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Full potential linearized augmented plane wave calculations of structural and electronic properties of BN, BP, BAs and BSb

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Abstract

A theoretical study of structural and electronic properties of boron compounds BN, BP, BAs and BSb is presented, using the full potential linearized augmented plane wave method. In this approach, the generalized gradient approximation was used for the exchange–correlation potential. Ground state properties such as lattice parameter, bulk modulus and its pressure derivative are calculated as well as structural transition pressure. The band structure is obtained for both zincblende and rocksalt structures. We also give the valence charge density at equilibrium lattice constant and at transition pressure. We show from the latter quantity the inverse role between cation and anion for BP, BAs and BSb. Results are discussed and compared with experimental and other theoretical data with reasonable agreement.

1. Introduction

Boron compounds have attracted increasing research interest over the past few years, as wide-gap semiconductors. These materials are of great technological interest for high-temperature, electronic and optical applications. This is due to their unique physical properties such as low densities, extremely high thermal conductivities, wide band-gap and large resistivities [1].

In addition to their interesting properties, these materials possess some peculiar characteristics that we discuss and try to explain in the present work. Among these peculiar characteristics is the inverse role between the cation and the anion in terms of charge transfer and the new phase transition. The latter aspect does not obey the Phillips diagram [2] established for $A^N B^{8-N}$ compounds, which predicts a metallic structure as the first new transition phase for weakly ionic compounds such as BP, BAs and BSb. BN is not concerned with the first anomalous point, in fact it can be viewed, at this point, less as a boron compound than a nitride.

These unusual behaviours appear to originate from the small core size of p electrons in B. Boron is expected to have a deep and localized pseudopotential compared to the atoms

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Table 1. The plane waves (PW), nearest-neighbour distance (NN) and muffin-tin radius (RMT) used for both zincblende (ZB) and rocksalt (RS) for BN, BAs and BSb.

	PW	NN (au)	RMT(au)	
			B	N, P, As, Sb
BN (ZB)	511	2.965 43	1.4	1.5
BP (ZB)	602	3.719 89	1.5	1.8
BAs (ZB)	579	3.914 63	1.5	2
BSb (ZB)	745	4.297 58	1.5	2.3
BN (RS)	398	3.309 85	1.5	1.5
BP (RS)	516	4.080 87	1.5	1.8
BAs (RS)	623	4.358 93	1.5	2
BSb (RS)	766	4.720 52	1.5	2.3

of elements from other rows. The reasons for these fundamental differences between these compounds and other III–V materials are apparent from band structures and charge density calculations.

The ground state and electronic properties have been calculated by Wentzcovitch *et al* [3, 4] and recently by Ferhat *et al* [5, 6] and Bouhafis *et al* [7]. The high-pressure structural phase transitions of BP and BAs were discussed by Wentzcovitch *et al* [8]. These theoretical studies used the local density approximation (LDA) within the density functional theory and the pseudopotential method.

The aim of this paper is to give a comparative and complementary study of electronic and structural properties to both experimental and other theoretical works for BN, BP, BAs and BSb, by using the full potential linearized augmented plane wave (FP-LAPW) method. After a brief description of the calculation details, we present a calculation of ground state properties as well as the high-pressure structural transition. The charge density obtained serves to illustrate the bonding behaviour under pressure and to explain the charge transfer and its effects on the phase transition. Finally we give the obtained band structure for both zincblende (ZB) and rocksalt (RS) structures and compare them with available theoretical works. Concluding remarks are presented at the end of the paper.

2. Computational details

In this work, we have employed the FP-LAPW. This method has been carried out using the WEIN97 code [9]. The exchange-correlation potential within the GGA is calculated using the scheme of Perdew *et al* [10]. The values of the sphere radii, the nearest-neighbour distance and the number of plane waves used in our calculation are listed in table 1. In table 2, special k -points used for the irreducible zone integration for the total energy as well as the plane wave cut-off are shown. Both the muffin-tin radius and the number of k -points are varied to ensure convergence.

