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Electronic and structural properties of BN and BP

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We present a pseudopotential study within the local-density formalism of the structural and electronic properties of zinc-blende BN and BP. The ground-state properties of these systems such as bulk moduli, lattice constants, cohesive energies, and frequencies of the TO phonon mode are in good agreement with experimental results. The valence charge density of BP shows two local maxima along the bond, which is similar to the case of diamond. In contrast, the charge density of BN is similar to that of a typical III-V compound semiconductor. The resulting band structures have some important features which are in disagreement with previously published work. Like most III-V compound semiconductors, the fundamental gap in BP decreases with decreasing volume. The corresponding gap in BN, however, increases with decreasing volume as was also found in diamond.

I. INTRODUCTION

There is considerable interest in the study of properties of zinc-blende BN and BP. From a technological point of view these materials have useful physical properties like extreme hardness, high melting points, and interesting dielectric and thermal characteristics.[1] From a more basic perspective, comparison of the two compounds is instructive since both can be isostructural to diamond, but BN has the largest heteropolar gaps of the III-V compounds,[2] while BP has one of the smallest heteropolar gaps (except for BA's). In fact, BP is even less ionic than SiC,[2] which can be viewed as being the isoelectronic IV-IV compound to BP.

The structural properties of these two compounds differ. BP is found in the zinc-blende structure; we find no reports of other phases. Although BN is normally found in the hexagonal phase (graphitelike),[3] the zinc-blende structure was synthesized[4] in 1957. Like diamond, BN is known to be a very hard material[5] and the only report of its bulk modulus (465±50 GPa) (Ref. 6) is an interpolation based on empirical relations for the elastic constants. This value is even larger than the accepted value for diamond (442 GPa).[7,8] The bulk modulus for BP was measured to be 173 (Ref. 9) and 267 GPa (Ref. 10).

Unfortunately there is limited experimental data on the electronic structure of these compounds. For BN, soft x-ray spectroscopy studies yielded widths of groups of valence bands and a value for the indirect gap of 6.0 eV.[11] Studies using uv absorption reported a minimum value of 6.4 eV for the indirect gap.[12] Although several theoretical calculations are available in the literature, their results differ considerably. The calculated indirect gap for BN is reported to be in a range from 3.0 to 10.5 eV.[13–23] This variation in theoretical gap values may be caused by difficulties in the treatment of the valence states in the absence of p core states.

For BP, optical reflectivity data provided some information about direct gaps,[24] and optical-absorption measurements gave an indirect gap of 2.0 eV.[25] There have been two theoretical calculations for the full band structure of BP.[18,23] Both have made use of adjustable parameters to reproduce the band gaps, but the topology of the reported bands in these studies differ significantly for both the valence- and conduction-band states.

Another property of interest is the behavior of the electronic states under volume compression. It is experimentally observed[3] that the indirect gap in diamond increases with decreasing volume. This behavior is different from that of other diamond and zinc-blende semiconductors,[3] and it appears to be related to the large relative energy separation of the atomic d states from the top of the valence band. Hence, studies of BN and BP should help to understand this effect. For BN, the behavior of the gap under pressure was studied by Zunger and Freeman.[19] These authors found an increasing gap with decreasing lattice constant, but in this first-principles calculation the gap at equilibrium volume is large compared to the experimental value. This provides further motivation to reexamine the behavior of the conduction states under volume compression using a different calculational technique. Another interesting electronic property to examine in BN and BP is the possibility of the existence of two local maxima in the total charge density along the bond, as is observed in diamond.[7] This effect is usually associated with the absence of p core states in first-row elements.

In the present work we use the total-energy pseudopotential technique employing the local-density approximation to calculate the following ground-state properties of BN and BP: bulk moduli, lattice constants, cohesive energies, frequencies of the TO(Γ) phonon mode, and total electronic charge densities. Although this approach fails to describe accurately the energies of excited states, it usually provides a qualitative description of these states; hence, we have used this approach to calculate the full band structure and the behavior of valence and conduction states under volume compression.

In Sec. II we briefly describe the method of calculation. In Sec. III the structural properties are presented and compared with other theoretical and experimental results. In Sec. IV, we present the results of the electronic properties and compare with previous band-structure calculations and experimental information. The behavior of the electronic states under volume compression and the total valence charge densities are also given. In Sec. V, concluding remarks are made.

