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B Bouhafs†, H Aourag†, M Ferhat‡ and M Certier§

† Computational Materials Science Laboratory, Physics Department, University of
Sidi-Bel-Abbes, 22000, Algeria
‡ Laboratoire de Physique, USTO, 31100-Oran, Algeria
§ LSOM—IUT Mesures Physiques, 57078-Metz Cédex 3, France

E-mail: `udlvrpg@ist.cerist.dz` (B Bouhafs)

Abstract.   We present first-principles calculations of the bonding properties for the series of boron
compounds BP, BAs, and BSb. The plane-wave pseudopotential approach to density functional
theory in the local density approximation has been used to calculate the equilibrium properties,
i.e., the ground-state energy, the lattice constant, the bulk modulus, its pressure derivative, and
the ionicity factor. The valence electron density is used to study the modification of the bonding
with respect to different pressures. The calculated electronic charge densities present an anomalous
behaviour which can be characterized by reversing the standard assignments for the anion and cation
in these compounds. The competition between the ionic and the covalent character in these materials
is discussed in relation to the charge transfer. Estimates of the ionicity and its pressure derivative
for the series of boron compounds are presented. The distribution of the valence charge density
suggests that the bonding in these materials is less ionic than in other zinc-blende compounds.

1. Introduction

Interest in solids formed from atoms with low atomic numbers has recently increased greatly
[1], because of the potentially unique properties of these materials. Some of the 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.

   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—the 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].

   The electronic valence configuration is $1s^2 2s^2 2p^1$ for boron atoms and $ns^2 np^3$ for group-V
elements ($n = 2$, 3, 4, and 5 for N, P, As, and Sb, respectively). These atomic configurations
may change with the compound due to the crystalline environment. This change is evaluated
while taking bonds in the purely ionic limit, and assigning electrons to the most electronegative
element of each bond, in order to obtain a net charge on atoms. The boron compounds are
strongly covalent since the electronegativity of the P (1.64), As (1.57), and Sb (1.31) anions

is 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 that BX, X being P, As, or Sb, compounds 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.

The anomalously deep-lying 2s and 2p levels have a marked effect on the ionicity of the boron-based semiconductors. Since, in the case of BP, BAs, or BSb, the anomalously deep valence levels belong to the group-III atom, the ionicity of these compounds compared to other III–V semiconductors is strongly reduced. 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. For BN, on the other hand, the deep valence levels are those of the group-V atom (N in this case) and that enhances the ionicity appreciably [2]. As we will show, the ion character in BP, BAs, and BSb is actually reversed, B playing the role of the anion. Independently, Wentzcovitch *et al* [9] came to the same conclusion and provided additional evidence for the inverted ion character on the basis of the behaviour of BP and BAs under high pressure.

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 be apparent from the charge-density calculations. In assessing the usefulness of these materials for device applications, it is important to understand their bonding properties, especially the ionicity factor (f_i), so that the properties for phase transitions can be assessed. Although there have been several studies for BN, BP, and BAs compounds [8–17], to our knowledge, except our published paper [18], there are no published reports of theoretical studies for BSb.

In this paper, we are interested in finding common trends and differences in the electronic charge density for the whole family of BX (X = P, As, Sb) crystals. So, as we want to analyse the evolution through the family, 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. 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 electron charge distribution. To perform this analysis, it is interesting to use the ionicity as the driving concept, through charge-density calculations obtained from density functional theory.

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 for the whole BX family, and concluding remarks are presented in section 4.

2. Calculation

The method used is based on the density functional theory (DFT) that determines the ground-state properties of an electron system from the knowledge of its density $\rho(r)$ [19]. This method requires only a specification of the ions present (by their atomic number). It allows us to map the many-electron problem onto a set of one-electron equations [20]. Then, the total energy

$E_T[\rho]$ of the system is written as a functional of $\rho(\boldsymbol{r})$.

In the equation that gives the functional $E_T[\rho]$ there appears the exchange and correlation energy E_{xc}, which is generally not known. For purposes of practical calculations, an approximation of this term has to be introduced. The Hohenberg–Kohn theorem [19] provides some motivation for using approximate methods to describe the exchange–correlation energy as a function of the electron density. The most commonly used approximation is referred to as the local density approximation (LDA).

Recent progress has been made going beyond the LDA by adding gradient terms of the electron density to the exchange–correlation energy or its corresponding potential. This has led to the generalized gradient approximation (GGA) in various parametrizations, e.g. the one given by Perdew *et al* ([21] or [22]).

It is recognized that non-local forms of the exchange and correlation potential, such as the GGA, may be important in systems where the wavefunctions have significant localized character, which is the case for boron. This more sophisticated approximation to E_{xc} relates the exchange–correlation energy also to the gradient of the electron density [21], but it usually retains an explicit density dependence. The GGA typically reduces the underestimation of the lattice parameters in crystals.

The calculation of the functional $E_T[\rho]$ also requires the use of atomic potentials. These potentials must produce the atomic core states as well as the valence states, and thus exhibit strong divergences. But, if one notices that the core states in crystals are similar to those in free atoms, one may replace potentials in the chemically important region beyond the core radius. In conjunction with the use of pseudopotentials, we use a plane-wave expansion for the wavefunction.

