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# First Principle Calculation of Pressure-Induced Phase Transition and Band Structure of Gallium Phosphide

*A first principle study of the electronic, structural and phase transition of the III-V binary compound semiconductor gallium phosphide (GaP) is performed under the framework of density functional theory (DFT). Structural transformation from the zinc-blende (ZB) to rocksalt (RS) structure is observed at a pressure of about 21.9 GPa and the dependence of the volume decrease of ZB to RS structure at the transition pressure is 14.11%. The variation of the energy band gap, elastic constants and debye's temperature with pressure are also obtained successfully. Our results are found to be in consistent with other experimental and theoretical results.*

**Keywords:** Density Functional Theory, Density of states (DOS), Band structure, Phase transition

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## 1. Introduction

Gallium phosphide is an important III-V compound semiconductor which has increasingly attracted attention theoretically and experimentally and can be used advantageously in a variety of technological areas. It is also considered to be of wide-band gap and hence making it a good candidate for room-temperature device applications such as top junction solar cells and multi junction solar cell system. The variation of band gap of GaP with pressure is important for the identification of some of the luminescent processes and for a better understanding of their origin. In recent years the study of the structural properties, phase diagram and effect of pressure has aroused considerable scientific interest. Two phases of GaP such as zinc-blende (ZB) and rock-salt (RS) has been found with phase transition taking place under pressure [1]. The ZB to RS structure phase transition has been found to occur around 18.8 GPa with unstable RS structure [2]. Using the density functional theory (DFT) Rashid et al. [3] have studied the structural and electronic properties of GaP and compared the lattice parameters, bulk modulus, pressure derivative of the bulk modulus with earlier data. A. Mujica and R. J. Needs [4] found that the simple cubic phase of GaP should be stable between 14.7 GPa and 20.3 GPa. The High-pressure properties of the zinc-blende structure have been determined by Raman scattering, ultrasonic measurements, fundamental absorption, and refractive-index measurements [5-7]. Even though GaP has been well known for a long time, calculations on the elastic properties and pressure variation of GaP are still very rare. In the present work, the phase transformation from zinc-blende to rocksalt structure along with the electronic structure, density of states (DOS), change in band

gap, and variation in mechanical properties is studied for better understanding of the semiconductor.

## 2. Computational Method

The calculation of GaP was performed within the framework of density functional theory (DFT) using the full potential linearised augmented plane wave (FP-LAPW) method [8]. The exchange-correlation effects are treated within the generalised gradient approximation of Perdew-Burke-Ernzerhof (PBE-GGA) scheme [9] as implemented in wien2k code [8,10,11]. This method is used as it is one of the most accurate methods in electronic structure calculation of crystals. In this method, the lattice is divided into non-overlapping atomic spheres surrounding each atomic sites and an interstitial region [12]. Inside the muffin tin (MT) region, the potential is a product of radial function and spherical harmonics and expanded up to order  $l = 10$ . For the interstitial regions that are outside the muffin tin spheres, the potentials are expanded in plane waves. 8000 k-points are used for the integration part which reduces to 256 irreducible k-points inside the Brillion zone. Convergence is obtained at  $R_{MT}K_{max} = 9.0$  where  $R_{MT}$  is the atomic sphere radii and  $K_{max}$  gives the plane wave cut-off.

## 3. Results and Discussion

### 3.1 Structural properties

The ground state lattice parameter of ZB and RS structure of GaP are obtained by optimisation of the structures. The total energy and the corresponding primitive cell volume are calculated by setting a series of different lattice constants for both the structures and the energy versus volume curves are shown in figure 1. From figure 1 it is clearly seen

that the ZB structure of GaP is more stable as compared to RS structure which is in good agreement with other previous results [1,4]. The zero pressure, lattice constant  $a_0$ , bulk modulus  $B_0$ , pressure derivative of the bulk modulus  $B_0'$  are obtained by fitting the calculated energy-volume points to the Birch-Murnaghan equation of states [13] and the obtained results are listed in table 1. It shows that our results are reasonably in agreement with the previous reported data [1, 4, 14-16].

