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# Structural properties of boron compounds at high pressure

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## Abstract

The present work employs the full potential linearized augmented plane wave (FP-LAPW) method to calculate the elastic and the bonding properties of the boron compounds BN, BP, BAs and BSb at high pressures. A numerical first principles calculation of the elastic constants is used to obtain  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for these compounds. The equilibrium lattice constant and the bulk modulus are also calculated. Our FP-LAPW calculations were performed to evaluate the total energy as a function of strain, after which the data were fitted to a polynomial function of strain to determine the elastic modulus. The experimental elastic constants are only available for BN and BP. Hence for BAs, the results are only compared with the available theoretical works. To our knowledge the elastic constants of BSb have not yet been measured or calculated, hence our results serve as a prediction for future study. In addition, we discuss the bonding parameter in terms of charge density at equilibrium and at transition volumes, which suggests that the bonding of BP, BAs and BSb are less ionic than in other zinc-blende compounds.

## 1. Introduction

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

The zinc-blende boron compounds BN, BP, BAs and BSb as a subgroup of this family possess some peculiar characteristics such as the inverse roles between the cation and the

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anion in terms of charge transfer and the new high-pressure phase transitions. The latter aspect does not obey the Phillips diagram [2] established for  $A^N B^{8-N}$  compounds, which predicts a metallic structure, as the first new phase for weakly ionic compounds such as BP, BAs and BSb. BN is not concerned with the first anomalous point, because it can be viewed less as a boron compound than a nitride. 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 the B core. Boron is expected to have a deep and localized potential compared with the atoms from other rows. The fundamental differences between these compounds and other III–V materials can be explained by 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 their phase transition properties can be investigated.

An additional aspect of this study is a systematic comparison of the high-pressure phase transition in a series of III–V semiconductors. The  $\beta$ -Sn structure is generally preferred by the low ionicity and the rock-salt structure by the high ionicity in zinc-blende compounds [3].

The structural and electronic properties of boron compounds have been calculated by Wentzcovitch *et al* [4, 5] and by Ferhat *et al* [6, 7]. The high-pressure structural phase transitions of BN, BP and BAs were also discussed by Wentzcovitch *et al* [8]. All of these theoretical studies were performed using the density functional theory (DFT) within the local density approximation (LDA) and the pseudopotential method. To best of our knowledge, except our previous paper [9], there are no other published reports on theoretical studies of boron compounds within the FP-LAPW method.

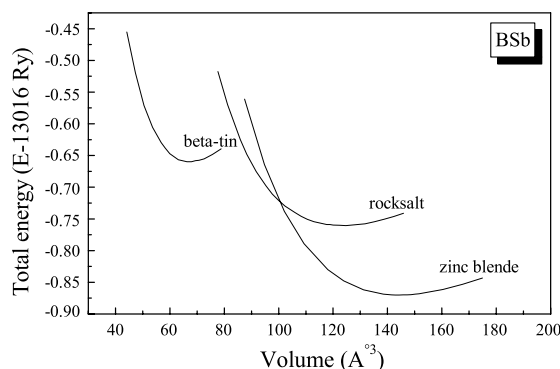
In this paper we used a numerical first-principles method, on the basis of a technique developed by Mehl *et al* [10, 11], to calculate the elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  of the boron compounds. Our calculations were performed using the full-potential linear augmented plane-wave method (FP-LAPW) to calculate the total energy as a function of strain, after which the data were fitted to a polynomial function of the strain to determine the elastic modulus.

To obtain a deeper understanding of elastic properties of compounds, we need to have a clear idea of the bonding properties. The charge density is an appropriate tool that permits us to better understand the bonding character of these compounds and FP-LAPW gives an accurate description of the valence charge density. We then correlate this latter quantity to the ionicity factor through an empirical formula [12], which has been successfully applied to other  $A^N B^{8-N}$  compounds.

