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Theoretical study of BN, BP, and BAs at high pressures

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The present work employs the total-energy pseudopotential technique to calculate the relative stabilities at high pressures of the zinc-blende β-Sn, and rocksalt structures in the series of compounds BN, BP, and BAs. For compressed volumes these compounds are shown to favor the rocksalt phase over β-Sn, even though BP and BAs are the least ionic of the III-V zinc-blende compounds. This indicates that the stability of the rocksalt structure under pressure depends on more than just the ionicity factor. The structural preference is analyzed in terms of charge densities. The charge rearrangements at different volumes are also studied. We find that for BN the charge associated with B decreases with volume compression while the charge associated with N increases. In BP and BAs the opposite trend is observed, with P and As behaving like B in BN. BN appears to behave like a typical III-V compound semiconductor in its charge distribution while BP and BAs are anomalous cases which can be characterized by reversing the standard assignments for the anions and cations in these compounds.

I. INTRODUCTION

The group of zinc-blende boron compounds, BN, BP, and BAs, displays rather peculiar behavior when compared to other compounds of the III-V family. Their unusual behavior appears to originate from the small core size and the absence of p electrons in the cores of the atoms belonging to the first row of the Periodic Table. These atoms are expected to have deep and localized pseudopotentials compared with the atoms from other rows.

BN exhibits solid phases[1] similar to the phases of carbon which also differ from those of the other group-IV solids. Normally BN is synthesized in hexagonal phases that have two- or three-layered stacking sequences. The two-layered form[2] has an *AaAa* . . . stacking sequence which is structurally different from hexagonal graphite which has an *ABAB* . . . stacking sequence. The three-layered form is similar to rhombohedral graphite: both have an *ABC* . . . stacking sequence. The denser zinc-blende and wurtzite forms are similar to cubic and hexagonal diamond and are produced directly (without catalysts) from the hexagonal phases under static[3,4] and dynamic compression.[5,6] The products of the compression, i.e., zinc-blende or wurtzite BN, depend on the relative amount of these two forms of hexagonal BN in the initial sample and the temperature at which the compression is performed.[3,5] The similarities between BN and C are also manifested in their electronic properties. Band-structure calculations have indicated[7,8] that the fundamental gap of zinc-blende BN increases with pressure, a behavior exhibited also by cubic diamond[9] but not by other zinc-blende and diamond semiconductors.[10] It has been shown[9] that this behavior occurs in atoms of the first row because of the large energy separation of the d atomic orbitals from the Fermi level and their absence in the bottom of the conduction band.

The compounds BP and BAs are also unusual. A special situation is created when the cation, usually the element of column III, belongs to the first row and the anion, usually the element of column V, belongs to a lower row in the Periodic Table. The very attractive B potential competes with the element V's potential for the valence charge, creating a situation of small heteropolarity and consequently small ionicity (in the Phillips's[11] as well as in the Pauling's sense[12]). The possibility of a reversal of the usual charge transfer with B behaving as an anion is not excluded. In particular there is theoretical as well as experimental evidence for this fact. According to the Phillips's scale of electronegativities[11] B is more electronegative than P, As, or Sb. Tight-binding calculations[13] have pointed out that the effective charges of BP and BAs are negative; this result is opposite to that found for other zinc-blende semiconductors. A soft-x-ray study of BAs,[14] in which the contribution of atomic orbitals to the valence- and conduction-band states is analyzed, suggests that there is a relative lack of p character associated with B in the bottom of the conduction band at point X in contrast to other III-V compounds where the column-III atom is identified as the cation. Finally, pseudopotential calculations[8,15] of the electronic structure of these compounds confirm the lack of p character of B in the bottom of the conduction bands and suggest that a large amount of p character is associated with the B atom in the top of the valence bands, as generally happens with a typical anion. These studies[8,15] also indicated that in the formation of the bonds in BP and BAs the charge moves from the antibonding region associated with the column-V element to the bonding region. Usually this rearrangement of charge in zinc-blende semiconductors is observed to proceed in the opposite way, with the charge leaving the antibonding region associated with the column-III element and going to the bonding region. These results suggest a comparative study of the behavior of the valence charge distribution in BN, BP, and BAs at high pressures would be useful.

Another aspect of this study is a systematic comparison of the high-pressure phase transitions in a series of III-V compound semiconductors which contain atoms of the first row. Phillips and Van Vechten developed an ionicity scale based on dielectric theory[11] which can be used to predict the first pressure-induced structural phase transitions. Broadly speaking, there are two likely candidates for crystalline structures into which the family of diamond and zinc-blende semiconductors transform under isotropic pressure. The β-Sn structure is generally preferred by the low-ionicity zinc-blende compounds while the rocksalt structure is preferred by the high-ionicity zinc-blende compounds. This trend is also the conclusion of a recent quantum-mechanical calculation[16] which studied the behavior of a hypothetical compound in the Ge row with an artificially changed heteropolarity in the potential. In this study the homopolarity of the compound was not varied therefore it may not be applicable to first row elements. An important exception to the above trends is the case of C, which is also in the first row of the Periodic Table. Calculations indicate that its first high-pressure phase is the B-8 "(BC8)" phase.[17] At high pressures, the simple cubic structure, which is equivalent to the rocksalt in a group-IV solid, has a lower energy than the β-Sn at high pressures.[18] It has been suggested that the lack of p states in the core and the large separation in energy of the d orbitals from the Fermi level in C contribute to this behavior.[18] In fact the β-Sn structure has recently been shown to be unstable.[19]

According to the Phillips and Van Vechten scale of ionicities, BP and BAs) are the least ionic compounds of the III-V family ($f_i = 0.006$ for BP and $f_i = 0.002$ for BAs), hence a calculation of the relative stability of these two structures for these compounds which are on the boundary that separates ionic from covalent compounds can provide interesting physical information. Phase transitions in these compounds have not been observed experimentally up to 68 GPa.[20]

In the present paper the total-energy pseudopotential technique is used to study the behavior of the charge densities under volume compression in the zinc-blende phase of these B compounds. In an attempt to quantify the observed charge rearrangements at different volumes, we calculated the amount of valence charge enclosed inside spheres of radii corresponding to the last closed contours of the charge-density plots when viewed in the (100) planes containing different atoms. This study allows us to make a comparison between the Pauling and the Phillips scales of electronegativities and to explore the different meanings of "ionicity" defined by these two authors. Using a pseudopotential total-energy approach[21] we also calculate the relative stability of the β-Sn structure with respect to the rocksalt in these compounds under pressure. The fact that these compounds do not fit naturally into schemes proposed to explain pressure versus ionicity phase diagrams[11,16] of III-V compounds is examined and a general scheme that could describe their behavior and that of other zinc-blende compounds at high pressures is described.

