

# Electronic and Structural Properties of $\text{Li}_3\text{AlP}_2$ and $\text{Li}_3\text{AlAs}_2$ from First Principles

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## Abstract

A detailed analysis of the electronic and structural properties of the filled tetrahedral semiconductors  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  has been performed, using the full potential linearized augmented plane wave method within the density functional theory. Experimental results about the structural properties, involves the positions of the elements Al and P(As). Since there were not any other efforts about the positions of the Li elements in these compounds, so to our knowledge there was no theoretical study about them till now. In the first step the interactional forces between atoms were minimized. The calculated internal coordinations of atoms agree well with the experimental results. Using these positions we obtained the equilibrium lattice constants, bulk modulus and their pressure derivative. In the second step the electronic properties of  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  have been studied. The study of total and partial electronic DOS indicate the main contribution of DOS consists of P(As)  $3p(4p)$  and P(As)  $3s(4s)$  states. Our band structure calculation verifies that  $\text{Li}_3\text{AlP}_2$  is an indirect gap semiconductor with a value of about 2.36 eV between valance band maximum occurring at H point and conduction band minimum occurring at  $\Gamma$  point; though the difference between the direct (2.38 eV) and indirect (2.36 eV) is very small. We also found that  $\text{Li}_3\text{AlAs}_2$  is a direct band gap (1.49 eV) in the center of BZ.

**Keywords:** Filled Tetrahedral Semiconductors, Electronic Properties, FP-LAPW, DFT

## 1. Introduction

$\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  are filled tetrahedral Nowotny-Juza compounds [1,2] with an orthorhombic structure and belong to the space group  $Ibca(73)$  [3] in contrast to cubic nitride semiconductors such as  $\text{Li}_3\text{AlN}_2$  and  $\text{Li}_3\text{GaN}_2$  [1,3]. Crystal structure of  $\text{Li}_3\text{AlP}_2$  depicted by Juza *et al.* [3] and has been grown by direct reaction of Li, Al, and P in an evacuated quartz ampoule [4]. A filled tetrahedral compound (such as  $\text{Li}_3\text{AlP}_2$ ) can be viewed as zincblend-like  $(\text{Li}_{0.5}\text{Al}_{0.5}\text{P})^-$  lattice filled with He-like  $\text{Li}^+$  ions at the empty tetrahedral sites. The available experimental studies on  $\text{Li}_3\text{AlP}_2$  are limited to growth and optical band gap [4]. Kuriyama *et al.* have grown  $\text{Li}_3\text{AlP}_2$  by direct reaction between Li, Al and P using photoacoustic spectroscopy method and obtained a band gap of 2.75 eV. (Unfortunately we do not have any experimental or theoretical information about  $\text{Li}_3\text{AlAs}_2$ ). From theoretical point of view, to our knowledge, there is no theoretical research on electronic and structural properties. More-

over, it seems that there is a lack of both experimental and theoretical data on electronic and structural properties of  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$ . In this work, we present the results of a systematic study of the electronic and structural properties of  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  obtained by full potential linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA) for the exchange correlation potential, within the density functional theory. This work is along the latest study that is performed on  $\text{Li}_3\text{AlN}_2$  and  $\text{Li}_3\text{GaN}_2$  about the electronic and optical properties of these compounds [5]. Our calculated results could serve as a reference for future theoretical and experimental works on these compound. The rest of this paper organized as follows. A brief description of our calculation method is given in Section 2. Section 3 contains the results and the conclusions are given in Section 4.

## 2. Calculation Method

The calculations presented in this work were performed

using the full potential linearized augmented plan wave (FP-LAPW) method. In this method no shape approximation on the potential or on the electronic charge density is made. The calculations of the electronic and structural properties have been done relativistically. We use the WIEN2K [6] implementation of the method which allows the inclusion of local orbitals in the basis, improving upon linearization and making possible a consistent treatment of the semicore and valence states in an energy window, hence ensuring proper orthogonality. The exchange correlation potential within the generalized gradient approximation (GGA) is calculated using the scheme of Perdew *et al.* [7]. The convergence parameter  $R_{MT}^{\min} k_{\max}$ , (the product of the smallest of the atomic sphere radii  $R_{MT}$  and the plane wave cutoff parameter  $k_{\max}$ ) which controls the size of the basis sets in these calculations, was set to 8. The maximum  $l$  quantum number for the wave function expansion inside the atomic sphere is confined to  $l_{\max} = 10$ . The  $G_{\max}$  parameter was taken to be  $12.0 \text{ Bohr}^{-1}$ . Brillouin-zone (BZ) integrations within the self-consistency cycles were performed via a tetrahedron method [8], using 170 K points in the irreducible BZ. For the calculation of the density of states (DOS) however, a denser sampling of the BZ was needed, where we used 427 K points. The muffin-tin radii of Lithium (Li), Aluminium (Al) Phosphor (P) and Arsenide (As) were chosen as  $(R_{MT}^{Li}, R_{MT}^{Al}, R_{MT}^{P(As)}) = (2.32, 2.16, 2.16) \text{ a.u.}$  for  $\text{Li}_3\text{AlP}_2$  and  $(2.41, 2.26, 2.26)$  for  $\text{Li}_3\text{AlAs}_2$ . All these values have been chosen in a way to ensure the convergence of the results.

