Published by
NIGERIAN SOCIETY OF PHYSICAL SCIENCES
Available online @ https://journal.nsps.org.ng/index.php/jnsps

J. Nig. Soc. Phys. Sci. 5 (2023) 1029

Journal of the Nigerian Society of Physical Sciences

# First Principles calculation of Half metallic proprieties of QCrAs (Q=Hf, Ti and Zr)

M. I. Babalola*, B. E. Iyorzo, S. O. Ebuwa

*Department of Physics, University of Benin, Nigeria*

## Abstract

The structural, electrical, magnetic, mechanical, and thermodynamic properties of some novel half-Heusler alloys QCrAs(Q=Hf, Ti and Zr) are investigated using first principles calculations. The results show that the three half Heusler alloys are half metals and they can find application in spintronics industries. They possess magnetic moment of $3\mu_B$. The mechanical properties shows that they are mechanically stable. The B/G ratio of the three half-Heusler alloys show that they are ductile in nature and the Poisson's ratio reveal that the plasticity of TiCrAs and ZrCrAs are higher than that of HfCrAs. The Debye temperature and average sound velocity of ZrCrAs is observed to be higher than the other two alloys. This implies that the thermal conductivity of ZrCrAs is the highest.

DOI:10.46481/jnsps.2023.1029

*Keywords:* Half Heusler, Half-metallic gap, Electronic band structure, Mechanical properties

*Article History :*
Received: 03 September 2022
Received in revised form: 01 November 2022
Accepted for publication: 08 November 2022
Published: 21 January 2023



Communicated by: K. Sakthipandi

## 1. Introduction

For many years now, the search for functional materials has been on the increase in the scientific community. Examples of functional materials include thermoelectric materials [1], piezoelectric materials [2], optoelectric materials [3], spintronic materials [4] etc. Of all materials that have been found and synthesized till date, the Heusler alloys and its family have been one of the most widely studied material [5-7], this is because they can be easily synthesized and have multifunctional capability which are very useful in technological industries. The Heusler family with this multifunctional capabilities include the full Heusler alloy [8], quaternary Heusler alloy [9], half Heusler alloy [10], binary Heusler alloy [11], and inverse Heusler alloy [12]. Interestingly, different characteristics of these Heusler family can be predicted just by knowing their valence electron count [13]. Some years back, Gautier and coworkers predicted over 300 half Heusler alloys [14], ever since then, more half Heusler alloys have been investigated till date. Half Heusler alloys having valence electrons greater or less than 18 can be said to be ferromagnetic, hence such half Heusler allloys could possess half-metallic properties which is useful in spintronics industries. One of the properties sough after in spintronics is the half-metallic property. The half-metallic property is described as a situation whereby a material having metallic nature in one spin channel and having semiconducting properties in another spin channel. This concept was discovered by De Groot and co-workers in 1983 [15]. Half-metals possess

*Corresponding author tel. no: +234 8060797955
*Email address:* michael.babalola@uniben.edu (M. I. Babalola)

100% spin-polarization at the Fermi level, thereby making it possible for them to be used as a spin valve to enhance giant magneto-resistance [16], spin injector electrode in tunnel magneto-resistance [17] and current perpendicular to plane giant magneto-resistance (CPP-GMR) in spintronics [18]. They also find application in spin torque devices [19] and magnetic tunnel junction (MTJ) devices [20]. Half-Heusler alloys UVW(XYZ) with half-metallic character are usually described as having the U atomic position occupied by one of the followings: main group 1 or 2 element, the rare earth metals and a transition metal [13]. The V atomic position is occupied a transaction metal which is less electropositive compared to U. The W atomic position is occupied by elements from a main group 3, 4 and 5. In this work, we use ab initio calculation to explore the half-metallic, mechanical and thermodynamic properties of the novel half Heusler alloys QCrAs (Q=Hf, Ti and Zr). The remaining portion of this work is divided into the following sections: Section 2 covers the computational specifics, Section 3 covers the discussion and results, and Section 4 concludes with a summary.

