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First-Principles Study: Some Physical Properties of Half-Heusler Alloys XCrBi (X = Hf, Ti and Zr)

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Abstract

The structural, electronic, and elastic properties and HfCrBi, TiCrBi and ZrCrBi alloys formed in the Half-Heusler Structure are studied using ab-initio density–functional theory. The equilibrium lattice constant and the elastic parameters were calculated. The computed elastic results prove that the alloys were mechanically stable. The Half-Heusler alloys TiCrBi and ZrCrBi studied are found to possess half-metallic character except for HfCrBi, showing metallic behavior in both spin-down and spin-up channels. All Half-Heusler alloys are mechanically and thermodynamically stable. .

1.Introduction

Heusler Compounds have been considered either experimentally or theoretically as long as they were discovered [1]. These Compounds are in the intermetallic category consisting of three elements in 1:1:1 (half- Heusler) or 2:1:1 (full Heusler) stoichiometric ratio. In Full-Heusler Alloys, X is normally a transition metal like Cu, Fe, Ni, Co, Ru; Y is mostly Mn, Cr, or V; and Z can be Al, Ga, Ge, Si, Sn in L21 Structure [2]. For half-Heusler alloys, the general formula is XYZ Where X can be a transition or alkali metal element, Y is another transition Metal element, generally Mn or Cr, and Z is a member of group IV elements or a Pnictide [3]. This material has the capability to perform as a metal when all electrons spin up and as a semiconductor when all electrons spin down. The peculiar behavior of the half-metals makes them a likely material in spintronics. The spin of electrons can be influenced to transfer and store information [2], this is the concept of spintronics. Few materials have been found to possess this half-metallic behavior such as full-Heusler alloys [3], ferromagnetic oxides [4], perovskite alloys [5], s-p binary compounds [6], dilute magnetic Semiconductors [7, binary transition-metals and Pnictide [8], [9], [10], Chalcogenides [11], [12] and half-Heusler (HH) alloys [13], [14], [15].

The half-metallic character of the HH alloys has been given more consideration. This is in view of their lattice matching with Semiconductors having a Zinc blende structure, a high Curie temperature, and the likelihood of epitaxial developing them on semiconductors [16].

In addition, since the HH alloys have the structure XYZ, there is an endless number of possible HH alloys that can be synthesized, due to their properties as half-metal which makes them possibilities for tunneling magnetoresistance (TMR), magnetic random access memories (MRAM) and giant magneto-resistance (GMR) [17] as existing and new areas that have not been scrutinized [18],19].

It is imperative to design newer HH alloys to a high standard and also regulate experimentalists in the future.

In this work, the structural, electronic, magnetic, mechanical, and thermodynamic properties of XCrBi (X=Hf, Ti, and Zr) HH alloys have been explored from first-principles calculations. The option X=Hf, Ti, and Zr as regards the fact that these elements are recognized to be economical and non-poisonous [20].

The remaining work is organized with section 2 displaying the methods used to conduct the calculation. Section 3, discusses the results and finally concludes with the conclusion in section 4.

2. Computational details

Structural, electronic, and magnetic properties of XCrBi (X=Hf, Ti, and Zr) alloys were formed with the Quantum Espresso [21] Program based on spin-polarized density functional theory (DFT). The kind of pseudopotential used in this study for the exchange–correlation functional is the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof for solids (PBEsol).

The structural parameters of XCrBi (X=Hf, Ti, and Zr) are optimized and a variable cell relaxation is performed.

The band Structure, along with the density of states (DOS) is computed with the kinetic cut-off of 680eV, 816eV, and 816eV for HfCrBi, TiCrBi, and ZrCrBi respectively with k-points of 6χ6χ6, 6χ6χ6 and 6χ6χ6 for HfCrBi, TiCrBi, and ZrCrBi respectively.

We attained excellent convergence.