This paper is divided as follows: In Sec. II we briefly describe the method of calculation; in Sec. III we report the results of calculations of the relative stability of the high-pressure phases, β-Sn, and rocksalt, of the three compounds and point out why these compounds do not fit well into some of the proposed schemes for the pressure versus ionicity phase diagrams for zinc-blende compounds. Section IV contains a study of the valence charge densities in the zinc-blende phase with volume compression and a discussion of the Pauling and Phillips scales of electronegativities and ionicities with respect to the calculated charge distributions, while Sec. V contains a discussion of the trends obtained in our calculation. Conclusions are given in Sec. VI.

II. METHOD OF CALCULATION

The pseudopotential total-energy method[21] within the local-density approximation[22] (LDA) is used to calculate the total energies per molecule of the solid in different structures. We generate standard ionic pseudopotentials[23] whose parameters are given in Table I and use the Wigner interpolation formula[24] for the exchange and correlation functional. The generated potentials are nonlocal, i.e., they are different for electronic orbitals with s, p, and d symmetries. These potentials were used in previous studies of these compounds.[8,15] The wave functions in the solid are expanded in a plane-wave basis with the same kinetic energy for all the phases considered; these are 60 Ry for BN and 20 Ry for BP and BAs.

The total energies are calculated self-consistently in the momentum space representation[25] and the diagonalization of the large Hamiltonian matrices in BN are done by using the residual minimization method.[26] The in-

TABLE I. Atomic configurations used in generating *ab initio* pseudopotentials. The values in parentheses are the cutoff radii of the respective orbital in atomic units a_0.

	Atomic Configurations
B	$2s^{1.5}(1.00), 2p^{0.5}(0.90), 3d^{0.5}(1.30)$
N	$2s^{2.0}(0.85), 2p^{1.8}(0.80), 3d^{0.5}(1.10)$
P	$3s^{2.0}(1.10), 3p^{1.7}(1.20), 3d^{0.5}(1.80)$
As	$4s^{2.0}(1.20), 4p^{1.7}(1.40), 4d^{0.5}(1.30)$

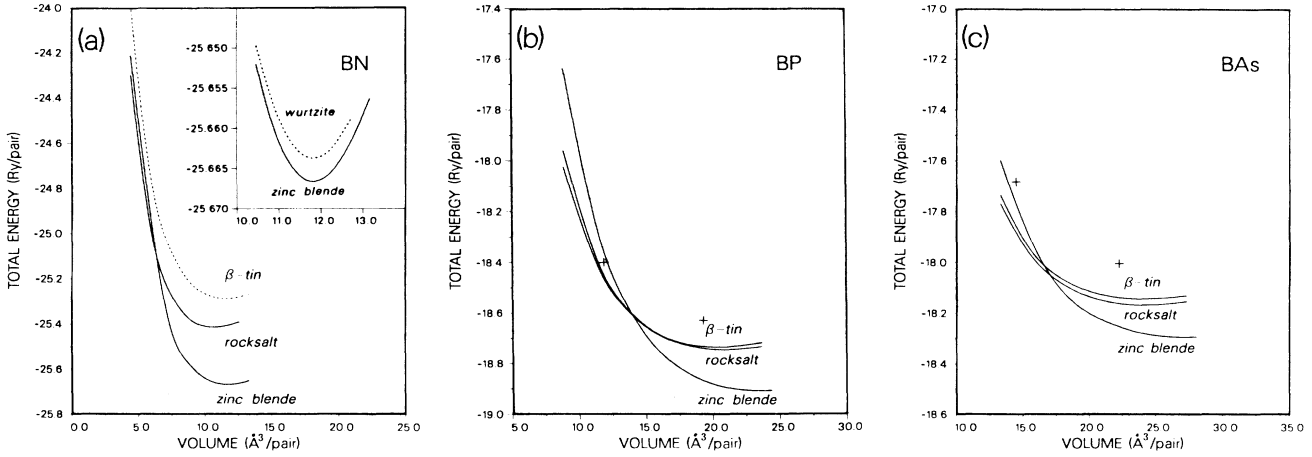

FIG. 1. Calculated total energies as a function of primitive cell volume. (a) BN in zinc-blende, rocksalt, and β-Sn (dashed curve) structures. (b) BP in zinc-blende, rocksalt, β-Sn, and CsCl structures. (c) BAs in zinc-blende, rocksalt, β-Sn, and CsCl structures. The results for the CsCl structure are indicated by the crosses.

tegrations over the Brillouin zones (BZ) are replaced by discrete sums over **k** points. The number of **k** points in the irreducible portion of the BZ change for different structures, but they are chosen to ensure an accuracy of better than 2 mRy/pair. For the insulating zinc-blende phase we chose 10 **k** points. Because of the existence of the Fermi surface, a much larger number of **k** points is used for the metallic phases. For the β-Sn and rocksalt structures we use 100 and 60 **k** points, respectively, although expansions up to 280 **k** points have been tested to assure the above precision.

