Calculation of the Band Structure and Band Splitting Energy of Boron Compounds (BX, X=N, P, As, Sb) using modified Becke-Johnson potential

Lalrintluanga Sailo[1], Ricky L. Ralte[2], Mary Lalchhuanawmi[1],
L.Zadeng[1] and Z.Pachuau[1]*

[1]*Department of Physics, Mizoram University, Aizawl – 796004.Mizoram, India*
[2]*Department of Electronics, Govt. Zirtiri Residential Science College, Aizawl-79600. Mizoram, India*

Abstract: *In this paper, we study the band structures of Boron compounds (BX, X=N, P, As, Sb) under III-V semiconductor compounds. Our calculations were performed using a Generalized Gradient Approximation (GGA) and the modified Becke-Johnson potential (mBJ) within the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. We have compared our results calculated by GGA and mBJ and we found that the mBJ approximation gives better results in semiconductor compounds compared to GGA. We also obtained the results on the band structures with the inclusion of Spin-Orbit Interaction(SOI) on both approximations and also compared the results. We have found that the inclusion of SOI affects the band structures and the splitting of degenerate valence band occurs on high symmetry Γ-point. We have also measured the value of the splitting energy and our results are similar to the experimental value.*

Keywords: *FP-LAPW, GGA, mBJ, spin-orbit interaction, band structure, splitting energy, pnictides.*

I. Introduction

The III-V semiconductors consist of two elements, one is from group III and another is from group V in the periodic table. III-V semiconductors are more important in optoelectronics because of their wide range of band gap. They have applications in specific areas such as wireless communications. III-nitrides (III-N) form a specific subgroup of the III-V compounds with basic crystal structures, Hexagonal wurtzite (WT) structure and cubic zinc blende structure (ZB). III-N semiconductors are characterized by high iconicity, very short bond length, low compressibility and high thermal conductivity [1-3]. These properties make the III-N semiconductors interesting and very useful. These materials can therefore be used for short wavelength light-emitting diodes (LED), laser diodes [4], and optical detectors, as well as for high temperature, high power, and high frequency devices [5, 6]. The Spin–Orbit Interaction is a relativistic effect whose magnitude increases with the atomic number. Consequently, it provides negligible contributions to the electronic structure of individual atoms and bulk materials made of light elements [7]. It is also the primary interaction responsible for most of the zero-field splitting and other properties of magnetic molecules [8]. Several relativistic methods have been developed in various schemes for the all-electron calculations for solids: the Augmented Plane Wave (APW) method [9], the Linearized Muffin Tin Orbital (LMTO) method [10-13], the Korringa Kohn Rostoker (KKR) method [14-17], and the Linear Combination of Atomic Orbitals (LCAO) method [18-22].

Density Functional Theory (DFT) has proven its worth in the past as an effective/leading theoretical technique for the calculation of various physical properties of solids, while at present it is unmatchable in accuracy and applicability and in the future, it is expected to grow further in all dimensions. The Kohn-Sham equations [23] are extensively solved with the Local Density Approximation (LDA) [23, 24] and Generalized Gradient Approximation (GGA) [25] for the structural, electronic, optical, magnetic and other physical properties of metals, semi-metals, semiconductors, insulators, superconductors, etc. Though, these calculations are effective for certain substances, but are ineffective in the calculations of the band structures of the highly correlated electron systems, with d or f orbital in the III-V compounds. In the case of III–V materials, it is important to include the localized 'd' orbitals. The localized 'd' orbitals play important role in the bonding process and hence their inclusion as valence orbitals is essential for a correct band structure [26] and optical spectra. LDA and GGA not only underestimate band gaps but also band dispersions, particularly the location of d energy level come out incorrectly. Thus the reason of the ineffectiveness of these techniques, especially the most commonly used LDA and GGA, is their inefficient treatment of the d state electrons.

In the present work, we have studied the electronic structures of AlX (X=P, As, Sb) compounds in zinc-blende structure with the modified Becke and Johnson (mBJ) [27] exchange potential in the framework of FP-LAPW method as implemented in the WIEN2k package [28]. We also studied the band structures of BX (X=N, P, As, Sb) with the inclusion of SOI and calculate the spin splitting energy by second variational method using WIEN2k.

