Effects of pressure on structural, mechanical, and electronic properties of chalcopyrite compound $CuAlS_2$

J. Geng[*], J. Wu
Nanchang Institute of Technology, Nanchang 330044, China

First-principles method is performed to investigate the structural, electronic, elastic and mechanical characteristics of the tetragonal $CuAlS_2$ in the pressure range from 0 to 10 GPa. The results indicated that both the lattice constant and cell volume decrease with the increase of pressure, which are matched well with available previous values. The pressure has a more significant influence on the *c* direction than the *a* and *b* direction. The obtained elastic constants reveal the tetragonal $CuAlS_2$ is mechanically stable between 0 and 10 GPa. The bulk, shear, and Young's modulus are evaluated by Voigt-Reuss-Hill approximation. All these elastic moduli exhibit a monotonic feature as a function of pressure. The Poisson's ratio, Pugh's criterion, and Cauchy pressure indicate that ternary chalcopyrite semiconductor $CuAlS_2$ is ductile against pressure. Meanwhile, the analysis of the electronic structures reveals that the states near the valence band top are derived from Cu 3d and S 3p orbitals, and the lowest conduction band is composed of Al 3p and S 3p orbitals. We expect that the findings predicted the physical properties of this compound will promote future experimental studies on $CuAlS_2$.

1. Introduction

Ternary chalcopyrite semiconductors have been extensively studied because of their large absorption coefficient and suitable band gap for applications to functional materials in electronics or in optoelectronics[1-4]. Among ternary chalcopyrite semiconductors, $CuAlS_2$ has a direct wide band gap of 3.5 eV at room temperature, making it suitable material for the use of light emitting devices in the blue and blue green region[5-6]. Also, this compound was proposed to act as window material for cascade thin films solar cell to improve quantum efficiency with UV region[7-8].

Recently, several experimental and theoretical works have been carried out on the electronic and optical properties of $CuAlS_2$ at ambient pressures. S. Sugan *et al.* studied the optical properties of ternary chalcopyrite compounds at room temperature using spectroscopic ellipsometry technique[9]. The ground-state structural, electronic, optical and thermal properties of the $CuAlS_2$ compound have been studied by U. P. Verma *et al.* employing the full potential

linearized augmented plane wave plus local orbitals method[10]. Jayalakshmi *et al.* studied the electronic structure and structural phase stability of chalcopyrite compounds $CuAlX_2$ (X=S, Se, Te) using the first principle self-consistent Tight Binding Linear Muffin-Tin (TB-LMTO) method within the local density approximation[11]. Early electronic structure calculations reveal that these compounds are direct band gap semiconductors. However, a very limited number of studies have been performed under pressure. The structure of ternary semiconductor $CuAlS_2$ is tetragonal and the space group is I-42d with four formula units per unit cell that lattice constants are a = 5.3336 $\mathring{A}$, c = 10.444 $\mathring{A}$ is similar to other fundamental chalcopyrite compounds[12]. It is known that changing the structure parameters will also change the physical properties. Meanwhile, pressure as an alternative to external stimuli of temperature has been proven to be an effective tool for changing the structural and physical properties of functional materials. High pressure studies of these chalcopyrite semiconductors have attracted considerable attention due to decrease in inter-atomic distance, which are significant changes in bonding, structures and electronic properties[13-14]. In addition, the chalcopyrite semiconductors have a relatively narrow energy gap, and the pressure induced changes of energy gap and electronic valence state have also attracted wide research interest[15-16]. These findings have important guiding significance for further development of the potential physical and chemical properties of $CuAlS_2$. In this work, we describe the pressure dependence of $CuAlS_2$ geometrical structure, electronic band structure and elastic properties up to 10 GPa. The information of lattice parameters, band structure, total density of states (DOS) and partial density of states (PDOS) under pressure are provided. Pressure-dependent bulk modulus, shear modulus, young modulus, and B/G ratio have been calculated for tetragonal $CuAlS_2$. The aim of the present study is to investigate the $CuAlS_2$ properties of interest in the tetragonal structure, with emphasis on their dependence on hydrostatic pressure. We believe that the above results can help to offer a theoretical basis for the experiments and applications of chalcopyrite semiconductors.

