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First Principle Calculations to Predict the Preferred Crystal and Structural Parameter of Indium Phosphate

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ABSTRACT

The structural and electronic properties and phase transition under pressure of Indium phosphide in Zinc-blende, Rock salt and wurtzite structure were studied using the first principle calculations based on the density functional theory by means of pseudo-potential plane-waves method. The calculation was performed with in the Generalise Gradient Approximations (GGA) within Perdew-Burke and Ernzerhof (PBE) exchange-correlation functional. On the basis of the Murnaghan equation of state, the transition pressure between the Zinc-Blende to RockSalt phases, Zinc-blende to Wurtzite and RockSalt to Wurtzite was investigated.

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1. INTRODUCTION

Indium Phosphide is a binary semiconductor composes of Indium and Phosphorus. It is a very promising material for several applications such as optoelectronic devices. eg. InP-base solar cell [1] and quantum-cascade laser [2]. With the recent advances in nanowires synthesis and nanoribbons, novel applications of InP based devices have also been Investigated such as photodetectors[3], flexile devices for wearable and disposable electronics[4] and polarized nanoscale light emitting diodes[5].

Besides optoelectronics, there is also considerable interest in the high pressure phases of InP. The reason is that, despite considerable work in the last few decades, the detailed understanding of the high pressure structures of InP and other semiconductors remains a challenge to theorists and experimentalists [6].

Having a good understanding of the relationship between the electronic and structural properties of the semiconductors and their pressure transition is very vital to nanostructures. This work studied the crystal structure of Indium Phosphide and its properties base on these three structures, Zinc-blende (ZB), Rock Salt (RS) and Wurtzite (WZ) structure. Each of these three phases has its unique physical properties.

Several methods have emerged in order to describe the electronic and structural properties of solid materials and molecule, one of which is the Density Functional Theory (DFT). It has shown significant value not only in the Interpretation of experiment but also in predicting important aspect of new properties and the design of new devices. Among the interesting phenomena is the pressure induced phase transition which is specially relevant to understanding the observed changes under pressure.

X-ray diffraction data shows that the transition is a structural transformation from one phase to another. In a previous work by Zhang et al[12], it was discovered that InP has a semiconductor to metallic transformation in the phase transition from Zinc-Blende to RockSalt structure of pressure between 10 and 13.3 Gpa [7-9]. Theoretical studies base on total energy calculations clearly predicts a first order phase transformation from ZB structure to the RS structure under hydrostatic pressure. All the results are experimentally proven with a phase transition pressure of about 10.0 Gpa[10] ,10.8 Gpa [11], 10.33 [12], and 10.5-11 Gpa [7]. Up to date, Arbouche et al, [13] studied the structural properties and phase stability in which the phase transition pressure of InP was about 7.35 Gpa. At higher pressure, the sequence of InP has shown up to 46 Gpa to be zinc-blende, Rock Salt and Cmcm like [14]. Further transition to 1mmm and Cscl structure were predicted even though it has not been confirm experimentally.

The zinc-Blende and the Wurtzite crystal structure are very much alike when you compare the [111] direction of the Zinc-Blende with the [001] direction of the Wurtzite[15].

The InP Zinc-Blende structure is a direct gap semiconductor, and the direct band gap energy at Γ point is 1.3ev and 1.4ev at room temperature and very low temperature respectively [15].

2. RESEARCH METHOD

We carried out first principle calculations using the Quantum Espresso. All calculations were performed based on the plane-wave pseudo-potential density functional theory (DFT). Ultrasoft Pseudopotentials (UPPs) were employed to describe the electron-ion Interaction. The effect of exchange-correlation interaction are treated within the generalize gradient approximations (GGA) of Perdew-Burke and Ernzerhof (PBE). Pseudo-atomic calculations are performed for In [Kr] d10 5s2 5p1 and P [Ne]3s23p3. The In 4d semi core electrons were left frozen in the core, which is justified by the fact that d-states are not energetically close to the valence s-states.

An scf calculation was carried out to test convergence of the total energy with respect to the plane wave cut-off and k-point sampling has been carefully examined. For each of the structure, a test for convergence with respect to kinetic energy cut-off, charge density and the brillioun zone sampling was carried out within the energy order of ~0.1 mRy and pressure of order ~0.5 kbar.

The lattice parameter of the Zinc-Blende and Rock salt was determined by doing the calculations for different lattice parameter and the equilibrium lattice parameter was obtained. Vc-relax calculations and atomic positioning was carried out on the wurtzite structure in order to obtain a more optimize data of the total energies. To take into account the effect of pressure on the wurtzite structure, all the geometric parameter (a, c and u) were optimize. Fittings with the murnaghan equation of state (EOS) of the computer Energy- Volume data provides values of the zero pressure bulk modulus (B0) and its pressure derivative (B0’) as well as the enthalpy-pressure curve was studied.

3. RESULTS AND DISCUSSIONS

Convergence Test

The convergence of kinetic energy cutoff (ecutwfc) was obtained by fixing the K-points and varying the ecutwfc at a regular interval. In the same way, for the charge density, I fixed the value at which ecutwfc converged and the K-point and then tested for different values of ecutrho in the order (ecutrho=4*ecutwfc). And finally, for the Brillioun sampling, I fixed the values of ecutwfc and ecutrho obtained and varied the K-Points. The results for which they converge are shown in the Table 1. Figure 1.1-1.3 shows the diagram of the crystal structures.

Table 1. Convergence parameter for InP Zinc-Blende, Rock Salt and Wurtzite Structure; kinetic energy cut-off for the plane wave basis, the charge density and Brillioun Zone sampling mesh.

