K is lower compared to the Seebeck coefficient at 1000 K, confirming that these are high-temperature thermoelectric materials. In Figs. 6 and 7, the Seebeck coefficient dropped with increase in hole concentration and was zero at approximately $2.0 \times 10^{20} (\text{cm}^{-3})$. Electrical conductivity increased with increase in hole concentration, therefore describing the inverse trend between electrical conductivity and Seebeck coefficient. This relationship is well understood in terms of the Fermi level location, that is, as the Fermi level moves downward into the valence band (or upward into the conduction band), the hole (or electron) carrier concentration increases exponentially. This results in an increase in electrical conductivity and a decrease in Seebeck coefficient. It is worth noting, as the Fermi level shifts out of the energy gap, the Seebeck coefficient diminishes rapidly, approaching zero due to the increased carrier symmetry. In comparison, electrical conductivity is strongly influenced by the energy state density and increases gradually as the Fermi level gets extensively

into the valence band or conduction band. From our calculations, the highest electrical conductivities were realized at 1000 K and at a hole concentration of $3.99 \times 10^{23} \text{cm}^{-3}$ with GW approximation, which is presented in Fig. 6(a)—right. These conductivities are 26.0 S/ms , 22.5 S/ms , and 22.5 S/ms for VRhSn, VRhSi, and VRhGe, as listed. At the same temperature, the values are lower without GW. At 1000 K, as well as at room temperature, electrical conductivity is highest in the p type. At a lower hole concentration of $2.14 \times 10^{23} \text{cm}^{-3}$, and a temperature of 1000 K, Solola *et al.* [46] obtained an electrical conductivity of 3.32 S/ms by use GGA-PBESol functionals on VRhGe material. This shows that this study agrees well with other previous studies. High electrical conductivity reported in the p type suggests a larger IEM compared to the n type.

3. Power factor

Figure 8(a) reports the power factor of VRhSn as the highest at 15.99 W/msK^2 (with GW) at a hole concentration of $0.98 \times 10^{21} \text{cm}^{-3}$ at 1000 K. At the same temperature and the same hole concentration, without GW [Fig. 8(b)], VRhSn gives a lower value of 13.99 W/msK^2 power factor. The power factor results in this study have been presented without lattice thermal conductivity.