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 the series of compounds, BP, BAs, and BSb, we apply the DFT within the LDA [19,20] in a plane-wave basis, with the norm-conserving non-local pseudopotentials of Bachelet, Hamann and Schlüter (BHS) [23] without empirical parameters, for both species of atoms. We adopt the Ceperley–Alder-type exchange–correlation potential [24], as parametrized by Perdew and Zunger [25]. 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 [20].

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

The wavefunctions are expended 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.

3. Results

3.1. Structural properties

First of all we have performed convergence tests of the total energy at different plane-wave cut-offs. We show in tables 1–3 the convergence of the total energy versus the energy cut-off for BP, BAs, and BSb compounds. The $\boldsymbol{k}$-space summation for the undistorted lattice

Table 1. Convergence behaviour of the lattice constant a (Å), the bulk modulus B_0 (Mbar), the derivative of the bulk modulus with respect to the pressure B'_0, and the minimum ground-state energy E_{min} (Ryd) with respect to the kinetic energy cut-off E_{cut} (Ryd) for BP. The total energy has been fitted to the Murnaghan equation of state.

E_{cut}	a	B_0	B'_0	E_{min}
16	4.552	1.36	6.69	−18.88335
20	4.532	1.66	3.29	−18.93825
24	4.513	1.63	4.06	−18.96769
30	4.504	1.67	3.32	−18.99497
35	4.488	1.72	3.90	−19.00951
40	4.484	1.70	3.60	−19.01908
60	4.475	1.72	3.76	−19.03526

Table 2. Convergence behaviour of the lattice constant a (Å), the bulk modulus B_0 (Mbar), the derivative of the bulk modulus with respect to the pressure B'_0, and the minimum ground-state energy E_{min} (Ryd) with respect to the kinetic energy cut-off E_{cut} (Ryd) for BAs. The total energy has been fitted to the Murnaghan equation of state.

E_{cut}	a	B_0	B'_0	E_{min}
16	4.808	1.25	4.69	−18.32797
20	4.758	1.41	4.37	−18.37879
24	4.750	1.32	4.31	−18.40359
30	4.744	1.40	3.92	−18.42992
35	4.734	1.39	3.98	−18.44412
40	4.728	1.44	4.00	−18.45425
60	4.718	1.44	4.02	−18.46869

Table 3. Convergence behaviour of the lattice constant a (Å), the bulk modulus B_0 (Mbar), the derivative of the bulk modulus with respect to the pressure B'_0, and the minimum ground-state energy E_{min} (Ryd) with respect to the kinetic energy cut-off E_{cut} (Ryd) for BSb. The total energy has been fitted to the Murnaghan equation of state.

E_{cut}	a	B_0	B'_0	E_{min}
16	5.232	0.87	6.14	−16.75421
20	5.193	0.96	5.28	−16.79413
24	5.190	1.03	3.92	−16.82295
30	5.173	1.04	4.11	−16.84922
35	5.161	1.10	4.13	−16.86218
40	5.156	1.08	4.03	−16.86991
60	5.148	1.10	4.15	−16.87925

was performed using a set of ten special points which correspond to a 4, 4, 4 mesh in the Monkhorst–Pack [26] notation. The total energies are computed for a selection of lattice constants. Our data result from a best fit with the Murnaghan equation of state [27] 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). From these tables we are able to estimate a value of the energy cut-off such that the total energies converge to within an accuracy of about 1%. From these tables, it is clear that cut-off energy values of at least 60 Ryd for BP and 40 Ryd for both BAs and BSb are needed in order to obtain reliable results. Thus, these are the cut-off energies that we used in the remainder of this work. The choice of these values is due to the fact that the calculation time increases considerably with the increase of the cut-off energy, and the above accuracy is

sufficient for this series of compounds. On the other hand, the choice of a smaller plane-wave cut-off energy for BAs and BSb than for BP is due to the fact that the number of plane waves increases with the unit-cell volume. The number of plane waves, N, for a given E_{cut} and at a given volume V of the unit cell, varies approximately as $N \simeq V(E_{\text{cut}})^{3/2}$. Consequently, scaling the cut-off energy with the lattice constant in all three compounds keeps the number of plane waves constant, corresponding to approximately 1200 plane waves. In our calculations we use approximately the same number of plane waves for all three compounds. We note that the variational properties of the total-energy functional guarantee only that the energy decreases with increasing number of basis functions. Our calculations show that the compared equilibrium lattice parameters were well converged with respect to E_{cut} (see tables 1–3). Thus we arrive at a very good description of the atomic structure of the boron compounds by using BHS pseudopotentials.

The computed equilibrium lattice constants are 4.475 Å, 4.728 Å, and 5.156 Å for BP, BAs, and BSb, respectively. From this, we see that the variations of the lattice constants are in correlation with the variation of the size of atoms in these compounds. From the best fit of the total energies, 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. Table 4 reports the equilibrium data calculated at the LDA level and compares them with those obtained at the LDA level using a plane-wave basis set (for BP and BAs, references [8, 9]), those previously obtained at the HF level using an all-electron basis set (for BP, reference [28]), and at the LDA level using a linear combination of atomic orbitals (LCAO) scheme (for BP, reference [29]). Our predicted values for B_0 agree with those determined by using the empirical formula of Cohen [30] 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.

Table 4. The volume, V, lattice constant, a, bulk modulus, B_0, and first derivative of bulk modulus, B_0', for BP, BAs, and BSb, in the zinc-blende structure.