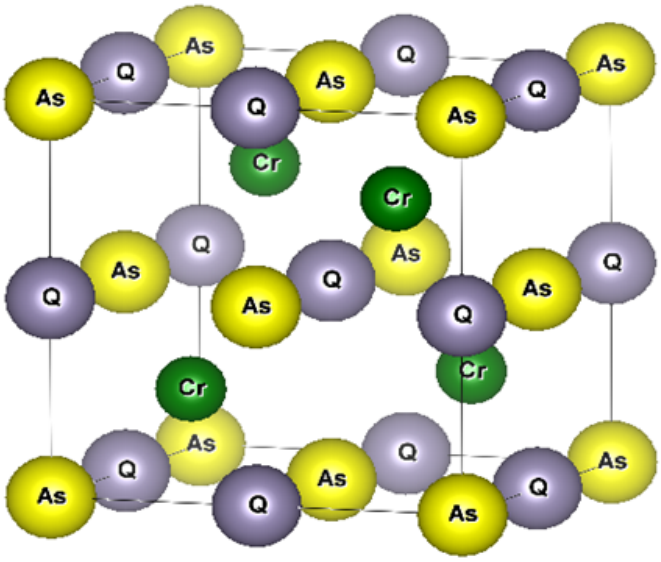


Figure 1. Unit cell of QCrAs (Q=Ti, Hf and Zr) HH alloys

## 2. Computational details

First principles spin-polarized density functional theory (SP-DFT) calculation has been used to perform the ground state properties of QCrAs(Q=Hf, Ti and Zr) alloys. A projected augmented wavefunction (PAW) type of the generalized gradient approximation (GGA) which is the choice of exchange correlation as implemented in the quantum espresso code[21] is used. The valence electron configurations of Hf($4f^{14}6s^25d^2$), Ti($4s^23d^2$),Cr($3d^54s^1$), As($4d^25s^2$) and Zr($5s^24d^2$) are used. An optimized value of 70Ry for the plane-wave basis set of the kinetic energy cutoff and a 9×9×9 k-point mesh are used to determine the structural parameters for the three half Heusler alloys. Optimizaion was carried out for various values of k-point starting with 4X4X4, 5X5X5, ... 15X15X15. At the end of the calculation, the difference between the last k-point and the others were observed. The difference between the energies of k-point 9X9X9 and the last k-point fell within the acceptable range of 0.1meV.Convergence threshold for all selfconsistency calculation is set at $10^{-6}$ Ry/atom. Spin-polarised was taken care of by introducing nspin which activates the magnetism in the compounds. Magnetic spins were allocated to the atoms of the transition metals using starting magnetization. Duriing band calculation, we used spin_component to distinguish between spin up and spin down components. The thermo pw package is used to compute the thermodynamic and mechanical properties [22].

## 3. Results and discussion

### 3.1. Structural properties

A cubic structure with MgAgAs type C1b structure forms during the crystallization of half Heusler alloys (UVW). They have space group of F-43m (No 216). The half Heusler stucture is seen as a combination of zincblende and rocksalt structure. Wyckoff locations 4b(1/2,1/2,1/2), 4c(1/4,1/4,1/4), and 4a (0,0,0) are occupied by the U, V, and W atoms, respectively. The unit cell of the half-Heusler alloy is shown in Fig. 1. The structural parameters such as the equilibrum lattice constant, bulk modulus and pressure derivative are computed by fitting the total energies versus lattice constant curve with the Murnaghan equation of state with the results presented in Table 1. Fig. 2 shows the ferromagnetic state and non magnetic state of the three half-Heusler alloys, and from the graph, their ferromagnetic state posses the lowest ground state energies. This implies that the three half-Heusler alloys are ferromagnetic in nature. The lattice constant of the three HH alloys satisfy the condition Ti<Zr<Hf, this could be as a result of the atomic mass satisfying the same condition. The half Heusler alloys QCrAs(Q=Hf, Ti and Zr) are novel and have no experimental and theoretical result to compare with. Nevertheless, the lattice constants of QCrAs(Q=Hf, Ti and Zr) when compared with results of QCrBi(Q=Hf, Ti and Zr) [23] are within reasonable range. The formation energies of the three alloys have also been computed using eq. 1 as shown in Table 1. QCrAs(Q=Hf, Ti and Zr) half Heusler alloys all have negative The formation energies of the three half-Heusler alloys have negative values and these indicate that they can be synthesized in experimentally.