III. STRUCTURAL PHASE TRANSITIONS

Although experiments indicate that the first high-pressure phase of III-V compounds is not unique and other structures should be considered, we restrict ourselves here to the β-Sn and rocksalt structures. Our goal is to determine which of these two structures is favored by zinc-blende semiconductors with low ionicities. Figure 1 contains the total-energy E_{tot} curves as a function of volume for the compounds in the three structures. These curves were fitted to the Murnaghan equation of state.[27] The calculated values for the static properties are listed in Table II and the transition pressures and volumes are summarized in Table III. For the zinc-blende phase of these compounds, more detailed comparisons with experimental data have been reported in Refs. 8 and 15.

The β-Sn structure can, in principle, be obtained from the zinc-blende structure by changing the c/a ratio of the tetragonal cell which for the zinc-blende structure is equal to $\sqrt{2}$ while in the β-Sn it is approximately 0.55. The rocksalt structure can in principle also be formed from the zincblende by displacing the anions along the diagonal of the cubic cell from $(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$ to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$, where a is the lattice constant. The E_{tot} versus volume curves for the β-Sn structures of BP and BAs were ob-

TABLE II. Lattice constants, bulk moduli, and cohesive energies for BN, BP, and BAs for various structural phases.

			a (Å)	c (Å)	c/a	B_0 (GPa)	E_{coh} (eV)
BN	Zinc-blende	Calc.	3.606			367	14.3
		Expt.	3.615[a]				13.2
	Rocksalt	Calc.	3.493			425	10.9
BP	Zinc-blende	Calc.	4.558			166	11.5
		Expt.	4.538[a]				10.2
	Rocksalt	Calc.	4.339			155	9.3
	β-Sn	Calc.	2.957	4.672	0.58	165	9.1
BAs	Zinc-blende	Calc.	4.777			145	10.6
		Expt.	4.777[a]				
	Rocksalt	Calc.	4.583			143	8.9
	β-Sn	Calc.	3.123	4.935	0.58	141	8.5

[a] Reference 1.

TABLE III. Transition pressures and transition volumes for the zinc-blende (ZB) to rocksalt (RS) structures. The volumes are given as fractions of the calculated equilibrium volumes in the ZB phase.

	P_t (Mbar)	V_t(ZB)	V_t(RS)
BN	11.1	0.45	0.42
BP	1.6	0.64	0.56
BAs	1.1	0.69	0.60

tained by minimizing the ratio c/a for volumes between $0.4V_0$ and $0.6V_0$ where V_0 is the equilibrium volume of the zinc-blende phase. This ratio was shown to be equal to 0.58 and is approximately constant with respect to volume change in this range of volumes. However for BN it was not possible to find a value of c/a at which this structure becomes metastable.[28] The dashed curve in Fig. 1(a) shows the total-energy curve for β-Sn for BN assuming a c/a ratio of 0.58.

We will examine each compound individually, starting with BN. In addition to the rocksalt and β-Sn phases, we have also examined the wurtzite structure for BN [see insert of Fig. 1(a)]. The total-energy curve of the wurtzite structure lies above that of zinc blende for all volumes considered, therefore there should be no pressure-induced transition from zinc blende to wurtzite. However, the wurtzite structure is only slightly higher in energy than the zinc-blende phase (≈ 4 mRy/pair).

For BN, the β-Sn structure is definitely higher in energy than the rocksalt structure. In fact the β-Sn structure is unstable. Figure 2 shows the total energy of BN for a wide range of c/a ratios for a volume equal to $0.45V_0$, where V_0 is the equilibrium volume in the zinc-blende structure. The E_{tot} versus c/a ratio curve has no local minimum around $c/a \approx 0.55$ although there is still some structure around this value. Similar behavior has recently been found in diamond.[19] As shown previously for the case of silicon,[29] the local minimum in the total-energy curve was caused by a local minimum in the Ewald energy around $c/a = 0.55$. In Si the behavior of the total energy follows that of the Ewald energy because the behavior of the electronic energy, which originates from a rather smooth metalliclike charge distribution, is also quite smooth. In BN the minimum in the Ewald energy still exists since its cause is purely geometrical, however the Ewald energy does not dominate because the charge distribution is far from uniform. Figure 3 shows the charge density for BN in the β-Sn structure at the transition volume and $c/a = 0.58$. As can be seen, even at such highly compressed volumes in which the electronic structure is metallic, the charge density is highly concentrated around the N atoms.

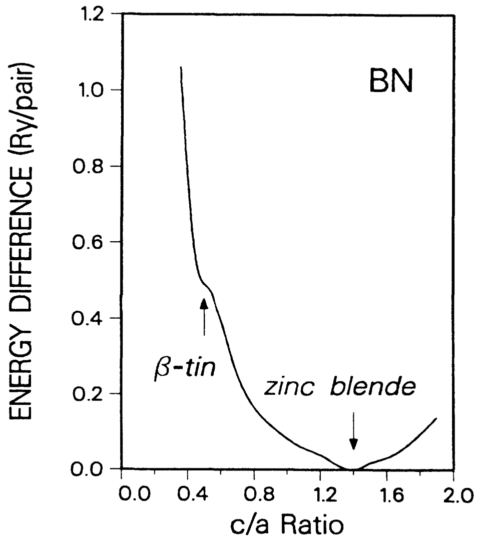

FIG. 2. Calculated total energies as a function of the c/a ratio for BN assuming a primitive cell volume equal to $0.45V_0$.

Figure 4(a) shows the charge-density contours of the high-pressure rocksalt phase of BN at the equilibrium volume of the zinc-blende structure V_0 and the transition volume in the rocksalt structure $0.42V_0$. These are displayed for both the (110) and (100) planes. If we take the last closed contour as an indication of the size of the atom, at the transition volume, the N atoms are much larger than the B atoms and the N atoms touch each other. This is the typical picture of a rocksalt compound where the larger atoms are packed into a fcc structure while the smaller atoms are fitted in between. A more detailed analysis of the charge density will be discussed in Sec. IV.