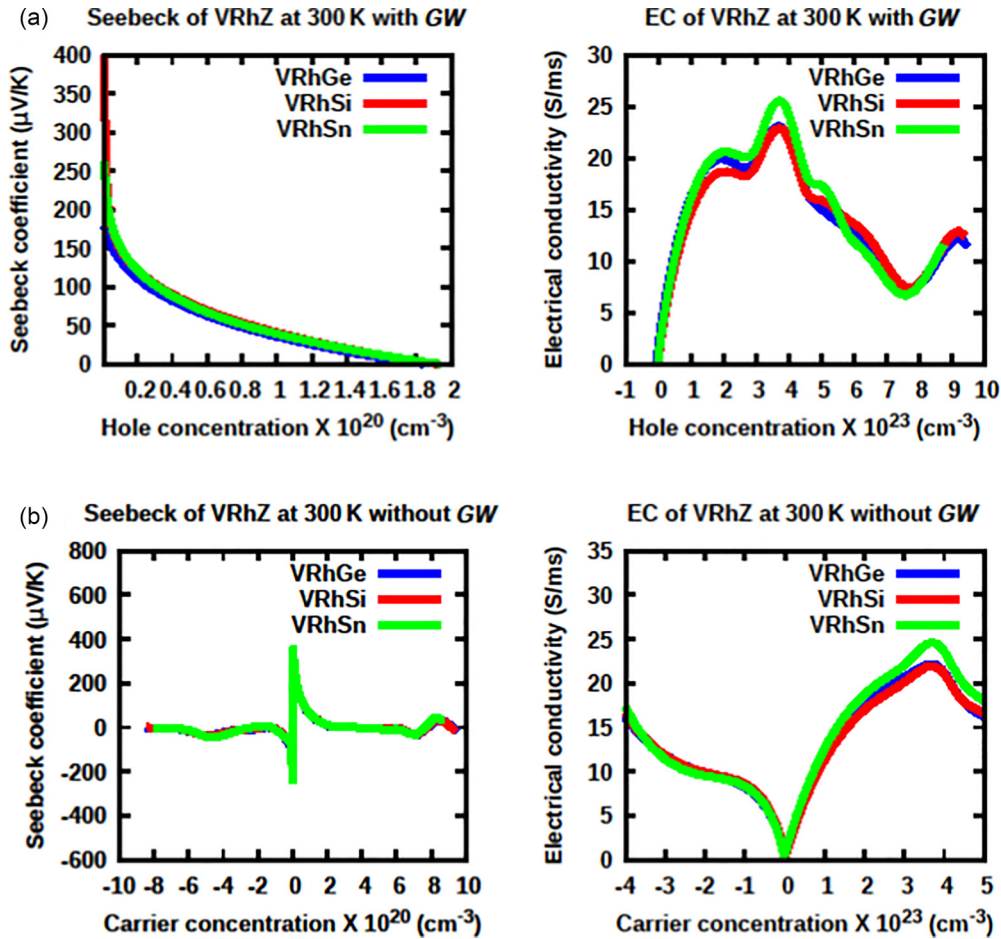


FIG. 7. Seebeck coefficient (left) and electrical conductivity (right) of VRhZ (Z = Ge, Si, and Sn) at 300 K: (a) with GW and (b) without GW.

For high ZT , the power factor is supposed to be high, and a small electron thermal conductivity. This is shown in Figs. 8 and 9 where the highest electron thermal conductivity is $0.45 \times 10^{-16} \text{ W/mK s}$ in VRhSn which also has the highest power factor of 15.99 W/msK^2 . This electronic thermal conductivity is too small compared to power factor therefore a high ZT . A similar trend is realized in all the investigated materials and reported in Tables IV and V. With holes as the carriers at 1000 K, in Fig. 8(a), VRhSn gave the highest electron thermal conductivity of $0.45 \times 10^{-16} \text{ W/mK s}$. At the same temperature, without GW in Fig. 8(b), electron carriers had a lower thermal conductivity which means that hole carriers are more preferred for a high ZT within the studied materials. Notably, based on the highest PF/τ at 1000 K, VRhZ (Z = Ge, Si, and Sn) half-Heusler materials are predicted to favor p -type behavior over n -type. The electronic thermal conductivity and power factor values, as illustrated in Fig. 9, are significantly reduced at room temperature compared to a temperature of 1000 K. Table VI depicts the carrier relaxation time analysis.

4. Lattice thermal conductivity

Acoustic phonon modes significantly influence thermal transport in semiconductors. The lattice thermal conductivity k_l in this study is obtained by use of the optimized Slack

model [36],

$$k_l = A \frac{\bar{M}_a n^{\frac{1}{3}} \delta \theta_a^3}{\gamma^2 T}, \quad (34)$$

where $\bar{M}_a$ refers to the average mass per atom, δ represents the cube root of the average atomic volume, n corresponds to the atomic count in the primitive cell that influences the total number of phonon branches, θ_a is defined as the Debye

TABLE V. Transport coefficients of VRhZ (Z = Ge, Si, and Sn) at room temperature, 300 K.

	VRhGe	VRhSi	VRhSn
ZT with GW	0.61	0.79	0.78
Without GW	0.88	0.86	0.88
EFF ($10^{-19} \text{ W}^{\frac{5}{3}} \text{ ms}^{-\frac{1}{3}} \text{ K}^{-2}$) with GW	0.65	0.47	0.45
Without GW	0.28	0.29	0.35
PF (W/msK^2) with GW	6.4	6.5	6.9
Without GW	4.9	5.2	5.3
σ (S/ms) with GW	22.5	22.5	26.0
Without GW	21.91	21.91	25
S ($\mu\text{V/K}$) with GW	200.2	225.4	225.6
Without GW	280.1	280.2	390.2
K_e (10^{-16} W/mK s) with GW	0.16	0.16	0.19
Without GW	0.14	0.14	0.18