Structure	Ecutwfc (Ry)	Ecutrho (Ry)	mesh
Zinc-Blende	45	180	8x8x8
Rock Salt	30	240	8x8x8
Wurtzite	45	270	6x6x6

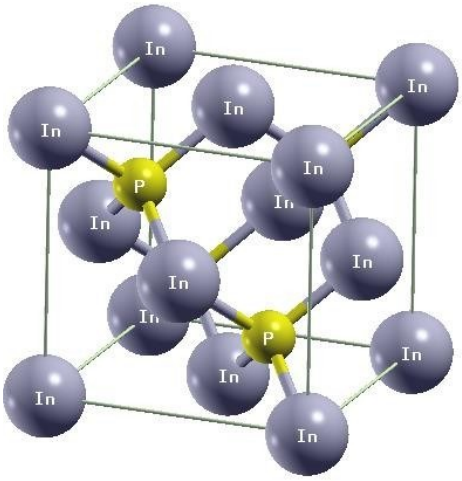


Figure 1.1. Xcrysden plot for Zinc-blende InP Structure

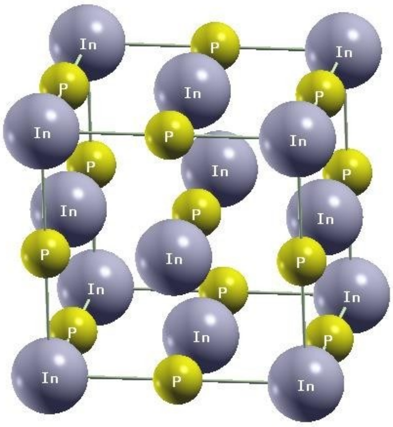


Figure 1.2. Xcrysden plot for Rock Salt InP Structure

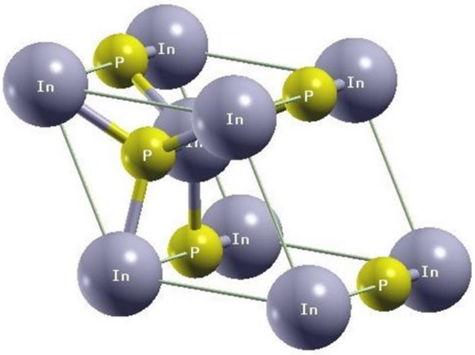


Figure 1.3. xcrysden plot of wurtzite structure of InP

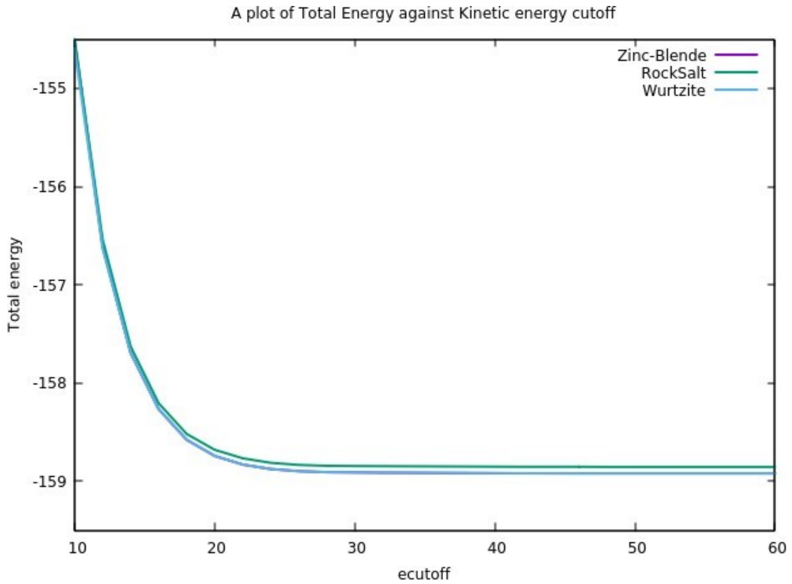


Figure 1.4. convergence of kinetic energy cutoff

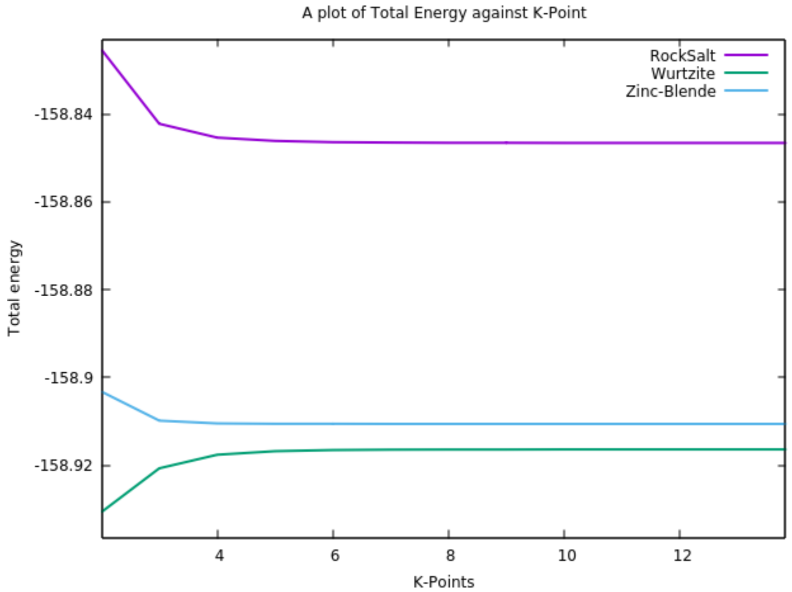


Figure 1.5. Convergence of K-Point

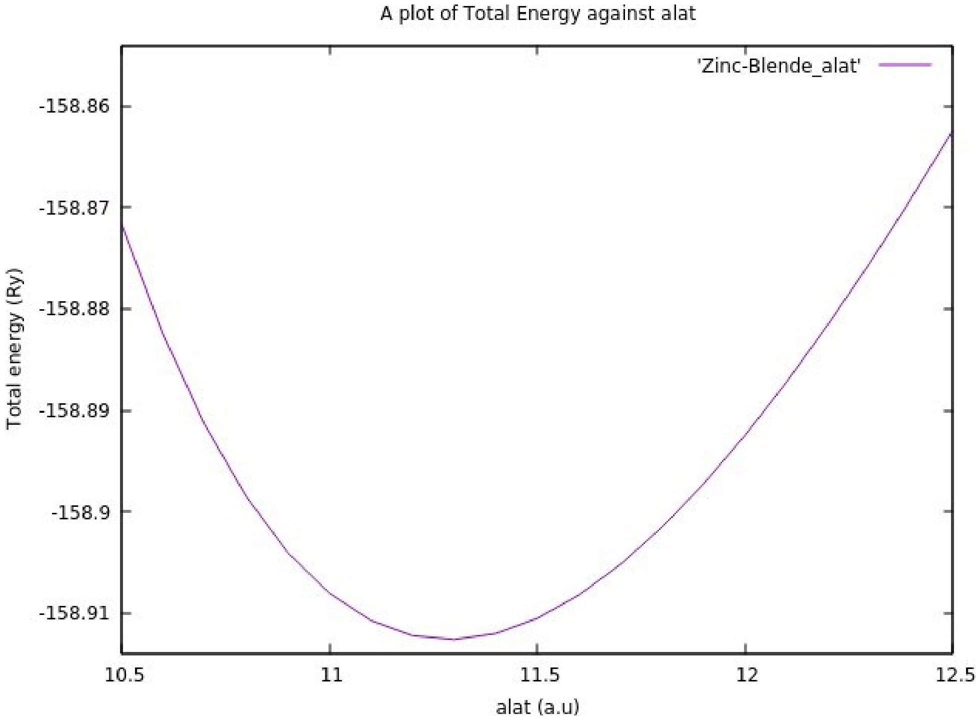
Structural properties

The result of this work for the lattice parameter equilibrium for the structures Zinc-Blende, Rock Salt and Wurtzite are obtained by minimization of the total energy with respect to the unit cell volume per molecule and fitting it to the murnaghan equation. The calculated parameters are compared with other