

First-principles study of structural and electronic properties of BSb

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 7995

(<http://iopscience.iop.org/0953-8984/10/36/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 17:16

Please note that [terms and conditions apply](#).

First-principles study of structural and electronic properties of BSb

M Ferhat[†], B Bouhaf[‡], A Zaoui[‡] and H Aourag[‡]

[†] Laboratoire de Physique, Institut du Tronc Commun, Université des Sciences et de la Technologie d'Oran (USTO), Oran, Algeria

[‡] Computational Materials Science Laboratory, Physics Department, University of Sidi-Bel-Abbes, 22000 Algeria

Received 11 February 1998, in final form 11 May 1998

Abstract. We have performed the first *ab initio* investigation of the boron compound BSb with zinc-blende structure, and have compared its structural and electronic properties with those of other boron compounds such as BN, BP, and BAs. The calculations are performed using a plane-wave expansion within the local density approximation and the pseudopotential approximation. Results are given for the lattice constant, bulk modulus, band structure, and total valence charge density. The electronic band structure of BSb proved to have features that differ from those of other III–V materials. It is found that BSb is less ionic than other III–V compounds, with an indirect band gap, and presents the same anomalous behaviour as BP and BAs.

1. Introduction

Despite their technological promise, boron compounds such as BN, BP, and BAs have received less attention than other III–V materials. Although they are members of the III–V semiconductor family, boron compounds have a number of remarkable properties which set them apart from other III–V materials and make them particularly worth studying. These compounds, such as BP and BAs, appear to be the least studied of the III–V semiconductor group. This is probably because of the difficulties involved in their synthesis. Furthermore, the boron compounds BP, BAs, and BSb 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 of elements from other rows. The reasons for these fundamental differences between these compounds and other III–V materials are apparent from band-structure and charge-density calculations. According to the Phillips scale of ionicity [1], BP and BAs are the most covalent of the III–V semiconductors, and there are interesting consequences of this property. It was found that BP and BAs have the smallest heteropolar gaps of the group III–V compounds.

There have been many first-principles theoretical studies [2, 3] of the structural properties of BN. Although there have been several theoretical studies of the boron compounds BP and BAs, little experimental work has been devoted to these compounds. The ground-state (equilibrium lattice constant and bulk modulus) and electronic properties have been calculated by Wentzcovitch *et al* [4, 5]. The high-pressure properties of BP and BAs were also discussed by Wentzcovitch *et al* [6]. All of these studies utilized the local density approximation (LDA) within density functional theory and the pseudopotential method. To

provide predictive information on the excitation energies of these compounds, Surh *et al* [7] employed the GW approximation to properly include the effects of exchange and correlation on the quasiparticle energies.

To broaden the search for candidate materials with the cation—usually of an element of column III—belonging to the first row and the anion—usually of an element of column V—belonging to a lower row in the periodic table, we have examined the properties of the last member of the boron compounds family, BSb. The description of these properties within models seems to be problematic because of the lack of experimental data and because the state of the BSb compound is intermediate between covalency and ionicity. In BSb, the very attractive B potential competes with the Sb potential for the valence charge, a situation of small heteropolarity and consequently small ionicity. In the past decade, it has become possible to compute with great accuracy a number of electronic and structural parameters of solids from first-principles calculations. This development has opened up many exciting possibilities for the study of condensed matter, since today it is possible to predict properties of solids which were formerly inaccessible to experiment. To provide a better understanding of the structural and electronic properties of BSb, first-principles calculations are certainly desirable. Although there have been a few studies of the structural and electronic structure of BN, BP, and BAs [8–13], to our knowledge there are no published reports of theoretical studies of BSb. The existence of this material in its zinc-blende form has not been reported, so its properties are unknown. In assessing the usefulness of BSb for device applications, it is important to understand its energy-band structure, and to predict the fundamental band gap. The second step is to determine the bonding properties of this compound, especially the ionicity factor (f_i), so that the properties exhibited during phase transitions can be assessed. We will make theoretical predictions for both the bulk modulus (B_0) and the ionicity factor (f_i) in this paper.

In this paper, we theoretically investigate the structural and electronic properties of BSb in the zinc-blende structure, and compare its properties to those of BN, BP, and BAs semiconductors. Our calculations are *ab initio*, and have used the local density approximation (LDA) within density functional theory and the pseudopotential approximation. Simple plane-wave expansions are used for the electron eigenstates. Although this approach fails to describe the energy of the excited states accurately, it usually provides very good results for ground-state properties.

