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ELECTRONIC PROPERTIES AND STRUCTURAL PHASE TRANSITION OF IV-IV AND III-V SEMICONDUCTORS UNDER PRESSURE: A FIRST PRINCIPLE APPROACH

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ABSTRACT
Binary semiconductors are one of the nominee materials for the manufacture of third-generation infrared photon detectors and ICs with ultra-high speed and ultra-low power consumption. In this work, we present the electronic properties of IV-IV (SiC) and III-V (GaSb, InSb) semiconductors in Zinc-blend (ZB), Rocksalt (RS), and Wurtzite (WZ) Phases and the structural Phase transition using first principle. Our result shows that SiC, GaSb and InSb crystallize as metals in the RS Phase but as semiconductors in the ZB (WZ) Phases with an energy gap of 1.30 eV (2.26 eV), 0.23 eV (0.14 eV) and 0.17 e V (0.21 eV) respectively; indicating that both GaSb and InSb are narrow bandgap semiconductors while SiC is a wide bandgap semiconductor. These results are in good agreement with other theoretical and experimental reports. A phase transition from ZB – RS and from WZ – RS phases is observed at a pressure of 9.72 GPa (7.65 GPa), 72.4 GPa (72.4 GPa) and 8.063 Gpa (8.063 Gpa) for InSb, SiC and GaSb respectively. This shows that under high pressure, the materials undergo a transition from the semiconducting (ZB or WZ) Phase to the metallic (RS) Phase.
Keywords: Semiconductors, SiC, GaSb, InSb, Phase Transition

INTRODUCTION

Binary semiconductors (IV-IV, III-V, and II-IV) have been widely used in electrical and optoelectronic devices, as well as an anode in rechargeable lithium batteries, over the previous century. As a result of these applications, they have become essential components of an advanced information society. These materials are valuable in thermo-photovoltaic cells and advanced device applications due to their great mobility (Adachi, 2004; Bolognesi, Dvorak, & Chow, 1998; Wachtler, Winter, & Besenhard, 2002; C. Wang, 2004; Zhu-Feng, Zi-Zhong, Mei-Chun, & Yong, 2003). Under applied pressure, these semiconductors undergo a sudden change in their atomic arrangement (structural phase transition). This is because under compression, the Gibbs free energy of various conceivable atomic configurations vary, and at some point, it becomes advantageous for the material to alter the kind of atomic arrangement. If the change is discontinuous or continuous, yet there is a change in crystal symmetry, the change is considered to be a phase transition, with the properties of high-pressure phases probably differing significantly from those of regular phases. Most group IV and III– V semiconductors have zinc-blende (ZB) and wurtzite (WZ) as common structures.

Pressure's effect on the electronic properties of III–V and other binary compounds can be studied experimentally in a variety of ways (Müller, Trommer, Cardona, & Vogl, 1980; K. Wong, Chim, Huang, & Zhu, 2008; K. M. Wong, 2009). In recent decades, however, theoretical and technological advances in density-functional theory (DFT) and pseudopotential calculations have provided researchers with effective methods for predicting electrical and energetic properties revealed by novel experimental approaches.

Naeemullah et. al (2014) investigated the pressure-induced structural Phase transition of III-Sb binary compounds from Zinc-blend to Rocksalt using TB-mBJ potential approximation. They found that a phase transition occurs from ZB to RS at 8.16 and 4.70 GPa for GaSb and InSb respectively (Naeemullah, Murtaza, Khenata, Mazharullah, & Omran, 2014). Wang (2002) has shown that the Zinc-blende structure of III-V semiconductors transforms to a rocksalt structure under pressure (S. Wang & Ye, 2002). Also, Varshney et. al., by formulating an effective interaction potential that incorporates the long-range Coulombic and covalence effects reported the structural Phase transition of GaSb and InSb from ZB to RS as 7.0 and 4.4GPa

respectively (Varshney, Joshi, Varshney, & Gorai et al. investigated the phase transition in SiC and found that at a pressure of 68.5 GPa the SiC structure transforms from ZB to RS (Gorai, Bhattacharya, & Kondayya, 2017). In this study, we carry out an in-depth investigation of the electronic properties and structural phase transition from ZB to RS, and WZ to RS of IV-IV and III-V semiconductors using the generalized gradient approximation. The results obtained are compared with experimental and other available theoretical results.