3. Results and discussion

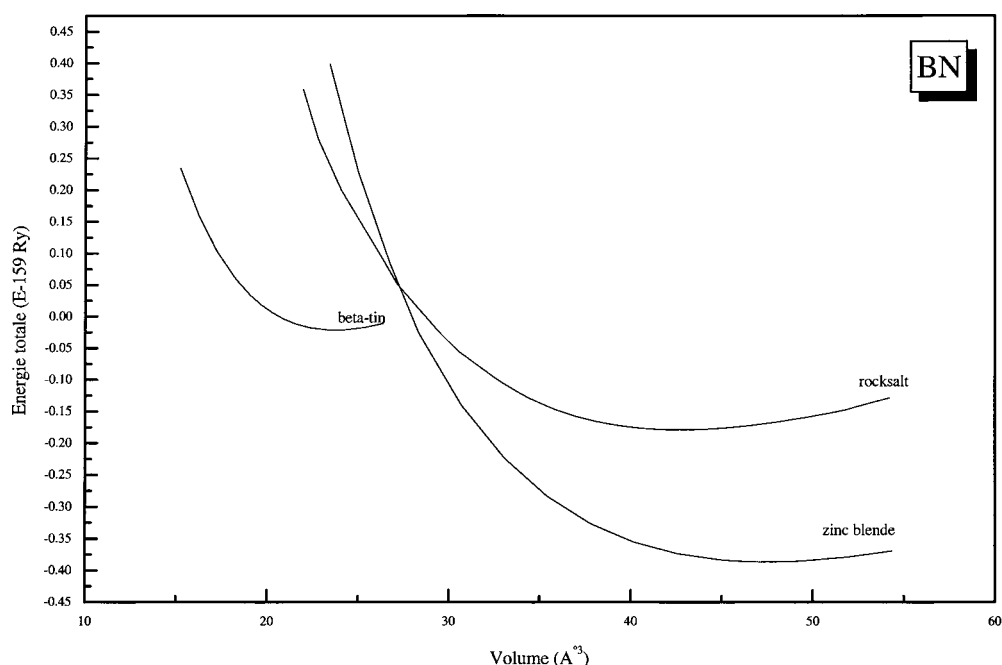
The variation of total energy as a function of volume is shown in figure 1 only for BN since the other corresponding curves are similar. The curves were obtained by calculating the total energy at many different volumes around equilibrium and by fitting the calculated values to the Murnaghan's equation of state [11]. The β -Sn structure is obtained by changing the c/a -ratio

Table 2. Calculated lattice constant, bulk modulus and its pressure derivative compared to experiment and other theoretical works of BN, BP, BAs and BSb for (ZB) and (RS) structures. The corresponding cut-off and the number of k points used are also listed for each compound for both structures.

(a)					
BN	Lattice constants (\AA)	B (Mbar)	B'	Cut-off (Ryd)	k points
ZB					
Present	3.623	3.68	3.32	64	30
Experiment	3.615[13, 14, 20]	3.69[13]	4[13]		
Other calculations	3.575[15] 3.576[16] 3.649[17], 3.606[8, 4], 3.623[18]	3.86[15], 3.97[16] 3.66[17], 3.67[8, 4] 3.65[18], 3.59[24]	3.6[16], 2.91[17] 3.94[18], 3.97[24]	60[8, 4, 24], 13.4[23], 160[15]	10 [18, 15, 24]
RS					
Present	3.503	3.99	2.53	64	47
Experiment					
Other calculations	3.493[8] 3.580[18], 3.500[19], 3.493[13],	4.25[8] 4.80[18], 4.06[19], 4.25[13]	4.59[18], 3.7[19]	60[8]	60[8]
(b)					
BP	Lattice constants (\AA)	B (Mbar)	B'	Cut-off (Ryd)	k points
ZB					
Present	4.546	1.70	3.07	20	30
Experiment	4.538[14, 20]	1.73[21]			
Other calculations	4.51[26] 4.53[25], 4.558[8, 4]	1.72[26] 1.52[25], 1.65[4], 1.66[8, 22]	3.7[26], 4.3[25]	80[15], 20[8, 4]	10[8]
RS					
Present	4.320	1.71	2.82	20	47
Experiment					
Other calculations	4.339[8]	1.55[8]		20[8]	60[8]
(c)					
BAs	Lattice constants (\AA)	B (Mbar)	B'	Cut-off (Ryd)	k points
ZB					
Present	4.784	1.37	3.49	20	30
Experiment	4.777[20]				
Other calculations	4.777[8, 3] 1.38[22]	1.45[8, 3] 1.38[22]		20[8, 3]	10[8, 3]
RS					
Present	4.619	1.35	3.44	20	47
Experiment					
Other calculations	4.583[8]	1.43[8]		20[8]	60[8]