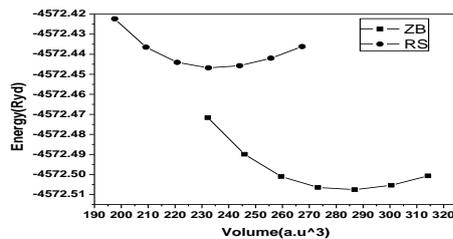


Fig. (1) Energy versus volume for different structure of GaP

Table (1) Lattice constants  $a_0$ , bulk modulus  $B_0$ , and pressure derivative of bulk modulus  $B_0'$  for ZB and RS structures of GaP at zero pressure

Structure		$a_0$ ( $\text{\AA}$ )	$B_0$ (GPa)	$B_0'$
ZB	Present work	5.523	77.709	4.347
	References	5.411 <sup>a</sup> ; 5.50 <sup>b</sup> ; 5.386 <sup>c</sup>	90.0 <sup>a</sup> ; 7.21 <sup>b</sup> ; 86.8 <sup>c</sup>	4.50 <sup>a</sup> ;4.88 <sup>b</sup> ; 4.00 <sup>c</sup>
RS	Present work	5.181	88.303	4.84
	References	5.165 <sup>d</sup> ; 5.160 <sup>e</sup>	87.3 <sup>d</sup> ; 87.59 <sup>e</sup>	3.78 <sup>d</sup> ; 4.54 <sup>e</sup>

<sup>a</sup>Ref. [4]; <sup>b</sup>Ref. [14]; <sup>c</sup>Ref. [15]; <sup>d</sup>Ref. [1]; <sup>e</sup>Ref. [16].

### 3.2 Phase transition and Elastic properties

For the determination of phase transition pressure at zero temperature, the usual condition of equal enthalpies i.e.  $H=E+PV$  is used. The enthalpy as a function of pressure is shown in figure 2. The phase transition of GaP from ZB to RS is found to occur at 21.9 GPa pressure. The obtained transition pressure is found to be in good agreement with other experimental and theoretical results which are shown in table 2. In figure 3, the normalised volume ( $V_p/V_0$ ) of ZB and RS of GaP at different pressure is shown. The relative volume is found to decrease as pressure increases for the two structures. During the phase transition,  $V_p/V_0$  of ZB phase is found to occur at 0.8293 and the RS phase at 0.6882. It clearly shows that the volume collapses at 14.11% indicating that ZB phase of GaP is more compressible as compare to RS phase. Hence the elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$  of GaP-ZB structure are calculated for the lattice volume corresponding to the pressure ranging from 0 GPa to 21.9 using the stress-strain method [20].

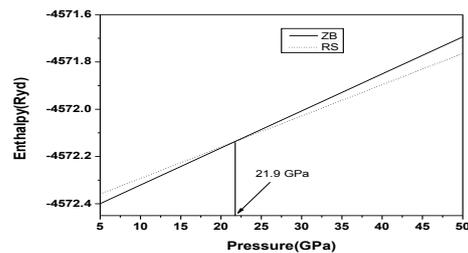


Fig. (2) Enthalpy as a function of pressure

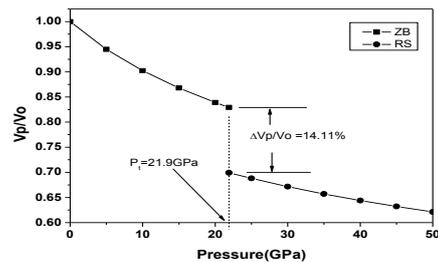


Fig. (3) Phase transition between ZB and RS structure of GaP at 21.9 GPa

For computing the elastic constants  $C_{ij}$ , the volume conserving technique is used [21]. The results are shown in figure 4. The results clearly show the mechanical stability conditions:  $(C_{11}+2C_{12})>0$ ;  $C_{11}C_{12}>0$ ;  $C_{44}>0$  are satisfied and hence the stable GaP-ZB structure can exist up to higher pressure of 21.9 GPa. Using the calculated elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ), the Debye's temperatures of the ZB phase at different pressures are obtained. From figure 4 and figure 5, it is also observed that the elastic constants as well as the Debye's temperature increases with increasing pressure.

Table (2) Transition pressure from ZB to RS in GaP

ZB - RS	Pressure (GPa)
Present work	21.9
Ref.1	21.9
Ref.17	24±0.3
Ref.7	22.0
Ref.18	21.5±0.8
Ref.19	21.7

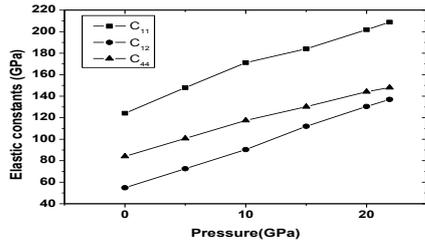


Fig. (4) Elastic constants ( $C_{11}, C_{12}, C_{44}$ ) as a function of pressure