COMPUTATIONAL DETAILS

The first principle calculation has been carried out using the Quantum ESPRESSO package (Giannozzi et al., 2009). The electron-ion interaction is described using ultrasoft pseudopotentials, with exchange-correlation energy being described by the generalized gradient approximation (GGA) in the scheme proposed by Perdew-Burke-Ernzerhorf (PBE) (Perdew, Burke, & Ernzerhof, 1996). Energy cut-off is set to 30 Ry for SIC and InSb, and 45 Ry for GaSb. To determine the structural properties of the materials, a $6 \times\times 6, 8 \times 8 \times 8$ and $10 \times 10 \times 10$ k-point mesh was used for the Brillouin zone integration for InSb, GaSb and SiC respectively. All structures were optimized using a variable cell relaxation until all the forces were smaller than 10^{-3} eV/A and the difference between the final total energy of the last two consecutive steps was less than 10^{-5} eV. A much denser k-point grid is adopted for the calculation of electronic properties. The phase transitions among the ZB, RS and WZ phases are obtained from the Gibbs free energy (eq. 1).

$$G = E + PV - TS \qquad (1)$$

Where; G is the Gibbs free energy, E is the internal energy, P is the pressure, T is the temperature and S is the entropy. Since all calculations are performed at T = 0 K, the Gibbs free energy becomes equal to the enthalpy ($H = E + PV$). At this temperature, the thermodynamically stable phase is the one with the lowest enthalpy at a given pressure. A transition occurs when the enthalpy of the lower pressure phase coincides with some other phase at high pressure which then becomes the stable phase above this pressure (Munjal, Sharma, Vyas, Joshi, & Sharma, 2012).

RESULTS AND DISCUSSION

Structural Properties

The ZB and RS structures possess a face-centered cubic packing arrangement with four molecules in their unit cell, while the WZ has a hexagonally packed lattice [Figure. 1 (a-c)]. Complete optimization of the structures was performed to determine the lattice parameters a *and* c for SiC, GaSb and InSb in the three Phases (ZB, RS and WZ). As shown in Table 1, the lattice constant a for SiC is 8.28 Å, 7.66 Å and 3.09 Å in the ZB, RS and WZ phase respectively. To obtain other structural properties (eg. Volume, bulk modulus), the data from the optimized structures were fitted in the Murnaghan equation of state (eq. 1) (Tyuterev & Vast, 2006) and the results are summarized in Table 1. These results are in good agreement with available experimental and other theoretical results as shown in Table 1.

$$P(V) = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \qquad (2)$$

Where; P is the pressure, V_0 and V are the initial and final Volumes, B_0 and B_0' are the bulk modulus and the first derivative of the bulk modulus.

