High temperature and pressure dependent structural and thermophysical properties of Co$_2$VN (N = Sn, Sb) ferromagnetic materials

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Abstract

Ab-initio framework investigation of structural stability and thermophysical behavior of two Co-based Heusler alloys is carried out using spin-polarized calculations at high temperature and pressure. The structural characterization in nonmagnetic and ferromagnetic states reveals the ordered ferromagnetic Cu$_2$MnAl-prototype structure as stable phase. The optimized lattice constant is found to be consistent with the available experimental value. The continuity in the P–V plot indicates the absence of any structural phase transition from highly symmetric cubic structure to other structural phase. The band structure profile shows perfect half-metallic character with integral 3.00 $\mu_B$ magnetic moment for Co$_2$VSn and 4.00 $\mu_B$ for Co$_2$VSb according to the Slater-Pauling rule. Elastic constants convey that these alloys are mechanically stable with a high Debye and melting temperatures. With the incorporation of modified version of Beck-Johnson potential these alloys displays a perfect half-metallic character having an indirect band gap of 1.12 eV and 1.34 eV in spin down orientation of Co$_2$VN (N = Sn, Sb) Heuslers respectively. The density of states along with their corresponding band structure delivers the semiconducting nature of alloys in spin down channel for the present set of alloys. Semi-classical Boltzmann theory for heat transport is used to check the applicability of the material for thermoelectric technology. Insight into variation of lattice thermal conductivity shows an exponential decreasing trend for both the compounds intriguing their experimental exploration. Also, a detailed description of thermodynamic behavior of the vital quantities like entropy, thermal expansion, Grüneisen parameter and specific heat were examined using quasi harmonic Debye approximation.

1. Introduction

Heusler alloys have been comprehensively and systematically studied in the fields of solid state physics and chemistry due to their remarkable and multidimensional chemical and physical properties [1–3]. These materials have grabbed lot of attention due to their peculiar properties like high spin polarization, interesting electronic structure (half-metallic/semiconducting/spin gapless nature), shape-memory effect, large curie temperatures, ferromagnetism and thermoelectric properties, which are used in various applications like magnetoresistive materials, spin valve generators, spin filters, transducers, shape memory devices and spintronics [4–10]. Among them half metallic ferromagnetic (HMF) are a class of materials that have been acknowledged by the world class researchers due to their application in spintronics/magneto electronics/ thermoelectrics [11–15]. Thus, spin-based electronics are expected to bring revolution in the field of information technology, memory devices and telecommunication. The addition of the spin degrees of freedom to the conventional electronic devices has several advantages like non-volatility, increased data processing speed and decreased electrical power consumption. In these materials spin resolved bands have special behavior, the
majority spin band shows metallic character while the minority spin band shows semiconducting/insulating behavior with a gap at Fermi level. The ferromagnetic material delivering half-metallic character is one of the typical behaviors of Heuslers to demonstrate 100% spin polarization at Fermi level [16–18]. One more important feature of these Heuslers is the likelihood by exhibiting Slater–Pauling (SP) rule which deliberates the degree of atomic disorder and exchange interactions strength, atomic ordering in the lattice, valence electron count [19, 20]. Slater–Pauling rule is a simple way to study ferromagnetic alloys and the interrelation between the valence electron concentration and the magnetic moments. It is well known that the Clh, Heusler alloys with three atoms per unit cell follow a simple rule that scales linearly with the number of valence electrons: 

\[ M_t = Z_t - 18 \]

where \( M_t \) represents the total spin magnetic moment and \( Z_t \) stands for the total number of valence electrons per unit cell, which was first noted by Kubler et al and the importance of which was also emphasized by Jung et al and Galanakis et al [19]. Since with 9 electron states occupied in the minority band for Clh Heusler alloys, \( Z_t - 18 \) is just the number of uncompensated electron spins. Namely, that is magnetic moment per unit cell. For ordered alloys with different kinds of atoms, it might be more convenient to work with all atoms of the unit cell. In the case of four atoms per unit cell, as in Heusler alloys like Co2MnGe with L21 structure, one has to subtract 24 from the accumulated number of valence electrons to find the magnetic moment per unit cell (\( M_t \)): 

\[ M_t = Z_t - 24 \]

with \( Z_t \) denoting the accumulated number of valence electrons in the unit cell containing four atoms [19]. In the case of Heusler alloys, the number 24 arises from the number of completely occupied minority bands that has to be 12 in the half-metallic state.

