Trends in band-gap pressure coefficients in boron compounds BP, BAs, and BSb

Trends in band-gap pressure coefficients in boron compounds BP, BAs, and BSb

Bachir Bouhafs†§, H Aourag† and M Certier‡

† Computational Materials Science Laboratory, Physics Department,
University of Sidi-Bel-Abbes, 22000 Algeria
‡ LSOM—IUT Mesures Physiques, 57078-Metz Cédex 3, France

E-mail: `bbouhafs@mail.univ-sba.dz`

Abstract. We have performed an *ab initio* investigation for a series of boron compounds, BP, BAs, and BSb, and have compared their structural and electronic properties with those of c-BN. The calculations are performed using a plane-wave expansion within the local density approximation and the pseudopotential approximation. Results are given for lattice constants, bulk moduli, band structures, and band-gap pressure coefficients. The electronic properties of these compounds are shown to have features that differ from those of other III–V materials. We found that the direct-band-gap pressure coefficient in boron compounds is nearly independent of the anion substitutions. As a result, this trend is similar to the one resulting from cation substitutions in other zinc-blende compounds. This is another anomalous behaviour which can be characterized by reversing the standard assignments for the anion and cation in these compounds.

1. Introduction

Interest in solids formed from atoms with low atomic numbers has recently increased greatly [1], because of the potential unique properties of these materials. Some of these properties are associated with the relatively strong chemical bonding characteristic of the second-row atoms. This leads to high melting points, which implies potential use as refractories, and large elastic constants which, in turn, are related to hardness, high sound velocities, and good thermal conductivities.

Boron compounds constitute a family of compounds that are written as BX, X being N, P, As, or Sb, which are group-V elements. Generally, compounds belonging to a given family present similar properties that gradually change with increasing atomic number. As the best example, one may consider III–V compounds. They have the same zinc-blende crystalline structure, with tetrahedral environment, the same sp^3 hybridization, and the same kind of semiconducting electronic structure.

On the basis of Harrison's [2] simple picture of the bonding in tetrahedral semiconductors, one can increase either the ionicity or the covalent interaction between the atoms. Since the covalent interaction is strong for early elements in the periodic table, in particular for the elements of the second row, such as B, C, and N, materials involving these elements can be used, such as diamond [3], c-BN [4], and a number of alternative materials such as SiC [5], BP, and their superlattice SiC/BP [6].

§ Fax: (213) 7 56 16 42.

The boron compounds are strongly covalent, since the electronegativities of the P (1.64), As (1.57), and Sb (1.31) anions are slightly smaller than that of the B (2.00) cation. In BN, the nitrogen N (3.00) is always the most electronegative element and will thus attract electrons from the boron atom towards it. However, this situation is inverted in BP, BAs, and BSb, where the boron is always the most electronegative element and will thus attract electrons towards it. From these electronegativity considerations, one can expect BX, X being P, As, or Sb, compounds to have a number of remarkable properties which set them apart from other III–V materials and make them particularly worthy of study. In addition, they are characterized by highly localized orbitals (B 2s, B 2p). Their main characteristic, namely the dominance of strongly localized orbitals, is of precisely the same nature as the obstacle that has hampered accurate band-structure calculations for group-III nitrides for a long time.

Furthermore, the boron compounds display rather peculiar behaviour when compared to other III–V compounds. Their unusual behaviour appears to originate from the small core size and the absence of p electrons in B. Boron is expected to have a deep and localized pseudopotential compared with the atoms from other rows. The reason for these fundamental differences between these compounds and other III–V materials can become apparent from the band-structure calculations. According to the Phillips scale of ionicity [7], BP and BAs are the most covalent of the III–V semiconductors, and there are interesting consequences of this property. These compounds are also known to have one of the smallest heteropolar gaps [7] and can be viewed as being isoelectronic to SiC [8]. Despite extensive studies, some interesting problems remain unresolved, and a number of basic properties are still unknown, e.g. the band-gap coefficients. When a calculation is available, there is always a lack of information about quantities in which we are interested. This has motivated us to explore their structural and electronic properties.

To provide a better understanding of the structural and electronic properties for these compounds, first-principles calculations are certainly desirable. Although there have been several studies for BN, BP, and BAs compounds [8–17], to our knowledge, except our published papers [18, 19], there are no published reports of theoretical studies for BSb.

We are interested in finding common trends and differences in the electronic structure for the whole family of BX (X = P, As, Sb) crystals. This choice has been suggested for the reason that the presence of anions belonging to three different periods of the periodic table allows us to analyse the influence of size on the physical properties. So, as we want to analyse this family of compounds systematically, we will use the same formalism for the calculation of a given property, even if there are some good calculations of the electronic structure for one compound or another. In this paper, we investigate theoretically the structural and electronic properties of BP, BAs, and BSb compounds in the zinc-blende structure, and compare their properties to those of cubic BN semiconductor. The *ab initio* plane-wave approach has been applied to the series of these compounds.

The remainder of the paper is organized as follows. Information on the calculation method is given in section 2. Section 3 is devoted to the analysis of the structural and electronic properties within the whole BX family, and concluding remarks are presented in section 4.

2. Calculation

For the series of compounds BP, BAs, and BSb, we apply the DFT within the LDA [20, 21] in a plane-wave basis, with the norm-conserving nonlocal pseudopotentials of Bachelet, Hamann, and Schlüter (BHS) [22] without empirical parameters for both species of atoms. We adopt the Ceperley–Alder-type exchange–correlation potential [23], as parametrized by Perdew and Zunger [24]. The calculation is computationally heavy as boron has a hard-core potential;

thus a large number of plane waves are required in order to achieve a good convergence in the solutions of the self-consistent Kohn–Sham equations [21].

On the basis of the previous successes of such calculations for related materials, we believe that our results are just as reliable and can be used to predict the structural and electronic properties that have not yet been established experimentally.

