

FIRST- PRINCIPLE CALCULATIONS OF ELECTRONIC PROPERTIES OF BORON COMPOUNDS BAs, BP AND BSb.

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ABSTRACT

We present first- principle calculations of electronic properties of the boron compounds BAs, BP and BSb, using the full potential linearized augmented plane wave method(FPLAPW) for both rock salt and zinc-blende structures. The calculations are performed using the local density approximation and the generalized gradient approximation for the exchange-correlation potential. At the equilibrium volume, for the zinc-blende structure, the band gaps for all materials are indirect from Γ to X. In the rock salt structure, the compounds have a metallic character. We also give the density of states and the charge density. We show from the latter quantity the inverse role between cation and anion for BP, BAs and BSb. Our results are discussed and compared with experimental and other recent theoretical studies with good agreement.

Key Words : first- principle calculations – FPLAPW – LDA - GGA

RESUME

Nous avons effectué des calculs de premier principe sur les propriétés électroniques des composés du bore BP, BAs et BSb en utilisant la méthode linéaire des ondes planes augmentées et linéarisées FP-LAPW..

Dans cette approche, l'approximation de la densité locale (LDA) et l'approximation du gradient généralisé(GGA) ont été utilisées pour la détermination du potentiel d'échange et de corrélation. Les trois composés ont été étudiés dans deux structures différentes : zinc-blende et NaCl. Au volume d'équilibre, le calcul de la structure de bandes dans la structure zinc-blende a montré l'existence d'un gap indirect dans la direction $\Gamma \rightarrow X$ pour les trois matériaux.

Dans la structure NaCl, ces composés ont un caractère métallique. Nous avons également calculé la densité d'états et de charge respectivement. De cette dernière quantité, nous avons montré le rôle inverse entre l'anion et le cation. Nos résultats ont été discutés et comparés à ceux de l'expérience et autres études théoriques récentes avec une bonne concordance

Mots clés : calculs du premier principe - - FPLAPW – LDA - GGA

INTRODUCTION

Boron compounds have attracted increasing research interest over the past few years, as wide gap semi conductors. These materials are of great technological interest for high temperature, electronic and optical applications[1,2,3,4].

The electronic valence configuration is $1s^2 2s^2 2p^1$ for boron atoms and $ns^2 np^3$ for group V elements. The boron compounds are strongly covalent since the electro negativity of the P(1.64), As(1.57) and Sb(1.3) anions is slightly smaller than that of the B(2.0) cation. In these materials, B is the most electronegative element and will thus attract electrons towards it. These materials possess a peculiar behaviour where compared to other III-V

compounds ; among this, is the inverse role between the cation and anion in terms of charge transfer, witch is confirmed by Wentzcovich et al [1]. Their unusual behaviour appears to originate from the small core size and the absence of p electrons in B. The reason for these fundamental differences between these compounds and other III-V materials is apparent from band structures and charge density calculations.

Only few theoretical and little experimental work have been devoted to the study of structural and electronic properties of these series of boron compounds. The structural properties of BP have been determined by Lambrecht et al [3] using linear muffin_tin orbitals (LMTO) method within local density approximation (LDA). Using the plane-

wave basis sets and pseudopotential approximation (PWPP) within LDA, the ground state and the high-pressure properties have been calculated by Wentzcovich et al [1] for BP and BAs, and by Ferhat et al [5] and Zaoui et al [6]. A comparative study of the structural and electronic properties of the series BP, BAs and BSb has been presented by Bouhafs et al [2,7] using the same approach.

In the following, using the full-potential linearized augmented plane wave (FP-LAPW) method, we present the electronic properties of the boron compounds BAs, BP and BSb. We have compared the results with available theoretical and experimental works. The concluding remarks are presented at the end of paper.