### 3. Results and Discussions

In this section, we express the structural and electronic properties of  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$ . The results of studying electronic and structural properties are in Sections 3.1 and 3.2 respectively.

#### 3.1. Total Energy Calculations

The orthorhombic phase of  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  has 96 atoms, 48 Li, 16 Al and 32 P (As), per primitive cell. A Point worth to mention is that the similar phosphors (Arsenides) in the cell are not equivalent. The Wyckoff position [3] of Li, Al, and P<sub>1</sub> (As<sub>1</sub>), P<sub>2</sub> (As<sub>2</sub>), P<sub>3</sub> (As<sub>3</sub>) and P<sub>4</sub> (As<sub>4</sub>) atoms are as follows:

$$\begin{aligned} \text{Li: } & 16f(x_1, y_1, z_1) & \text{Al: } & 16f(x_2, y_2, z_2) \\ \text{P}_1 \text{ (As): } & 8a(0, 0, 0) & \text{P}_2 \text{ (As): } & 8c(u, 0, 0.25) \\ \text{P}_3 \text{ (As): } & 8d(0.25, v, 0) & \text{P}_4 \text{ (As): } & 8e(0, 0.25, w) \end{aligned}$$

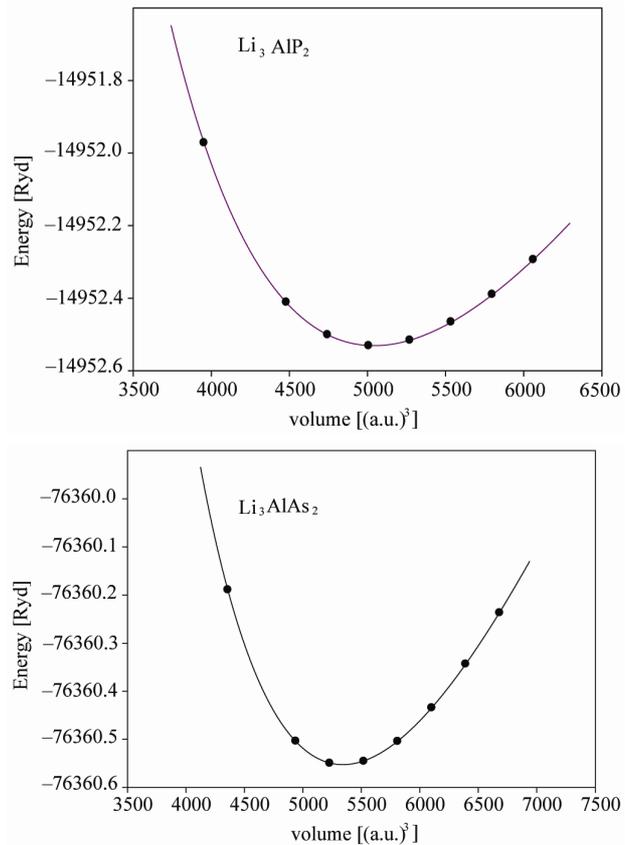
The structure of  $\text{Li}_3\text{AlP}_2$  ( $\text{Li}_3\text{AlAs}_2$ ) is characterized by three Lattice parameters  $a$ ,  $b$  and  $c$ , and the internal parameters of atoms.

In our Literature survey, we did not find any theoretical works on calculating the lattice parameters and internal parameters for these compounds and nor any theoretical work on electronic and structural properties of them. Therefore to our knowledge, this part of the work can be considered as the first ab initio calculation for these compounds.

Experimental information about these compounds involves the positions of Al and P(As) and there is no information about the position of Li. In this work we first optimized the internal parameters by relaxing the atomic positions inside a unit cell using experimental lattice parameters [3]; the force on each atom after relaxation decreased to less than  $0.5 \text{ mryd/a.u.}$  We then used the optimized internal parameters to calculate the total energy of primitive unit cell as a function of their volume and fitted the results with Murnaghan equation of state [9] (**Figure 1**).