result and are given in the table 2. The result I obtain is in good agreement with other experimental result by kabita[17] with lattice constant 5.97 Å, Paul [18] 5.9 Å and Madelung[19] 5.87 Å.

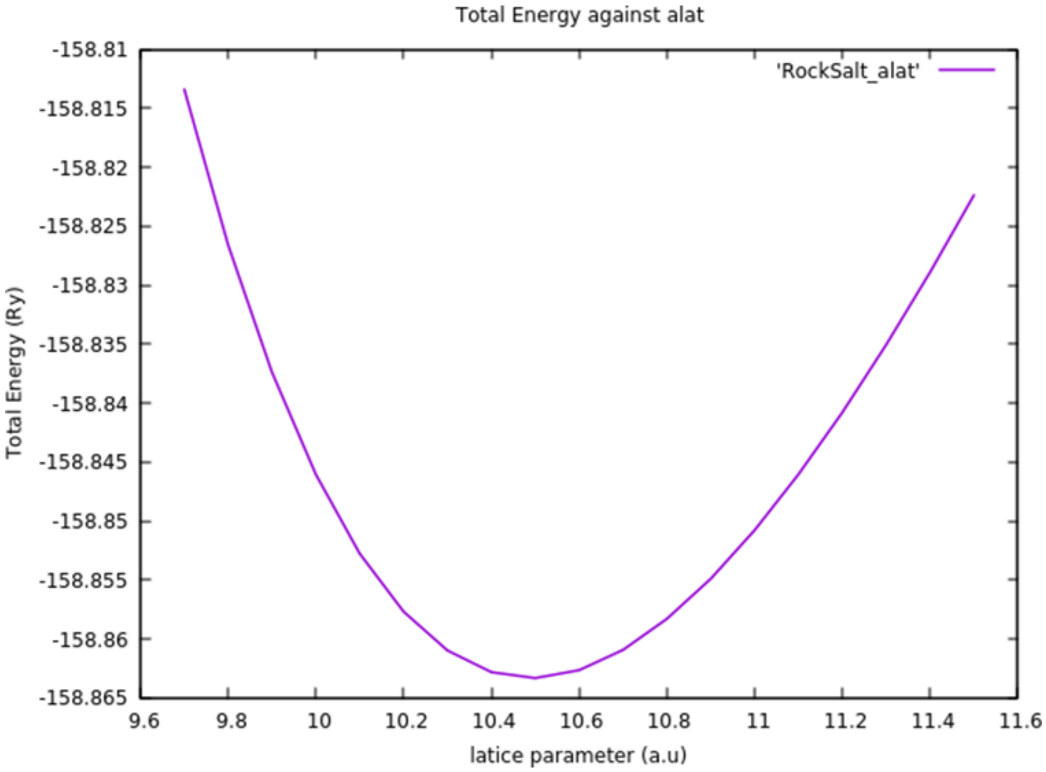
For the Zinc-blende, I have obtain from the equation of state that the bulk modulus and pressure derivative is B0=57.5 Gpa and B0'=4.83, which is lower than the experimental value reported by kabita[17] of B0 =60.5 Gpa and B0'=4.64. for the Rock Salt structure, I got B0 =69.9 Gpa, B0'=5.02, which is smaller than the value reported by Kabita[17] of 74.78 Gpa and for the wurtzite structure, I obtain the Bulk modulus as B0 =49.5 Gpa and B0'=5.75. 49.5 Gpa which is lower than the value reported by Branicio et al of 60.88 Gpa and 5.195[20]. The Table. 2 shows detail on the values of the lattice parameter for the different structures. Figure 2. Shows the plot of the lattice parameter for the three structures.

