



Analysis of structural, electrical, magnetic and mechanical properties of Half-Heusler CoVZ (Z= Pb and Sn) compounds using First Principle

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Using first principle techniques, the structural, electrical, elastic, and magnetic properties of Half-Heusler CoVZ (Z= Pb and Sn) compounds having the space group F-43_m have been observed. Here, we employ WIEN2k-implemented full potential linearized augmented plane wave (FP-LAPW) technique. The compounds CoVZ (Z= Pb and Sn) has a finite band gap of 0.68 and 0.67 eV, respectively, close to the Fermi level as implemented in the WIEN2k algorithm. It is discovered that these substances are semiconducting in nature. These compounds, CoVZ (Z= Pb and Sn), represents 0.0 μ B magnetic moment and are ductile in nature. The value of bond index is positive and greater than 12 for both the compounds which is representing metallic behavior and hard nature for aforesaid compounds. The values of Poisson ratio for both the compounds lie between 0 and 0.5.

Keywords: Semiconducting, Band gap, Density of State, Magnetic Moment, Band Structure

Introduction

It was the year of 1903, when Friedrich Heusler exposed a ferromagnetic material at 300 K [1]. He was a German mining engineer and chemist. This is a great finding by Friedrich Heusler in those days. He framed a Heusler compound by taking two elements of Cu, one element of Mn and one element of Al at room temperature. Heusler found that these three non-magnetic elements show magnetism at room temperature, when studied as a compound. CuMnSb, Cu₂MnAl, and Cu₂MnSn are the first compounds studied by Friedrich Heusler [2]. In the year 1903, structure of Heusler prepared compounds are unknown. A special class of materials described by Heusler is lie at the edge of compounds and alloys, by merging the characteristics of both. Heusler compounds are constructed from chemical stability of covalent lattice and in a lattice single sites can be replaced with distinct species, act as alloys. The uniqueness of these materials is perfectly described by covalency and tenability in compactly. Crystal structure of Co₂MnAl is described by Otto Heusler and Bradley in the year 1934 [3-4]. This structure contains four

interpenetrating fcc sub lattices. Out of thus, two belongs to same elements. At presently, it is known that Mn is anti-ferromagnetic but the concept of anti-ferromagnetism was unknown before Neel's work in 1936 [5]. In the same continuation, after Heusler, Nowotny and Juza, represent their results for different group (main group element) of materials and in present days these are known as Nowotny-juza Phases. L. Castelliz established the link between Heusler compounds and Nowotny-juza Phases by firstly synthesizing NiMnSb. Now, these Phases are known as half Heusler compounds, whose structure is described with one empty fcc sub lattice out of four interpenetrating fcc sub lattices in full Heusler compounds [6-7]. A chain of compounds could be framed among half and full Heusler by filling the fourth sub lattice. The structure of half Heusler compounds is represented by $\chi\gamma Z$. Whereas, full Heusler compounds structure is represented by $\chi_2\gamma Z$. In these structures, χ and γ belong to d block whereas Z belongs to p block. Due to presence of two elements at χ position in full Heusler compounds, it can be characterized in different forms; such as inverse Heusler can be obtained by swapping of χ element with γ and quaternary Heusler can be obtained by swapping χ with fourth distinct element [8-9].

Half Heusler compounds have a structure that combines zinc blend type sub lattices with rock salt. The structure of these compounds can be described with one empty fcc sub lattice from available four interpenetrating fcc sub lattices in full Heusler compounds [10–13]. This class of materials can be represented as $\chi\gamma Z$ type structure. This face-centered cubic structure contains structurbericht designation C1b having space group F-43 m with their composition 1:1:1[14–15].