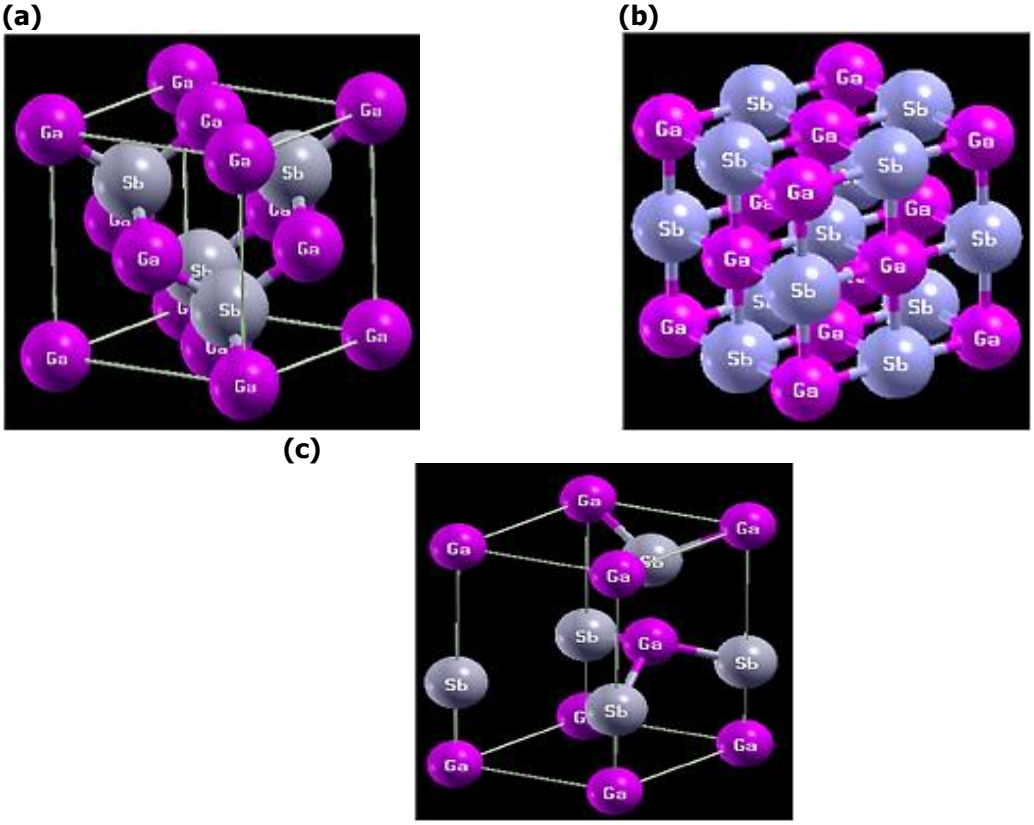


Figure 1*. Structure of GaSb in*; (a) *Zinc blende phase, (b) Rock salt phase and (c) wurtzite phase*

Table 1: Calculated Structural Properties, band gap energy and transition Pressures

		a (Å)	*c* (Å)	*B*(GPa)	PT(GPa)	Band gap (**eV**)
SiC	Zinc Blende **(ZB)**					
	This work	8.28		208.4	72.4	1.302
	Others	8.28[a], 8.27[b]		208[a], 213[b]		1.53[c], 1.40[d]
	Experimental	-		-		2.39[e]
	Rock Salt (**RS**)					
	This work	7.66		257.8		
	Others	8.24[f]		278.4[e]		
	Experimental	-		-		
	Wurtzite **(WZ)**					
	This work	3.09	5.07	209.3	72.4	2.26
	Others	3.06[g], 3.12[h]	5.07[f], 5.03[g]	216[g]	75.4[i]	2.14[g]
	Experimental	-	-	-	100[j]	3.33[k]
GaSb	Zinc Blende **(ZB)**					
	This work	6.21		49.1	8.06	0.23
	Others	5.98[l], 6.21[m]		56.7[l], 44.6[m]	7[n], 8.16[o]	0.54[l], 0.50[p]
	Experimental	6.08[q]		56.0[q]	6.2[r]	0.81[s]
	Rock Salt (**RS**)					
	This work	5.85		47.7	4.63	-
	Others	5.72[o]		51.00[o]		
	Experimental	-		-	-	-
	Wurtzite **(WZ)**					
	This work	4.23	7.11	53.1	8.06	0.14
	Others	4.23[l], 4.31[t]	6.92[l], 8.14[t]	55.80[l]		0.16[l], 0.50[t]
	Experimental	-	-	-		-
InSb	Zinc Blende **(ZB)**					
	This work	6.67		46.50	9.72	0.09
	Others	6.48[o], 6.34[l]		46.78[o], 47.60[l]	4.70[o]	0.0[o], 0.21[l]
	Experimental	-		46.0[u]		0.20[u]
	Rock Salt (**RS**)					
	This work	6.13		61.0	-	-
	Others	6.02[o]		61.63[o]		
	Experimental	-		-	-	-
	Wurtzite **(WZ)**					
	This work	4.40	7.40	46.80	7.65	0.10[l]
	Others	4.47[l]	7.33[l]	46.88[l]	-	0.21[l]
	Experimental	-	-	-	-	-