CALCULATION

In this work the calculations were carried out by the code Wien 97 [8] which is the implementation of the FP-LAPW method. For the determination of the exchange-correlation potential, we take the Perdew–Wang local density approximation (LDA) [9], and the Perdew–Burke–Erzerhof generalized gradient approximation (GGA) [10]. Both zinc-blende and rocksalt structures are studied. The LAPW method expands the Kohn-Sham orbitals in atomic like orbitals inside the atomic muffin-tin (MT) spheres and plane waves in the interstitial region. Relativistic effects are taken into account within the scalar-relativistic approximation, but the spin-orbit coupling is neglected because it was checked to have little effect on our main conclusions. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut off $l_{\max} = 10$, and in Fourier series in the interstitial region. We use a parameter $R_{\text{MT}} K_{\max} = 8$ which determine matrix size, where R_{MT} denotes the smallest atomic sphere radius and K_{\max} gives the magnitude of the largest K vector in the plane wave expansion. All the calculations were carried out at the theoretical equilibrium lattice constants. We chose the muffin-tin radii of B, As, P and Sb to be 1.5, 2.0, 2.0 and 2.0 a.u. respectively.

RESULTS

Electronic band structure and density of states

The band structures for zinc-blende and rocksalt structures were calculated along the high symmetry directions in the Brillouin zone (figures 1 and 2). For the zinc-blende structure, our calculations shows an indirect gap near X ($X_{15v} \rightarrow \Delta_{\min}$) for all compounds. Besides, we notice the metallic character of the band structure of these compounds in the rock salt structure (Figure 2). Using the equilibrium lattice parameters, we have obtained energy gaps of 1.24 eV for BP, 1.21 eV for BAs

and 0.71 eV for BSb. This underestimation of energy gaps is caused, however by the generalized gradient approximation and local density approximation. This is mainly due to the fact that LDA and GGA have simple forms that are not sufficiently flexible to accurately reproduce both exchange-correlation energy and its charge derivative. Table 1 gives a summary for the most important calculated band-gaps in the zinc-blende structure of our compounds and compared with the experimental and theoretical ones. The values found by using approximations GGA and LDA are only slightly different. All in all, GGA did not make an appreciable improvement of the results. Our values are in good agreement with the theoretical ones. As a result, the calculated energy gap E_g for BP is underestimated by about 50% for both LDA and GGA compared to experiment. In rocksalt structure, these materials were not the subject of former work, from where the absence of comparison. The density of states of zinc-blende BP is shown in figure 3. One notices, in correlation to the curve of electronic band structure, that the lower part of the valence band is dominated by P s states and the upper part by B and P p states, the B s states contributing to both parts of the valence band. The same behaviour is observed for BAs and BSb which is in agreement with that of Wentzcovich [1].

The electronic charge density

The electronic charge density of our compounds differs from that of typical III-V semiconductors. The important characteristic of these materials is the shift of the density toward the B atom. The ionic character is reversed, B plays the role of anion. Usually, this rearrangement of charge in zinc-blende semiconductors is observed to proceed in the opposite way. Similar conclusions have been established from other ab-initio calculations [1,2,5]. This unusual behaviour of boron compounds can be attributed to the lack of cancellation of the p pseudopotential of B which results in the p pseudopotential being much deeper than that of As, P and Sb. The charge transfer indicates the degree of the ionicity of the bonding which is not enough large as it appears in figures 4 and 5; there remains a considerable degree of covalent character in the BX (X= P, As, Sb). The bond charge is large and located close to half way between the nearest atoms. It is noted that the chemical bonding is strongly covalent. Another aspect directly linked to the charge transfer is the ionicity factor. To give a quantitative measure of the ionicity for these compounds, we use the Pauling's definition [19] of a single bond and the Phillips electronegativity values for B, P, As and Sb [19]. We can obtain a rapid estimate of the ionicity factor

for these compounds by using the following equation:

$$f_i = 1 - \exp\left[-(\chi_A - \chi_B)^2 / 4\right] \quad (1)$$

The results obtained for the ionicity factor are summarised in table 2. Our results suggest the following ionicity order BP > BAs > BSb, f_i decreases as the anion gets heavier.