Thermoelectric (TE) materials are in the center of worldwide research activities due to their ability to convert waste heat into electricity [21–23]. Thermoelectricity is based upon two principles, due to Seebeck and Peltier, which in general, convert residual heat into electricity and vice versa. The maximum efficiency (\( \eta_{\text{max}} \)) of a TE device is calculated by the cold and hot side temperatures (\( T_h \) and \( T_c \)) and the intrinsic figure of merit (\( zT \)) through the following equation,

\[
\eta_{\text{max}} = \frac{\sqrt{T_c} + zT}{\sqrt{T_c} + zT - 1} \frac{1}{1 + \frac{T_c}{T_h}} \left[ 1 - \frac{T_c}{T_h} \right]
\]  

For a given temperature difference, the conversion efficiency depends upon the value of \( zT \). The higher the value of \( zT \) the higher is the conversion efficiency. From the theoretical and experimental studies, the Heuslers alloys have been predicted by the researchers demonstrating half-metallicity in Fe2YSi [24], Full Heuslers Co-based nanowires: deposition parameter variation of static and energetic properties [25], experimental and theoretical Ti-based Heuslers Ti2YAl [26], Co2YS [27] respectively. The recent experimental study in the field of thin films of Heuslers including Cr2CoGa [28], Co2MnGe [29], CoZFeAl [30], Fe2CoSi [31], Fe2CrGa [32], Co2MnSi [33], Co2FeSn [34] and Cu2MnAl, Co2MnSi, Co2MnGe and Co2MnSn [35] also possesses some novel properties which includes spin transfer torque for RAM and perpendicular magnetic anisotropy (PMA) [36]. Motivated by above-mentioned properties and keeping in view the multi-dimensional applications of these materials we have investigated the structural, magneto–electronic, mechanical, transport and thermal properties of Co2VN (\( N = \) Sn, Sb) Heuslers at high temperature and pressure. Therefore, our results would act as a guide for experimentalists for synthesis of such ferromagnetic Heusler compounds.

2. Computational details

Highly accurate and precise ground state properties are computed from high-throughput density functional theory (DFT) calculations using full-potential linearly augmented plane wave method (FP-LAPW) method implemented in the WEIN2k code [37]. The unknown exchange–correlation function in the Khon–Sham equations is generally approximated by well-known methods such as generalized gradient approximation (GGA). The GGA additionally includes the information gathered from gradient in the electron density. So, (GGA) [38] along with (GGA + U) [39] with onsite coulomb interaction (U) have to be selected by substituting U by Ueff. Here, \( U_{\text{eff}} = U - J \) where, J is the onsite exchange interaction and U is the on-set coulomb term after being optimized to deliver more precise band profiles for present set of alloys. In the present study, Co possesses seven valence electrons in the d-orbital and Coulomb potential (\( U_{\text{eff}} \)) was varied by adjusting J = 0–0.4. The optimized Ueff for Co was initiated to be 0.44 Ry (5.98 eV). Since GGA and GGA + U formulism are somehow in adequate to explain the magneto–electronic structure of correlated systems accurately. Therefore, modified Becke Johnson (mBJ) [40] has been employed to figure out the exchange correlation which mainly assembled of d and f-states. In FP-LAPW method, the crystal is divided into the non-overlapping muffin-tin spheres centered at each nuclei and the interstitial regions among them. The basis functions are expanded into the spherical harmonic functions within the muffin-tin sphere and the Fourier series within the interstitial region. The convergence of the basis set was controlled by a cutoff parameter \( R_{\text{MT}} K_{\text{max}} = 8 \), here \( R_{\text{MT}} \) shows the smallest
radii of the muffin tin sphere and $K_{\text{max}}$ represents the largest reciprocal lattice vector in the plane wave expansion. The cutoff energy was limited by $-6$ Ry value. In the self-consistent iteration cycle, the charge convergence value was set to 0.0001 e. In order to construct the charge density in each self-consistency step, the tetrahedron method with a $k$ points in the irreducible wedge ($3000$ $k$-points in the full BZ) was used at the Brillouin zone (BZ) integration. Elastic constants are taken from cubic-elastic code for the present set of alloys [41]. By using the calculation for band occupation, the Boltzmann transport theory is used to figure out the transport coefficients [42]. Gibbs2 simulation package is used to calculate the thermodynamic properties [43]. The typical code needs the energy band structure altogether lattice’s group symmetry. Hence, tensor of the electrical conductivity usually is achieved by doing the Fourier expansion expressed as:

$$\sigma_{\alpha \beta}(i, k) = e^2 \tau_{\alpha \beta}(i, k) v_{\alpha}(i, k)$$

(2)

Where the term and $\tau_{\alpha \beta}$ and $\tau$ illustrates the relaxation of time and charge of en electron respectively and $v_{\alpha}(i, k)$ represents $\alpha$ component with $i$ band index of the group velocity and is demonstrated as,

$$v_{\alpha}(i, k) = \frac{1}{\hbar} \frac{\partial \varepsilon_{i, \alpha}}{\partial k_{\alpha}}$$