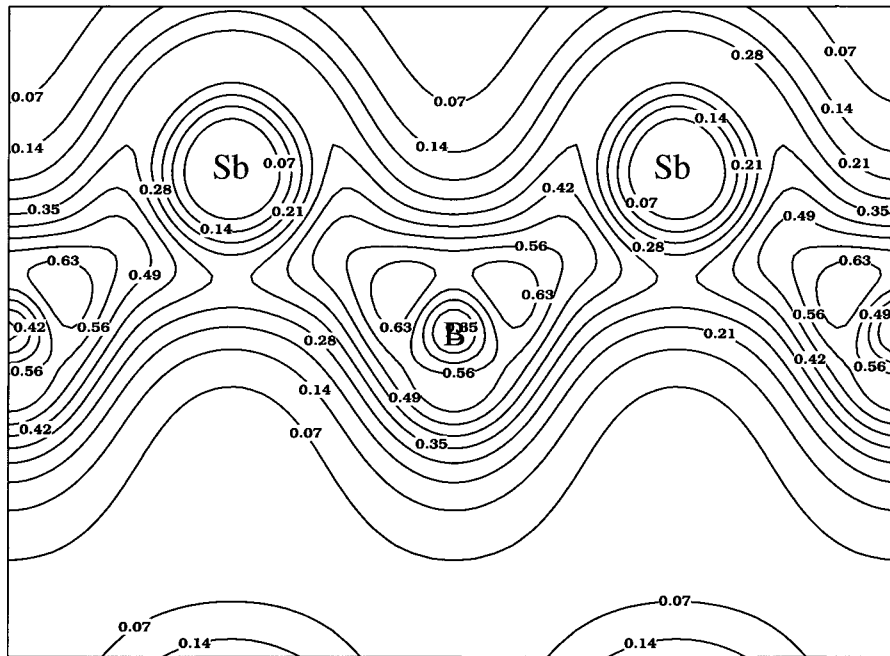
Table 2. (Continued)
(d)

BSb	Lattice constants (Å)	B (Mbar)	B'	Cut-off (Ryd)	k points
ZB					
Present	5.252	1.03	3.62	20	30
Other calculations	5.12[6]	115[6], 108[22]	5.28[6]	23[6]	6[6]
RS					
Present	4.979	1.08	3.89	20	30
Other calculations					

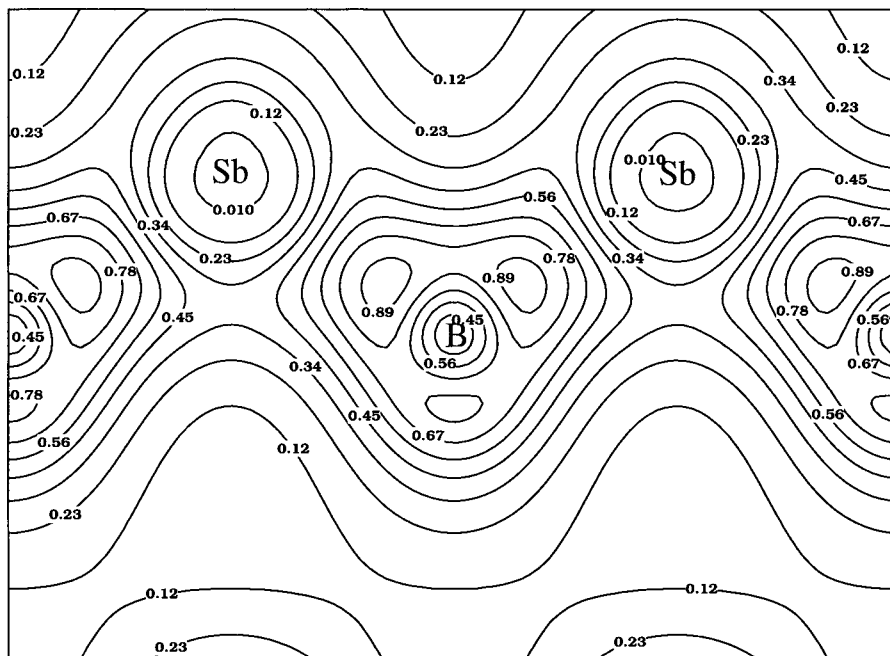
**Figure 1.** Variation of the total energy with volume for ZB, rocksalt and beta-tin structures of BN.

of the tetragonal cell, which is approximately 0.55. The shift observed between the beta-tin structure and ZB one is not too large, since the energetic differences between the equilibrium value of ZB structure and beta-tin are around 0.36 for BN and 0.2 for BP, BAs and BSb. These values are in the same order of magnitude as those of Wentzcovitch *et al* [8]. The other difference concerns the shift between the total equilibrium volume of both structures. As mentioned in [8], the beta-tin is unstable, and due to the different methods ([8] and our calculation) used to find the ideal ratio c/a , we should expect this difference. In all cases, this does not affect the value of transition volume and does not affect the nature of the first new phase under pressure, which remains RS.

