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STRUCTURAL, THERMAL, AND ELECTRONIC INVESTIGATION OF $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) HALF-HEUSLER ALLOYS[†]

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This article presents the theoretical evaluation of the structural, mechanical, thermal and electrical properties of half-Heusler $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys in the framework of density functional theory (DFT) that is implemented in WIEN2k code. Equilibrium lattice parameters are found agree with previous literature. Several calculated mechanical properties are revealed that all studied alloys are mechanically stable. According to the critical values for B/G, Ni-doped $ZrCoBi$ alloys are ductile, whereas $ZrCoBi$ and $ZrNiBi$ are brittle. The band structure and density of states of the present compounds show that $ZrCoBi$ has a semiconducting nature, while Ni-doped $ZrCoBi$ has a half-metallic nature. The structural reforms, brought to $ZrCoBi$ as the Ni-dopant concentration increases at the site of Co-atom, showed an increase in its metallicity, conductivity and ductility, and a decrease in its rigidity, stiffness, minimum thermal conductivity, melting and Debye temperatures. According to the results obtained, $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys could have potential thermal and electronic applications.
Keywords: ZrCoBi; First principles; Half-Heusler compounds; Electronic structure; Ni/Co Substitution
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Heusler alloys have been exploring since their first find in 1903 by Friedrich Heusler [1] for their promising characteristics, such as semi-metallicity [2], tunable band gap [3], magnetism [4], thermoelectricity [5], etc. Accordingly, they can be utilized, for instance, in piezoelectric [6], spintronics [7], optoelectronic [8], thermoelectric [9], shape memory alloys [10], and solar cell applications [11]. Half-Heusler alloys, with crystallize of $MgAgAs$ structure, have a 1:1:1 stoichiometry formulation XYZ with the $F\bar{4}3m$ space group [1]. X and Y atoms are the d- or f-block rare-earth or transition elements and Z is the p-lock element [12]. The half-Heusler alloys which have 18 valence electrons (VE) exhibit semiconductors behavior, and the other alloys own a metallic character. The semiconductors half-Heusler alloys are closed-shell species, non-magnetic and semiconducting [13].

Nasir Mehmood et al. [14] have studied the structural, mechanical, elastic, electronic, magnetic, and optical properties theoretically of half-Heusler alloys RhCrZ (Z = Si, Ge). They found that both alloys are half-metallic, ductile, weak ferromagnetic, optically metallic and become transparent above 17 and 13 eV, respectively. Osafile O.E. et al. [15] reported a ductile half-metallic character in the γ- phase of the novel half-Heusler ZrMnAs (VE=16) alloy. They showed that ZrMnAs had a promising application in spintronics devices.

Bismuth-based materials have recently attracted many researchers. Yazdani-Kachoei, M. et al. [16] have investigated the structural and electronic properties of ZrCoBi and ZrRhBi. They found that these alloys have high Seebeck coefficient and low electrical conductivity making them good candidates for thermoelectric applications. Gokhan Surucu et al. [17] have shown that γ-phase structure of XCoBi (X: Ti, Zr, Hf) half-Heusler alloys has the most stability structure depending on the computed formation enthalpies, Cauchy pressures and energy-volume dependencies. Hangtian Zhu et al. [18] have studied the thermoelectric performance of ZrCoBi-based half-Heuslers. They demonstrated that the ZrCoBi-based half-Heuslers are quite promising for mid- and high-temperature thermoelectric power generation.

Therefore, it is worthy to study this promising field to enhance its usage capability as well as to discover new compounds for further investigations. In this study, I aim to use the ab-initio calculations to investigate the structural, mechanical, thermal and electronic properties of Co substituting by Ni atoms in the half-Heusler ZrCoBi alloy, with concentration of 25%, 75% and 100%.

This paper is arranged as follows: Section "METHOD OF CALCULATIONS" describes the calculations method; Section "RESULTS AND DISCUSSION" presents the results and discussion of the calculated parameters. While, Section "CONCLUSION" recaps the mentioned and analyzed results.

METHOD OF CALCULATIONS

In this study, the calculations were performed using Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method that depend on the density functional theory (DFT) [19], which is implemented in WIEN2k code [20]. For exchange-correlation (XC) potential, the generalized gradient approximation Perdew-Burke-Ernzerhof (PBE-GGA) is used [21]. The structural and electronic properties of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys were computed with 3000 k-points. The plane wave is applied in the interstitial site with a cutoff energy of K_{max} = 8.0 /R_{MT} where R_{MT} is the smallest of all atomic sphere radii. The k-points and $K_{max}R_{MT}$ values were estimated by the convergence test. The muffin-tin sphere radii (MT) were chosen to be 2.35,

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2.35 (2.37) and 2.47 a.u. for Zr, Co (Ni) and Bi, respectively. The self-consistent calculations are converged when the determined total energy and charge of the crystal became lower than 0.1×10^{-3} Ry and 0.1×10^{-3} e, respectively. The three independent elastic constants (C_{11}, C_{12} and C_{44}) are calculated from stress tensor matrix under small strains. These constants are used to investigate the elastic and thermal properties. The elastic constants, Cij, were obtained by Charpin method using ElaStic code which is integrated within WIEN2k code [22]. The elastic constants are used to investigate the elastic and thermal properties.