2. Computational details

The basic physical properties of the tetragonal chalcopyrite phase $CuAlS_2$ under high pressure were calculated using the Vienna *ab*-initio Simulation Package (VASP) software package[17-18]. Exchange and correlation interactions were formulated with the corrected density functional of the local density approximations (LDA-CA-PZ) in conjunction with ultrasoft pseudopotentials[19-20]. The valence electrons of Cu, Al, and S atoms are $3d^{10}4s^1$, $4s^24p^1$, and $3s^23p^4$, respectively. The kinetic energy cutoff for the plane-wave basis was set to be 950 eV, yielding a convergence for the total energy better than 5×10^{-6} eV/atom. Brillouin zone integration was performed using the Monkhorst-Pack grid of 5×5×6. The convergence criteria for max force, max tress, and SCF iterations were 0.01eV/Å, 0.02 GPa, and 5×10^{-7} eV/atom, respectively.

3. Results and discussion

3.1. Structural optimization properties

The interest of our study is understanding the qualitative behavior of the ternary chalcopyrite semiconductors under compressive and tensile pressures. The electronic band structure of a material, as well as its optical properties change under external pressure. The physical properties of materials are correlated with the lattice deformations. To optimize the lattice constants at different pressures, the experimental lattice constants as functions of pressure were firstly used as initial values. The optimized lattice parameters and the volume at zero pressure are given in Table 1 together with the available experimental data[12]. Optimized lattice constants of tetragonal $CuAlS_2$ without pressure are a=b=5.266 $\dot{A}$, and c=10.419 $\dot{A}$. One appreciates the very good agreement between our results and the available experimental data. The maximum relative difference between the calculated lattice parameters and the corresponding experimental counterparts does not exceed 2%. This constitutes the first proof of the reliability of the current calculations.

Table 1. The values of equilibrium lattice constants and volume of tetragonal chalcopyrite compound $CuAlS_2$.

Method $V(\text{Å}^3)$	$a = b$ (Å)	c (Å)	c/a	
GGA	5.414	10.507	1.941	307.96
LDA	5.266	10.419	1.978	288.94
[10]Cal.	5.341	10.571	1.979	----
[12]Exp.	5.334	10.444	1.958	297.11

To explore the effect of pressure on the structural parameters of tetragonal $CuAlS_2$, the lattice parameters and elastic constants were calculated at several reduced volumes, each of which corresponds to the system under pressure. Figure 1 gives the pressure-dependent lattice parameters a (b), and c of tetragonal $CuAlS_2$ from 0 to 10 GPa. It can be clearly seen that both lattice parameters are decreased with increasing pressure. By increasing the applied pressure from 0 to 10 GPa, the lattice constants a (b) and c decrease slightly from 5.266 to 5.111 Å and from 10.419 to 10.151 Å, respectively. The lattice parameter c decreases slightly faster than the lattice parameter a (b). This suggests that the lattice parameter c is more sensitive to external pressure than a and b. Meanwhile, the unit cell volume of tetragonal $CuAlS_2$ compound is also decreased with increasing pressure as shown in Fig. 1 (b). When the pressure increases to 10 GPa, the volume compression is

