



First Principles Study of the Structural and Electronic Properties of Polymorphs of CuI

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Abstract

The structural and electronic properties of zinc blende, rock-salt and wurtzite polymorphs of Copper (I) Iodide were investigated using the first principles method within the frame work of Density functional theory. The lattice constants obtained were comparable with the experiments. Energy versus cell volume calculations showthat the zinc blende and wurtzite structure are preferred over the rock salt at ambient pressure. The zinc blende and wurtzite structure showed a direct band gap both at zero and finite pressure while the rock salt structure showed a metallic band structure. The cohesive and formation energies of each structure were also calculated. Our results are in agreement with the available experimental and theoretical results.

Keywords: CuI, Density functional theory, Cohesive energy, Formation energy, Electronic structure.

1. Introduction

Transition metal chalcogenides (TMC) have attracted a lot of attention because of their enormous interesting properties (Chibueze et al., 2019; Chibueze, 2019; Ighodalo et al., 2017).CuI is an important class of TMC with tetrahedral coordinated zinc blende lattice structure under normal conditions. It has been studied extensively both experimentally and theoretically because of its vast applications in optical absorption measurements (Ves et al., 1981), electronic devices such as solar cells (Rusop et al, 2004), electrophotography, thermoelectric devices as well as photographic materials (Chaudhuri et al, 1990). CuI has high ionic conductivity ($\sim 0.1 \text{ S cm}^{-1}$), wide band gap ($\sim 3.1 \text{ eV}$), and large excitonic binding energy ($\sim 62 \text{ meV}$) and as such it has interesting physical and chemical properties (Adipranoto et al., 2009; Lewonczuk et al., 1994; Perera and Tennakone, 2003). It has been reported that the band gap of CuI reduces when itis doped with metallic ions (Ighodalo, et al., 2017).In a pure

semiconductor, there are enough electrons to occupy the valence band, and none left to occupy the conduction band. At a finite temperature however, some electrons would gain enough energy to migrate to occupy some states in the conduction band, leaving behind holes and unoccupied orbitals in the valence band. CuI can exist in zinc blende, rhombohedral, hexagonal(wurtzite), tetragonal, rock-salt and orthorhombic structures and these different structural phases display different properties. A transition from the predominant zinc blende phase at room temperature and pressure to rocksalt phase at about 9.6 GPa has been reported by Zhu *et al.* (2012). Bioud, *et al.* (2017) predicted a direct phase transition from the zinc blende to rocksalt phase at about 6.9 GPa. Under ambient pressure, the zinc blende phase transits to the rock salt phase at a temperature of 673K (Ves, 1981).

When CuI solid is heated, it changes its structure at 643 K from the zinc blende to the wurtzite and loses this structure at 673 K. This wurtzite phase co-exists with the rhombohedral phase within temperatures of 645-668K (Keen and Hull, 1995). At ambient temperature, under the influence of pressure, the wurtzite phase is found to be competing with the zinc blende phase, but it has a slightly higher energy, which suggests co-existence (Hernández-Cocoletzi *et al.*, 2009). Several experimental works have been done on CuI but works done on both wurtzite and rock salt phase the compound are scanty. Moreover, the formation and cohesive energy of wurtzite and rock salt phase have not received adequate attention in the literature. In this research work, we performed first principle comparative study of the structural and electronic properties of zinc blende, wurtzite and rock salt structures of CuI within

density functional theory (DFT) using the generalized gradient approximation (GGA).

2. Computational Details

Ab-initio DFT calculations were performed for the structural and electronic properties of zinc blende, wurtzite and rock salt polymorphs of CuI using generalized gradient approximation (GGA) with the Wu and Cohen exchange correlation (Wu and Cohen, 2006) as implemented in Quantum-Espresso code (Giannozzi *et al.*, 2009). The Kohn-Sham functions were expanded in a Plane wave basis sets with kinetic energy and augmented density cut-offs of 50 Ry and 400 Ry respectively. At this cut-off, the total energy is converged to within 1 mRy/atom as shown in figure 1.