Finally, the mechanical and thermodynamic properties of XCrBi (X=Hf, Ti, and Zr) are explored with the assistance of a code called thermo-pw [22].

3.0. Results and discussion

3.1 Structural Properties

Half-Heusler is generally described as XYZ with the space group F-43m (No216). The XYZ atoms occupy the 4b(0.50,0.50,0.50), 4c(0.25,0.25,0.25), and 4a(0,0,0) Wyckoff sites respectively.

Fig.1 Shows the crystal structure of HH alloys. Moreover: in this work, we used other Wyckoff sites given as X(0.00,0.00,0.00), Y(0.25,0.25,0.25), and Z(0.50,0.50,0.50) used by [23], 24] and also utilized in this study.

In Fig 2, the total energy E as a function of lattice constant has been computed for both the non-magnetic states and ferromagnetic states of the HH alloys XCrBi (X=Hf, Ti, and Zr). For the respective HH alloys, the ferromagnetic state has lower energy in contrast with the nonmagnetic state, concerning these results, it is inferred that the three HH alloys are ferromagnetic.

To attain the bulk Modules, equilibrium lattice parameters, and the pressure derivatives of XCrBi (X=Hf, Ti, and Zr) the total energies versus the lattice parameters for the ferromagnetic states is filled to the Murnaghan equation of state. The results are conferred in Table 1.

Table1; Calculate lattice parameters (a(Å)) the magnetic state (Mg) magnetic derivative (B$^{'}$), magnetic moment (μB), non-magnetic (NM) and ferromagnetic (FM), Theory (Ref. 26).

Compounds	Sources	M_g	a(Å)	B$^{'}$	μ_B
HfCrBi	This work	FM NM	6.4055 6.2684	64.6 93.7	3.11 -
	Theory	FM NM	6.5020 6.4020	82.7 99.6	2.97 -
TiCrBi	This work	FM NM	6.2568 6.0903	62.9 89.3	3.04 -
	Theory	FM NM	6.2568 6.0903	74.8 101.0	3.01 -
ZrCrBi	This work	FM NM	6.4218 6.2871	63.9 90.9	3.04 -
	Theory	FM NM	6.4218 6.2871	80.5 96.8	3.01 -

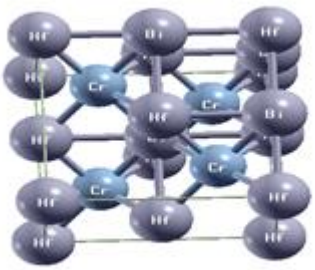


Figure 1(a): Crystal structure of HfCrBi HH alloy.

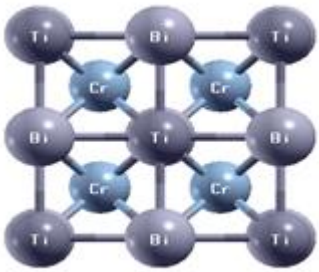


Figure 1(b): Crystal structure of TiCrBi HH alloy.