[a] (Van Ginhoven, Chartier, Meis, Weber, & Corrales, 2006)
[b] (Ziambaras & Schröder, 2003)
[c] (Liu et al., 2009)
[d] (Bui, 2012)
[e] (Jiang & Cheung, 2009)
[f] (Durandurdu, 2007)
[g] (Vashishta, Kalia, Nakano, & Rino, 2007)
[h] (Zhang, Cui, Ruan, & Zhang, 2014)
[i] (Rössler, 2011)
[j] (Yoshida, Onodera, Ueno, Takemura, & Shimomura, 1993)
[k] (Park, Cheong, Lee, & Chang, 1994)
[l] (S. Wang & Ye, 2002)
[m] (Salehi, Badehian, & Farbod, 2014)
[n] (Varshney et al., 2010)
[o] (Naeemullah et al., 2014)
[p] (De & Pryor, 2010)
[q] (Paufler, 1983)
[r] (Yu, Spain, & Skelton, 1978)
[s] (Tit, Obaidat, Reshak, & Alawadhi, 2010)
[t] (Gmitra & Fabian, 2016)
[u] (Vurgaftman, Meyer, & Ram-Mohan, 2001)

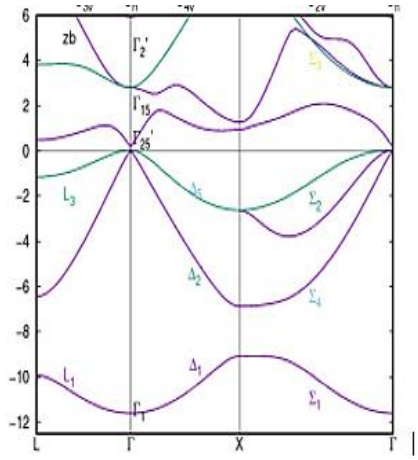
Electronic Properties

The electronic band structure of GaSb, InSb and SiC was investigated at the high symmetry points of the ZB, RS and WZ Brillouin zone. The electronic energy bands calculated are shown in Figures 2 and 3, with the zero of the energy set at the top of the valence band for all three structures. The Fermi level at zero has been normalized by subtracting the energy with the Fermi energy value to make it a reference energy level. The conduction and the valence bands are defined as the nearest energy states above and below the Fermi level, respectively.

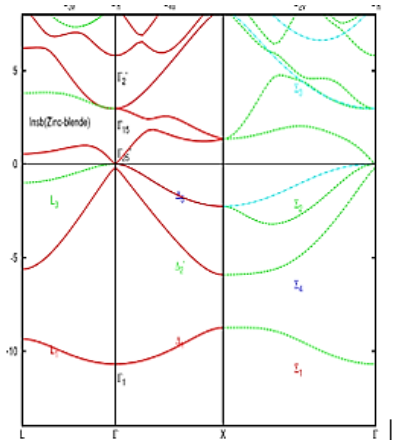
Figure 2, clearly shows that in the ZB Phase, both GaSb and InSb have a direct bandgap located at the Γ symmetric point with a bandgap energy of 0.234 eV and 0.01 eV respectively. SiC – ZB phase (figure 3) on the other hand possess an indirect bandgap energy, measured from the top of the valence band, at the Γ point, to the bottom of the conduction band at the X point. The calculated energy gap is 1.302 eV, which is comparable with other theoretical data that used a similar computational approach: 1.37 eV (Karch, Pavone, Windl, Strauch, & Bechstedt, 1995) and 1.53 eV (Bui, 2012), but low compared to experimental data. This is of course because DFT underestimates bandgap value by about 50%, resulting in lower electrical bandgap energy than the actual value (Gali, 2011). Notwithstanding, the energy bandgap of 1.302 eV found is still in good agreement with the experimental data, because the bandgap error in wide bandgap semiconductors, like ZB-SiC, was quantitatively analyzed as roughly 1.0 eV (Gali, 2011).