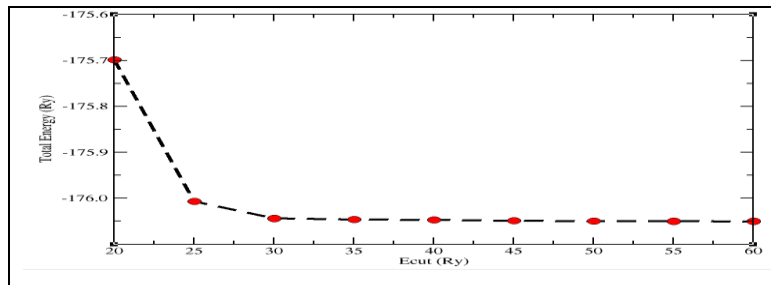


Fig 1: Total energy vs cut-off energy.

The interaction between valence electrons and ions were described using the scalar relativistic ultrasoft pseudopotential. The electrons in the Cu 4s, 4p, 3d and I 5s, 5p orbitals are taken as the valence electrons. Brillouin zone integration was done over $8 \times 8 \times 8$, $9 \times 9 \times 6$ and $8 \times 8 \times 8$ k-points grids for the zinc blende, wurtzite and rock-salt phases, respectively, sampled by Monkhorst-Pack scheme (Monkhorst and Pack, 1976) using the ordinary Gaussian spreading. The optimization criteria for the ionic geometry relaxation was 0.0001 Ry for total energy and 0.001 Ry/au for the Hellmann-Feynman forces.

3. Results and Discussion

a. Structural properties and stability

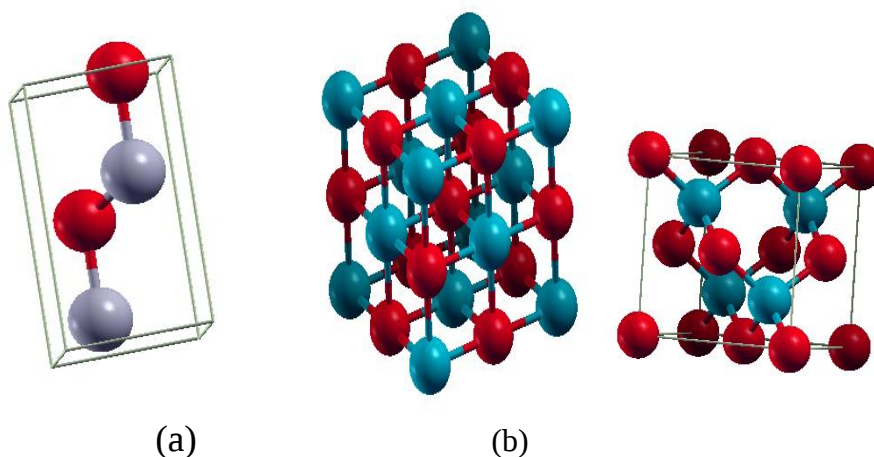


Fig. 2. Crystal structure of CuI polymorphs (a) Wurtzite (w-CuI) (b) Rock salt (c) Zincblende (ZB-CuI).

Crystal structure of wurtzite (w-CuI), rock salt and Zincblende (ZB-CuI) polymorphs of CuI are shown in Figure 2. The graph of total energy as a function of unit cell volume for the three polymorphs of CuI is shown in Figure 3. It can be seen from the figure that ZB-CuI has the least energy (and therefore highest stability) at large volumes (or low pressures). This is in agreement with literature since the experimental work (high resolution x-ray diffraction) of Keen and Hull (1994) revealed that the ground state of CuI is the zinc blende structure (ZB). It can be seen also from the figure that ZB-CuI and w-CuI compete for stability throughout the various volume points. The results in the figure suggest a coexistence of both wurtzite and zinc blende structures in the ground state of CuI. This is also in agreement with the literature (Palomino-Rojas et al., 2007; Cocolletzi et al., 2009). The rock-salt phase takes over at lesser volume (higher pressure) regions. As energy is a measure of stability, the rock-salt phase is less stable at low volumes, compared to ZB-CuI and w-CuI at the equilibrium volume.