(3)

Seebeck tensors, electrical conductivity and the group velocity can be determined as following relations expressed as:

$$S_{ij}(T, \mu) = \sum_{\alpha} (\sigma^{-1})_{\alpha \beta} v_{\alpha \beta}$$

$$\sigma_{\alpha \beta}(T, \mu) = \frac{1}{8\pi^2} \sum_i \int \sigma_{\alpha \beta}(i, k) \left( -\frac{\partial f(T, \mu)}{\partial \varepsilon} \right) dk$$

(5)

$$v_{\alpha \beta}(T, \mu) = \frac{1}{8\pi^2} \sum_i \int \sigma_{\alpha \beta}(i, k) [\varepsilon(k) - \mu] \left( -\frac{\partial f(T, \mu)}{\partial \varepsilon} \right) dk$$

(6)

Here, $f$ indicates the Fermi–Dirac function.

3. Results and discussion

The various properties of the materials under consideration have been discussed in the following sections.

3.1. Structural and mechanical stability

Heusler alloys are known as intermetallic compounds displaying various magnetic, electronic and various physical properties. The Heusler alloys with general formula $X_2YZ$ are known as full-Heusler alloys. These compounds are ternary inter-metallic, where $X$, $Y$ transition metals (TM) atoms and $Z$ is a main group ($sp$) valence element. The primitive cell of the $L2_1$-type structure comprises of four interpenetrating FCC sub lattices. The unit cell contains four atoms as basis such that the $X$ atom is placed at $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, with center of inversion symmetry, and $Y$, $Z$ atoms are situated at $(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ and $(0, 0, 0)$, respectively. The $X$ atoms, occupying the two different sub-lattices are chemically equivalent as the environment of the one sub-lattice is the same as the environment of the second one but rotated by $90^\circ$. Here, we have tried to confirm the energy analysis by minimizing the Birch Murnaghan’s equation [44] in both the non-magnetic with (no spin-polarization) and
ferromagnetic (spin-polarized) and is demonstrated in figure 1 to define the exact ground state. The associated lattice parameters as well as atomic positions were completely relaxed within the present calculation process. It is notified from the stability curves and other theoretical calculated results that the minimum energy of these Heuslers supports the ferromagnetic phase rather than non-magnetic phase. Howsoever, the stability components of Co$_2$VN ($N = \text{Sn, Sb}$) Heuslers are illustrated form table 1 and the structure is demonstrated in figure 2 where Co$_2$VN ($N = \text{Sn, Sb}$) Heuslers prefers Cu$_2$MnAl type.

An elastic property expresses the potential of a material to get back to its original shape upon removal of deforming force. The elastic constants of a material determine the response to an applied stress. These constants are important because of due to the fact that these parameters are related to behaviors of materials, including hardness, durability, strength, reliability, and performance required to designate the type of application and fabrication [51, 52]. The number of independent elastic constants required for a system is directly related to symmetry of structure. More symmetric the structure less is the number elastic constant required. For cubic structures, the number of elastic constants reduces to three $C_{11}$, $C_{12}$ and $C_{44}$. In order to determine them, we

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**Table 1.** The calculated values of lattice parameter ($a_0$ in Å), Cohesive energy (eV atom$^{-1}$), and Formation energy (eV unit$^{-1}$ cell) for Co$_2$VN ($N = \text{Sn, Sb}$) Heuslers.

| Alloys    | Magnetic phase | $a_0$ | Previous | Experimental | $E_{\text{cohesive}}$ | $E_{\text{formation}}$ |
|-----------|----------------|-------|----------|--------------|-----------------------|------------------------|
| Co$_2$VSn | FM             | 5.97  | [45–47]  | [48, 49]     | 4.11                  | −1.63                  |
| Co$_2$VSb | FM             | 6.07  | [50]     | —            | 4.45                  | −1.74                  |

**Table 2.** The calculated values of elastic constants and its associated parameters for Co$_2$VN ($N = \text{Sn, Sb}$) Heuslers.