Figures 4(b) and 4(c) show equivalent contours for BP and BAs; both differ from BN but are similar to each other. Despite the extremely low ionicities of these compounds, the rocksalt structure is still more favorable than the β-Sn at high pressures, however, the energy difference between β-Sn and rocksalt is much smaller than in the case of BN. For BP it should be pointed out that the minimum difference of the energies between the two phases is as small as 3 mRy/pair which is within the limit of precision of the calculation. Since the calculated transition pressure for BP is around 1.6 Mbar, it is possible to determine the high-pressure phase with a diamond anvil cell experiment. So far, no phase transitions have been observed up to 0.68 Mbar.[20] In view of the fact that calculations indicate that other low-ionicity compounds such as BAs and SiC also prefer the rocksalt structure over the β-Sn, we will discuss our results assuming that the rocksalt structure is also more favorable for BP.

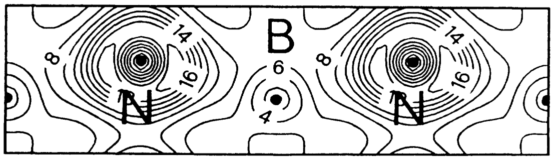

FIG. 3. Valence charge density distribution for BN in the β-Sn structure assuming primitive cell volume equal to $0.45V_0$ and c/a ratio equal 0.58.

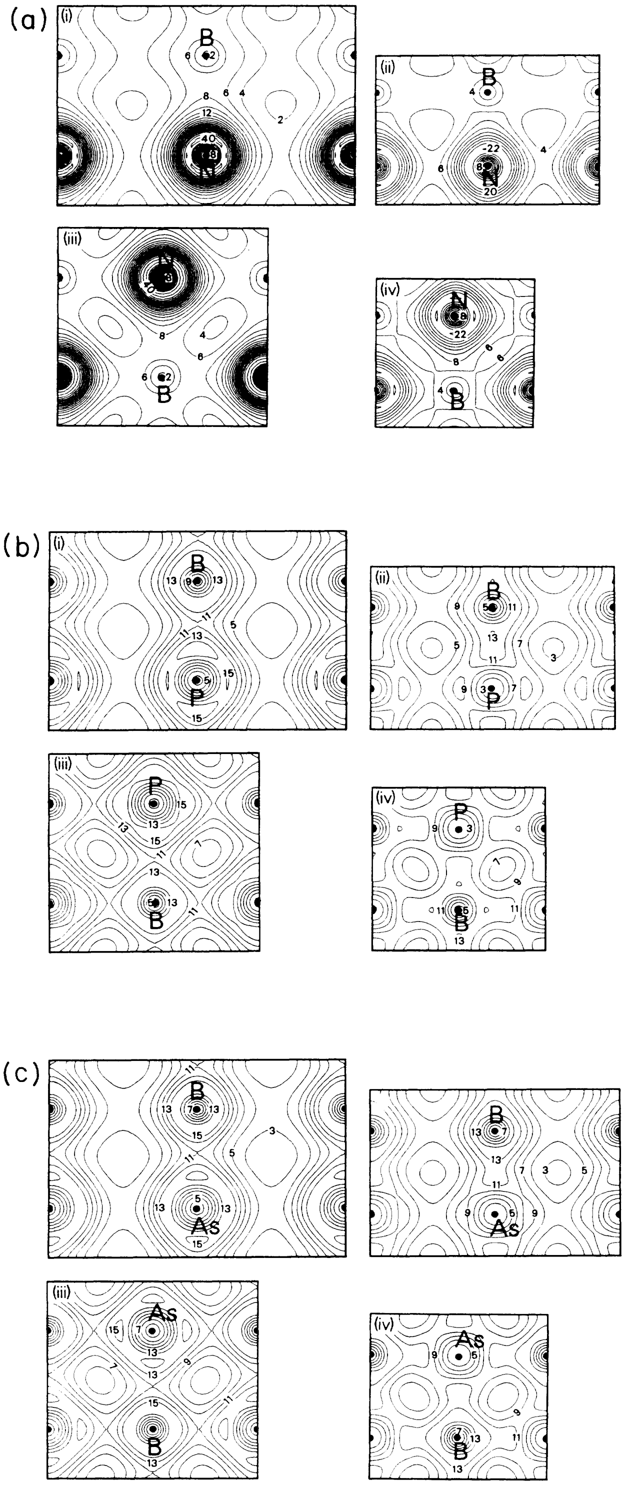

FIG. 4. Valence charge distribution in the rocksalt structure for (a) BN, (b) BP, and (c) BAs. The charge contours are shown in (i) the (110) plane at the equilibrium volumes of the zinc-blende structure and (ii) the (110) plane at the transition volumes in the rocksalt structure; (iii) and (iv) are the same as above for the (100) plane. The lengths are scaled by the ratio of lengths in real space, and the charge densities are in units of electrons per primitive cell volume.

Unlike BN, BP, and BAs show unconventional charge distributions in the rocksalt structure [see Figs. 4(b) and 4(c)]. At the transition volume, both atoms are similar in size. This is more typical for the CsCl structure. We have also calculated the total energies for the CsCl structure for a few volumes. We observe that this structure is at higher energies than either the β-Sn or rocksalt, hence it does not compete as a high-pressure phase in this range of volumes. This is in agreement with previous calculations in III-V compounds.[30] It is therefore evident that size effects are not the only determining factor for the structural stability of BP and BAs.

The transverse optical phonon mode at $\mathbf{k}=0$ corresponds to atomic dislacements along the path that can take the zinc-blende to the rocksalt structure. We have examined the stability of this mode with volume change. For small changes in volume the frequency of this mode was observed to increase[31] with decreasing volume indicating that the energy barrier along this path also increases. The calculated frequency of this mode in BP at $V=0.65V_0$, where V_0 is the equilibrium volume, is 61 THz which is much larger than $\Omega_{\text{TO}}(\Gamma)=23$ THz at V_0. Therefore, the transition is not driven by the softening of this mode.