The wavefunctions are expanded in a set of plane waves of wavevector $(\boldsymbol{k} + \boldsymbol{G})$, where $\boldsymbol{k}$ is the wavevector in the first Brillouin zone and $\boldsymbol{G}$ is a reciprocal-lattice vector. The only plane waves included in the expansion are those whose kinetic energy is less than a specified energy cut-off, which should be tested to be sufficient for the convergence. We have performed convergence tests of the total energy at different values of kinetic energy cut-off. The $\boldsymbol{k}$-space summation was performed using a set of ten special points which correspond to a 4, 4, 4 mesh in the Monkhorst–Pack [25] notation. Details of the calculations on the same compounds have been given in an earlier publication [19].

3. Results

3.1. Structural properties

The total energies are computed for a selection of lattice constants. Our data result from a best fit with the Murnaghan equation of state [26] built up with 10–11 points, in the range $V_{equ}(1 \pm 0.05)$ (V_{equ} is the equilibrium volume of the unit cell).

The computed equilibrium lattice constants are 4.475 Å, 4.728 Å, and 5.156 Å for BP, BAs, and BSb, respectively. From these fits, we also calculated the values of the bulk moduli to be 1.72 Mbar, 1.44 Mbar, and 1.08 Mbar, and their pressure derivatives to be 3.76, 4.00, and 4.03, for BP, BAs, and BSb, respectively. In table 1 we summarize our data at equilibrium and compare them with those obtained from other calculations at the LDA level using a plane-wave basis set (for BP and BAs; references [8, 9]), those previously obtained at the Hartree–Fock (HF) level using an all-electron basis set (for BP; reference [27]), and at the LDA level using a linear combination of atomic orbitals (LCAO) scheme (for BP; reference [28]). It is well known that the HF calculations overestimate the lattice parameters. This result was confirmed for the BP compound, since the mean overestimation is 1.3% with respect to the experimental data. LDA calculations significantly improve the agreement with experiment. For comparison, experimental results when available are also given. Our predicted values for B_0 agree with those determined by using the empirical formula of Cohen [29] which seems to be valid for the series of boron compounds. These compounds involving second-row elements also have comparatively smaller cell volumes and larger bulk moduli than other III–V compounds. This implies that the homopolar gaps (E_h) computed using the scaling relation [29] are relatively large and the values of the ionicity (f_i) are reduced accordingly.

To verify the accuracy of these results, several tests have been performed using different kinetic energy cut-offs as well as different sets of special points. The structural parameters calculated with ten special points and kinetic energy cut-offs of 60 Ryd for BP and 40 Ryd for BAs and BSb are well converged. Thus we arrive at a very good description of the atomic structure of the boron compounds by using BHS pseudopotentials.

3.2. Electronic properties

Let us now discuss the results of our electronic band-structure calculations employing the BHS pseudopotentials. To allow for a more meaningful comparison with the theoretical literature data of references [6, 8, 10, 16, 18], the calculations of the band structures for the series of

Table 1. The lattice constant, a, bulk modulus, B_0, first derivative of bulk modulus, B'_0, and homopolar gap for BP, BAs, and BSb compared to those for the BN compound, in the zinc-blende structure.

		a (Å)		B_0 (Mbar)			B'_0		E_h
BN		3.611[a]		3.67[a]	3.70[b]		3.05[a]		12.5[b]
		3.62[c]		3.65[c]			3.94[c]		
		3.615[d]		3.69[d]			4.0[d]		
BP	4.475[e]	4.558[a]	1.72[e]	1.66[a]	1.74[b]	3.76[e]			7.3[b]
		4.526[f]		1.66[f]					
		4.598[g]		1.70[g]					
		4.538[h,i]		1.73[j]					
		4.474[k]		1.72[k]					
		4.51[l]		1.72[l]			3.7[l]		
BAs	4.728[e]	4.777[a]	1.44[e]	1.45[a]	1.43[b]	4.00[e]			6.5[b]
BSb	5.156[e]	5.12[m]	1.08[e]	1.15[m]	1.06[b]	4.03[e]	5.28[m]		5.3[b]

[a] References [8, 9].
[b] Calculated using the empirical relation of reference [29].
[c] Our values taken from reference [4] using MD simulation.
[d] Experimental values taken from reference [36].
[e] This work.
[f] Reference [28].
[g] Reference [27].
[h] Reference [37].
[i] Reference [38].
[j] Reference [15].
[k] Reference [10].
[l] Reference [6].
[m] Reference [18].

boron compounds have been carried out at the calculated lattice constants. Using standard pseudopotentials, we obtain good general agreement with the *ab initio* literature data.

As far as the respective band gaps are concerned, our results are in close agreement with the results of Rodriguez-Hernández *et al* [10] for BP. The deviations between our results and those of Wentzcovitch *et al* [8], for BP and BAs, seem to be due to differences between the methodologies used in the calculations.

Our calculated electronic band structures for BP, BAs, and BSb along the various symmetry lines are given in figure 1. There is an overall topological resemblance of the present band structures and those calculated by Wentzcovitch *et al* [8], Rodriguez-Hernández *et al* [10], Surh *et al* [16], and Ferhat *et al* [18].

The lower parts of the valence bands are dominated by P 3s, As 4s, and Sb 5s states in BP, BAs, and BSb, respectively. The upper parts are dominated by B and P p states in BP, B and As p states in BAs, and B and Sb p states in BSb. The B s states contribute to both parts of the valence bands. Our estimates of the full valence bandwidths are 15.78 eV for BP, 15.71 eV for BAs, and 14.03 eV for BSb. All materials are found to have indirect band gaps, where the conduction band minima are along the Δ direction. Figure 1 shows the indirect band gap near X ($\Gamma_{15v} \rightarrow \Delta_{min}$) for all of these compounds.