ZB

GaSb

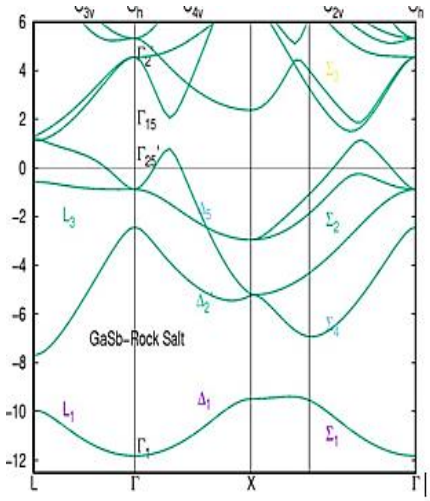


InSb

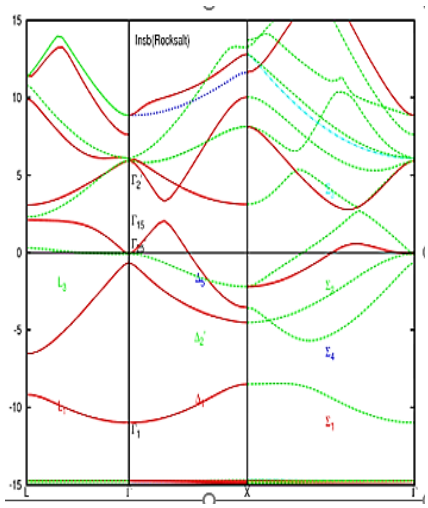


RS

GaSb



InSb



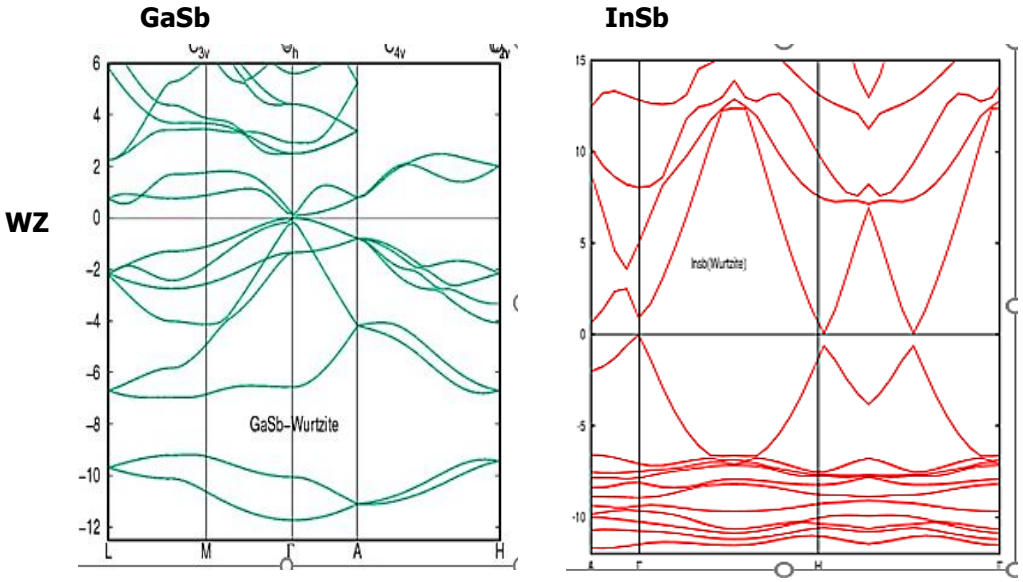


***Figure 2**. Band Structure of GaSb and InSB in ZB, RS and WZ phases.*

For the RS Phases, both SiC, GaSb and InSb have no distinct bandgap as compared to ZB and WZ structures. This suggests that in the Rocksalt phase, all three materials exhibit a metallic nature. This occurs when pressure is applied leading to an overlapping among the neighboring atoms. Hence the bandgap closes. Also, Figures 2 and 4c show that WZ-GaSb and WZ-InSb again have a direct bandgap located at the Γ point while WZ-SiC has an indirect bandgap with all valence band maximum