The preference for the rocksalt structure at high pressures in low-ionicity compounds like BP and BAs indicates that ionicity may not be the only factor involved. In order to gain a more detailed understanding of the zinc-blende to rocksalt transition, we will analyze the charge distribution in more detail in the next section.

IV. BEHAVIOR OF THE VALENCE CHARGE UNDER COMPRESSION

The motivation of this study is to achieve a better understanding of the electronic density distribution at compressed volumes which is fundamental to a study of the mechanisms for the pressure-induced phase transitions. Furthermore, the effective charge is of interest and although we will not compute effective charges precisely, we will use this concept to guide our discussion of the electronic structure. In this series of B compounds a systematic comparison between the valence charge distributions at normal and high pressures is of interest because it appears that in BP and BAs the anion and cation are reversed. In this study we adopt the following procedure: We compare the valence charge densities in the (110) and (100) planes for these three compounds at the equilibrium volume and at the compressed volume. The compressed volumes correspond to the volumes at which the zinc-blende to rocksalt transitions occur (see Table III). In an attempt to quantify the description of the charge distribution we calculate the valence charge enclosed by spheres around the atoms which have radii equal to the average radii of the last closed contours of the figures around the atoms in the (100) plane. This procedure does not lead to a rigorous description of the charge transfer but it is a useful way to describe the redistribution of charge observed in the contour plots.

Figures 5(a)–5(c) show the valence charge density contours in the (110) plane and the (100) planes containing

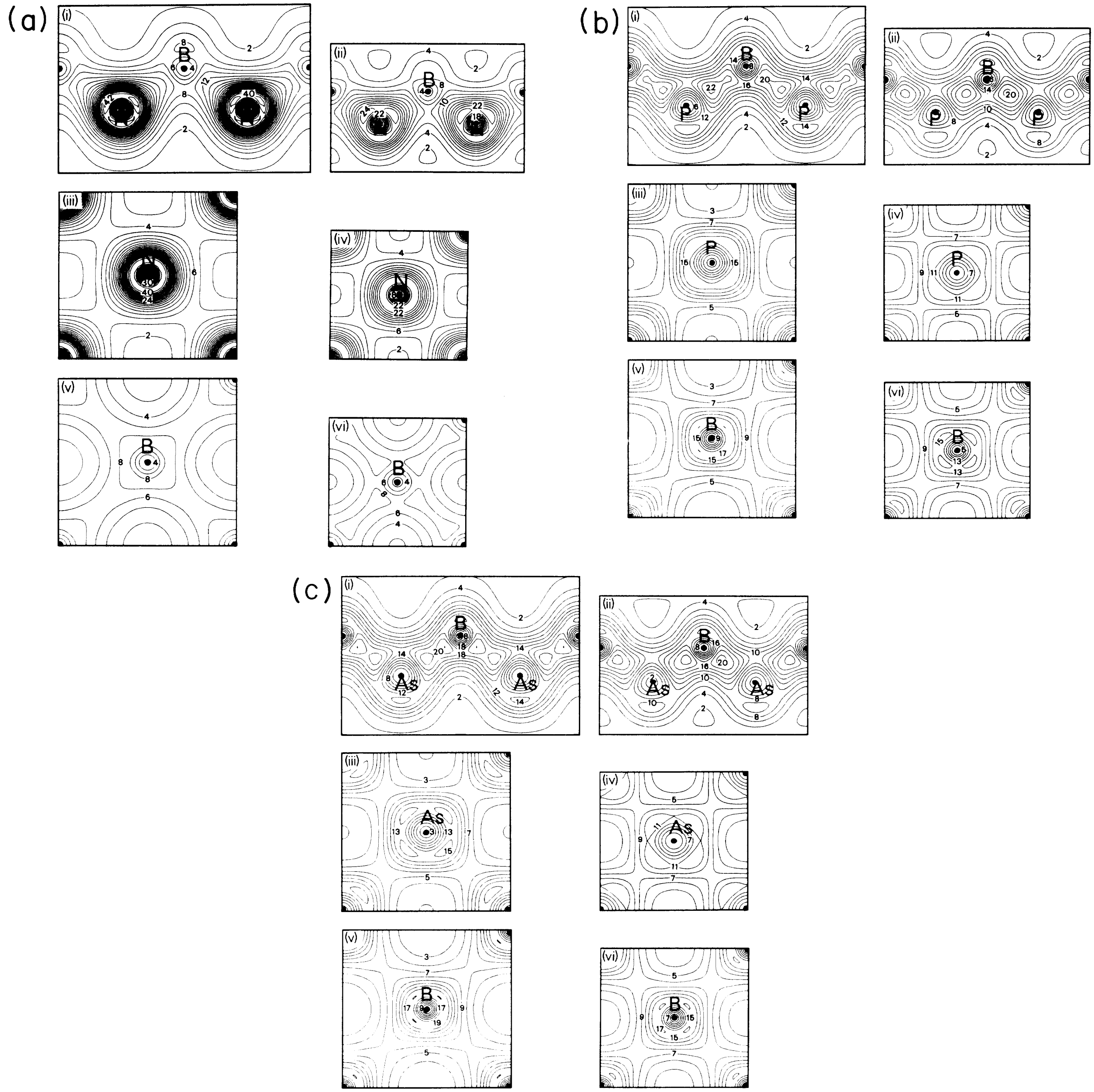

FIG. 5. Valence charge distribution in the zinc-blende structure for (a) BN, (b) BP, and (c) BAs. The charge contours are shown in (i) the (110) plane at the equilibrium volumes and (ii) the (110) plane at the transition volumes; (iii) and (iv) are the same as above for the (100) plane containing the group-V atom; (v) and (vi) are the same as above for the (100) plane containing the group-III atom. The lengths are scaled by the ratio of lengths in real space, and the charge densities are in units of electrons per primitive cell volume.

the column-III or -V atoms at equilibrium and compressed volumes in the three compounds in the zinc-blende structure. The ratio of the sizes of these figures are equal to the ratio of cell sizes in real space and the charges are normalized by e/V, where V is the volume considered. These plots show that as the atoms of column V are changed from N to As, the compounds become less ionic, i.e., the charge becomes more uniformly distributed between the atoms.