II. METHOD

The calculations are based on the pseudopotential—total-energy scheme[26] using the local-density approximation (LDA) (Ref. 27) for electron-electron interactions. The nonlocal ionic pseudopotentials *s*, *p*, and *d* symmetries are generated by the method proposed by Hamann, Schlüter, and Chiang,[28] and the Wigner interpolation formula[29] is used for the exchange and correlation functional. They reproduce eigenvalues and excitation energies converged to within 1.5 mRy for excited configurations in a range of 1.5 Ry for N and to within 1 mRy over a range of 1.5 Ry for B. The pseudopotentials of P used here were previously employed to study structural properties of black phosphorus.[30]

The crystal total energies are calculated self-consistently in the momentum space representation.[31] The wave functions are expanded in terms of plane waves with a kinetic energy cutoff $E_{\rm PW}$ of 60 and 20 Ry for BN and BP, respectively. The large $E_{\rm PW}$ for BN is required because of the strongly attractive character of the *p* potential of N. The corresponding number of plane waves is approximately 950 and 350 per molecule for BN and BP, respectively. To diagonalize the large Hamiltonian matrix of BN, the residual minimization method is used.[32] For the summation over the Brillouin zone, a uniform grid of ten **k** points is chosen. The total energies are computed as a function of volume and then fitted to the Murnaghan equation of state.[33] Thus, the ground-state properties, such as lattice constants and bulk moduli, can be obtained. To investigate the behavior of the electronic states under pressure, we reduce the volume up to 50% of the equilibrium volume.

III. STRUCTURAL PROPERTIES

The calculated ground-state energies plotted as functions of the volume for the two compounds are shown in Figs. 1 and 2. The computed equilibrium lattice constant *a*, bulk modulus B_0, cohesive energy $E_{\rm coh}$, and frequency of the transverse-optical vibrational mode at $q=0$, TO(Γ), are given in Table I. For both BN and BP, the calculated lattice constants are in good agreement with the measured values[3] to within 0.4%. Comparisons with available reported data for the bulk moduli suggest that the theoretical results are underestimated in both cases. However, the reported value for BN was estimated[6] using the relation between bulk modulus and the elastic constants which were interpolated by using empirical relations and not directly measured.[34] For BP, the value of B_0 obtained using the measured elastic constants is 173 GPa,[9] which is in good agreement with our calculated value, while the value obtained by adjusting the Murnaghan's equation to the measured volume versus pressure curve is 267 GPa.[10] The reason for this disagreement between results obtained by using different experimental techniques, is not clear. It is interesting to compare our results for B_0 with the values obtained using the

TABLE I. Lattice constants, bulk moduli, cohesive energies, and phonon frequencies of the TO(Γ) modes for BN and BP in the zinc-blende structure.

		a (A)	B_0 (GPa)	$E_{\rm coh}$ (eV)	$f_{\rm TO}$ (THz)
BN	Expt.	3.615[a]	465[b]	13.2[c]	31.6[d]
					32.0[e]
	Calc.	3.606[f]	367[f]	14.3[f]	30.1[f]
			367[g]	12.8[h]	
				12.2[i]	
BP	Expt.	4.538[a]	173[j]	10.24[c]	23.9[d]
			267[k]		24.6[e]
	Calc.	4.558[f]	165[f]	11.5[f]	23.0[f]
			166[g]		

[a] Reference 3.
[b] Interpolated using empirical relations for the elastic constants (Ref. 6).
[c] Estimation using Refs. 38 and 39 (see the text).
[d] Raman spectroscopy (Ref. 6).
[e] ir absorption (Ref. 41).
[f] This calculation.
[g] Empirical relation $1761d^{-3.5}$ (Ref. 35).
[h] *Ab initio* calculation (Ref. 19).
[i] HF exact exchange with final corrections of correlation (Ref. 22).
[j] Brillouin scattering (Ref. 9).
[k] High pressure *in situ* x-ray diffraction (Ref. 10).

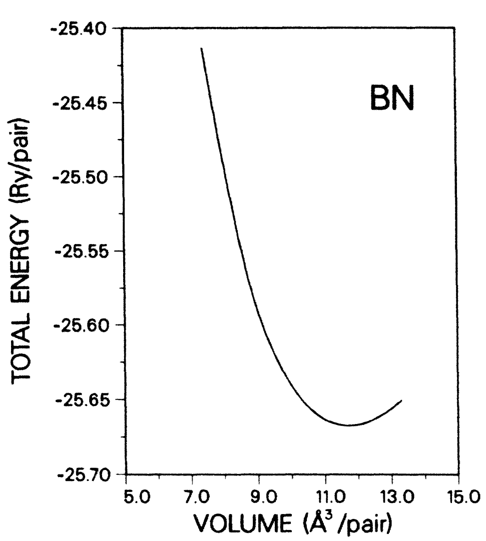

FIG. 1. Calculated total energies as a function of primitive cell volume in the zinc-blende BN. The experimental equilibrium volume is 11.704 Å ^{3}.

empirical relation[35] $B_0=1761d^{-3.5}$, where d is the nearest-neighbor distance in angstroms. This relation gives $B_0=367$ and 166 GPa for BN and BP, respectively, in excellent agreement with our results.