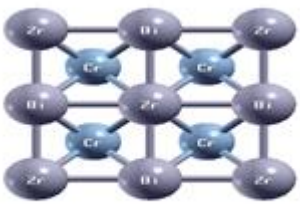


Figure 1(c): Crystal structure of ZrCrBi HH alloy

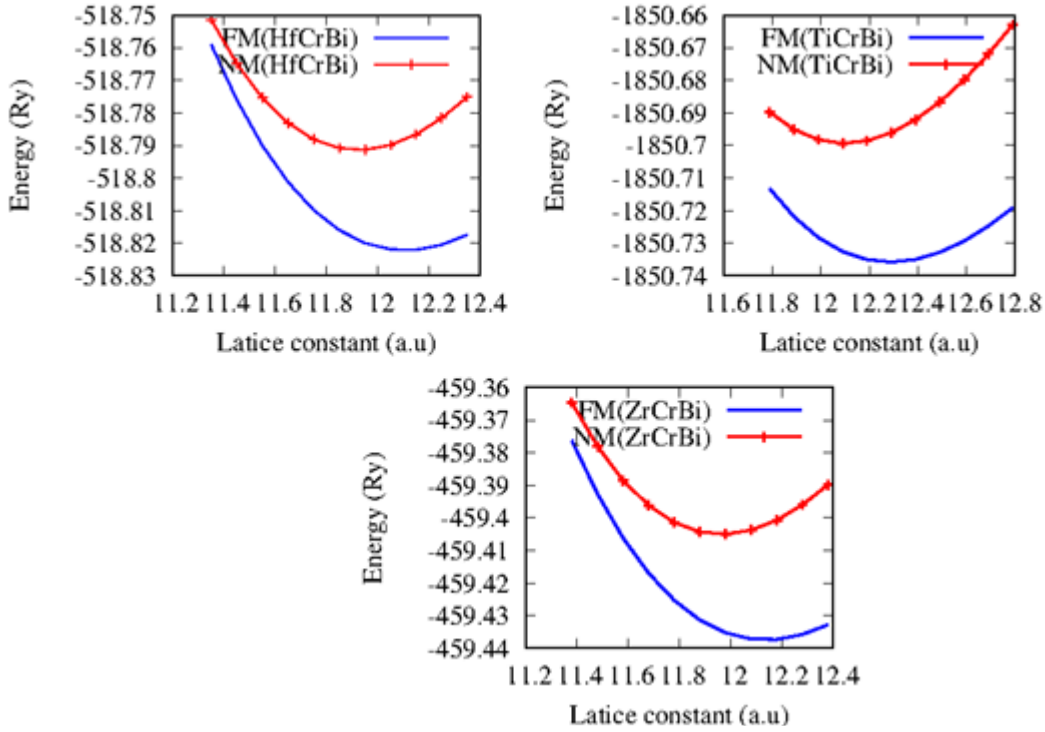


Figure 2: Total energies versus lattice constant for XCrBi (X=Hf, Ti and Zr) (a) HfCrBi (b) TiCrBi and (c) ZrCrBi HH alloys in the non-magnetic state (NM) and ferromagnetic state (FM).