For the zinc-blende structure in the (110) planes of BP and BAs at the equilibrium volume it is observed that the bond has a double hump similar to diamond. This originates from the low ionicity of these compounds as well as the absence of p states in the B core which is responsible for the localized nature of the p states of B.[8,15] At the transition volumes, the two humps are fused into one and an increase of charge in the interstitial regions is observed. In the (100) plane the regions associated with specific atoms are identified with closed contours separating them. When the contours in these planes are compared at the normal and compressed volumes an interesting effect is revealed; the regions associated with the atoms seem to change at different rates indicating that the charges associated with the atoms also change at different rates. These changes are quantified in Table IV which lists the average radii of the last closed contours of the figures around the atoms in the (100) planes and the valence charges enclosed inside the corresponding spheres. As can be seen, the summation of the net charges calculated in this way, i.e., the values in parentheses which include the core charges, are not zero. This arises from the fact that the charge in the interstitial region is not associated with any atom. The results indicate that for BN, the region associated with B decreases as well as its associated charge and the corresponding region for N decreases more slowly while its charge increases. In BP and BAs we observe the opposite trend, with P and As behaving like B in BN and B like N in BN respectively.

Behavior similar to BN was observed in GaAs.[32] The observed trend suggests that the relative electron attraction of N with respect to B in BN, increases with increasing pressure, while in BP and BAs the same statement is true about B with respect to P and As. We believe that the behavior of BN is typical of a III-V compound semiconductor while BP and BAs are anomalous cases which can be understood by redefining the anion and cation in these compounds.

Another approach used to study the above trends is to examine the differences between the self-consistent charges and a superposition of atomic charges and this was shown to yield consistent results. The charge rearrangements performed at the equilibrium volume are enhanced at compressed volumes. Although this analysis is not rigorous, it gives a consistent picture of the charge rearrangements and a change of 5% in the radii chosen does not affect the observed trends. Larger changes in the radii would blur the effect.

The above charge-density study motivates further comparisons between the calculated results and empirical schemes for determining atomic sizes and ionicities as well as electronegativities. The charge-density plots for BN indicate that most of the valence charge is concentrated around N. As shown in Table IV, the radii of the last closed contours around this atom is larger than the one around B. This ratio of sizes differs from the empirically determined ratios of covalent radii[11,12] which attribute a larger dimension to B than to N. Our calculations indicate that the larger dimension of the region associated with N is not only due to the more concentrated character of the atomic valence charge of N, which seems to be preserved in the solid, but also due to a large charge rearrangement. In particular the region around N contains more than five electrons.

The high degree of asymmetry observed in the valence charge distribution of BN also illustrates an important aspect concerning the definition of ionicities introduced by Phillips.[11] Phillip's approach is convenient and widely used to classify the tetrahedrically coordinated $A^N B^{8-N}$ compounds. The idea of asymmetry in the valence charge distribution for these compounds is often associated with the concept of ionicity.[12,33] This results from the way in which ionicities are defined with a dependence on only one parameter. As defined by Pauling,[12] ionicity is taken as an increasing function of the empirically determined difference of electronegativities with an upper bound equal to one. According to Coulson,[33] ionicity is the relative difference of occupation of hybridized orbitals centered on atoms A and B, respectively. The definition of ionicity as introduced by Phillips is based on a band-gap model which is described by two parameters C and E_h. The heteropolar gap C is the magnitude of the energy gap produced by the antisymmetric part of the potential $[\frac{1}{2}(V_A - V_B)]$, while E_h, the homopolar gap, is produced by the symmetric part of the potential $[\frac{1}{2}(V_A + V_B)]$.

TABLE IV. Average radii (in Å) of the last closed contours around the atoms in the (100) planes containing the column-III or -V elements and valence charges e_0 and e_t (in units of e) enclosed inside the corresponding spheres at the normal and transition pressures. The values in parentheses include the core charges.

	BN	BP	BAs
r_0^{III}	0.731	1.043	1.095
r_0^{V}	0.992	1.275	1.338
r_t^{III}	0.369	1.020	1.051
r_t^{V}	0.860	1.060	1.092
e_0^{III}	$-1.17(+1.83)$	$-2.56(+0.44)$	$-2.69(+0.31)$
e_0^{V}	$-5.28(-0.28)$	$-4.37(+0.63)$	$-4.25(+0.75)$
e_t^{III}	$-0.23(+2.77)$	$-3.57(-0.57)$	$-3.34(-0.34)$
e_t^{V}	$-5.83(-0.83)$	$-3.54(+1.47)$	$-3.14(+1.86)$

The average optical gap E_g is given by

$$E_g^2=E_h^2+C^2 \tag{1}$$

and the three parameters C, E_h, and E_g are then empirically determined by measurements of the static dielectric constant in A^NB^{8-N} compounds. Ionicities are then defined as

$$f_i=\frac{C^2}{E_h^2+C^2} \tag{2}$$

which is the relative ionic character of the average optical gap.

According to this model, the asymmetry in the valence charge distribution, which reflects the *absolute* asymmetric character of the potential, should be correlated with the parameter C and not with the ionicity f_i, which is only an indicator of the *relative* asymmetric character of the potential. This interpretation is suggested by the more strongly asymmetric character of the charge distribution in BN ($f_i=0.256$ and $C=7.71$ eV) when compared with GaAs's charge,[34] for example ($f_i=0.310$ and $C=2.90$ eV).