	V (Å^3)	a (Å)		B_0 (Mbar)			B_0'	
BP	22.403[a]	4.475[a]	4.558[b]	1.72[a]	1.66[b]	1.74[k]	3.76[a]	
			4.526[c]		1.66[c]			
			4.598[d]		1.70[d]			
			4.538[e,f]		1.73[j]			
			4.474[g]		1.72[g]			
			4.51[h]		1.72[h]			3.7[h]
BAs	26.422[a]	4.728[a]	4.777[b]	1.44[a]	1.45[b]	1.43[k]	4.00[a]	
BSb	34.267[a]	5.156[a]	5.12[i]	1.08[a]	1.15[i]	1.06[k]	4.03[a]	5.28[i]

[a] This work.
[b] References [8].
[c] Reference [29].
[d] Reference [28].
[e] Reference [39].
[f] Reference [40].
[g] Reference [10].
[h] Reference [6].
[i] Reference [18].
[j] Reference [15].
[k] Calculated using the empirical relation of reference [30].

3.2. The electronic charge density

The electronic charge density of BP, BAs, and BSb differs considerably from that of typical III–V semiconductors. The important feature in these compounds 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 densities along the bond in figure 1. The overall shapes of the charge distributions suggest a highly covalent B–anion bonding. This figure presents a slightly higher peak close to B. This feature was also found by Cohen's group [8] for BP and BAs. 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 of P, As, and Sb. 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.

To illustrate the degree of covalency in the boron compounds, figure 1 shows the typical features of the covalently bonded semiconductors. The bond charge is large and located close to half-way between the two nearest atoms. However, important differences appear. In fact, we note that with respect to silicon, a fully covalent semiconductor for which the isoelectronic curves are symmetric [31], the bond charge in these compounds is slightly disturbed by the electron charge transfer from one atom to another (a semi-covalent bond). The net charge transfer from the anion (P, As, or Sb) to B, which indicates the degree of the ionicity of the bonding, is not as large as suggested by figure 1; there remains a considerable degree of covalent character in the cation–anion bond. We notice that the chemical bonding is strongly covalent, i.e. a weak charge is transferred from the anion to B. Usually this rearrangement of charge in zinc-blende semiconductors is observed to proceed in the opposite way.

The competition between the ionic and covalent character in boron compounds can be related to the charge transfer between cation and anion. This charge transfer increases as the difference in the electronegativity values of the two atoms increases. Charge distributions in agreement with these expectations have been calculated by Wentzcovitch *et al* [8] for BP and BAs. 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 or other III–V materials.

The charge densities in figure 2 indicate a predominantly covalent character of the chemical bond accompanied by a small charge transfer from one atom to the other. These two features also indicate that the ionicity decreases on going from BP to BSb, i.e. when the anion goes down from P to Sb. Other features should also be noted. The BX (X = P, As, Sb) compound charge transfer is reversed, and boron is negatively charged. Similar conclusions have been established from other *ab initio* calculations [8]. These results also confirm the theoretical analysis of Lichanot and Causà [29] using an *ab initio* LCAO method which shows a significant electron charge transfer from P to B in BP.

Visual comparison of the corresponding charge-density plots leads to the conclusion that the boron compounds present a charge distribution similar to that found in SiC. This is in accordance with the fact that the key feature shared by the boron compounds and SiC is the presence of the element of the second row, B in the former and C in the latter.

The most pronounced effect of pressure on the charge density is the substantial increase in the background charge density in the non-bonding areas with a corresponding decrease in the peaks. We also note that the ratio of the peak heights around the B atom (in the bonding and non-bonding directions) remains roughly unaltered, indicating no radial change in the degree of covalency.
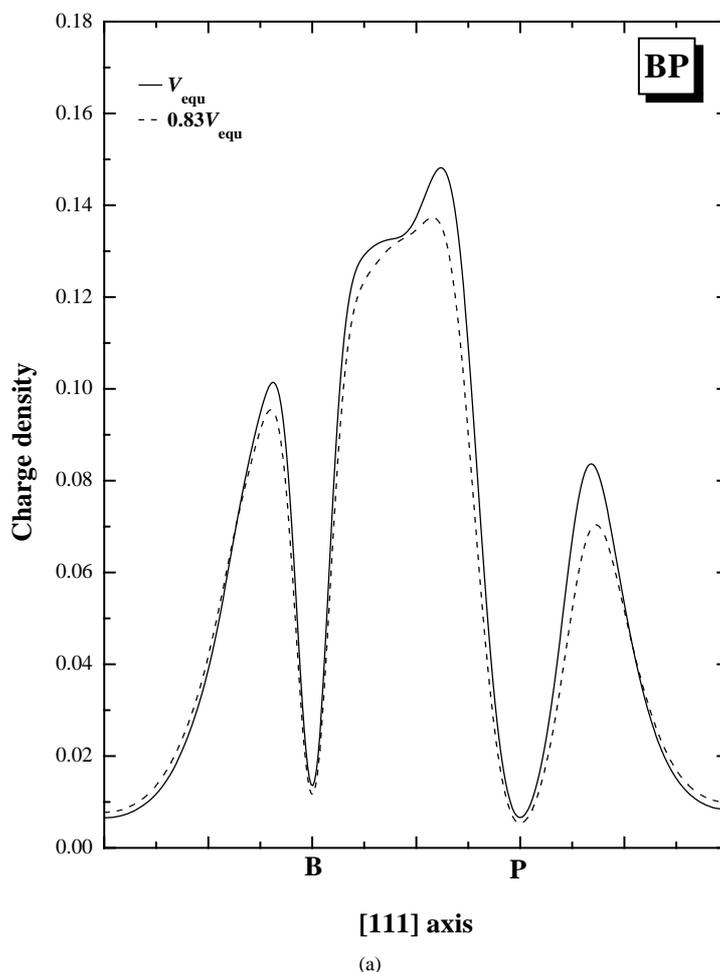
Figure 1. Plots for the zinc-blende phase of: (a) BP, (b) BAs, (c) BSb; valence charge densities along the bond at the equilibrium volume and under compression.