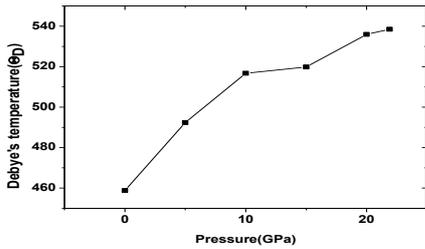


Fig. (5) Debye's temperature as a function of pressure

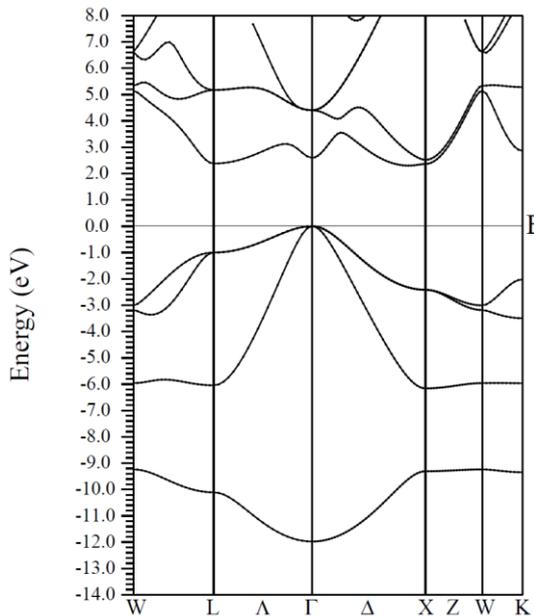
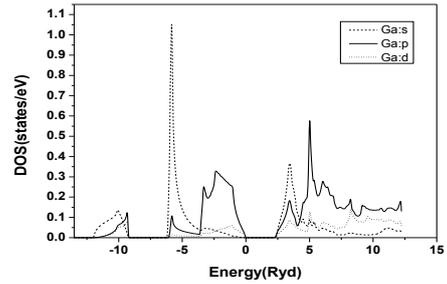


Fig. (6) Energy band diagram of GaP ZB structure at zero pressure

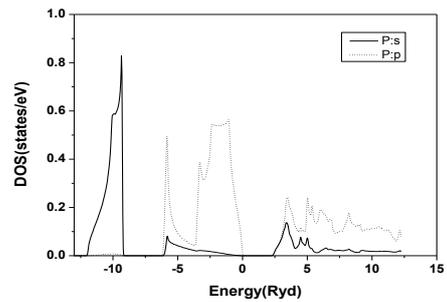
**3.3 Band structure and Density of states**

The energy band diagram of GaP-ZB at zero pressure is shown in figure 6 and the partial DOS of Ga and P in GaP-ZB are shown in figure 7 (a) and 7 (b) respectively. In the band diagram, one can observe that the valance band maximum occurs at the  $\Gamma$  point and the minimum conduction band occurs at L point. Hence GaP-ZB is found to be an indirect band gap semiconductor material of 2.3 eV. From the partial DOS one can observe that the lowest band appears in energy band diagram is mainly contributed from s-non metal (P atom)

orbital and the valance band is mainly contributed by the s-metal (Ga- atom) orbital and p-non metal orbital with little contribution from the p-metal orbital. The contribution of the s, p orbitals of metal and non-metal in Density of States (DOS) in the lowest and valence band is found to decrease with increase in pressure. The variation of band gap of GaP-ZB structure under pressure ranging from 0 GPa to 21.9 GPa is shown in figure 8 and observed that there is increase in band gap with increase of pressure.



(a)



(b)

Fig. (7) (a) Partial DOS of Ga in GaP, (b) Partial DOS of P in GaP

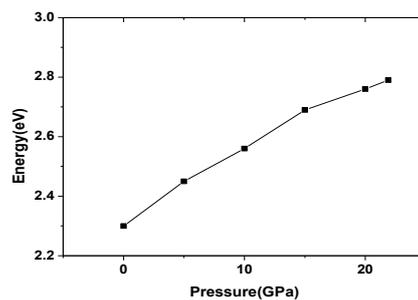


Fig. (8) Pressure versus energy band gap in GaP

**4. Conclusion**

In this paper we present a detailed study of pressure induced phase transition and electronic structure of GaP from ZB to RS structure. The phase transition from ZB to RS structure is obtained at 21.9 GPa and ZB phase is found to be more stable. During the phase transition, the relative volume of ZB phase is occurred at 0.8293 and the RS phase at

0.6882 and volume collapses at 14.11% indicating that ZB phase of GaP is more compressible as compare to RS phase. The calculated equilibrium lattice parameter, bulk modulus and pressure derivative of the bulk modulus are found to be in good agreement with the other experimental and theoretical studies. The Debye's temperature calculated from the elastic constants is increased with increase in pressure. GaP-ZB phase is found to be an indirect band gap semiconductor material of 2.3eV and band gap increases with increase in pressure. The partial DOS shows the main contributions from s, p orbital of non metal-P atom and p, d orbital of metal-Ga atom in the band diagram of GaP.

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