V/V_0 =91.75%, ($V = 265.11$ Å^3, $V_0 = 288.94$ Å^3). This is because, when we increased the

pressure then the interaction of Cu, Al and S atoms becomes stronger and therefore the bond length among these atoms becomes shorter as a result the lattice parameters become smaller with pressure. This similar behavior was often observed in chalcopyrite compound such as $CuMSe_2$ (M=Al and Ga), and $AgGaS_2$[21-23].
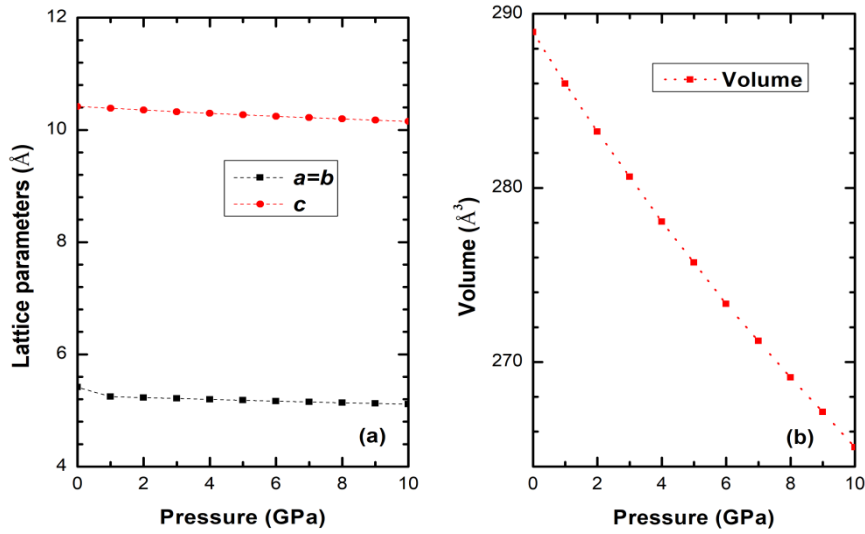
Fig. 1. The lattice constants (a, c) and cell volume of tetragonal CuAlS$_2$ as a function of pressure.

Moreover, according to the change of unit cell volume with pressure, we can obtain the equation of state for the tetragonal CuAlS$_2$ (Fig. 1(b)). In the present study, we use the third-order Birch-Murnaghan equation to fit the relationship between cell volume (V) and pressure (P)[24]:

$$P = \frac{3}{2} B_0 [\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}] \times \left\{1 + \frac{3}{4}(B_0' - 4)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\},$$ where B_0 is the bulk modulus,

B_0' is the derivative of bulk modulus at ambient pressure, and V_0 the volume at ambient pressure. The bulk modulus at ambient pressure and temperature is $B_0 = 78.5$ GPa and its derivative is $B'_0 = 5.27$. It agrees well with the previous theoretical values[21].