Table 2. Lattice constant ‘a (Å)’, bulk modulus ‘B0(GPa)’ and pressure derivative of bulk modulus (B0’) of ZB, RS and WZ structure of InP at zero pressure

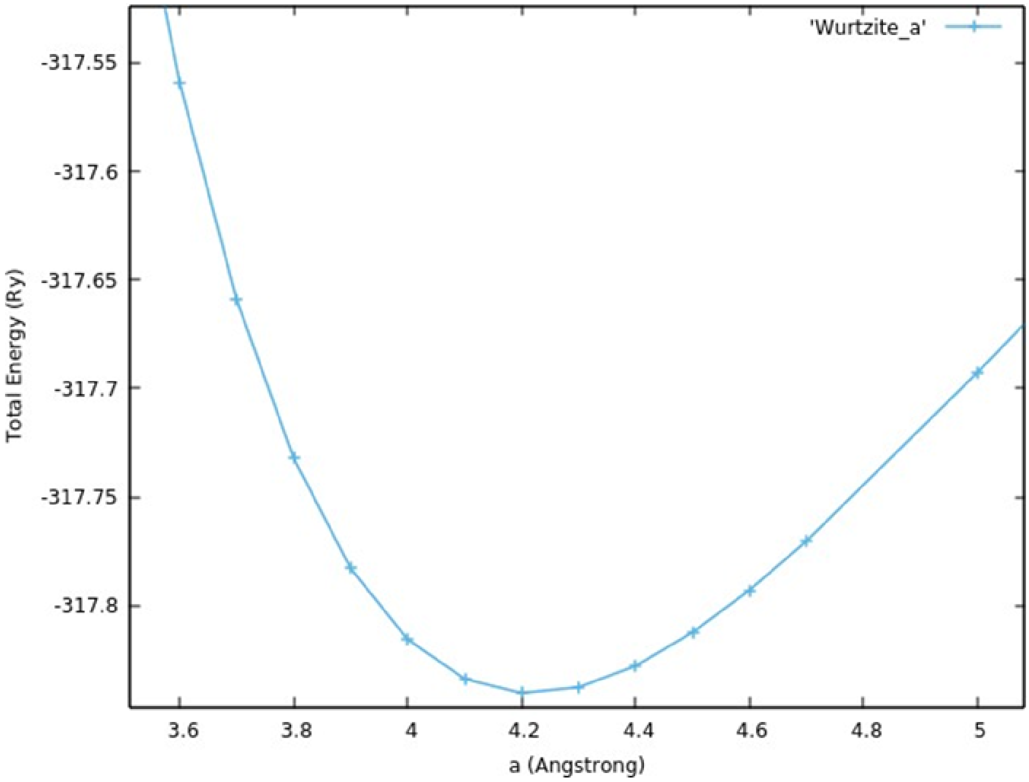
Structure	**a (Å)**	**c (Å)**	**u**	**B_0 (Gpa)**	**B_0’**
Zinc-Blende	This work: 5.961 Other Exp.: 5.729[21] 5.867[23] 5.702[24]			57.5 73.6[21] 72.0[23] 76.14[24]	4.83 4.479[21]
Rock Salt	This work: 5.552 Other Exp.: 5.515[21] 5.55[22]			69.9 73.36[21] 79.12[22]	5.02 5.08[21] 4.34[22]
Wurtzite	This work: 4.200 Other Exp.: 4.150[25]	6.898 6.625[25]	0.375 0.3750[25]	49.5 73.06[25]	5.75 4.4913[25]



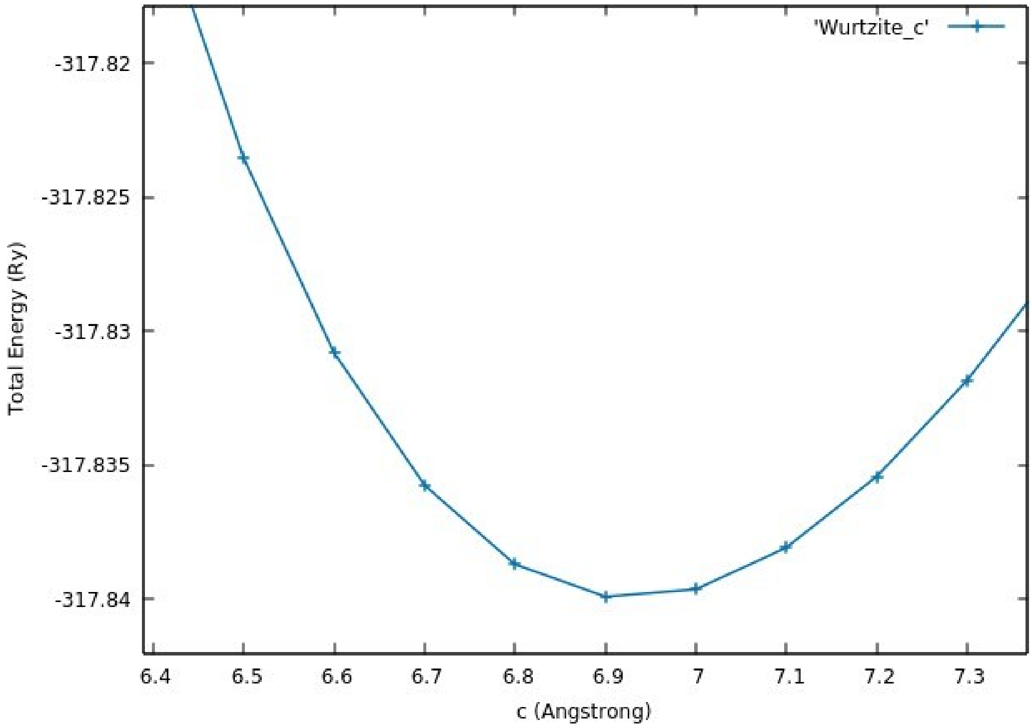
(a)


Total Energy against alat
'RockSalt_alat'
Total Energy (Ry)
-158.81
-158.815
-158.82
-158.825
-158.83
-158.835
-158.84
-158.845
-158.85
-158.855
-158.86
-158.865
9.6
9.8
10
10.2
10.4
10.6
10.8
11
11.2
11.4
11.6
latice parameter (a.u)

(b)


'Wurtzite_a'
Total Energy (Ry)
-317.55
-317.6
-317.65
-317.7
-317.75
-317.8
3.6
3.8
4
4.2
4.4
4.6
4.8
5
a (Angstrong)

(c)



(d)

Figure 2. Lattice parameters (a) Zinc-Blende (b) Rock Salt, (c) and (d) Wurtzite

Phase transition

The estimation of zero-temperature phase transition pressure between Zinc-Blende, Rock Salt and Wurtzite structure of InP can be obtained from the usual condition of equal enthalpies. In order words the pressure at which enthalpy H, of the three phases is the same.