In rocksalt structure, as the figure 6 shows it, the charge is uniformly distributed; it is the characteristic of the metal bonding.

CONCLUSION

We have performed first principles FPLAPW calculations to study the electronic properties of boron compounds for both zinc-blende and rocksalt structures. Our results are in good agreement with the experimental data and with the other theoretical calculations. From the investigation of the electronic band structure, it is found that the compounds have an indirect gap in the zinc-blende structure and presented a metallic character in the rocksalt one. In zinc-blende structure, these materials are strongly covalent. The results are of capital importance for the study of the various properties of these materials.

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	$\Gamma_{1v} \rightarrow \Gamma_{15v}$		$\Gamma_{15v} \rightarrow \Gamma_{15c}$		$\Gamma_{15v} \rightarrow X_{1c}$		$\Gamma_{15v} \rightarrow \Delta_{min}$	
BA s	15.37 ^a	16.00 [11] [*]	3.26 ^a	4.00 [12]	1.42 ^a	1.33 [2]	1.12 ^a	0.67 [15] [*]
	15.22 ^b	16.63 [12]	3.25 ^b	4.20 [13]	1.46 ^b	1.86 [13]	1.21 ^b	1.60 [13]
		16.70 [13]		1.46 [14] [*]				1.25 [1]
		15.17 [1]		3.30 [1]				1.06 [2]
		15.71[2]						
BP	15.58 ^a	17.00 [16]	3.40 ^a	5.00 [14] [*]	1.52 ^a	1.5 [2,3]	1.15 ^a	2.40 [18] [*]
	15.39 ^b	15.30 [1]	3.38 ^b	3.30 [1]	1.65 ^b	2.00 [13]	1.24 ^b	1.20 [1]
		16.80 [13]		4.40 [13]				1.90 [13]
		15.78 [2]		3.45 [2,1]				1.14 [17]
		15.55 [3]		3.55 [3]				1.35 [13]
							1.23 [2]	
	13.36 ^a	14.35 [5]	2.96 ^a	3.06 [5]	1.55 ^a	1.27 [5]	0.56 ^a	0.52 [5]
	13.54 ^b	14.03 [2]	2.43 ^b	3.05 [2]	1.42 ^b	1.32 [2]	0.71 ^b	0.62 [2]
BSb								

^a This work using LDA

^b This work using GGA

^{*} Experiment

Table 1: Electron band eigen values for the lowest conduction band and the valence bandwidths for zinc-blende BAs, BP and BSb. All of the energies are in eV.

	$ \chi_A - \chi_B $	f_i (Pauling)	f_i (Zaoui) [20]	f_i (Phillips) [19]
BP	0.36	0.032	0.074	0.006
BAs	0.43	0.044	0.026	0.002
BSb	0.69	0.112	0.019	

Table2. The calculated ionicity factor f_i of BAs, BP and BSb.

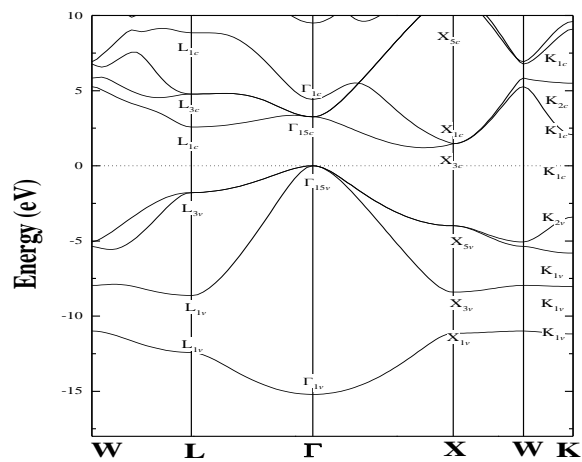


Figure 1: The electronic band structure of zinc-blende BA at the calculated lattice parameter using the GGA.