Computational Particulars

Ab initio principle calculations executed by means of the 'full potential Linearized Augmented Plane Wave (FP-LAPW)' approach provided in the WIEN2k simulation package [16–17] to describe the interaction between atomic core and valence electrons. The valence electrons are taken into consideration when extending the electronic wave function. At Perdew-Burke-Ernzerhof (PBE), the energy of exchange-correlation is defined using the generalized gradient approximation (GGA) [18–19]. We employed the spin-polarized Density Functional Theory's (SDFT) FP-LAPW approach to optimize the shape of the electronic structure. In order to extend the spherical harmonics in the atomic sphere, the value of l_{\max} is assumed to be 6. Up to $G_{\max}=12$, the charge density as well as potential in the middle area were produced as Fourier series with a wave vector. According to the alloys examined, Table 1 provides the muffin-Tin radii of each atomic sphere [20]. $RMT \times K_{\max}$ is the convergence criterion that LAPW employs.

Table 1: The Muffin-Tin Radii of each atomic sphere for the optimized lattice parameter of each specific alloy are shown to avoid overlapping of spheres during the SCF cycle,

Compounds	Atoms	RMT
CoVPb	Co	2.16
	V	2.08
	Pb	1.79
CoVSn	Co	2.21
	V	2.12
	Sn	2.12

We have fixed the energy between these two states at $-6.0Ry$. Relativistic core states and semi-relativistic valence states are distinguished. The SCF cycle is considered to have converged when, between successive iterations, the energy difference and the integration of the absolute charge density difference are fewer than $10^{-5}Ry$ and 0.001 Coulomb/f.u., correspondingly. Wien2k keeps overall K-point count for irreducible Brillouin zones at 1000. Based on first principle total energy or stress computations, Elastic_1.0 is used to compute the full second-order elastic stiffness tensor for crystal structures. The maximum absolute value of Lagrangian strain is 0.5, and the numeral of deformed strain structures is fixed at 11.

Results and Discussion

The lattice parameters are calculated and the minimum energy for the previously specified substances is measured in the first stage. One can derive the equilibrium lattice parameters by minimizing the energy in relation to the volume.

Structural Properties

Half-Heusler compounds crystallise in the fcc having space group $F-43_m$ and structurbericht designation $C1b$. These compounds can be understood as follows: V and Z in $CoVZ$ compounds, γ and Z in $Mn\gamma Z$ compounds at $(1/2, 1/2, 1/2)$ position, and Mn with Ru, Fe, Ni, and Pd create zinc blende sublattice ordered in a primitive cell with Wyckoff positions $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$. Volume optimization was carried out using the Murnaghan equation, which describes the energy and pressure values as a function of volume and can be applied to any feasible configuration of each component [20–23]:

$$E(V) = E_0 + \left[\frac{BV}{B_P} \left(\frac{1}{(B_P-1)} \left(\frac{V_0}{V} \right)^{B_P} + 1 \right) - \frac{BV_0}{(B_P-1)} \right] \quad (1)$$

$$P(V) = \frac{B}{B_P} \left\{ \left(\frac{V_0}{V} \right)^{B_P} - 1 \right\} \quad (2)$$