RESULTS AND DISCUSSION

Structural properties

In the first step, the ground state structure characteristics of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys have been carried out at 0 K and 0 GPA. The cubic half-Heusler $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys, which has $F\bar{4}3m$ space group, have Wyckoff positions at (0, 0, 0)a, $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$b, and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$c for Zr, Co (Ni) and Bi atoms, respectively. The optimized lattice constant (a) and bulk modulus (B) are calculated using Birch-Murnaghan's equation of states [23], as listed in Table 1 and shown in Fig. 1. The computed lattice parameters of ZrCoBi and ZrNiBi alloys are in agreement with the experimental study explained in ref. [24]. It is found that the unit cell volume of ZrCoBi increases directly with Ni-dopant concentration. This allows us to predict that ductility of alloys decreases as going from ZrCoBi to ZrNiBi alloy.

Table 1. The calculated lattice constant (a in Å), bulk modulus (B in GPa) and formation energy (ΔH_f in eV/unit cell) of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys.

Alloys	a (Å)	B (GPa)	ΔH_f (eV/unit cell)
$ZrCoBi$	6.232 6.179 [24]	126.10	-3.76
$ZrCo_{0.75}Ni_{0.25}Bi$	6.258	114.526	-14.47
$ZrCo_{0.25}Ni_{0.75}Bi$	6.280	99.695	-13.49
$ZrNiBi$	6.291 6.148 [24]	103.544	-3.26

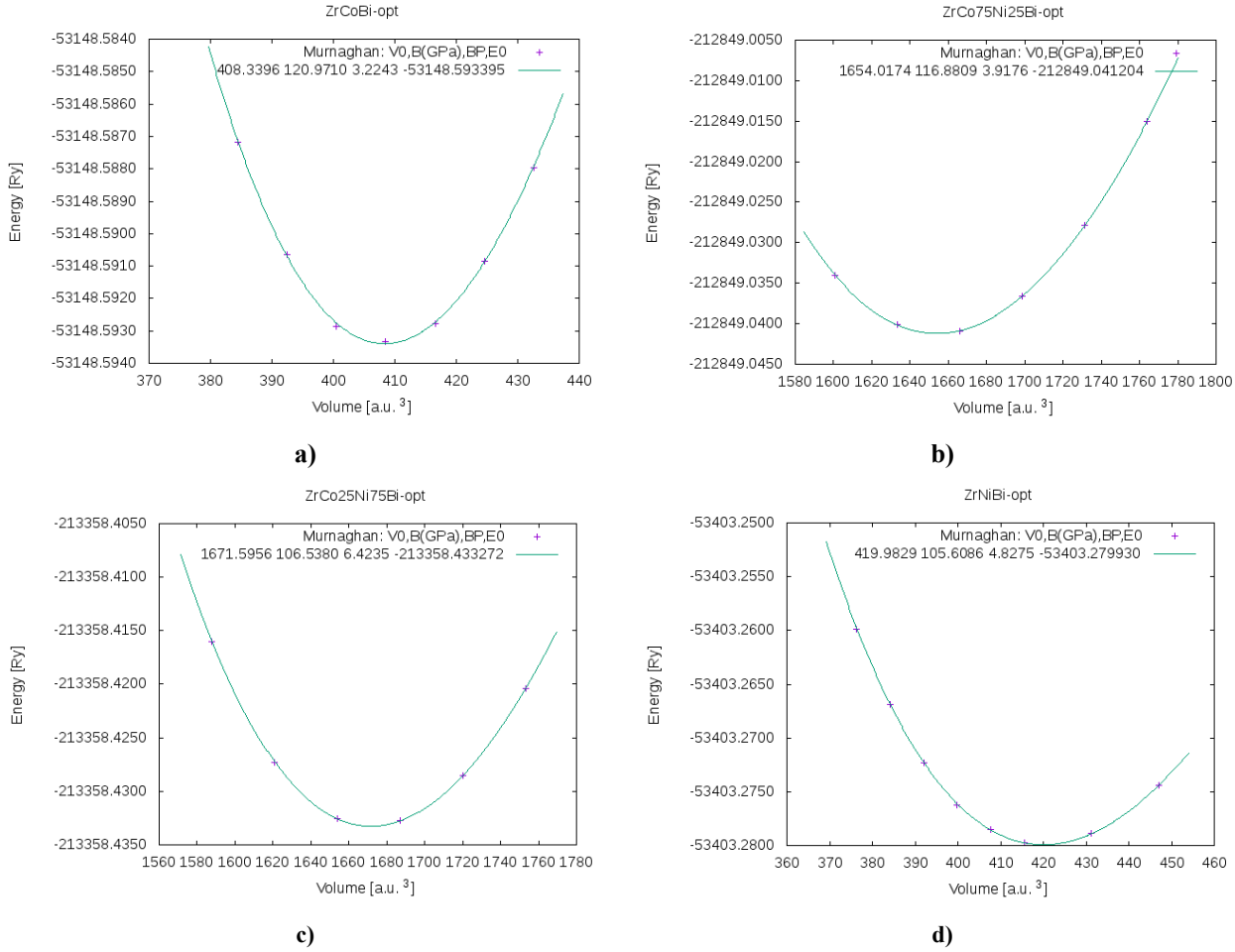

Figure 1. The energy-volume optimization graphs of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys (a) $ZrCoBi$; (b) $ZrCo_{0.75}Ni_{0.25}Bi$; (c) $ZrCo_{0.25}Ni_{0.75}Bi$; (d) $ZrNiBi$.