Shown in figure 3 are contour plots in the (110) plane of the valence charge density calculated under volume compression for BP, BAs, and BSb. There is a small amount of electronic charge transferred from the bonding region to the non-bonding region.

The location of the unaltered isodensity curves around the B nucleus can be due, on one hand, to the large attraction of this nucleus characterized by its small radius and, on the other hand, to the diffuse character of the p orbitals of P, As, and Sb coming close to the B nucleus without p core electrons.

3.3. The ionicity factor in boron compounds

The charge densities presented allow us to analyse the nature of the bonds in these compounds according to a classical chemical concept such as ionicity. While this concept is not very well founded, it is undoubtedly useful for classifying compounds with different chemical and
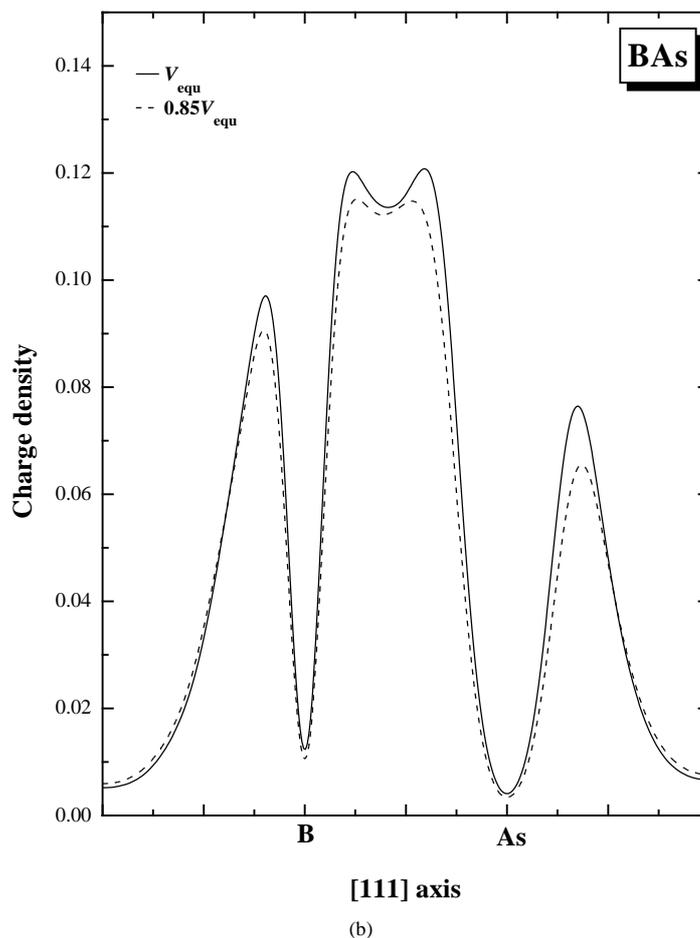
Figure 1. (Continued)

physical properties into different categories. To obtain an estimate of the value of the ionicity factor for BP, BAs, and BSb compounds, we have used two different approaches: (i) the Garcia and Cohen approach based on the valence charge-density calculation [32], and (ii) the Pauling definition based on the electronegativity values of the elements. 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 results for the ionicity in these compounds has made it difficult to assess the accuracy of the various approaches.

The charge asymmetry of a cation–anion bond was suggested to be a measure of the ionic character, and thus of the ionicity of binary compounds [32]. The Garcia and Cohen ionicity factor is defined as

$$f_i = \sqrt{S_s/S_a} \tag{1}$$

where S_s, S_a are the measures of the strength of the symmetric and antisymmetric components
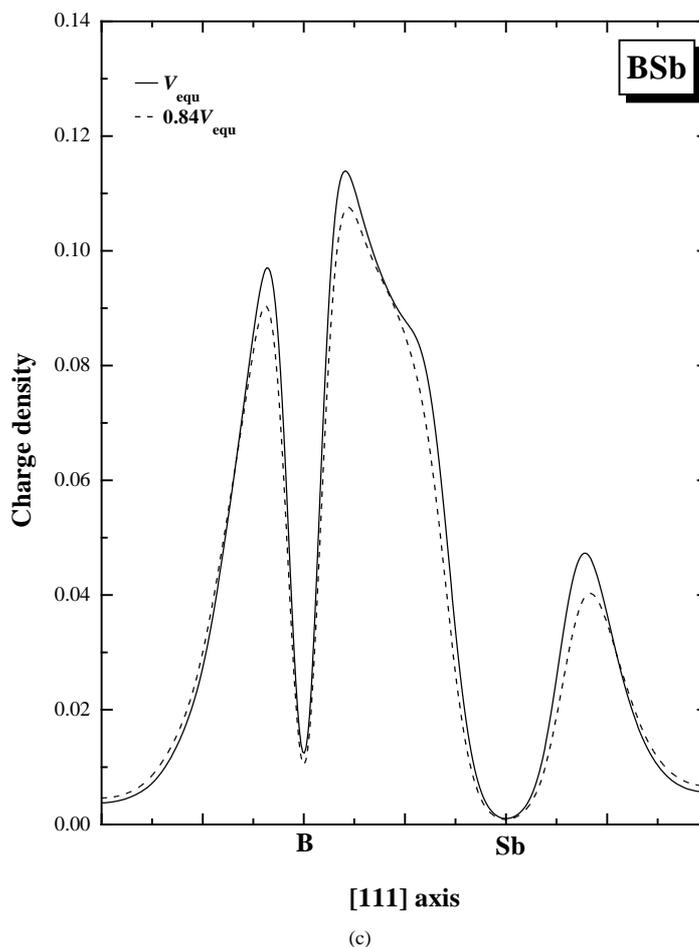
(c)