The remainder of the paper is organized as follows. In section 2 we describe the computational approach used to calculate the structural and electronic properties. Electronic band-structure and charge-density results are presented and discussed in section 3, and concluding remarks are presented in section 4.

2. The method of calculation

The use of pseudopotentials in the density functional formalism [14, 15] has proved to be very successful in calculating and predicting the ground-state properties of solids. The LDA and pseudopotential approximations have been used in a number of similar calculations with great success. This success can be mainly attributed to the introduction of so-called norm-conserving pseudopotentials [16–18], which have the desired property of being transferable to environments other than the one in which they are generated.

Our calculations are *ab initio* and require no experimental input or fitting parameters. However, there are a number of decisions which must first be made. In particular, one must choose the type of pseudopotential to be used, as well as the approximate analytic form to be used for the exchange–correlation functional.

For BSb, we apply the density functional theory within the local density approximation [14, 15] in a plane-wave basis, with the norm-conserving nonlocal pseudopotentials of Bachelet, Hamann and Schlüter [17]. We adopt the Ceperley–Alder-type exchange–correlation potential [19], as parametrized by Perdew and Zunger [20].

The wavefunctions are expanded in a complete set of plane waves with the wavevector $\mathbf{k} + \mathbf{G}$, where \mathbf{k} is the wavevector in the first Brillouin zone and \mathbf{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, $E_c = 23$ Ryd, which has been found by testing to be sufficient to ensure convergence. We have scaled the cut-off with respect to the lattice constant to keep the number of plane waves constant at approximately 440. The total structural energy is calculated self-consistently with six special \mathbf{k} -points [21] in the irreducible wedge of the Brillouin zone.

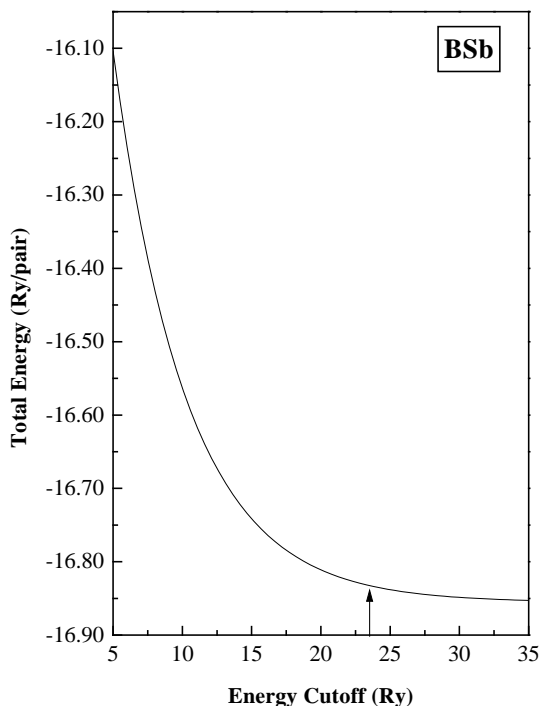


Figure 1. The convergence of the total energy versus the energy cut-off for BSb.

3. Results

3.1. Structural properties

We show in figure 1 the convergence of the total energy versus the energy cut-off for BSb. The lattice parameter a used for this convergence study is 5.1 Å. From this curve we are able to estimate a value for the energy cut-off such that the total energy converges to within an accuracy of 4%. On the basis of this test and practical considerations, we have chosen an energy cut-off value of 23 Ryd for our calculations. This is the energy cut-off that we then used for the remainder of this work.