The most prominent features of the present band structures are as follows:

(i) Δ_{min} is close to X_{3c} instead of X_{1c} as was found in most III–V semiconductors, GaAs for example;
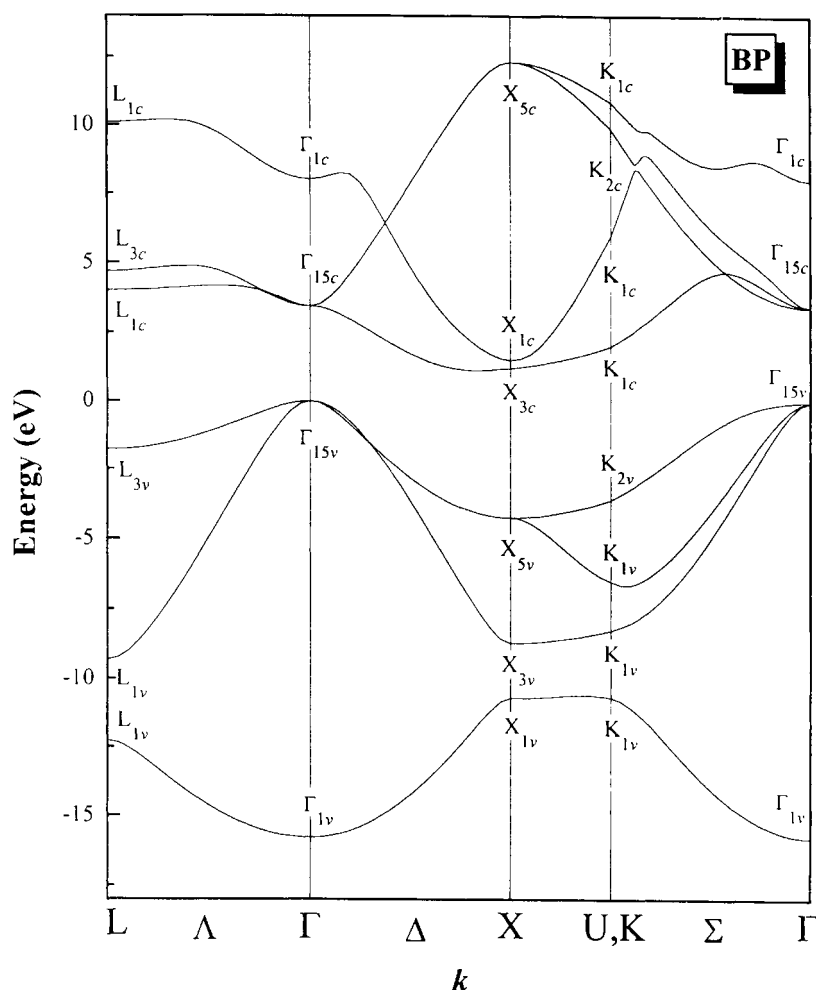
Figure 1. The band structure at the predicted equilibrium lattice constant in the zinc-blende structure of (a) BP, (b) BAs, and (c) BSb.

(ii) the Γ_{15c} band is below the Γ_{1c} band, in contrast to the case for other III–V compounds where the Γ_{1c} state is below the Γ_{15c} state.

This exchange of the order of the states at the bottom of the conduction bands at Γ and X points is a common feature of the covalent semiconductors BP, BAs [8], and BSb [18,19]. The large component of p states of B in the upper valence bands and its absence at the bottom of the conduction bands suggest that in this compound B resembles an anion.

   The important features of the band structures (bandwidths, band gaps), comparing the LDA and the first-principles quasi-particle calculations based on the GW-approximation (which evaluates the electron self-energy to the first order in the electron Green's function G and the screened Coulomb interaction W) (compiled from references [6,8,10,16,18,19]), of BN, BP, BAs, and BSb in the zinc-blende structure are listed in table 2. It is interesting to note that BSb has a small band-gap value compared to that found for BP and BAs. Also the width of the BSb valence band is slightly smaller than those of BP and BAs. Since the band gaps of BP,
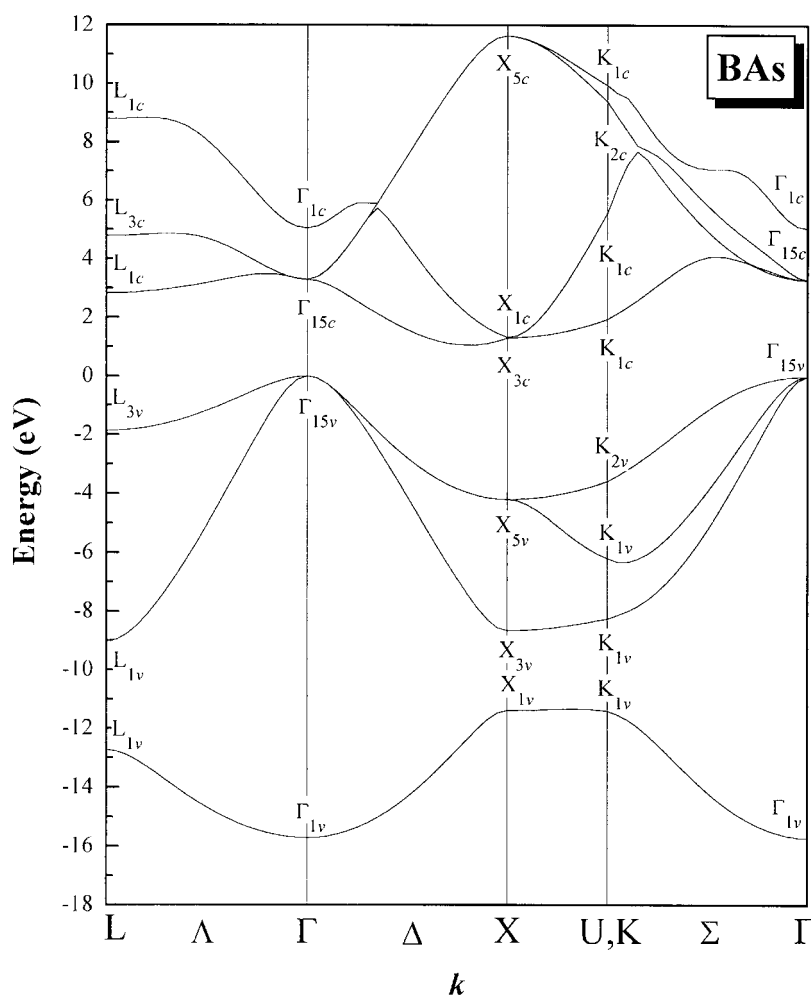
Figure 1. (Continued)

BAs, and BSb are seriously underestimated in the LDA, these band gaps may be larger than those indicated in table 2.