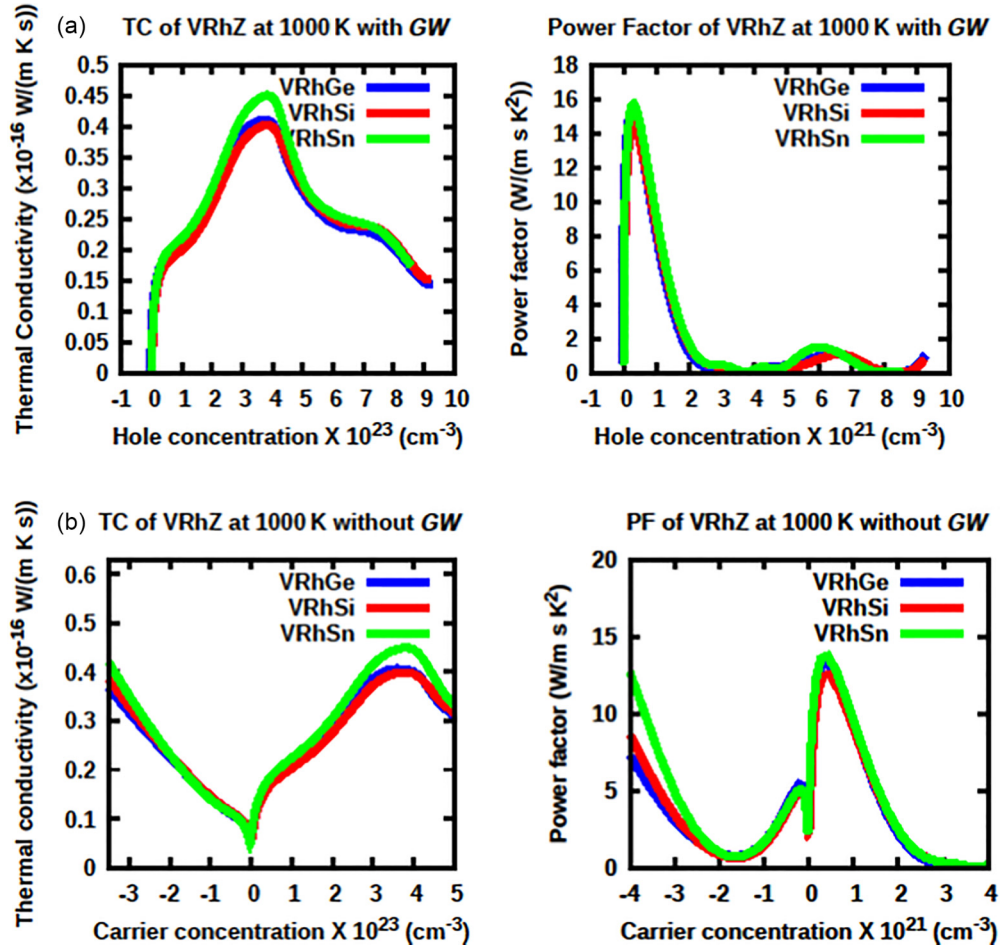


FIG. 8. Electron thermal conductivity (left) and power factor (right) of VRhZ (Z = Ge, Si, and Sn) at 1000 K: (a) with *GW* and (b) without *GW*.

temperature for acoustic vibrations, γ denotes the Grüneisen parameter, T refers to the thermodynamic (absolute) temperature, and A is a coefficient in the optimized slack model formulated as

$$A = \frac{2.436 \times 10^{-6}}{1 - \frac{0.514}{\gamma} + \frac{0.228}{\gamma^2}}, \quad (35)$$

where γ stands for the Grüneisen parameter.

Based on the evaluated bulk modulus B and shear modulus G , the velocities of longitudinal and shear waves (V_L and V_S) can be calculated as

$$V_L = \left(\frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}} \quad \text{and} \quad V_S = \left(\frac{G}{\rho} \right)^{\frac{1}{2}}, \quad (36)$$

such that ρ denotes the material's mass density.

Hence, the average sound velocity v_a can be determined as

$$v_a = \left[\frac{1}{3} \left(\frac{1}{V_L^3} + \frac{2}{V_S^3} \right) \right]^{-\frac{1}{3}}. \quad (37)$$

Based on the obtained sound velocity, the acoustic Debye temperature can be determined,

$$\theta_a = \frac{h}{K_B} \left[\frac{3\rho_n}{4\pi} \right]^{\frac{1}{3}} v_a n^{-\frac{1}{3}}, \quad (38)$$

where h stands for the Planck's constant, K_B denotes the Boltzmann constant, and ρ_n refers to atoms per unit volume. The Grüneisen parameter measures the degree of anharmonicity in the system, and this is described by the variation of

TABLE VI. Simulated values of effective masses; m_h^* for holes, m_e^* for electrons in units of the free electron mass m_e , deformation potentials, elastic constants, and carrier relaxation time (τ) at 300 K for VRhZ (Z = Si, Ge, and Sn).