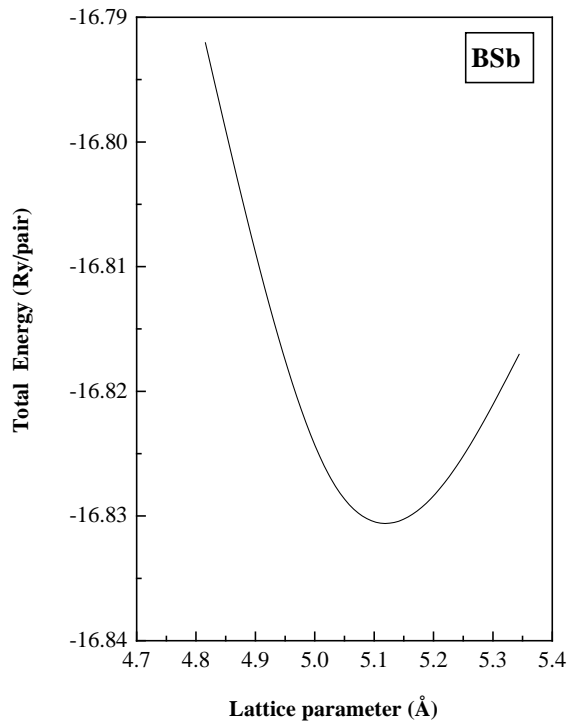


Figure 2. The calculated total energy as a function of the lattice parameter for zinc-blende BSb.

The calculated ground-state energy plotted as a function of the lattice constant for BSb in the zinc-blende structure is shown in figure 2. The total energy is computed for a selection of lattice constants from 4.8 Å to 5.3 Å and then fitted to the linear Murnaghan equation of state [22]. The computed equilibrium lattice constant is 5.12 Å. From this fit we also calculated the value of the bulk modulus to be 115.8 GPa and its pressure derivative to be 5.28. None of these properties have been measured or calculated previously. Our results for BSb are given in table 1. In order to give some comparison, the *ab initio* calculation results for the structural properties for BN, BP, and BAs in the zinc-blende structure are also listed in table 1. These compounds have smaller lattice constants and larger bulk moduli than other III–V compounds. Despite some differences in detail, the general features of the equilibrium structural results are very similar.

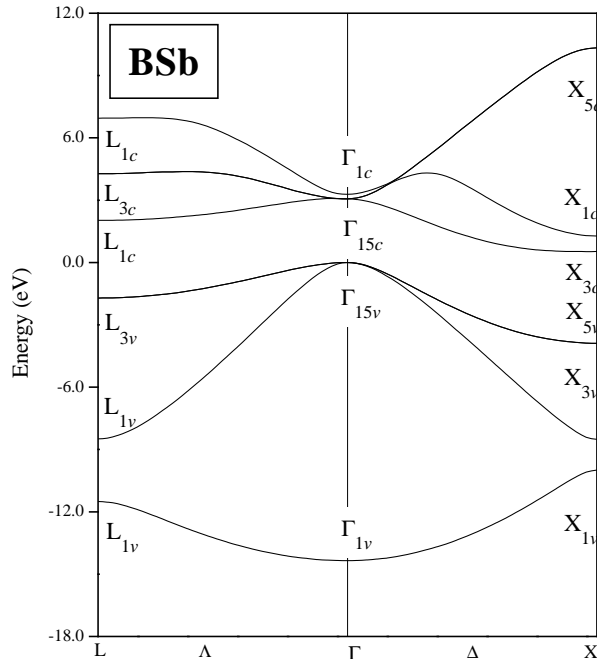
The key feature shared by the boron compounds is that they contain an element of the second row of the periodic table. Since the latter boron compounds do not have p-like core states below the 2p valence level, the covalent component of the bonding is stronger than for other III–V semiconductors. This leads to small lattice constants, high cohesive energies, and large bulk moduli.

3.2. Electronic properties

3.2.1. The electronic band structure. The electronic band structure of zinc-blende BSb is shown in figure 3. There is an overall topological resemblance of the present band structure and those calculated by Wentzcovitch *et al* [4, 5] for BP and BAs compounds. The lower part of the valence band is dominated by Sb 5s states and the upper part by B and Sb p

Table 1. The lattice constant and bulk modulus for BSb compared to those for the other boron compounds BN, BP, and BAs, in the zinc-blende structure.

	a (Å)	B (GPa)	B'
BN	3.606 ^a	367 ^a	367 ^b
BP	4.558 ^a	166 ^a	166 ^b
BAs	4.777 ^a	145 ^a	138 ^b
BSb	5.12 ^c	115 ^c	108 ^b 5.28 ^c

^a References [4–6].^b Calculated using the empirical relation of reference [29].^c This work.**Figure 3.** The electronic band structure of zinc-blende BSb at the calculated equilibrium volume.

states, the B s states contributing to both parts of the valence band. Our estimation of the full valence bandwidth is 11.504 eV. Figure 3 shows an indirect gap near X ($\Gamma_{15v} \rightarrow \Delta_{\min}$) with a very small magnitude of 0.527 eV. Table 2 summarizes the important features of the band structure of BSb.