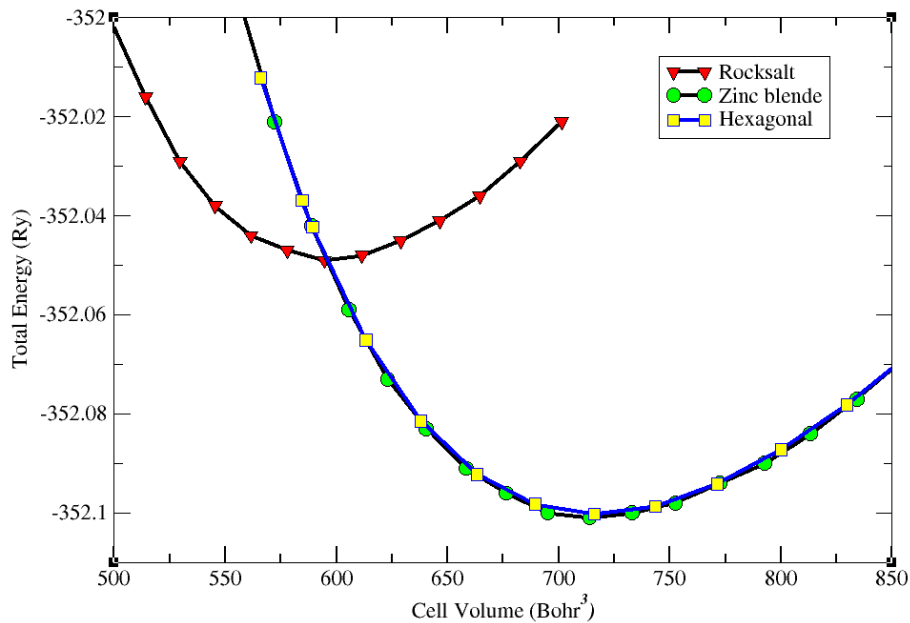


Fig 3: The graph of the total energy against Cell volume.

The graph of the total energy against Cell volume for both ZB-CuI, w-CuI and rock-salt-CuI phase we calculated is shown in figure 8.

The formation energies of ZB-CuI, w-CuI and rock-salt-CuI were obtained as 2.635 eV, 2.632 eV and 2.277 eV respectively. Their cohesive energies were also obtained as 8.513eV, 8.510 eV and 8.156 eV respectively. Our theoretical results as well as other results are presented in Table 1. From the table, our calculated lattice parameters and the volume for zinc blende-CuI were found to be 5.975 Å and 53.34 Å³ respectively. Our calculated value for the lattice parameter is in agreement with theoretical calculated result of 6.08 Å obtained by Coccoletzi *et al.* (2009). Similarly, our calculated value for unit cell volume of 53.34 Å³ is also in agreement with 56.0 Å³ (Zhu, *et al.*, 2012), 56.29 Å³ (Coccoletzi *et al.*, 2009) and 56.83 Å³ (Keen and Hull, 1995). We obtained formation energy of -2.635 eV for the ZB-CuI. Unfortunately, we could not find any previous work in the literature to compare our result. Our cohesive energy of -8.513 eV is comparable with -7.63 eV obtained by Hernández-Coccoletzi *et al.* (2009) and -5.32 eV obtained by Harrison (1980). For the Wurtzite-CuI, our calculated lattice constants “a” and “c” of value 4.206 and 6.924 respectively compares well with 4.30 and 7.181 respectively obtained by Hernández-Coccoletzi, *et al.* (2009) and our calculated unit cell volume of 106.101 Å³ is also in fair agreement with 57.56 Å³ obtained by them (Hernández-Coccoletzi, *et al.*, 2009).

Furthermore, for the rock-salt-CuI, our calculated lattice parameters and the unit cell volume were found to be 5.613 Å and 44.21 Å³ respectively as also shown in Table 1. Our calculated value for the lattice parameters of 5.613 Å is in agreement with theoretical calculated result of 5.733 Å obtained by Zhu, *et al.* (2012). Similarly, our calculated value for unit cell volume of 44.21 Å³ is also in agreement with 47.1 Å³ (Zhu, *et al.*, 2012). Our formation energy value of -2.277 eV could not be compared with any work available in literature but our cohesive energy

of -8.156 eV compares well with -8.02 eV (Hernández-Cocoletzi, *et al.* (2009). Again, we obtained a metallic band gap at zero pressure but an indirect band gap of 2.54 eV was reported by (Yüce *et al.*, 2007). Generally, our theoretical calculated results are in line with other available theoretical calculations done with DFT (Zhu, *et al*, 2012), (Hernández-Cocoletzi, *et al.*, 2009) and with experimental observations (Keen and Hull, 1995; Yashima, *et al*, 2006).

