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First-principles study of the structural and electronic properties of III-phosphides

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Abstract

We use density functional theory and different forms of the exchange-correlation approximation to calculate the structural and electronic properties of tetrahedrally coordinated III-phosphide semiconductors. The computed results for structural properties using generalized gradient approximation (GGA) agree well with the experimental data. For reliable description of energy band gap values, another form of GGA developed by Engel and Vosko has been applied. As anticipated, boron phosphide was found to be the hardest compound due to the strong B–P covalent bonding.
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1. Introduction

Knowledge of physical properties of crystalline materials plays a vital role in developing new technologies. Such materials include III-phosphide binary compounds, namely boron phosphide (BP), aluminum phosphide (AlP), gallium phosphide (GaP) and indium phosphide InP, which are common-anion III–V semiconductors. At ambient conditions, these compounds crystallize in the zincblende structure with a space group F$\bar{4}$3m [1–3] and have an indirect band gap, with the exception of InP. Recently, these compounds have attracted a great deal of attention, [1–30] anticipating fabrication of important electronic devices. Boron phosphide is classified as a refractory material and has resemblance with silicon carbide electronically [10,20]. Like boron arsenide and boron antimonide, BP shows a strong covalent nature and exhibits an unusual behavior due to small core and absence of p electrons in the core of the boron atom compared to other III–V

compounds [11]. Similarly, GaP is in use as a material for light-emitting diodes, and InP has particular importance in the designing of transferred-electron devices [21].

Motivated by the technological significance of these materials, III-phosphides have been the subject of various theoretical investigations, from empirical [22] to first-principles based on the density functional theory (DFT) [31,32]. Most of these studies have been undertaken using the pseudo-potential [33] or full-potential linearized-augmented plane wave (FP-LAPW) method; one of the most accurate computational schemes for the study of crystalline solids, within local density approximation (LDA) [34] or generalized gradient approximation (GGA) [35]. Although LDA and GGA give good results for ground state properties, usually they underestimate energy band gap values. Another form of GGA proposed by Engel and Vosko (GGA-EV) [36] successfully explains the electronic properties of different solids [37–47]. To the best of our knowledge, GGA-EV has not yet been used for theoretical study of the electronic properties of III-phosphides. For structural properties only few computational investigations using GGA [35] have been reported. Therefore,

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a comprehensive and accurate theoretical description of III-phosphides is indispensable for better understanding of these compounds.

The aim of this work is to carry out a thorough DFT study of the structural and electronic properties of zincblende structure BP, AlP, GaP and InP semiconductors. We calculate lattice parameters, bulk modulus, cohesive energy and band gap for each compound, with different exchange-correlation approximations. The paper is organized as follows: Section 2 describes computational details. Results and discussions are presented in Section 3 (structural properties) and Section 4 (electronic properties). The last section summarizes our work.

2. Computational details

The zincblende structure has an FCC lattice with two atoms per basis point and the atoms associated to each basis are located at R(0, 0, 0)and X(1/4, 1/4, 1/4), where R≡B, Al, Ga, In and X≡P. Our calculations were performed using WIEN2k code [48–53] based on the full-potential linear-augmented plane wave plus local orbital method (FP-(L)APW + lo). In this scheme as described in Refs. [48–53], a crystal unit cell is partitioned into two regions: non-overlapping Muffin-Tin (MT) spheres centered on nuclei and the remaining interstitial region. In both the regions, Kohn–Sham wave functions, charge density and potential are expanded in different sets of basis functions. For the wave functions, inside the MT spheres a linear combination of the atomic wave functions times the spherical harmonics was used. In the interstitial region, plane waves are used. The maximum quantum number for expansion of wave functions inside the MT sphere was $l_{max} = 10$, and the energy cutoff for plane wave expansion in the interstitial region was set to $K_{max} = 8.0/R_{MT}$ (Ryd)$^{1/2}$. The charge density and potential are expanded into lattice harmonics inside MT spheres and as a Fourier series in the remaining space. Fourier expansion of charge density was truncated at $G_{max} = 14$(Ryd)$^{1/2}$. The R_{MT} (R_{MT} is the smallest MT radii in the unit cell) values for B, Al, Ga, In and P are taken as 1.5, 1.9, 2.0, 2.1, 2.4 and 2.0 bohr, respectively. Reciprocal space integration was performed using an improved tetrahedron method [54] and a set of 30 irreducible special k-points. A suitable choice of exchange-correlation energy functional plays an important role in the accurate calculations of various properties of solids. For the structural properties, we used the local density approximation (LDA) [34] developed by Perdew and Wang and generalized gradient approximation (GGA-PBE) [35] developed by Perdew, Burke and Ernzerhof. For band structure study another form of GGA developed by Engel and Vosko (GGA-EV) [36] is used. Our calculations for the valence electrons were performed in a scalar-relativistic limit, while the core electrons were treated fully relativistically. The spin–orbit coupling was not taken into account, on account of having a negligible effect on the

