Transactions of the Nigerian Association of Mathematical Physics
Volume 15, (April –June, 2021 Issue), pp121 – 126

THE EFFECTS OF PRESSURE ON THE STRUCTURAL, ELECTRONIC AND MECHANICAL PROPERTIES OF THE HALF HEUSLER ALLOY VRuSb

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Abstract

The Physical properties of VRuSb half Heusler alloy have been investigated under pressure from first principles calculation based on the density functional theory (DFT). VRuSb was found to be a semiconductor at zero pressure and as pressure increases a semiconductor to metal transition was observed at 10Gpa. Mechanical stability was observed on VRuSb and as pressure increases the parameters associated with mechanical properties increased, VRuSb is also found to be ductile in nature from the B/G ratio result.

***Keywords*:** HalfHeusler, Semiconductor, Electronic Properties, Mechanical properties.

1.0 Introduction

Heusler compounds have gained the interest of researchers due to their important applications in spintronics, optoelectronics, and thermo-electrics[1].The need for good and reliable materials for production is on the high rise as well. It is important to produce materials with high efficiency and ability to withstand harsh working conditions. In this work, we have gone through the properties of a ternary half Heusler compound to determine its properties and have exerted pressure on these properties and measured significant changes.Heusler compounds are magnetic intermetallics with face-centered cubic crystal structure and a composition of XYZ (half-Heuslers) or X_2YZ (full-Heuslers), where X and Y are transition metals and Z is in the p-block. Many of these compounds exhibit properties relevant to spintronics, such as magneto resistance, variations of the Hall effect, Ferro-, antiferro-, and ferrimagnetism, half- and semimetallicity, semi conductivity with spin filter ability, superconductivity, and topological band structure. Their magnetism results from a double-exchange mechanism between neighboring magnetic ions. Manganese, which sits at the body centers of the cubic structure, was the magnetic ion in the first Heusler compound discovered [2].Half-Heusler compounds are generally represented by the formula XYZ, where Y and Z form a rock salt structure having the lattice points (0, 0, 0) and (0.5, 0.5, 0.5) respectively and X atom located at the octahedral voids at one of the lattice points either at (0.25, 0.25, 0.25) or (0.75, 0.75, 0.75). This is the stable crystal structure of half Heusler alloys at ambient conditions. Just like the Full-Heusler, X and Y are transition metal elements and Z is a metal element in the P-block. Half-Heusler alloys usually crystallize in a cubic structure.

Conductors are the materials or substances which allow electricity to flow through them on application of an electric field. They conduct electricity because they allow electrons to flow easily inside them from atom to atom as a result of an overlap between the conduction band and the partially filled valence band. This accounts for high conductivity in metals. The conductivity of metals decreases with increase in temperature.[3]

Semiconductors are materials which have a conductivity between conductors (generally metals) and nonconductors or insulators (such as most ceramics). Semiconductors can be pure elements, such as silicon or germanium, or compounds such as gallium arsenide or cadmium selenide. In a process called doping, small amounts of impurities are added to pure semiconductors causing large changes in the conductivity of the material. The most commonly used semiconductors are silicon (Si) and Gallium Arsenide (GaAs).In semiconductors, the valance band and conduction band are separated by a forbidden energy gap（Eg）of sufficient width, and the Fermi energy（E_f） is between the valence and conduction band. To get to the conduction band, the electron has to gain enough energy to jump the band gap. Once this is done, it can conduct.[3,4].In semiconductors at room temperature, the band gap is smaller, there is enough thermal energy to allow electrons to jump the gap fairly easily and make the transitions in conduction band, given the semiconductor limited conductivity. At low temperature, no electron possesses sufficient energy to occupy the conduction band and thus no movement of charge is possible. At absolute zero, semiconductors are perfect insulators, The density of electrons in conduction band at room temperature is not as high as in metals, thus cannot conduct current as good as metal. The electrical conductivity of semiconductor is not as high as metal but also not as poor as electrical insulator. That is why, this type of material is called semiconductor - means half conductor.

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Hardness is a measure of the resistance to localized plastic deformation induced by either mechanical indentation or abrasion. In general, different materials differ in their hardness; for example hard metals such as titanium and beryllium are harder than soft metals such as sodium and metallic tin, or wood and common plastics. Materials which show low resistance to these localized plastic deformations are known as soft materials .[5,6].