To test the dependence of a and B_0 on the exchange and correlation functional, we also use the Hedin and Lundqvist formulation.[36] We find that the bulk modulus increases by about 3% while the lattice constant decreases by about 1%. Furthermore, the values of a and B_0 are found to be rather insensitive to different sampling of **k** points in the Brillouin-zone integrations. With two **k** points, the lattice constants change by less than 0.1% while the variation of the bulk modulus are of the order of 3%.

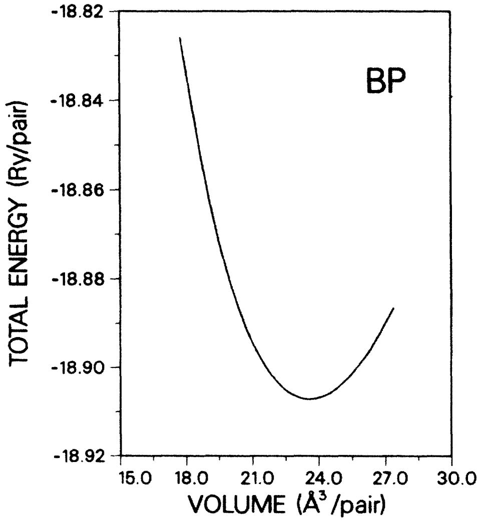

FIG. 2. Calculated total energies as a function of primitive cell volume in the zinc-blende BP. The experimental equilibrium volume is 23.685 Å ^{3}.

The cohesive energies are obtained by subtracting the total energies of the isolated atoms from the total ground-state energy of the solid. An estimation of the error caused by the finite number of plane waves used in the calculation suggests that the cohesive energies would change by approximately 1 eV/pair when E_{PW} is extrapolated to infinite. A correction due to zero-point vibrational energy was estimated by using the Debye model ($E_{\text{ZP}}=\frac{9}{4}k_B\Theta_D$, where Θ_D is the Debye temperature). For BN this correction was approximately 0.34 eV/pair ($\Theta_D=1700$ K) (Ref. 3) and for BP, approximately 0.18 eV/pair ($\Theta_D=985$ K) (Ref. 3). A final correction was made to take into account the spin polarization energy of the atoms. The estimates were obtained using polarized and unpolarized atomic calculations[37] and are equal to 2.5, 1.7, and 0.9 eV for N, P, and B, respectively. The experimental cohesive energies are obtained by adding the heat of formation[38] to the heat of atomization of the elements.[39]

The frequency of the transverse optical phonon mode at Γ in the Brillouin zone is calculated using the frozen-phonon approximation.[40] This phonon mode is simulated by displacing one ion with respect to the other in the unit cell along the [111] direction. The coefficients of even terms up to fourth order in the Taylor expansion of the increase in energy $\Delta E(u)$, where u is the displacement of the ions from the equilibrium position, were obtained by plotting the quantity

$$\overline{\Delta E}(u)=[\Delta E(u)+\Delta E(-u)]/2u^2 \tag{1}$$

versus u^2. Since $\overline{\Delta E}(u)$ drops odd powers in u, the intercept at $u^2=0$ gives the coefficient of the second power term. The calculated frequencies are smaller by approximately 4% than the experimental values.[6,41]

IV. ELECTRONIC PROPERTIES

A. Band structures

The important features of the band structure of BN are given in Table II where available experimental data and the results of previous calculations are reported in chronological order. In 1952, Philipp and Taft[42] mentioned that crude reflectivity data on BN indicated structure in the region of 9 to 10 eV and a prominent peak at 14.5 eV which supported the idea of large direct gaps. In 1968 the K-band x-ray emission spectra[11] reported upper bound values of 6 eV for the indirect gap and 22 eV for the full valence bandwidth. uv absorption experiments[12] gave a lower bound value of 6.4 eV for the indirect gap, and K and L x-ray emission spectra[43] yielded profiles of the density of states.

On the theoretical side, an early band structure of BN was reported in 1960 by Kleinman and Phillips.[13] By treating the antisymmetric pseudopotential as a perturbation to the crystal Hamiltonian of diamond, they obtained an indirect gap ($\Gamma_{15}^{v}\rightarrow X_1^{c}$) of 10.5 eV. Next, a calculation[14] using linear combinations of bond orbitals yielded values for the bandwidths substantially different from the previous calculation. The symmetrized orthogonalized-plane-wave (OPW) method[15] predicted an indirect gap