results. More details of this scheme of calculations are available elsewhere [48–53].

3. Structural properties

The structural properties of BP, AlP, GaP and InP were computed using LDA and GGA [35]. For each compound, total energy per primitive cell was calculated at different volumes over a range of $\pm 10\%$ around the equilibrium value, and then by fitting the Murnaghan equation of states [55] to the resulting data; equilibrium lattice parameters, bulk modulus, its pressure derivative, and cohesive energy were calculated. The obtained values are listed in Table 1 together with available experimental and theoretical results for comparison. As a sample, the energy–volume curve of BP within LDA is shown in Fig. 1.

From Table 1 it is observed that, compared to experiment, our calculated lattice parameters are slightly underestimated with LDA and overestimated with GGA. However, all results agree with the experimental numbers within 1% and 2% for LDA and GGA, respectively. Moreover, our results have an overall agreement with other barely available DFT calculations.

Bulk modulus, as a measure of the hardness of materials, was calculated for all compounds (Table 1). Our computed values for bulk moduli using LDA are close to the measured data, while GGA underestimates it. As shown in Table 1, BP has a much higher bulk modulus because of the strong covalent bonding between B and P atoms. The calculated pressure derivatives of bulk moduli are also shown in Table 1.

The cohesive energy (difference between the total energy of isolated atoms and the total energy of the crystal unit cell) of III-phosphides was also calculated precisely by performing both calculations at the same level of accuracy. The results as given in Table 1 indicate that LDA generally gives higher values than the experiment, while GGA provides a good agreement. This is due to 'over-binding problem' of LDA. GGA effectively improves cohesive energies by considering gradient corrections. To our knowledge, the cohesive energy of III-phosphides is not calculated within DFT and the reported Hartree–Fock-based values [5,8] are significantly lower than the experimental values.

4. Electronic properties

For a consistent and comparable study of electronic band structure and energy band gap with different exchange-correlation approximations, the experimental lattice parameters were used. The Kohn–Sham energy eigenvalues were calculated using the (FP-L(APW + lo)) method along high-symmetry directions in the first Brillouin zone. For the exchange correlation potential, LDA, GGA-PBE and GGA-EV have been used. Energy band gap values thus calculated are given in Table 2 along with other computations as well as the experimental data

Table 1
The lattice parameter (*a*) bulk modulus (*B*) its pressure derivative (*B*′) and cohesive energy per unit cell (E_{coh}) of BP, AlP, GaP and InP compounds