| Parameter                  | Co$_2$VSn$^{36}$ | Co$_2$VSb |
|----------------------------|------------------|-----------|
| Elastic Constants          |                  |           |
| $C_{11}$ (GPa)             | 233.23           | 284.78    |
| $C_{12}$ (GPa)             | 151.49           | 123.87    |
| $C_{44}$ (GPa)             | 115.53           | 154.58    |
| Bulk modulus; $B$ (GPa)    | $B_v$ = $B_R = (C_{11} + 2C_{12})/3$ | 275.76 | 177.50    |
| Voigt shear modulus; $G_V$ (GPa) | $= (C_{11} + C_{12} + 3C_{44})/3$ | 109.35 | 124.89    |
| Young’s Modulus (GPa)      | $= 9B_G/(3B + G)$ | 200.177 | 291.67    |
| Cauchy’s pressure; $C_P$ (GPa) | $= C_{11} - C_{14}$ | 35.96  | −30.71    |
| Poisson’s Ratio; $\nu$     | $= (3B - Y)/(6B)$ | 0.31    | 0.25      |
| Frantsevich’s ratio (G/B)  | 0.33             | 0.67      |
| Lamé Constants             |                  |           |
| $\mu$ (GPa)                | $= Y/(2(1 + \nu))$ | 90.85  | 119.53    |
| $\lambda$ (GPa)            | $= \nu Y/(1 + \nu) + (1 + 2\nu)$ | 28.15  | 24.12     |
| Kleinman parameter $\xi$ (g cm$^{-3}$) | $= C_{11} + 8C_{12}/7C_{11} + 2C_{12}$ | 0.83  | 0.56      |
| Melting temperature (K)    | $T_m \pm 300$    | 1931.62   | 2236.33   |

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that these alloys preserve their lattice structures over wide range of temperatures. The cohesive energy is an important parameter that affects the stability of a material. The melting temperatures for these alloys are 1931.62 K and 2236.33 K with a standard error of ±300 K [53–56].

We have used the rhombohedral and tetrahedral distortions on the cubic structure under volume conserving constrain. The requirement on these elastic constants leads to the following restrictions $C_{11} > 0$, $C_{12} > 0$, $C_{44} > 0$, $(C_{11} - C_{12}) > 0$, and $C_{12} < B < C_{11}$ defined by Born-Haung [53–56]. The detailed discussion of different parameters has been precisely written here shown in table 2. The shear modulus is concerned with the deformation of a solid when it experiences a force parallel to one of its surfaces while its opposite face experiences an opposing force. The determination of hardness or strength of a material is related to the Bulk modulus (B). It also determines the strength against the brittleness. The materials with large bulk modulus are more strong compared to those with small value of bulk modulus. The calculated values of bulk modulus for the present alloys suggest these alloys have high facture strength.

Young’s modulus is a mechanical property that measures the stiffness of a solid material. It defines the relationship between stress (force per unit area) and strain (proportional deformation) in a material in the linear elasticity regime of a uniaxial deformation. The calculated values of Young’s modulus of these alloys indicating they are stiff in nature. Ductile and brittle nature of an alloy can also be determined through the elastic constants ($C_p$). The nature of the atomic binding is related to the ductile or brittle nature and can be revealed by the Cauchy pressure [57]. For metallic bonding with ductile nature, the $C_p$ is positive. Moreover, for brittle materials with directional and angular bonding character, it has negative value. From the observed in table 2, it is clear that Co$_2$VSn is ductile and Co$_2$VSb is brittle in nature. Brittle and ductile nature can also be interpreted by Pugh’s ductility index ($B/G$). According to the Pugh’s criterion, the low (high) $B/G$ ratio is coupled with the brittle (ductile) nature of the materials. The key values separating brittleness and ductility is 1.75, below this value material possess brittle nature and if $B/G > 1.75$ material has ductile nature. The calculated value for Co$_2$VSn lie above the critical value indicates its ductile nature while for Co$_2$VSb it lies below the critical value indicating its brittle nature. The ratio of transverse contraction strain to longitudinal extension strain in the direction of applied force is known as Poison’s ratio. It is another criterion that has been verified experimentally to determine ductile or brittle nature of an alloy and is defined by relation. The critical value of $\nu$ to differentiate brittle and ductile materials is 0.26. Materials with $0.26 < \nu < 0.5$ are regarded as ductile materials, for $0.12 < \nu < 0.26$ materials are supposed to be brittle. The calculated value of $\nu$ in table 2, indicates similar results for Co$_2$VN ($N = \text{Sn, Sb}$) Heuslers as shown by $C_p$ and $B/G$ values. We have also calculated Lamé Constants that recommends the elastic stress components of a material to the isotropic deformable of strain at a definite point. Bond twisting along with the bond lengthening can be designated through the Kleinman parameter. These alloys deliver a significant value of Kleinman parameter, hence demonstrates their strengthened against various external forces and lends its strong support in engineering purposes. Melting temperature is also an indicator of atomic bonding strength and there is relationship with Young’s modulus. The general trend is that a higher melting temperature indicates a higher modulus and vice versa. Ordering of the crystalline lattice is energetically favorable which means that crystalline structures are generally more stable thermally as well as chemically. We have calculated the melting temperature of Co$_2$VN ($N = \text{Sn, Sb}$) alloys from Fine’s relation [58].

$$T_m = [553(K) + (5.911)C_{11}] \pm 300 \text{ K}$$

(7)