Figure 1. (Continued)

of the charge density, respectively, and are defined as [32]

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

In the present work we attempt to show that the ionicity factor in 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 the Pauling's definition [7] of the ionicity of a single bond and the Phillips electronegativity values for B, N, P, As, and Sb [7]. Our aim is to show that this expression gives a good approximation for the ionicity factors of BN, BP, BAs, and BSb. We can obtain a rapid estimate of the ionicity factor for these compounds by using the following equation:
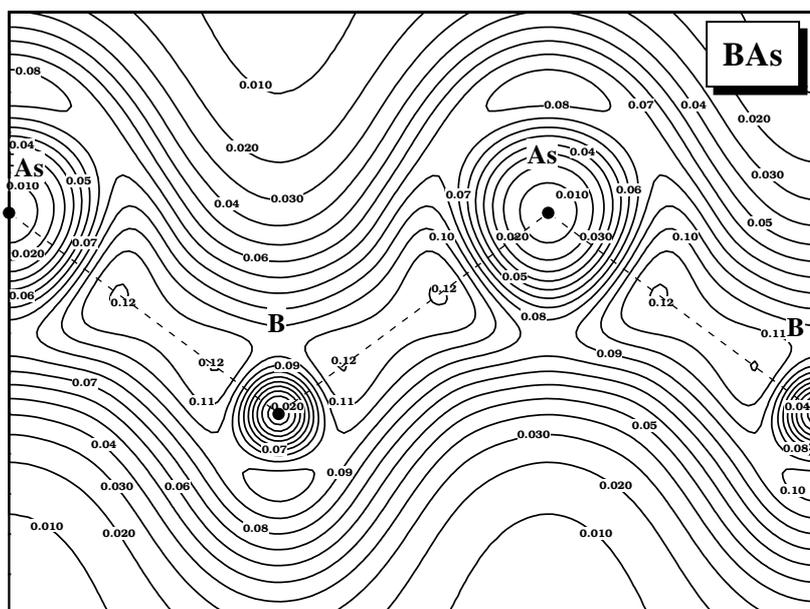
$$f_i^P = 1 - \exp[-[\chi_A - \chi_B]^2/4] \tag{2}$$

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

The calculated ionicity values for BP, BAs, and BSb compared with those of BN are summarized in table 5. For the series of BP, BAs, and BSb compounds, we see from table 5
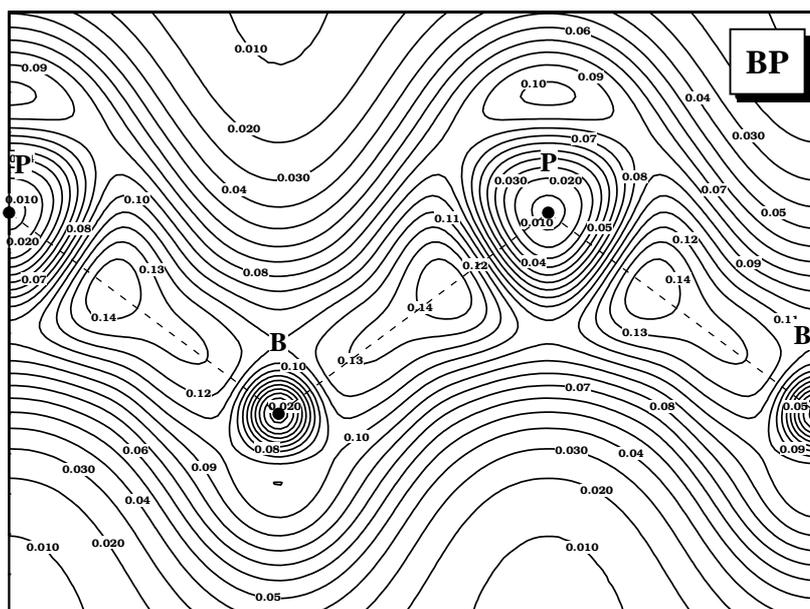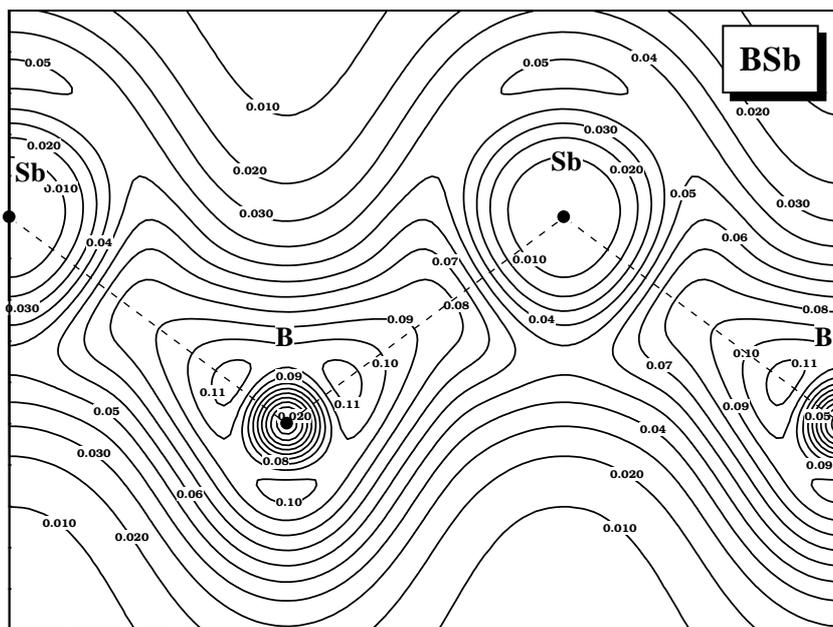
(a)

