

## First-principles study of structural and electronic properties of GaP and InP

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### Abstract

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*The full-potential linearized augmented plane wave method (FP-LAPW) within the generalized gradient approximation (GGA) is used to calculate the structural and electronic properties of zinc blende GaP and InP. In this approach we obtained ground state properties such as equilibrium lattice constants, bulk modulus and its pressure derivative which are in good agreement with previous results. However our study shows that the GGA underestimates the energy band gap of both semiconductors.*

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**Keywords:** Full-Potential Linearized Augmented Plane Wave (FP-LAPW), Density Functional Theory (DFT), Generalized Gradient Approximation (GGA)

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### 1.0 Introduction

GaP and InP belong to the group III-V semiconductors crystallizing in the zinc blende structure. These semiconductors which are widely used in modern technology have received a lot of attention. However we still need first principles method in other to appreciate fully these semiconductors. The density functional theory (DFT), [1] provides such a method.

The DFT has been very successful for calculating the electronic structure of solids and molecules. Approximations enter the DFT through the exchange correlation term. Thus the primary task in the solution is choosing good approximation for the exchange correlation energy. The local density approximation (LDA), [2] is one such approximation. The LDA assumes that the exchange correlation energy arising from a volume element in an inhomogeneous system is the same as if that volume element would be embedded in a homogeneous electron gas of that same density. There are more sophisticated approximations involving both the spin density and the gradient of density. This is called the Generalized Gradient Approximation (GGA).

In this work, we shall use the generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE-GGA) [3] within the full potential linearized augmented plane wave (FP-LAPW) method [4,5] to study the electronic and structural properties of GaP and InP.

The paper is arranged as follows: section 2 will be devoted to the computational procedure while the results and discussion will appear in section 3. Finally conclusions will be drawn in section 4.

### 2.0 Method of calculation

The basic approach in density functional theory formalism is to solve the Kohn-Sham (K-S) equations which have the form of the single-particles Schrödinger equation:

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$$\left[ -\frac{1}{2}\nabla^2 + v_{eff}(r) \right] \psi_i = \epsilon_i \psi_i \quad (2.1)$$

and applying

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2 \quad (2.2)$$

where the single particle wave functions  $\psi_i(r)$  are the  $N$  lowest energy solutions of the  $K$ - $S$  equations, and the effective potential  $v_{eff}$  is given by

$$v_{eff}(r) = v(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}(r) \quad (2.3)$$

where  $n(r)$  is the ground state density corresponding to the external potential  $v(r)$  and  $v_{xc}$  the exchange correlation potential defined as the functional derivative of the exchange correlation energy :

$$v_{xc} = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \quad (2.4)$$

Equations 2.1, 2.2 and 2.3 are solved self-consistently. A successful approximation to the exchange correlation energy is the generalized gradient approximation (GGA). Within the GGA, the exchange correlation energy  $E_{xc}$  takes the form

$$E_{xc}^{GGA}[n \downarrow, n \uparrow] = \int d^3r f(n \uparrow, n \downarrow, \nabla n \uparrow, \nabla n \downarrow) \quad (2.5)$$

The LAPW method is a procedure for solving the  $K$ - $S$  equations for the ground state density, total energy and  $K$ - $S$  eigenvalues of a many electron system by introducing a bases set which is well adapted to the problem. In this method, the unit cell is divided into two regions: non-overlapping muffin tin spheres surrounding every atom and the interstitial region between the spheres.

The LAPW basis functions  $\phi_{kn}$  which are used for the expansion of the  $KS$  wavefunctions

$$\psi_k = \sum_n C_n \phi_{kn} \quad (2.6)$$

are defined as

$$\phi_{k_n} = \frac{1}{\sqrt{\Omega}} e^{ik_n r} \quad (2.7)$$

interstitial region

$$= \left[ \sum_{lm} A_{lm,k_n} u_l(r, E_l) + B_{lm,k_n} \dot{u}_l(r, E) \right] Y_{lm}(r)$$

inside sphere, where  $u_\ell(r, E_\ell)$  is the regular solution of the radial Schrödinger equation for energy  $E_\ell$ ,  $\dot{u}_\ell(r, E_\ell)$  is the energy derivative of  $u_\ell$  taken at the same energy  $E_\ell$ .