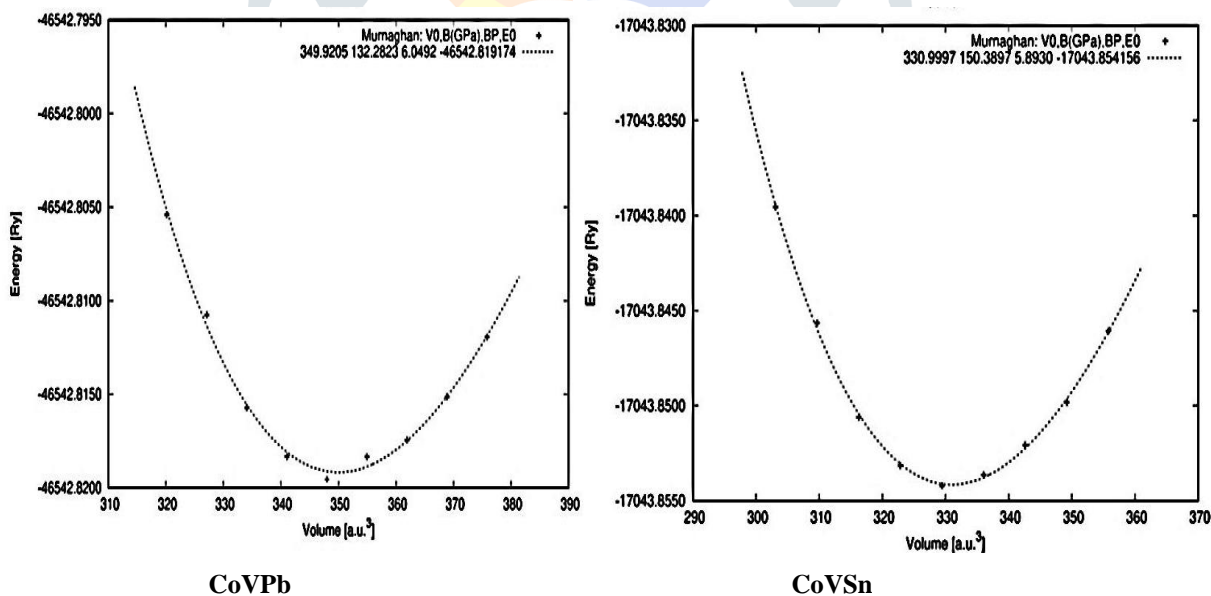


Figure1: The volume vs. energy curves

For further studies, only that arrangement which has minimum energy and electro negativity order is to be considered [24-27]

Table 2 Electronegativity for different elements

Elements	Electronegativity
Co	01.87
V	01.64
Pb	01.80
Sn	01.96

Table 3: Observed values of band gap (B.G.), equilibrium volume (Eq.V.) and minimum energy (M.E.)

Compound	Energy (Ry)	Equilibrium Volume (a.u.) ³	B.G. (eV)
CoVPb	-46542.82	349.92	0.68
CoVSn	-17043.85	331.00	0.67

Table 4: Observed values of the lattice parameter (a_0), Eq.V., bulk modulus (BM), pressure derivative of elasticity modulus (BP) and M.E. during optimization

Composite	Lattice Parameter (Å)	Equilibrium Volume (a.u.) ³	BM (GigaPascal)	BP	(M.E.) (Rydberg)
CoVPb	4.89	349.92	132.28	6.05	-46542.82
CoVSn	4.78	331.00	150.39	5.89	-17043.85

Electronic Properties

We first examine the full DOS configuration of both compounds in order to analyze the electrical structure of all alloys. 3-d metal atom states, which vary from -0.5 to +4.3 eV, hybridize with one another in partial DOS, as shown in Figure 2. This is because the half-metallic band difference in some compounds is a significant factor. The density

of state allows for the investigation of the CoVZ ($Z=\text{Pb}$ and Sn) chemical bonding property. The hybridization between the d -states of Co and V is the primary mechanism of the chemical bond, as can be seen from the partial densities of the figure 2. A chemical bond can be both covalent and ionic at the same time. Covalent because both transition elements' d states are strongly hybridized and degenerate over a large portion of their extension, and ionic because the relative quantities of Co and V's 3- d states differ below and above the Fermi point, favoring V's 3- d states. Moreover, the compounds CoVZ ($Z=\text{Pb}$ and Sn) contain 18 valence electrons. The semiconductor behavior of these half-Heusler materials can be identified in large part by looking at the electronic structure. We also computed the total DOS using the equilibrium lattice parameter in order to examine the electrical image of these materials.