H=E+PV
Where E = energy,
P= pressure and V=volume

The **figure 3.1** shows the energy volume curve for the three different structures of InP in consideration. It indicate that the phase transition pressure from Zinc-Blende to Rock Salt structure is about 14.68 Gpa with a large volume collapse of 21.4% which is higher than other reported values by kabita[17] of 9.3 Gpa with a volume collapse of 16.4% and 11 and 10.2 Gpa[21] and even with experimental report of between 10 Gpa to 13 Gpa[26]. It can be seen from the diagram that the most stable phase of InP is the Zinc-Blende with volume of 357.52 (au)^3 at minimum energy. We could see from the plot that the different between the energy of the Zinc-Blende and wurtzite is ΔE=0.002 Ry, which is comparable to the experimental value reported by Branicio et al [20] as ΔE=0.0057ev, indicating a positive stalking fault energy.

The figure 3.2 gives more information on the phase transition between the structures. wurtzite and Rock salt is found to be 14.68 Gpa, even though there is no available literature for me to compare. There is no transition between Zinc-Blende to wurtzite structure.

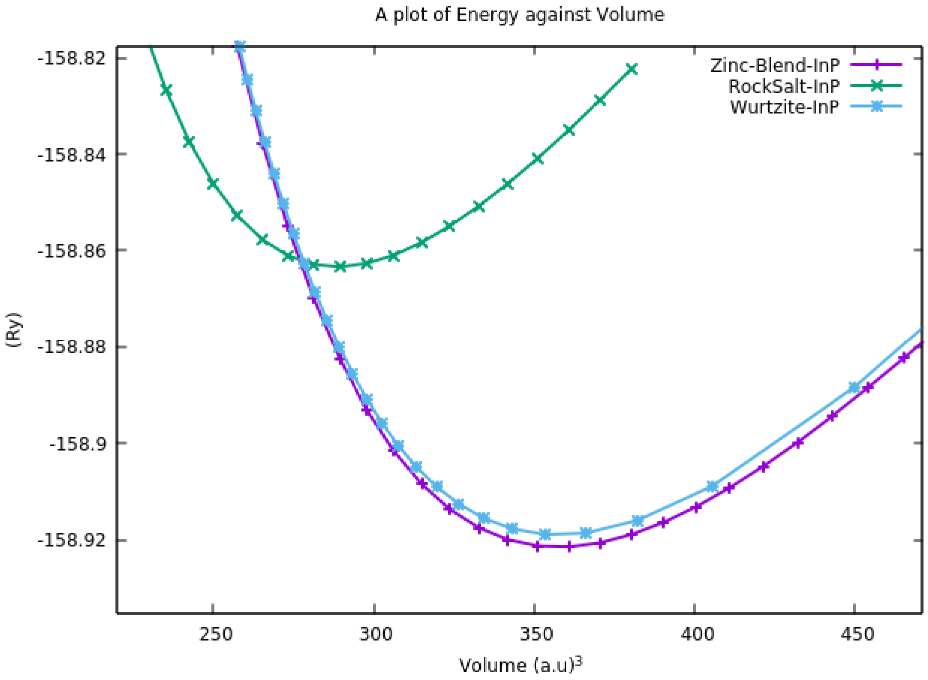


Figure 3.1. Energy-Volume Curve for ZB, RS and WZ structure of InP

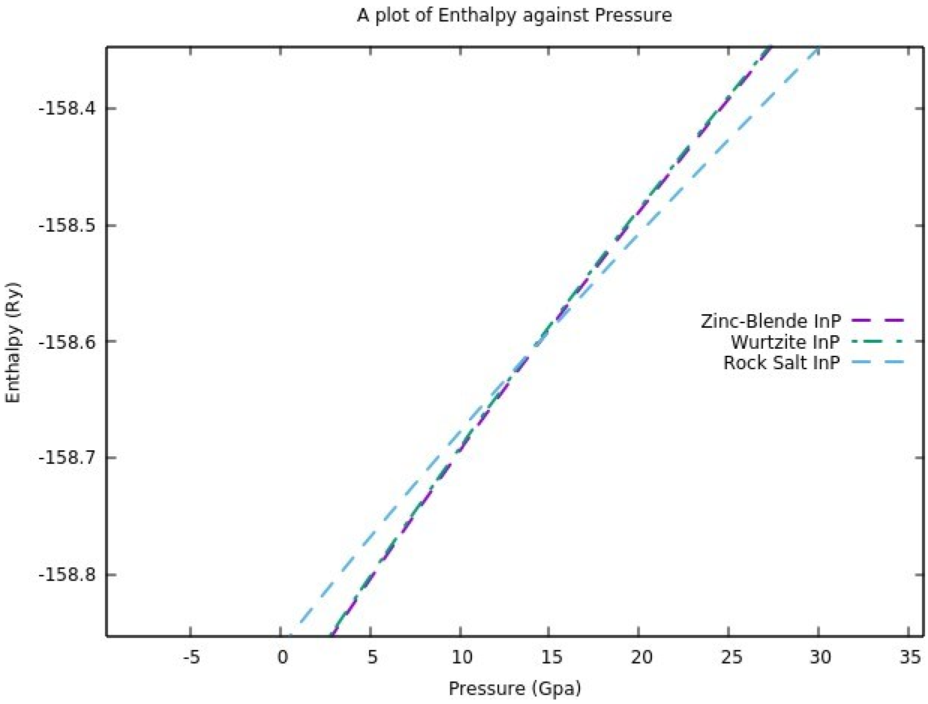


Figure 3.2. Energy versus pressure for the three structures of InP

There are other transitions of InP to other structures as the pressure Increase. In this study we studied the structural transformation of Zinc-Blend to Rock salt wih increase in pressure. In a work by Rino, there is a transition from Rock Salt (RS) to Rhombohedra (RH) structure at 14 Gpa and from the Rhombohedra (RH) to Caesium Chloride (CsCl) at 70 Gpa. The RS → RH is a weakly first order transition while the others are typical first order transitions which are accompanied with large volume drop and hysteresis in the reverse transformation.