Alloy	m_h^* (m_e)	m_e^* (m_e)	D_p^c (eV)	D_p^v (eV)	C_{ii} (111)	C_{ii} (110)	C_{ii} (100)	τ_h (ps)	τ_e (ps)
VRhSi	2.94	0.91	1.76	0.75	259.90	252.82	241.01	3.45	3.65
VRhGe	3.56	0.92	-0.56	-0.37	286.39	284.24	276.81	10.84	35.46
VRhSn	3.62	0.98	-3.39	-0.39	298.78	287.22	285.92	328.05	140.88

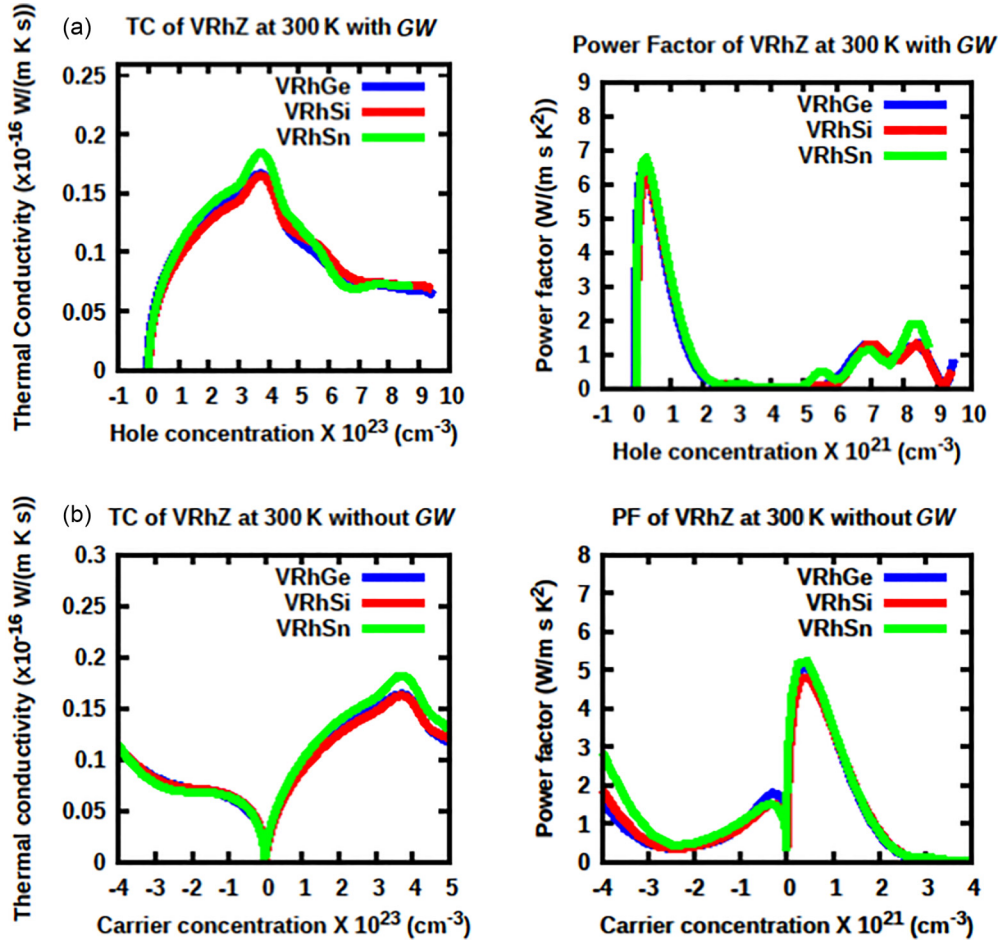


FIG. 9. Electron thermal conductivity (left) and power factor (right) of VRhZ ($Z = \text{Ge, Si, and Sn}$) at 300 K: (a) with GW and (b) without GW.

phonon frequency (ω) as a function of volume change (V):

$$\gamma = -\frac{V}{\omega} \left[\frac{\partial \omega}{\partial V} \right], \quad (39)$$

given that $\omega = vq$, where v denotes long-wavelength sound velocity and q denotes wave vector. Substituting Eq. (36) into Eq. (39),

$$\gamma_L = -\frac{1}{2} \frac{V}{B + \frac{4G}{3}} \frac{\partial (B + \frac{4G}{3})}{\partial V} - \frac{1}{6}, \quad (40)$$

$$\gamma_S = -\frac{1}{2} \frac{V}{G} \frac{\partial G}{\partial V} - \frac{1}{6}, \quad (41)$$

$$\gamma = \sqrt{[\gamma_L^2 + 2\gamma_S^2]}/3. \quad (42)$$

By utilizing the obtained θ_a [Eq. (38)] and γ [Eqs. (40)–(42)], lattice thermal conductivity k_l was computed using the optimized slack model [Eq. (34)] and the results are presented in Table VII.