located at Γ point and conduction band minimum located at K point. The calculated band gap values are 2.26, 0.09 and 7.11 eV respectively.

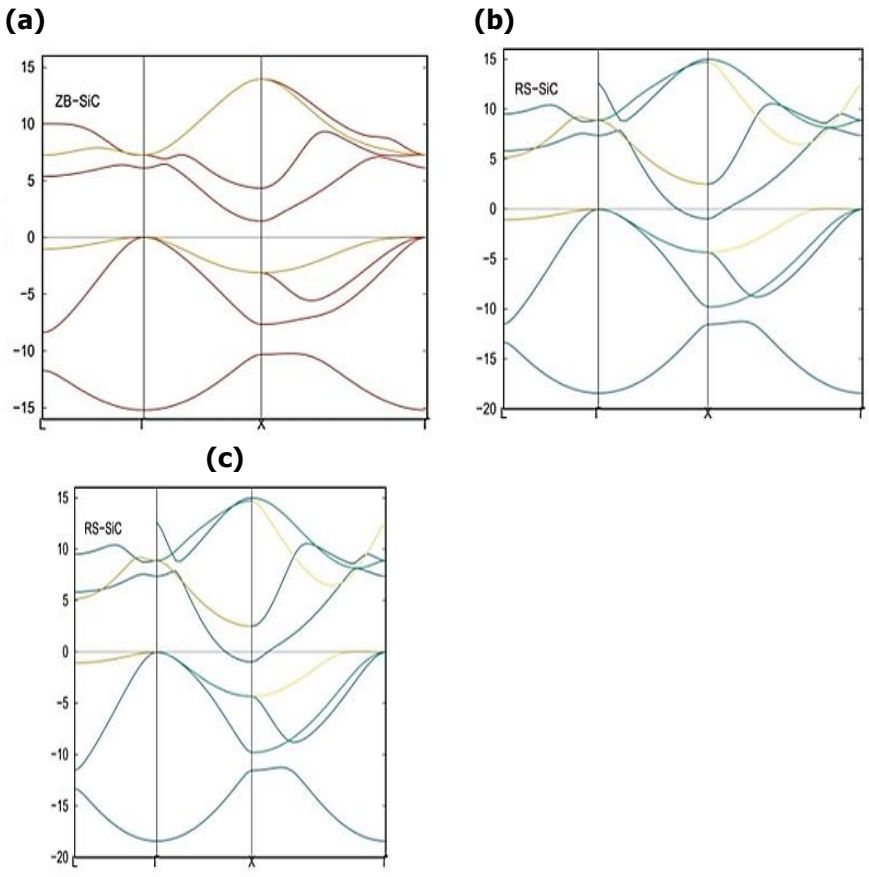


Figure 4. *Band Structure of SiC in; (a) ZB Phase, (b) RS Phase and (c) WZ Phase*

Phase Transition

The energy-volume calculation was performed to study the stability of different phases of SiC, GaSb and InSb. The computed total energy as a function of volume for the three phases being studied is shown in figure 5. Accordingly, the Zinc Blende phase is found to be the most stable for all three systems since it has the lowest minimum energy. This is in good agreement with other results (Vashishta et al., 2007) and (S. Wang & Ye, 2002).

