

Band gap correction in Nowontny-Juza ordered and disordered LiMgP semiconductor via TB-mBJ approach

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ABSTRACT

First principles density functional theory (DFT) based full potential calculations has been used to investigate the electronic properties of $\text{LiMgP}_{1-x}\text{As}_x$ ($x = 0, 0.25$). The exchange and correlation (XC) effects were taken into account by a semi local, orbital independent modified Becke-Johnson (TB-mBJ) exchange potential as coupled with Local Density Approximation (LDA) correlation to correct the band gap anomaly. The band gaps of LiMgP semiconductor with TB-mBJ approach were found to be in good agreement with corresponding experimental results. Further, the decrease in band gap has been observed in LiMgP via introducing sp-element (As) disorder.

Key words: LiMgP semiconductor, TB-mBJ approach.

1. Introduction

Filled tetrahedral semiconductors with chemical composition XYZ where X, Y are main group/transition metal cations and Z is main group anion are famous as Nowontny-Zuha compounds after the names of Nowontny [1] and Zuha [2] who synthesized and characterized them firstly. They are promising materials for optoelectronic applications and closely related to more familiar III-V compounds such as AlN. Due to the existence of wide band gaps, these compounds are also the potential candidates mainly in thin film solar cells as buffer layer materials [3-7].

Beleanu et al. [8] synthesized the ternary LiMgX ($X = \text{P, As and Sb}$) by solid state reaction method and established the semiconducting behavior for these. They reported the variation of band gap and response of the dielectric function in synthesized LiMgX ($X = \text{P and As}$) compounds. There exist many band structure calculations for LiMgP and LiMgAs but not much regarding the effect of sp-element disorder on electronic band gap and semiconducting nature of LiMgP. Moreover, no experimental data is available for disordered structure of LiMgP. With this motivation, we have planned to simulate sp-element; As disorder in LiMgP and to report the analyze electronic properties of $\text{LiMgP}_{1-x}\text{As}_x$ ($x = 0, 0.25$), as calculated by first principles approach.

2. Theoretical Details

Filled tetrahedral LiMgP semiconductor crystallizes in $C1_b$ structures and belongs to space group $F\bar{4}3m$ (No. 216). The present first-principles calculations were performed using the full potential augmented plane wave plus local

orbitals (FP-LAPW) method as implemented in the WIEN2k software and based on the density functional theory (DFT) [9]. The exchange correlation potential was first tested by the generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof parametrization [10]. Further, we also used the Tran-Blaha approach, a modified version of Becke-Johnson exchange potential [11] as coupled with local density approximation (LDA) correlation; the so-called TB-mBJ formalism, for the calculation of electronic and optical properties. The TB-mBJ functionals [11] was mainly called to cross check the accuracy of GGA predictions and to improve the band gap of LiMgP semiconductor. The values of other parameters were selected as $G_{\text{max}} = 12$ and the muffin-tin sphere radii R_{MT} for Li, Mg and P/As as 1.6, 2.1 and 2.0 a.u., respectively. The convergence of the basis set for all computations is controlled by a cutoff parameter $R_{\text{MT}}k_{\text{max}} = 7$ (R_{MT} is the smallest muffin-tin radius of a particular atom and k_{max} is the cutoff for the plane wave). We have used an appropriate set of k-points, $10 \times 10 \times 10$ Monkhorst-Pack sampling, to compute the total energy within the desired convergence limit.

3. Results and Discussion

Filled tetrahedral LiMgP semiconductor compounds in the pure form crystallizes in $C1_b$ structure which is a similar structure to famous semi Heusler alloys [12]. In order to simulate the sp-element; As disorder in LiMgP (i.e. $\text{LiMgP}_{0.75}\text{As}_{0.25}$ compound), one out of four P atoms in $1 \times 1 \times 1$ supercell of LiMgP was replaced

by As atom. The unit cell of LiMgP is presented in Fig.1, which contains three atoms as basis with Li atom at (0,0,0), Mg at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), P at ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) and a void at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) in Wyckoff coordinates.

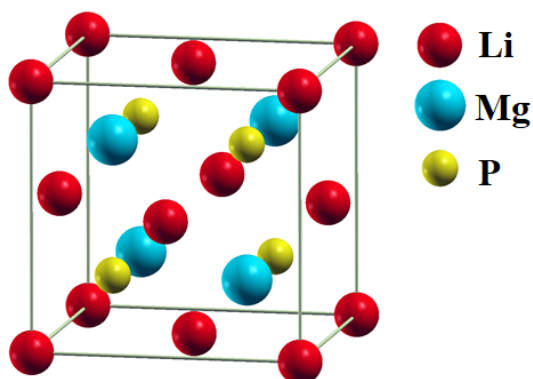


Fig. 1: Unit cell of pristine LiMgP compound.

In Fig. 2, the comparison of the total density of states (DOS) within GGA and TB-mBJ formalism is portrayed. The valence band

(VB) is found to be filled upto Fermi level (E_F) for both pure and disordered LiMgP semiconducting compounds. It is observed that the GGA underestimates the band gap for LiMgP (Table-I) whereas TB-mBJ functional produces better band splitting. Thus, the conduction band (CB) in both compounds shift upwards in energy as compared to that in GGA and that the difference between VB maximum and CB minimum increases. In this way, the band gaps come closer to corresponding experimental values [12-13] with TB-mBJ (Table-I). Comparing TB-mBJ based DOS of LiMgP and LiMgP_{0.75}As_{0.25}, we found that the total DOS for LiMgP_{0.75}As_{0.25} shifts slightly lower in energy as compared to that of LiMgP throughout entire conduction band (CB) which leads to slight decrease in the value of band gap. This decrease may be attributed to the increase in atomic radius of As in comparison with P. However, there is a qualitative similarity of total DOS of both compounds which clearly establishes the identical optical response.