Table 1: Lattice constant and formation and cohesive energy of zinc blende, wurtzite and rock salt structures of CuI

Crystal Structure	Space group	Lattice constant (Å)			Unit cell volume (Å ³)		
		This work	Experiment other work	Theoretic other work	This work	Expt. Other work	Theoretical other work
Zinc Blende	F43m or 126	a=5.975	6.054 ^A	A=6.074 ^F	53.34	56.83 ^H	56.0 ^F
Wurtzite	P6 ₃ m or 186	A=4.206 C=6.924	-	a=4.30 ^D c=7.181	106.101	-	57.56 ^D
Rock-salt	Fm3m or 225	a=5.613	-	a=5.733 ^F	44.21	-	47.1 ^F
Crystal Structure	Formation energy (eV)				Cohesive Energy (eV)		
	This work	Expt. other work	Theoretical other work		This work	Experimental other work	Theoretical other work
Zinc Blende	-2.635	-	-		-8.513	-5.32 ^C	-7.63 ^C
Wurtzite	-2.632	-	-		-8.510	-	-7.60 ^D
Rock-salt	-2.277	-	-		-8.156	-	-8.02 ^D

A= (Yashima, *et al*, 2006); B= (Keen and Hull, 1995); C= (Harrison, 1980)

D= (Hernández-Cocoletzi, *et al* 2009); E= (Yüce, *et al*, 2007); F= (Zhu, *et al*, 2012).

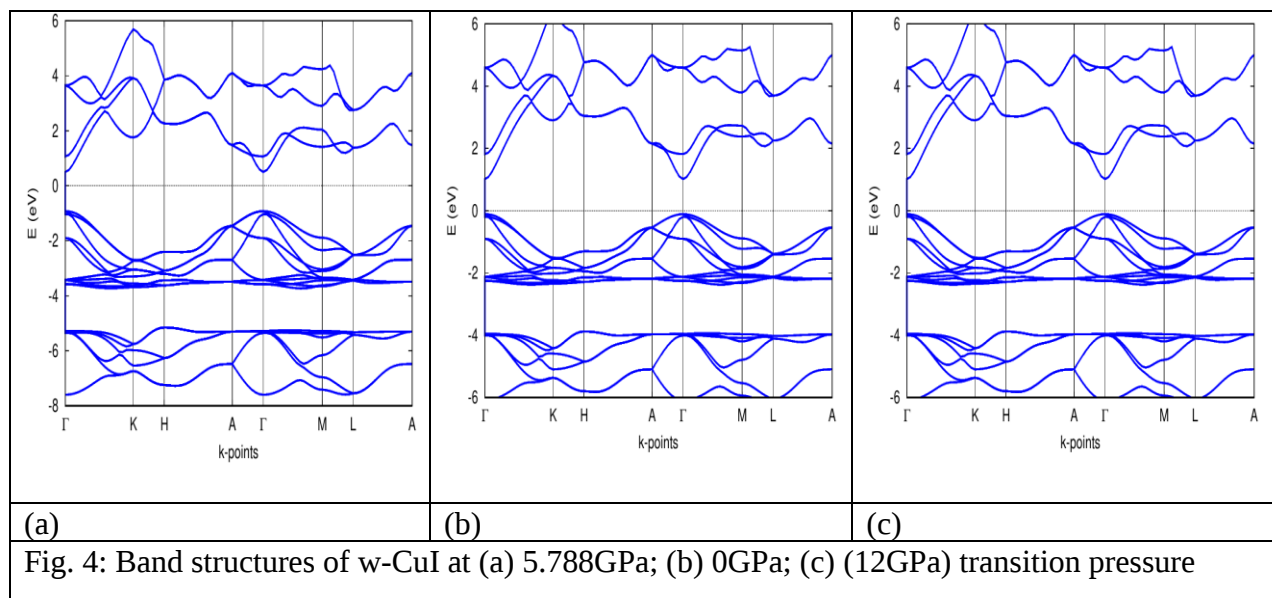
b. Electronic properties

The band structures of three CuI polymorphs were obtained at room temperatures for various pressures. The Band structures of wurtzite phase of CuI at 5.788 GPa, 0 GPa and rock salt-w CuI phase transition pressure of 12 GPa are shown in Figure 4. The top of the valence band for wurtzite phase of CuI (w-CuI) is three-fold degenerate at all the pressures considered. Direct band gaps were obtained at the Γ point and band gaps are 1.45 eV, 1.16 eV and 1.80 eV at pressure of 5.788 eV, 0 GPa and 12 GPa respectively as presented in Table 2. The density of states is presented in Figure 5.