($\Gamma^v_{15}\rightarrow X^c_1$) of 3.0 eV, which is smaller than the corresponding gap in diamond[3] (5.4 eV). This result appeared unusual since, in general, gaps increase in going from a group-IV material to the corresponding III-V compound. An augmented-plane-wave (APW) calculation[16] yielded no direct transitions in the range of 14.5 eV,[17] which is the energy of the prominent peak that was observed in the reflectivity spectrum.[42] A nonlocal empirical-pseudopotential method (EPM) calculation[18] gave larger gap and larger valence bandwidths than the values predicted by x-ray spectroscopy. This work also yielded a direct gap ($\Gamma^v_{15}\rightarrow \Gamma^c_1$) in disagreement with previous calculations. An *ab initio* calculation[19] using the LDA to describe the exchange and correlation potentials gave an indirect gap ($\Gamma^v_{15}\rightarrow \Delta_{\min}$) of 8.7 eV, which is larger than the two previous experimental estimates. A plane-wave-Gaussian (PWG) mixed basis method was applied[20] yielding a direct gap of 9.2 eV at X, and an indirect gap ($\Gamma^v_{15}\rightarrow X^c_1$) of 4.3 eV. Another nonlocal EPM calculation[21] produced essentially the same features as the previous EPM calculation. A Hartree-Fock (HF) exact exchange calculation[22] reported large bandwidths and gaps. The most recent calculation was carried out by Huang and Ching[23] using a minimum-basis semi-*ab-initio* approach in which a gap of 7.0 eV was obtained by adjusting the exchange-correlation

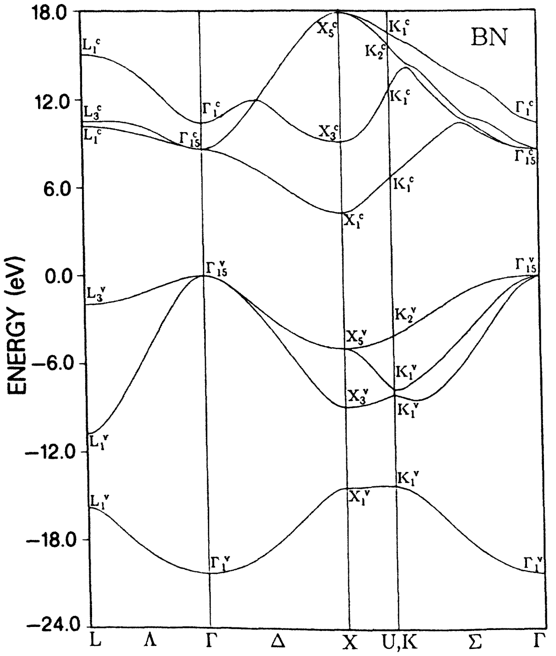

FIG. 3. Electronic band structure of zinc-blende BN at the calculated equilibrium volume. Energies are measured from the top of the valence band.

TABLE II. Summary of important features of the band structure of BN. The values interpolated from published figures are denoted by asterisks.

	Lower valence band (eV)	Upper valence band (eV)	Full valence band (eV)	Minimum gaps (eV) indirect	Minimum gaps (eV) direct
			Theoretical		
a	5.6	3.6	18.0	10.5 ($\Gamma^v_{15}\rightarrow X^c_1$)	14.3 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
b	7.0	5.1	12.6		
c	5.0	12.7*	23.2*	3.0 ($\Gamma^v_{15}\rightarrow X^c_1$)	7.6 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
d	4.5	8.0	17.8	7.2 ($\Gamma^v_{15}\rightarrow X^c_1$)	8.9 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
e	6.8*	16.5	27.5	7.6 ($\Gamma^v_{15}\rightarrow X^c_1$) or ($\Gamma^v_{15}\rightarrow L^c_1$)	8.4 ($\Gamma^v_{15}\rightarrow \Gamma^c_1$)
f	5.1	9.0	19.1	8.7 ($\Gamma^v_{15}\rightarrow \Delta_{\min}$)	10.8 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
g	6.5*	11.3*	20.4	4.3 ($\Gamma^v_{15}\rightarrow X^c_1$) or ($\Gamma^v_{15}\rightarrow K^c_1$)	9.2 ($X^v_5\rightarrow X^c_1$)
h	7.3	14.0	27.4	8.0 ($\Gamma^v_{15}\rightarrow X^c_1$) or ($\Gamma^v_{15}\rightarrow L^c_1$)	14.3 ($\Gamma^v_{15}\rightarrow \Gamma^c_1$)
i	9.3*	15.0*	30.0*	11.3*($\Gamma^c_{15}\rightarrow X^c_1$)	14.6 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
j	5.5	9.7	19.9	7.0 ($\Gamma^v_{15}\rightarrow X^c_1$)	9.9 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
k	5.9	10.8	20.3	4.2 ($\Gamma^v_{15}\rightarrow X^c_1$)	8.6 ($\Gamma^v_{15}\rightarrow \Gamma^c_{15}$)
			Experimental		
l			<22.0	<6.0	
m				≈ 6.4	

[a] OPW pseudopotential (Ref. 13).

[b] Linear combination of bonding orbitals (Ref. 14).

[c] OPW (Ref. 15).

[d] APW (Ref. 16).

[e] Nonlocal EPM (Ref. 18).

[f] *Ab initio* calculation (Ref. 19).

[g] PWG (Ref. 20).

[h] Nonlocal EPM (Ref. 21).