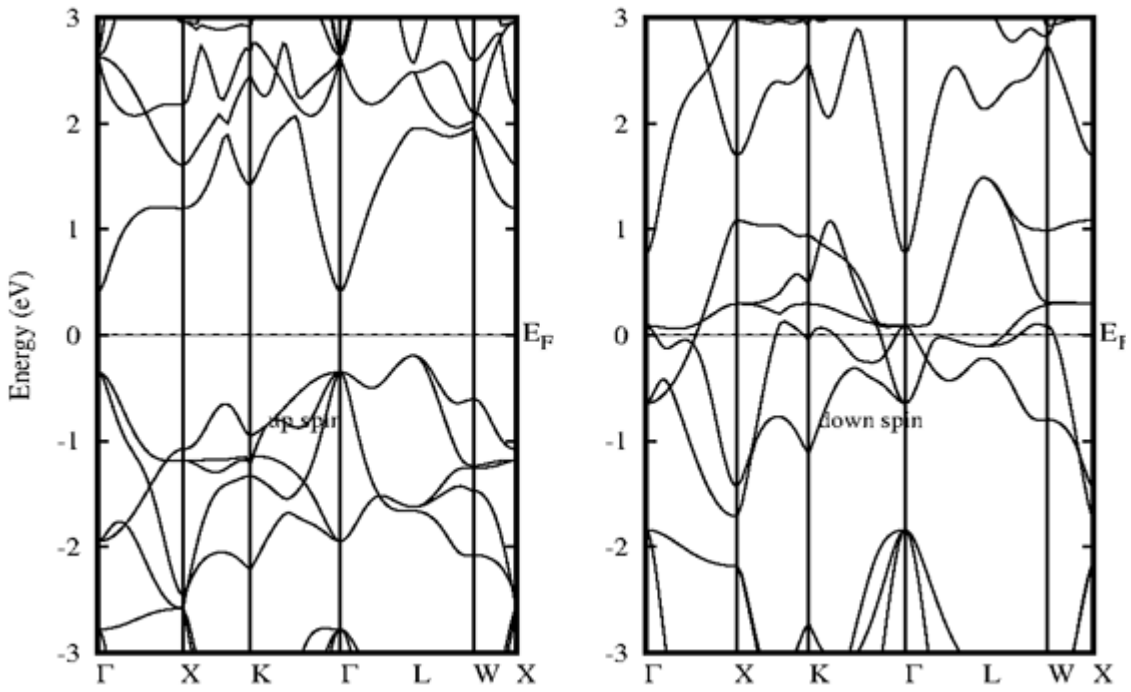


Figure3: The calculated band structures of HfCrBi for both spin channels.

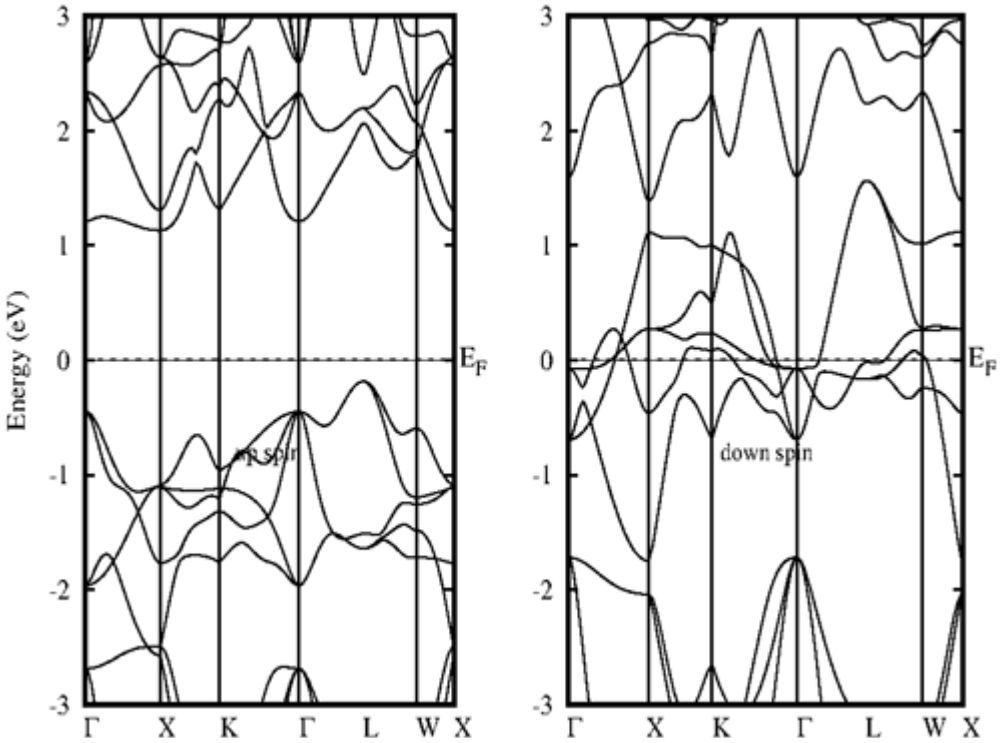


Figure 4: The calculated band structure of TiCrBi for both spin channels

3.2 Electronic and Magnetic Properties

After the structural optimization, the ferromagnetic states of XCrBi (X=Hf, Ti, and Zr) are used instantly to calculate the spin-resolved electronic band structures. The electronic structures of HfCrBi, TiCrBi, and ZrCrBi are shown in Fig. 3, 4, and 5.