Table 2: Electronic band gap of zinc blende (ZB), wurtzite and rock-salt (RS) structures of CuI at zero, ZB-RS transition pressure and at a pressure between zero and transition pressure.

Crystal Structure	Band gap type	Band gap (eV)				
		This work			Experiment Other work	Theoretical other work
		0 GPa	P _{MIDDLE}	ZB-RS transition Pressure		
Zinc Blende	direct	2.024	2.154	2.068	2.95 ^C	1.13 ^F
Wurtzite	direct	2.024	2.068	2.111	-	-
Rock salt	metallic	0.0	-	-	-	Indirect 2.54 ^E

C= (Harrison, 1980); E= (Yüce, et al, 2007); F= (Zhu, et al, 2012).



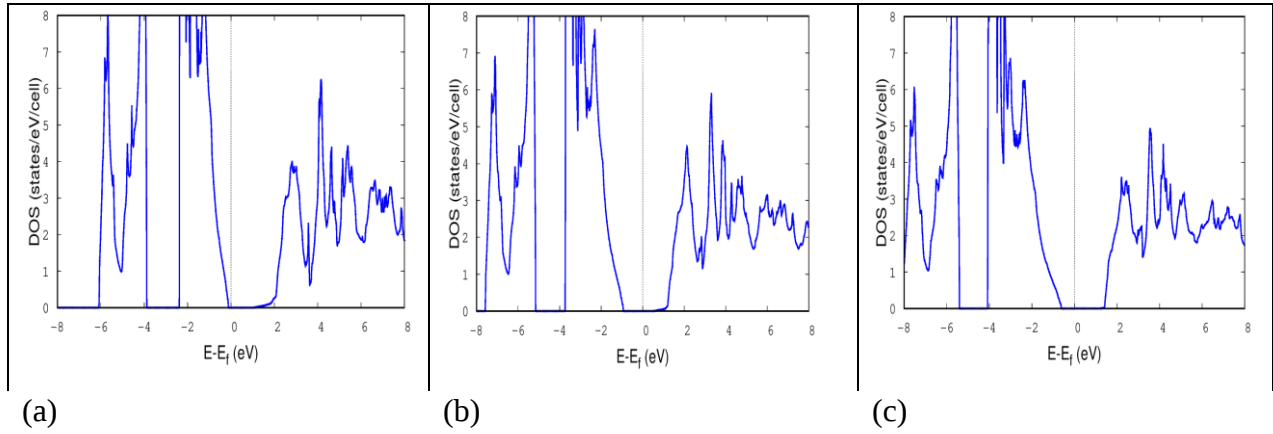


Fig. 5. Density of states for the w-CuI at (a) 5.788 GPa; (b) 0 GPa; (c) (12 GPa) transition pressure.

Figure 6(a) is the band structure of rock-salt-CuI. From the figure, the top of the valence band and the bottom of the conduction band crosses the Fermi level, thereby creating zero energy gap. This implies that rock-salt-CuI is a conductor and metal. Due to its metallic band gap, rock-salt-CuI is not a good material to use as a semiconductor, and thus is of little interest in solar cell applications. The density of states for rock salt-CuI is presented in Figure 6(b). The band structures of ZB-CuI at 5.73 GPa, 0 GPa and 14.73 GPa (transition pressure) are presented in Figure 7. Similar to w-CuI, the band structure of the ZB-CuI is seen to remain fairly similar throughout the various pressures. ZB-CuI has direct band gap of 1.31 eV, 1.09 eV and 1.71 eV at 5.73 GPa, 0 GPa and 14.73 GPa respectively.