It is well known that the *GW*-calculations give energy band gaps in excellent agreement with experiment, as shown by Surh *et al* [16] for such semiconductors as BN, BP, and BAs. It is interesting to note that the band structure derived from *ab initio* calculations within the local density functional formalism cannot be used directly to compare with the *GW*-calculations. LDA band structures are well known to underestimate the band gap in semiconductors. Our calculated band gaps listed in table 3 are underestimated by 40% and 35% for BP and BAs, respectively. For BSb we will make the *ad hoc* assumption that the band-gap correction is proportional to the correction for the BAs compound. Thus, for BSb, for which we predict an LDA band gap of 0.62 eV, a correction of 35% was made, to give an adjusted band gap of 0.88 eV. Both BAs and BSb have minima in their conduction bands in the ΓX direction, but if we assume that the correction corresponds to a rigid shift of all the conduction bands, then the correction should work equally well for other conduction band minima.
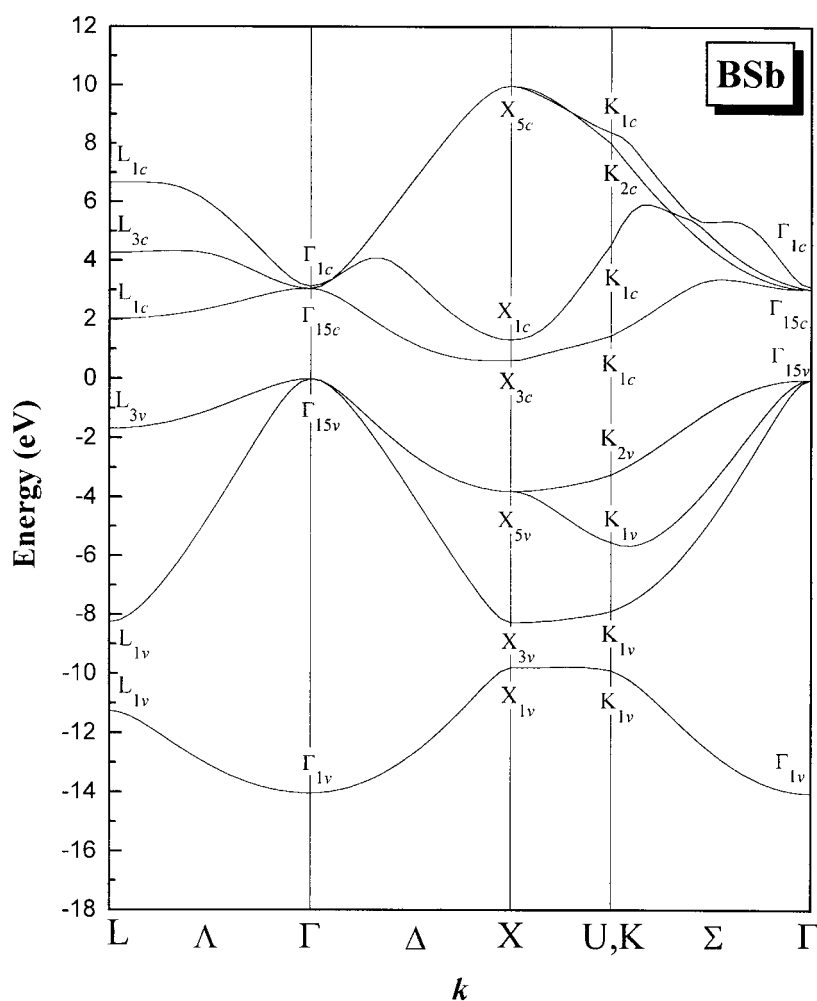
Figure 1. (Continued)

3.3. Band-gap pressure coefficients

The LDA does not accurately describe the eigenvalues of the electronic states, which causes quantitative underestimations of band gaps. It is precisely these quantities that are least well predicted by the LDA in the DFT. However, the pressure derivatives of conduction band states [30] and their relative positions are given reasonably well within the LDA. We also note that the LDA tends to underestimate the band-gap pressure coefficients, but it at least reproduces the experimental trend quite well. The underestimation of the pressure coefficients can probably be attributed to the LDA, but at a small percentage compared to the absolute band gaps. However, since the GW-calculation of the self-energy correction to the gap indicates that the correction is typically a rigid shift of the whole conduction band, the pressure coefficient of the band gap within the LDA is, at least, more reliable than the absolute gap size. We therefore assume that the band states calculated within the LDA show the qualitatively correct ordering and dependence on cell volume.

Table 2. Electron band eigenvalues for the lowest conduction band and the valence bandwidths for BN, BP, BAs, and BSb. All of the energies are in eV.