The goal of this paper is to apply the full-potential linearized augmented plane-wave method to calculate the elastic properties of the boron compounds and also to understand the extreme ionicity character of such zinc-blende compounds in terms of charge density under pressure. The paper is organized as follows. In section 2 we briefly give the computational details. In section 3 we present the results of our calculations. The conclusion is contained in section 4.

## 2. Method of calculation

We employed the FP-LAPW method in order to calculate the structural and electronic properties of boron compounds. This method, that was carried out using the WIEN97 code [13], has been proven to be most appropriate to describe electronic states for such compounds [9]. The exchange–correlation potential was calculated by the generalized gradient approximation (GGA) using the scheme of Perdew *et al* [14]. We performed convergence tests for the total energy at different plane-wave cut-offs and finally we used 64 Ryd for BN and 20 Ryd for BP, BAs and BSb. The numbers of  $k$ -points in the irreducible Brillouin zone for different structures



**Figure 1.** Variation of total energy with volume for zinc-blende, rock-salt and beta-tin structures of BSb.

**Table 1.** Number of plane waves (PW), nearest-neighbour distance (NN-dist) and muffin-tin radius (RMT) used for both zinc-blende and rock-salt for BN, BP, BAs and BSb.

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

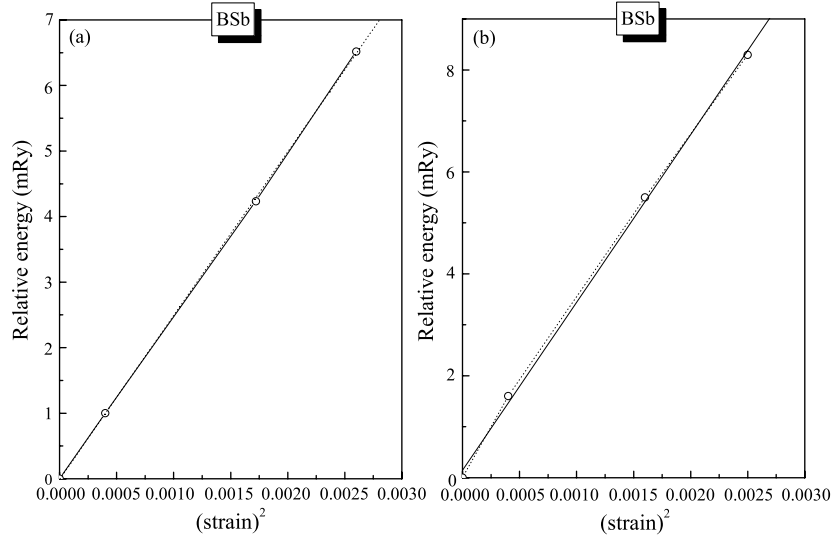
were chosen to ensure enough accuracy. For the insulating zinc-blende phase we chose 30  $k$ -points while for the  $\beta$ -Sn and rock-salt structures we used 58 and 47  $k$ -points, respectively. The values of the sphere radius, the nearest-neighbour distance and the number of plane waves used in the interstitial region are listed in table 1. Both the muffin-tin radius and the number of  $k$ -points were varied to ensure convergence.

### 3. Results and discussion

#### 3.1. Elastic properties

The variations of total energy as a function of volume are similar for different compounds, hence we only display the results obtained for BSb in figure 1. The curves were obtained by calculating the total energy at many different volumes around equilibrium and by fitting the calculated values to the Murnaghan equation of state [15]. The  $\beta$ -Sn structure is obtained by changing the  $c/a$ -ratio of the tetragonal cell [8], which is approximately 0.55. It is obvious from these curves that the zinc-blende is the most stable structure at ambient pressure, which is consistent with the experimental results. For compressed volumes, the boron compounds BN, BP, BAs and BSb are shown to favour the rock-salt phase over  $\beta$ -Sn in spite of the fact that BP, BAs and BSb are the least ionic among zinc-blende compounds.