In order to study the stability of $ZrCo_{1-x}Ni_xBi$ alloys, the formation energy (ΔH_f) are calculated by comparing the fully minimized total energies ($E_{ZrCo_{1-x}Ni_xBi}$) with content atoms (E_{atom}) energies. ΔH_f is represented mathematically by

$$\Delta H_f = E_{ZrCo_{1-x}Ni_xBi} - n_{Zr}E_{Zr} - n_{Co}E_{Co} - n_{Ni}E_{Ni} - n_{Bi}E_{Bi} \quad (1)$$

where, n_{Zr}, n_{Co}, n_{Ni} and n_{Bi} are Zr, Co, Ni and Bi atoms numbers in the $ZrCo_{1-x}Ni_xBi$ unit cell, respectively.

The computed ΔH_f values for current compounds are negative, see Table 1, suggesting that these compounds are thermodynamically stable and can be synthesized experimentally.

The determination of three elastic constants, C11, C12 and C44, of a cubic alloy takes an important role. These constants are utilized to understand the mechanical characteristics. For instance, studying alloy behavior under mechanical stress provides acquaintance about its elastic rigidity and stability. Stress-strain method that is implemented in ab initio calculations makes it possible to determine these values with high precision. The calculated elastic parameters of the present alloys are listed in Table 2. The calculated values of Cij satisfy the mentioned criteria formulae, $(C_{11} + 2C_{12})/3 > 0$; $C_{44} > 0$; $(C_{11} - C_{12})/2 > 0$; $C_{12} < B < C_{11}$, which is confirmed that the alloys are mechanically stable [25]. Moreover, it is noticed that C_{11} constant is quite higher than C_{12} and C_{44} constants for all studied alloys, leading to the fact that the alloys have higher resistance to be compressed in the x-direction. It is found that C_{11} values are 257.98%, 295.42%, 250.02%, and 220.73% higher than C_{44} for ZrCoBi, $ZrCo_{0.75}Ni_{0.25}Bi$, $ZrCo_{0.25}Ni_{0.75}Bi$, ZrNiBi, respectively. Hence, ZrNiBi alloy has the lowest resistance, while $ZrCo_{0.75}Ni_{0.25}Bi$ has the highest resistance. Ni-doping modifies the whole alloy's microstructure and consequently increases its resistance to be compressed [26].

Table 2: The determined bulk modulus (B in GPa), shear modulus (G in GPa), Young's modulus (E in GPa), the three independent elastic constants (C_{11}, C_{12} and C_{44} in GPa), B/G ratio, Vicker's hardness (H_v in GPa), Cauchy pressure ($C_{12} - C_{44}$ in GPa), elastic anisotropy (A) and Kleinman parameter (ξ) of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1)

Properties		$ZrCoBi$	$ZrCo_{0.75}Ni_{0.25}Bi$	$ZrCo_{0.25}Ni_{0.75}Bi$	$ZrNiBi$
$B = (C_{11} + 2C_{12})/3$	(GPa)	126.048	114.798	100.071	104.134
G		81.662	60.663	51.535	89.086
E		201.476	154.733	131.954	207.957
C_{11}		257.585	212.045	173.141	249.533
C_{12}		60.279	66.175	63.537	31.435
C_{44}		71.955	53.625	49.465	77.801
B/G		1.544	1.892	1.942	1.169
H_v (GPa)		12.681	8.150	7.051	18.501
Cauchy pressure $(C_{12} - C_{44})$ (GPa)		-11.6755	12.5497	14.0711	-46.3662
ξ		0.385	0.459	0.509	0.277
A		0.729	0.735	0.907	0.713

The bulk modulus, $B = (C_{11} + 2C_{12})/3$, describes the resistance to fracture deformation. The calculated B values from Cij agrees those determined by Birch-Murnaghan's equation of state, see Table 1. This assures the reliability of the computed elastic constants in the present study. The bulk modulus is found to decrease with increasing of the concentration of Ni-dopant and the unit cell volume; which articulates that the rigidity diminishes as going from ZrCoBi to $ZrCo_{0.25}Ni_{0.75}Bi$, with a minute increase in the rigidity in ZrNiBi alloy.