The melting temperatures for these alloys are 1931.62 K and 2236.33 K with a standard error of ±300 K suggests that these alloys preserve their lattice structures over wide range of temperatures. The cohesive energy is an
important thermo-dynamical feature defines its strength capability of the material and can be measured experimentally by the process of heat of sublimation. It conveys us about the bond strength of a material, which is equal to the energy needed to break the intermolecular physical links. It is regarded a dynamic quantity by which all thermodynamic parameters as well as chemical bonding can be elucidated. The prediction of cohesive energy within the first principles has been calculated for Co\textsubscript{2}VN (N = Sn, Sb) Heuslers. The calculated values of cohesive energy for these alloys are 4.11 eV atom\(^{-1}\) and 4.45 eV atom\(^{-1}\) for Co\textsubscript{2}VSn and Co\textsubscript{2}VSb respectively. The calculated values illustrated that the atoms are robustly withheld each other in a crystal lattice and will preserve their respective structures over extensive range of external forces. Heusler alloys can be synthesized and form stable phases. In order to demonstrate that Co\textsubscript{2}VN (N = Sn, Sb) Heuslers could be synthesized experimentally, we calculated the formation energy \(E_f\) by subtracting the sum of equilibrium total energies for the constituent elements from the equilibrium total energies of corresponding alloys by using the formula. The calculated formation energies turn out to be negative, which indicates that these alloys can easily be synthesized experimentally. The calculated formation energies for Co\textsubscript{2}VSn and Co\textsubscript{2}VSb are \(-1.63\) (eV unit\(^{-1}\) cell), \(-1.74\) (eV unit\(^{-1}\) cell) respectively comes out to be negative signifying that these alloys can be experimentally synthesized.

To analyze the pressure effect on the structural properties, Gibbs 2 code is incorporated to generate pressure-volume (P–V) data by calculating unit cell volumes under a series of applied hydrostatic pressures and is represented in figure 3. The continuity in P–V plot indicates the absence of any structural phase transition from highly symmetric cubic structure to other structural phase.

3.2. Electronic and magnetic properties
The electronic structure study of a material is highly desired for the application based perspective. The efficiency of a material for spintronic device application is characteristically represented by the energy gaps, the value of which paves the way to manipulate the desired physical properties in a significant manner. The basis of band
profile, are used to describe the electronic structure of Co$_2$VN ($N = Sn, Sb$) Heuslers is illustrated in figure 4 along with high-symmetry Brillouin zone (BZ), nature and type of band profile is represented in table 3. The materials possessing smart magneto-electronic profile are immensely required in numerous scientific fields. By using GGA formalism, the energy levels are crossing at Fermi level in up-down spin channel, hence exhibiting metallic character for Co$_2$VSb alloy. However at Fermi level Co$_2$VSn shows a semiconducting gap of 0.46 eV in spin down channel and metallic nature in spin up channel delivering half-metallicity. As we know that the transition metal systems are usually highly correlated, so to further elucidate this discrepancy has to be needed. Since the GGA method underestimates the band gap, so some sophisticated methods have been adopted in order to obtain the precise band structure. To eliminate the vagueness, the GGA + U method has been adopted. The current value of U was precisely chosen for Co-d orbital electrons is 5.98 eV. However, the Hubbard correction is insufficient for these Heuslers to define the band occupation. So, we have used mBJ potential to define effective and accurate band profile. The important benefit of the mBJ is the inbuilt potential due to which the accurate examination of the band gap energies have been investigated for Co$_2$VN ($N = Sn, Sb$) Heuslers. Mostly the origin of half-metallic nature of Co$_2$VN ($N = Sn, Sb$) Heuslers can be examined by presenting the possible hybridization among the constituent atoms schematically and usually there are three interactions which are responsible for the origin of gap in materials; these are classified as (i) charge transfer band gap (ii) covalent band gap and (iii) d-d orbital hybridization band gap. The energy gap in Heusler alloys arises mainly due to d-d hybridization, so the origin of this gap can be predicted by d-d hybridization between the energy levels in both majority and minority spin channels schematically. The degeneracy of d-states is lifted when it is acted by external fields (octahedral or tetrahedral), thus creating a triply degenerated 3t$_{2g}$ and doubly degenerated 2e$_g$ states (bonding) along with formation of anti-bonding states due to crystal field splitting. The transition metal atom d-states in presence of crystal field are decomposed into double degenerate e.g. ($d_{x^2-y^2}$, $d_{z^2}$) and triple degenerate t$_{2g}$($d_{x^3}$, $d_{x^2}$, $d_{y^2}$) states. The existence of metallic nature in one spin channel and semiconducting exhibits 100% spin polarization in region of Fermi level.