The structural phase transition is determined by calculating the Gibbs free energy ( $G$ ) [19] for the two phases, which is given by  $G = E_0 + PV + TS$ . Since the theoretical calculations



**Figure 2.** (a) Energy as a function of the square of the orthorhombic strain, used to determine  $C_{11} - C_{12}$  in zinc-blende structures for BSb. The solid line is the linear fit. (b) Energy as a function of the square of the orthorhombic strain, used to determine  $C_{11} - C_{12}$  in rock-salt structures for BSb. The solid line is the linear fit.

**Table 2.** Calculated value for pressure and corresponding transition volume from zinc-blende to rock-salt structures for BN, BP, BAs and BSb. Comparison is made with the available theoretical data.

		BN	BP	BAs	BSb
$P_t$ (GPa)	Present	6.24 (GGA)	1.28	0.95	0.68
	Theoretical	11.1 [8]	1.6 [8]	1.1 [8]	2.16 [21]
$V_t$ ( $\text{\AA}^3$ )	Present	26.654 (GGA)	64.287	76.403	107.520
	Theoretical	19.693 [8]	53.028 [8]	65.405 [8]	85.300 [21]

are performed at  $T = 0$  K, Gibbs free energy becomes equal to the enthalpy,  $H = E_0 + PV$ . For a given pressure, a stable structure is one for which the enthalpy has its lowest value. Hence the common tangent to the curves in figure 1 indicates the phase transition pressure. Following such a procedure the zinc-blende to rock-salt transition pressures were calculated and are compared with other available theoretical results in table 2. It is clearly seen that our GGA calculated transition pressure 6.24 GPa for BN is substantially lower than the value of 11.1 GPa obtained in [8] by using the LDA-pseudopotential approach. To trace the source of this discrepancy we recalculated the phase transition pressure by the LDA-FPLAPW method and found a value of 9.45 GPa with transition volume  $V_t = 23.196 \text{ \AA}^3$ . This result confirms the fact that most of this discrepancy is rooted in the different exchange–correlation schemes.

The elastic constants are determined using the method discussed in detail in [10, 11]. Following this method and considering the fact that the compounds have cubic structure, we calculated the shear modulus  $C_{11} - C_{12}$  from the volume-conserving orthorhombic strain tensor:

$$\begin{bmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \frac{\delta^2}{(1-\delta^2)} \end{bmatrix}.$$

**Table 3.** Calculated lattice constant, bulk modulus and elastic constant parameters in the zinc-blende structure at equilibrium volume compared to experiment and other theoretical works.

		BN	BP	BAs	BSb
Lattice constants (Å)	Present	3.623	4.546	4.784	5.252
	Experimental	3.615 [17, 18]	4.538 [18]	4.777 [20]	
	Theoretical	3.606 [8]	4.558 [8]	4.777 [8]	5.12 [7]
$B$ (Mbar)	Present	3.68	1.70	1.37	1.03
	Experimental	3.69 [17]	1.73 [19]		
	Theoretical	3.67 [8]	1.65 [8]	1.45 [8]	115 [7]
$C_{11}$ (Mbar)		3.86 [28]	1.72 [28]		
	Present	7.51	3.29	2.51	1.92
	Experimental	7.12 [24]	3.15 [27]		
	Theoretical	8.37 [25]	3.59 [28]	2.79 [6]	
		8.30 [26]	3.60 [6]		
$C_{12}$ (Mbar)		9.90 [6]			
		8.44 [28]			
	Present	1.765	0.975	0.798	0.585
	Experimental		1.00 [27]		
	Theoretical	1.82 [25]	0.81 [28]	1.20 [6]	
$C_{44}$ (Mbar)		4.20 [26]	1.55 [6]		
		4.41 [6]			
		1.9 [28]			
	Present	4.36	1.54	1.27	1.05
	Experimental		1.60 [27]		
	4.93 [25]	2.02 [28]	1.13 [6]		
	4.50 [26]	1.46 [6]			
	3.94 [6]				
	4.83 [28]				

Application of this strain changes the total energy from its unstrained value to

$$E(\delta) = E(-\delta) = E(0) + (C_{11} - C_{12})V\delta^2 + 0(\delta^4) \quad (1)$$

where  $E(0)$  is the energy of the unstrained lattice and  $V$  is the unit cell volume.