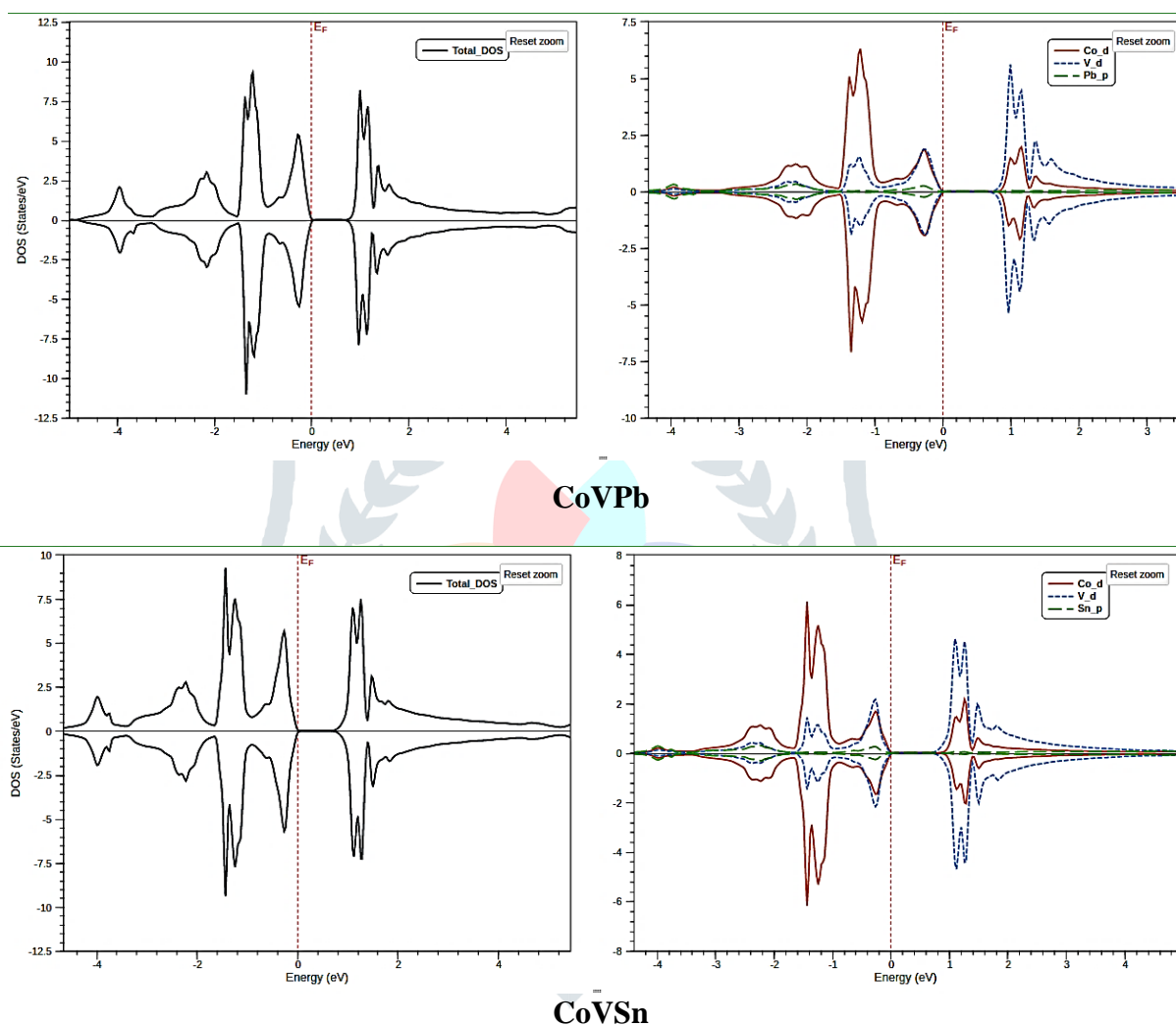


Figure 2: Total density of states of both the compounds at their equilibrium lattice constant

