IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 1 Issue 9, November 2014.
www.ijiset.com
ISSN 2348 – 7968

Study of band structure and spin splitting energy in Gallium (GaX, X=P,As,Sb) compounds using GGA and mBJ-GGA method

Ricky Ralte*, Aldrin Malsawmtluanga, Lalrintluanga Sailo, Lalnunpuia and Z. Pachuau
Department of Physics, Mizoram University, Aizawl – 796004.Mizoram, India

ABSTRACT

We studied the band structures of Gallium compounds (GaX, X=P,As,Sb) under III-V semiconductor compounds in this paper. Our calculations were performed using a generalized gradient approximation (GGA) and the modified Becke-Johnson potential (mBJ) within the Wien2k code. 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: *DFT, FP-LAPW, GGA, mBJ-GGA, spin-orbit interaction, band structure, splitting energy.*

1. INTRODUCTION

The classical analysis of spin-orbit interaction (SOI) in hydrogen like atoms by Thomas[1] played an important role in supporting the hypothesis of electron spin, as given by Uhlenbeck and Goudsmit[2] in 1925. The latter successfully explained the multiplet structure of atom spectra and the anomalous Zeeman effect based on an assumption about the proper magnetic moment of the electron, which is associated with the self-rotational motion of the electron (spin). However, their prediction of a SOI in the hydrogen atom was twice the measured value. This discrepancy was removed by Thomas[1] in 1926 by applying a classical relativistic approach. Later, the problem of SOI was solved by the relativistic quantum electron theory of Dirac[3].

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[4] are extensively solved with the local density approximation (LDA)[4,5] and generalized gradient approximation (GGA)[6] 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 like 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[7] 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 this paper, we have studied the electronic structures of GaX(X=P,As,Sb) compounds in zinc-blende

ISSN 2348 – 7968

structure with the modified Becke and Johnson (mBJ)[8] exchange potential in the framework of full-potential linearized augmented plane wave (FP-LAWP) method as implemented in the WIEN2K package[9]. We also studied the band structures of GaX(X=P,As,Sb) with the inclusion of SOI and calculate the spin splitting energy by second variational method using Wien2K[9].

2. FORMALISM

The Kohn-Sham[4] equation is given as

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

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; $V_{xc} = \delta E_{xc}[\rho]/\delta\rho$.

To solve the Kohn-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 Local Density Approximation (LDA), which was followed by the Generalized Gradient Approximation (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[9] using either the LDA or the GGA which is the modified Becke and Johnson (mBJ) potential[8].

In the present, work we have studied the electronic structures of Gallium compounds (GaX, X=P,As,Sb) in the zinc-blende structures with the modified Becke and Johnson (mBJ) potential[8]. The mBJ potential is given as follows[8,10,11]

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

where $\rho_\sigma = \sum_{i=1}^{N_\sigma}\left|\psi_{i,\sigma}\right|^2$,is the electron density,

$t_\sigma = \left(1/2\right)\sum_{i=1}^{N_\sigma}\nabla\psi_{i,\sigma}^{*}.\nabla\psi_{i,\sigma}$ is the kinetic energy density and

$v_{x,\sigma}^{BR}$, is the Becke-Roussel (BR) potential[11]. The 'c' stands for

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

α and β are free parameters. The Wien2k code[9] 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}:

$$H\psi = \varepsilon\psi + H_{so}\psi \qquad (3)$$

where H_{so}[12] has the form:

$$H_{so} = \frac{\hbar^2}{2Mc^2}\frac{1}{r}\frac{dV}{dr}\begin{pmatrix}\vec{\sigma}\cdot\vec{l} & 0\\ 0 & 0\end{pmatrix}$$

with $\vec{\sigma}$ as the Pauli spin matrices.