Compounds	Method	*a* (Å)	*B* (GPa)	*B*′	E_{Coh} (eV)
BP					
Present work	FP-LDA	**4.498**	**176**	**3.92**	**12.50**
	FP-GGA	**4.555**	**162**	**3.86**	**10.69**
Experiment	–	4.538 [1]	173 [2]	–	10.4 [1]
Other calculations	LMTO-LDA	4.56 [5]	168 [5]	–	–
	PP-LDA	4.475 [9]	172 [9]	3.76 [9]	–
	PP-LDA	4.478 [12]	173 [12]	3.71 [12]	–
	FP-LDA	4.501 [13]	176 [13]	3.68 [13]	–
	FP-GGA	4.554 [13]	160 [13]	4.02 [13]	–
	FP-GGA	4.546 [10]	170 [10]	3.07 [10]	–
	FP-GGA	4.546 [15]	170 [15]	–	–
	PP-GGA	–	164 [16]	–	–
	PP-LDA	4.464 [17]	176 [17]	4.00 [17]	–
	HF	4.6 [3]	171 [3]	–	6.4 [3]
	HF	–	–	–	0.23 [6]
	HF	4.584 [7]	195 [7]	–	–
AlP					
Present work	FP-LDA	**5.436**	**89**	**4.14**	**9.62**
	FP-GGA	**5.511**	**82**	**3.99**	**8.24**
Experiment	–	5.451 [1]	86 [1]	–	8.40 [1]
	PP-LDA	5.417 [11]	89 [11]	4.04 [11]	–
Other calculations	HF	5.520 [3]	96 [3]	–	5.7 [3]
	HF	–	–	–	0.198[6]
	HF	5.535 [7]	101[7]	–	–
GaP					
Present work	FP-LDA	**5.398**	**91**	**4.76**	**8.70**
	FP-GGA	**5.512**	**76**	**4.60**	**7.06**
Experiment	–	5.450 [1]	91 [1]	–	7.30 [1]
Other calculations	LMTO-LDA	5.358 [4]	98 [4]	–	–
	PP-LDA	5.322 [11]	92 [11]	4.34 [11]	–
	HF	5.560 [3]	95 [3]	–	4.20 [3]
	HF	–	–	–	0.147 [6]
	HF	5.530 [7]	–	–	–
InP					
Present work	FP-LDA	**5.838**	**71**	**4.78**	**8.03**
	FP-GGA	**5.968**	**62**	**4.04**	**6.45**
Experiment	–	5.869 [1]	72 [1]	–	6.60 [1]
Other calculations	PP-LDA	5.729 [11]	74 [11]	4.48 [11]	–
	HF	5.930 [3]	76 [3]	–	3.90 [3]
	HF	–	–	–	0.142 [6]
	HF	5.953 [7]	–	–	–

Values in bold faces are our results.

for comparison. Important features of our computations are discussed below.

The general features of band structures are essentially the same within all exchange-correlation approximations, and the main difference is in the numerical values of the energy band gap (Table 2). Maximum of the valance band occurs at Γ point while the minimum of the conduction band for BP and GaP is along the $\Delta - X$ line, and at the X and Γ points for AlP and InP, respectively, which is also clear from figures (Figs. 2–5). This leads to indirect gaps for all compounds, except for InP that has a direct Γ–Γ gap.

Regarding the energy band gap (Table 2), GGA provides slightly enhanced values to LDA, indicating similar treatment of exchange-correlation potential in these two approximations. Both LDA and GGA give underestimated

band gaps compared to experiment because they are developed for accurate description of exchange-correlation energy. In contrast, GGA-EV gives much better results (Table 2), which are close to experimental values as it is formulated for better treatment of exchange-correlation potential. Notably, it is for the first time that GGA-EV is applied for the band structure calculation of phosphides.

5. Conclusion

The following observations are noticeable:

1. No comprehensive theoretical work is available on the study of structural as well as electronic properties of III-phosphides. Our work gives a comprehensive study of these properties.
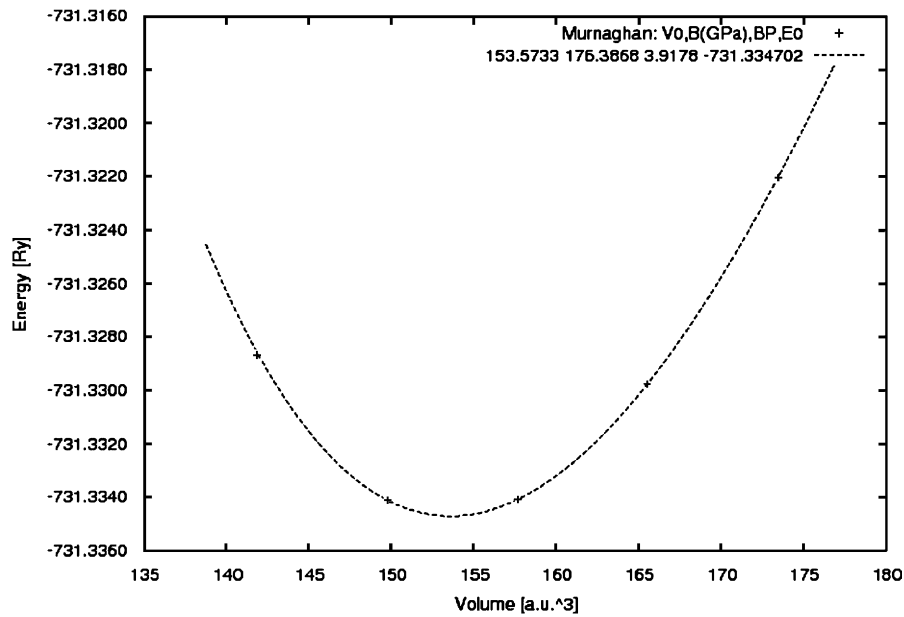
Fig. 1. The total energy vs. primitive cell volume for zb-BP with LDA.