The elastic anisotropy of any material leads to the generation of microcracks and lattice distortion during and after the production process that limits its durability in practical applications. Therefore, evaluating the anisotropy factor, $A = 2C_{44}/(C_{11} - C_{12})$, of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys is necessary for development purposes. The alloy is presumed to be fully isotropic for $A = 1$, else the alloy is anisotropic. The $ZrCo_{1-x}Ni_xBi$ alloys are considered anisotropic as all calculated A values are deviating from 1 with $ZrCo_{0.25}Ni_{0.75}Bi$ being the lowest anisotropic alloy compared to the other alloys, as listed in Table 2.

Pugh's index of ductility ratio (B/G) value is used to examine the ductile and brittle character of the alloys. The alloy assumes brittle if this ratio is less than 1.75, otherwise it behaves in a ductile nature [27]. From the results in Table 2, I predict that the ZrCoBi and ZrNiBi alloys have a brittle nature with ZrCoBi is more rigidity than ZrNiBi. Whereas $ZrCo_{0.75}Ni_{0.25}Bi$ and $ZrCo_{0.25}Ni_{0.75}Bi$ classify as ductile alloys and ZrCo0.25Ni0.75Bi is more ductility than ZrCo0.75Ni0.25Bi.

I have also calculated the shear Modulus ($G = \left(\frac{1}{2}\right)(C_{11} - C_{12})$, to comprehend the dynamical stability of the alloys. The present alloys display a dynamical stability structure since $G > 0$.

The Young's modulus ($E = (9BG)/((3B) + G)$ is used to examine the stiffness of the alloys. Strong covalent bonds, where the alloys have also high rigidity, are expected when Young's modulus has a high value. Our results point out that the alloys stiffness decreases as increases the concentration of Ni-doped atom. This decreasing is due to the replacement of weak ionic bonds over covalent bonds in this case. Vicker's hardness criteria, $H_V = 0.92(G/B)^{1.137}G^{0.708}$, is used to check the alloys resisting ability. It is figured out that as Ni-dopant concentration increases, the alloy resistance ability to be dented

decreases. Pettifor and Johnson [28,29] suggested that the Cauchy pressure ($C_{12} - C_{44}$) parameter explains the nature of atomic bonding domination in the alloys. It is typically negative for directional bonding where the covalent bonds are majority. In this case the material resists against the shear strain (C_{44}) more strongly than with the volume change (C_{12}), whereas it is positive when ionic bonding is dominant. As shown in Table 2, the Cauchy pressure for ZrCoBi and ZrNiBi has a negative value, which portrays that the covalent bonding is a majority. While, for $ZrCo_{1-x}Ni_xBi$ (x = 0.25 and 0.75) Cauchy pressure's value becomes positive upon alloying with Ni, pointing out a domination of ionic bonding for the Ni-doped alloys. Additionally, the dimensionless Kleinman parameter (ξ) is used to examine the prospect of the alloys to be stretched or bended. If ξ is close to zero (one), maximum bond stretching (bending) is expected, respectively. Among the studied alloys, $ZrCo_{0.25}Ni_{0.75}Bi$ has the highest ξ, while ZrNiBi has the smallest ξ. This leads to the fact that $ZrCo_{0.25}Ni_{0.75}Bi$ (ZrNiBi) alloy possesses minimum (maximum) bond stretching, respectively.

Thermal properties

In this subsection, I inspect the thermal characteristics, such as minimum thermal conductivity (Λ_{min}), sound velocities, Debye (Θ) and melting (T_M) temperatures, as listed in Table 3. The Debye temperature, $\Theta = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{\frac{1}{3}} V_m$, is an important parameter correlating with many physical and thermal properties of materials [27]. Where N_A, k and h are Avogadro, Boltzmann's and Plank's constants; M and ρ are molecular weight and density of the alloy; n is atoms number in a single cell and V_m stands for average sound velocity. V_m, $V_m = \left[\frac{1}{3}\left(\frac{2}{\upsilon_t^3} + \frac{1}{\upsilon_l^3}\right)\right]^{-\left(\frac{1}{3}\right)}$, can be calculated straight forward from the computed longitudinal ($\upsilon_l = \sqrt{\frac{3B+4G}{3\rho}}$) and transverse ($\upsilon_t = \sqrt{\frac{G}{\rho}}$) acoustic velocities. According to the results listed in Table 3, it is found that longitudinal acoustic velocity is larger than transverse acoustic velocity for all examined alloys. Additionally, longitudinal acoustic velocity specifically along [100] directions is the highest. The computed melting temperature $\left(T_M 553 + \frac{(5.91 \times C_{11})}{GPa}\right)$ and Debye values suggest that the present alloys are tolerable candidates in electronic high-temperature applications. The suggested operational temperature T for electronic apparatuses must be restricted between Debye and melting temperatures, i.e. ($\theta < T < T_M$).

Table 3. The average wave velocity (V_M in km/s), the longitudinal elastic wave velocity (υ_l in km/s), the transverse elastic wave velocity (υ_t in km/s), Debye temperature (Θ in K), melting temperature (T_M in K), the longitudinal and transverse sound velocities along specific directions ([100], [110], and [111]), minimum thermal conductivity at 0 K ($\Lambda_{min}(WK^{-1}m^{-1})$), and minimum thermal conductivity along specific directions ([100], [110], and [111]) of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1).