$$E_f(QCrAs) = E_T(QCrAs) - (E(Q) + E(Cr) + E(As)) \quad (1)$$

The ground state energies of each element are represented as E(Q), E(Cr) and E(As)), while $E_T$(QCrAs) is the sum of the energies in the HH compounds. The formation energies for each HH are displayed in Table 1. The compounds can be synthesized experimentally if the formation energies have a negative value.

### 3.2. Magnetic and electronic properties

The magnetic and electronic properties of the three half Heusler alloys QCrAs (Q=Hf, Ti and Zr) have been computed

Table 1. Computed lattice parameters a, bulk moduli (B), pressure derivatives (B'), magnetic states $M_g$ magnetic moment (MM), and the formation energy $E_f$ of QCrAs (Q=Hf, Ti and Zr

| Compounds | a(Å) | B(GPa) | B' | $M_g$ | MM($\mu_B$) | $E_f$ (eV) |
|---|---|---|---|---|---|---|
| TiCrAs | 5.87 | 116.80 | 6.20 | FM | 3.012 | -1.58 |
| | 5.81 | 128.90 | 4.33 | NM | - | |
| ZrCrAs | 6.10 | 103.50 | 4.28 | FM | 3.026 | -1.44 |
| | 6.02 | 117.80 | 4.30 | NM | - | |
| HfCrAs | 6.07 | 108.50 | 4.61 | FM | 2.988 | -1.62 |
| | 5.98 | 122.10 | 4.16 | NM | - | |

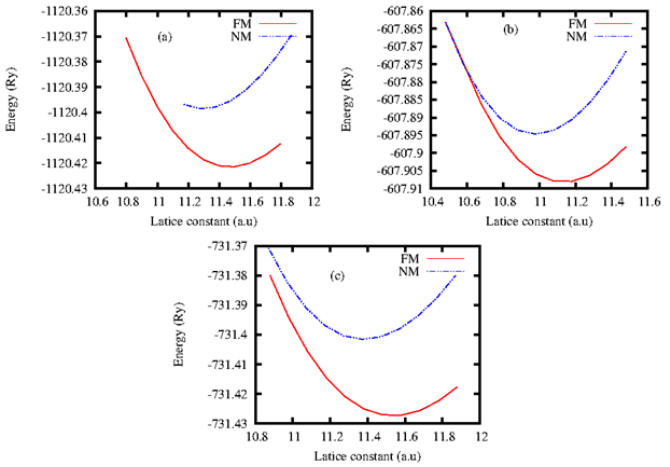


Figure 2. Total energies of XCrAs (X=Hf, Ti, and Zr) against lattice constants in ferromagnetic (FM) and non-magnetic (NM) states (a)HfCrAs, (b) TiCrAs and (c) ZrCrAs