The transition pressure between the different phases of SiC, GaSb and InSb is determined by direct differentiation of the calculated energy-volume curves. **InSb**SiC, GaSb and InSb undergo first-order structural phase transition from zinc blende to rock salt under pressure (C. Wang, 2004) (Red'Ko, Milenin, & Milenin, 2017).

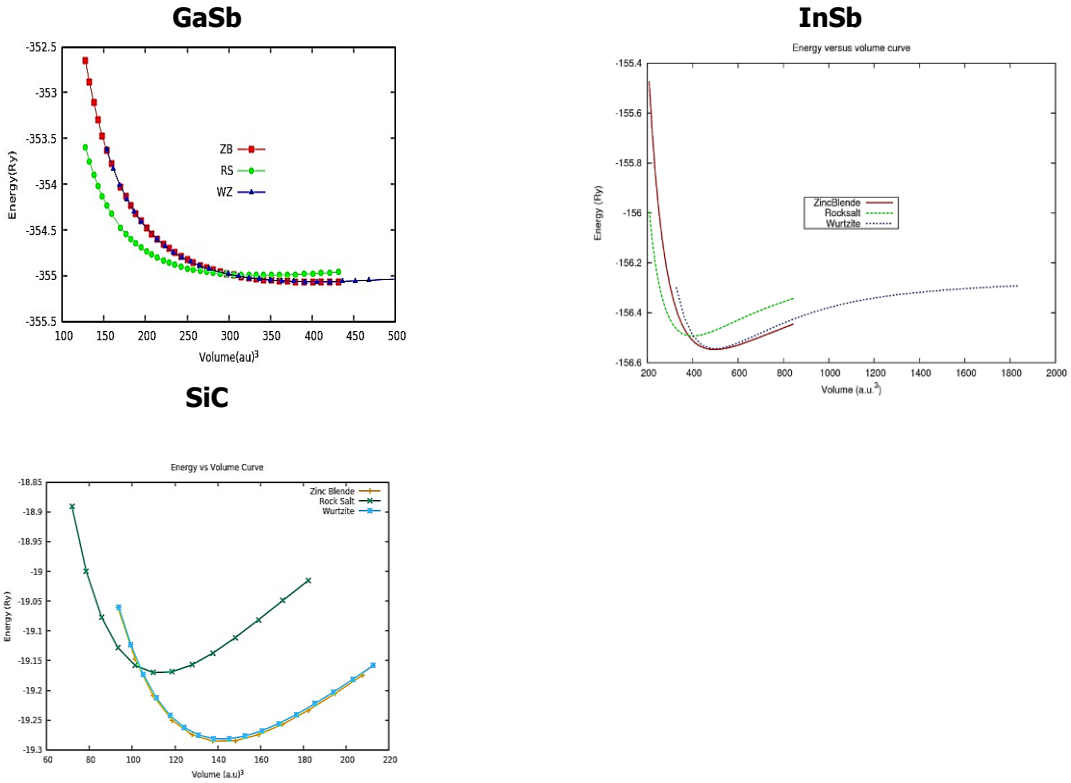


Figure 5. *Energy vs Volume curve of GaSb, InSb and SiC*

From the calculation of enthalpies (figure 6), the phase transition pressure from ZB-RS and WZ-RS were found to be 9.72 GPa (7.65 GPa), 72.4 GPa (72.4 GPa) and 8.063 Gpa (8.063 Gpa) for InSb, SiC and GaSb respectively. These results are in good agreement with other theoretical results [6], [9], [10]. Table 4, summarizes the presently calculated structural phase transition pressures along with experimental and other theoretical results. The crossing of two enthalpy curves indicates a pressure-induced phase transition between these two phases. The computed enthalpy curve of the Zinc Blende, Wurtzite, and Rock Salt phases is plotted as a function of pressure. Accordingly, the enthalpy curve of the Zinc Blende or Wurtzite phase crosses with that of the Rock Salt phase around 72 GPa, for SiC and 8.06 GPa for GaSb indicating a first-order phase transition between Zinc-Blende or Wurtzite and the Rock Salt phases.