3.2. Electronic properties

The influence of pressure on the band gap energy of tetragonal CuAlS$_2$ was also explored through LDA functional-based calculations. The band structures for tetragonal CuAlS$_2$ under different pressure are plotted in Fig. 2 (a)-(c). The band structure calculations have been carried out following a path along the highest symmetry points Z, A, M, G, R, and X. The internal coordinates of these points are (0, 0, 0.5), (0.5, 0.5, 0.5), (0.5, 0.5, 0), (0, 0, 0), (0, 0.5, 0.5), and (0, 0.5, 0) in the first Brillouin zone, respectively. At zero pressure, both the conduction band minima (CBM) and valence band maxima (VBM) are positioned at G point, indicating that the band gap of tetragonal CuAlS$_2$ is of direct character. Additionally, the calculated band gap of 2.3 eV for tetragonal CuAlS$_2$ is in good agreement with the theoretical result of 2.2 eV, which is much smaller than the experimental value value of 3.49 eV, due to the well-known underestimation of conduction band state energies in density functional theory calculations[25-26].
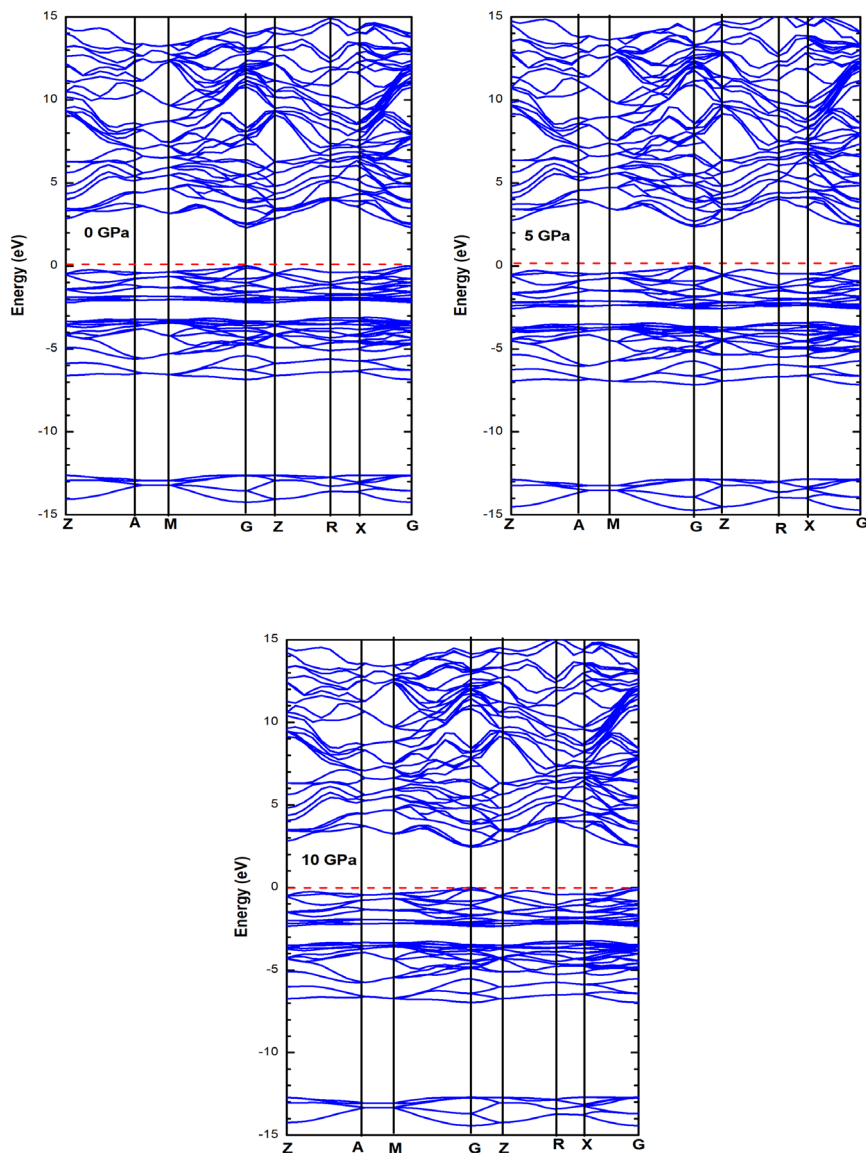
Fig. 2. Energy band structure for tetragonal CuAlS₂ at 0 and 10 GPa.

To further analyze the electronic behavior of tetragonal $CuAlS_2$, the energy distribution of different electronic states can be visualized using partial density of states (PDOS) and total density of states (TDOS). Fig. 3 (a)-(c), show the total density of states (TDOS) and partial density of states (PDOS) of tetragonal $CuAlS_2$ at 0, 5 GPa, and at 10 GPa pressures, respectively. And the DOS shows that the band gap of tetragonal $CuAlS_2$ is controlled by the Cu 3d and S 3p states (valence band) and the Al 3p and S 3p states (conduction band). These results agree with the previous calculation results[11]. However, as the pressure increases, the conduction and valence band shift to higher and lower energies, respectively. The shifts of the conduction and valence band result in an increasing band gap. The pressure dependence of the band gap is shown in Fig. 4, clearly indicating the band gap expend with increasing pressure. As the pressure increases from 0 to 10 GPa, the band gap increases from 2.3 to 2.45 eV. These results can be explained by the