Hence the phase transition of InP with pressure is as thus;

ZB → RS → RH → CsCl

Band Structure and Density of State

The energy band diagram for the three structures Zinc-Blende, Rock salt and Wurtzite is also studied and reported thus;

From figure (4.1) shows that for the Zinc-blende structure, the maximum of the valence band is at Γ and it coincided with the minimum of the conduction band which is also at Γ. We could see the presence of the band gap which makes it a direct band gap semiconductor.

The band gap was calculated and found to be 0.9123 eV, which is smaller than experimental value of 1.42 eV[17] and also with the theoretical value of 1.40 eV[16], But it is better than other LDA results of 0.62 eV and GGA result of 0.85 eV[27]. figure (4.2) of the DOS shows the presence of the band gap at the Fermi level.

For the Rock Salt structure, we could see that in figure (4.3) and figure (4.4) there is no presence energy band gap at the Fermi Level between the valence band and the conduction band, which tells the metallic nature of the compound in the rocksalt phase. This is as a result of an overlapping among the states of the neighbouring atoms when pressure is applied. This resulted to the broadening of the valence and conduction band, hence narrowing and eventually closing the band gap. This agrees with a result reported by kabita[17].

For the wurtzite structure, we found its direct band gap nature. As seen in figure (4.5) that the valence band maximum and the conduction band minimum are laying at the Γ –point of symmetry. The band gap energy is found to be 0.698 eV, which is lower than the Experimental values reported of 1.474 eV[28] and 1.4936 eV[29]. The presence of the band gap is also shown in figure 4.6 of the DOS.