(b)

Figure 2. Contour plots of the total valence charge densities of: (a) BP, (b) BAs, (c) BSb, in the (110) plane. The equilibrium volume V_0 is used.

(c)

Figure 2. (Continued)

Table 5. The calculated ionicity factor f_i, of BP, BAs, and BSb compared to that for BN. The differences in electronegativities, $|\chi_A - \chi_B|$, are also listed for comparison.

| | | $|\chi_A - \chi_B|$ | | f_i | |
		Calculated	Garcia	Calculated	Phillips
BN	1.00		0.485[b]	0.221[c]	0.256[d]
BP	0.36	0.16[a]	0.085[b]	0.032[c]	0.006[d]
BAs	0.43	0.15[a]	0.116[b]	0.044[c]	0.002[d]
BSb	0.69	0.12[a]		0.112[c]	

[a] Calculated by using the Garcia and Cohen approach [32].
[b] Reference [32].
[c] Estimated by using Pauling's definition [7].
[d] Reference [7].

that the ionicity (f_i) decreases when the group-V anion is changed from P to Sb. This effect is similar to the one caused by the increase of the anion atomic number in other III–V compounds. For zinc-blende compounds, e.g. AlX, GaX, and InX (X = P, As, Sb), f_i decreases as the anion gets heavier [7].

In the light of the charge-density plots, it is clear that the degree of ionicity of the B–X chemical bond deceases from BP to BAs and to BSb. Considering the low degree of ionicity of the bond, and correlating this ionicity with the magnitude of the electron charge transfer, our results suggest the following ionicity order: BP > BAs > BSb. These conclusions confirm perfectly the order of the ionicity scale as calculated by Phillips [7] but present a reverse ordering of BP and BAs for the ionicity calculated by Garcia and Cohen [32].
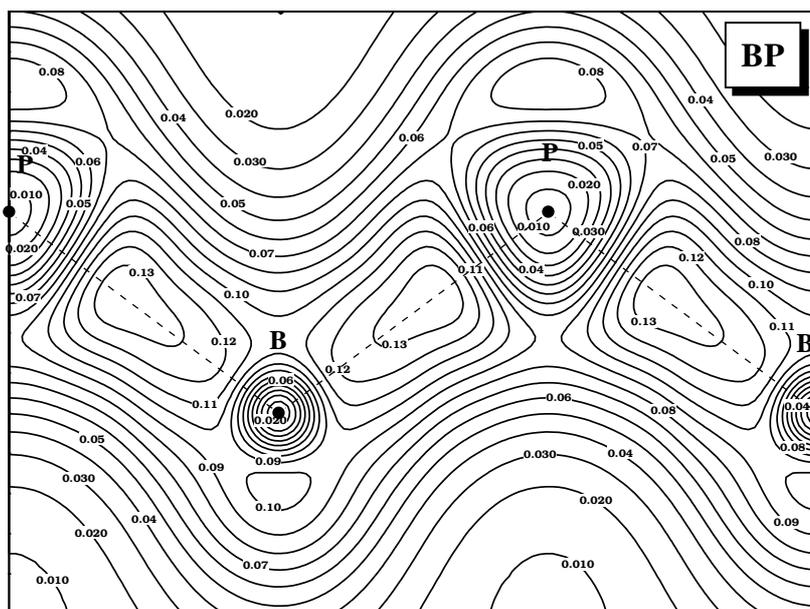
(a)
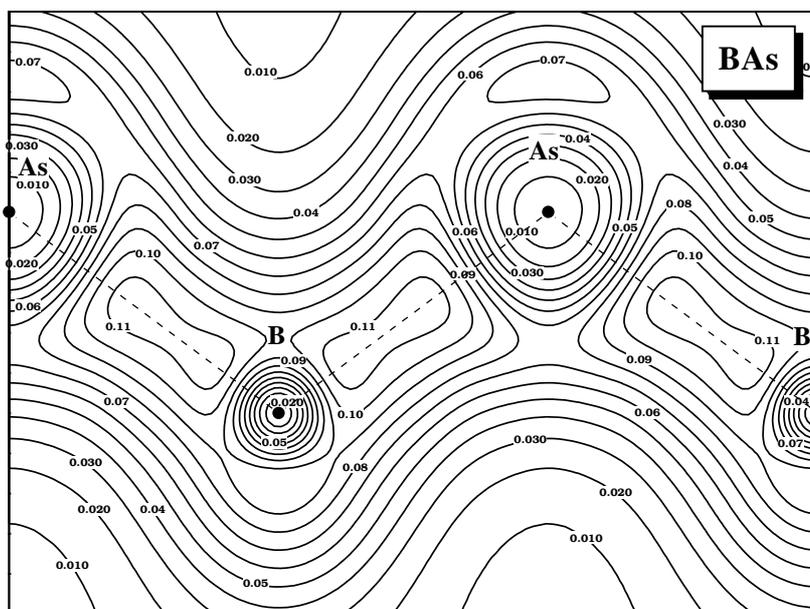
(b)