shortened distance between the atoms when compressed, leading to a change in the interaction potentials. Due to the decrease of lattice constants under high pressure, the atoms become closer to each other, which leads to the decreased free orbit spacing between the outer valence electrons of each atom, the enhanced interaction between them, and thus the decreased band gap. To determine the pressure coefficient, we fitted the direct band gap to determine the pressure coefficient, we fitted the direct band gap ($E_g(P)$) with a quadratic function: $E_g(P)=E_g(0)+aP+bP^2$, and obtained $a=0.016$ eV/GPa and $b=3.41 \times 10^{-4}$ eV/(GPa)^2.
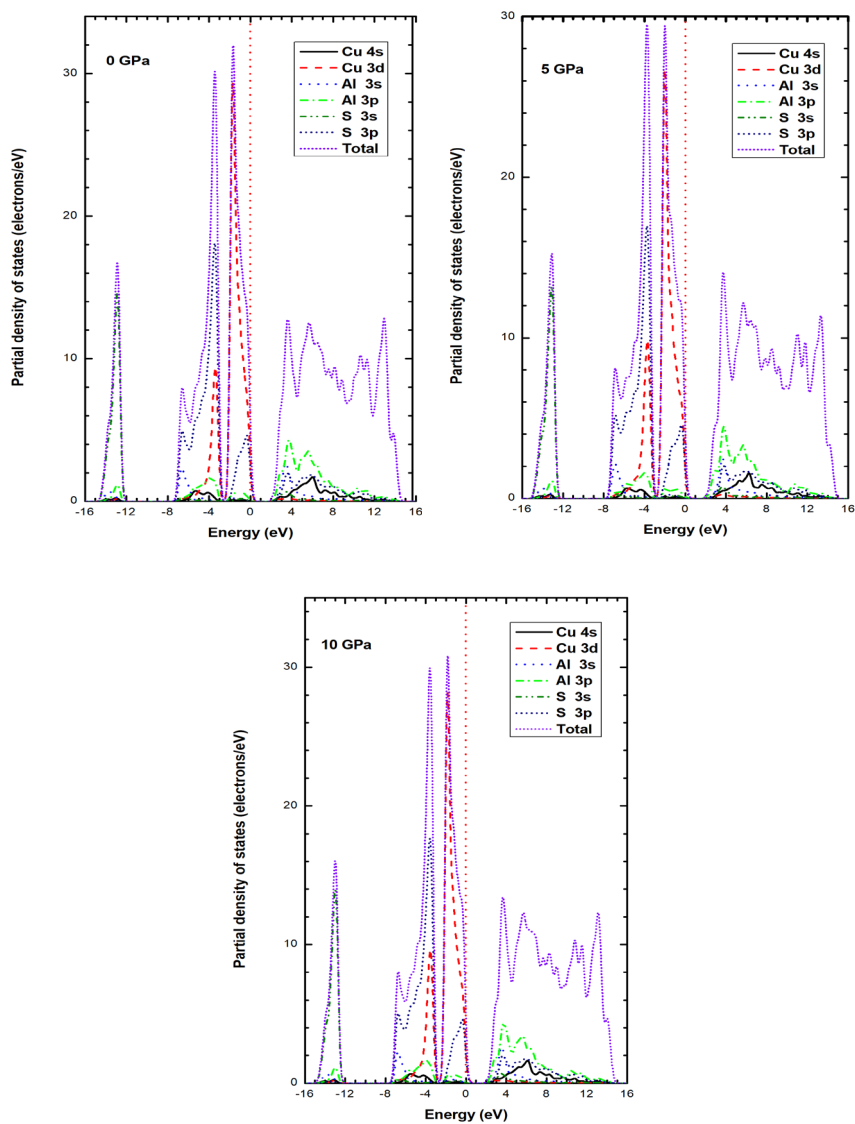