It is obvious from these curves that the ZB structure is the most stable at ambient pressure, which is consistent with the experimental results. The corresponding equilibrium lattice



(a)



(b)

Figure 2. (a) Valence charge distribution on the (1 - 1 0) plane in the ZB structure at the equilibrium volume for BSb. (b) Valence charge distribution on the (1 - 1 0) plane in the ZB structure at the transition volume of BSb.

Table 3. Calculated value for transition pressure and corresponding transition volume from ZB to RS structures for BN, BP, BAs and BSb. Comparison is made with the available theoretical data.

	P_t (Mbar)		V_t (\AA^3)	
	Present work	Other calculations	Present work	Other calculations
BN	5.55	11.1[8]	28.345	19.693[8]
BP	1.11	1.6[8]	65.995	53.028[8]
BAs	0.93	1.1[8]	76.908	65.405[8]
BSb	0.53	2.16[12]	108.752	85.300[12]

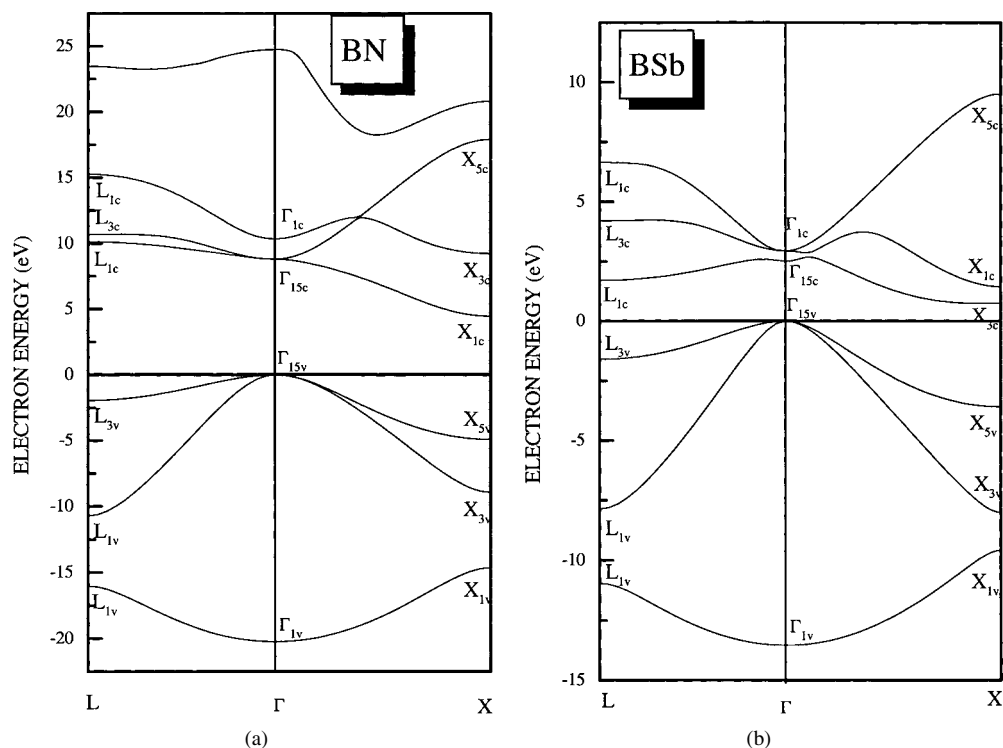


Figure 3. Band structure along the principal high-symmetry points in ZB structure at equilibrium volume for BN (a) and BSb (b).

parameter, bulk modulus and its pressure derivative are given in table 2 for each compound for both ZB and RS structures. We see, from this table, that our calculated values are in better agreement with experiment than the other calculations.

The pressure value for the structural phase transition (P_t) to the RS phase was determined by the common tangent of the two $E-V$ curves, ZB and RS, shown in figure 1. This value is compared with other available theoretical results in table 3. The calculated P_t is in reasonable agreement with the other theoretical calculations for BN, BP and BAs.