Figure 3. Contour plots of the total valence charge densities of: (a) BP, (b) BAs, (c) BSb, in the (110) plane. The volumes of transition from the zinc-blende to rock-salt structures of $0.85V_0$ for BP, $0.83V_0$ for BAs, and $0.84V_0$ for BSb are used.
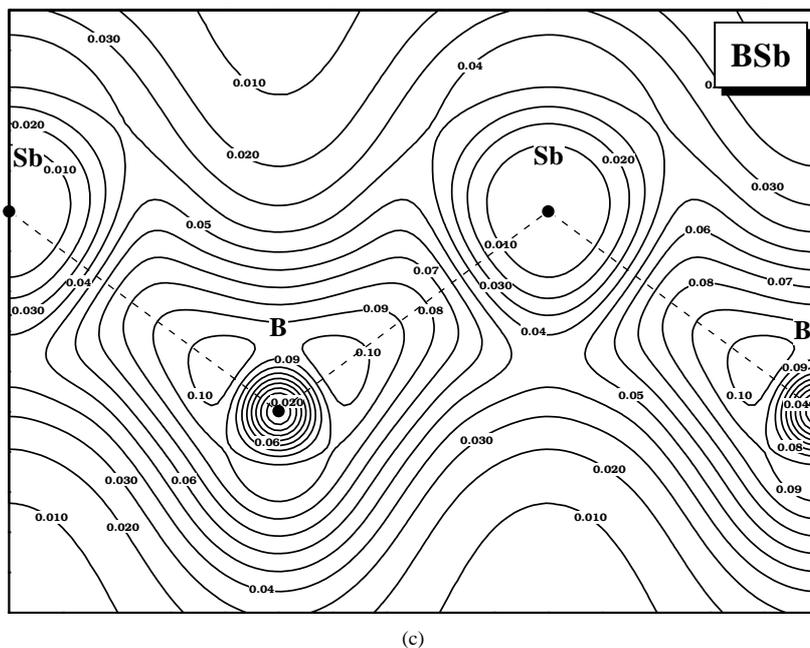
(c)

Figure 3. (Continued)

For the borides BP, BAs, and BSb there is instead a reduction in ionicity. We note that as a result of the small degree of ionic character of the series of BP, BAs, and BSb compounds, these materials share many similar properties. These results suggest a weak ionic character for this series of compounds, which are the most covalent III–V compounds. Their ionicity is so low that the ionic character is reversed. The group-III element, B, becomes the anion, where more charges are placed around it than P, As, and Sb, while in BN most of the valence charge was found concentrated around N [8] (see table 5 for comparison). Behaviour similar to this was observed by Wentzcovitch *et al* [8] for BP and BAs. 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 [6].

Another trend displayed by our calculation concerns the correlation between (i) the difference of electronegativities between the cation and anion and (ii) the ionicity. If we consider the isoelectronic series of semiconductors BP, BAs, and BSb, based on the Garcia ionicity scale, the ionicity decreases from 0.16 (when using Garcia's approach) in BP to a minimum of 0.12 in BSb. This is in agreement with the expectation that the ionicity decreases as the difference in the core size of cation–anion atoms increases. Our results suggest that the ionicity factor in the boron compounds decreases when the difference of the electronegativities increases. For instance, the ionicity decreases with increasing electronegativity mismatch between the cation and anion. The results indicate that BSb exhibits a slightly smaller ionicity value than BP and BAs. This is a very interesting result with regard to the structural phase transitions of this compound.

We notice that in these compounds the direction of the charge transfer (P → B in BP, As → B in BAs, and Sb → B in BSb) coincides with the atomic electronegativity difference

(B having a larger electronegativity value than P, As, and Sb; see table 5). In BN (B having a smaller electronegativity value than N), the usual normal trends remain as found for other III–V materials. The value of the electronegativity of B being larger than those of P, As, and Sb indicates 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 almost ionic bonding in the BN compound in this family.