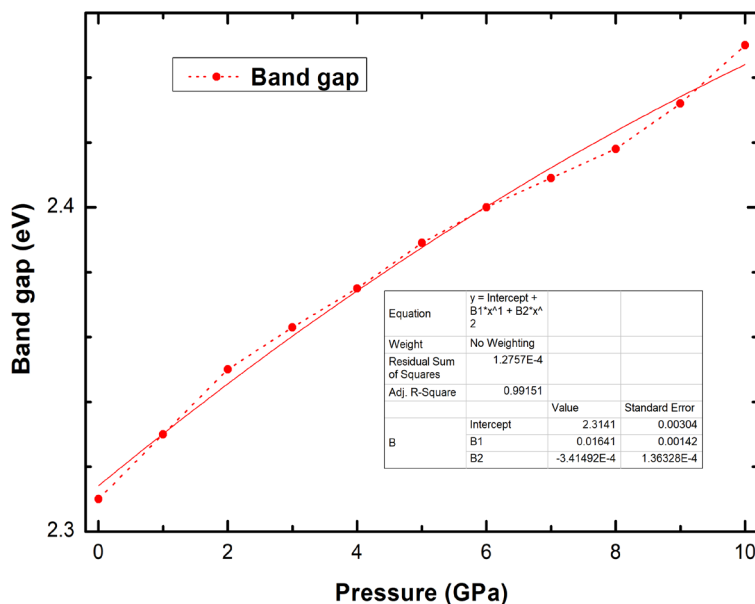*Fig. 3. The total and partial density of states for tetragonal chalcopyrite compound CuAlS$_2$ at 0, 5 GPa, and 10 GPa.*

Fig. 4. The pressure variations of energy band gaps for tetragonal CuAlS₂.

3.3. Elastic constants and mechanical properties

Elastic constants convey information about the mechanical stability, stiffness, strength, hardness, ductility and brittleness of the material. Moreover, the method of calculating the single crystal elastic constants (C_{ij}) under high pressure in this paper is the same as that in Ref. [27]. In this method, $G - G_0 = \frac{1}{2}V_0 \sum_{ij} C_{ij} e_i e_j$, G_0 is the equilibrium Gibbs free energy, V_0 is the equilibrium volume, and G is the strain Gibbs free energy. The strain tensor is defined as that in Ref. [28]. The tetragonal chalcopyrite phase CuAlS₂ has six independent elastic constants (C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, C_{13},)[28]. It requires six strains to obtain them are summarized in Table 2. Our calculated results at zero pressure were very close to the theoretical data[29], which shows that the elastic constants calculated by LDA are reliable in this paper. As a tetragonal structure[30], the mechanical stability criteria are given by $C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, ($C_{11}-C_{12}$)>0, ($C_{11}+ C_{33}-2C_{13}$)>0, and [$2(C_{11}+C_{12})+ C_{33}+4 C_{13}$]>0. It is seen that the elastic constant values calculated are found to be in harmony with the well-known Born criteria for the tetragonal structure under both zero pressure and 10 GPa pressure. This is in association with the fact that the tetragonal chalcopyrite phase CuAlS₂ compound is mechanically stable in the pressure limits performed.

Table 2. Elastic constants of tetragonal chalcopyrite compound CuAlS₂ at 0 GPa.

Pressure (GPa)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
0	52.18	124.12	78.37	80.97	127.18	51.68
Ref. [29]	108.2	57.3	60.8	117.9	55.1	54.7