Properties	$ZrCoBi$	$ZrCo_{0.75}Ni_{0.25}Bi$	$ZrCo_{0.25}Ni_{0.75}Bi$	$ZrNiBi$
$V_M(km/s)$	3.190	2.763	2.549	3.309
$\upsilon_l(km/s)$	4.883	4.457	4.140	4.758
$\upsilon_t(km/s)$	2.879	2.481	2.287	3.008
Θ (K)	349.315	333.034	307.193	362.375
$T_M \pm 300$ (K)	2075.329	1806.184	1576.263	2027.737
$\upsilon_l[100](km/s)$	5.113	4.639	4.193	5.034
$\upsilon_l[110](km/s)$	4.840	4.423	4.128	4.708
$\upsilon_l[111](km/s)$	4.746	4.348	4.106	4.594
$\upsilon_t[100](km/s)$	2.702	2.333	2.241	2.811
$\upsilon_t[110](km/s)$	4.475	3.848	3.336	4.706
$\upsilon_t[111](km/s)$	3.018	2.598	2.320	3.165
$\Lambda_{min}(WK^{-1}m^{-1})$	0.3171	0.3401	0.3146	0.3211
$\Lambda_{min}[100](WK^{-1}m^{-1})$	0.3134	0.3359	0.3132	0.3176
$\Lambda_{min}[110](WK^{-1}m^{-1})$	0.4110	0.4375	0.3899	0.4208
$\Lambda_{min}[111](WK^{-1}m^{-1})$	0.3213	0.3446	0.3158	0.3256

Knowing thermal conductivity is vital to ease predicting the thermal characteristics of a specific alloy. The thermal conductivity decreases with elevating temperature up to a particular limit which is referred to as minimum thermal conductivity (Λ_{min}). The determination of minimum thermal conductivity is important to enhance the thermal performance of the alloys under investigation. I have calculated Λ_{min} by Cahill model [30] that is given by the following formula:

$$\Lambda_{min} = \frac{(k_b)}{2.48}(n_o)^{\frac{2}{3}}(\upsilon_l + 2\upsilon_t), \text{ at } 0K \text{ for all alloys} \quad (2)$$

where n_o is the atoms number per unit volume.

To extend our knowledge of the minimum thermal conductivity effect along specific directions. Where these directions make is easy to grow crystals intentionally to design maximal or minimal thermally conductive devices. From our results enlisted in Table 3, I have observed that all $ZrCo_{1-x}Ni_xBi$ alloys have low thermal conductivity making them good candidates for high temperature applications such as thermal barrier coatings. However, it is found that $ZrCo_{0.25}Ni_{0.75}Bi$ has the smallest value of minimum thermal conductivity in all studied directions. The reduced value of thermal conductivity can be a result of substitutional point defect scattering induced by the Ni-dopant [31].

Electronic properties

The partial, total density of states (PDOS and TDOS), and band structure of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloy are shown in Figs. 2 and 3, respectively. The properties of the studied alloys are demonstrated based on the electron's behavior around the Fermi level. Figures 2a and 3a show the semiconductor nature of ZrCoBi alloy with a band gap value of 0.99 eV. This gap is confined between the d-states of Zr and Co and p-state of Bi in the valence band at Γ symmetry line the X symmetry line of d-states for Zr and Co in the conduction band. The computed band gap value of ZrCoBi agrees with that found in the previous literatures [32].