The most prominent features of the band structure of BSb are: (i) Δ_{\min} is close to X_{3c} instead of X_{1c} as was found for most III–V semiconductors; and (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 is a common feature for the covalent semiconductors BP, BAs, and BSb [4, 5]. This is a manifestation of the relative energies of the p and s levels, and thus is a result of the absence of a p -like core for $2p$ wavefunctions. The Γ_{1v} state is composed primarily of anion orbitals. The conduction band state Γ_{1c} is complementary to Γ_{1v} in being its antibonding counterpart. However, whereas the bonding Γ_{1v} state is mostly contributed

Table 2. A summary of the important features of the band structure of BSb (the energies are in eV).

L_{1v}	-11.504	Γ_{1v}	-14.350	X_{1v}	-9.991
L_{1v}	-8.487	Γ_{15v}	0.0	X_{3v}	-8.516
L_{3v}	-1.712	Γ_{15c}	3.061	X_{5v}	-3.885
L_{1c}	2.027	Γ_{1c}	3.284	X_{3c}	0.528
L_{3c}	4.272			X_{1c}	1.274
L_{1c}	6.947			X_{5c}	10.330

by anion s orbitals, the antibonding Γ_{1c} state also contains a sizable contribution from the cation s orbitals. One might note that BN has Γ_{1c} lower than Γ_{15c} , while BSb has the order reversed compared to that for BN, the p -like (Γ_{15c}) state lying below the s -like Γ_{1c} state. The conduction band state in BN is purely s -like, and, being an antibonding state, has important B s components.

The valence band state X_{1v} is seen to be an anion s state (with some cation p character) in BSb. Its antibonding counterpart is the conduction band state X_{1c} . The conduction band state X_{3c} is complementary to X_{1c} . Note that having chosen the origin of our coordinate system at the cation site, we find the X_{3c} state in BSb to be lower in energy than the X_{1c} state, and hence X_{1c} and X_{3c} interchange their roles compared to the case in which the origin was chosen to be at the anion site [23]. The difference between these states is that X_{3c} states have associated charge densities, which are concentrated mostly in the interstitial regions close to the anions, while X_{1c} states have associated charge densities in the interstitial regions close to the cations. The symmetries are such that X_{3c} and X_{3v} have s states centred on the cation and p states centred on the anion, while for X_{1c} and X_{1v} this order is reversed.

Table 3. 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.

	BN		BP		BAs		BSb
	LDA	GW	LDA	GW	LDA	GW	This work
$\Gamma_{15v} \rightarrow \Gamma_{15c}$	8.6 ^a	11.4 ^b	3.3 ^a	4.4 ^b	3.3 ^a	4.2 ^b	3.06
$\Gamma_{15v} \rightarrow X_{1c}$	4.2 ^a	6.3 ^b		2.0 ^b		1.86 ^b	1.274
$\Gamma_{15v} \rightarrow \Delta_{\min}$			1.2 ^a	1.9 ^b	1.25 ^a	1.6 ^b	0.527
$\Gamma_{1v} \rightarrow \Gamma_{15v}$	20.3 ^a	23.1 ^b	15.3 ^a	16.8 ^b	15.17 ^a	16.7 ^b	14.35

^a References [4, 5].

^b Reference [7].

The important features of the band structures (bandwidths, gaps)—comparing the LDA and GW calculations (compiled from references [4, 5, 7]) for BN, BP, BAs, and BSb in the zinc-blende structure—are listed in table 3. All of the materials are found to be indirect, with the conduction band minima along the Δ direction, except BN in which the lowest conduction band minimum occurs at X. It is interesting to note that BSb has a small band-gap value compared to those 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 and BAs are seriously underestimated in the LDA, the band gap of BSb may be larger than that indicated in table 3.

It is well known that the GW calculations give energy band gaps in excellent agreement

with experiment, as shown by Surh *et al* [7] 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 for semiconductors. The band gaps listed in table 3 are underestimated by 2.1, 0.7, and 0.35 eV for BN, 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 compound BAs. Thus, for BSb, for which we predict a LDA band gap of 0.527 eV, a correction of 0.35 eV is added, to give an adjusted band gap of 0.87 eV.

Both BAs and BSb have minima in their conduction bands in the X direction, but if we assume that the correction corresponds to a rigid shift of all of the conduction bands, then the correction should work equally well for other conduction band minima.