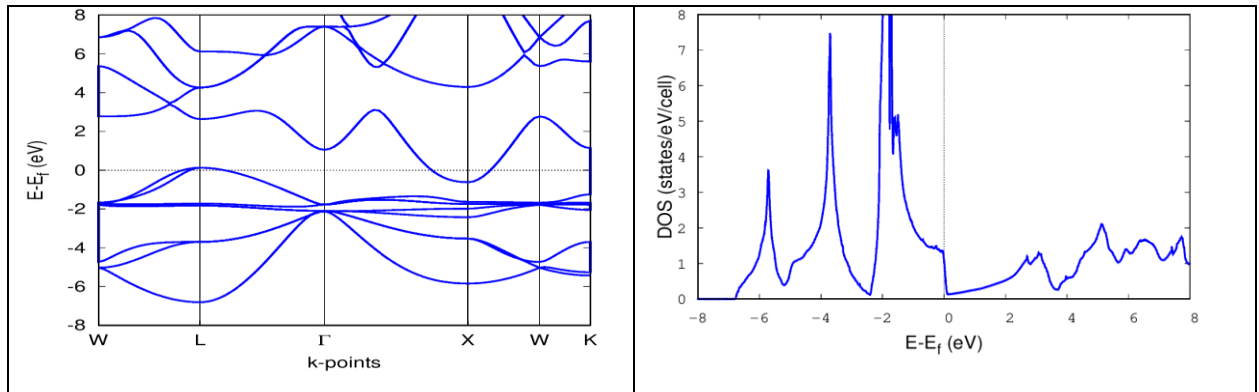


Fig. 6(a): Band structure of rock-salt-CuI.

Fig. 6(b): Density of States for rock salt-CuI.

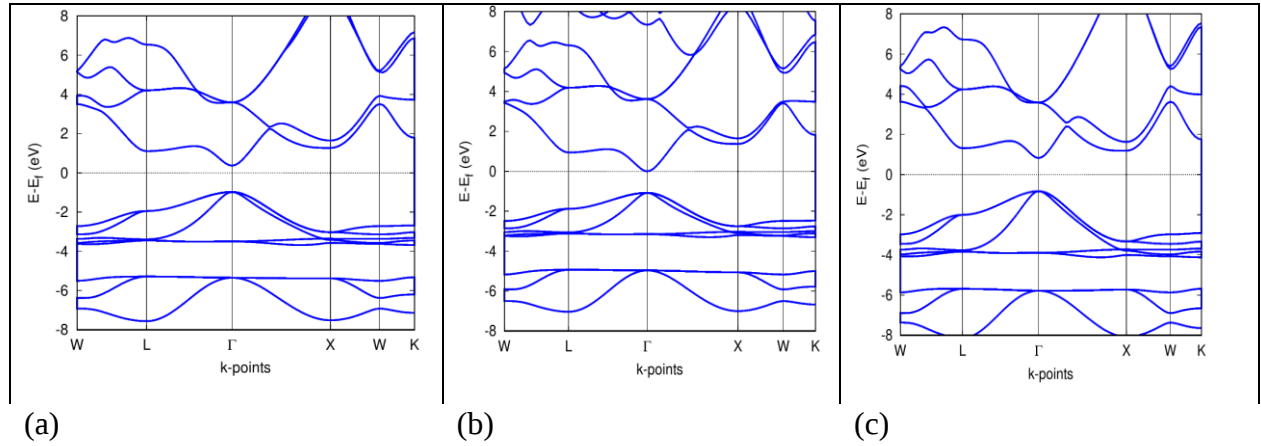


Fig. 7: Band structures of ZB-CuI at (a) 5.73 GPa (middle pressure); (b) 0 GPa (zero pressure); (c) 14.73 GPa (transition pressure).

. The density of states (Figure 8) reveal the same band gap size as the electronic band structure. Also, the direct band gap of 2.024 eV we obtained at zero pressure is in fair agreement with 2.95 eV (Harrison, 1980) and 1.13 eV (Zhu, *et al*, 2012).