Next, we tried to figure out the magnetic properties which decide the capability of these materials in spin based technological fields and covers its attention towards the most remarkable applications such as spintronics.
random memory shape devices, spin injectors, spin filters, etc. The magnetic calculation is carried out through GGA and GGA + U and mBJ formalisms are illustrated in table 4. For full Heusler alloys with an L21 structure (the present study follows the same rule), the origin of the band-gap and the $M_t = Z_t - 24$ rule are well understood from the discussions of Galanakis et al based on first-principles calculations and the group theory.

Figure 6. Representation of partial density of states of Co$_2$VN ($N = $ Sn, Sb) Heuslers by mBJ formulism.

Figure 7. Calculated Seebeck coefficients ($S$) and total Seebeck coefficient ($S_t$) with temperature for Co$_2$VN ($N = $ Sn, Sb) Heuslers.
Figure 8. Graphical variation of electrical conductivity as a function of temperature for Co$_2$VN ($N = Sn, Sb$) Heuslers.

Figure 9. The variation of lattice thermal conductivity with temperature for Co$_2$VN ($N = Sn, Sb$) Heuslers.

Figure 10. Variation of power factor (a) and figure of merit (b) with temperature for Co$_2$VN ($N = Sn, Sb$) Heuslers.
They have demonstrated that in full-Heusler alloys with an L21 structure Cu2MnGe-prototype, the d–d hybridizations between the Co atoms are very important despite of their being next-nearest-neighbors to each other. This situation leads to the bonding $t_{2g}$ and $e_{g}$ states and anti-bonding $t_{1u}$ and $e_{u}$ states. The $t_{2g}$ and $e_{g}$ states are hybridized with the d states of the Mn atom, but the $t_{1u}$ and $e_{u}$ states cannot couple with any of the d states of Mn due to the lack of symmetry. The $t_{1u}$ states are below the Fermi level and they are occupied, whereas the $e_{u}$ states are just above the Fermi level. Therefore, the minority occupied bands accommodate a total of 12 electrons ($1s, 3p$, and 8d electrons), and the total magnetic moment $M_t = Z_t - 24$ follows. Recent experimental and theoretical research reveals that the full-Heusler alloys with an Hg2CuTi-type structure can also belong to the family of half-metallic materials. These types of alloys mostly follow the $M_t = Z_t - 18$ rule instead of the $M_t = Z_t - 24$ rule. Thus the present study (following $M_t = Z_t - 24$ rule) delivers the magnetism from the alloys with the maximum contribution of Co-supplies to the lattice structure. The total DOS is illustrated in the figure which elucidates the consequence of mBJ potential mainly on the electronic profiles. The different energy states are shifted predominantly from the Fermi level offers the band gap there. Further the clarification of the energy states which are primarily linked with the bands (i.e., to analyses the visibility of the states), we have plotted partial density of states displayed in figure. Whereas, properties of $N = \{\text{Sn, Sb}\}$ states are typically far from the valance band, thus don’t perform any significant character in defining the electronic band profile i.e. their contribution of magnetic character is least around the Fermi level in comparison to Cobalt which supplies most contribution. On comparing the pDOS of the two alloys we examine the d-states of transition atoms through Fermi level delivers half metallic character of alloys. In Co-based alloy, both $d_{2g}$ as well $d_{eg}$-states are below Fermi signifies in p-d hybridization in up-spin channel. However in down-spin $d_{2g}$-states are at Fermi level while $d_{eg}$ states are empty lie above Fermi level. The overall combination of ferromagnetic spins alignments constitutes
the net magnetism in their corresponding structures. Hence, the sufficient magnetism comprising these Heuslers may lend their extending stand in high performance spin electronic devices.

3.3. Thermoelectric-transport properties
The presence of parabolic bands near the Fermi level in the electronic band structure expects the charge carriers to have low effective mass and hence high mobility. As evident from the band structures (spin down) the materials present the semiconducting nature and bands are almost flat in the conduction band, thus both the materials are believed to be a prominent to show significant thermoelectric performance [59–61]. For a material to have high thermoelectric performance, it should hold high electrical conductivity, large Seebeck coefficient and low thermal conductivity. The thermoelectric properties like electrical conductivity ($\sigma$), thermal conductivity ($\kappa_{\text{tot}}$) and Seebeck coefficient ($S$) for both the spin configurations were computed for both the materials in the temperature range of 0 K to 800 K. Insight towards Seebeck coefficient ($S$) shows the application of these materials towards thermoelectric purposes and various energy harvesting technologies. One can observe that Seebeck coefficient of Co$_2$VN (N = Sn, Sb) Heuslers against the temperature ranging from (0–800) K and is represented in figure 7. The entire Seebeck value for Co$_2$VSn Heusler delivers rising trend from 5 $\mu$V K$^{-1}$ at 100 K to a value of 37 $\mu$V K$^{-1}$ at a temperature of 800 K for up spin channel. However in case of down channel $S$ exhibits decreasing value from 2706 $\mu$V K$^{-1}$ at 50 K to a value 407 $\mu$V K$^{-1}$ at 800 K. In case of Co$_2$VSn, the value of $S$ shows linear trend from $-15$ $\mu$V K$^{-1}$ at 100 K to a value of $-82$ $\mu$V K$^{-1}$ at 550 K in up spin configuration, however an exponential decay trend is followed in down channel configuration and varies form $-748$ $\mu$V K$^{-1}$ at 100 K to a value of $-300$ $\mu$V K$^{-1}$ at 550 K temperature. The negative and positive value of total Seebeck coefficient shows that Heuslers are $p$-type and $n$-type semiconductor depends on holes and electrons are as suppliers. The nature of the decreasing phenomena is due to the main reason of increasing in the carrier concentration $n$. The increasing carrier concentration is inversely proportional to the Seebeck coefficient and is expressed by the following equation:
Here, \( m^* \) is effective mass and \( n \) designates the carrier concentrations.