Another interesting aspect of the charge rearrangements is shown in Table IV for BP and BAs. The values of the net charges listed inside the parentheses show that even at the equilibrium volume, P and As lose more electrons than B. (The positive net charges arises from the presence of electrons beyond the limits of the spheres which are not associated with any of the atoms.) This fact indicates that the electron attraction of B (neutral B) is greater than that of P or As in these compounds. This effect is consistent with the Phillips value of electronegativities for atoms in tetrahedrically coordinated environments introduced by Phillips.[11] These values were based on the empirically determined electronegativities as defined by Pauling but included the effect of valence electron screening. The new values for the electronegativities were adjusted to agree with the previous values for the atoms of the first row, and the differences between the two definitions then appeared in the other rows of the Periodic Table. The inclusion of screening effects resulted in decreasing values of the electronegativities for the atoms in the lower rows with respect to the previous values. These new values which now attribute a larger value of electronegativity to B than to P or As seem to be appropriate for indicating the charge rearrangements observed in BP and BAs.

The valence charge rearrangements at high pressures have also been addressed using a different approach. An attempt has been made by Sanjurjo *et al.*[31] to describe these effects quantitatively in terms of transverse charges which are defined in terms of the splittings of the TO- and LO-phonon modes at the zone center. In general the transverse charges are viewed as the charges associated with the atoms in a dynamical situation in contrast to the effective charges for a static situation. This work showed that in BN and BP the splittings between the TO(Γ) and LO(Γ) modes decrease with increasing pressure. The interpretation of this experimental fact was that the polarization densities developed with the atomic displacements in the LO mode decrease with increasing pressure, i.e., the transverse effective charges associated with the atoms when these are displaced from their equilibrium positions decrease with increasing pressure. Our results indicate that the behavior of the static effective charge is quite different. For all the compounds studied, the charge rearrangements performed at equilibrium volume are even more enhanced at the compressed volumes considered, although the charge rearrangements in BP and BAs are clearly reversed with respect to BN.

V. DISCUSSION

The behavior of BP and BAs can be viewed as anomalous since the empirical approach[11] and quantum-mechanical calculations of model systems[16,35] indicate that zinc-blende compounds with low ionicities prefer β-Sn to the rocksalt structure at high pressures. These studies were based on results obtained for zinc-blende compounds with relatively large volumes and did not include compounds containing elements of the first row which have smaller equilibrium volumes. It was shown by the model system study[16] that for a family of A^NB^{8-N} compounds in the same row of the Periodic Table, increasing heteropolar character makes the rocksalt structure more favorable than the β-Sn at high pressures. The transition pressure to rocksalt decreases with increasing ionicity and the rocksalt structure eventually becomes stable at zero pressure. For such a family of compounds the equilibrium volume remains roughly constant and so does the homopolar gap E_h, which is related to the equilibrium volume. Using scaling arguments based on the group-IV elements, Phillips chose E_h to be proportional to $d^{-2.5}$, where d is the nearest-neighbor distance.

Calculational results are presented in Table II. The major trends are summarized as follows: (a) Variations of the bulk moduli and equilibrium volume among different phases within a given compound are smaller than the variations between compounds. In particular, the differences in bulk moduli between phases appear to scale inversely with the equilibrium volume in the zinc-blende structure V_0, i.e., the larger the volume, the smaller the changes in the bulk moduli. (b) The differences in equilibrium volume between phases scale directly with V_0, i.e., the larger the volume in the zinc-blende phase, the larger the differences in the equilibrium volumes of high-pressure phases. (c) The difference in cohesion between the zinc-blende and the rocksalt phase decreases with decreasing heteropolarity. This trend is opposite to the trend observed for a family of A^NB^{8-N} compounds with approximately the same volume and confined to the same row of the Periodic Table. This indicates that the effects of volume, i.e., homopolar character, are dominating in the sequence of compounds considered.

The trends in the transition pressures and transition volumes observed in Table III can then be interpreted in light of the above observations. We note that the transition pressure P_t depends on the following factors: (a) the bulk modulus B_0 (the larger B_0, the larger P_t), (b) the difference in equilibrium volumes ΔV_0 for different phases (the larger ΔV_0, the smaller P_t), and (c) the difference in cohesion ΔE_{coh} between the phases (the larger ΔE_{coh}, the larger P_t). In the sequence of compounds considered all these factors are dominated by volume effects which add up coherently, therefore the transition pressures are also dominated by volume effects, i.e., the larger the volume the smaller the transition pressure. This behavior appears to be typical of similar sequences of compounds[36] and was also observed in a comparative first-principles study of Ga and Al compounds under pressure.[30,32] A similar argument can be extended to the observed trends in the transition volumes.

Another trend displayed by our calculation concerns the relative stability between the two high-pressure phases. We note that in this sequence the difference in energies between the rocksalt and the β-Sn phases does not change systematically as the column-V elements are replaced. In particular, this difference in energies decreases when N is replaced by P and increases when P is replaced by As. In previous *ab initio* studies of these structures in similar sequences of compounds[30,32] it was observed that the rocksalt phase becomes more stable with respect to the β-Sn whenever the column-V element is replaced and the difference of electronegativities between the atoms increases. Our findings therefore suggest that the difference of electronegativities in the boron compounds decreases when replacing N by P but increases by replacing P by As. This behavior is conveniently described by the Phillips scale of electronegativities[11] which attributes electronegativities X for the elements involved in these compounds in the following order: $X_{\text{N}} > X_{\text{B}} > X_{\text{P}} > X_{\text{As}}$. Therefore the behavior of the high-pressure phases in these compounds also indicates that in BP and BAs the usual assignments of cation and anion should be reversed.

