Full Potential – Linearized Augmented Plane Wave (FP-LAPW) in the Framework of Density Functional Theory

C.A. Madu and B.N Onwuagba
Department of Physics, Federal University of Technology Owerri, Nigeria
E-mail: cadamadu@yahoo.com

Abstract

Full Potential-Linearized Augmented Plane Wave (FP-LAPW) method was used in the framework of Density Functional Theory (DFT) using the Generalized Gradient Approximation (GGA) to study the electronic and structural properties of some semiconductors. The results obtained are quite good and compare favourably with some previous experimental and theoretical results. The applications are useful, interesting and exciting.

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

PACS Nos: 71.15.Ap; 71.15.-m

1. Introduction

The density functional theory [1] has proved to be very good for self-consistent-field electronic structure calculations of the ground-state properties of atoms, molecules and solids. The Kohn-Sham [2] equations are the basic equations of density functional theory. The Linearized Augmented Plane Wave [3] method has proved to be one of the most efficient schemes for solving the Kohn-Sham equations for the ground-state density, total energy and Kohn-Sham eigenvalues (energy bands) of a many electron system. However the Kohn-Sham equations contain the exchange correlation energy through which approximation enter the DFT. The success of DFT lies on good approximation for the exchange correlation energy. In recent years the most popular approximation to the exchange correlation, energy is the generalized gradient approximation (GGA) [4] which depends on both the density and its gradient at each point in space. The LAPW uses the muffin-tin approximation in which the potential is spherically
averaged around each atomic site. In the LAPW method, the unit cell is divided into two regions—non-overlapping atomic spheres called the muffin-tin region and an interstitial region. The charge densities around the atoms are then written as a linear combination of radial functions times spherical harmonics and a Fourier series in the interstitial region.

In this work we present self-consistent first-principles calculations for the electronic and structural properties of BP and AlP which are zincblende semiconductors. We employ the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method within the DFT. The exchange correlation energy is calculated using the Generalized Gradient Approximation GGA which depends on both the spin densities and their gradients. The Perdew, Burke and Ernzerhof PBE [5] version of GGA is used. The paper is arranged as follows: in section 2 we will briefly describe the computational method used in getting the structural and electronic properties of BP and AlP. In section 3 we will display our results and use it to compare with previous theoretical and experimental data. The conclusion will be drawn in Section 4.

2. Method of Calculations

In this section we present the technique used in the calculation of the band structure of BP and AlP. All the computations are done using the FP-LAPW method within the Density Functional Theory. The exchange correlation potential was calculated within the Generalized Gradient Approximation using the Perdew-Burke-Ernzerhof (PBE-GGA) scheme. The method is implemented using the WIEN2K [6] code. In this code a basis set is obtained by the unit cell into non-overlapping atomic spheres and an interstitial region.

The sphere radii (in atomic units) used in the calculations for B, Al and P are 1.4, 1.8 and 1.8 respectively. Inside these spheres the charge densities are written as a linear combination of radial functions times spherical harmonics and a Fourier series in the interstitial region. To obtain energy eigenvalues convergence, the basis function was expanded up to \( R_{MT} K_{\text{max}} = 7.5 \) for BP and AlP where \( R_{MT} \) is the interstitial plane wave cut-off. The convergence criterion was specified as charge to a value of 0.0001. The Brillouin zone integrations were carried out with 116k-points for BP and 91k-points for AlP respectively in the irreducible part of the Brillouin zone.
3. Results and Discussion.

The total energy of the semi-conductors was calculated as a function of the lattice constant using the FP-LAPW method and the PBE-GGA form of exchange correlation energy without spin-orbit coupling. The calculated total energies are then fitted to the Murnaghan equation of state [7]. The equilibrium lattice constant $a$, bulk modulus $B$ and the pressure derivative of the bulk modulus $B'$ for the semiconductors along with experimental values (where available) and results by earlier workers are listed in Table 1.

### Table 1 Structural parameters of BP and AlP

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Other calculated values</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BP</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>AlP</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$(Mbar)</td>
<td>0.8169</td>
<td>0.90 0.88</td>
<td>0.86[11]</td>
</tr>
<tr>
<td>$B'$</td>
<td>4.2303</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium lattice constants of the zinc blende BP and AlP overestimate the experimental lattice constants by 1.15% and 1.73% respectively. With this small difference we can conclude that the calculated values of the structural properties are in reasonable agreement with experiment. An earlier computation by Onwuagba [9] using the tight-binding linear muffin-tin orbital (TB-LMTO) method found the lattice constant of BP to be 4.61Å which is 1.54% higher than experimental value. However, our result for the lattice constant of AlP overestimates that by Rodriguez-Hernandez and Munoz [12] by 2.08%. This overestimation of lattice constants is characteristic of the GGA.
The electronic band structure of these semiconductors was also calculated. The calculations were done along the high symmetry lines of the Brillouin zone. The experimental lattice constants were used in the calculations.

We display the relativistic band structures of the semiconductors in figures 1(a and b).

The graphs are for a plane through the Brillouin zone, surrounded by the k-points W-L-Λ-Γ-Δ-X-Z-W-K. The position of the Fermi level is shown by the zero of the energy scale. The positions of symmetry points are indicated by vertical lines.

In the two compounds BP and AlP, the valence band maximum occurred at the Γ-point while the conduction band minimum is at the X-point thus predicting all to be indirect band gap (Γ-X) materials. The calculated energy band gaps for BP and AlP are shown in Table 2.
Table 2: Energy band gaps (eV) for BP and AlP

<table>
<thead>
<tr>
<th></th>
<th>Present Work</th>
<th>Experiment</th>
<th>Other calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>1.3376</td>
<td>2.05[11]</td>
<td>1.31, 2.33 2.18,</td>
</tr>
</tbody>
</table>

Overall the present values of the energy band gaps of the compounds underestimate the experimental values. This has been corroborated by earlier workers. Okoye [14] found underestimation of up to 54% using the GGA as exchange correlation energy. It has been suggested that the band gap problem likely occurs due to the lack of non-locality and energy dependence in the exchange–correlation potential used in density functional formalism. However, the overall band profiles obtained are in agreement with those by earlier workers.

Fig. 2 (a and b) show the total density of states for BP and AlP at the equilibrium lattice constant within the GGA.
The prominent peaks to the left of the Fermi level i.e. the valance bands arise primarily from the P atom while the peaks in the conduction band are due to B and Al. For AlP the first prominent peak is at -10eV. By comparing with the partial density of states it is found that the P atom is responsible for this peak while the sharp peak at -5eV is contributed mainly by the Al atom. The band gaps correspond to that observed in the band structure.

4. Conclusion

In this paper we have done an analysis of the electronic and structural properties of BP and AlP using the FP-LAPW method. The exchange-correlation energy used is PBE-GGA. The results give band structures that are in agreement with previous theoretical studies. Our results show that BP and AlP have indirect gap (Γ – X). The results of the structural properties are also in reasonable agreement with the results by previous workers and experimental data.

Acknowledgements

The authors would like to thank Professor P Blaha and his team for providing the WIEN 2K code used in the computations.

5. REFERENCES

7. Murnaghan F.D.; Proc Natl. Acad. Sci. 30 244 (1944) .