Malleability is characterized by a material's ability to deform plastically without failure under compressive stress. [7]Historically, materials were considered malleable if they were amenable to forming by hammering or rolling). [8]Lead is an example of a material which is, relatively, malleable but not ductile.

Ductility is a mechanical property commonly described as a material's amenability to drawing (e.g. into wire). In materials science, ductility is defined by the degree to which a material can sustain plastic deformation under tensile stress before failure. Ductility is an important consideration in engineering and manufacturing, defining a material's suitability for certain manufacturing operations (such as cold working) and its capacity to absorb mechanical overload. Materials that are generally described as ductile include gold and copper.

Bencherif et al[9] studied the elastic, optoelectronic, and thermal properties of XRuSb (X ¼ V, Nb, Ta) compounds using density functional theory. They found that these materials are semiconductors in nature. Kaur et al [10] also using Density functional theory (DFT), worked on the half heusler compounds XRuSb (X = V, Nb, Ta), discovering their photoelectric properties and from their results, that these materials were identified as good thermoelectric materials with narrow band gaps and flat electronic bands in the valence band.

If VRuSb is to be used in the factory for engineering purposes, it will definitely undergo some form of pressure during machining. The aim of this paper is to investigate the effects of the applied pressure on the structural, electronic and mechanical properties of the compound.

2.0 Methodology

First principles calculations performed based on the density functional theory as implemented in the Quantum Espresso simulation package [11]The generalized gradient approximation (GGA) [12] with the Perdew-Burke-Ernzerhof (PBE) functional was used as the exchange correlation energy.55 Ryd was used as the kinetic energy cut-off value for plane wave expansion. The Brillouin zone integration is performed with 11 × 11 × 11 Monkhorst pack [13]k-mesh and the self-consistent convergence of energy is 10−6 eV/atom. To obtain ground state structural parameters like equilibrium volume, equilibrium lattice constant, bulk modulus and its pressure derivatives, we calculated the total energy at a wide range of lattice constants around the available experimental lattice parameters and fitted energy vs. volume curve with Birch Murnaghan equation of state [14]. Elastic constants are computed by an elastic code [15] using Quantum ESPRESSO input files. Elastic moduli (Young's, bulk and shear modulus), Zener anisotropic factor, Poisson's ratio are derived from second-order elastic constants. The Zener anisotropic factor can be calculated as

$$\mathbf{A} = \frac{2C_{44}}{(C_{11}-C_{12})} \quad (1)$$

Bulk modulus (Bv), shear modulus according to Voigt (Gv) and Reuss (GR) formula are given by

$$\mathbf{B_V} = \frac{(C_{11}+C_{12}+C_{44})+2(C_{12}+C_{13}+C_{23})}{9V} \quad (2)$$

$$\mathbf{B} = \frac{14710.5164\,a^2}{9V} \quad (3)$$

$$\mathbf{G_V} = \frac{(C_{11}+C_{12}+C_{44})-(C_{12}+C_{13}+C_{23})+3(C_{44}+C_{55}+C_{66})}{15V} \quad (4)$$

$$\mathbf{G} = \frac{14710.5164\,a}{6V} \quad (5)$$

$$\mathbf{C_{44}} = \frac{14710.5164\,a^2}{3V} \quad (6)$$

$$\mathbf{C_{11}} = \frac{3B_K+4G}{3} \quad (7)$$

$$\mathbf{C_{12}} = \frac{3B_K-2G}{3} \quad (8)$$

Young's modulus and Poisson's ratio were obtained from the bulk modulus and shear modulus as follows:

$$\mathbf{E} = \frac{9GB_K}{G+3B_K} \quad (9)$$

$$\mathbf{n} = \frac{0.5(B_K-0.6667G)}{B_K+0.3333G} \quad (10)$$

3.0 Results

3.1 Structural Properties

The structural properties of ***VRuSb*** have been computed and are presented in this section. Table 1 shows the lattice parameters of ***VRuSb*** at zero pressure and at higher pressures. It is observed that from Table 1, the lattice contants , unit cell

volume decreases as pressure increases . The bulk modulus on the other hand increases as pressure increases. The unit cell structure of ***VRuSb*** is presented in figure 1 and it is seen that it is face centered cubic structure.

