Effect of Spin-orbit coupling on the Band structures of Aluminium compounds (AlX, X=P,As,Sb) using modified Becke-Johnson potential

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Abstract

In this paper, we have studied the band structures of Aluminium compounds (AlX, X=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). We have compared our results calculated by GGA and mBJ and 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 coupling on both approximations and then compared the results. We have found that the inclusion of spin-orbit coupling 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, spin-orbit coupling, band structure, splitting energy.

Introduction

The spin–orbit coupling 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[1]. It is also the primary interaction responsible for most of the zero-field splitting and other properties of magnetic molecules[2]. Several relativistic methods have been developed in various schemes for the all-electron calculations for solids: the augmented-plane-wave (APW) method[3], the linearized muffin-tin-orbital (LMTO) method[4-7], the Korringa-Kohn-Rostoker (KKR) method[8-12] and the linear-combination-of-atomic-orbitals (LCAO) method[13-17].

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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[18] are extensively solved with the local density approximation (LDA)[18,19] and generalized gradient approximation (GGA)[20] 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[21] 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 Aluminium compounds AlX(X=P,As,Sb) in zinc-blende structure with the modified Becke and Johnson (mBJ)[22] exchange potential in the framework of full-potential linearized augmented plane wave (FP-LAWP) method as implemented in the WIEN2k package[23]. We also studied the band structures of AlX(X=P,As,Sb) with the inclusion of spin-orbit coupling and calculate the spin splitting energy by second variational method.

Formalism

The Kohn-Sham[18] 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 used. 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[23] using either the LDA or the GGA, which is the modified Becke and Johnson (mBJ) potential[22].

In the present work, we have studied the electronic structures of Aluminium compounds (AlX, X=P,As,Sb) in the zinc-blende structures with the modified Becke and Johnson (mBJ) potential[22]. The mBJ potential is given as follows[22,24,25]

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

where $\rho_\sigma = \sum_{i=1}^{N_\sigma} |\psi_{i,\sigma}|^2$, 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[26]. The 'c' stands for

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

α and β are free parameters. The Wien2k code[23] defines $\alpha = -0.012$ and $\beta = 1.023$ Bohr.

With the inclusion of spin orbit coupling, we have the total Hamiltonian with the spin-orbit Hamiltonian H_{so}:

$$H\psi = \varepsilon\psi + H_{so}\psi \tag{3}$$

where H_{so}[27] has the form: $H_{so} = \dfrac{\hbar^2}{2Mc^2}\dfrac{1}{r}\dfrac{dV}{dr}\begin{pmatrix} \vec{\sigma}\vec{l} & 0 \\ 0 & 0 \end{pmatrix}$ with $\overset{u}{\sigma}$ as the Pauli spin

matrices.

Results and Discussion
(a) Without spin–orbit coupling

We have calculated the band structures of AlX(X=P,As,Sb) by using GGA and mBJ [22] potential within the full potential linearized augmented plane wave (FP-LAWP) method as implemented in Wien2k code[23].

Figure (1) and (2) gives the results of GGA and mBJ calculations without the spin-orbit coupling on band structure of AlX(X=P,As,Sb).
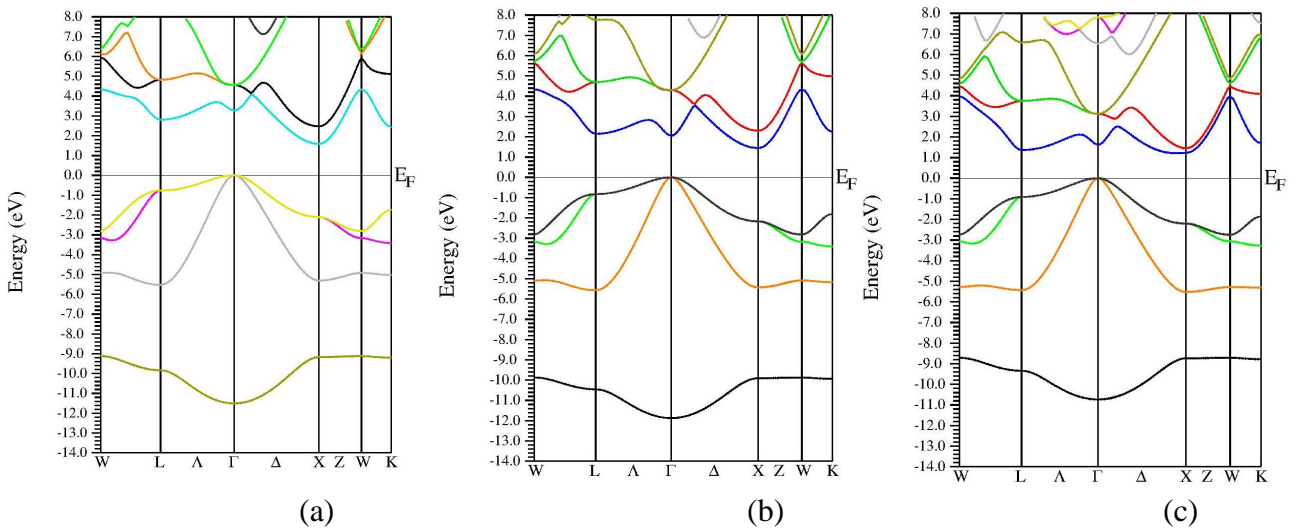

(a)   (b)   (c)

Fig.1. Band structures using GGA without spin orbit coupling for (a) AlP (b) AlAs and (c) AlSb.