3. RESULTS AND DISCUSSION

3.1. Band structure of GaX(X=P,As,Sb) without spin–orbit interaction(SOI)

We have calculated the band structures of GaX(X=P,As,Sb) by using GGA and mBJ-GGA [8] potential within the full potential linearized augmented plane wave (FP-LAWP) method as implemented in Wien2k code[9]. The electronic band structure of GaX without SOI calculated by DFT/FP-LAPW- GGA is shown in Fig 1. We have seen that in GaP compound, the band gap is a indirect band gap because the top of valence band lying at high symmetry point and the lowest of conduction band are lying at the X valley i.e 1.65 eV. But in GaAs and GaSb, the band gap is a direct band gap, because the top of valence band and the lowest of conduction band are lying at high symmetry Γ point at k=0, i.e 0.5 eV and 0.6 eV respectively. Comparing to the experimental value[13],

ISSN 2348 – 7968

these energy gaps are very small and deviation percentage with the experimental values are 29.79%, 67.08% and 92.61% for GaP, GaAs and GaSb respectively.

We have also calculated the band gap of GaX by using the modified Becke-Johnson potential combined with the generalized gradient approximation (mBJ-GGA) [8] in order to obtain a corrected value of the gap energy (closer to experiment [13]) which is shown in Fig. 2. It shows that, the energy band gap are GaP = 2.25 eV, GaAs = 1.65 eV and GaSb = 1.93 eV. and the deviation percentage with the experimental values are4.26%, 8.62% and 14.53% for GaP, GaAs and GaSb respectively. The comparison of band energy(Eg) calculated by GGA, mBJ-GGA and the experimental value[13] are shown in Table 1.

3.2. Band structure of GaX(X=P,As,Sb) with spin–orbit interaction(SOI)

We have calculated the band structures of GaX(X=P,As,Sb) by using GGA and mBJ [8] potential within FP-LAWP method as implemented in Wien2k code[9] with the inclusion of SOI term.

In the band structure of GaX(X=P,As,Sb) calculated using GGA and mBJ-GGA method with the inclusion of SOI term, we have found that the SOI has no effect on the band energy between valence band and conduction band in both cases. But due to the SOI, the valence band split into two parts in both cases as shown in Fig 3 and Fig 4. The lower splitting valence band is called split-off band. We have calculated the splitting between the split-off bands and the upper splitting valence bands at the point which are 0.06 eV, 0.32 eV and 0.71 eV for GaP, GaAs and GaSb respectively. These values are in good agreement with the experimental value[13]. The comparisons of spin splitting energy of GaX(X=P,As,Sb) between our calculated value and the experimental value is shown in Table 2. The upper splitting valence band has two band which are called heavy-hole (HH) band and light-hole (LH) band. The names heavy and light hole band come from the fact that the effective masses of these two sets of bands are different.

4. CONCLUSION

In this paper, we have found that the calculation of band energy in III-V semiconductor using mBJ-GGA gives more accurate result than GGA. We can concluded that mBJ is an efficient theoretical technique for the calculation of the band structures of GaX (X=P,As,Sb) under III-V semiconductors. We have also found that the SOI effects the valence band of GaX(X=P,As,Sb) semiconductor compounds. It splits the top of valence band and the splitting energy of valence band is different in different compounds and also the values increase with atomic number (Table 1). But, mBJ-GGA potential does not affect the spin splitting energy and has the same splitting energy in both cases (Table 2).