Since BSb is the least studied among this group of compounds, we consider the present high-pressure structural phase transition as a prediction study. We confirm this result with the only existing one, which was recently performed by Zaoui and Ferhat [12] using LDA within density functional theory and the pseudopotential method.

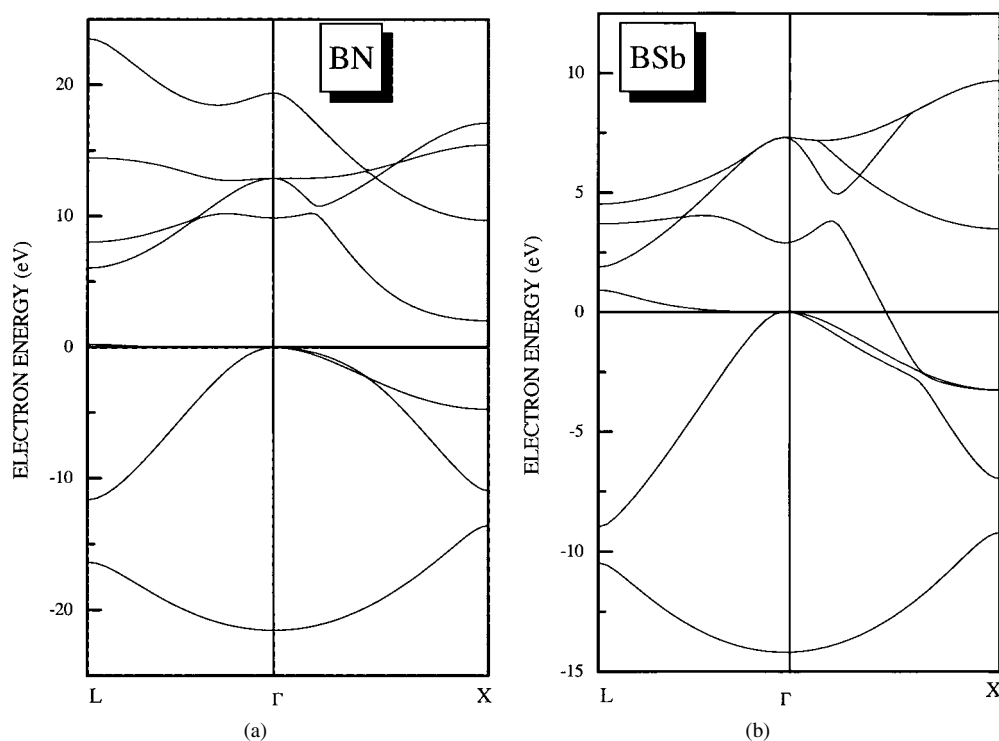


Figure 4. Band structure along the principal high-symmetry points in rocksalt structure at equilibrium volume for BN (a) and BSb (b).

The remarkable feature to note from these results is the fact that all the boron compounds studied have the rocksalt structure as a new first transition pressure. This is confirmed in the work of Wentzcovitch *et al* [8]. The latter work and ours are different, of course, in the methods used (pseudopotential and FLAPW), but mainly by the use of LDA and GGA to calculate the total energy for each compound in different structures. The use of GGA in our calculations is more appropriate than LDA and gives a good description of structural properties such as lattice parameter and bulk modulus as well as the transition volume.

This result seems anomalous for BP, BAs and BSb if we consider their ionicity values, which are supposed to be too small, according to the Phillips ionicity scale [2] (see, for additional evidence, [6] and [7] concerning the ionicity calculation of boron compounds). Phillips' diagram of phase predicts a metallic structure as a new phase transition for the $A^N B^{8-N}$ compounds with a low ionicity value, while the compounds that show a medium or a very pronounced ionic character translate to the rocksalt structure first and to the metallic one under more pressure.

This phenomenon could be explained by the anomalous charge transfer in this kind of material. Indeed, the calculated electronic charge density for the sum of valence bands for zincblende structure shows a localization of charges near the cation side instead of the anion one. Figure 2 displays this valence charge density for BSb; the same behaviour is observed for the others. The reversed role of anion and cation is due to the highly localized orbitals 2s and 2p of B. This could also be explained by the difference between their electronegativities, that is very small (2.0 for B, 1.64 for P, 1.57 for As and 1.31 for Sb). The electronegativity of nitrogen (3.0) is more important than that of B.

Table 4. Summary of the band-gaps and the valence band width of the band structure of BN, BP, BAs and BSb in the ZB structure. The energy is given in eV and it is compared to other theoretical works and to available experimental data.