For the elastic modulus  $C_{44}$ , we used the volume-conserving monoclinic strain tensor

$$\begin{bmatrix} 0 & \frac{1}{2}\delta & 0 \\ \frac{1}{2}\delta & 0 & 0 \\ 0 & 0 & \frac{\delta^2}{(4-\delta^2)} \end{bmatrix}$$

which changes the total energy to

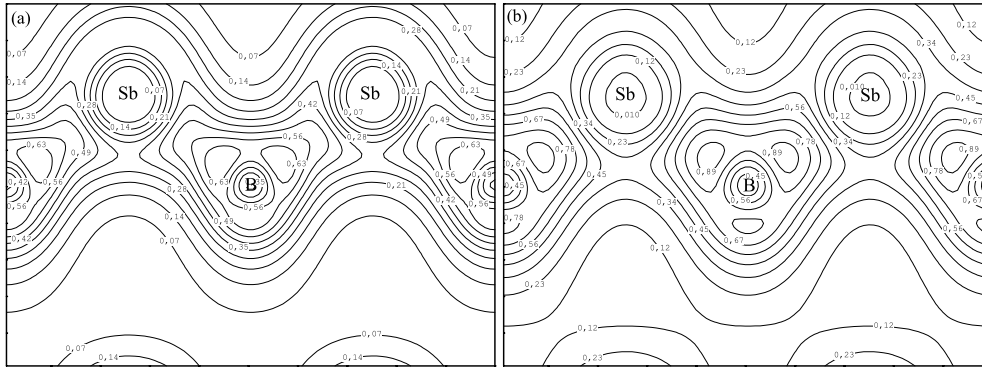
$$E(\delta) = E(-\delta) = E(0) + \frac{1}{2}C_{44}V\delta^2 + 0[\delta^4]. \quad (2)$$

For an isotropic cubic crystal, the bulk modulus is given by [16]

$$B = \frac{1}{3}(C_{11} + 2C_{12}). \quad (3)$$

Figure 2 shows the variation of relative energy with respect to the square of the orthorhombic strain, used to determine  $C_{11} - C_{12}$  in zinc-blende for BSb. The error bars are not shown since they are too small.

The calculated lattice parameter, bulk modulus and elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for the zinc-blende structure are given in table 3. It is clearly seen that our marginally overestimated GGA results of the lattice parameters are in good agreement with the experimental and other calculated values; considering the fact that as a general trend the GGA overestimates the lattice



**Figure 3.** (a) Valence charge distribution in the zinc-blende structure for BSb. The charge contours are shown in the  $(1\bar{1}0)$  plane at the equilibrium volume. (b) Valence charge distribution in the zinc-blende structure for BSb. The charge contours are shown in the  $(1\bar{1}0)$  plane at the transition volume.

**Table 4.** Calculated lattice constant, bulk modulus and elastic constant parameters in the rock-salt structure.

		BN	BP	BA <sub>s</sub>	BSb
Lattice constants ( $\text{\AA}$ )	Present	3.503	4.320	4.619	4.979
	Theoretical	3.493 [8]	4.339 [8]	4.583 [8]	
$B$ (Mbar)	Present	3.99	1.71	1.35	1.08
	Theoretical	4.25 [8]	1.55 [8]	1.43 [8]	
$C_{11}$ (Mbar)	Present	8.16	3.41	2.76	2.38
$C_{12}$ (Mbar)	Present	1.90	0.86	0.64	0.43
$C_{44}$ (Mbar)	Present	5.92	2.48	1.89	1.54

parameters while the LDA underestimates them. The bulk modulus decreases in going from BN to BSb (from the lower to the higher atomic number). Hence we conclude that BN is less compressible than the other compounds.