Our optimized internal parameters and lattice parameters are compared with experimental results in **Tables 1** and **2**.

It is evident from this data that our results agree rather well with experimental work. By calculating the total energy at different volumes and fitting the results with



**Figure 1.** Total energy versus primitive unit cell volume of  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$ .

**Table 1. Lattice parameters, atomic position, bulk modulus (B) and its pressure derivative (B) of  $\text{Li}_3\text{AlP}_2$ . Experimental results are included for comparison.**

Properties	Present	Experimental
a (Å), b (Å), c (Å)	11.29, 11.43, 11.55	11.47 <sup>a</sup> , 11.61 <sup>a</sup> , 11.73 <sup>a</sup> 11.43 <sup>b</sup> , 11.93 <sup>b</sup> , 12.03 <sup>b</sup>
B (GPa)	46.35	-
B	4.161	-
Li ( $x_1, y_1, z_1$ )	(0.162, 0.37, 0.10)	-
Al ( $x_2, y_2, z_2$ )	(0.121, 0.10, 0.129)	(0.121, 0.121, 0.121)
P <sub>2</sub> (u, 0, 0.25)	(0.24, 0, 0.25)	(0.233, 0, 0.25)
P <sub>3</sub> (0.25, v, 0)	(0.25, 0.19, 0)	(0.25, 0.233, 0)
P <sub>4</sub> (0, 0.25, w)	(0, 0.25, 0.20)	(0, 0.25, 0.233)

<sup>a</sup>Ref [3]; <sup>b</sup>Ref [4].**Table 2. Lattice parameters, atomic position, bulk modulus (B) and its pressure derivative (B) of  $\text{Li}_3\text{AlAs}_2$ . Experimental results are included for comparison.**

Properties	Present	Experimental
a (Å), b (Å), c (Å)	11.54, 11.65, 11.78	11.87 <sup>a</sup> , 11.98 <sup>a</sup> , 12.11 <sup>a</sup>
B (GPa)	41.13	-
B	4.26	-
Li ( $x_1, y_1, z_1$ )	(0.153, 0.367, 0.103)	-
Al ( $x_2, y_2, z_2$ )	(0.113, 0.107, 0.14)	(0.121, 0.121, 0.121)
P <sub>2</sub> (u, 0, 0.25)	(0.251, 0, 0.25)	(0.233, 0, 0.25)
P <sub>3</sub> (0.25, v, 0)	(0.25, 0.185, 0)	(0.25, 0.233, 0)
P <sub>4</sub> (0, 0.25, w)	(0, 0.25, 0.243)	(0, 0.25, 0.233)

<sup>a</sup>Ref [3].

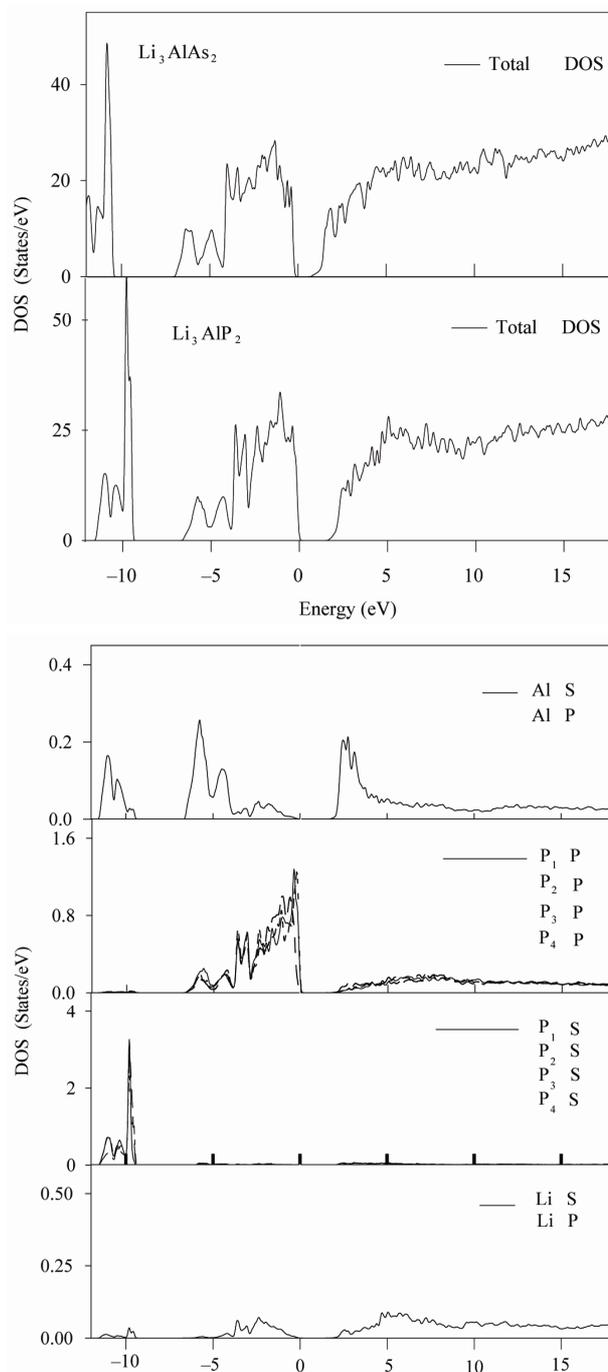
Murnaghan equation of state. We obtained the equilibrium lattice constants, bulk modulus and their pressure derivative. We show the energy—volume curve for  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  structure in **Figure 1** and compare the results with available experimental results in **Tables 1** and **2**.