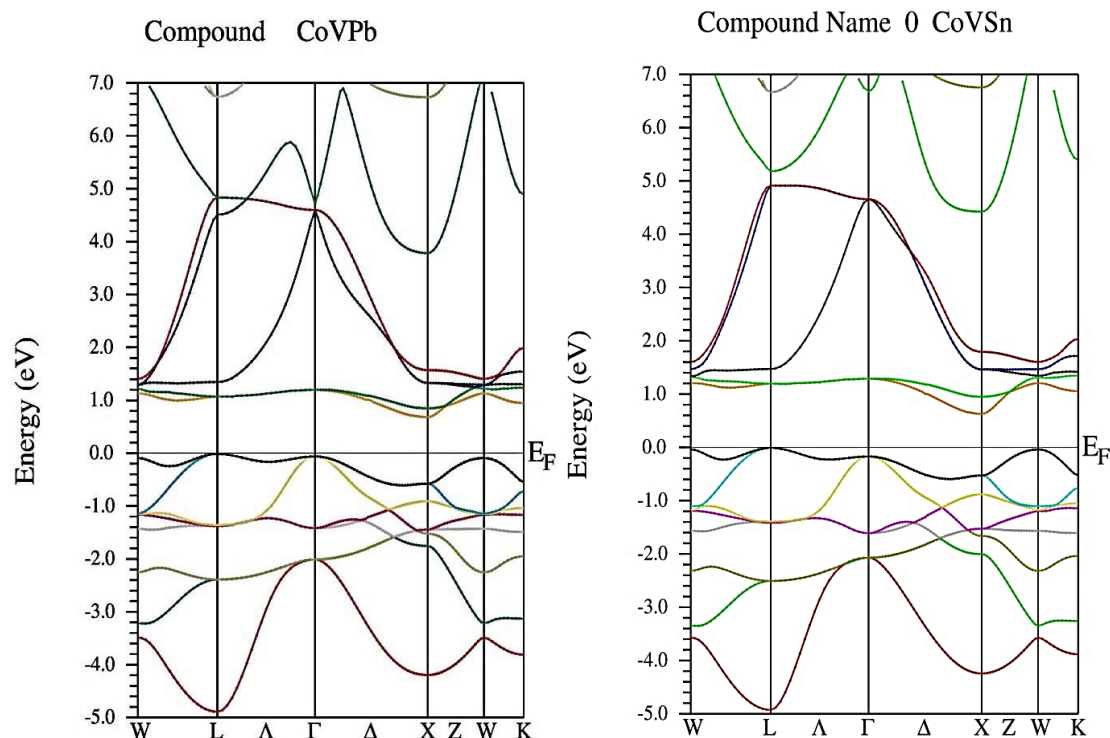


Figure 3: Band Structures of the Compounds CoVPb and CoVSn

Table 5: Total band gap and band transition between special points of first Brillion zone

Compound	E_g (eV)	BAND Transition	Compound	E_g (eV)	BAND Transition
CoVPb	0.68	L→X	CoVAs	0.67	L→X

Magnetic properties

By calculating the difference between the up and down spin states, the Galanakis model determines the spin magnetic moment of these materials [28–30]. The peculiar behavior of these compounds is explained by the underlying magnetic moment, which for these compounds obeys the Slater-Pauling rule as illustrated below.

$$M_t = Z_t - 18;$$

Where M_t : total magnetic moment/ f.u and

Z_t : total number of valence electrons.

For example, Co, V, Pb and Sn atoms have 9, 5, 4 and 4 valence electrons count.

Table 6: Total magnetic moment per formula unit of the compounds CoVPb and CoVSn

Compound	Total Magnetic Moment Per Formula (μB) (Using WIEN2k)
CoVPb	0.0
CoVSn	0.0

In addition, the spin polarization P is defined by

$$P = \frac{n \uparrow - n \downarrow}{n \uparrow + n \downarrow} \times 100\%$$

Where, $n \uparrow (E_f)$ and $n \downarrow (E_f)$ are the spin-dependent density of states around the Fermi level.

The table below lists the total magnetic moment and valence electron count for each formula unit [31–34]. The estimated outcome is in decent accord to the theoretical value [35].