REFERENCES

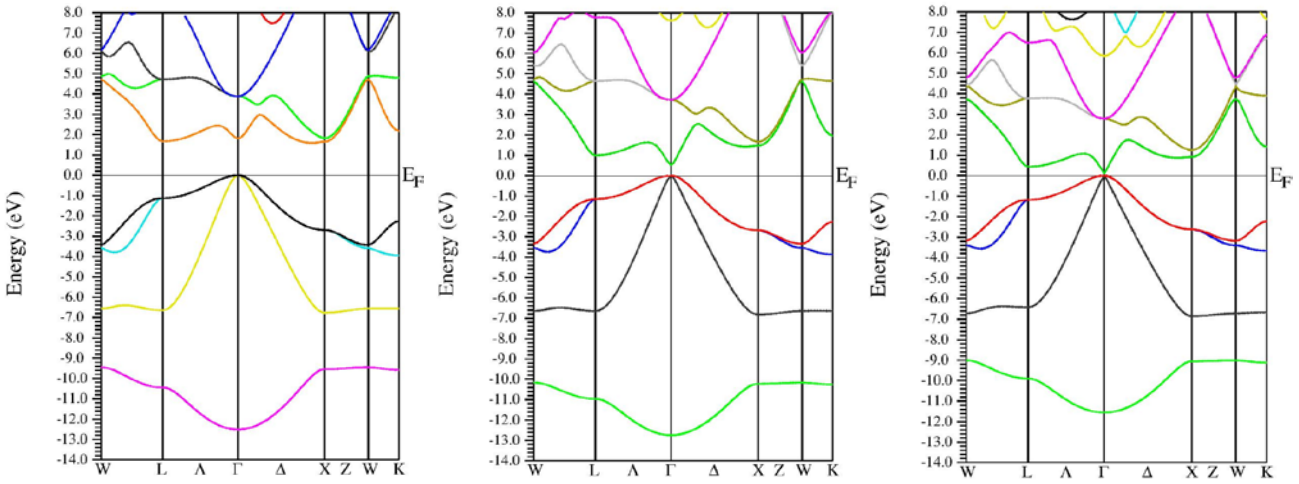
1. L. H. Thomas, “The motion of the spinning electron,” Nature London, **117**, 514, 1926.
2 G. E. Uhlenbeck and S. Goudsmit, “Spinning electrons and the structure of spectra,” Nature London, **117**, 264–265, 1926.
3. P. A. M. Dirac, “The Quantum theory of the electron,” Proc. R. Soc. London, Ser. A, **117**, 610–624 (1928).
4. W. Kohn, and L. J. Sham, “Self-Consistent Equations Including Exchange and Correlation Effects,” Phys. Rev., **140** A1133-A1138, 1965.
5. J. P. Perdew and Y. Wang, “Accurate and simple analytic representation of the electron-gas correlation energy,” Phys. Rev. B., **45** 13244-13249, 1992.
6. J. P. Perdew, B. Kieron and E. Matthias,“ Generalized Gradient Approximation Made Simple,” Phys. Rev. Lett., **78** 1396, 1997.
7. P. Schroer, K. Peter and P. Johannes, “First-principles

ISSN 2348 – 7968

calculation of the electronic structure of the wurtzite semiconductors ZnO and ZnS," Phys. Rev. B,. **47** 6971-6979, 1993.

8. A. D. Becke and E. R. Johnson, "A simple effective potential for exchange ," J. Chem. Phys., **124**, 221101-221105, 2006.
9. Blaha, P. *et al.*, , WIEN2K: An Augmented Plane Wave and Local Orbitals Program for Calculating Crystal Properties, edited by K. Schwarz, Vienna University of Technology, Austria, 2008.
10. F. Tran and P. Blaha, "Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential," Phys. Rev. Lett., **102**, 226401-226405, 2009.
11. F. Tran, B. Peter and S. Karlheinz, "Band gap calculations with Becke–Johnson exchange potential," J. Phys. Condens. Matter., **19**, 196208-196216, 2007.
12. P. Novak, "Calculation of spin-orbit coupling,"(1997) (at http://www. wien2k.at/ reg_user/textbooks)
13. I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, "Band parameters for III–V compound semiconductors and their alloys", J. Appl. Phys., **89**, 5815-5875, 2001.

Figures



(a) (b) (c)

Fig.1. Band structures using GGA without SOI for (a) GaP (b) GaAs and (c) GaSb.