### 3.2. Electronic Structure

Our calculated density of states (DOS) and electronic band structure for  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  are given in **Figures 2** and **3**. Due to the close similarity between the results obtained for these compounds, the Partial Dos are given only for  $\text{Li}_3\text{AlP}_2$ . Major contribution to occupied part of the DOS come from the P (As) 3s (4s) and 3p (4p) states along with Al 3s and 3p states.

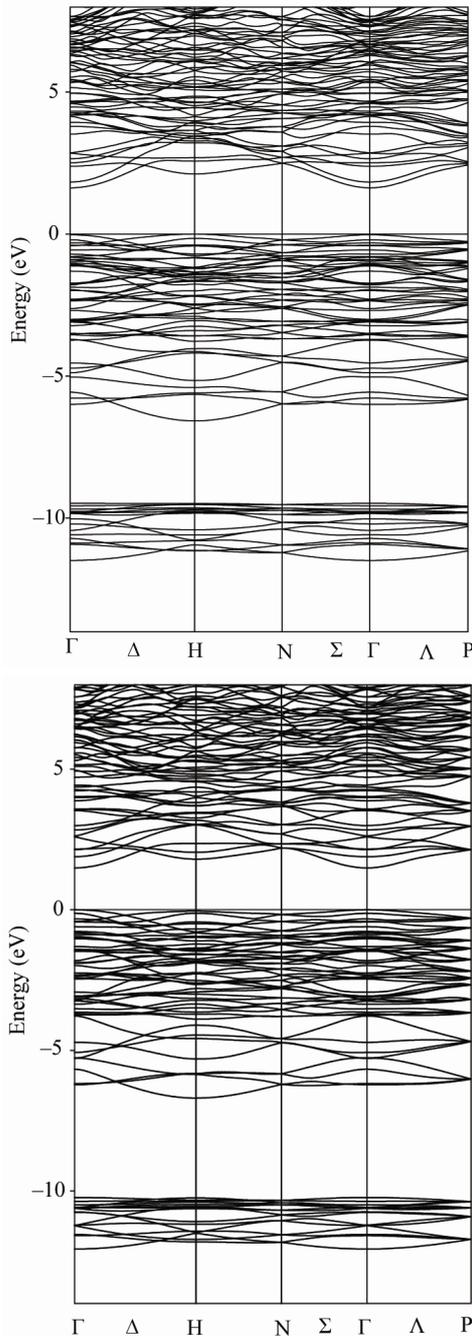
The first structure in the low lying energy side of the DOS consists of a peak centered on -10 (-11) eV for  $\text{Li}_3\text{AlP}_2$  ( $\text{Li}_3\text{AlAs}_2$ ) and originates from P (As) s states and Al s and p states, corresponding to the lowest lying bands in **Figure 3**.

The next structure which is separated from the first by a gap of 2.53 eV (3.28) for  $\text{Li}_3\text{AlP}_2$  ( $\text{Li}_3\text{AlAs}_2$ ) is a broad

**Figure 2. Total DOS for two compounds (left) and partial density of states for  $\text{Li}_3\text{AlP}_2$  (right).**

peak that is situated between -6.7 (-7.0) eV and the Fermi level, corresponding, to the valence bands shown in the band structure in **Figure 3**. From the partial DOS, it is seen that just below the Fermi level, the bands are dominated by the P (As) p states and Al p states.