The partial density of state (PDOS) of HfCrBi, TiCrBi, and ZrCrBi are exhibited in fig 6. It is observed in fig.3 that both spin channels for HfCrBi denote metallic conduct denoting that HfCrBi is not half-metallic, even if it is affirmed to be ferromagnetic. Figs 4 and 5 indicate that the two alloys have a semiconducting gap near the Fermi energy for spin-up channels when a metallic characteristic is established near the Fermi energy in the spin-down channels denoting that the two HH alloys are half-metals.

In Figs 6 (a), (b), and (c), it is indicated that TiCrBi and ZrCrBi are half-metals, HfCrBi which is metallic in both spin directions. the ZrCrBi and TiCrBi alloys are known to be direct-band semiconductors. The d orbitals of the atom possessing the Y position and the X are separated into doublet and triplet states, this is recognized as the crystal field effect. In between the two new states created, the triplet states have the higher energy. It is the triplet state that connects with the P state of the atom in the X position which creates bonding and anti-bonding.

In the course of the connection of the trip state of the atom in the Y atomic position and the P orbitals of the atom in the X atomic positions, the orbitals in the triplet state generally gain more electrons for being more electronegative, hereby possessing higher local magnetic moments (MM).

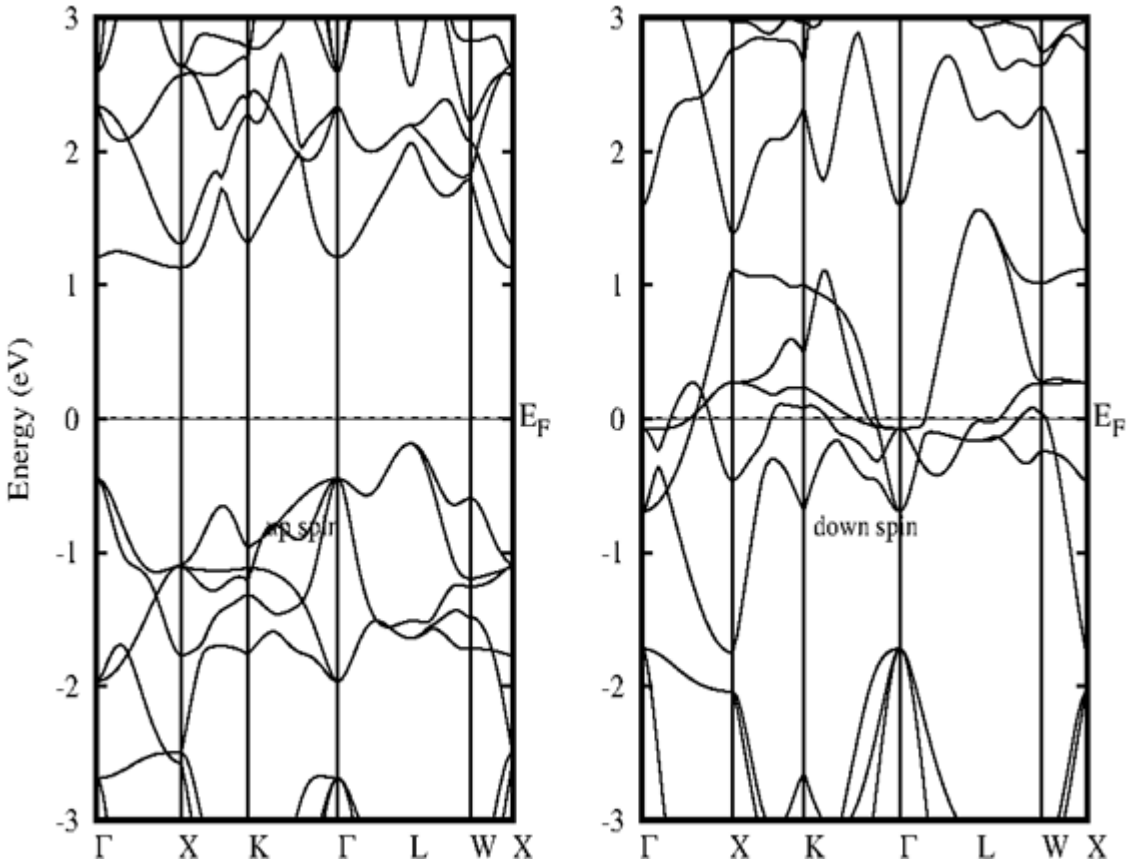


Figure 5: The calculated band structure of ZrCrBi for both spin channels.