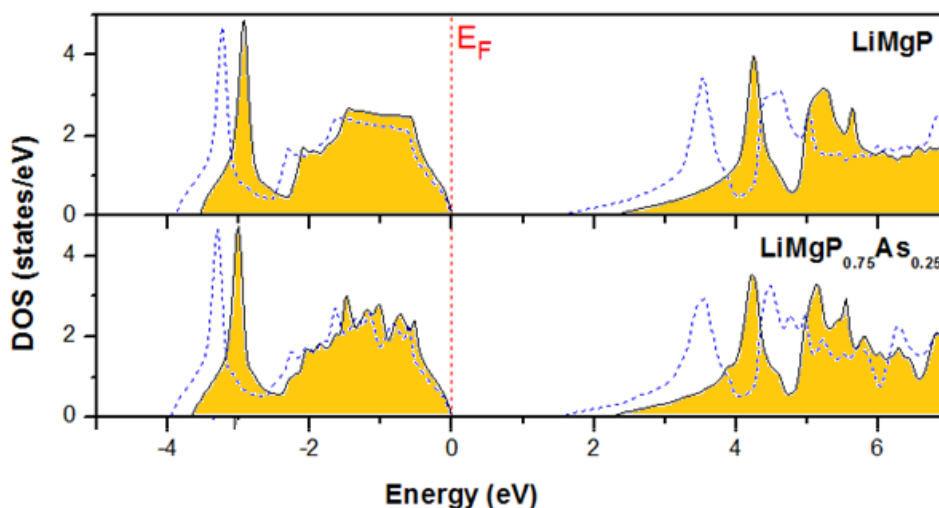


Fig. 2: Calculated total DOS of LiMgP_{1-x}As_x (x = 0, 0.25), Blue dotted and black solid lines represent DOS using GGA within TB-mBJ formalism.

Table: Theoretical and experimental band gap (E_g) of LiMgP_{1-x}As_x (x = 0, 0.25).

Compound	This work		Expt.
	GGA	TB-mBJ	
LiMgP	1.52	2.30	2.43 ^a
LiMgP _{0.75} As _{0.25}	1.48	2.19	2.29 ^b

^aRef. 13, ^bRef. 14 (For LiMgAs)

In order to understand the bonding mechanism, the valence electronic charge density map has been constructed in Fig. 3 along the (110) plane. A detailed description of charge densities within the FPLAPW method was presented by Blaha and Schwarz [15]. In LiMgP, the Mg layer is sandwiched between Li and P layers. Further, the charge transfer from P to Mg is clearly visible. The covalent binding is predicted

among Li and P atoms whereas in between Mg and P, polar covalent character can be traced. Due to the involvement of P in bond formation with both Li and Mg atoms, the consideration of Se-disorder at P sites become important.

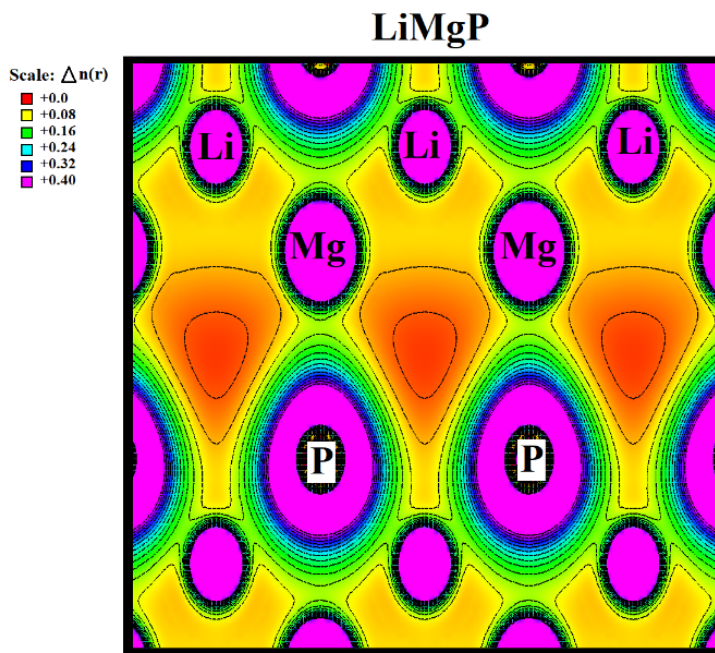


Fig. 3:The valence electronic density plot for LiMgP in units of $e/\text{\AA}^3$ along (110) plane within TB-mBJ formalism

4. CONCLUSIONS

In short, we have presented a DFT based full potential investigation of electronic properties of $\text{LiMgAs}_x\text{P}_{1-x}$ ($x = 0, 0.25$) compounds. We have observed that TB-mBJ is flexible to reproduce accurately both the XC energy and its charge derivative. Thus the band gaps with TB-MBJ come out to be very close to experimental values. A slight decrease in the band gap has been observed in LiMgP via introducing sp-element (As) disorder. The calculated band gaps were found to be in good agreement with corresponding experimental data. The valence electronic charge density maps have been reported along the (110) plane to explain the bonding mechanism.

5. References

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