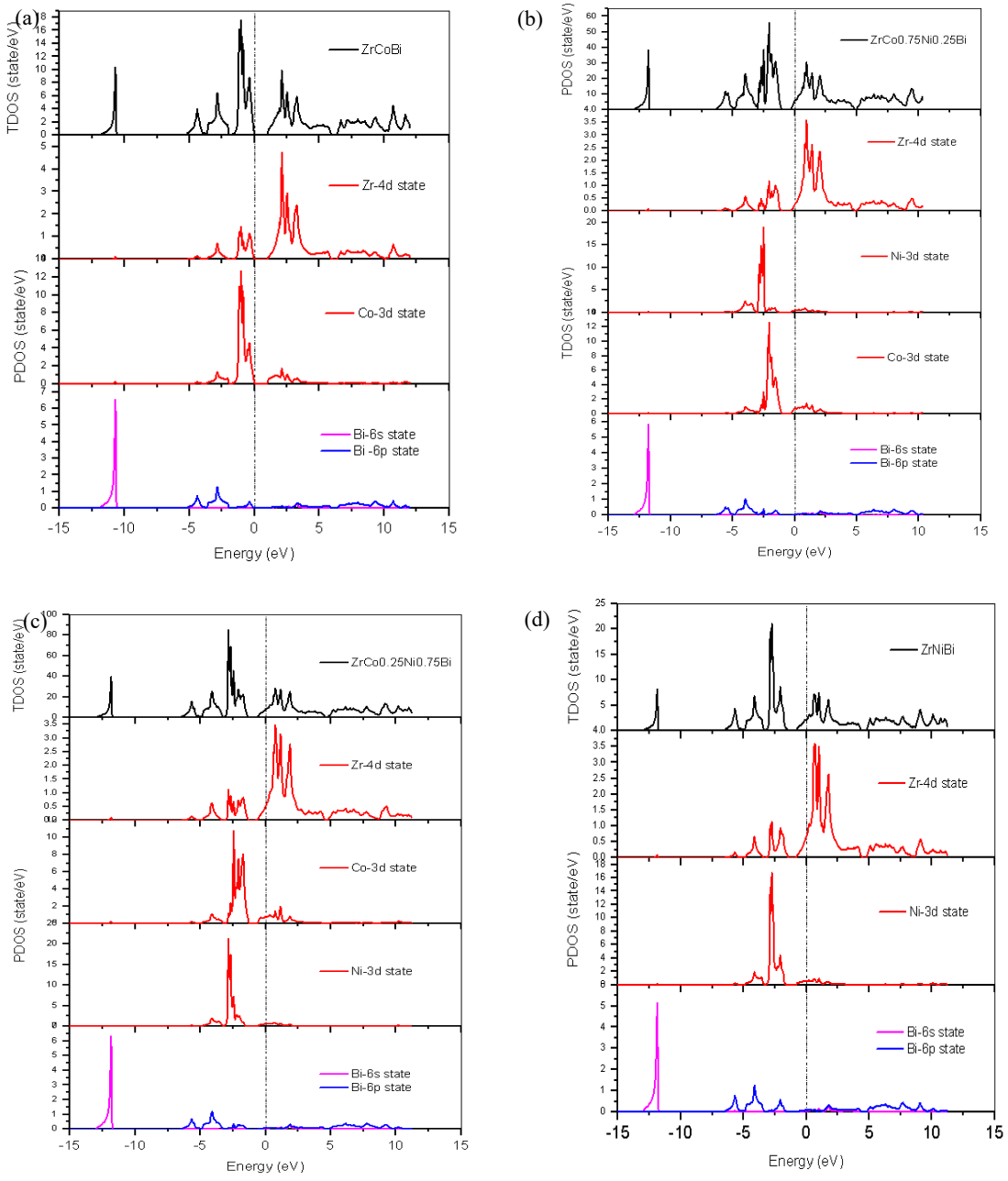

Figure 2. Graphs for density of states (TDOS and PDOS) of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1). The dashed lines represent Fermi level: (a) $ZrCoBi$; (b) $ZrCo_{0.75}Ni_{0.25}Bi$; (c) $ZrCo_{0.25}Ni_{0.75}Bi$; (d) $ZrNiBi$