Hence, in our conclusion majority of the local magnetic moments (MM) that constitute the local magnetic moments (MM) are upcoming from the atoms situated in the Y atomic position. The Y atom is leftover with some electrons when they constitute the local magnetic moments.
From Fig 6(a), there is a band crossing of the Fermi energy by the Hf's and the Bi-s orbital despite the crystal field splitting of the Cr-d orbitals split into the doublet and triplet states around the Fermi energy thereby making a gap in the spin-up channels. It is noticed that above the Fermi energy in the conduction band that there is a hybridization of the Bi-p orbital and the Cr-d orbital. The expression of the Slater-Pauling rules relates the number of the valence electrons per formula unit VN and the total magnetic moment per formula unit M by M=|VN-18|. This helps to check, the half-Heusler alloy is by nature ferromagnetic.

3.3 Mechanical and Thermodynamic properties

The criterion connected with the mechanical properties includes the elastic constants, the shear modulus, the young modulus, Poisson's ratio, the anisotropic factor, and the B/G ratio. These parameters have been calculated for HfCrBi, TiCrBi, and ZrCrBi as presented in Table 2, it is noticed that the three alloys are mechanically stable as established by the mechanical stability criteria displayed in equation 1 below [25-26].

$C11>0, C44>0, C11>C12, C11+C12>0, C11-C12>0$ (1)

Where C11, C12, and C44 are the elastic constant regularly linked with cubic materials.