Table 7: Theoretical values of magnetic moment according to the Slater-Pauling rule and their corresponding spin polarizing nature

Compound	Z_t	$M_t (\mu\text{B})$	Spin Polarization
CoVPb	18	0	Unpolarized
CoVSn	18	0	Unpolarized

Mechanical Properties

Elastic constant is used to analyze hardness, stress, and all pressure-induced structural deformations. The Poisson ratio, Young's modulus, shear modulus and melting temperature of solids are studied. For cubic crystal, only three different elastic constants: C_{11} , C_{12} , and C_{44} . The elastic constant tensors (in Voigt notation) arising from the alteration in internal energy deformation are represented by the C_{ij} in this instance [36–38]. The modulus of rigidity considers the solid's resistance to shear deformation-preserving volume, while modulus of incompressibility B describes the solid's resistance to volume variation.

In the study and creation of materials, elastic structures are important. Taylor's expansion of the elastic energy or stress in terms of the applied strain characterizes elastic tensors of any order. It is necessary to determine the three second-order elastic constants (SOEC), C_{11} , C_{12} , and C_{44} , in order to characterize the dynamic and mechanical behavior of the composites under study. There are only three different elastic constants for cubic crystal formations, according to Hooke's law: C_{11} , C_{12} , and C_{44} . $C_{11}=C_{22}=C_{33}$, $C_{12}=C_{13}=C_{23}$, and $C_{44}=C_{55}=C_{66}$ are the results of the symmetry of the second-order elastic constant matrix in Voigt notation. The compound's stability is confirmed by

the fact that none of the elastic constant matrix's Eigen values are zero. Aside from this requirement, the Born's theory-based stability criteria are as follows: $C_{11}>0$, $C_{44}>0$, $C_{11}>|C_{12}|$, and $(C_{11}+ 2C_{12}) >0$.

The researched χVZ compounds are mechanically stable because the elastic constants of the cubic crystals are thought to be compatible with the aforementioned stability requirements [39-40].

Table 8: Elastic constants of CoVZ (Z= Pb and Sn)

Compound	Elastic constant			B (GigaPa)	G (GigaPa)	E (GPa)	Pugh ratio	ν	A
	C_{11}	C_{12}	C_{44}						
CoVPb	204.64	105.99	83.22	138.87	67.47	174.20	2.058	0.29	1.69
CoVSn	224.12	109.10	91.98	147.44	76.19	194.98	1.935	0.28	1.60

From the study of the above table, we observe that both the Materials satisfy the classical mechanical stability criteria of elastic constants. If the value of anisotropy constant=1, the material is isotropic; if it is not equal to unity, composite is anisotropic, So, the results reveal that both the compounds are anisotropic in nature. The compounds CoVZ (Z= Pb and Sn) having Pugh ratio greater than 1.75, so these are ductile. The stiffness and flexibility of a material can be ascertained using the Bond index (B_I), i.e. $C_P = C_{12} - C_{44}$. The material is considered metallic if the value is positive; nonmetallic if the value is negative. The above results reveal that the value of $B_I >12$, representing the compounds CoVZ (Z= Pb and Sn) are metallic and hard in nature. The values of Poisson ratio for the compounds CoVZ (Z= Pb and Sn) are 0.29 and 0.28 respectively.

Conclusions

The compounds CoVPb and CoVSn exhibit semiconducting behavior with finite band gaps of 0.68 and 0.67 eV correspondingly, according to results of the research. These compounds, CoVZ (Z= Pb and Sn), have estimated magnetic moments of 0.0 and 0.0 μ_B . These findings demonstrate that the estimated magnetic moment approves fit to the behavior of Slater-Pauling. The Compounds CoVZ (Z=Pb,Sn) are ductile type. The value of B_I is positive representing metallic behavior by both the compounds and hard in nature whereas Poisson ratio for both the compounds lie between 0 and 0.5.

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