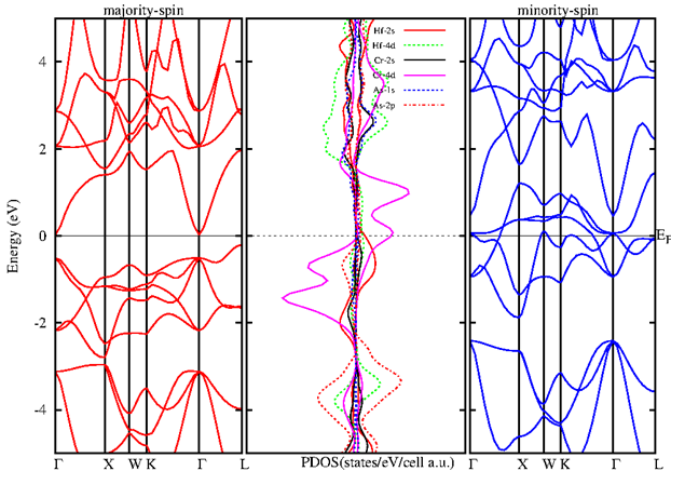


Figure 3. HfCrAs band structures for both spin channels

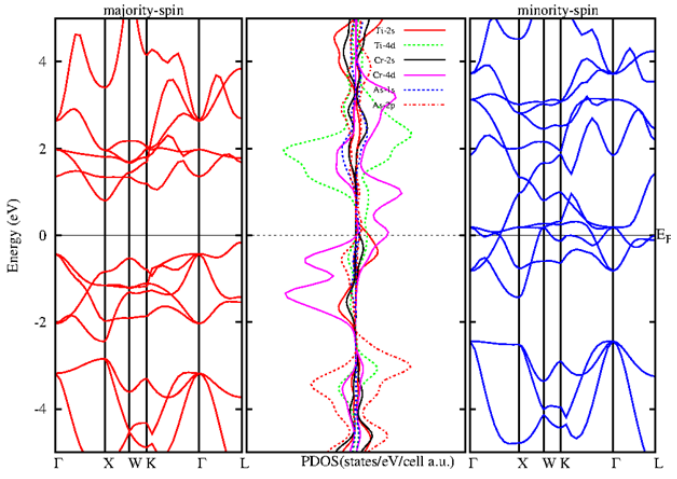


Figure 4. TiCrAs band structures for both spin channels

using the spin-resolved DFT technique. The total magnetic moment that results from the contributions of the local moments of each atom in the HH alloys is shown in Table 1. The MM obtained in Table 1 are in agreement with the MM predicted by Slater-Pauling rule. M=|$V_N$-18|, where $V_N$ is the valence electrons count (VEC) per formula unit and M is the total magnetic moment per formula unit, gives the Slater-Pauling rule. The valence electrons for each element are: Hf ( $5d^26s^2$), Ti($3d^24s^2$), Zr( $4d^25s^2$) Cr( $3d^54s^1$) and As($4s^24p^3$). The value of $V_N$ for each HH alloy is 15, hence the predicted MM from Slater-Pauling rule is $3\mu_B$. The magnetic moment computed are approximately $3\mu_B$. The idea behind the magnetic moment can be explained from the crystal field splitting of the d-orbital of the atom occupying the V atomic position (the Cr element) [24]. The Cr atom with the As atom form a tetrahedral position thereby hybridizing to form $[CrAs]^{4-}$. The resulting ion interact with Q(=Hf, Ti and Zr)$^{4+}$ ion during which electrons are exchanged. The $Cr^-$ ion gains one extra electron during this process thereby making it possess seven electrons. The seven electrons are the shared among the triplet and doublet states leaving three unpaired electrons which constitute the total MM of the compounds. Figures 3, 4, and 5 display the electronic band structure for both spin channels along with the corresponding partial density of states (PDOS) for each alloy. It is evident from the PDOS that the three HH alloys are half-metallic with their spin up channels being semiconductors and their spin down channels being metals. These results suggest that the three compounds are half-metals. The highest occupied molecular orbit (lowest occupied molecular orbit) HOMO (LUMO) for HfCrAs, TiCrAs and ZrCrAs are 12.8334eV (12.6114eV), 12.1927eV (11.8789eV) and 12.7092eV (12.3076eV) respectively. The band gap of HfCrAs, TiCrAs and ZrCrAs are 0.222eV, 0.3138eV and 0.4016eV respectively.