Upon slight compression, the charge flow causes a very small decrease of the ionicity. Figure 4 displays these variations with respect to the pressure. This figure shows a clear deviation from a linear variation of ionicity character for these compounds. The results indicate that these materials exhibit a lower bond polarity, and intrinsically lower degree of ionicity character than BN (see table 5 for comparison). This result confirms the overall trends observed for the charge densities.
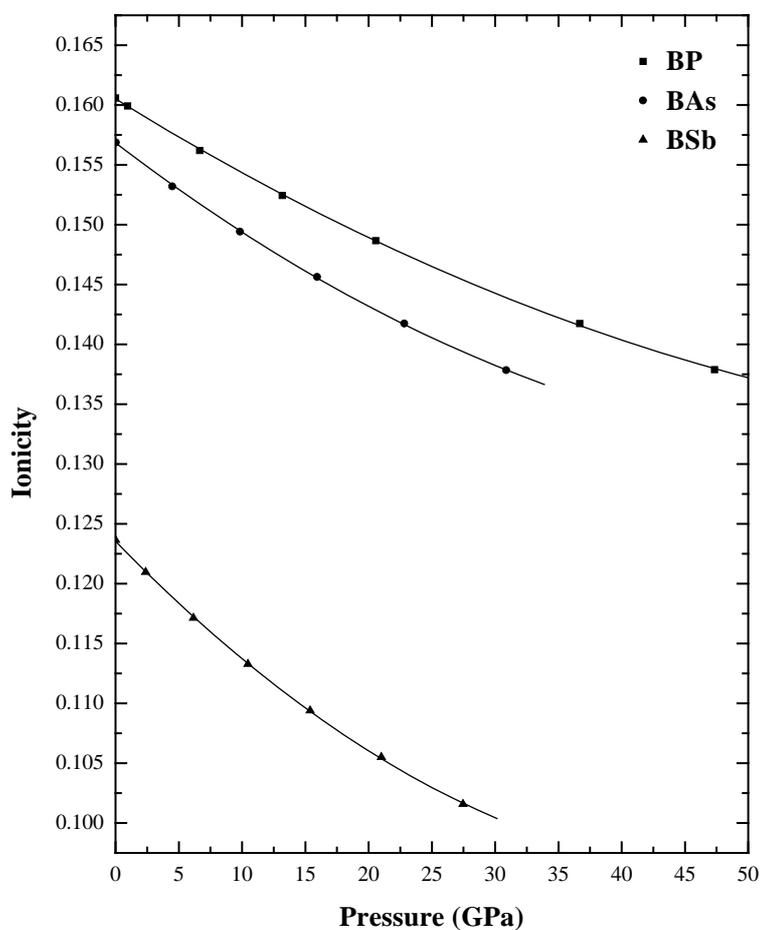

Figure 4. The variation of the ionicity of BP, BAs, and BSb under pressure.

We have calculated f_i for different pressures up to the pressure of the transition to a rock-salt structure. A least-squares fit of these results exhibits a linear dependence of the ionic

character with pressure as follows:

$$f_i = 0.16\text{--}6.5 \times 10^{-4} p \qquad \text{for BP}$$
$$f_i = 0.15\text{--}8.1 \times 10^{-4} p \qquad \text{for BAs}$$
$$f_i = 0.12\text{--}10.9 \times 10^{-4} p \qquad \text{for BSb.}$$

We notice that in these compounds the ionic character decreases with pressure. The pressure derivatives for BP and BAs are nearly the same, whereas that of BSb is slightly greater. On the basis of these results, we may therefore predict that the pressure for the transition to a rock-salt structure for BP and BAs should be higher than that for BSb. The ionicity for BSb decreases more rapidly than those for BP and BAs, which could be an indication that BSb can be transformed more easily than BP and BAs.

4. Concluding remarks

We have performed a self-consistent pseudopotential 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 equilibrium lattice constants, bulk moduli, and their first derivatives are described equally well by the LDA.

(ii) From the investigation of the valence charge density, it is found that BP and BAs compounds have a small difference in their chemical bonding, and that consequently their ionicity values are very close (0.16 for BP and 0.15 for BAs). As mentioned above, our calculation supports the suggestion made by Cohen *et al*. For BSb, we predict a very small ionicity value (0.12), which indicates that BSb is the more covalent material in the III–V zinc-blende family.

(iii) 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.

(iv) In this study, we have also investigated these boron zinc-blende materials under pressure. Despite the small charge transfer, the valence charge density in these boron materials remains covalently distributed. The competition between the ionic and covalent character is due to the similarity in the strengths of the chemical bonds for the series of BP, BAs, and BSb compounds.

The reported calculations provide new structural and electronic results from first principles for these compounds. The results reveal the fundamental importance of the chemical bonding nature and the ionicity in determining the properties of these compounds. This study is part of a larger theoretical effort to explore the nature and properties of boron-based materials. In contrast to BN, which had more strongly ionic character, BP, BAs, and BSb are apparently more strongly covalent.

The speed of the convergence for this series of compounds is low. A future test of some other algorithms is necessary—for example, the original Car–Parrinello method [33], the conjugate gradient method [34, 35], etc. The materials which we can study by means of pseudopotentials with a plane-wave basis is fairly limited. For example, B, C, O, N (with deep 2p potentials), and so on cannot be treated so accurately. It is necessary to devise more recent variants of pseudopotentials then those of BHS [23], e.g. the optimized soft pseudopotentials of Troullier and Martins [36] or those of Rappe *et al* [37] or the ultra-soft pseudopotentials

of Vanderbilt [38], which exhibit a considerably faster convergence with respect to cut-off energy (E_{cut}). Although there remain a few problems in the present calculations, our results are sufficiently accurate when compared to other data available in the literature.

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