[i] HF exact exchange (Ref. 22).

[j] Semi—*ab-initio* approach (Ref. 23).

[k] Present calculation.

[l] Soft x-ray spectroscopy (Ref. 11).

[m] uv absorption (Ref. 12).

potential.

Our calculated band structure is shown in Fig. 3. The full valence bandwidth is equal to 20.3 eV, which is in good agreement with the value of ≈22 eV reported by soft x-ray spectroscopy, and an indirect gap ($\Gamma_{15}^{v} \rightarrow X_1^c$) equal to 4.2 eV. Considering that the LDA has been used in this calculation, an underestimation of the gap by 30% to 50% is expected. A rigid shift of the conduction bands upward by approximately 30% of the actual value of the gap, i.e., 1.8 eV, would bring the calculated gap closer to the reported experimental value of ≈6 eV. At L we observe that the conduction states L_1^c and L_3^c have a small energy separation. The calculated transitions $L_3^v \rightarrow L_1^c$ and $L_3^v \rightarrow L_3^c$ correspond to 12.1 and 12.6 eV, respectively. If the shift of 1.8 eV is assumed, these transitions become 13.9 and 14.4 eV, which are close to the value of 14.5 eV of the reported strong peak in the reflectivity spectrum.[42] The lowest conduction state at Γ is reported by the majority of the calculations as being Γ_{15}^c; however, the EPM calculations[18,21] have reported Γ_1^c as the lowest conduction state. Although the energy at Γ_1^c is lowered with respect to the Γ_{15}^c state as ionicity increases, BN is isoelectronic to diamond which has Γ_1^c above Γ_{15}^c.[7] However the more ionic compound in the series, BeO, has Γ_1^c below Γ_{15}^c,[44] hence both orderings are possible in BN. We obtain a minimum direct gap ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$) of 8.6 eV.

Table III gives experimental information about BP together with results of previous calculations; the calculated band structure is shown in Fig. 4. The reflectivity spectrum of BP reported[24] three main peaks at ≈5.0, 6.9, and 8.0 eV which were tentatively assigned to direct transitions $\Gamma_{15}^v \rightarrow \Gamma_{15}^c$, $X_5^c \rightarrow X_1^c$, and $L_3^v \rightarrow L_3^c$, respectively. An indirect gap of 2 eV was obtained by optical-absorption experiments.[25] Although x-ray band spectra have been reported[43] no numerical values for the bandwidths were explicitly mentioned. A rough estimation of the full valence bandwidth yields a maximum value of approximately 17 eV. A theoretical estimate of the band gaps was made by Van Vechten in 1969 using a quantum dielectric theory of electronegativity.[45] The values of transitions predicted by the reflectivity spectrum as well as the indirect gap were well reproduced by adjusting an external parameter corresponding to the dielectrically defined difference of electronegativity. An EPM calculation[18] was done to reproduce the gap and the reflectivity spectrum adjusting the pseudopotential form factors. This study led to a minimum direct gap at L and the lowest conduction state was obtained at Γ_1^c. A recent band-structure calculation[23]

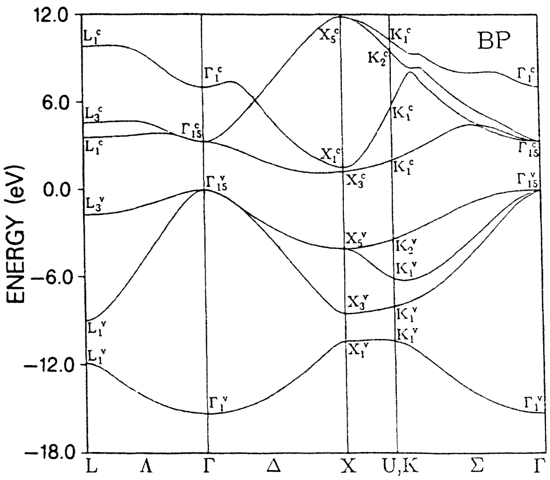

FIG. 4. Electronic band structure of zinc-blende BP at the calculated equilibrium volume. Energies are measured from the top of the valence band.

TABLE III. Summary of important features of the band structure of BP. The values interpolated from published figures are denoted by asterisks.

	Lower valence band (eV)	Upper valence band (eV)	Full valence band (eV)	Minimum gaps (eV) indirect	direct
			Theoretical		
a					4.9 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)
b	5.7*	11.3*	17.9*	2.2 ($\Gamma_{15}^v \rightarrow X_1^c$)	5.0 ($L_3^v \rightarrow L_1^c$)
c	2.6	6.2	11.8	≈2.0 ($\Gamma_{15}^v \rightarrow L_1^c$)	≈2.0 ($\Gamma_{15}^v \rightarrow \Gamma_1^c$)
d	4.9	9.0	15.3	1.2 ($\Gamma_{15}^v \rightarrow \Delta_{\min}$)	3.3 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)
			Experimental		
e					5.0 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)
f				2.0 ($\Gamma_{15}^v \rightarrow X_1^c$)	
g			< 17*		

[a] Quantum dielectric theory (Ref. 45).