In this section we present the computational techniques used in the study of the structural and electronic properties of GaP and InP which crystallizes in the zinc blende structure. We have used the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN 2k code [6] to calculate the electronic and structural properties of GaP and InP. In this calculation the exchange and correlation potential is incorporated in the GGA by using the scheme of Perdew-Burke and Ernzerhof [3].

The optimized sphere radii of Ga and In are each 2.4 atomic units while that of P is 2.0 atomic units in both cases. In the spheres both the charge densities and the potentials are expanded in terms of crystal harmonics up to angular momenta  $\ell = 6$ . Brillouin zone intergrations have been done using 116  $k$ -points in the irreducible part of the Brillouin zone. Well converged solutions were obtained at  $R_{MT}K_{max} = 9$ , where  $R_{MT}$  is the atomic sphere radii and  $K_{max}$  is the interstitial plane wave cut-off.

### 3.0 Results and discussions

To calculate the ground state bulk properties of GaP and InP, the total energies are calculated for different volumes around the equilibrium cell volume. The plots of calculated total energies versus volumes for the semiconductors are shown in figure 3.1. The calculated total energies are fitted to the Murnaghan's [7] equation of state in order to obtain the ground state properties such as the equilibrium lattice constant  $a_0$ , the

**Table 3.1:** Structural properties of GaP and InP.

	Present work	Other calculated values	Experiment
GaP			
a (Å)	5.5134	5.34[8] 5.45 [9]	5.4505[10]
B(Mbar)	0.7678	0.90[8] 1.127[9]	0.89[10]
B'	0.4339		
InP			
a (Å)	5.9703		5.8687[10]
B(Mbar)	0.5950	0.67(11)	0.71[10]
B'	4.5287		

**Table 3.2:** Energy band gaps (eV) for GaP and InP

	Present work	Other calculated values	Experiment
GaP	1.8204	1.50, 2.52[12]	2.39[13]
InP	0.6864	0.43, 1.55[12]	1.42[13]