	$\Gamma_{15v} \rightarrow \Gamma_{15c}$	$\Gamma_{15v} \rightarrow X_{1c}$	$\Gamma_{15v} \rightarrow \Delta_{min}$	$\Gamma_{1v} \rightarrow \Gamma_{15v}$	
BN	8.6[a]	4.2[a]		20.3[a]	LDA
	8.80[b]	4.38[b]			
	11.4[c]	6.3[c]		23.1[c]	GW
BP	3.45[d]	1.51[d]	1.12[d] (0.85, 0, 0)	15.78[d]	LDA
	3.3[a]		1.2[a]	15.3[a]	
	3.55[e]	1.51[e]	1.35[e]	15.55[e]	
	3.45[a]		1.14[b]		
	4.4[c]	2.0[c]	1.9[c]	16.8[c]	GW
BAs	3.30[d]	1.33[d]	1.06[d] (0.80, 0, 0)	15.71[d]	LDA
	3.3[a]		1.25[a]	15.17[a]	
	4.2[c]	1.86[c]	1.6[c]	16.7[c]	GW
BSb	3.05[d]	1.32[d]	0.62[d] (0.95, 0, 0)	14.03[d]	LDA
	3.06[f]	1.274[f]	0.527[f]	14.35[f]	

[a] Reference [8].
[b] Reference [10].
[c] Reference [16].
[d] This work.
[e] Reference [6].
[f] Reference [18].

Table 3. Calculated linear and quadratic pressure coefficients of important band gaps for BP, BAs, and BSb compounds. $E_i(p) = E_i(0) + bp + cp^2$, $b = \partial E_i/\partial p$ in eV Mbar^{-1}, $c = \partial^2 E_i/\partial p^2$ in eV Mbar^{-2}.

	Γ_{15v}–Γ_{15c}		Γ_{15v}–Γ_{1c}		Γ_{15v}–X_{3c}		Γ_{15v}–X_{1c}		Γ_{15v}–L_{1c}		Γ_{15v}–Δ_{min}	
	b	c	b	c	b	c	b	c	b	c	b	c
SiC			5.5[a]				−0.34[a]		3.95[a]			
BP	1.01	−0.17	8.54	−4.54	−1.03	0.53	−0.37	0.39	3.98	−4.66	−0.72	0.37
BAs	0.79	0.07	8.52	−6.16	−0.52	−0.11	−0.87	0.93	3.99	−2.36	−0.58	0.31
BSb	1.77	−1.09	6.70	−7.94	−0.91	0.83	−0.16	0.37	4.73	−3.71	−0.90	0.80

[a]Reference [5].

In order to investigate the effects of the cell volume on the size of the energy gap and position of the conduction band minimum of the boron-based materials, the band energies at selected symmetry points are examined as a function of cell volume. The results of our calculation for the direct and indirect band gaps for BP, BAs, and BSb versus the volume are shown in figure 2. At the equilibrium volume, the band gaps for all materials are indirect from Γ to Δ. As for typical semiconductors, the fundamental gap decreases when the volume is compressed. The behaviour of the band-gap variation under pressure is very similar to that found in all III–V materials. The energy dependence of the state at X closely follows the minimum along Δ.

Although the minimum direct gap in BP, BAs, and BSb is from Γ_{15v} to the Γ_{15c} level at the equilibrium volume, the dependence of the Γ_{15c} level on the volume compression is small. It is the next Γ state, Γ_{1c}, which changes most rapidly with change in cell volume and is therefore of interest in this study. Figure 2 also shows that the band gaps at Γ (with Γ_{1c} symmetry) and
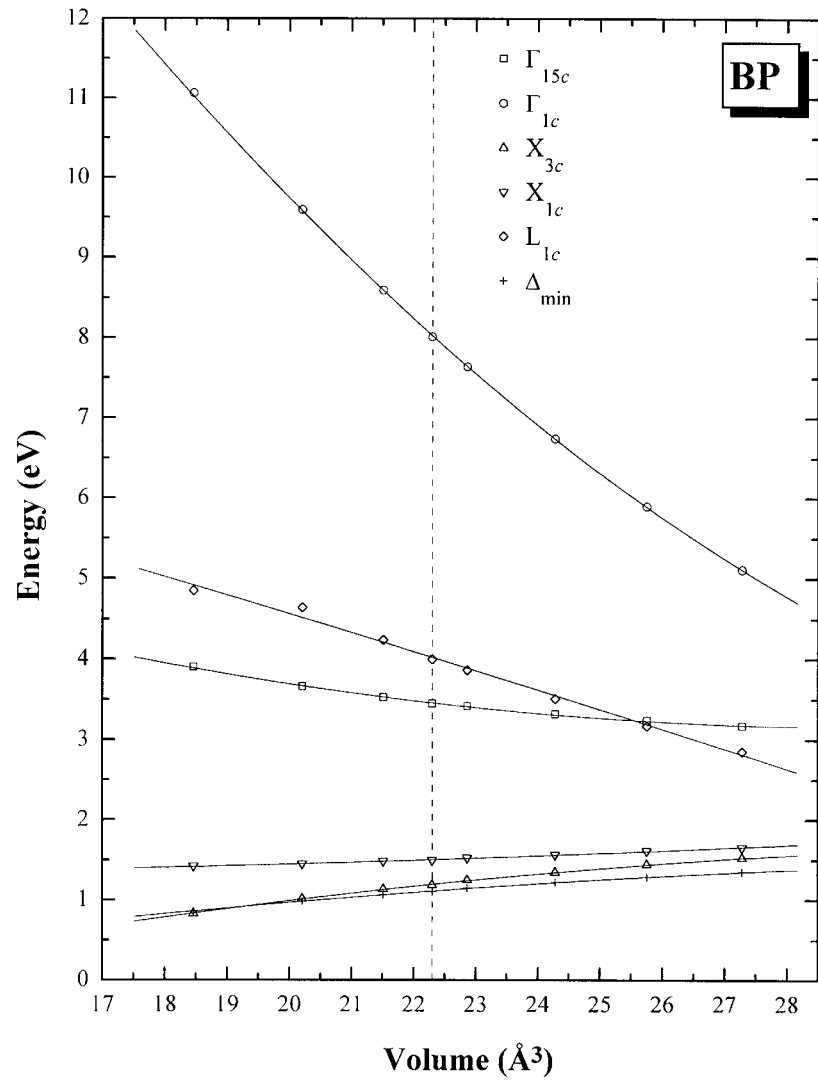
Figure 2. Band-edge levels as a function of volume for (a) BP, (b) BAs, and (c) BSb. The calculated equilibrium volume is denoted by the dashed vertical line.