[b] EPM (Ref. 18).

[c] Semi—*ab-initio* approach (Ref. 23).

[d] Present calculation.

[e] Optical reflectivity (Ref. 24).

[f] Optical absorption (Ref. 25).

[g] Soft x-ray spectroscopy (Ref. 43).

using a semi-*ab-initio* approach obtained an indirect gap ($\Gamma_{15}^c \rightarrow L_1^c$) of 2.0 eV and a comparable direct gap ($\Gamma_{15}^c \rightarrow \Gamma_1^c$) of approximately 2.0 eV.

The present calculation gives an indirect gap ($\Gamma_{15}^c \rightarrow \Delta_{\min}$) of 1.2 eV and direct gap ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$) of 3.3 eV. At X we obtain the lowest conduction state with symmetry X_3^c instead of X_1^c, as most of the III-V compound semiconductors. The difference between these two states is subtle and their labels can be exchanged under a change of origin, but X_1^c, being a typical antibonding state, has an associated charge density that is mostly concentrated in the interstitial region close to the cation[46] while in X_3^c the charge is mainly in the interstitial close to the anion. This same ordering of levels at X was observed in BAs,[47,48] which also has a very small ionicity. Further comparison with experiment is difficult because of the lack of experimental data, but summarizing, the calculated full valence bandwidth of 15.3 eV is comparable with the estimated measured value of 17.0 eV and an indirect gap of 1.2 eV is in the expected range of values that an LDA type of calculation should yield.

B. Behavior of electronic states under compression

The behavior of the electronic states under pressure is studied by calculating the energy eigenvalues with respect to Γ_{15}^v at several highly symmetric points in the Brillouin zone for different volumes ranging from $V_0/2$ to V_0, where V_0 is the calculated equilibrium volume. The results for BN are shown in Fig. 5. It is observed that the full valence bandwidth increases by 50% when the volume is reduced by 50%. The fundamental gap ($\Gamma_{15}^v \rightarrow X_1^c$) increases from 4.2 to 5.3 eV for this compression of volume. This behavior is different from that observed in other semiconductors, but similar behavior was found in diamond.[3,49] One possible origin of the different behavior of the band gaps under pressure for C and BN is the relatively large energy separation of the d excited atomic orbitals from the Fermi level which reduces the d-state contribution to the lowest conduction state at X. Consequently, the energy gap does not decrease as it would if the d states participated more effectively. When the volume changes from V_0 to $V_0/2$, the ionic gap ($X_1^v \rightarrow L_1^v$) decreases from 3.7 to 1.3 eV, while the energy separation of the levels X_1^v and X_3^v, which is related to the heteropolar gap C,[2] decreases from 5.5 to 4.6 eV. For the conduction states, Γ_1^c, L_1^c, and X_5^c are the most sensitive to the compression. This behavior is in qualitative agreement with the calculation of Zunger and Freeman.[19]

Figure 6 shows the behavior of the electronic states of BP under volume compression. Like typical semiconductors, the energy between X_1^c and Γ_{15}^v, which is very close to the fundamental gap, decreases from 1.3 to 0.2 eV when the volume is compressed to $V_0/2$. In the valence bands, we find that the L_1^v state crosses the X_1^v state at approximately 0.7 V_0, closing the ionic gap.

C. Charge densities

In Fig. 7, the valence charge-density contours of BN are plotted in the $(1\bar{1}0)$ plane. The valence charge density is strongly localized in the region close to the N atom and one local maximum in the charge density is seen along the bond. The value of the charge density at the peak position is approximately 42 electrons per unit cell, while for BeO, its isoelectronic II-VI compound,[44] this value is about 60 electrons per unit cell. In diamond, the isoelectronic IV-IV compound, the maximum value of the charge

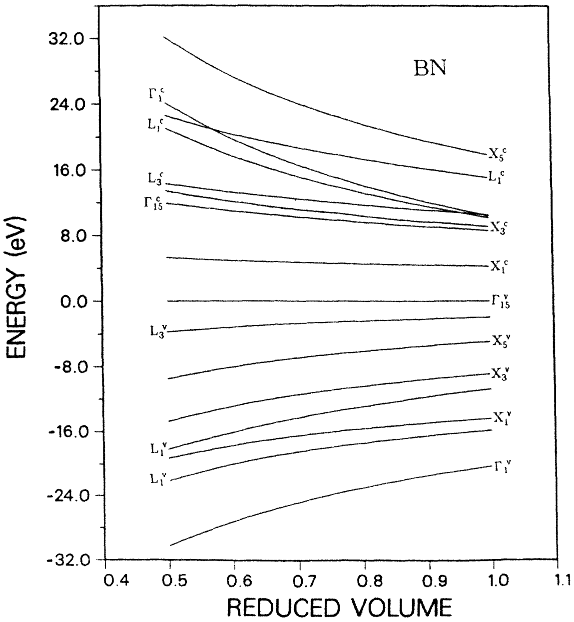

FIG. 5. Volume dependence of the valence- and conduction-band energies for BN. The volumes are normalized by the calculated equilibrium volume.