Further, to study the effect of pressure on the mechanical properties of the tetragonal $CuAlS_2$, the elastic constants have been calculated over a wide range of pressure, from 0 to 10 GPa, are shown in Fig. 5. From this figure we observed the linear response of the elastic constants with increasing pressure. With the influence of pressure effect lattice parameters and volume become shorter and for this reason the change of elastic constants occurred. For the tetragonal crystal under external pressure (P), the mechanical stability can be checked by the following criteria[31]: C_{11}-P>0, C_{33}-P >0, C_{44}-P >0, C_{66}-P >0, (C_{11}-C_{12}-2P)>0, (C_{11}+ C_{33}-2C_{13}) -4P>0, and [2(C_{11}+C_{12})+ C_{33}+4 C_{13}]+3P>0. It is obvious that the elastic constants of $CuAlS_2$ satisfy all of the conditions above when the pressure is below 10 GPa, indicating that the tetragonal $CuAlS_2$ is mechanically stable below 10 GPa. Since values of C_{11} and C_{33} are more than about two times the values of C_{44}, C_{66}, C_{12}, and C_{13}, this shows that tetragonal $CuAlS_2$ structure has more resistance to compression than to shear at di□erent pressures. In the tetragonal system, C_{11} and C_{33} reflect the compression resistance and atomic bonding characteristics along the *a* direction and *c* direction, respectively. Under the pressure range of 0-10 GPa, the phenomenon of C_{33}>C_{11} indicates that the tetragonal $CuAlS_2$ has stronger compression resistance in the *c* directions than in the *a* and *b* direction, which is in accordance with the above analysis. To our knowledge, no experimental data for the pressure derivative of elastic constants of this compound has been given. Thus, the obtained results can be served as a prediction for future investigations.
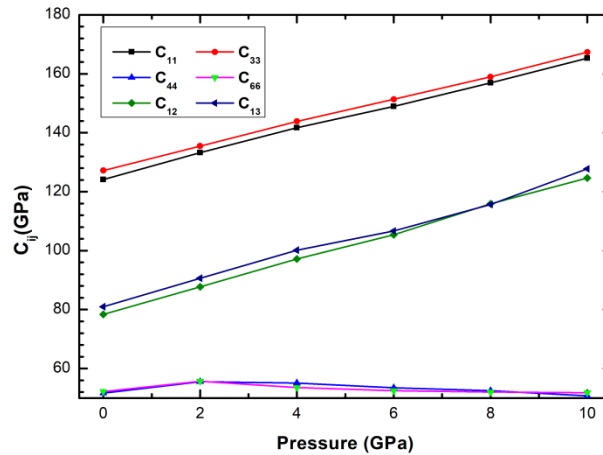

Fig. 5. The elastic constants of tetragonal chalcopyrite compound $CuAlS_2$ as functions of pressures.

The elastic parameters such as bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (*υ*) are very important parameters to understand the mechanical behavior of materials. So, it is very significant to know the variations of these parameters in accordance with pressure. Here, we use the Voigt-Reuss-Hill approximation to express the bulk modulus (B), shear modulus (G), and Young's modulus (E)[32]. For the tetragonal crystal, the expression of B, G, E, and Poisson' ratio *υ* can be found in Ref. [33]. The calculated results of tetragonal $CuAlS_2$ under pressure up to 10 GPa are shown in Fig. 6. It is shown that the bulk modulus B of tetragonal $CuAlS_2$ increase rapidly with the increasing pressure. However, the shear modulus (G) and