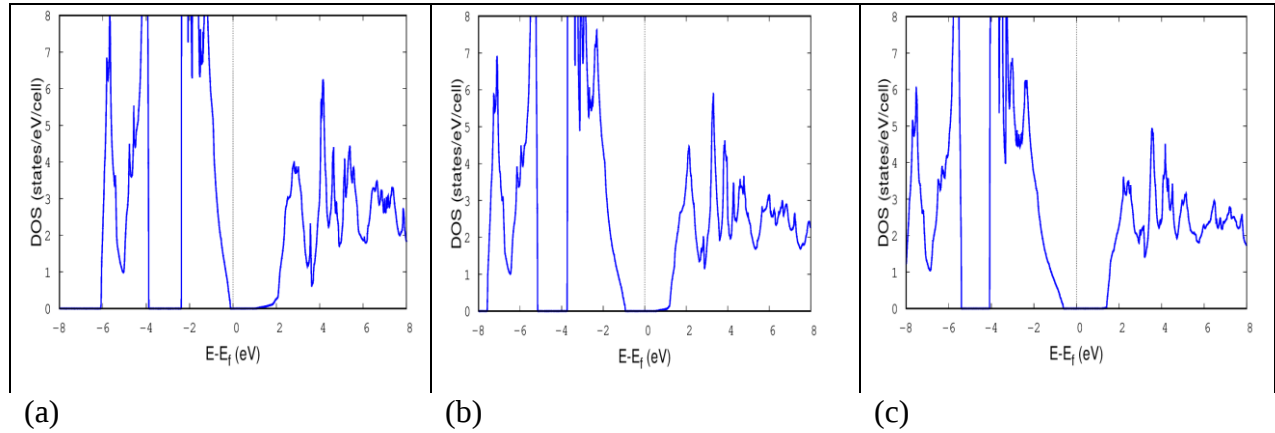


Fig. 8. Density of states for the w-CuI at (a) 5.788 GPa; (b) 0 GPa; (c) (12 GPa) transition pressure.

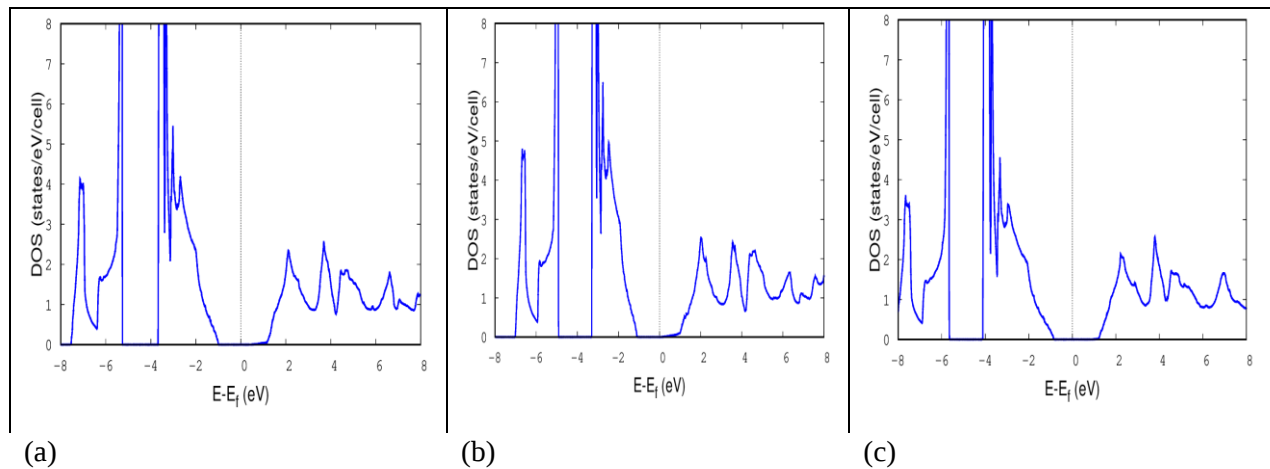


Fig. 7. Density of states for the ZB-CuI at (a) 5.73GPa (middle pressure); (b) 0GPa (zero pressure); (c) 14.73GPa (transition pressure).

4. Conclusion

The structural and electronic properties of the wurtzite, rock-salt and zinc-blende polymorphs of copper (I) iodide have been studied using the first principles density functional theory. The zinc blende phase at ambient pressure has the most stable structure relative to the wurtzite and rock-salt phases. The zinc-blende phase transits to rock-salt phase at a pressure of 14.73 GPa. The wurtzite phase appears to be in stability competition with the zinc blende phase, but the zinc blende has slightly lower energy of about 2 meV. Rock-salt-CuI was found to have a metallic band structure and as such is a metal. The zinc blende and wurtzite have direct band gaps close to experimental results. ZB-CuI has the lowest formation and cohesive energies, where the negative signs denote feasibility of synthesis. We observe that our DFT calculations using WC-GGA for exchange correlation exaggerated the cohesive energies and the transition pressure but underestimated the lattice parameters when compared with other available theoretical and experimental results. Nevertheless, the results of this work are found to be in fairly comparable with the experimental data.

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