II. Formalism

The Kohn-Sham [23] equation is given as

$$\left[T + V_H + V_{xc} + V_{ext}\right]\psi_i(r) = \varepsilon_i \psi_i \tag{1}$$

where T is the kinetic energy operator, V_H is the Hartree potential, V_{ext} is the external potential and V_{xc} is the exchange and correlation potential;

$$V_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho} \tag{2}$$

To solve the Khon-Sham equation, an explicit expression for $E_{xc}[\rho]$ is needed. The exact expression is unknown and hence an approximation is needed. The first and best known approximation is the LDA, which was followed by the GGA. These potentials reproduce rather well the band structure in metallic systems but fail to reproduce the gap of semiconductors. As a possible solution to this problem, the new potential reproduces the experimental gap of semiconductors with accuracy of several orders of magnitude better than the previous version of the WIEN2k code [28] using either the LDA or the GGA, which is the modified Becke and Johnson (mBJ) potential [27]. In the present work, we have studied the electronic structures of Boron compounds (BX, X=N, P, As, Sb) in the zinc-blende structures with the modified Becke and Johnson (mBJ) potential [27]. The mBJ potential is given as follows [29, 30, 31]:

$$V_{x,\sigma}^{MBJ}(r) = c v_{x,\sigma}^{BR}(r) + (3c - 2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(r)}{\rho_\sigma(r)}} \tag{3}$$

where $\rho_\sigma = \sum_{i=1}^{N_\sigma}\left|\psi_{i,\sigma}\right|^2$ is the electron density, $t_\sigma = \left(\frac{1}{2}\right)\sum_{i=1}^{N_\sigma}\nabla \psi_{i,\sigma}^* . \nabla \psi_{i,\sigma}$ is the kinetic energy density and $v_{x,\sigma}^{BR}$, is the Becke-Roussel (BR) potential [31]. The parameter 'c' stands for

$$c = \alpha + \beta\left(\frac{1}{V_{cell}}\int d^3 r \frac{|\nabla\rho(r)|}{\rho(r)}\right)^{1/2} \tag{4}$$

α and β are free parameters. The WIEN2k code [28] defines $\alpha = -0.012$ and $\beta = 1.023$ Bohr.
With the inclusion of SOI, we have the total Hamiltonian with the spin-orbit Hamiltonian H_{so}:

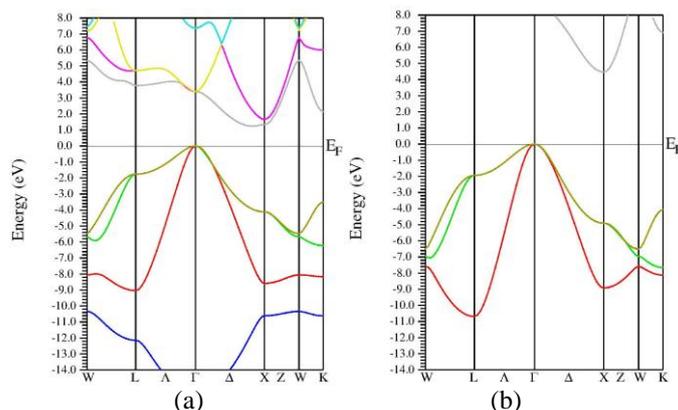$$H\psi = \varepsilon\psi + H_{so}\psi \tag{5}$$

where H_{so}[32] has the form:

$$H_{so} = \frac{\hbar}{2Mc^2}\frac{1}{r}\frac{dV}{dr}\begin{pmatrix}\vec{\sigma}\vec{l} & 0 \\ 0 & 0\end{pmatrix} \tag{6}$$
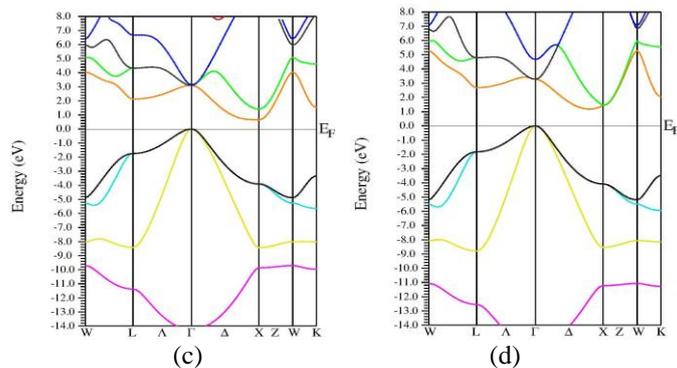
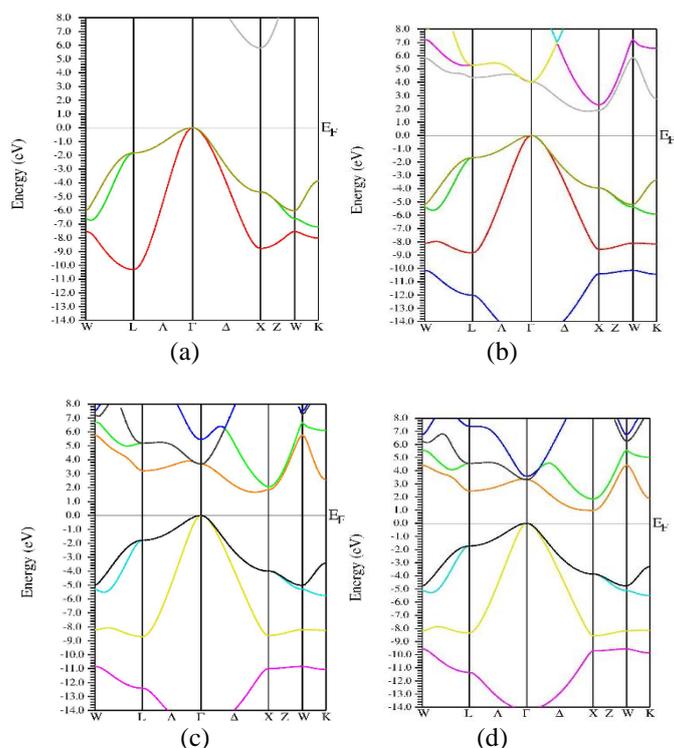with $\vec{\sigma}$ as the Pauli spin matrices.

III. Results And Discussion

(A) Without spin–orbit interaction

We have calculated the band structures of BX (X=N, P, As, Sb) by using GGA and mBJ [27] potential within the FP-LAWP method as implemented in WIEN2k code [28]. Figures (1) and (2) gives the results of GGA and mBJ calculations without SOI on the band structures of BX (X=N, P, As, Sb).
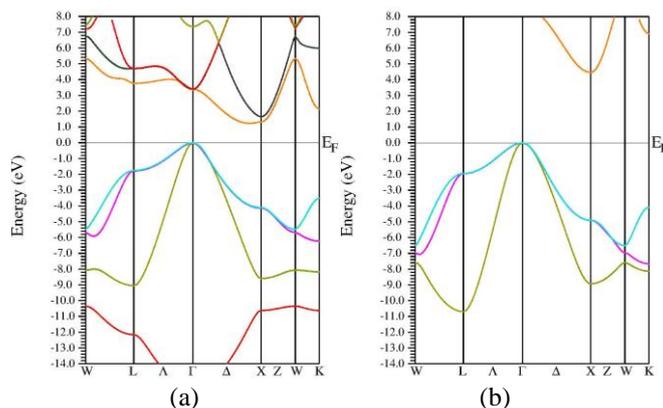

(a)   (b)

(c)　　　　　　　　　　(d)

Fig.1. Band structures using GGA without SOI for (a) BN (b) BP (c) BAs (d) BSb

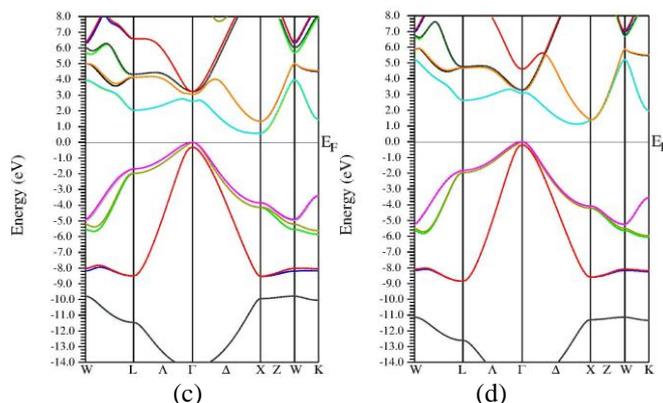(a)　　　　　　　　　　(b)