To understand this feature qualitatively, we consider a simple molecular-orbital picture. The states of interest are Γ_{1c} and Γ_{15c} , which can be described qualitatively in our tight-binding model as follows.

(i) Retaining the cation s orbital (with energy E_{sc}) and the anion s orbital (with energy E_{sa}). Since both have the same symmetry representation Γ_1 , they can interact through the coupling matrix V_{ss} forming a lower-energy bonding state (weighted more by the lower-energy E_{sa}):

$$\varepsilon(\Gamma_{1v}) = \frac{(E_{sa} + E_{sc})}{2} - \left[\left(\frac{(E_{sa} - E_{sc})}{2} \right)^2 + V_{ss}^2 \right]^{1/2} \quad (1)$$

and an antibonding state (weighted more by a higher-energy E_{sc}):

$$\varepsilon(\Gamma_{1c}) = \frac{(E_{sa} + E_{sc})}{2} + \left[\left(\frac{(E_{sa} - E_{sc})}{2} \right)^2 + V_{ss}^2 \right]^{1/2}. \quad (2)$$

The two states E_{sa} and E_{sc} will repel each other; the bonding state is lowered relative to E_{sa} and the antibonding state is pushed upwards relative to E_{sc} by the same amount of energy ΔE_{ss} [13]. BSb is characterized by this strong level repulsion or s-s interaction ΔE_{ss} . We can obtain this s-s interaction by calculating $\varepsilon(\Gamma_{1c}) - E_{sc}$.

(ii) Retaining the cation p orbital (with energy E_{pc}) and the anion p orbital (with energy E_{pa}). Since they have the same symmetry representation Γ_{15} , they can interact through the coupling matrix V_{pp} forming a lower-energy bonding state:

$$\varepsilon(\Gamma_{15v}) = \frac{(E_{pa} + E_{pc})}{2} - \left[\left(\frac{(E_{pa} - E_{pc})}{2} \right)^2 + V_{pp}^2 \right]^{1/2} \quad (3)$$

and an antibonding state:

$$\varepsilon(\Gamma_{15c}) = \frac{(E_{pa} + E_{pc})}{2} + \left[\left(\frac{(E_{pa} - E_{pc})}{2} \right)^2 + V_{pp}^2 \right]^{1/2}. \quad (4)$$

The two states E_{pa} and E_{pc} will repel each other; the bonding state is lowered relative to E_{pa} and the antibonding state is pushed upwards relative to E_{pc} by the same amount of energy ΔE_{pp} ($\Delta E_{pp} = \varepsilon(\Gamma_{15c}) - E_{pc}$). Hence Γ_{1c} and Γ_{15c} are formed by the level repulsions (i) and (ii) respectively.

The calculated level repulsions ΔE_{ss} and ΔE_{pp} for BN and BSb, and for the other III-V compounds AlP, GaAs, and InSb, are given in table 4. For all of these compounds

Table 4. The calculated s–s and p–p interactions (in eV).

	ΔE_{ss}	ΔE_{pp}
AIP	4.86	1.32
GaAs	4.21	1.04
InSb	3.70	0.59
BN	11.93	3.60
BSb	7.86	1.33

except BSb, the values of ΔE_{ss} and ΔE_{pp} are taken from reference [13], while for BSb, the tight-binding parameters [24] used are fitted to our calculated energy gaps. For BN and BSb, we see an increase of the s–s repulsion effect compared with the case for other III–V compounds. However, the p–p repulsion effect is important only for BN, while it has the same magnitude for BSb, AIP, GaAs, and InSb. As a consequence, in BSb the cation s orbital and the anion s orbital interact very strongly and Γ_{1c} is pushed to above Γ_{15c} . This strong s–s interaction causes the direct gap of BSb to be of Γ_{15c} symmetry. In contrast, the direct gap found in BN is of Γ_{1c} symmetry, and the reason for this is that in BN the p–p interaction is also strong compared to the case for BSb. This p–p interactions tend to compensate for the changes in the s–s interaction. No such compensation takes place in the BSb compound. Therefore the band structure of BSb is very different from those of the other compound semiconductors. The parameter V_{ss} represents overlaps between the s orbitals on the anion and on the cation separated by the nearest-neighbour distance, and its value mainly influences the shift of the conduction band edge. It seems therefore that the physical mechanism leading to inversion of the Γ_{1c} and Γ_{15c} states in BSb is the s–s repulsion effect.