G. Electron fitness function and effective mass

Traditional, in adequate thermoelectric materials, for example, $\text{Si}_{1-x}\text{Ge}_x$ materials, high-temperature conditions lead to increased carrier mobility μ and diminished k_l . A typical

characteristic of these compounds is that their energy gaps are influenced by s or p electronic states near the Fermi levels, accountable for low effective mass m^* in the density of states and enhanced μ . Thermoelectric semiconductors characterized by light bands and extremely low effective masses m^* ($0.1m_e - 1.0m_e$) typically require a moderately low optimal carrier density, that is, ρ_{opt} should be in the range of $(10^{19} - 10^{20}) \text{ cm}^{-3}$. This means a small amount of carrier density is sufficient to achieve optimal power factor performance and therefore their ZT . This was experimentally realized by Fu *et al.* [82]. Our results in Figs. 10 and 11 confirm these experimental findings. At 1000 K, in Fig. 10, optimal EFF and ZT is realized at zero carrier concentrations. At this temperature, the two parameters, EFF and ZT , dropped to zero at $2.5 \times 10^{20} \text{ cm}^{-3}$ hole concentration and to zero at $-2.5 \times 10^{20} \text{ cm}^{-3}$ electron concentration. At 300 K in Fig. 11, the reported data on EFF and ZT are less than those reported at 1000 K. This means the investigated compounds are high-temperature thermoelectric materials.

EFF gives a reflection on the electronic characteristics of thermoelectric efficiency. It additionally analyzes how band structure complexity impacts thermoelectric capability, in that it decouples σ and S [83] but does not give the origin of the complexity. EFF is expressed as a function of volumetric density of electronic states N and the power factor per

TABLE VII. Calculated sound velocities in m/s (longitudinal and shear), Grüneisen parameter (γ), primitive unit cell volume V (in $\text{\AA}^3$), average mass per atom $\bar{M}_a$ (in u), Debye temperature θ_D (in K), acoustic Debye temperature θ_a (in K), and lattice thermal conductivity k_l in W/mK at 300 K for VRhZ ($Z = \text{Si, Ge, Sn}$).

Alloy	V_L	V_S	V	γ	$\bar{M}_a$	θ_D	θ_a	k_l	Reference
VRhSn	4616.45	2108.02	51.84	1.42	72.04	360.95	252.09	6.18	This work 6.0 Expt. [80]
VRhGe	3284.71	2069.78	48.25	1.13	69.21	364.24	226.33	5.72	This work 6.0 Expt. [80]
VRhSi	3228.65	2016.86	48.06	1.04	66.73	442.50	208.76	5.46	This work 4.8 Expt. [81]

scattering time, that is, $\text{EFF} = \frac{PF}{\tau N^{2/3}}$. The EFF of holes and electrons for VRhZ ($Z = \text{Ge, Si, and Sn}$) with and without GW was calculated with the use of TRANSM code, which is a postprocessing code to analyze data modeled using Boltzmann statistics and transport equations. The realized results are depicted in Figs. 10 and 11. When computed with GW , EFF has a maximum peak value of $7.9 \times 10^{-20} W^{5/3} ms^{-1/3} K^{-2}$ in regions of zero charge carriers. EFF approaches zero as the density of charge carriers rises. An optimum value of $7.9 \times 10^{-20} W^{5/3} ms^{-1/3} K^{-2}$ indicates that there is a pow-

erful decoupling between σ and S , which means that the compounds VRhZ ($Z = \text{Ge, Si, and Sn}$) are good thermoelectric materials, VRhSn being the best among the studied compounds. The maximum EFF of VRhZ ($Z = \text{Ge, Si, and Sn}$) with GW at 1000 K are $6.9 \times 10^{-20} W^{5/3} ms^{-1/3} K^{-2}$, $6.6 \times 10^{-20} W^{5/3} ms^{-1/3} K^{-2}$, and $7.9 \times 10^{-20} W^{5/3} ms^{-1/3} K^{-2}$, representing VRhGe, VRhSi, and VRhSn, while without GW these outputs are reduced. At room temperature (Fig. 11), the EFF values are very low compared to EFF values at 1000 K. At 1000 K, the calculated ZT , using GW approximation for the