Young's modulus (E) of tetragonal $CuAlS_2$ increase linearly with pressure and reach their maxima at 2 GPa from where it starts to fall as pressure increases. The ratio between the bulk and the shear modulus (B/G), Poisson's ratio (υ), and Cauchy pressure (C_{13}-C_{44} and C_{12}-C_{66}) have been proposed by Pugh to predict brittle or ductile behavior of materials[34-35]. Crystal with B/G > 1.75, $υ$> 0.26, or C_{13}-C_{44}>0, C_{12}-C_{66}>0 is classified as ductile material. For the tetragonal $CuAlS_2$, From Fig. 6 (b), it is observed that B/G increases with pressure with a maximum value of 3.63 at 10 GPa and obtain the ductility. That of $υ$ is between 0.315-0.374, which is greater than 0.26. And that of C_{12}-C_{44} are positive. They all prove that the tetragonal $CuAlS_2$ is ductile.
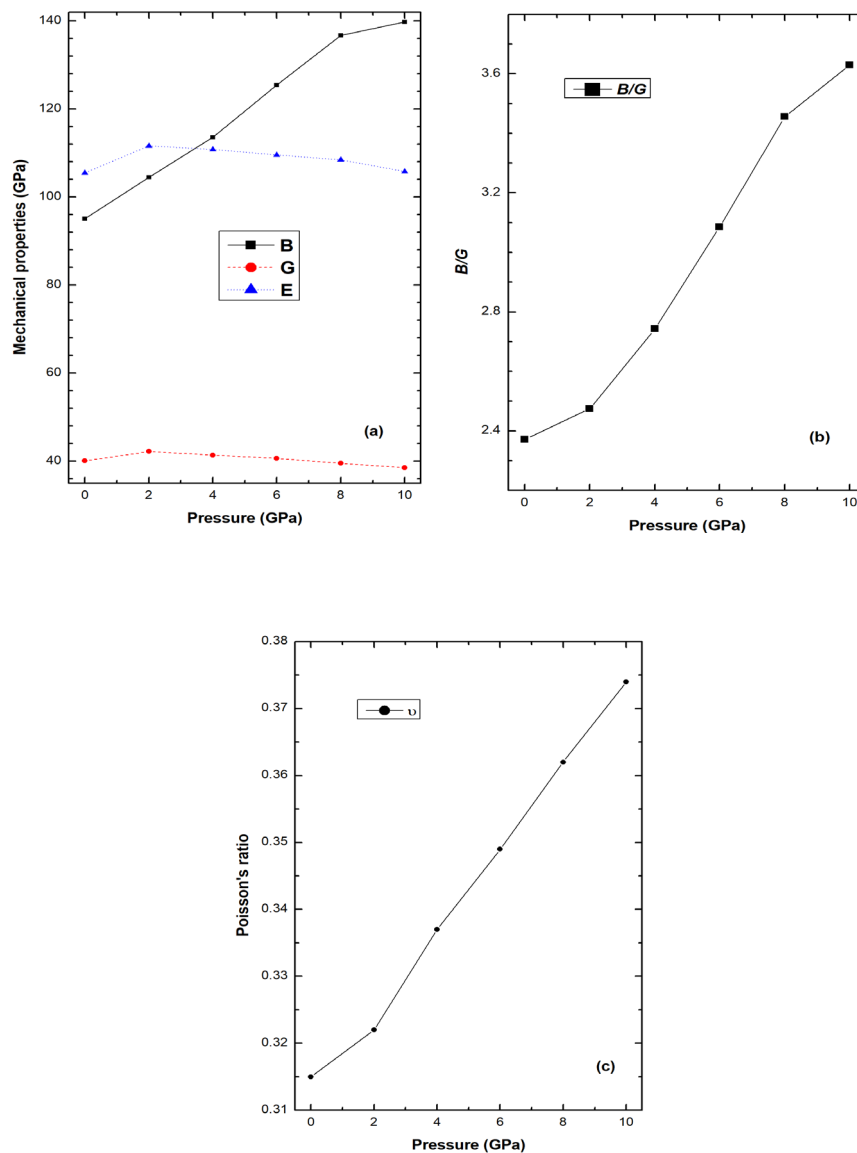
Fig. 6. The bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (υ)
of tetragonal chalcopyrite compound $CuAlS_2$ at given pressures.

4. Conclusion

In present work, based on the first-principles, the structural, mechanical, and electronic properties of ternary chalcopyrite semiconductor $CuAlS_2$ have been calculated under various pressures from 0 to 10 GPa. The obtained structure parameters were in fairly good agreement with the experimental and theoretical values. The mechanical properties like Shear modulus, Young's modulus, and Poisson's ratio are also calculated. According to the present results, we observe that these compounds in mechanically stable. Meanwhile, the analysis of the electronic structures reveals that the states near the valence band top are derived from Cu 3d and S 3p orbitals, and the lowest conduction band is composed of Al 3p and S 3p orbitals. We expect that the findings predicted the physical properties of this compound will promote future experimental studies on $CuAlS_2$.

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