Table 2
The energy band gap (E_g) properties of BP, AlP, GaP and InP. XC: Exchange correlation approximation

Compounds	Methods	XC	Eg (ev)	Type of band-gap
BP				
Present work	FP-LAPW	LDA	**1.18**	Indirect ($\Gamma - \Delta_{min}$)
		GGA	**1.24**	Indirect ($\Gamma - \Delta_{min}$)
		GGA-EV	**1.86**	Indirect ($\Gamma - \Delta_{min}$)
Experiment	–	–	2.10 [1]	Indirect ($\Gamma - \Delta_{min}$)
–	–	–	2.00 [8]	Indirect ($\Gamma - \Delta_{min}$)
Other Calculations	LMTO	LDA	1.10 [5]	Indirect ($\Gamma - \Delta_{min}$)
	PP-PW	LDA	1.53 [5]	Indirect ($\Gamma - \Delta_{min}$)
	PP-PW	LDA	1.12 [9]	Indirect ($\Gamma - \Delta_{min}$)
	FP-LAPW	GGA	1.25 [10]	Indirect ($\Gamma - \Delta_{min}$)
	FP-LAPW	LDA	1.15 [13]	Indirect ($\Gamma - \Delta_{min}$)
	FP-LAPW	GGA	1.24 [13]	Indirect ($\Gamma - \Delta_{min}$)
	PP-PW	GGA	1.28 [16]	Indirect ($\Gamma - \Delta_{min}$)
AlP				
Present work	FP-LAPW	LDA	**1.44**	Indirect ($\Gamma - X$)
		GGA	**1.57**	Indirect ($\Gamma - X$)
		GGA-EV	**2.50**	Indirect ($\Gamma - X$)
Experiment	–	–	2.500 [1]	Indirect ($\Gamma - X$)
GaP				
Present work	FP-LAPW	LDA	**1.44**	Indirect ($\Gamma - \Delta_{min}$)
		GGA	**1.59**	Indirect ($\Gamma - \Delta_{min}$)
		GGA-EV	**2.32**	Indirect ($\Gamma - \Delta_{min}$)
Experiment		–	2.350 [1]	Indirect ($\Gamma - \Delta_{min}$)
Other calculations	LMTO	LDA	1.360 [4]	Indirect ($\Gamma - \Delta_{min}$)
	PP-PW	LDA	2.438 [11]	Indirect ($\Gamma - \Delta_{min}$)
InP				
Present work	FP-LAPW	LDA	**0.62**	Direct ($\Gamma - \Gamma$)
		GGA	**0.85**	Direct ($\Gamma - \Gamma$)
		GGA-EV	**1.50**	Direct ($\Gamma - \Gamma$)
Experiment	–	–	1.424 [1]	Direct ($\Gamma - \Gamma$)
–	–	–	1.350 [14]	Direct ($\Gamma - \Gamma$)
Other calculations	PP-PW	LDA	1.232 [11]	Direct ($\Gamma - \Gamma$)