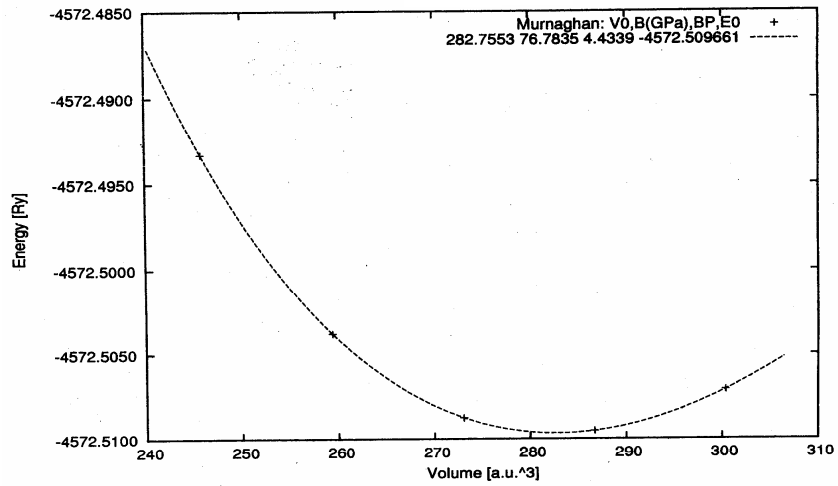


Figure 3.1a: Energy versus volume curve for GaP

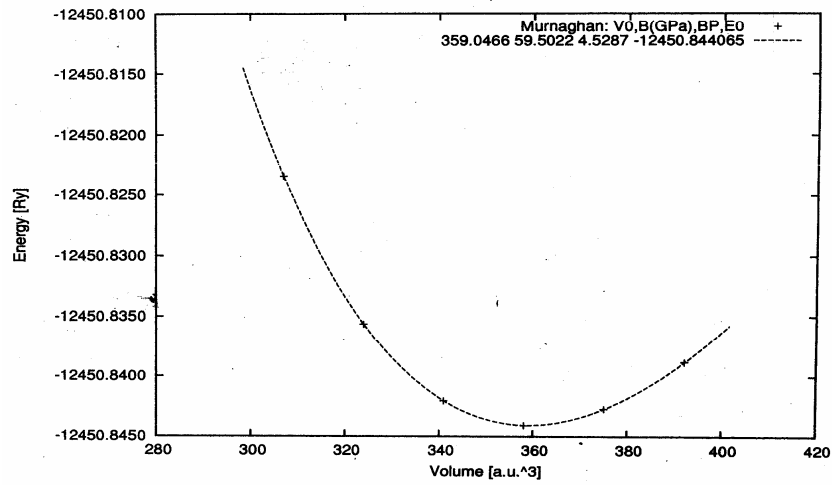
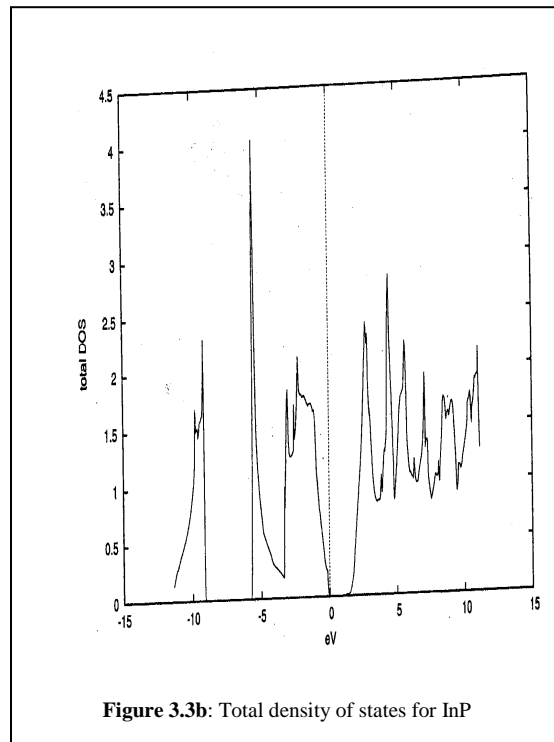
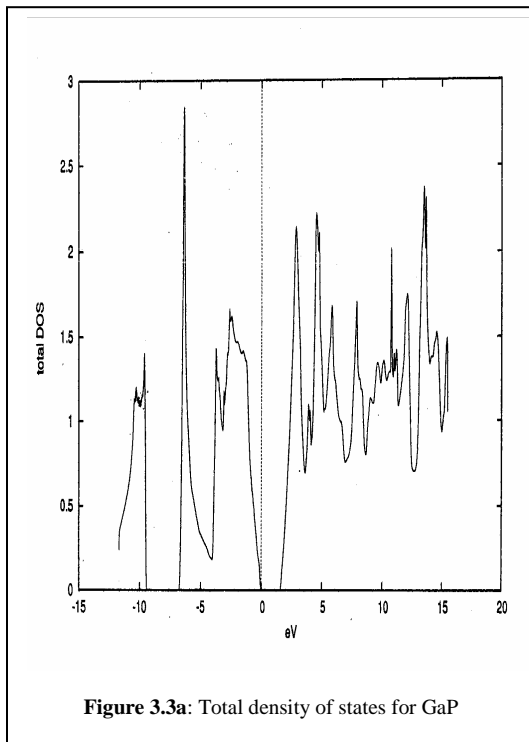
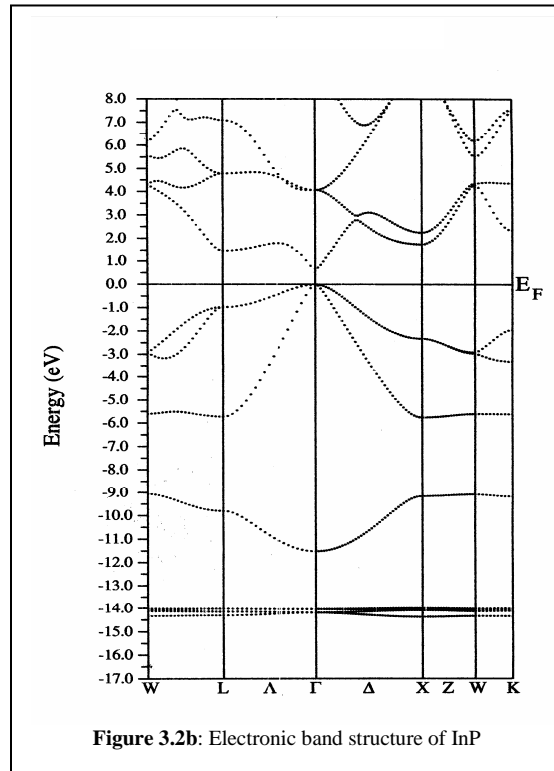
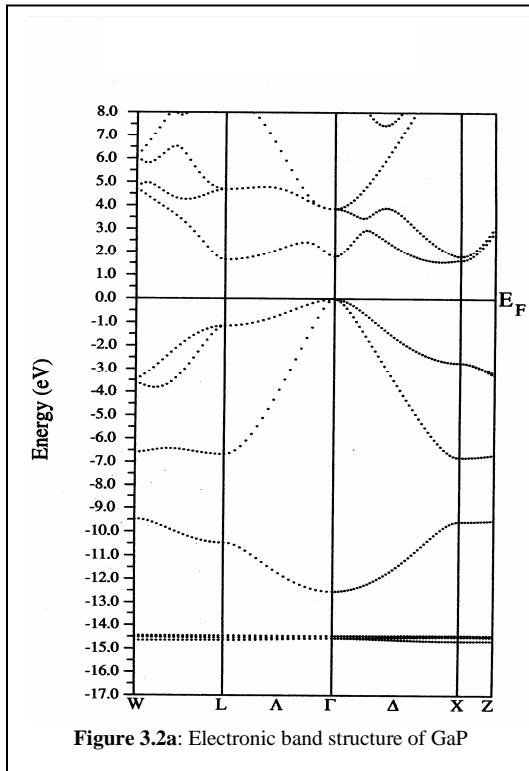