Figure 8 shows the variation of electrical conductivity \( (\sigma/\tau) \), where spin-up state is metallic nature as conductivity is displaying a decaying trend with temperature. In case of spin-down state, a semiconducting behavior of conductivity is displayed. One can observe that with the rise in temperature the electrical conductivity also shows rising trend. It is due to the reason that rises in carrier concentration the \( \sigma \) also increases at higher temperature. The carrier concentration and electrical conductivity are interrelated by the mathematical equation

\[
\sigma = n \mu
\]

where \( \mu \) is the mobility. Positive temperature dependency at high temperature of \( \sigma/\tau \) is because of increasing carrier concentration. The lattice thermal conductivity \( (\kappa) \) consists mainly of two parts phonon \( \kappa_\text{L} \) and electronic \( \kappa_\text{e} \) contribution. By employing the Boltzmann theory, we calculate the electronic part \( \kappa_\text{e} \), on the other hand the lattice part \( \kappa_\text{L} \) is calculated through quasi-harmonic Debye approximation. Through Slacks equation \( K_\text{L} \) is well-defined as,

\[
K_\text{L} = \frac{A \theta_D V^{1/3} m}{\gamma^2 n^{2/3} T}
\]

Where \( A \) is a collection of physical constants \( (A \sim 3.1 \times 10^{-8}) \) and \( \gamma \) is Grüneisen parameter. The calculated value of total thermal conductivity for \( \text{Co}_2\text{VN} \) \((N = \text{Sn, Sb}) \) Heuslers in up-down channel as a function temperature is illustrated in figure 9. In up-spin alignment \( \kappa_\text{e}/\tau \) with temperature increases linearly, however in down alignment a small changes up-to 400 K beyond which a swift change can be observed. With the increase in temperature the total electronic thermal conductivity delivers an increasing trend. The thermal conductivity rises form \( 5.34 \times 10^{15} \) at 300 K to \( 17.43 \times 10^{15} \) at 1200 K for \( \text{Co}_2\text{VSn} \), and \( 5.17 \times 10^{15} \) \( \text{W} \)(Kms)\(^{-1} \) at 300 K to \( 15.9 \times 10^{15} \) \( \text{W} \)(Kms)\(^{-1} \) for \( \text{Co}_2\text{VSb} \) Heuslers. The total thermal conductivity shows the decreasing trend up to some temperature and then increases slowly as the electronic thermal conductivity becomes dominant at
higher temperatures. Recently, Co$_2$MnAs alloy predicted with a PF $0.40 \times 10^{-5}$ W m K$^{-2}$ at 0 K and 0 GPa. Enamullah et al evaluates PF of Co-based Heuslers nearly equal to $0.80 \times 10^{-5}$ W m K$^{-2}$ at room temperature. However, Sofi et al explored the Power factor of approximately $1.20$ W m K$^{-2}$ for Co$_2$SeSb and $1.80$ W m K$^{-2}$ for Co$_2$TiSb at 0 K and 0 GPa. On comparing the Power factor of above said materials, the current study delivers a significant PF and illustrates in figure 10(a). At 0 GPa and 0 K the predicted PF for Co$_2$VN (N = Sn, Sb) Heuslers is $2.95 \times 10^{-5}$ W m K$^{-2}$, $3.72 \times 10^{-5}$ W m K$^{-2}$ respectively. The present set of Heusler materials demonstrates the value of PF high in comparison with the Co-based Heuslers at 0 K and 0 GPa. Thus, we conclude that Co$_2$VN (N = Sn, Sb) Heuslers creates its possibility in thermoelectric applicability. To define the significance of a material for a TE generation purposes, ZT calculation is the best parameter. The deviation of ZT with temperature is described in figure 10(b). The calculated value of ZT for Co$_2$VSn is 0.14 and that of Co$_2$VSb is 0.13 at 1200 K respectively. This efficient capability conveys that the present set of alloys find a possible stand for thermoelectric purposes.