3.2.2. The charge density and the ionicity factor. To illustrate the degree of covalency in BSb, we perform charge-density calculations. The electronic charge density of BSb differs considerably from that of typical III–V semiconductors. The important feature in BSb is the remarkable shift of the charge density toward the B atom. This is immediately apparent from the real-space representation of the valence charge density along the bond in figure 4. The overall shape of the charge distribution suggests a highly covalent B–Sb bonding like in BP and BAs. The net charge transfer from Sb to B, which indicates the degree of the ionicity of the bonding, is not as large as is suggested by figure 4; there remains a considerable degree of covalent character in the B–Sb bond. A charge distributed covalently along the bond is found. We notice that the chemical bonding is strongly covalent—i.e., a weak charge is transferred from Sb to B. This figure presents a slightly higher peak close to B. This feature is also found for BP and BAs [4, 5]. This behaviour is unusual and not typical for 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 that of Sb. 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 the B ion resembles an anion. BSb appears to behave like the typical boron compounds BP and BAs in its charge distribution. The similarity of our results for BSb to those for other boron compounds such as BP and BAs suggest the interpretation that in this material the B ion resembles an anion instead of a cation as was found for BP and BAs [6]. Like BP and BAs, BSb is another anomalous case which can be characterized by reversing the standard assignments for the anion and cation in this compound.

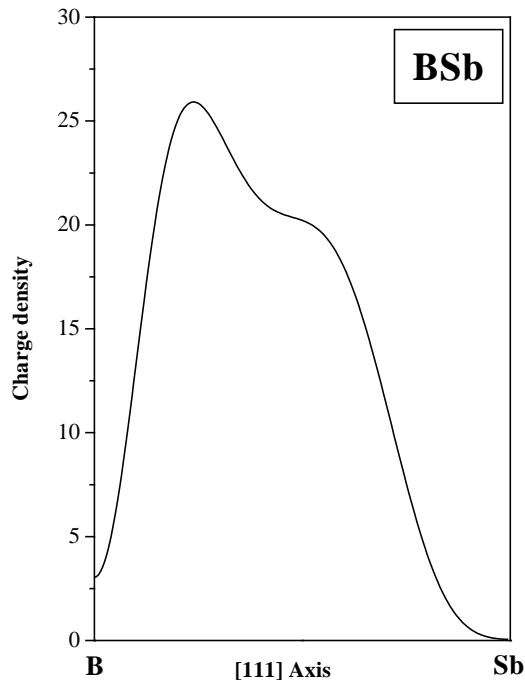


Figure 4. The total valence charge density along the bond of BSb.

The ionic character of BSb can be related to the charge transfer between the cation and anion. In BSb the bonding charge is displaced from the mid-point between the atoms towards the B atoms. This displacement increases as the difference between the electronegativity values of the two atoms increases. Charge distributions in agreement with these expectations have been calculated by Wentzcovitch *et al* [4, 5] for BP and BAs using an *ab initio* method. The driving force behind the displacement of the bonding charge is the greater ability of B in these compounds to attract electrons compared to N in BN. The bonding characteristics do not change from BN to the isoelectronic series of semiconductors BP, BAs, and BSb, which present an opposite charge transfer compared to BN and other III–V materials.

The charge asymmetry of a cation–anion bond was suggested to be a measure of the degree of ionic character, and thus of the ionicity of binary compounds [25]. The Garcia and Cohen ionicity factor is defined as

$$f_i = \sqrt{S_s/S_a} \quad (5)$$

where S_s , S_a are measures of the strengths of the symmetric and antisymmetric components of the charge density, respectively, and are defined as [25]

$$S_{s/a} \equiv (1/V_0) \int_{V_0} \rho_{s/a}^2 d^3r.$$

To obtain an estimate of the value of the ionicity factor for the compound BSb, we use two different approaches: first the approach of Christensen *et al* based on the tight-binding parameters [27], and second the Garcia and Cohen approach based on the valence charge-density calculation [25]. The scaling law introduced by Garcia and Cohen was found to be successful in predicting the f_i -behaviour for a wide variety of semiconductors, although BP and BAs were checked against the Phillips ionicity scale. The large scatter in theoretical

Table 5. The calculated ionicity factor, f_i , of BSb compared to those for the other boron compounds BN, BP, and BAs. The $|X_{1v}-X_{3v}|$ band splittings, and the differences in electronegativities, $|\chi_A - \chi_B|$, are also listed for comparison.