Figure 3.1b: Energy versus volume curve for InP



bulk modulus  $B$  and the pressure derivative of the bulk modulus  $B'$ . The calculated equilibrium parameters ( $a_0$ ,  $B$ ,  $B'$ ) are given in Table 3.1. Available experimental data and results from previous first principles calculations are presented for comparison.

The observation in Table 1 is that the present study slightly overestimates the experimental lattice constant of GaP and InP by 1.15% and 1.73%. Thus we conclude that the calculated values of the structural properties are in reasonable agreement with experiment.

The electronic band structure of these fcc compounds which crystallize in the zinc blende structure have been calculated along the high symmetry lines of the Brillouin zone. These calculations are carried out using the experimental values of the lattice constants. In figure 2, the relativistic band structures of GaP and InP determined without spin-orbit coupling are displayed. The graphs are for a plane through the Brillouin zone, surrounded by the k-points W-L- $\Lambda$ - $\Gamma$ - $\Delta$ -X-Z-W-K. The zero of the energy scale shows the position of the Fermi level. The positions of symmetry points are indicated by vertical lines.

For GaP, the energy gap is indirect ( $\Gamma$ -X) with the valence band maximum (VBM) occurred at the  $\Gamma$ -point and the conduction band minimum (CBM) at X. The energy gap for InP is direct ( $\Gamma$ - $\Gamma$ ) with both the valence band maximum and the conduction band minimum at the  $\Gamma$  point. This is in agreement with the earlier results. The calculated indirect and direct band gaps for GaP and InP as well as some previous theoretical results and experimental data are presented in Table 3.2.

It is observed that both the indirect and the direct band gaps are underestimated by the PBE-GGA calculations. This may be attributed to the neglect of spin-orbit coupling that improves equilibrium properties of densely-packed solids and their surfaces.

The total density of states (DOS) for GaP and InP are shown in figure 3.3. The position of the peaks and general structures are in agreement with earlier calculations. The band gaps also correspond to that observed in the band structure.

#### 4 0 Conclusion

We have used the generalized gradient approximations within the full potential linearized augmented plane wave method to study the structural and electronic properties of zinc blende GaP and InP. We used the GGA as the exchange-correlation potential which gave us good structural properties. However the band gaps were underestimated showing the need for a better description of the exchange correlation functional. GaP was observed to have indirect band gap while InP has a direct gap.

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