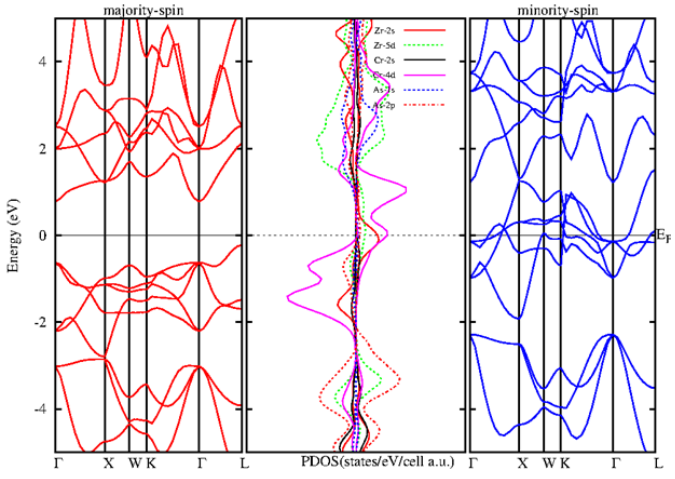


Figure 5. ZrCrAs band structures for both spin channels

Table 2. Computed elastic constants $C_{ij}$ , shear moduli $G$, Young moduli $E$, B/G ratio with the Poisson's ratio $v$ of QCrAs (Q=Hf, Ti and Zr)

| Compounds | HfCrAs | TiCrAs | ZrCrAs |
|---|---|---|---|
| $C_{11}$ *(GPa)* | 108.62 | 105.18 | 116.00 |
| $C_{12}$ *(GPa)* | 116.61 | 101.07 | 104.19 |
| $C_{44}$ *(GPa)* | 11.78 | 19.61 | 11.79 |
| *E(GPa)* | 16.15 | 24.69 | 26.08 |
| *G(GPa)* | 5.47 | 8.51 | 8.93 |
| *B/G* | 19.8 | 13.7 | 11.6 |
| *v* | 0.6385 | 0.4508 | 0.4597 |

### *3.3. Mechanical Properties*

For QCrAs (Q=Ti, Zr, and Hf), the parameters that make up the mechanical properties are calculated and are shown in Table 2. These parameters include the elastic constants, the Young's modulus, the shear modulus, and Poisson's ratio. The elastic constants typically related to cubic materials are $\boldsymbol{C}_{11}$, $\boldsymbol{C}_{12}$ and $\boldsymbol{C}_{44}$. They describe the response of materials to external forces. The cubic structure's mechanical stability criteria are specified as $C_{11} > 0$, $C_{44} > 0$, $C_{11} > C_{12}$ and $C_{11}+2C_{12} > 0$, $C_{11}-C_{12} > 0$. Once this criteria is satisfied then the material is said to be mechanically stable. According to the results in Table 2, ZrCrAs has the strongest resistance to linear and shear deformation when compared to TiCrAs and HfCrAs. The B/G ratio of the three half-Heusler alloys are greater than the critical value of 1.75, it means the three alloys are ductile. The Poisson's ratio determines a compound's plasticity. The critical value for metals and their alloys is $0<v<0.5$. The lower the value, the greater the plasticity. TiCrAs and ZrCrAs fall within the criteria and they have better plasticity compared to HfCrAs.

### *3.4. Thermodynamic Properties*

The results of the thermodynamic properties of QCrAs (Q=Ti, Zr, and Hf) are shown in Table 3 and Figure 6. The constant volume heat capacity of the three compounds are similar while the Debye temperature of ZrCrAs has the highest value implying that it has higher thermal conductivity than the other half Heusler alloys. The zero-point energy of the three alloys are

Table 3. Computed heat capacities $C_v$ at 300K, zero point energies $E_o$, Debye temperatures $\Theta_D$, and the sound velocity $V_{av}$ of the HH alloys

| Compounds | $C_v$ (J/Kmol) | $E_o$ (kJ/Nmol) | $\Theta_D$(K) | $V_{av}$(m/s) |
|---|---|---|---|---|
| HfCrAs | 74.7 | 2.263 | 80.616 | 717.68 |
| TiCrAs | 74.7 | 2.218 | 79.004 | 682.86 |
| ZrCrAs | 74.6 | 2.643 | 94.152 | 843.28 |