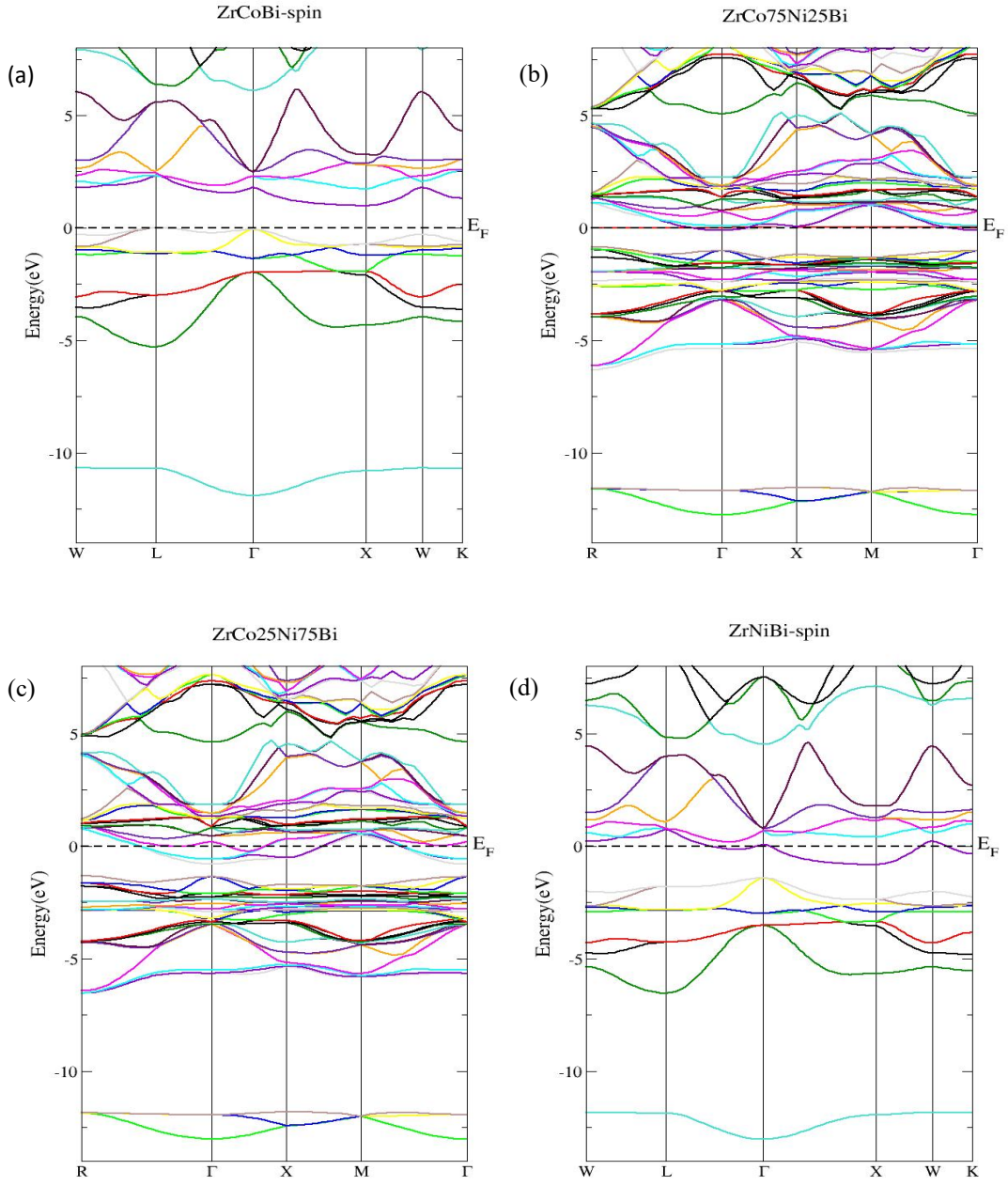

Figure 3. Graphs for energy band structure along the symmetry points of $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1). The dashed lines represent Fermi level: (a) $ZrCoBi$; (b) $ZrCo_{0.75}Ni_{0.25}Bi$; (c) $ZrCo_{0.25}Ni_{0.75}Bi$; (d) $ZrNiBi$.

It is noticed that Ni-doping increases the number of valence electrons, and shifts the electronic states of the content atoms for the ZrCoBi alloy to the low energy level. The d-state of Zi and Co crosses Fermi level and changes the alloy nature from semiconducting to half-metallicity. This doping changes the band gap to the direct (Γ-Γ) and decreases this gap to 0.62 and 0.24 eV for ZrCo0.75Ni0.25Bi and ZrCo0.25Ni0.75Bi, respectively. Our electronic results agrees with the previous calculations [33,34].

In order to study the bonding nature of $ZrCo_{1-x}Ni_xBi$ alloys, the charge density difference is also performed. Figure 4 displays the charge density difference along (110) plane that uses to explain the bonding nature of the $ZrCo_{1-x}Ni_xBi$ alloys. The charge contours are perfectly spherical and isolated around $Co-Ni$, $Bi-Co$, $Bi-Ni$ and $Zr-Bi$ atoms that denote the ionic bonding among them. However, the charge contours for Zr are not completely spherical and dented which means the electronic orbit is not fully filled. The charges transfer from Zr to Co and Ni due to the electronegativity difference. This creates the induced dipole moment toward Zr atom. The charge contours around Zr – Co and Zr – Ni atoms denote the covalent bonding among them. The $Zr-Bi$ and $Bi-Co$ ($Bi-Ni$) ionic bonds are existed due to pd-hybridization between Zr 3d and Bi 5p states and from pd-hybridization of Bi 5p and Co 3d (Ni 3d), respectively. It can be assumed that bonding nature of the current alloys is a mixed between a covalent and ionic bond.