	Present	Experiment	Other calculations
BN			
Direct gap ($\Gamma_{15V} \rightarrow \Gamma_{15C}$)	8.79	14.5[14]	8.60[4], 11.4[30], 11.40[5], 8.61[27] 8.80[23], 8.8[15]
Indirect gap ($\Gamma_{15V} \rightarrow X_{1C}$)	4.45	6.0[29] 6.4[28] 6.00– 6.4[14]	4.2[4], 6.3[30], 6.31[5], 4.19[27], 4.40[23], 4.38[15]
V. bandwidth ($\Gamma_{1V} \rightarrow \Gamma_{15V}$)	20.23	22.0[29]	20.1[4], 23.1[30], 23.10[5], 20.6[27], 20.1[23], 20.44[15]
BP			
Direct gap ($\Gamma_{15V} \rightarrow \Gamma_{15C}$)	3.37	5.0[32]	3.3[4], 4.40[30], 4.40[5], 3.45[15], 3.55[26]
Indirect gap ($\Gamma_{15V} \rightarrow \Delta_{min}$)	1.25	2.4[13]	1.2[4], 1.9[30], 1.14[15], 1.35[26]
V. bandwidth ($\Gamma_{1V} \rightarrow \Gamma_{15V}$)	15.38	17[31]	15.3[4], 16.80[30], 16.8[5], 15.75[15], 15.55[26]
BAs			
Direct gap ($\Gamma_{15V} \rightarrow \Gamma_{15C}$)	3.25	1.46[32]	4.00[5], 4.20[30],
Indirect gap ($\Gamma_{15V} \rightarrow \Delta_{min}$)	1.23	0.67[27]	1.60[30], 1.25[3]
V. bandwidth ($\Gamma_{1V} \rightarrow \Gamma_{15V}$)	15.22	16.0[28]	16.63[5], 16.70[30], 15.17[3]
BSb			
Direct gap ($\Gamma_{15V} \rightarrow \Gamma_{15C}$)	2.51	—	3.06[6]
Indirect gap ($\Gamma_{15V} \rightarrow \Delta_{min}$)	0.75	—	0.527[6]
($\Gamma_{15V} \rightarrow X_{1C}$)	1.44	—	1.274[6]
V. bandwidth ($\Gamma_{1V} \rightarrow \Gamma_{15V}$)	13.53	—	14.35[6]

Another aspect directly linked to the charge transfer is the ionicity parameter. From our point of view, this concept should play an essential role in the fact that the new phase transition does not follow the same rule as described by Phillips' diagram. It seems that there is incoherence between the calculated ionicity value and the charge transfer, which reflects a negative value for these compounds.

From figure 2(a) to figure 2(b), we can remark that the charge density moves under pressure towards the bond centre, which means that the system becomes less ionic. This is a common behaviour for all the $A^N B^{8-N}$ compounds, but the translation in this case is from the inverse sense. This could be a reason why the system changes, under pressure, to a new phase, different from what we would expect.

The band structure for ZB and RS structures of BN and BSb were calculated along the high-symmetry directions in the Brillouin zone (figures 3 and 4). BP and BAs have the same trends than BSb in both structures. Table 4 gives a summary for the most important

calculated band-gap in the zincblende structure of boron compounds and compared with the experimental and theoretical ones. The overall band profile is found in agreement with the available theoretical works. Besides, we notice the metallic character of the band structure of these compounds, except for BN, in the RS structure (see figure 4(b) for BSb).

Since our calculations are *ab initio*, the underestimation of the transition band-gap was expected. Nevertheless, the obtained values are in good agreement with the experimental ones. It is then an interesting question whether the exact DF formalism would give a band gap substantially closer to the experimental value, so that the poor band gap is due to the LDA approximation itself, or due to the discontinuity inherent in the exchange-correlation potential. It is fair to conclude that GGA can improve quantities derived from the total energy, such as equilibrium lattice constant and bulk modulus. However, quantities that are based on single particle energies such as band-gap as excited states are involved.

4. Conclusion

We have presented a theoretical analysis of the structural and electronic properties of boron compounds using the FP-LAPW method. The use of GGA for the exchange-correlation potential permitted us to obtain good structural parameters. The calculated band-gap was also in good agreement with the experimental data and agrees well with the other theoretical calculations. The results regarding the high pressure structural phase transition agrees with the available theoretical works in this subject and show the importance of the inverted charge transfer in the nature of the new phase under pressure.

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