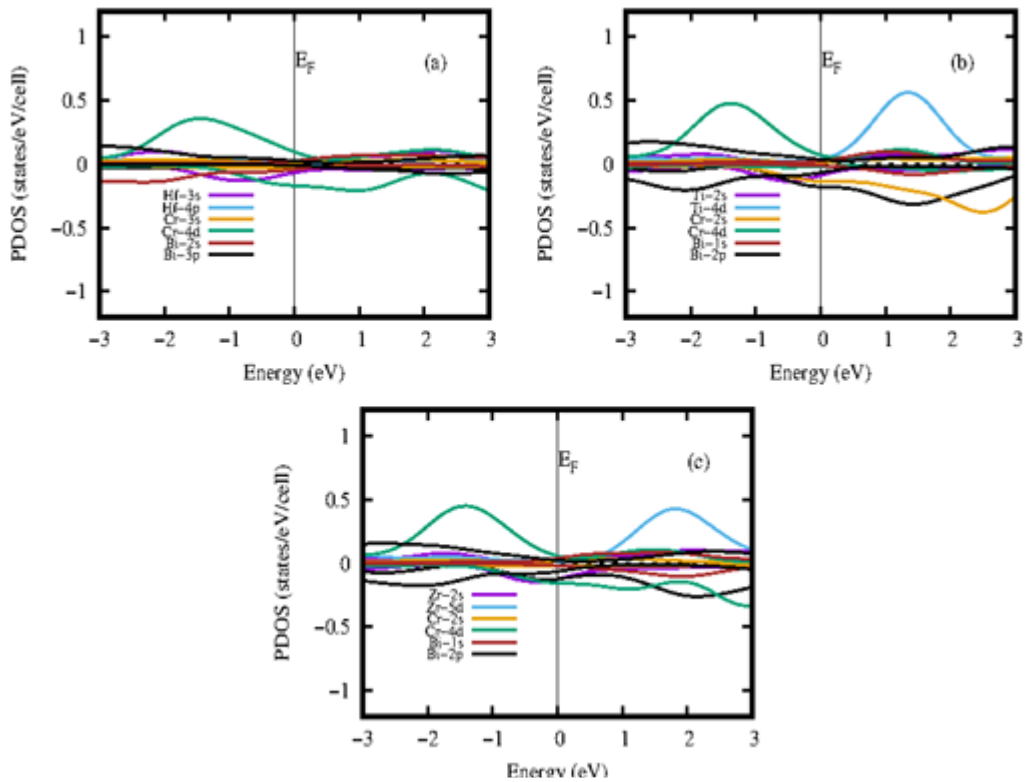


Figure 6: The calculated partial density of states of (a) HfCrBi (b) TiCrBi and (c) ZrCrBi for both spin channels.

The Young modulus and shear modulus computed indicates how resistive a compound can be when subjected to volume and shear deformation respectively. More so, the B/G ratio is a vital parameter that discloses if a material is ductile or brittle in nature the critical value of the B/G ratio is 1·75· if B/G ratio greater 1·75 than, the material is ductile but ratios 3·37, 5·03, 3·56 for HfCrBi, TiCrBi, and ZrCrBi evidently depict that the alloys are ductile·

3.4. Lattice Dynamics

The phonon dispersion spectra of the three Half-Heusler alloys been examine, have three acoustic modes and six (6) optical modes are sufficient to have real frequencies, this indicates that the compounds in Half-Heusler structure are stable since there is no negative frequencies. Fig.8 (a-c) are plots of phonon dispersion spectra along Γ→X→ K→ Γ → L→ W→X brillouin zone for HfCrBi, TiCrBi and ZrCrBi compounds respectively. To the best of my knowledge, there is no study in literature examining the vibrational properties of these alloys for us to compare experimental data. The three (3) acoustic modes of the compounds are different quantitatively and similar qualitatively and a similar appearance is the peaks of their dispersion are observed at point L. The six (6) optical modes are in the frequency range of 150 cm^{-1} to 250 cm^{-1}, and are seen to be entirely similar, and can be associated with the corresponding contribution from Hf, Ti and Zr.

Table 2; The Calculated elastic constants C11, C12 and C44, Young Modulus E, Shear Modulus G, anisotropy A, Bulk Modulus B, B/G ratio and the Poisson's ratio of HfCrBi, TiCrBi and ZrCrBi, Theory (Ref. 26).

Compounds	Sources	HfCrBi	TiCrBi	ZrCrBi
C_{11} (GPa)	This work Theory	159.80 105.91	151.34 80.81	152.69 106.96
C_{12} (GPa)	This work Theory	84.30 70.06	94.86 52.27	84.61 71.47
C44 (GPa)	This work Theory	29.06 26.12	18.88 31.03	27.53 26.35
B (GPa)	This work	109.47	113.69	107.30
E (GPa)	This work	88.80	63.64	82.66
A	This work	0.77	0.67	0.81
B/G	This work	3.37	5.03	3.56
ν	This work	0.37	0.41	0.37

Table 3: The Calculated specific heat capacity C_v (J / Kmol) at 300K, Debye temperature θ_D(K), Zero-point energy E_o (KJ/Nmol), and the average sound velocity V_{av} (M/S) for the three compounds.

Compounds	C_v	θ_D	E_o	V_{av}
HfCrBi	73.39	202.60	5.69	1875.62
TiCrBi	73.46	198.75	5.58	1793.04
ZrCrBi	73.03	218.76	6.14	2032.07