Table 1*Lattice Parameter**(Å),** Unit cell Volume**(a.u^3)** Bulk Modulus **(GPa)**and pressure derivative* of VRuSb at 0Gpa

a (Å)	***V_o(a.u^3)***	***B (GPa)***	***B'***
11.4160	1487.79	162.8	4.30

VRuSb possesses a Face-Centered Cubic structure as shown in the diagram below

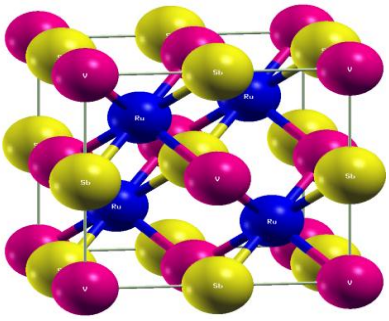

Fig 1 FCC Structure of VRuSb at 0GPa pressure

When pressure was exerted, some differences were observed in the lattice parameters and the unit cell volume.

Table 2*Lattice Parameter**(Å)** and Unit cell Volume**(a.u^3)**at pressures from 5GPa to 40GPa*

Pressure (GPa)	***a (Å)***	***V_o (a.u^3)***
5	11.3060	1445.2
10	11.2906	1408.54
20	11.0471	1308.57
30	10.9107	1289.85
40	10.9734	1257.4

3.2 Electronic Properties

The electronic properties of ***VRuSb*** from first principles calculation have been computed and are presented in fig. 2 to 7 as electronic band structure and partial density of state (PDOS). Fig 2 is the electronic band structure of ***VRuSb*** at zero pressure with an indirect band gap of 0.27eV. Figs 3 to 7 are the electronic band structure as well as their corresponding PDOS for 5GPa, 10 GPa, 20GPa, 30GPa and 40 GPa respectively. It is observed that at 10GPa there was no gap between the conduction band minimum and the valence band maximum. This indicate metallic behavior.With these results a semiconductor to metallic transition was observed to be at 10GPa. Above the 10GPa pressure the Half Heusleralloy remain metallic.

The PDOS of the Half Heusleralloy show the contribution of the various orbitals around the Fermi energy. There is a metallic bonding between the Ru orbital and the V orbital which is responsible for the ductile behavior of ***VRuSb.***