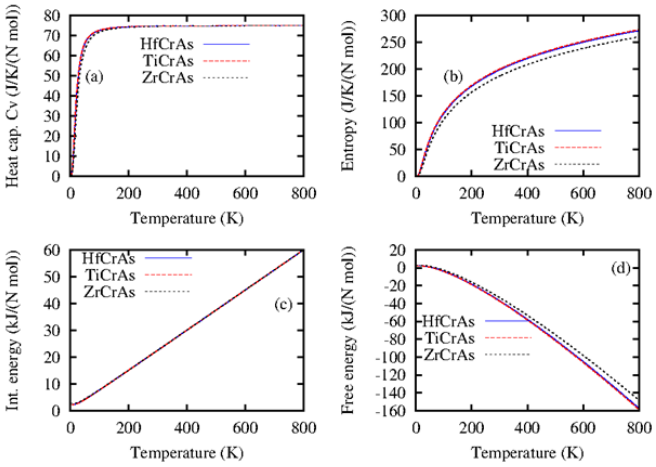


Figure 6. Thermodynamic characteristics of QCrAs (Q=Hf, Ti, and Zr), showing the heat capacity, the entropy, the internal energy, and the Gibb's free energy in (a), (b), (c), and (d), respectively

close and it gives information about the vibrational energies of materials at absolute zero temperature. The heat capacities, entropy, internal energy of QCrAs (Q=Hf, Ti and Zr) increase as the temperatures increase. The free energies of the three HH alloys decrease as the temperatures increase. This is the usual trend of most compounds.

## 4. Conclusion

The spin-polarization DFT calculation used to analyze the electronic properties of QCrAs (Q=Hf, Ti, and Zr) alloys reveals that all studied HH alloys are half metals. With the half metallic properties they can find application in spintronic industries. The HH alloys are all mechanically stable. The thermodynamic quantities such as the specific heat capacity at constant volume, internal energies and zero-point energies for the three HH alloys are similar.

## Acknowledgements

We are grateful to the Marie Curie Library of the Abdus Salam International Centre, for Theoretical Physics (ICTP) for permission to use the ejds resources for the reference articles used in this study

## References

[1] C. Hu, K. Xia, X. Chen, X. Zhao & T. Zhu, "Transport mechanisms and property optimization of p-type (Zr, Hf) CoSb half-Heusler thermoelectric materials", Materials Today Physics **7** (2018) 69.

[2] R. Hinchet, U. Khan, C. Falconi & S.W. Kim, "Piezoelectric properties in two-dimensional materials: Simulations and experiments", Materials Today **21** (2018) 611.

[3] M. V. Shisode, A.V. Humbe, P. B. Kharat & K. M. Jadhav, "Influence of Ba 2+ on opto-electric properties of nanocrystalline BiFeO 3 multiferroic", Journal of Electronic Materials **48** (2019) 358.

[4] S. A. Khandy, I. Islam, D. C. Gupta & A. Laref, "Full Heusler alloys (Co2TaSi and Co2TaGe) as potential spintronic materials with tunable band profiles", Journal of Solid State Chemistry **270** (2019) 173.

[5] O. Amrich, M. E. A. Monir, H. Baltach, S. B. Omran, X. W. Sun, X. Wang, Y. Al-Douri, A. Bouhemadou & R. Khenata, "Half-metallic ferrimagnetic characteristics of Co 2 YZ (Z= P, As, Sb, and Bi) new full-Heusler alloys: a DFT study", Journal of Superconductivity and Novel Magnetism **31** (2018) 241.

[6] P. D. Patel, S. B. Pillai, S. M. Shinde, S. D. Gupta & P. K. Jha, "Electronic, magnetic, thermoelectric and lattice dynamical properties of full heusler alloy Mn2RhSi: DFT study", Physica B: Condensed Matter **550** (2018) 376.

[7] N. S. Chauhan, S. Bathula, A. Vishwakarma, R. Bhardwaj, K. K. Johari, B. Gahtori, M. Saravanan & A. Dhar, "Compositional tuning of ZrNiSn half-Heusler alloys: Thermoelectric characteristics and performance analysis", Journal of Physics and Chemistry of Solids **123** (2018) 105.

[8] T. Yang, J. You, L. Hao, R. Khenata, Z. Y. Wang & X. Wang, "Structural configuration and phase stability in full Heusler alloys Cr2ZnSi and Cr2ZnGe", Journal of Magnetism and Magnetic Materials **498** (2020) 166188.

[9] S. Idrissi, S Ziti, H. Labrim, L. Bahmad, I. El Housni, R. Khalladi, S. Mtougui & N. El Mekkaoui, "Half-metallic behavior and magnetic proprieties of the quaternary Heusler alloys YFeCrZ (Z= Al, Sb and Sn)", Journal of Alloys and Compounds **820** (2020) 153373.