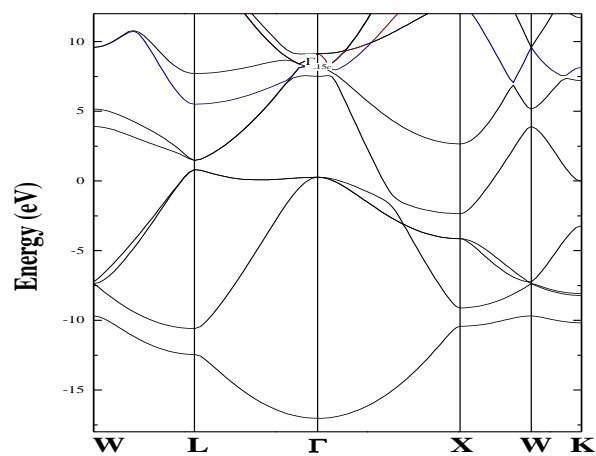


Figure 2: The electronic band structure of rocksalt BP at the calculated lattice parameter using the LDA

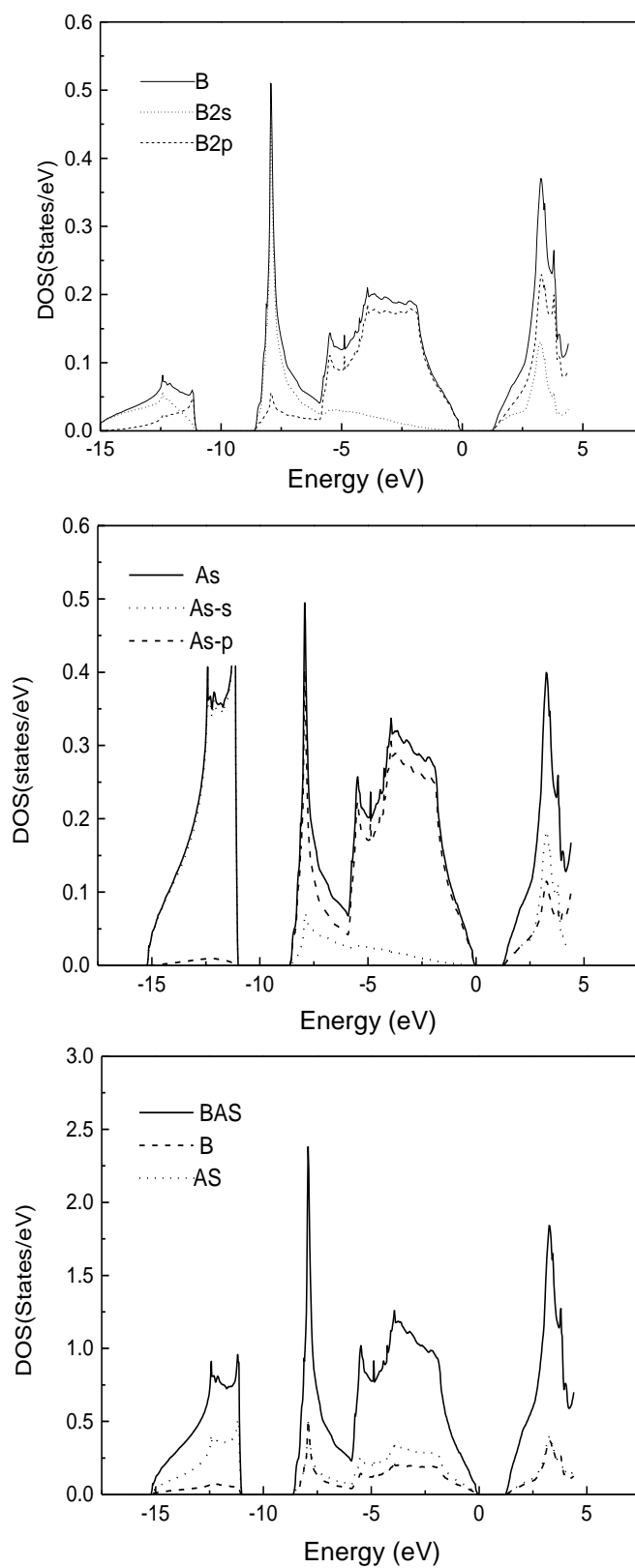


Figure 3: Calculated density of states of BAs at the equilibrium lattice constant using the GGA.

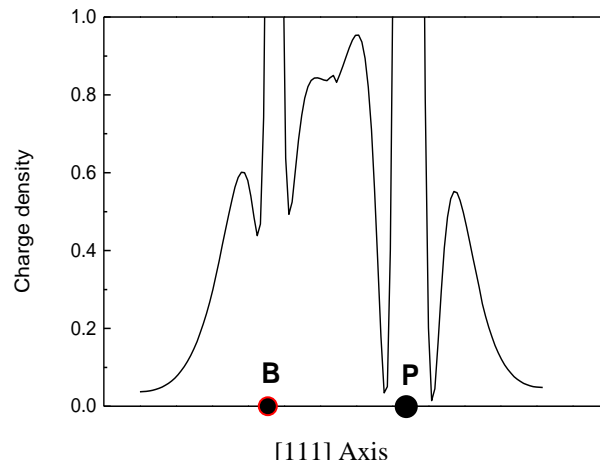


Figure 4: Total valence charge density along the [111] direction for BP in the zinc-blende structure at equilibrium lattice constant.