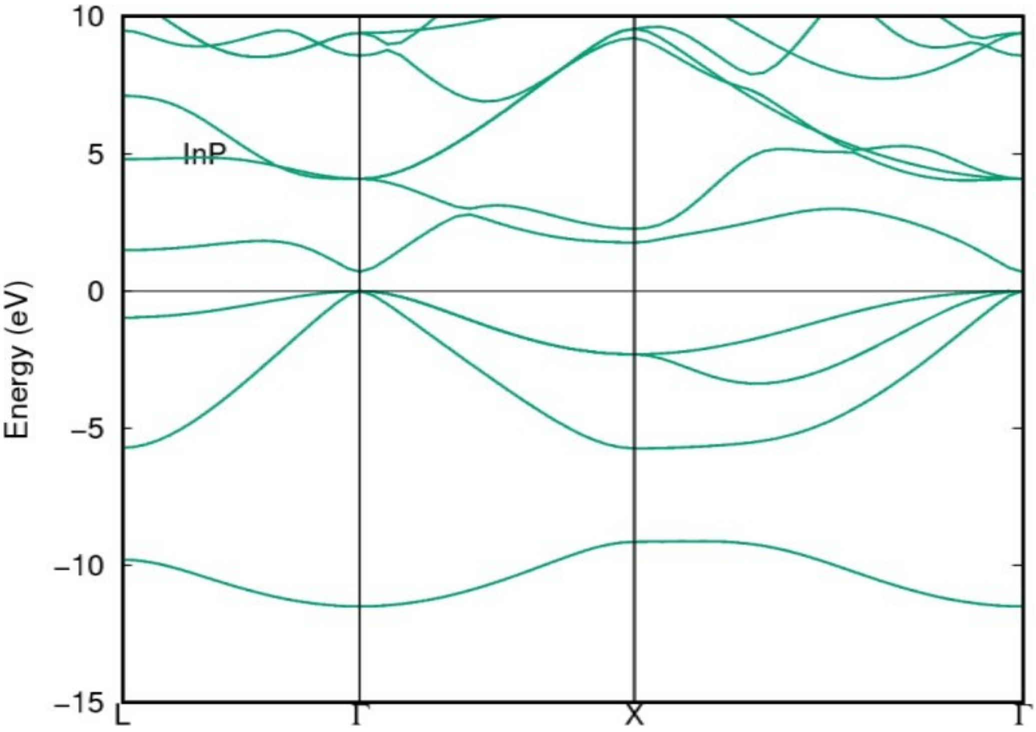


Figure 4.1. band structure of Zinc-Blende InP

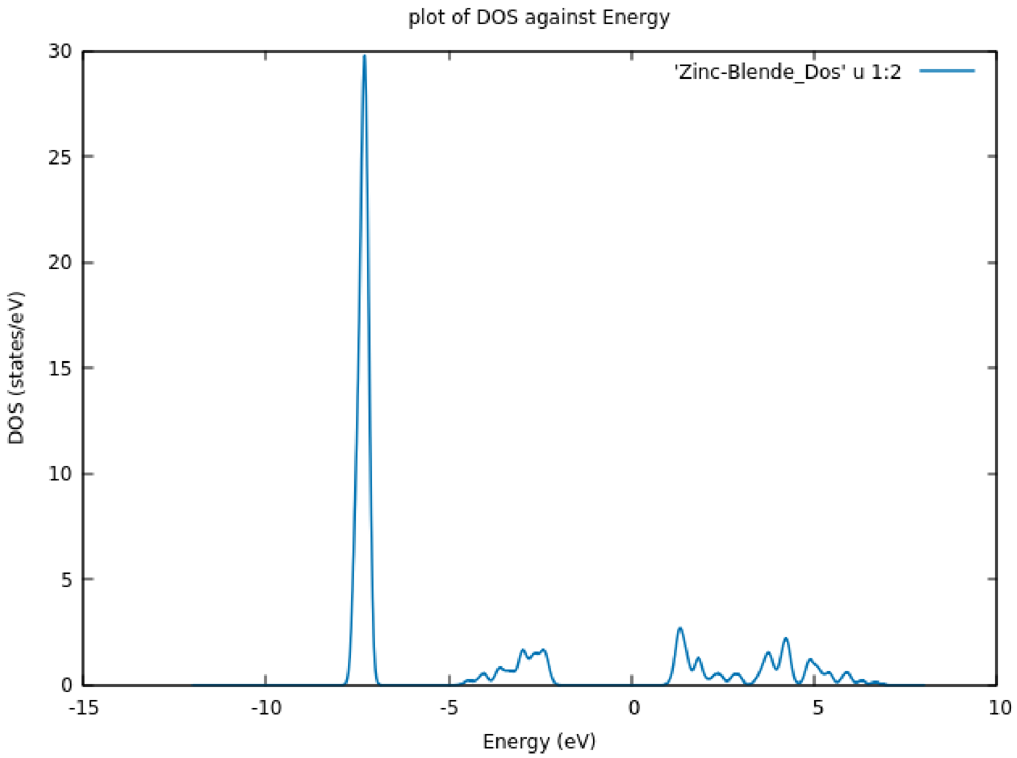


Figure 4.2. Density of state of Zinc-Blende InP

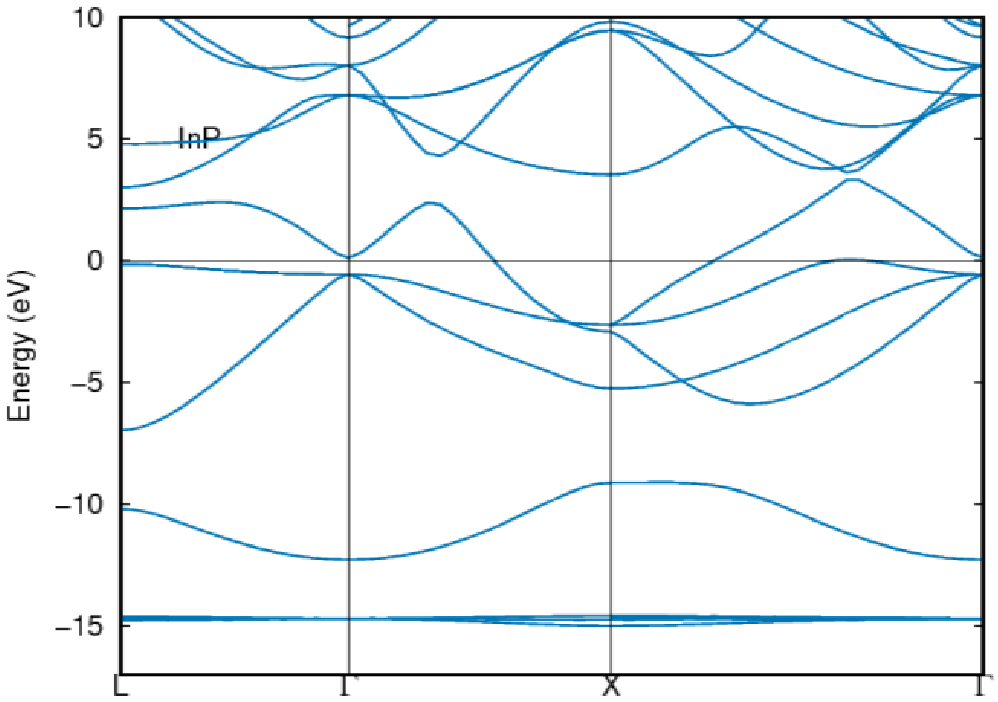


Figure 4.3. Density of state of RockSalt InP

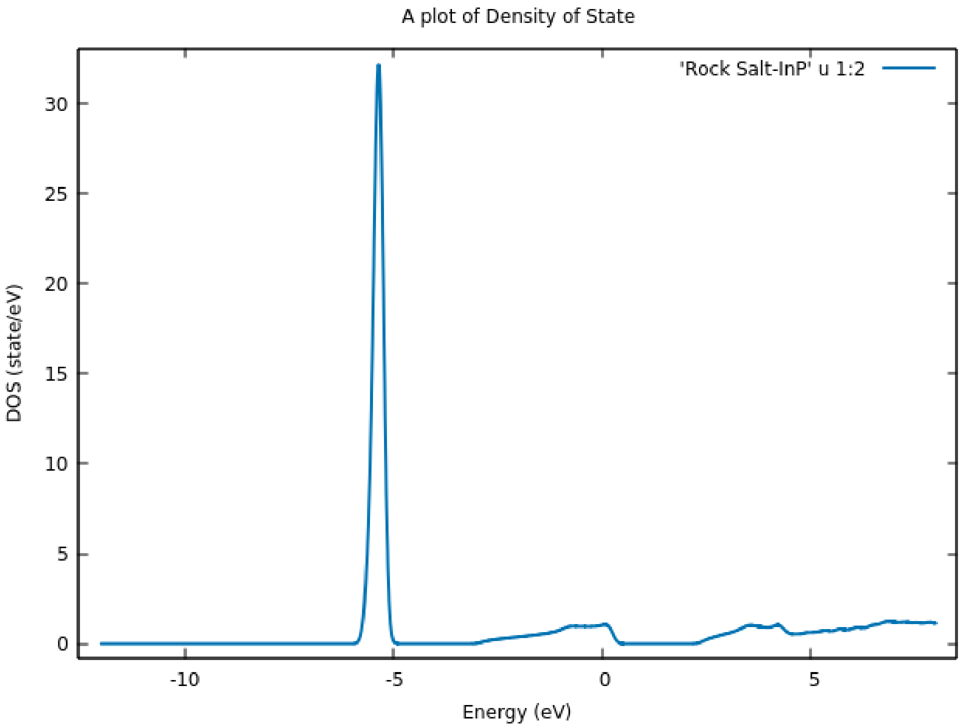


Figure 4.4. Density of state of Rock Salt InP

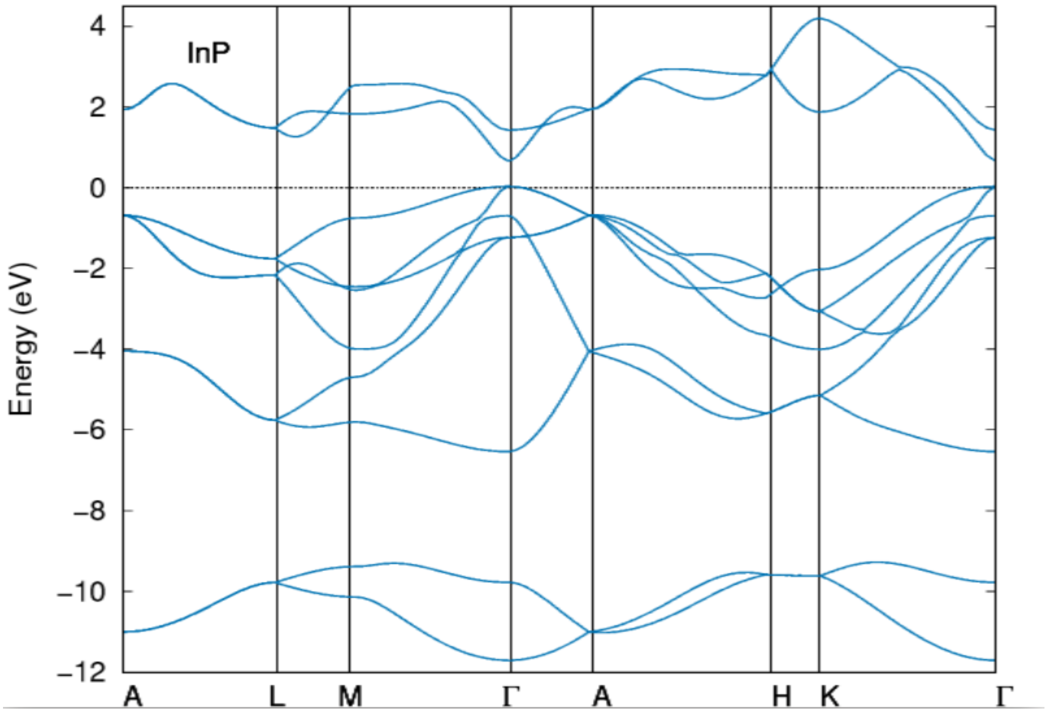


Figure 4.5. Band structure of Wurtzite InP

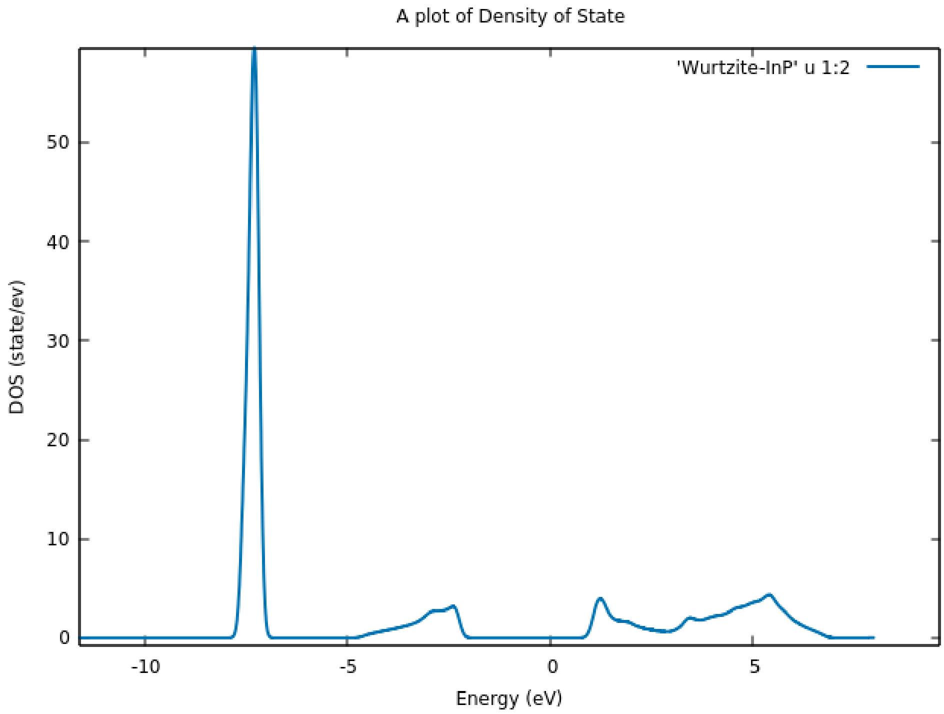


Figure 4.6. Density of state of Wurtzite InP

4. CONCLUSION

The structural and Electronic properties of InP was studied in the phases of Zinc-Blende, RockSalt and Wurtzite. The lattice parameter of the Zinc-Blende is found to be 5.961 Å which is 1.5% higher than the theoretical value of 5.868 Å. For the Rocksalt, the lattice parameter is found to be 5.552 Å and for wurtzite a=4.2 Å, c=6.898 Å and u=0.371.

The Energy-Volume Curve shows that the transition from Zinc-Blende to Rocksalt 14.68 Gpa with 21.4% Volume collapse. It also predicts the stability of the Zinc-Blende Phase which has its equilibrium Volume at the minimum energy. The Enthalpy-Pressure shows the pressure phase transition of the ZB to RS as 14.68 Gpa and that there is no transition between the zinc- blende and wurtzite phase.

It was discovered from the band structure that the Zinc-Blende and Wurtzite are direct band gap semiconductor with band gap energy 0.9123 eV and 0.698 eV respectively, which are lower than the experimental values reported. Under pressure, ZB undergoes a transition from semiconductor to the metallic nature of RockSalt structure.

We can say that the InP Zinc-Blende structure is the most preferred structure of InP at ambient condition and this is in agreement with existing experiment/observations.

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