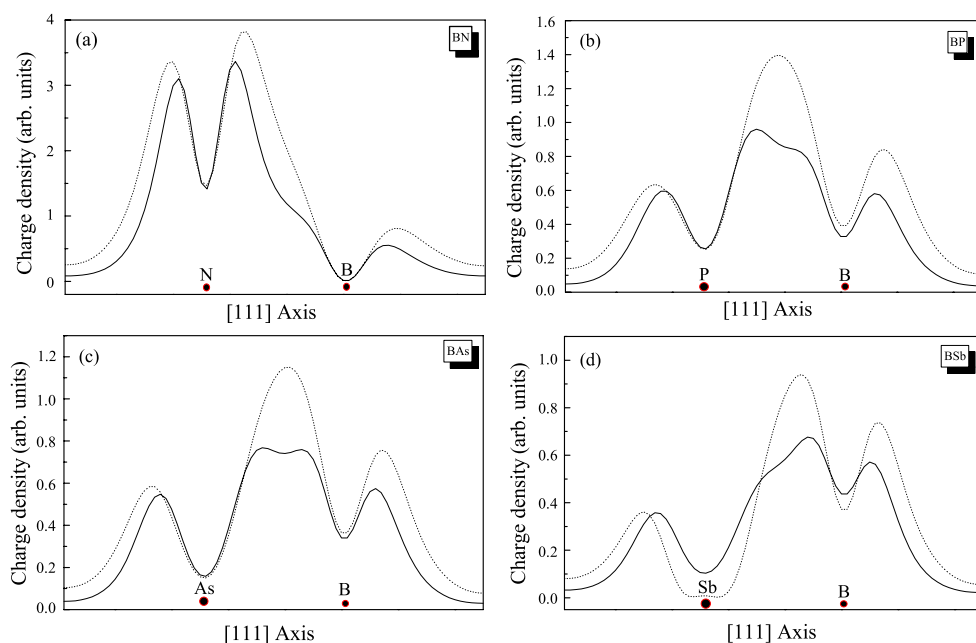
The calculated elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for the rock-salt structure along with their corresponding equilibrium lattice constants and bulk moduli are listed in table 4.

To our knowledge the elastic constants of rock-salt structure for boron compounds as well as the lattice parameter and the bulk modulus of the BSb have not yet been measured or calculated. Hence our results can be considered as a prediction for these properties of BSb. Additionally, it is clearly seen that BP, BA<sub>s</sub> and BSb have rather similar compressibility, while BN is considerably harder.

Finally, we calculated the structural properties of  $\beta$ -Sn and have listed the corresponding equilibrium lattice parameters ( $a$ ,  $c$ ) and the bulk modulus ( $B$ ) in table 5. The equilibrium volume and the bulk modulus that we obtained for BP and BA<sub>s</sub> are a little bigger than the corresponding values that have been calculated within the LDA [8]. This is consistent with the general trend of the LDA.

### 3.2. Bonding properties

The electronic charge density is an important property of solids and can be only described accurately in the context of first-principles studies. In our work the charge density is derived from highly converged wavefunctions, hence the result is very reliable.



**Figure 4.** (a) Total valence charge densities along the  $\langle 111 \rangle$  direction for BN in zinc-blende structures at equilibrium volume (solid curve) and the transition volume (dashed curve). (b) Total valence charge densities along the  $\langle 111 \rangle$  direction for BP in zinc-blende structures at equilibrium volume (solid curve) and the transition volume (dashed curve). (c) Total valence charge densities along the  $\langle 111 \rangle$  direction for BAs in zinc-blende structures at equilibrium volume (solid curve) and the transition volume (dashed curve). (d) Total valence charge densities along the  $\langle 111 \rangle$  direction for BSb in zinc-blende structures at equilibrium volume (solid curve) and the transition volume (dashed curve).