### 3.4. Thermodynamic properties

To govern the importance of the effect of pressure and temperature characteristics, we have employing modified version of quasi-harmonic approximation (QHA) [62, 63]. As there are no such results to show that these alloys can behave under varying pressure and temperature conditions. Therefore our study will be helpful for experimentalists to synthesis Co$_2$VN alloys. Thermodynamic properties are essential to construct the materials carrier capability and it also relates the effect and cause effect of dynamics and microstructure of the material. The exact or correct temperature variation of the thermodynamic properties can be attained by assuming the lattice vibrations to be quantized. We have calculated the deviation of heat capacity ($C_v$), Grüneisen parameter ($\gamma$), thermal expansion coefficient ($\alpha$), entropy ($S$) at different temperatures and pressures. These thermal quantities were varied from 0–400 K and 0–20 GPa. Heat capacity is a measure to show the capacity of a material...
to store heat as the temperature changes. From this, we can get the information about different properties like lattice vibration etc. Since in solids volume does not change appreciably with application of temperature, so we here reported the specific heat at constant volume \((C_V)\) shown in figure 11. From this graph, we can see that \(C_V\) increases with temperature due to increase in atomic vibrations. At high temperatures, \(C_V\) tends towards a constant value showing the Dulong and Petit limit \([64]\). However, at lower temperature \(C_V\) changes abruptly with temperature obeying Debye \(T^3\) law.

Thermal expansion \((\alpha)\) is the tendency of matter to change its shape, area, volume, and density in response to a change in temperature. The graphical representation with respect to temperature and pressure variation for the present Heusler alloys is displayed in figure 12. The sharp rising trend of \((\alpha)\) followed at lower temperatures while it attains a constant value at higher temperature. The Grüneisen parameter \((\gamma)\) is used to designate the thermo-mechanical properties and clarifies the association between change in volume in case of crystals and frequency associated with phonon. It is also considered a significant dynamical property used to quantify the relationship between elastic and thermal description of solids and is directly connected with them. Here in the present case the Grüneisen parameter \((\gamma)\) shows an increasing inclining trend with increase in temperature, but on the other hand shows radical decrease with increase in pressure. The calculated value of Grüneisen parameter at pressure 0 GPa and temperature 300 K for Co2VSn and Co2VSB is 2.07 and 2.41 respectively shown in figure 13. Entropy of the material delivers information a crucial understanding related to the vibrational properties which exhibits the vital significance the presentation of several dispositive’s like heat pumps, heat engines and refrigerators etc. At fixed pressures the entropy at ambient conditions is exhibited in figure 14. From the plots we observed that entropy increases from 0 K to 650 K. Additionally, the obtained values of entropy suggests the value of 45.33 Jmol\(^{-1}\) K\(^{-1}\) for Co2VSn and 47.04 Jmol\(^{-1}\) K\(^{-1}\) for Co2VSB Heuslers, designate that Co2VSB is less ordered than Co2VSn at ambient conditions. Beyond the temperature 650 K the extensive property becomes very high. This is mainly due to the vibrational entropy increases of the material with the rising temperature and shows a declining trend with the rise in cohesive energy.

4. Conclusions

By using the Full potential linearized augmented plane wave method based on the density function theory we have carried out \textit{ab-initio} calculations of Co-based full Heusler alloy. The observed band structures was found to be indirect having \(n\)-type semiconducting nature at Fermi level. The strongly dependent elastic constants and cohesive/formation energies illustrates the stability of these alloys. Transport parameters, viz. electrical and thermal conductivity, Seebeck coefficient, power factor and \(zT\) have been calculated by using the BoltzTraP code. Meanwhile, thermodynamic properties of Co2VN viz thermal expansion coefficient, unit cell volume and Grüneisen parameter as a function of the temperature and pressure are evaluated by means of quasi-harmonic Debye model. The outcomes display that entropy increases with increase in the temperature. Grüneisen parameter is more sensitive to pressure than temperature, while as specific heat significantly depends on temperature and follows \(T^3\) law. These materials show the possible TE performance with the significant \(zT\) value. Hence, our conclusions will play a starting place to guide experimentalists for developing the high temperature TE materials.

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Data availability statement

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

Conflict of interest

The authors declare that they don’t have any conflict of interest.
**Author’s statement**

All the calculations and manuscript writing have been done by Shakeel Ahmad Sofi under the supervision of Dinesh C Gupta.

**Supplementary material**

Supplementary material is available online at stacks.iop.org/MRX/7/125701/mmedia.

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