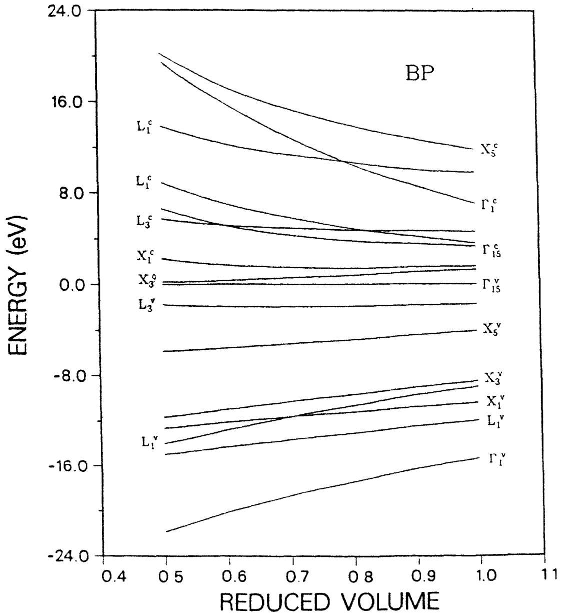

FIG. 6. Volume dependence of the valence- and conduction-band energies in BP. The volume is normalized by the calculated equilibrium volume.

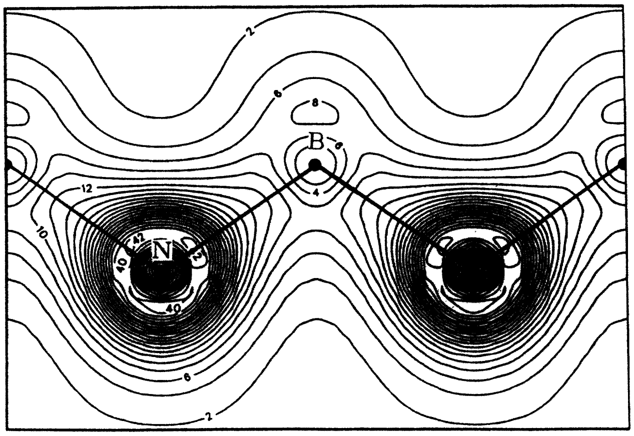

FIG. 7. Total valence charge-density contours of BN in the (110) plane. Units are in e/V_0, where V_0 is the calculated equilibrium volume. The contour intervals are 2.0 e/V_0.

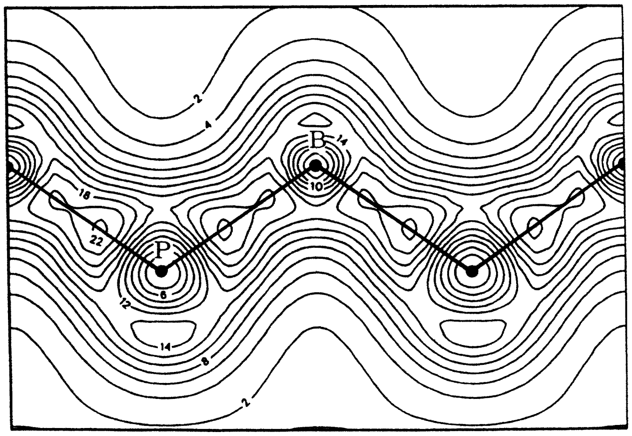

FIG. 9. Total valence charge-density contours of BP in the (110) plane. Units are in e/V_0, where V_0 is the calculated equilibrium volume. The contour intervals are 2.0 e/V_0.

density is 23 electrons per unit cell; however, there are two local maxima along the bond. Figure 8 shows a linear plot of the charge density and the contributions from the first and the upper three valence bands. An angular momentum decomposition[46] of the states in the valence bands shows that the s and p states of the N atom give the main contributions to the humps closer to this atom in the dotted and dashed lines. Hence, the charge of BN is similar to those of typical III-V compounds.

The valence charge-density contours of BP are plotted in Fig. 9. Compared to BN the charge density of BP is more equally distributed between the two atoms, as is expected of a compound with small ionicity ($f_i = 0.006$).[2] As shown in Fig. 10, the charge density reveals two distinct local maxima along the bond as in the case of diamond. This behavior results from the relatively localized p state of the B atom and the small ionicity in this compound. Similar charge densities were also found in BAs (Ref. 48) and in the isoelectronic IV-IV compound SiC.[50] From the angular momentum decomposition of the valence states, we find that the lowest band is mainly contributed by the s state of the P atom. However, the upper three valence bands have comparable contributions from the p states of both B and P atoms, resulting in the double humps of the valence charge density (see Fig. 10).