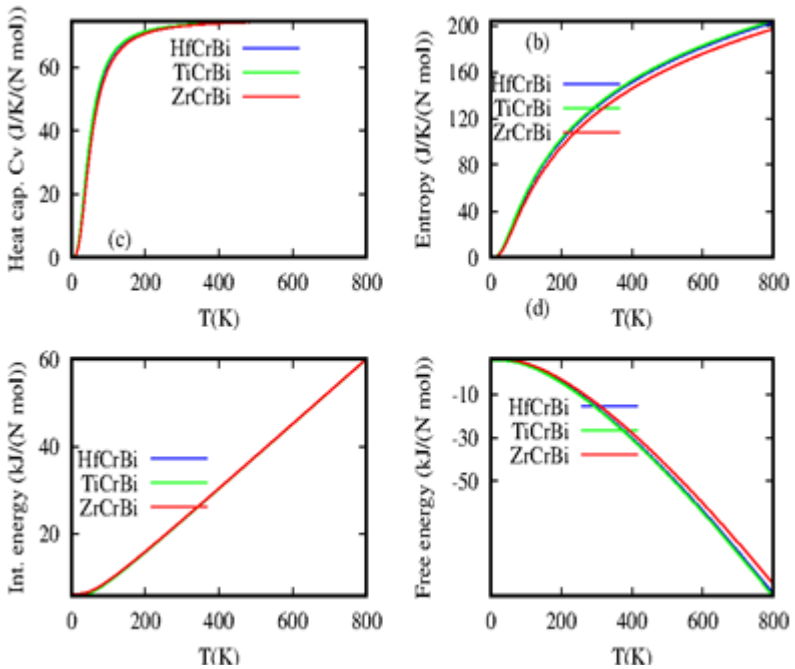
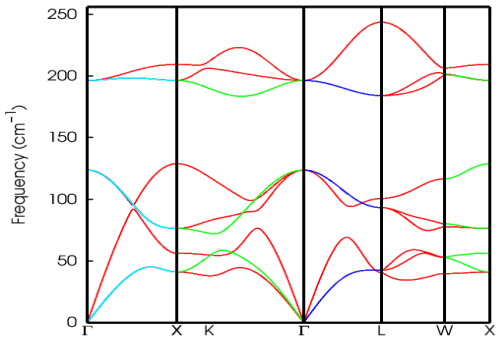
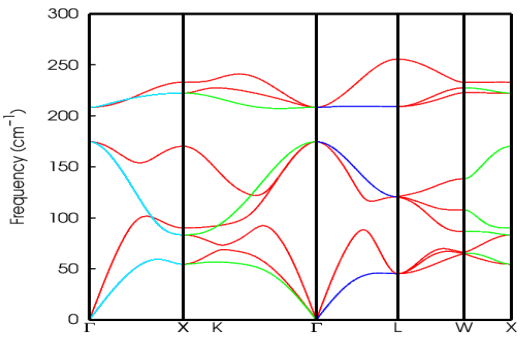


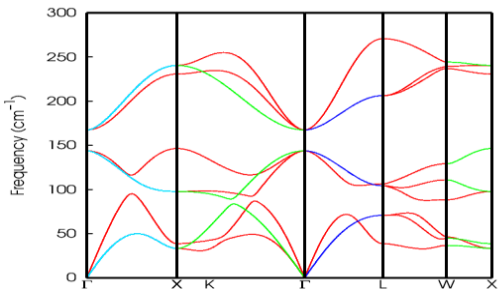
Fig.7: The Calculated (a) Specific heat capacity, (b) the entropy (c) internal energy and (d) Gibb's free energy for XCrBi (X=Hf, Ti and Zr)



(a) HfCrBi



(b) TiCrBi



(c) ZrCrBi

Fig.8: Phonon dispersion spectra for (a) HfCrBi (b) TiCrBi (c) ZrCrBi half-Heusler compounds.

4.0 **Conclusion**

We have examined the structural, elastic and electronic properties of DFT Calculation. The electronic properties indicates that TiCrBi and ZrCrBi are half–metals excluding HfCrBi which nearly have a gapless state close to the Fermi energy. The three HH alloys are found to be thermodynamically, and mechanically stable and are ductile because their B/G is greater than the critical value of 1·75·

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