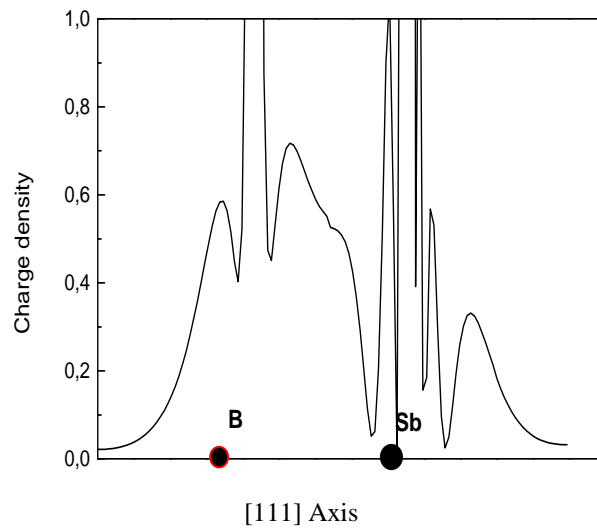


Figure 5: Total valence charge density along the [111] direction for BSb in the zinc-blende structure at equilibrium lattice constant.

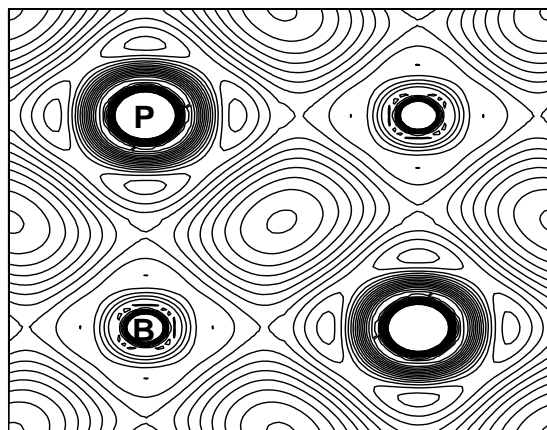


Figure 6: Contour plot of the total valence charge density of BP in rocksalt structure in the (110) plane at the equilibrium lattice constant.