(a)   (b)   (c)
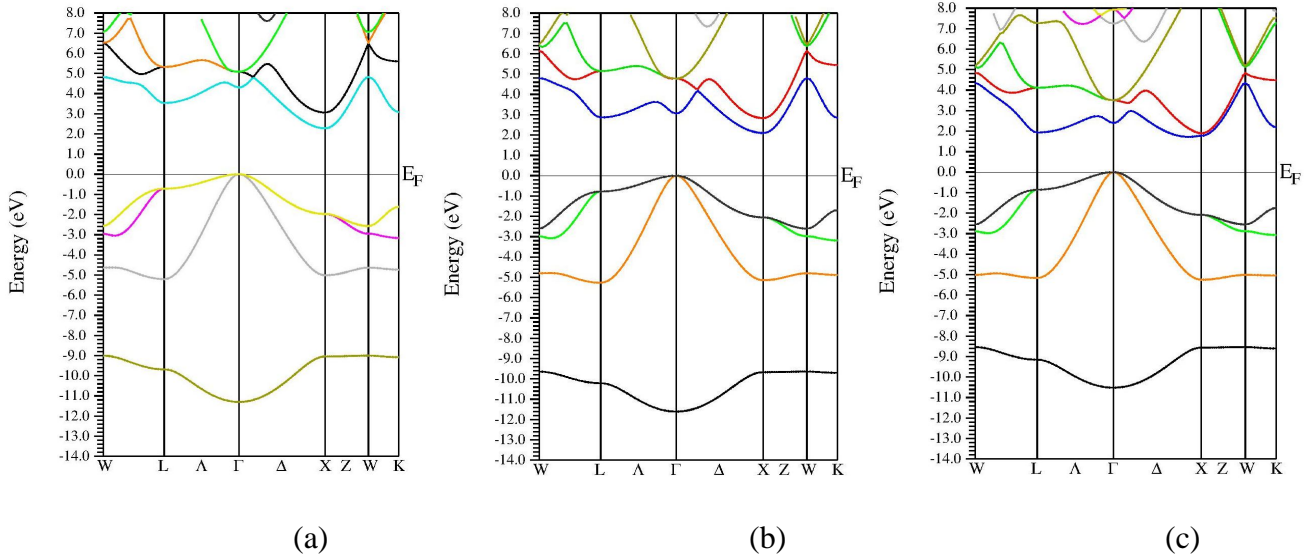
Fig.2. Band structures using mBJ without spin orbit coupling for (a) AlP, (b) AlAs and (c) AlSb.

(b)   With spin–orbit coupling

          We have also calculated the band structures of AlX(X=P,As,Sb) by using GGA and mBJ [22] potential within FP-LAWP method as implemented in Wien2k code[23] with the inclusion of spin-orbit coupling term.

          Figure (3) and (4) gives the results of GGA and mBJ calculations with the spin-orbit coupling on the band structures of AlX(X=P,As,Sb).
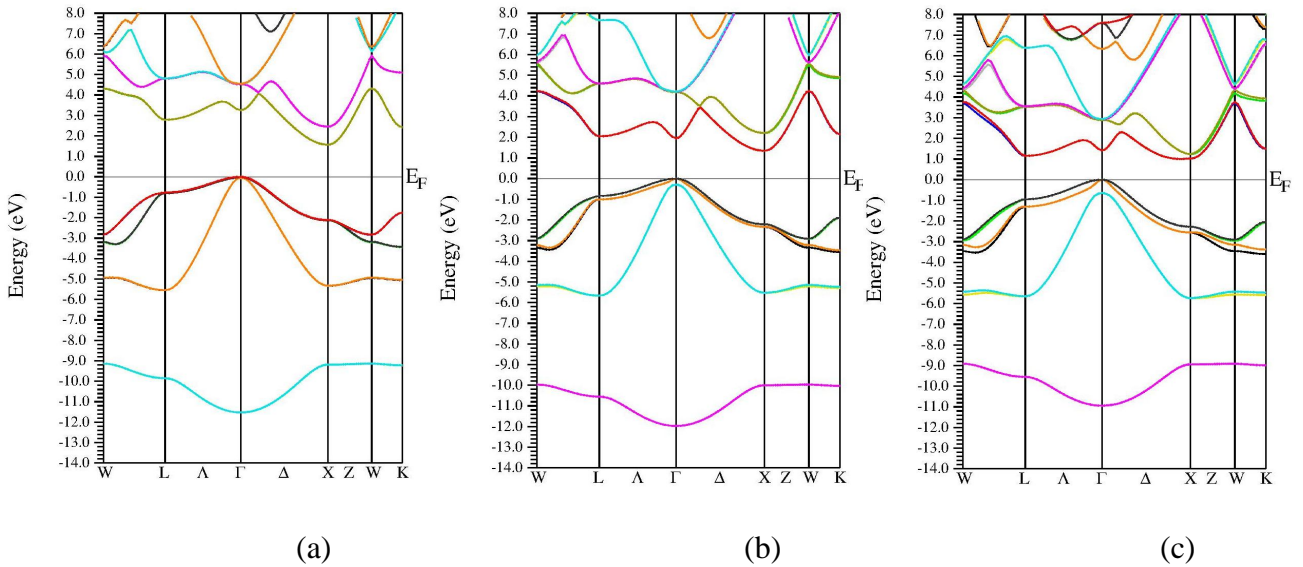