ISSN 2348 – 7968

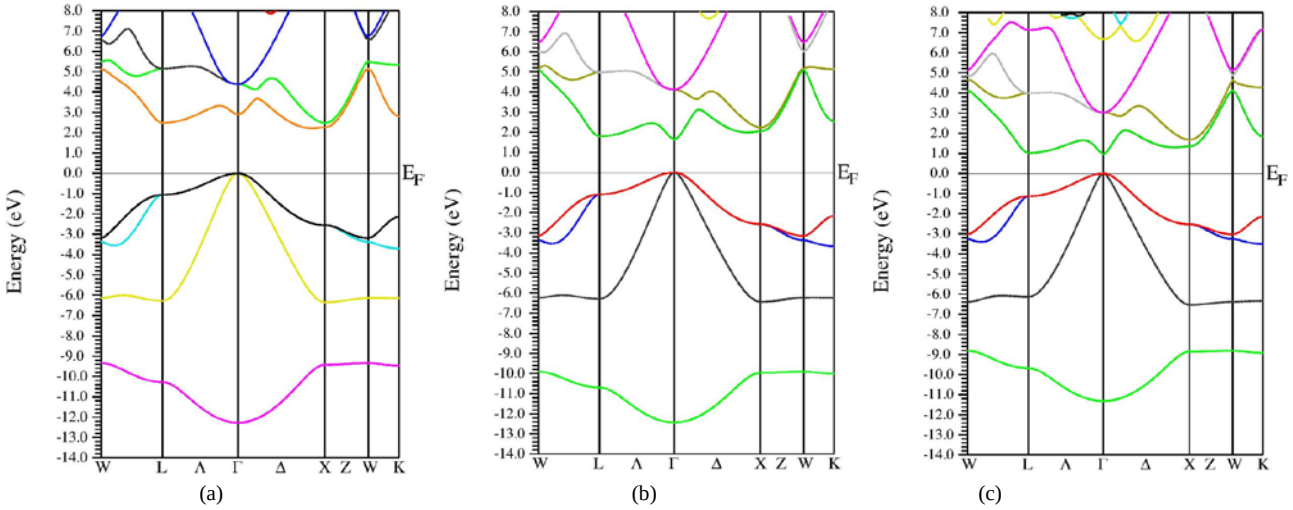


Fig.2. Band structures using mBJ without SOI for (a) GaP, (b) GaAs and (c) GaSb.

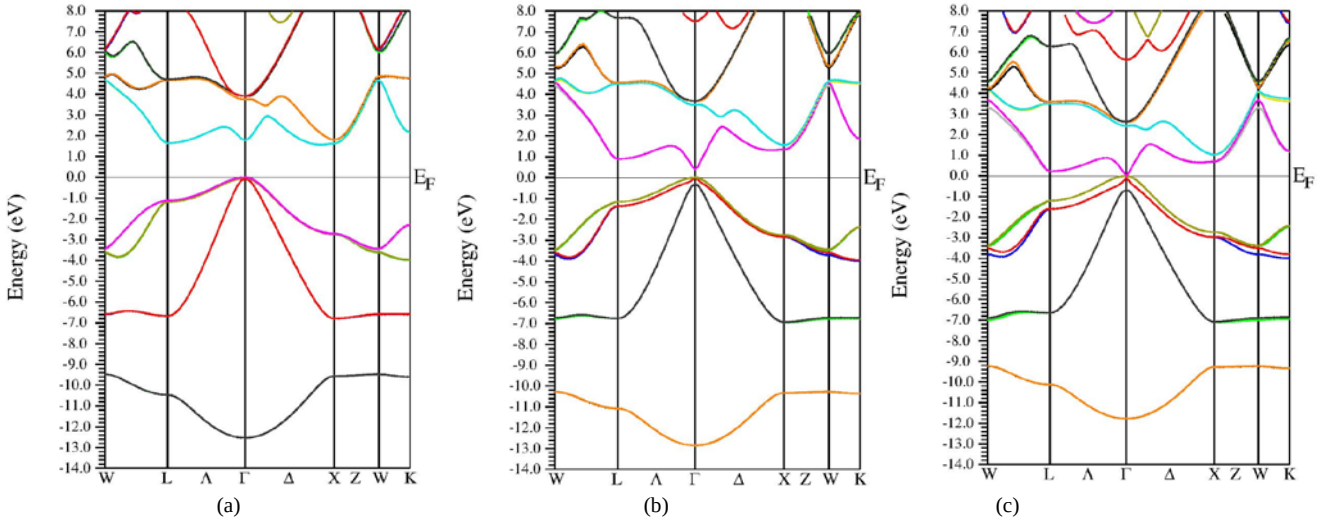


Fig.3. Band structures using GGA with SOI for (a) GaP (b) GaAs and (c) GaSb.