The preference for the rocksalt structure over the β-Sn as the first high-pressure phase in this sequence of compounds as well as the simple cubic structure in diamond is a very important aspect that ionicity or heteropolarity arguments do not explain satisfactory. It has been suggested that in carbon, which is also a first row element, this behavior is caused by the lack of p states in the core and also by the large energy separation of the d orbitals from the Fermi level,[18] which makes the stabilization of a metallic structure like β-Sn more difficult. These ideas are currently under investigation in a model study of a homopolar semiconductor by introducing an extra attractive (repulsive) character to the nonlocal p and d components of its pseudopotential.[37] This procedure artificially increases (decreases) the binding energy of these atomic states and enhances their role in the stabilization of the two examined high-pressure phases. These hypothesis are not easily checked in the above compounds because a perturbation of B's potentials, which is the first row element in BP and BAs, also perturbs their heteropolarities, which by itself plays a very important role in the stabilization of the rocksalt phase.[16]

Preliminary quantitative results of such a study indicate that the large energy separation of the d states from the Fermi level is not the cause of this behavior. In fact the simple cubic as well as the β-Sn phase are metallic and show approximately the same amount of d character in the occupied states, and lowering the energy of the d states also lowers the energy of these phases with respect to the diamond structure but not with respect to each other, and the overall effect is just a decrease in the transition pressure. On the other side, the binding energy of the p states seems to affect the relative stability of the rocksalt and β-Sn phases. A sharper effect caused by lowering the binding energy of the p states is an increase in the transition pressure since the energy of the diamond structure, which has a relatively larger p character, is lowered by a larger amount.

It has been suggested recently that the stability of the rocksalt structure with respect to zinc blende is accompanied by a closing of the gap in the zinc-blende structure.[38] However for the first-row compounds discussed here, at the transition volumes the zinc-blende phases are still insulators. For example, in the zinc-blende phase, the fundamental gap of BN opens under volume compression,[8] and $E_g = 6.6$ eV at the transition volume. After the transition, the gap remains approximately 6.6 eV. As discussed earlier, this transition may not be the first high-pressure phase change since other intermediary phases not considered here may become energetically more favorable.

The band structure of these compounds in the rocksalt phase at the transition volume is shown in Fig. 6. The dispersions along the main symmetry lines differ from typical dispersions of rocksalt compounds stable at zero pressure. The insulating phase of BN has an indirect gap $\Delta_1^v \rightarrow \Gamma_{15}^c$ while typical rocksalt compounds have direct gaps $\Gamma_{15}^v \rightarrow \Gamma_1^c$. The slightly ionic compounds BP and BAs are semimetal and metal, respectively. This is caused by a systematic lowering of the conduction bands relative to the valence bands with decreasing ionicity and a crossing of bands of the same symmetry along the Δ line.

VI. CONCLUSIONS

We have calculated the relative stability of the β-Sn and rocksalt phases at high pressures for BN, BP, and BAs. The calculations indicate that these compounds favor the rocksalt phase at compressed volumes even though BP and BAs are the least ionic of the III-V zinc-blende compounds. In BN the β-Sn structure is shown to be unstable even at highly compressed volumes. The preference for the rocksalt structure over the β-Sn as the first high-pressure phase in this sequence of compounds as well as the simple cubic in diamond is a very important aspect that arguments based on ionicities or heteropolarities cannot explain. The strong volume dependence of the transition pressures as well as the similarities between the structural energies of equivalent solid phases of BN and C, imply that beside the strong role played by the heteropolar character of the compound there is an important contribution to the high-pressure phase stabilities due to their homopolar character. To unfold the consequences of different

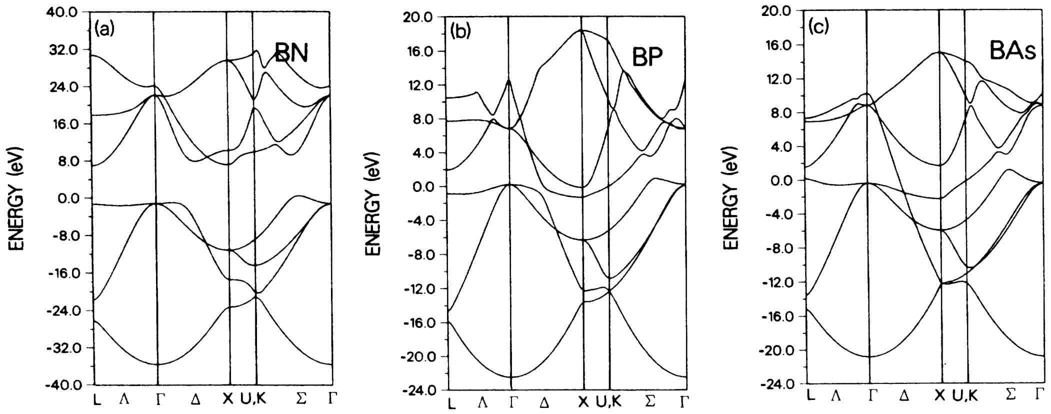

FIG. 6. Band structures of (a) BN, (b) BP, and (c) BAs at the transition volumes in the rocksalt structure.

homopolarities, a systematic study in a model homopolar semiconductor is currently under investigation and preliminary results indicate that the relative contributions of each component of the pseudopotential, i.e., nonlocality, can be a determining factor to the relative stability of the high-pressure phases. The lack of consistency of these compounds with the proposed high-pressure versus ionicity phase diagrams for zinc-blende semiconductors indicate that to achieve a unified description of the relative stability of the β-Sn and rocksalt structures at high pressures for the whole family of $A^N B^{8-N}$ semiconductors, the effects of both heteropolar and homopolar character should be considered separately.

We have also described the valence charge rearrangements with volume compression in the zinc-blende phase of BN, BP, and BAs by computing the charges inside spheres with radii corresponding to the last closed contours around the atoms in the (100) plane. The results show that in BN the charge transfer from B to N increases with decreasing volume while in BP and BAs this charge transfer also increases but has the opposite trend with P and As behaving like B in BN. We believe that the behavior of BN is typical of most III-V compound semiconductors while BP and BAs are anomalous cases which can be understood by reversing the usual assignments of anion and cation in these compounds. This reversal of assignments is appropriately described by the Phillips's scale of electronegativities, which can also be conveniently used to interpret the trends in the relative stabilities between the high-pressure phases in this sequence of compounds.

The conduction properties in the rocksalt phase of these compounds have been investigated and contrary to results suggested by model quantum-mechanical calculation for third-row compounds, BN remains insulator while BP is a semimetal and BAs is a metal.

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