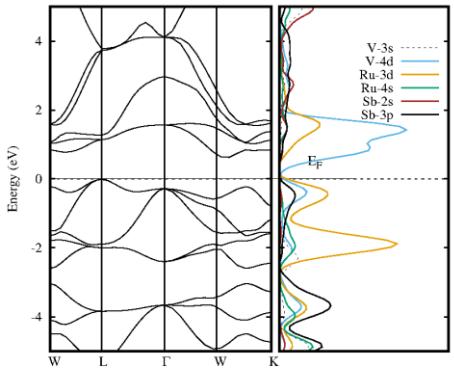

Fig 2: Band Structure and DOS at 0GPa

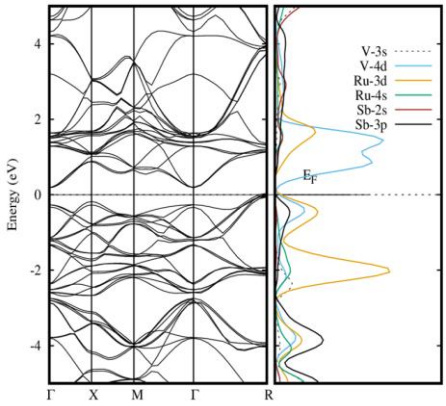

Fig 3. Band Structure and DOS at 5GPa

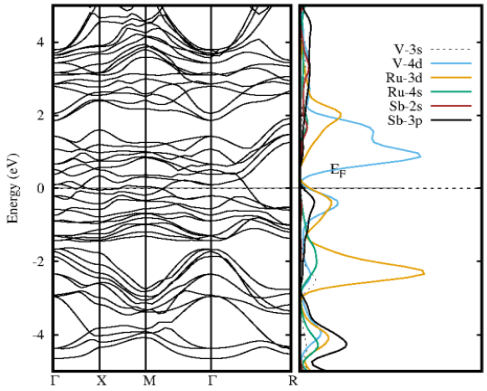

Fig 4. Band Structure and DOS at 10GPa

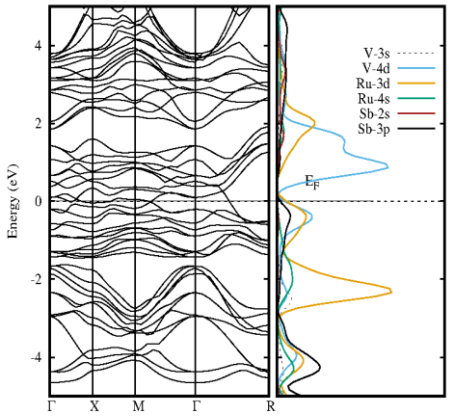

Fig 5. Band Structure and DOS at 20GPa

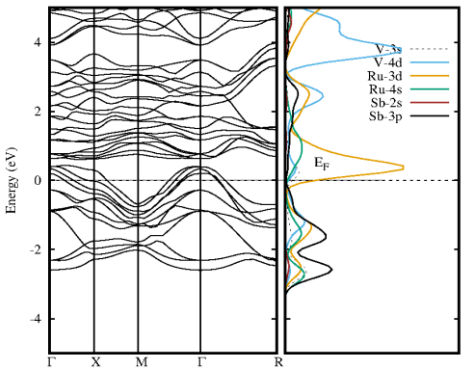

Fig 6. Band Structure and DOS at 30GPa

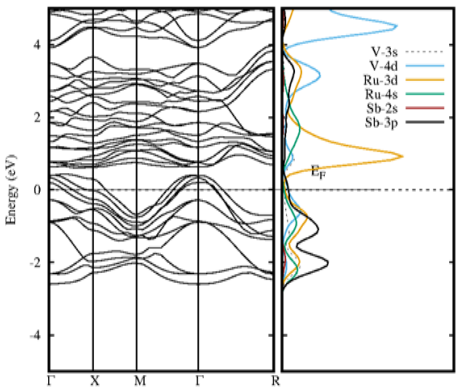

Fig 7. Band Structure and DOS at 40GPa

3.3 Mechanical Properties

The mechanical properties of VRuSb have also been computed and are presented in figs 8-12. The parameters associated with the mechanical properties include the elastic constants C_{11}, C_{12} and C_{44} for a cubic structure, the young modulus, Shear modulus and bulk modulus. The poisons ratio and the anisotropic factor as well as the B/G ratio are also computed. From our results it is seen that VRuSb satisfies the mechanical stability criteria gotte from the relation $C_{11}>0$, $C_{44}>0$, $C_{11}>C_{12}$ and $(C_{11}+2C_{12})>0$.The B/G ratio indicates that VRuSb is ductile in nature since its value is greater than the critical value of 1.75. For a value less than 1.75. than the material is brittle. The Youngs modulus and Shear modulus show how resistive the material is to tensile and shear deformation. At higher pressure the parameters increases, hence making the material more ductile, more stiff to deformation. The anisotropy is the measure of a material deviation from isotropy. As pressure increases, VRuSb tends towards isotropic system. The poisson ratio. Also increases as the pressure increases showing also its metallic behavior.

Table 3 *Mechanical Properties of VRuSb at different pressures*

MECHANICAL PROPERTIES									
	C_{11}	C_{12}	C_{44}	B (GPa)	G (GPa)	E (GPa)	A	V	B/G
0	234.30	129.27	35.35	164.28	52.51	142.383	0.673	0.3556	3.128
10	304.275	188.984	45.667	227.415	57.645	159.462	0.792	0.380	3.945
20	320.323	196.517	53.751	237.785	61.903	170.881	0.868	0.380	3.841
30	358.968	227.725	60.889	271.473	65.621	182.184	0.928	0.388	4.137
40	396.248	257.309	66.542	303.622	69.469	193.640	0.958	0.394	4.371