[10] G. Rogl, S. Ghosh, L. Wang, J. Bursik, A. Grytsiv, M. Kerber, E. Bauer, R.C. Mallik, X.Q Chen, M. Zehetbauer & P. Rogl, "Half-Heusler alloys: Enhancement of ZT after severe plastic deformation (ultra-low thermal conductivity)", Acta Materialia, **183** (2020) 285.

[11] Y. Zhou, J. M. Zhang, Y. H. Huang & X. M. Wei, "The structural, electronic, magnetic and mechanical properties of d0 binary Heusler alloys XF3 (X= Be, Mg, Ca, Sr, Ba)", Journal of Physics and Chemistry of Solids **138** (2020) 109246.

[12] Y. Chen, B. Wu, H. Yuan, Y. Feng & H. Chen, "The defect-induced changes of the electronic and magnetic properties in the inverse Heusler alloy Ti2CoAl", Journal of Solid State Chemistry **221** (2015) 311.

[13] T. Graf, C. Felser & S. S. Parkin, "Simple rules for the understanding of Heusler compounds", Progress in solid state chemistry **39** (2011) 1.

[14] R. Gautier, X. Zhang, L. Hu, L. Yu, Y. Lin, T.O. Sunde, D. Chon, K.R. Poeppelmeier & A. Zunger, "Prediction and accelerated laboratory discovery of previously unknown 18-electron ABX compounds", Nature chemistry **7** (2015) 308.

[15] R. A. De Groot, F.M. Mueller, G. G. Van Engen & K. H. J. Buschow, "New class of materials: half-metallic ferromagnets", Physical Review Letters 50 (1983) 2024.

[16] G. Binasch, P. Grünberg, F. Saurenbach & W. Zinn, "Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange", Physical review B **39** (1989) 4828.

[17] Y. Fujita, M. Yamada, M. Tsukahara, T. Oka, S. Yamada, T. Kanashima, K. Sawano & K. Hamaya, "Spin transport and relaxation up to 250 k in heavily doped n-type Ge detected using Co 2 FeAl 0.5 Si 0.5 electrodes", Physical Review Applied **8** (2017) 014007.

[18] Y. Sakuraba, K. Izumi, T. Iwase, S. Bosu, K. Saito, K. Takanashi, Y. Miura, K. Futatsukawa, K. Abe & M. Shirai, "Mechanism of large magnetoresistance in Co 2 MnSi/Ag/Co 2 MnSi devices with current perpendicular to the plane", Physical Review B **82** (2010) 094444.

[19] F. Wu, S. Mizukami, D. Watanabe, E.P. Sajitha, H. Naganuma, M. Oogane, Y. Ando & T. Miyazaki, "Structural and Magnetic Properties of Perpendicular Magnetized $Mn_{2.5}Ga$ Epitaxial Films", IEEE transactions on magnetics **46** (2010) 1863.

[20] S. Ikeda, K. Miura, H. Yamamoto, K. Mizunuma, H.D. Gan, M. Endo, S. Kanai, J. Hayakawa, F. Matsukura & H. Ohno, "A perpendicular-anisotropy CoFeB–MgO magnetic tunnel junction", Nature materials **9** (2010) 721.

[21] P. Giannozzi et al., "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials", Journal of physics: Condensed matter **21** (2009) 395502.

[22] A. Dal Corso, "Elastic constants of beryllium: a first-principles investigation", Journal of Physics: Condensed Matter **28** (2016) 075401.

[23] M. I. Babalola, B. E. Iyorzor & O. G. Okocha, "Origin of half-metallicity in XCrBi (X= Hf, Ti, and Zr) half-Heusler alloys", Materials Research Express **6** (2019) 126301.

[24] B. E. Iyorzor & M. I. Babalola, "Half-metallic Characteristics of the Novel Half Heusler Alloys XCrSb (X= Ti, Zr, Hf)", Journal of the Nigerian Society of Physical Sciences **3** (2022) 138.