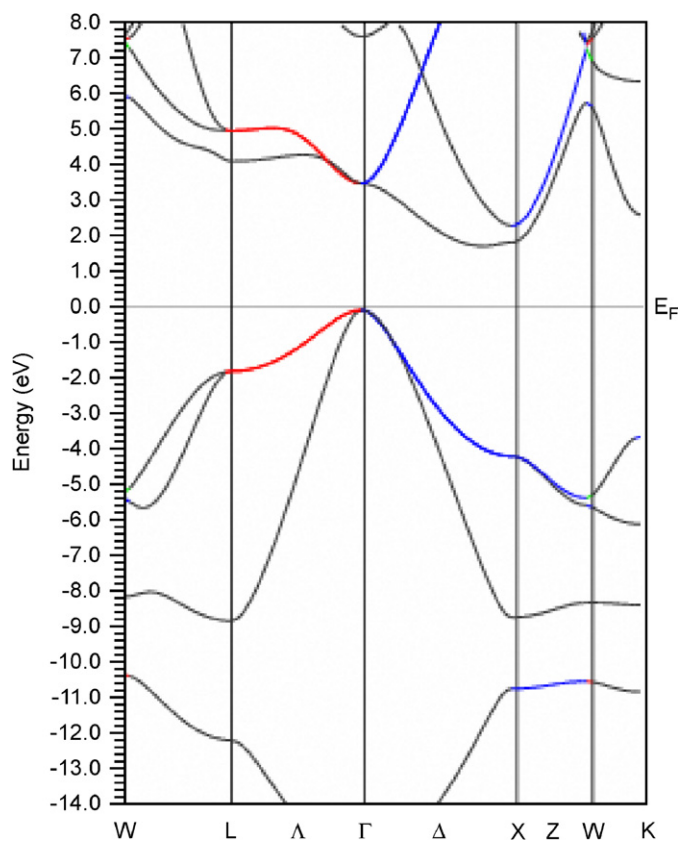Values in bold faces are our results.

Fig. 2. Band structure of zb-BP with GGA-EV.
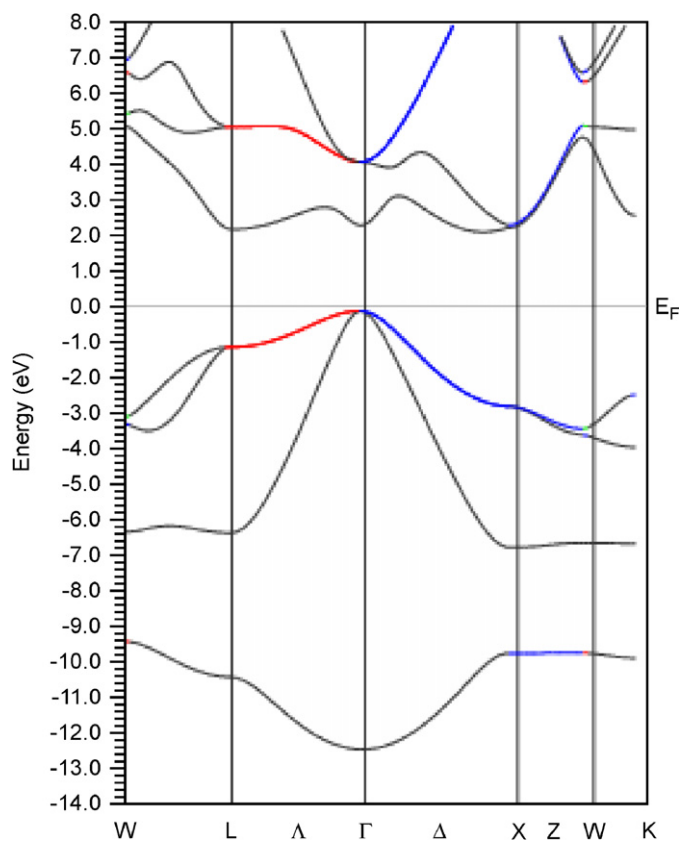

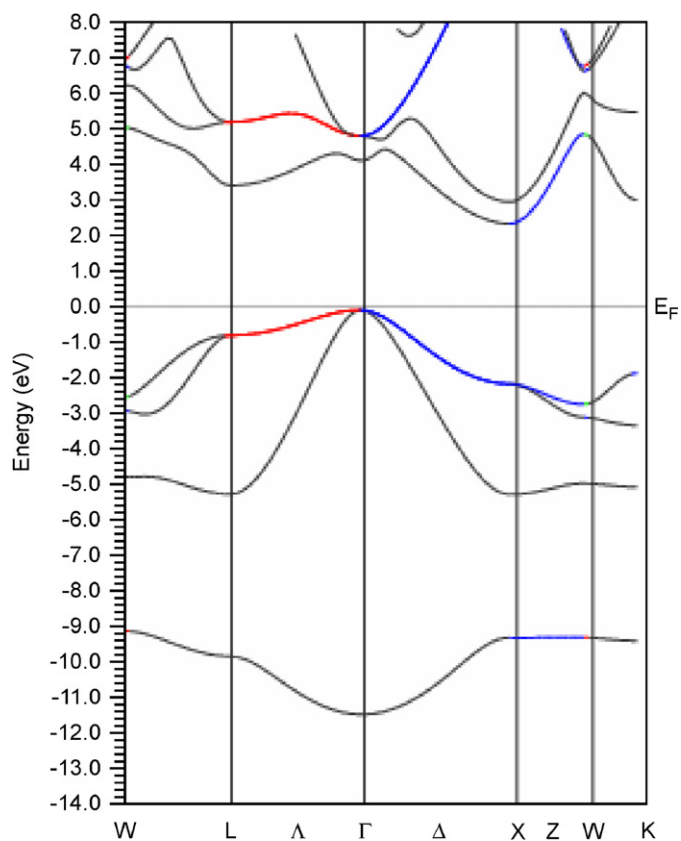Fig. 4. Band structure of zb-GaP with GGA-EV.