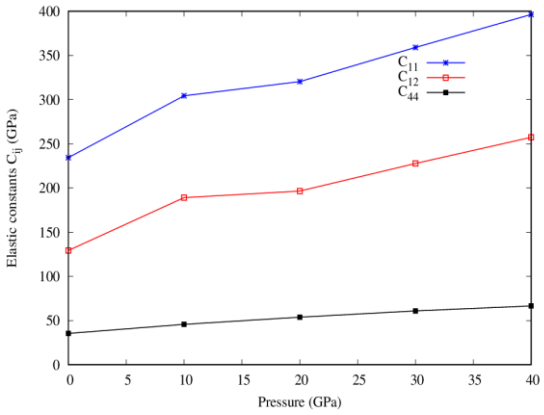

Fig 8. Variation of Elastic constants with pressure

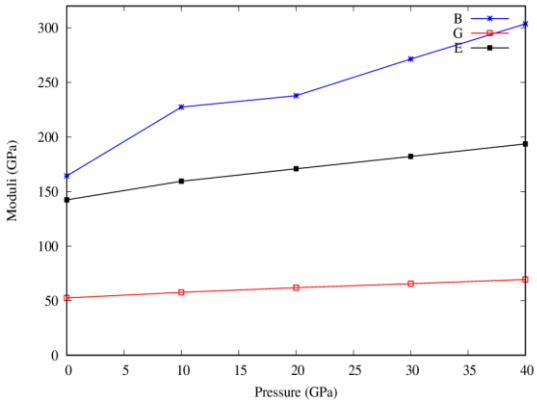

Fig 9. Variation of Bulk Modulus (B), Shear Modulus (G) and Elastic Modulus (E) with pressure

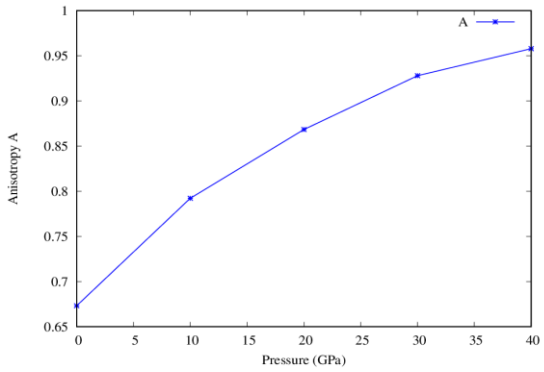

Fig 10. Variation of Zener Anisotropic ratio with pressure

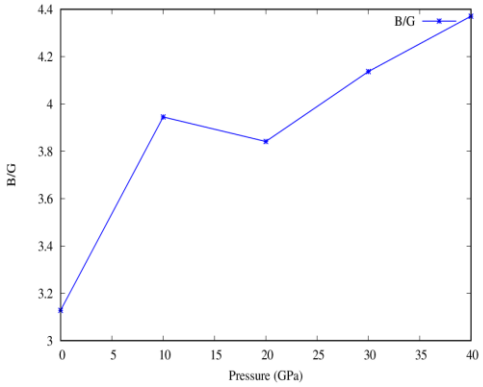

Fig 11. Variation of B/G ratio with pressure

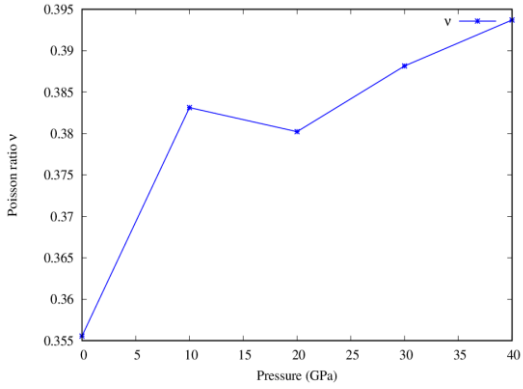

Fig 12. Variation of Poisson's Ratio with pressure

4.0 Conclusion

Physical properties of VRuSb half Heusler alloy have been investigated under pressure from first principles calculation. A semiconductor to metallic transition was achieved at 10GPa. The mechanical properties indicate that VRuSb is mechanically stable and it is found to be ductile in nature. As pressure increases the mechanical properties increase as well thereby increasing the materials stiffness to all types of deformation.

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