	$ X_{1v}-X_{3v} $	$ \chi_A - \chi_B $	f_i		
BN	5.5 ^a	1.00	0.485 ^b	0.256 ^c	0.221 ^d
BP	1.9 ^a	0.36	0.085 ^b	0.006 ^c	0.032 ^d
BAs	2.7 ^a	0.43	0.116 ^b	0.002 ^c	0.044 ^d
BSb	1.47 ^e	0.69	0.12 ^f	0.03 ^g	0.112 ^d

^a Reference [7].

^b Reference [25].

^c Reference [1].

^d Estimated using Pauling's definition [1].

^e This work.

^f Calculated by using the Garcia and Cohen approach [25].

^g Calculated by using the tight-binding approach [27].

results for the ionicity of these compounds has made it difficult to assess the accuracy of the various approaches. The calculated ionicity values for BSb compared with those of BN, BP, and BAs are summarized in table 5. We found a value of 0.12, which is close to that found by Garcia and Cohen for BAs (0.116). We can note that as a result of the small degree of ionic character of BSb, this compound shares many properties with BP and BAs. These results suggest a weakly ionic character for BSb, which is the most covalent III–V compound. The ionicity of BSb is so low that the ionic character is reversed. The ion of the group-III element, B, in BSb becomes the anion, where more charge is placed around it than around Sb, while in BN most of the valence charge was found concentrated around N [5]. Behaviour similar to that of BSb was observed for BP and BAs [4, 5]. This fact indicates that the electron attraction of B is greater than that of P, As, and Sb in BP, BAs, and BSb, respectively. This has been noted to have important effects for the bonding at interfaces between these and related materials [12].

In the present work we attempt to show that the ionicity factor for the boron compounds can be related to the difference in electronegativities of the two atoms. To give a quantitative measure of the ionicity for these compounds, we use Pauling's definition [1] of the ionicity of a single bond and the Phillips electronegativity values for B, N, P, As, and Sb [1]. Our aim is to show that this expression gives a good approximation for the ionicity factor for BN, BP, BAs, and BSb. We can obtain a quick estimation of the ionicity factors of these compounds by using the following equation:

$$f_i^P = 1 - \exp[-(\chi_A - \chi_B)^2/4] \quad (6)$$

where χ_A , χ_B are the electronegativities of atoms A and B, respectively.

For the borides BP, BAs, and BSb there is instead a reduction in ionicity. The result found here for BSb is also in agreement with our value calculated when using the Garcia and Cohen approach (see table 5 for a comparison).

Another trend displayed by our calculation concerns the correlation between the difference in electronegativities between the cation and the anion and the ionicity. Consider the isoelectronic series of semiconductors BP, BAs, and BSb. According to the Garcia and Cohen ionicity scale, the ionicity increases from 0.085 (0.032 when using Pauling's definition) for BP to a maximum of 0.12 (0.112 when using Pauling's definition) for BSb. This is in agreement with the expectation that the ionicity increases as the difference in the core size of the cation–anion atoms increases. Our results suggest that the ionicity factor

for the boron compounds increases when the difference in electronegativities increases.

We notice that in BSb the direction of charge transfer ($\text{Sb} \rightarrow \text{B}$) coincides with the atomic electronegativity difference (B having a larger electronegativity value than Sb; see table 5). In BN (B having a smaller electronegativity value than N) the usual normal trend persists, as found for other III–V materials. The larger value of the electronegativity for B compared to P, As, and Sb mirrors the charge rearrangements observed in BP, BAs, and BSb. The bonding characteristics change from the highly covalent bonding in BP, BAs, and BSb to the bonding of the almost ionic BN compound in this family.

A correlation between the ionic bonding and electronic properties in these compounds exists as predicted by Phillips [1]. An interesting feature linked to the ionicity is the gap between the first and second valence bands at X. This gap is related to the cation and anion potentials. This ‘antisymmetric’ gap has been proposed as a measure of the crystal ionicity [26]. The partially ionic character of BSb leads to the opening of a gap in the valence band of 1.47 eV separating the X_{1v} and the X_{3v} valence bands. We notice the small splitting for this compound compared to other III–V materials. This can also be seen clearly in certain band splittings, e.g. the X_{1v} – X_{3v} splitting, in these compounds, as can be seen in table 5. For instance, the X_{1v} – X_{3v} splitting increases with increasing electronegativity mismatch between the cation and anion, and thus with increasing ionicity. The results indicate that BSb exhibits a slightly smaller splitting than BP and BAs. This result cannot affect the conclusion reached above, since this difference is an order of magnitude smaller than the calculated bandwidth for this compound. This is a very interesting result in view of the structural phase transitions of this compound.