(c)　　　　　　　　　　(d)

Fig.2. Band structures using mBJ without SOI for (a) BN (b) BP (c) BAs (d) BSb
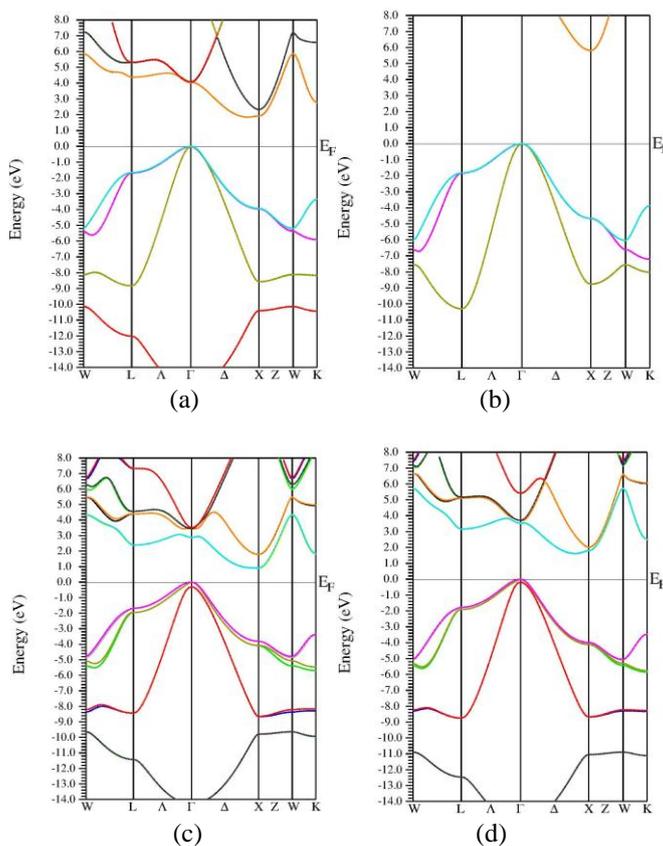
(B) With spin–orbit interaction

　　　　We have also calculated the band structures of BX (X=N, P, As, Sb) by using GGA and mBJ [27] potential within FP-LAWP method as implemented in WIEN2k code [28] with the inclusion of SOI term. Figures (3) and (4) gives the results of GGA and mBJ calculations with SOI on the band structures of BX (X=N, P, As, Sb).

(a)　　　　　　　　　　(b)

(c)   (d)

Fig.3. Band structures using GGA with SOI for (a) BN (b) BP (c) BAs (d) BSb

(a)   (b)

(c)   (d)

Fig.4. Band structures using mBJ with SOI for (a) BN (b) BP (c) BAs (d) BSb

Table 1: Comparison of energy bang gap and spin splitting energy in BX (X=N, P, As, Sb)

Name of Compounds	Energy band gap (eV)			Spin splitting energy (eV)	
	Our calculation		Expt.	Our calculation	
	GGA	mBJ	value[33]	GGA	mBJ
BN	4.2	5.8	6.2	0	0
BP	1.3	1.8	2.1	0.05	0.05
BAs	0.67	0.78	0.67	0.20	0.20
BSb	0.6	1.0	0.527	0.30	0.30

IV. Conclusions

In Figs. 1 and 2, we have the band structures of BX (X=N, P, As, Sb) by using GGA and mBJ method without spin orbit interaction. We have measured the band energy and found that the modified Becke-Johnson exchange potential can predict the band gap in better agreement with the experimental results [33] as shown in Table 1. We can conclude that mBJ is an efficient theoretical technique for the calculation of the band structures of BX (X=N, P, As, Sb) under III-V semiconductors.

When the spin orbit interaction is included, the splitting of valence band occurs on high symmetry Γ-point which is shown in Fig. 3 and Fig. 4. We have also measured the splitting energy which is shown in Table 1. In this work, we have found that the spin-orbit interaction effects the valence band of BX (X=N, P, As, Sb) semiconductor compounds. It is clear that the splitting energy of valence band is different in different compounds and its values increases with atomic number. We have also found that the modified Becke-Johnson (mBJ) potential gives more accurate result than GGA in the calculation of energy band gap of compound semiconductors. However, the mBJ potential does not effect the spin splitting energy.

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