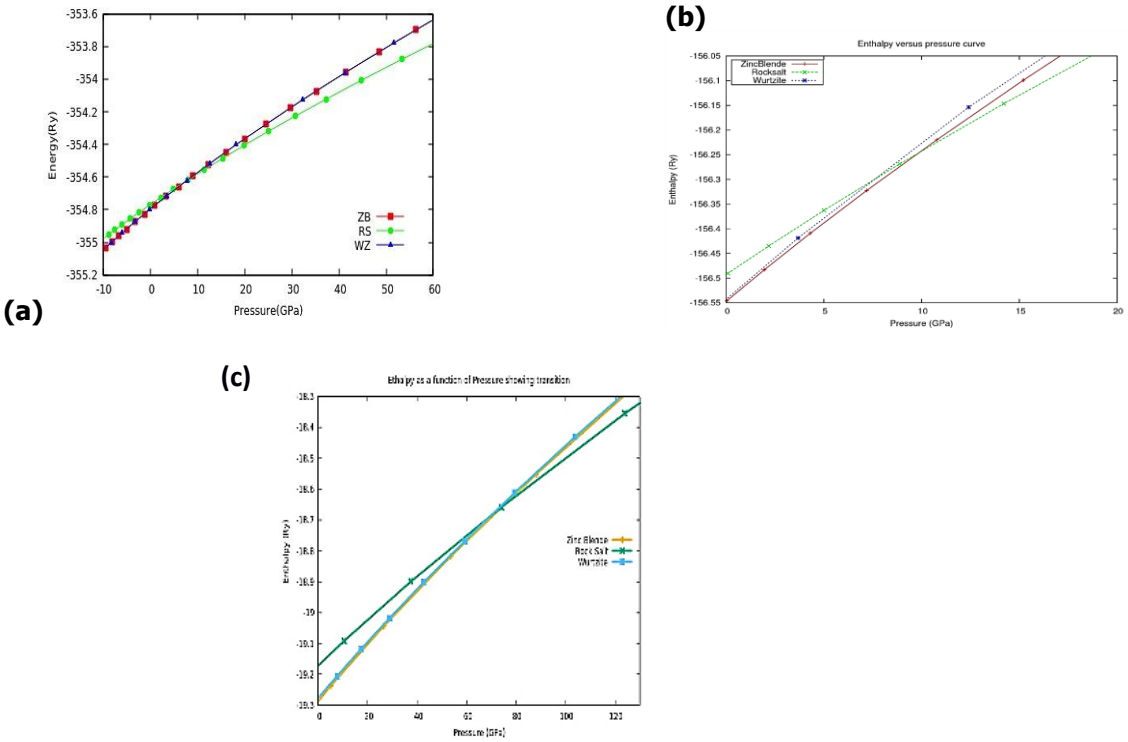


Figure 6. *Enthalpy against Pressure curve of; (a) GaSb (b) InSb and (c) SiC*

CONCLUSION

We have studied the electronic properties and structural Phase transition of SiC, GaSb and InSb semiconductors in zincblende, rocksalt and wurtzite phases by the means of DFT. It was observed that the zinc blende phase is the stable structure of SiC, GaSb and InSb due to the lowest minimum ground state energy. A phase transition from ZB – RS phase and from WZ – RS phase was also found to exist at 9.72 GPa (7.65 GPa), 72.4 GPa (72.4 GPa) and 8.063 Gpa (8.063 Gpa) for InSb, SiC and GaSb respectively. The band structure and enthalpy-pressure calculations lead to the conclusion that SiC, GaSb and InSb all undergo a transition from semiconducting (WZ or ZB phase) to metallic nature (RS phase) at the structural transition pressure with a volume reduction of about 19.7% for SiC.

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