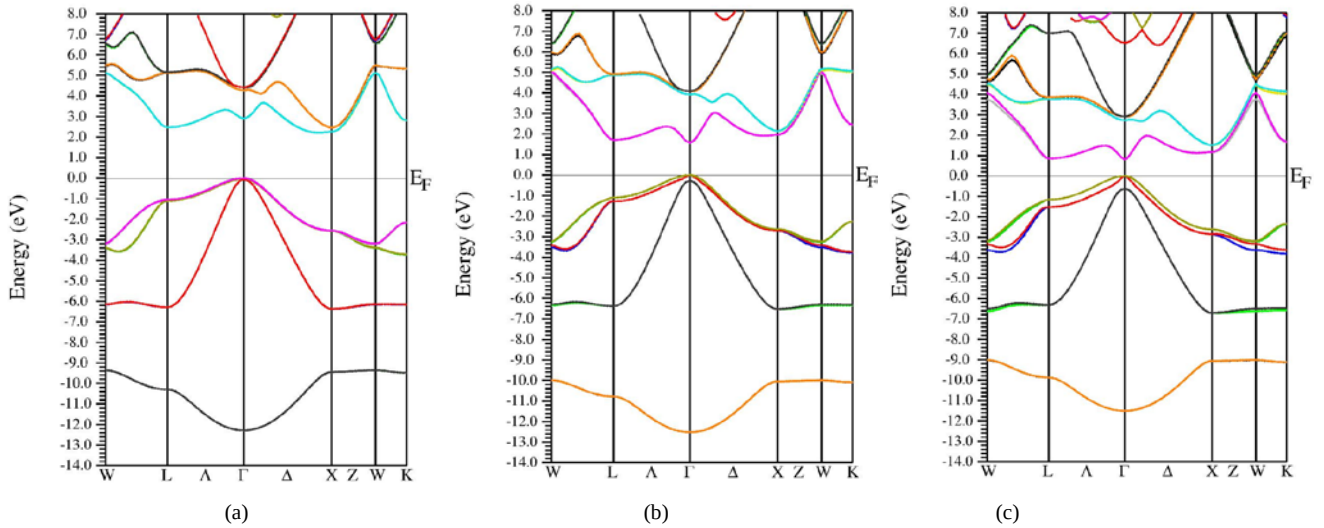


Fig.4. Band structures using mBJ with SOI for (a) GaP (b) GaAs and (c) GaSb.

ISSN 2348 – 7968

Tables:

Table 1: Energies of GaX(X=P,As,Sb) calculated by the GGA and mBJ-GGA approach without SOI. The last column gives the deviation in percentage of our calculated values from the experimental values [13].

Sl. No.	Compounds	Energy Band Gap E_g (in eV)			Deviation (in %)	
		Our calculations		Experimental results[13]		
		GGA	mBJ-GGA		GGA	mBJ-GGA
1	GaP	1.65	2.25	2.350	29.79	4.26
2	GaAs	0.5	1.65	1.519	67.08	8.62
3	GaSb	0.06	0.93	0.812	92.61	14.53

Table 2: Comparison of spin splitting energy in AlX(X=P,As,Sb) calculated by the GGA and mBJ-GGA approach with SOI. The last column gives the deviation in percentage of our calculated values from the experimental values [13].

Sl. No.	Compounds	Spin Splitting Energy (in eV)			Deviation (in %)	
		Our calculations		Experimental results[13]		
		GGA	mBJ-GGA		GGA	mBJ-GGA
1	GaP	0.06	0.06	0.08	25.00	25.00
2	GaAs	0.32	0.32	0.34	5.88	5.88
3	GaSb	0.71	0.71	0.76	6.58	6.58