(This figure is in colour only in the electronic version)

**Table 5.** Calculated lattice constants and bulk moduli in  $\beta$ -Sn structure.

		BN	BP	BAs	BSb
Lattice constants, $a$ ( $\text{\AA}$ )	Present	2.468	3.007	3.253	3.496
	Theoretical		2.957 [8]	3.123 [8]	
Lattice constants, $c$ ( $\text{\AA}$ )	Present	3.90	4.751	5.141	5.524
	Theoretical		4.672 [8]	4.935 [8]	
$B$ (Mbar)	Present	6.64	2.82	1.961	1.35
	Theoretical		1.65 [8]	1.41 [8]	

We calculated the valence charge density distribution for zinc-blende BSb in the  $(1\bar{1}0)$  plane at equilibrium and also at transition volumes as shown in figure 3. The density profiles in the zinc-blende structure at the equilibrium volume and at the transition volume of BN, BP, BAs and BSb are shown in figure 4. It is clearly seen that the charge density moves under pressure towards the bond centre, which means that the system becomes less ionic.

Although ionic charges play a decisive role in the physics of compounds they are still quantities difficult to assess in a consistent and meaningful way. Even if we know the distribution of the valence charge in a semiconductor, the ionic charges are still arbitrary; depending on the way the space is divided and assigned to individual atoms. Following an



**Table 6.** Calculated ionicity values of boron compounds BN, BP, BAs and BSb for zinc-blende structure at equilibrium volume  $V_0$  and at the transition volume  $V_t$  compared with those of Phillips and Garcia.

	$f_i$   present		$f_i$ (Phillips) [2]	$f_i$ (Garcia) [23]	Other calculations [7]
	Volume $V_0$	Volume $V_t$			
BN	0.567	0.503	0.256	0.485	0.221
BP	0.074	0.055	0.006	0.085	0.032
BAs	0.026	0.017	0.002	0.116	0.044
BSb	0.019	0.009			0.112

empirical formula [12], the total area occupied by the valence charge density is divided into two parts with respect to the centre.  $S_C$  is the area of the cation side and  $S_A$  the area of the anion side, and the ionicity factor is written as

$$f_i = \left( \frac{S_A}{S_A + \lambda S_C} \right)^\lambda \quad (4)$$

where  $\lambda$  is a parameter separating the highly ionic elements from the weakly ionic ones.  $\lambda = -1$  for elemental and III–V semiconductors;  $\lambda = +1$  for II–VI and II–VII semiconductors.

The calculated ionicity values for BP, BAs, BSb and BN are summarized in table 6. It is clearly seen that the ionicity ( $f_i$ ) decreases when the group V anion changes from N to Sb. This behaviour is similar to that 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 [2]. In the light of the charge density plots, it is clear that the degree of ionicity for the B–X chemical bond decreases from BP to BAs and 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: BN > BP > BAs > BSb. Such a conclusion confirms perfectly the order of the ionicity scale suggested by Phillips [2] but present a reverse ordering for the ionicity of BP and BAs calculated by Garcia and Cohen [23]. A point worth considering is that the value of the ionicity factor for all studied compounds, except BN, is very low. The small degree of ionic character in BN, BAs and BSb not only causes similar properties for these materials, but in addition to that it reverses the ionic character of the elements. The group III element B becomes the anion, with more charges placed around it rather than P, As and Sb, while in BN most of the valence charges are concentrated around N [4]. Similar behaviour has been observed by Wentzcovitch *et al* [8], using the pseudopotential approach, which is different from our full potential method. Hence we can conclude that the electron attraction of N is greater than P, As and Sb respectively. This behaviour has been noted to have important effects for the bonding at interfaces [22].

We finally calculated the ionicity factor ( $f_i$ ) at the transition volume, and found that upon compression, the charge flow causes a very small decrease of the ionicity.