There is a main feature in the broad structure above the Fermi level up to 20 eV, containing a broad peak



**Figure 3.** Energy band structure of  $\text{Li}_3\text{AlP}_2$  (left) and  $\text{Li}_3\text{AlAs}_2$  (right).

from  $p$  and  $s$  states of Aluminium (below 5 eV) and  $p$  and  $s$  states of Lithium (above 5 eV).

In  $\text{Li}_3\text{AlP}_2$  we found an indirect band gap between the top of phosphor valence P bands maximum occurring at the H point and the bottom of the Al  $s$  bands occurring at the  $\Gamma$  point. The difference between the calculated indirect band gap and the direct band gap at the center of BZ is too small. The indirect band gap value is 2.36 eV

while the direct is 2.38 eV. The calculated values of the band gap for  $\text{Li}_3\text{AlP}_2$  confirms the well known expectation that the theoretical band gaps are on the whole underestimated within GGA, in comparison with experimental value (2.75 eV) [4]. In  $\text{Li}_3\text{AlAs}_2$  we found a direct band gap (1.49 eV) at the BZ center. Unfortunately we do not have any experimental information for comparison.

#### 4. Conclusions

We have applied FP-LAPW method to study the electronic and structural properties of the filled tetrahedral semiconductors  $\text{Li}_3\text{AlP}_2$  and  $\text{Li}_3\text{AlAs}_2$  within density functional theory. During this study the positions of Li, Al, and P (As) have been obtained for the first time. Using these positions the structural parameters such as equilibrium lattice constants, bulk modulus and their pressure derivative have been calculated. The electronic properties such as total and partial electronic DOS and band structure have been calculated. The study of density of states indicated the main contribution of DOS consists of P (As)  $3p$  ( $4p$ ) and P (As)  $3s$  ( $4s$ ) states. The nature of the fundamental gap in  $\text{Li}_3\text{AlAs}_2$  was found to be direct. According to our results,  $\text{Li}_3\text{AlP}_2$  could be considered a material with a direct gap, because the difference between the direct (2.38 eV) and indirect (2.36 eV between H and  $\Gamma$  points) gap is very small. The calculated value of the band gap is in good agreement with experimental value (2.75 eV). Unfortunately in  $\text{Li}_3\text{AlAs}_2$  we do not have any experimental result for comparison.

#### 5. References

- [1] R. Juza and F. Hund, "Die Ternären Nitride  $\text{Li}_3\text{AlN}_2$  und  $\text{Li}_3\text{GaN}_2$ ," *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 257, 1948, pp. 13-25.
- [2] R. Juza, K. Langer and K. V. Benda, "Ternary Nitrides, Phosphides and Arsenides of Lithium," *Angewandte Chemie International Edition*, Vol. 7, No. 5, 1968, pp. 360-370. [doi:10.1002/anie.196803601](https://doi.org/10.1002/anie.196803601)
- [3] R. Juza and W. Schulz, "Herstellung und Eigenschaften der Verbindungen  $\text{Li}_3\text{AlP}_2$  und  $\text{Li}_3\text{AlAs}_2$ ," *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 269, 1952, pp. 1-12.
- [4] K. Kuriyama, J. Anzawa and K. Kushida, "Growth and Band Gap of the Filled Tetrahedral Semiconductor of  $\text{Li}_3\text{AlP}_2$ ," *Crystal Growth*, Vol. 310, 2008, pp. 2298-2300.
- [5] M. Dadsetani, S. Namjoo and H. Nejati, "Optical Study of Filled Tetrahedral Compounds  $\text{Li}_3\text{AlN}_2$  and  $\text{Li}_3\text{GaN}_2$ ," *Electronic Materials*, Vol. 39, No. 8, 2010, pp. 1186-1193.
- [6] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kavanicka

- and J. Luitz, "Wien2k: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties," Vienna University of Technology, Vienna, 2001.
- [7] P. Perdew, K. Burke and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Physical Review Letters*, Vol. 77, 1996, pp. 3865-3868.  
[doi:10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865)
- [8] O. Jepsen and O. K. Andersen, "Improved Tetrahedron Method for Brillouin-Zone Integrations," *Physical Review B*, Vol. 49, 1994, pp. 16223-16233.
- [9] F. Birch, "Finite Elastic Strain of Cubic Crystals," *Physical Review B*, Vol. 71, 1947, pp. 809-824.  
[doi:10.1103/PhysRev.71.809](https://doi.org/10.1103/PhysRev.71.809)