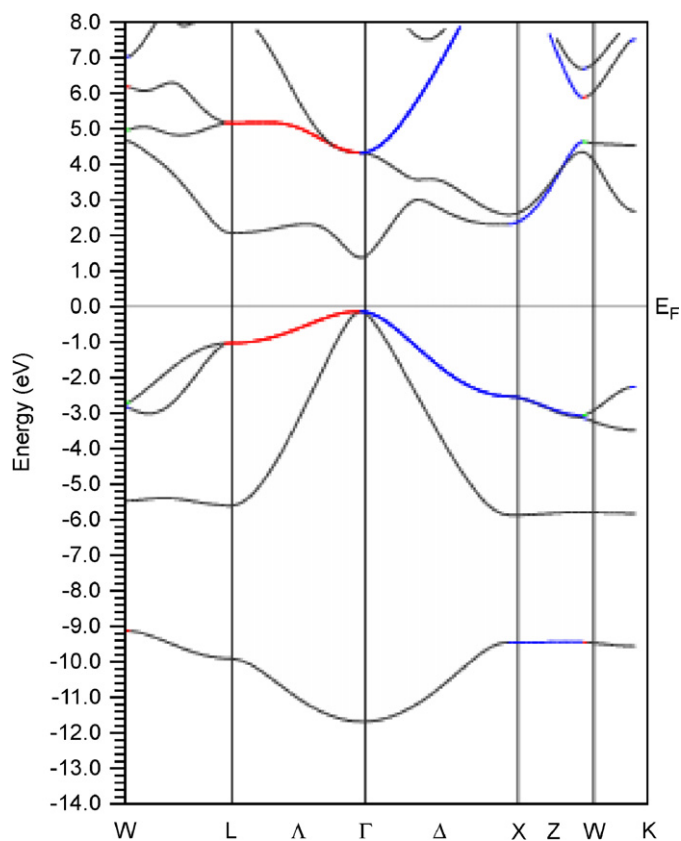Fig. 3. Band structure of zb-AlP with GGA-EV.

Fig. 5. Band structure of zb-InP with GGA-EV.

2. To our knowledge, there is no study available with DFT for cohesive energy for III-phosphides. Our results are a first attempt in this direction. There is also no study with GGA for lattice parameters and bulk moduli except for BP.

3. No electronic band structure calculations have been reported with GGA-EV within DFT. We have undertaken an in-depth study in this direction.

4. No theoretical work is reported for the electronic band gap of AlP, GaP and InP in literature with WIEN2k using GGA as an exchange correlation potential. Our work also encompasses this important aspect.

5. Calculations based on LDA and GGA for all phosphides give lower values for the band gap compared to GGA-EV. It is well known that LDA and GGA underestimate the energy band gap for semiconductors. This is because in LDA uniform electron gas approximation is applied and GGA, having a simple form, is not sufficiently flexible to reproduce accurate results for exchange-correlation energy and its charge derivative simultaneously. GGA-EV has been developed in such a way that it optimizes the exchange correlation potential at the cost of less accuracy in exchange-correlation energy. In this way it yields better band splitting and properties, which are mostly dependent on exchange correlation potential. We observe that GGA-EV results for electronic properties are in excellent agreement with the experiment.

6. No theoretical calculation is found for AlP in literature. Our results therefore provide an estimate of this important compound.

Acknowledgments

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