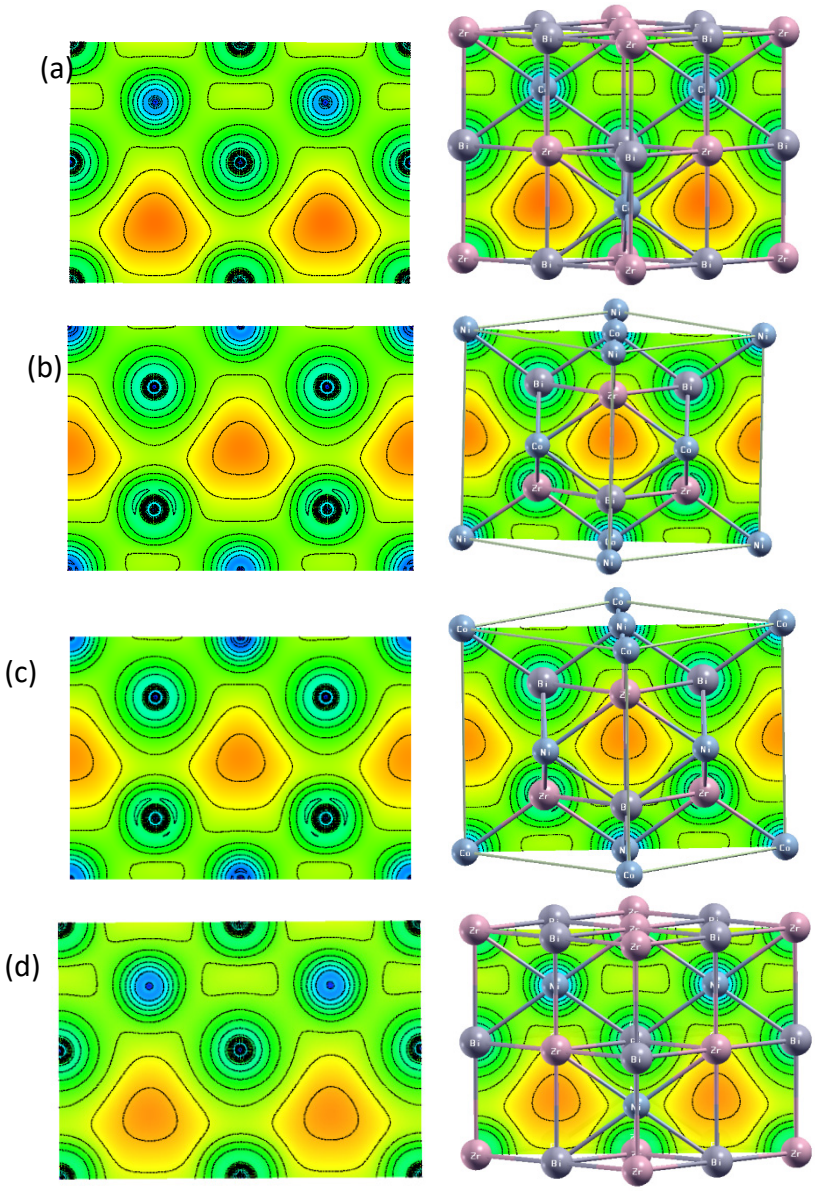

Figure 4. The charge density difference diagrams along (110) plane of (a) $ZrCoBi$, (b) $ZrCo_{0.75}Ni_{0.25}Bi$, (c) $ZrCo_{0.25}Ni_{0.75}Bi$, and (d) $ZrNiBi$

CONCLUSION

In this article, I have carried out ab initio study on $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys, predicting their structural, thermal and electronic characteristics using full-potential linearized augmented plane wave method.

I enumerate the important conclusions of our DFT calculations as follows:

(i) All studied alloys are mechanically, thermodynamical stable and can be formed depending on formation energy, elastic constants and elastic moduli criteria.

(ii) It is found that $ZrCo_{1-x}Ni_xBi$ elastic moduli, rigidity, stiffness, resistance to be dented, Debye and melting temperatures, minimum thermal conductivity, and band gap energy decrease as Ni-atom concentration in Co site increases.

(iii) It is also found that $ZrCo_{1-x}Ni_xBi$ ductility, metallicity, conductivity, and ionic bonding nature increase as Ni-atom concentration in Co site increases.

(iv) The band gab calculation shows that $ZrCoBi$ exhibits a semiconducting behavior, whereas Ni-doped $ZrCo_{1-x}Ni_xBi$ has a metallic character.

(v) C_{11} for all studied alloys are larger than C_{12} and C_{44}, hence all alloys have higher resistance to be compressed in x-direction.

(vi) $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) alloys show an anisotropic character.

(vii) Cauchy pressure calculation discloses that covalent bonding dominates in $ZrCoBi$ and $ZrNiBi$, while ionic bonding dominates in Ni-doped $ZrCo_{1-x}Ni_xBi$ alloys

(viii) It is noticed that the smallest value of minimum thermal conductivity occurs for $ZrCo_{0.25}Ni_{0.75}Bi$ in all studied directions. Therefore, the half- Heusler alloys $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) would be useful for high-temperature thermal device applications.

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СТРУКТУРНІ, ТЕРМІЧНІ ТА ЕЛЕКТРОННІ ДОСЛІДЖЕННЯ НАПІВ-ГЕЙСЛЕРОВИХ СПЛАВІВ $ZrCo_{1-x}Ni_xBi$ (x=0, 0,25, 0,75 і 1)

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У статті представлено теоретичну оцінку структурних, механічних, теплових та електричних властивостей напівгейслерових сплавів $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) в рамках теорії функціоналу щільності (DFT), яка реалізована в коді WIEN2k. Знайдено, що параметри рівноважної решітки узгоджуються з попередньою літературою. Декілька розрахункових механічних властивостей показують, що всі досліджувані сплави є механічно стійкими. Відповідно до критичних значень B/G, леговані Ni сплави ZrCoBi є пластичними, тоді як ZrCoBi та ZrNiBi крихкі. Зонна структура та щільність станів цих сполук показують, що ZrCoBi має напівпровідникову природу, тоді як легований Ni ZrCoBi має напівметалеву природу. Структурні реформи, внесені до ZrCoBi у міру збільшення концентрації Ni-допанту на місці Co-атома, показали збільшення його металічності, провідності та пластичності, а також зниження його жорсткості, стисливісті, мінімальної теплопровідності, температур плавлення та Дебая. Згідно з отриманими результатами, сплави $ZrCo_{1-x}Ni_xBi$ (x = 0, 0.25, 0.75 and 1) можуть мати потенційне термічне та електронне застосування.

Ключові слова: ZrCoBi; першопринципи; сполуки напів-Гейслера; електронна структура; заміщення Ni/Co