L points present a nonlinear variation while at the X point it is linear.

We also calculated the first pressure derivative coefficients for the boron compounds. To include the effect of changes in the volume (V) on the band gap we used the following equation:

$$a_g^i = \frac{\mathrm{d}E_g^i}{\mathrm{d}p} = -\left(\frac{1}{B}\right)\frac{\mathrm{d}E_g^i}{\mathrm{d}\ln V}. \tag{1}$$

The pressure coefficients are obtained near the calculated equilibrium positions. Table 3 lists the resultant values for the boron compounds. The calculated linear and quadratic pressure coefficients are listed for each band (Γ, X, L) and compared with those of SiC. There are no experimental results for the boron compounds available to us. The predicted pressure coefficients for BP, BAs, and BSb are found to have the same order of magnitude as for SiC.
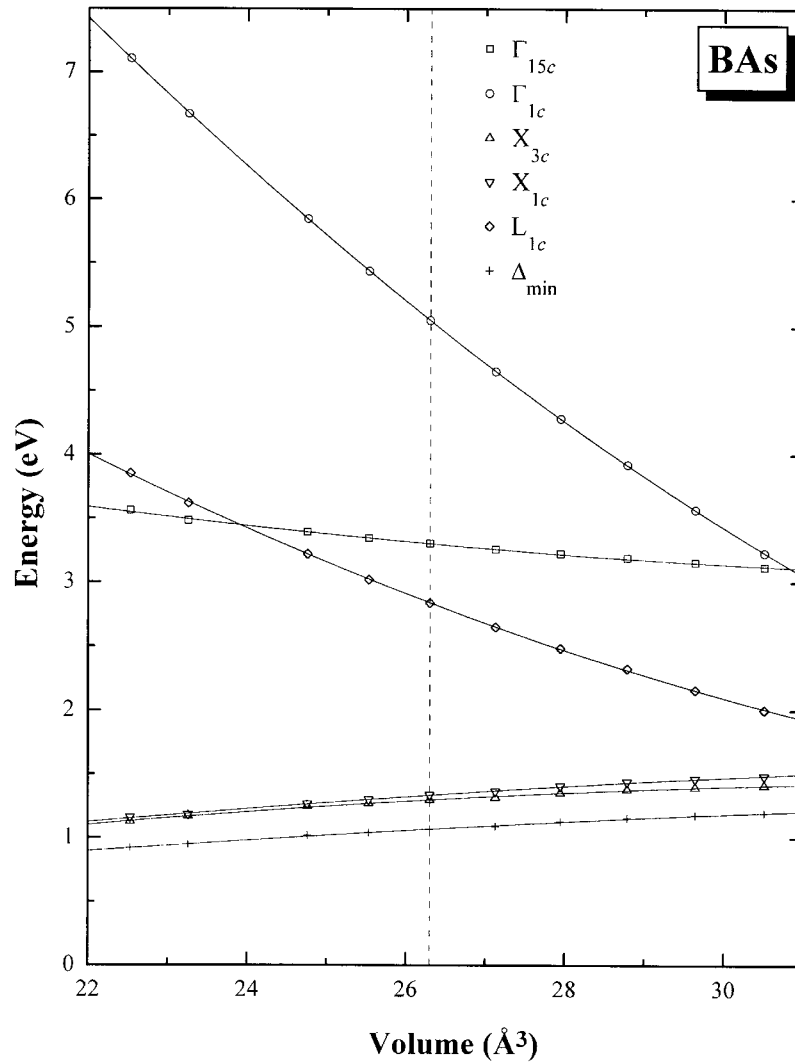
Figure 2. (Continued)

In table 4, we compare the band-gap pressure coefficients for the Γ_{15v}–Γ_{1c} transition for the boron materials with those of the corresponding III–V compounds. From this we see that:

(i) The direct-band-gap pressure coefficient of Γ_{1c} symmetry in boron compounds is fairly constant when the group-V element is changed from P to Sb.

(ii) For zinc-blende compounds, e.g., GaX, and InX (X $=$ As, Sb), we see that $a_g^{\Gamma_{15v}-\Gamma_{1c}}$ increases significantly as the atomic number of the group-V element increases [31–35].