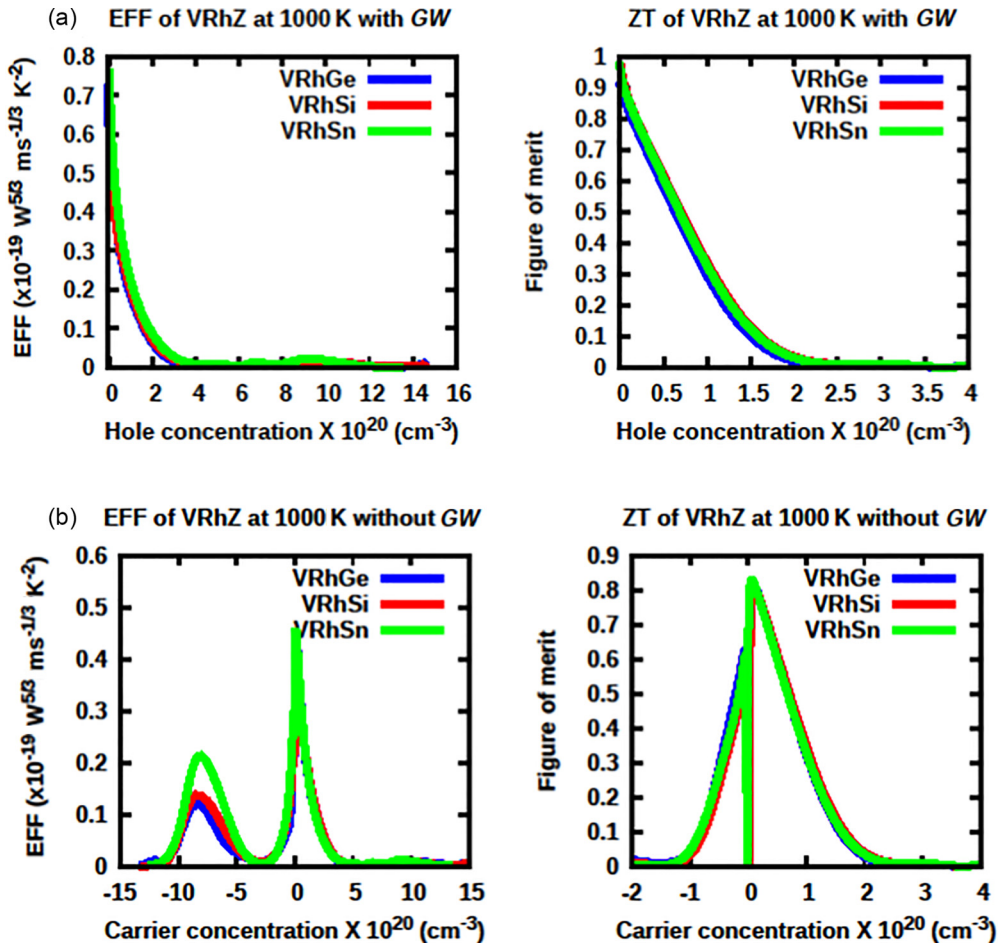


FIG. 10. EFF (left) and figure of merit (right) of VRhZ ($Z = \text{Ge, Si, and Sn}$) at 1000 K: (a) with GW and (b) without GW .