(a)   (b)   (c)

Fig.3. Band structures using GGA with spin orbit coupling for (a) AlP (b) AlAs and (c) AlSb.
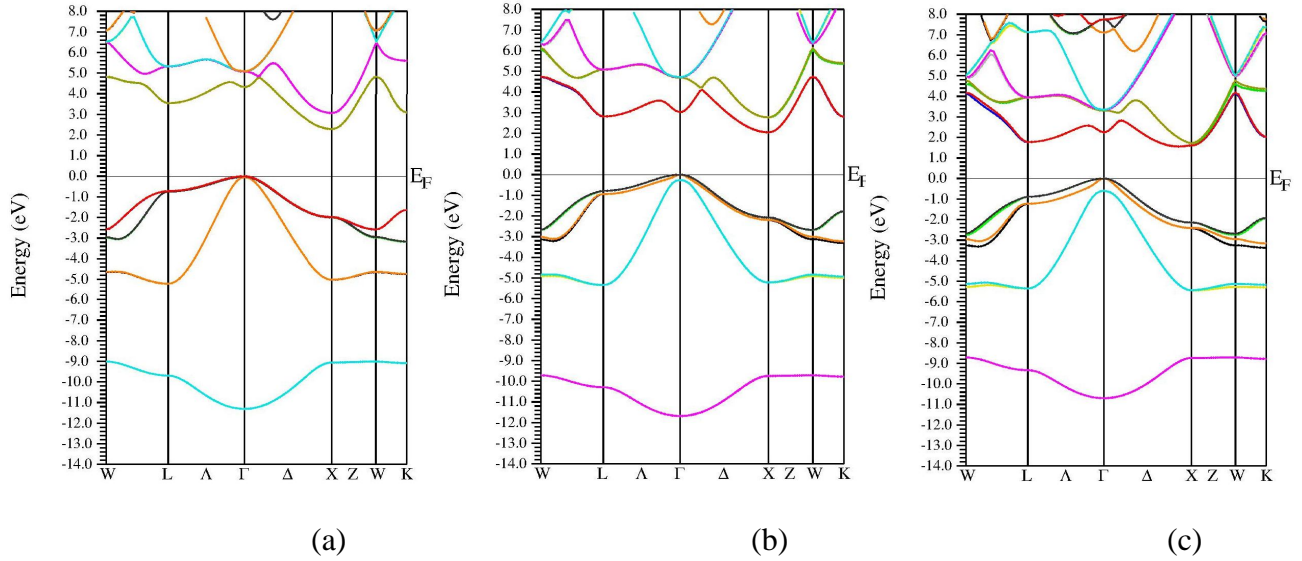
(a) (b) (c)

Fig.4. Band structures using mBJ with spin orbit coupling for (a)AlP (b) AlAs and (c) AlSb.

In Figs. 1 and 2, we have the band structures of AlX(X=P,As,Sb) calculated by using GGA and mBJ method without spin orbit coupling. 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[28,29] shown in Table 1. We can concluded that mBJ is an efficient theoretical technique for the calculation of the band structures of AlX (X=P,As,Sb) under III-V semiconductors.

When the spin orbit coupling is included, the splitting of valence band occurs on high symmetry Γ point which is shown in Figs. 3 and Fig. 4. We have also measured the splitting energy which is shown in Table 1.

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

Sl. No.	Name of Compounds	Energy band gap (eV)			Spin splitting energy (eV)		
		Our calculation		Expt. value	Our calculation		Expt. value
		GGA	mBJ		GGA	mBJ	
1.	AlP	1.6	2.3	2.4[a]	0.05	0.05	0.05[a],0.07[b]
2.	AlAs	1.4	2.1	2.153[a]	0.25	0.23	0.275[a],0.28[b]
3.	AlSb	1.2	1.7	1.686[a]	0.62	0.62	0.673[a],0.67[b]

[a][Ref. 28], [b][Ref.29]

In this paper, we have found that the spin-orbit coupling effects the valence band of AlX(X=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 semiconductor energy band gap. However, the mBJ potential does not effect the spin splitting energy.

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