#### 4. Conclusions

We have applied FP-LAPW method to study the elastic and the bonding properties of BN, BP, BAs and BSb compounds. A numerical first-principles method was used to calculate the elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for these compounds. We calculated the total energy as a function of strain, and fitted the data with a polynomial function to determine the elastic modulus. The bonding character has been discussed in terms of the charge density and shows a strong localization of charge around the anion in BN, and it is covalently distributed in the

BP, BAs and BSb compounds. Due to the similarity in the strengths of the chemical bonds in BP, BAs and BSb compounds, their ionicity factors are close to each other and significantly smaller than the related value in BN. These results are in agreement with the analysis of the charge density behaviour and compare well with the Phillips and Garcia ionicity scale.

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### References

- [1] Glass J T, Messier R and Fujimori N 1990 *Diamond, Silicon Carbide and Related Wide Gap Semiconductors* (MRS Symp. Proc. N0162) (Pittsburgh, PA: Materials Research Society)
- [2] Phillips J C 1973 *Bond and Bands in Semiconductors* (New York: Academic)
- [3] Chelikowsky J R 1986 *Phys. Rev. Lett.* **56** 96
- [4] Wentzcovitch R and Cohen M L 1986 *J. Phys. C: Solid State Phys.* **19** 6791
- [5] Wentzcovitch R, Chang K J and Cohen M L 1986 *Phys. Rev. B* **34** 1071
- [6] Ferhat M, Zaoui A, Certier M and Aourag H 1998 *Physica B* **252** 229
- [7] Ferhat M, Bouhafs B, Zaoui A and Aourag H 1998 *J. Phys.: Condens. Matter* **10** 7995
- [8] Wentzcovitch R M, Cohen M L and Lam P K 1987 *Phys. Rev. B* **36** 6058
- [9] Zaoui A and El Haj Hassan F 2001 *J. Phys.: Condens. Matter* **13** 253
- [10] Mehl M J 1993 *Phys. Rev. B* **47** 2493
- [11] Mehl M J, Osburn J E, Papaconstantopoulos D A and Klein B M 1990 *Phys. Rev. B* **41** 10311  
Mehl M J, Osburn J E, Papaconstantopoulos D A and Klein B M 1991 *Phys. Rev. B* **42** 5362 (erratum)
- [12] Zaoui A, Ferhat M, Khelifa B, Dufour J P and Aourag H 1994 *Phys. Status Solidi b* **185** 163
- [13] Blaha P, Schwarz K and Luitz J 1997 *WIEN97, a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* Technical University of Vienna (ISBN 3-9501031-0-4)  
This is an improved and updated Unix version of the original copyrighted WIEN code, which was published by Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
- [14] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [15] Murnaghan F D 1944 *Proc. Natl Acad. Sci. USA* **30** 5390
- [16] Schreiber E, Anderson O L and Soga N 1973 *Elastic Constants and their Measurement* (New York: McGraw-Hill)
- [17] Knittle E, Wentzcovitch R M, Jeanloz R and Cohen M L 1989 *Nature* **337** 349
- [18] *Landolt-Börnstein New Series* 1982 Group III, vol 17a (Berlin: Springer)
- [19] Wettling W and Windscheif J 1984 *Solid State Commun.* **50** 33
- [20] Madelung O (ed) 1972 *Landolt-Börnstein New Series* vol 3 (Berlin: Springer)
- [21] Zaoui A and Ferhat M 2001 *Phys. Status Solidi b* **225** 15
- [22] Lambrecht W R L and Segall B 1991 *Phys. Rev. B* **43** 7070
- [23] Garcia A and Cohen M L 1993 *Phys. Rev. B* **47** 4215
- [24] Steigmeir E F 1963 *Appl. Phys. Lett.* **3** 6
- [25] Kim K, Lambrecht W R and Segall B 1996 *Phys. Rev. B* **53** 16310
- [26] Sokolovskii T D 1983 *Izv. Akad. Nauk SSSR Neorg. Mater.* **19** 1484
- [27] Wettling W and Windscheif J 1984 *Solid State Commun.* **50** 33
- [28] Hernandez P R, Diaz M G and Munoz A 1995 *Phys. Rev. B* **51** 14705