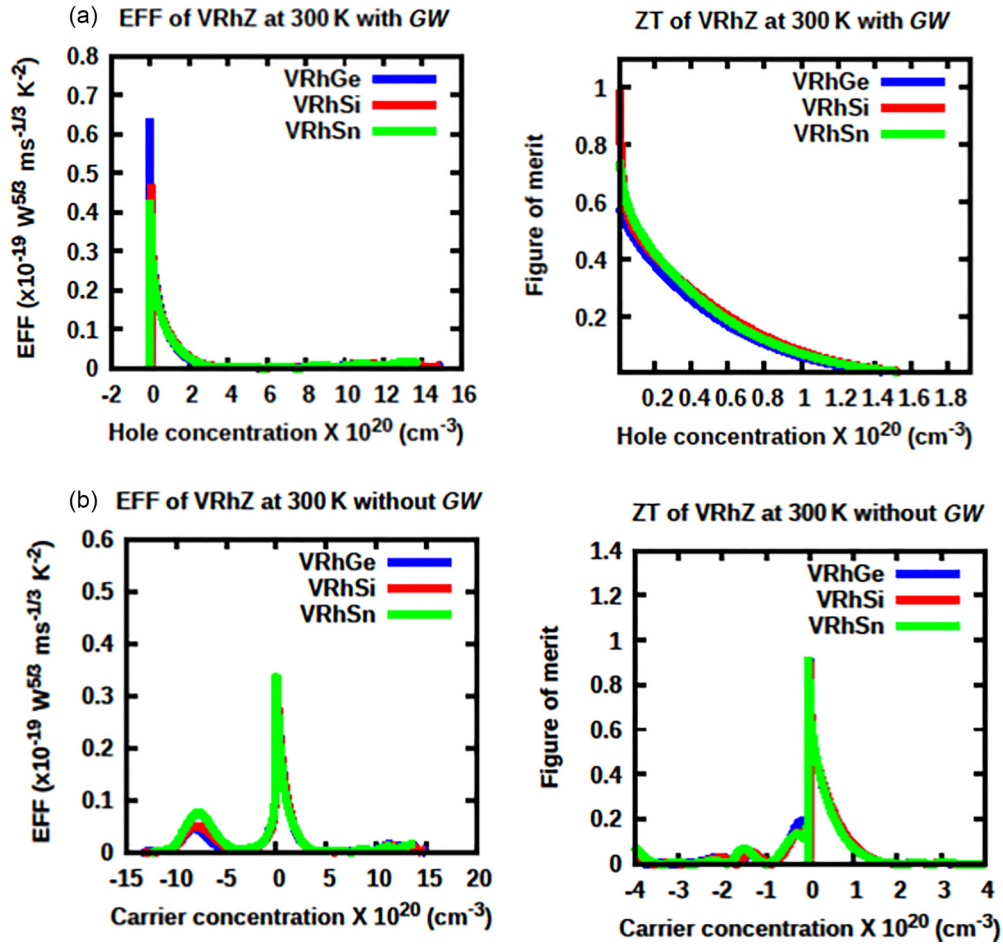


FIG. 11. EFF (left) and figure of merit (right) of VRhZ ($Z = \text{Ge, Si, and Sn}$) at 300 K: (a) with *GW* and (b) without *GW*.

studied alloys is 0.91, 0.99, and 0.99 for VRhGe, VRhSi, and VRhSn, correspondingly. The ZT values without *GW* approximation are 0.81, 0.81, and 0.82 for VRhGe, VRhSi, and VRhSn, correspondingly. At room temperature, the values of ZT without *GW* are slightly higher at 0.88, 0.86, and 0.88 for VRhGe, VRhSi, and VRhSn as listed. From the ZT findings, it is conclusively realized that the best temperature for high thermoelectric performance of the investigated materials is 1000 K with *GW*. Our main goal is to find materials with the largest possible values of ZT and this has been achieved. The ZT values obtained in this study are comparable to those of a good thermoelectric candidate from previous studies [84].

Effective mass of holes and electrons with *GW* and without *GW* at conduction band minimum and VBM was computed. Using outputs from Boltzmann transport analysis, the effective mass was evaluated through the TRANSM tool. The free electron theory approximation states that the Seebeck coefficient is linearly dependent on effective mass. Feng *et al.* [79] described the inverse relationship between electrical conductivity and Seebeck coefficient. They suggested that heavier effective mass supports the Seebeck coefficient while lighter effective mass supports electrical conductivity.

Figure 12 presents the inverse effect mass (IEM) with respect to carrier concentration. The negative scale of carrier concentration corresponds to the *n* type [Fig. 12(b)] while the

positive scale of carrier concentration indicates the *p* type. As seen in Fig. 12, for the *n* type, the IEM slowly decreased before gradually increasing. In the *p* type, it exhibits a sharp decline followed by a gradual rise with increasing carrier concentration from 0 cm^{-3} . The peak IEM values were observed for both acceptor and donor at zero charge carrier density, which shows that the *p* type exhibits a larger IEM compared to the *n* type. The high IEM in the acceptor results in improved electrical conductivity, therefore the studied compounds are well-suited for thermoelectric systems.