For boron compounds, $-\mathrm{d}E_g^{\Gamma_{15v}-\Gamma_{1c}}/\mathrm{d}\ln V$ decreases when the atomic number of the group-V element increases, and the bond length is shorter than in other III–V compounds. Thus, the cation–anion s–s coupling in boron compounds is stronger than in other III–V compounds. However, since, in semiconductor compounds, the bulk modulus is inversely proportional [29] to the bond length, the smaller atomic size of boron causes the bulk modulus to be larger in
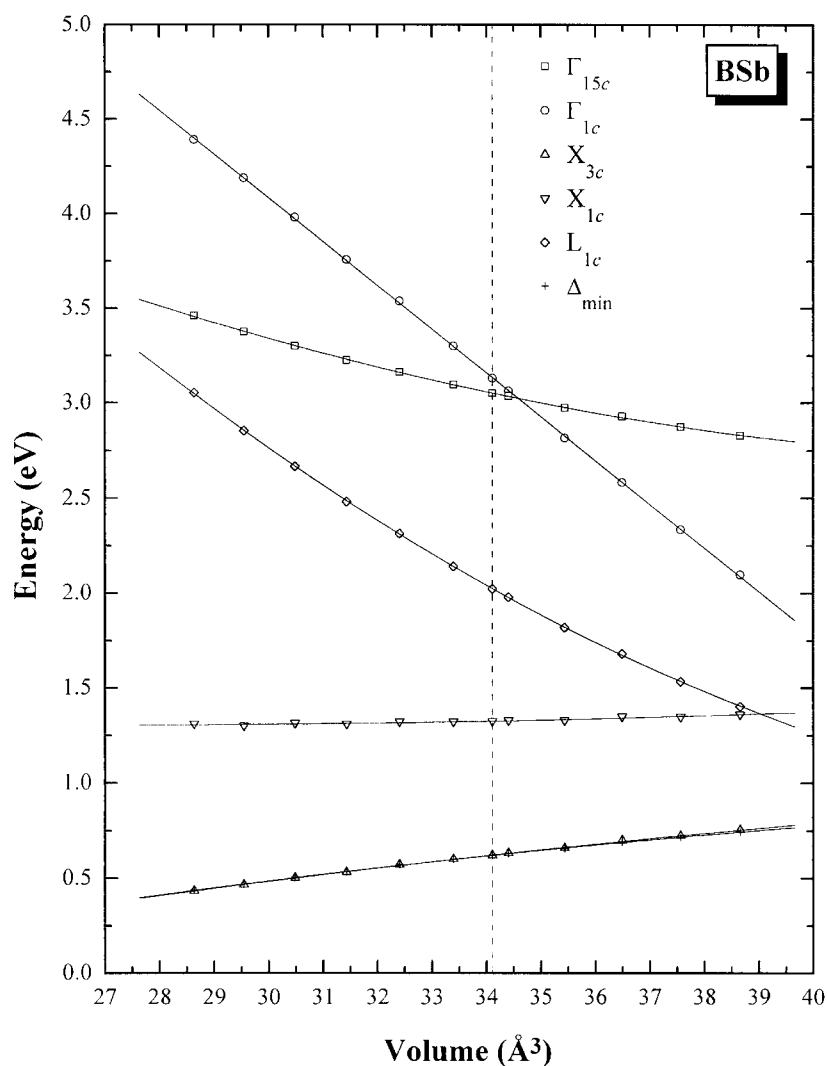
Figure 2. (Continued)

the boron compounds than in other III–V compounds. Thus, for

$$a_g^{\Gamma_{15v}-\Gamma_{1c}} = -(1/B)\, dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$$

the reduction in $-dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$ when the atomic number of the group-V element increases is partially offset by the increase in $1/B$. For the series of BP, BAs, and BSb compounds, this cancellation of the two effects is nearly complete, so $a_g^{\Gamma_{15v}-\Gamma_{1c}}$ is nearly independent of the group-V element. This effect is similar to the one caused by the increase of the atomic number of the group-III element in other III–V compounds.

In III–V compounds, $-dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$ changes little when the atomic number of the group-V element increases (see table 4) unlike the case for the group-III elements. This is because the anion–cation s–s coupling does not change much when the atomic number of the group-V element increases. This constancy reflects again a cancellation of two effects: on one

Table 4. Band-gap pressure coefficients for the $\Gamma_{15v}-\Gamma_{1c}$ transition for the boron compounds BP, BAs, and BSb compared with those of the corresponding III–V materials. The bulk moduli given in table 1 are used.

Compound	$-dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$ (in eV)	$1/B$ (in Mbar^{-1})	$a_g = dE_g^{\Gamma_{15v}-\Gamma_{1c}}/dp$ (in eV Mbar^{-1})
BP	15.2[a]	0.58[a]	8.84[a]
BAs	12.8[a]	0.69[a]	8.88[a]
BSb	7.7[a]	0.92[a]	7.13[a]
GaAs	7.25[b]	1.35[b]	9.8[b], 10.8[c]
GaSb	7.01[b]	1.81[b]	12.7[b], 14.0[c]
InAs	4.88[b]	1.66[b]	8.1[b], 9.6–10.8[c]
InSb	5.54[b]	2.16[b]	11.9[b], 14.0[c]

[a] These values are calculated from the product $-(1/B)\,dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$. The values of the deformation potentials $-dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$ are determined by fitting the $E_g^{\Gamma_{15v}-\Gamma_{1c}}(\ln V)$ curve. The values of the pressure coefficients obtained are slightly modified from those obtained from a direct fitting of the $E_g^{\Gamma_{15v}-\Gamma_{1c}}(p)$ curve and given in table 3.
[b] Recent first-principles calculation [31].
[c] Experimental values taken from references [32–35].

hand, changing P → As → Sb raises the group-V-element orbital energy, thus increasing the coupling with the group-III-element s orbital. On the other hand, heavier group-V elements mean a longer bond length, which acts to reduce the coupling. However, since the bond length increases significantly as the group-V element gets heavier, the bulk moduli decrease significantly. The net result is that the product $-(1/B)\,dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$ increases significantly when P → As → Sb. The small dependence of $a_g^{\Gamma_{15v}-\Gamma_{1c}}$ on the group-V element in boron compounds suggests the interpretation that in this series of compounds B, which is a group-III element, resembles an anion instead of a cation as discussed by Wentzcovitch and Cohen [8] using the LDA within the DFT and the pseudopotential method, Lambrecht and Segall [6] using the linear muffin-tin orbital method (LMTO) within the local density functional, and Surh *et al* [16] by using the *GW*-approximation. As occurs in the charge transfer of BP, BAs, and BSb, the trend in the direct-band-gap pressure coefficients is another anomalous case which can be characterized by reversing the standard assignments for the anion and cation in these compounds. We summarize our observations in table 5, which explains the observed trends.

Table 5. Observed chemical trends for the pressure coefficient of the direct band gap for the $\Gamma_{15v}-\Gamma_{1c}$ transition in boron compounds compared to other III–V compounds.