4. Conclusion

We have performed first-principles pseudopotential calculations to study the structural and electronic properties of BSb. We have calculated ground-state properties of BSb including the lattice constant and bulk modulus. The valence charge density in this material is covalently distributed and similar to that of BAs. From the investigation of the charge density, it is found that BSb shows a small difference in chemical bonding and ionicity compared to BAs. This material is predicted to have an indirect band gap by the present first-principles calculation. An indirect gap of about 0.527 eV is found. Due to the similarity in the strengths of the chemical bonds for the series BP, BAs, and BSb of compounds, the ionicity in these materials is smaller.

The reported calculations provide the first structural and electronic results obtained from first principles for this compound. The results reveal the fundamental importance of the nature of the chemical bonding and the ionicity in determining the properties of this compound.

Acknowledgment

One of the authors (MF) wishes to thank the International Centre for Theoretical Physics (ICTP), Trieste, for providing the supportive environment in which this work was initiated.

References

- [1] Phillips J C 1973 *Bonds and Bands in Semiconductors* (New York: Academic)
- [2] Rodríguez-Hernández P, González-Díaz M and Muñoz A 1995 *Phys. Rev. B* **51** 14 705

- [3] Edgar J H (ed) 1994 *Properties of Group III Nitrides (Electronic Materials Information Service (EMIS) Datareviews Series)* (London: Institute of Electrical Engineers)
- [4] Wentzcovitch R M and Cohen M L 1986 *J. Phys. C: Solid State Phys.* **19** 6791
- [5] Wentzcovitch R M, Chang K J and Cohen M L 1986 *Phys. Rev. B* **34** 1071
- [6] Wentzcovitch R M, Cohen M L and Lam P K 1987 *Phys. Rev. B* **36** 6058
- [7] Surh M P, Louie S G and Cohen M L 1991 *Phys. Rev. B* **43** 9126
- [8] Huang M Z and Ching W Y 1985 *J. Phys. Chem. Solids* **46** 977
- [9] Chrenko R M 1974 *Solid State Commun.* **14** 511
- [10] Sanjuro J A, López-Cruz E, Vogl P and Cardona M 1983 *Phys. Rev. B* **28** 4579
- [11] Wettling W and Windscheif J 1984 *Solid State Commun.* **50** 33
- [12] Lambrecht W R L and Segall B 1991 *Phys. Rev. B* **43** 7070
- [13] Ferhat M, Zaoui A, Certier M and Khelifa B 1996 *Phys. Status Solidi b* **195** 415
- [14] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
- [15] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1113
- [16] Bachelet G B, Greenside H S, Baraff G A and Schlüter M 1981 *Phys. Rev. B* **24** 4745
- [17] Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev. B* **26** 4199
- [18] Hamann D R, Schlüter M and Chiang C 1979 *Phys. Rev. Lett.* **43** 1494
- [19] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
- [20] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [21] Chadi D J and Cohen M L 1975 *Phys. Status Solidi b* **68** 405
- [22] Murnaghan F D 1944 *Proc. Natl Acad. Sci. USA* **30** 5390
- [23] Wood D M, Zunger A and de Groot R 1985 *Phys. Rev. B* **31** 2570
- [24] Vogl P, Hjalmarson H P and Dow J D 1983 *J. Phys. Chem. Solids* **44** 365
- [25] Garcia A and Cohen M L 1993 *Phys. Rev. B* **47** 4215
- [26] Chelikowski J R, Wagener J J, Weaver J H and Jin A 1989 *Phys. Rev. B* **40** 9644
- [27] Christensen N E, Satpaty S and Pawlowska Z 1987 *Phys. Rev. B* **36** 1032
- [28] Cody G D 1984 *Semiconductors and Semimetals* vol 21B, ed J I Pankove (New York: Academic) p 11 and references therein
- [29] Cohen M L 1985 *Phys. Rev. B* **32** 7988