IV. CONCLUSION

Structural stability, electronic band structure, Seebeck coefficient, $\sigma/\tau S^2\sigma/\tau$, EFF, and IEM of VRhGe, VRhSi, and VRhSn half-Heusler materials are explored by use of the DFT formalism as implemented in QE code. The interaction between electrons and ions has been approximated using plane-wave-based pseudopotentials. Thermoelectric characteristics, EFF and IEM of VRhZ ($Z = \text{Ge, Si, and Sn}$) have been comprehensively described with the γ phase of all the alloys confirmed to be the most stable configuration. Phonon dispersion analysis confirms the presence of dynamical stability while at elevated temperature of 900 K, the AIMD calculations provide evidence of thermal stability. This work

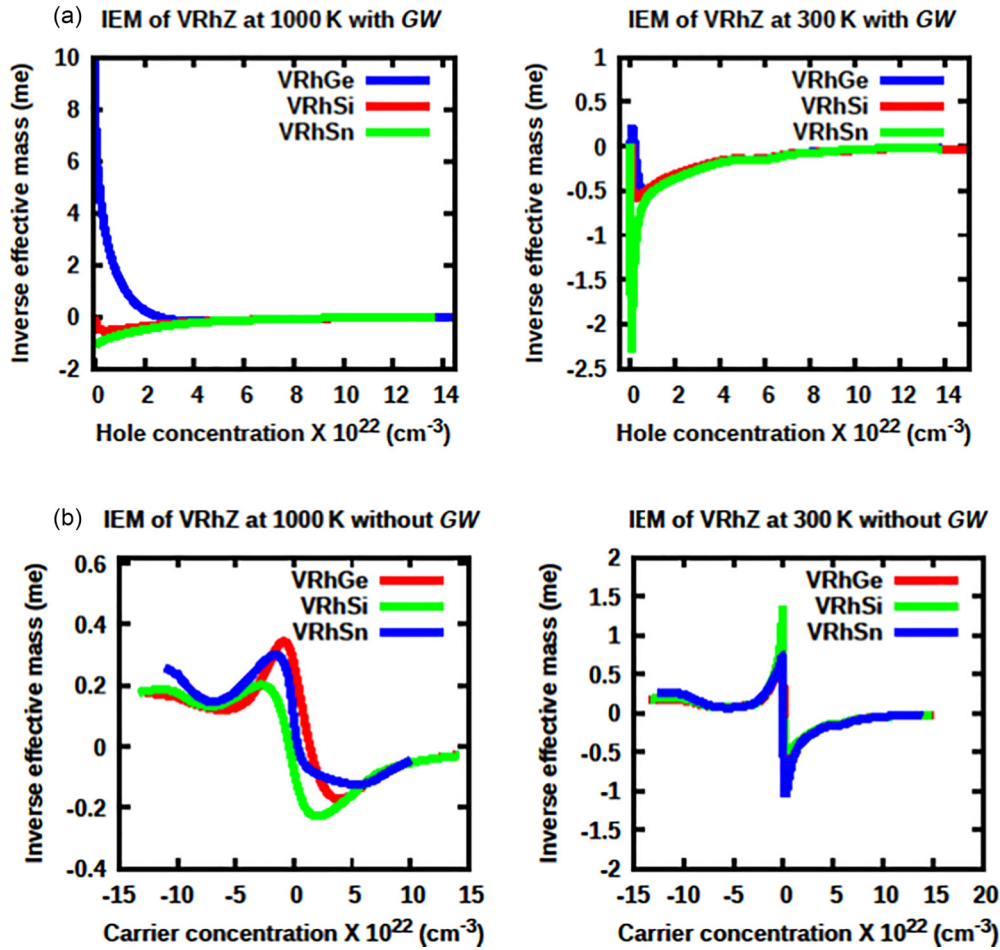


FIG. 12. Inverse effective mass of VRhZ ($Z = \text{Ge, Si, and Sn}$): (a) with *GW* and (b) without *GW*.

predicts VRhZ ($Z = \text{Ge, Si, and Sn}$) half Heusler materials as indirect-gap semiconductors dominated by hole conduction; therefore, they are recommended substitutes in thermoelectric applications. The investigated half Heusler materials indicate lattice dynamical stability, mechanical ductility, ionic bonding, and anisotropic elastic behavior, in agreement with half Heusler alloys classification. Our current results correlate reasonably well with results of examined properties for other half Heusler compound families and have the potential to act as guideline data for additional computational and experimental research on VRhGe, VRhSi, and VRhSn half Heusler materials.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available because they contain commercially sensitive information. The data are available from the authors upon reasonable request.

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