	III–V		BP, BAs, BSb
Atomic number of the group-V element:	Increases	Constant	Increases
Atomic number of the group-III element:	Constant	Increases	Constant
$1/B$:	Increases	Increases	Increases
$-dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$:	Nearly unchanged	Decreases	Decreases
$dE_g^{\Gamma_{15v}-\Gamma_{1c}}/dp = -(1/B)\,dE_g^{\Gamma_{15v}-\Gamma_{1c}}/d\ln V$:	Strongly increases	Nearly unchanged	Nearly unchanged

4. Concluding remarks

We have performed a pseudopotential self-consistent calculation for the boron compounds BP, BAs, and BSb. The results are summarized as follows:

(i) We have verified through calculations on boron-based semiconducting systems that the ground-state properties of these compounds including the equilibrium lattice constants, bulk moduli, and their first derivatives are described equally well by the LDA.

(ii) The LDA eigenvalue spectrum differs significantly from experimental observations and generally agrees more closely with other *ab initio* calculations. We have predicted that boron-based compounds have the following band-gap orderings: X, Γ, L for BP; and X, L, Γ for BAs and BSb. These materials are predicted to have indirect band gaps by the present first-principles calculation.

(iii) In this study, we have also investigated $a_g^{\Gamma_{15v}-\Gamma_{1c}}$ theoretically for these boron zinc-blende materials. We have predicted the first pressure coefficients for these materials, and found an anomalous behaviour in the trend of these coefficients compared to those of the corresponding III–V compounds. On the basis of the observed chemical trends in $a_g^{\Gamma_{15v}-\Gamma_{1c}}$, we show that group-V-element replacements have a smaller effect in boron compounds than in other III–V compounds. Our results suggest the interpretation that in these materials B resembles an anion instead of a cation. This behaviour is unusual and not typical for other III–V semiconductors, and can be attributed to the lack of cancellation of the p pseudopotential of B which results in the p pseudopotential being much deeper than those of P, As, and Sb.

References

[1] Glass J T, Messier R and Fujimori N (ed) 1990 *Diamond, Silicon Carbide and Related Wide Band-Gap Semiconductors (MRS Symp. Proc. No 162)* (Pittsburgh, PA: Materials Research Society)
[2] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco, CA: Freeman)
[3] Laref A, Bouhafs B, Aourag H and Bouarissa N 1998 *J. Phys.: Condens. Matter* **10** 3195
[4] Sekkal W, Bouhafs B, Aourag H and Certier M 1998 *J. Phys.: Condens. Matter* **10** 4975
[5] Cheong B H, Chang K J and Cohen M L 1991 *Phys. Rev.* B **44** 1053
[6] Lambrecht W R L and Segall B 1991 *Phys. Rev.* B **43** 7070
[7] Phillips J C 1973 *Bonds and Bands in Semiconductors* (New York: Academic)
[8] Wentzcovitch R M, Chang K J and Cohen M L 1986 *Phys. Rev.* B **34** 1071
    Wentzcovitch R M and Cohen M L 1986 *J. Phys. C: Solid State Phys.* **19** 6791
[9] Wentzcovitch R M, Cohen M L and Lam P K 1987 *Phys. Rev.* B **36** 6058
[10] Rodriguez-Hernández P, Gongález-Diaz M and Muñoz A 1995 *Phys. Rev.* B **51** 14 705
[11] Edgar J H 1994 *Properties of Group III Nitrides (Electronic Materials Information Service (EMIS) Datareviews Series)* (London: IEE)
[12] Huang M Z and Ching W Y 1985 *J. Phys. Chem. Solids.* **46** 977
[13] Chrenko R M 1974 *Solid State Commun.* **14** 511
[14] Sanjuro J A, López-Cruz E, Vogl P and Cardona M 1983 *Phys. Rev.* B **28** 4579
[15] Wettling W and Windscheif J 1983 *Solid State Commun.* **50** 33
[16] Surh M P, Louie S G and Cohen M L 1991 *Phys. Rev.* B **43** 9126
[17] Ferhat M, Zaoui A, Certier M and Khelifa B 1996 *Phys. Status Solidi* b **195** 415
[18] Ferhat M, Bouhafs B, Zaoui A and Aourag H 1998 *J. Phys.: Condens. Matter* **10** 7995
[19] Bouhafs B, Aourag H, Ferhat M and Certier M 1999 *J. Phys.: Condens. Matter* **11** 5781
[20] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[21] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[22] Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev.* B **26** 4199
[23] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[24] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[25] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[26] Murnaghan F D 1944 *Proc. Natl Acad. Sci. USA* **30** 5390
[27] Orlando R, Dovesi R, Roetti C and Saunders V R 1990 *J. Phys.: Condens. Matter* **2** 7769
[28] Lichanot A and Causà M 1997 *J. Phys.: Condens. Matter* **9** 3139
[29] Cohen M L 1985 *Phys. Rev.* B **32** 7988
    Lam P K, Cohen M L and Martinez G 1987 *Phys. Rev.* B **35** 9190

[30] Fahy S, Chang K J, Louie S G and Cohen M L 1987 *Phys. Rev.* B **35** 5856
[31] Su-Huai, Zunger A, Choi In-Hwan and Yu P Y 1998 *Phys. Rev.* B **58** R1710
[32] Goni A R, Syassen K and Cardona M 1987 *Phys. Rev.* B **36** 1581
[33] Tsay J, Mita S and Bendow B 1974 *Phys. Rev.* B **10** 1476
[34] Guillaume C B and Lavallard P 1970 *J. Phys. Chem. Solids* **31** 411
[35] Huant S, Dmowski L, Baj M and Brunel L C 1984 *Phys. Status Solidi* b **125** 215
[36] Knittle E, Wentzcovitch R M, Jeanloz R and Cohen M L 1989 *Nature* **337** 349
[37] *Landolt–Börnstein New Series* 1982 Group III, vol 17a, ed O Madelung (Berlin: Springer)
[38] Weast R C, Astle M J and Beyer W H 1987 *Handbook of Chemistry and Physics* 67th edn (West Palm Beach, FL: Chemical Rubber Company Press)