It should be noted that although the charge distribution of BP is similar to the charge density of diamond, which has the largest bulk modulus, the bulk modulus of BP is smaller than the value of BN. This behavior is in agreement with the observed fact that the bulk modulus in zinc-blende semiconductors depends primarily on the average density of valence electrons, i.e., the lattice con-

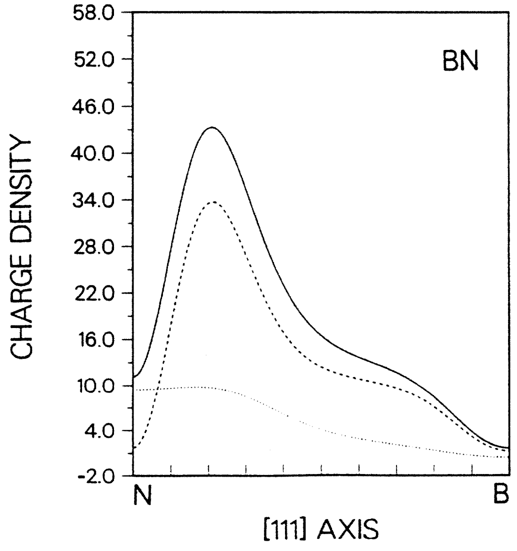

FIG. 8. Total valence charge density along the bond of BN; — — —, contribution from the upper three valence bands; · · · ·, contribution from the first band.

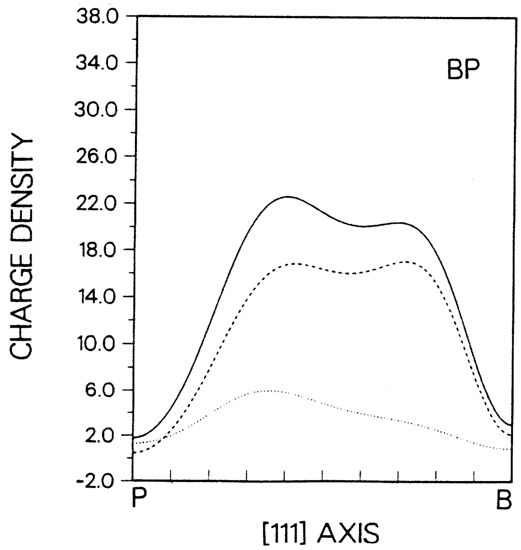

FIG. 10. Total valence charge density along the bond of BP; — — —, contribution from the upper three valence bands; · · · ·, contribution from the first band.

stant. This dependence is expressed in the empirical relation[35] $B_0 = 1761d^{-3.5}$, where d is the nearest-neighbor distance. The details of the charge distribution due to ionicity or covalency play a secondary role in the value of the bulk modulus.

V. CONCLUSIONS

We have calculated ground-state properties of BN and BP, some of which have not been measured previously. The calculated lattice constants, the phonon frequencies of the TO(Γ) mode, and the cohesive energies agree with the experimental values to within 0.4%, 4%, and 13%, respectively. The calculated value for BP agrees well with one previous experimental value although there is disagreement between results obtained by using different experimental techniques. The calculated bulk-modulus of BN is smaller than a previously reported value which was interpolated by using empirical relations for the elastic constants. We believe that this interpolation is not able to give accurate values for the elastic constants of compounds in the second row of the Periodic Table as BN and diamond, so our calculation suggests further experimental investigation in the field.

The calculated band structures differ considerably from previous calculations and the main differences are in the conduction bands. For BP the present calculation yields an indirect gap $(\Gamma_{15}^{v} \rightarrow \Delta_{\min})$ of 1.2 eV, where $\Delta_{\min}$ is close to X_3^c instead of X_1^c, and a direct gap $(\Gamma_{15}^{v} \rightarrow \Gamma_{15}^{c})$ of 3.3 eV. In BN, an indirect gap $(\Gamma_{15}^{v} \rightarrow X_1^c)$ of 4.2 eV and a direct gap $(\Gamma_{15}^{v} \rightarrow \Gamma_{15}^{c})$ of 8.6 eV are obtained. These values are small compared to the experimental determinations but this is expected since we have used the local-density formalism. The calculated valence bandwidths are in good agreement with experimental values.

Finally, we have found different behaviors for the fundamental gaps of BN and BP under volume compression. With increasing pressure the gap of BP decreases as is found in most semiconductors and insulators. In contrast, the gap of BN increases as in the case of diamond which is also in the first row of the Periodic Table. The valence charge densities were also shown to be different; in BP, as well as in diamond, two local maxima are found along the bond, while for BN, the charge density is similar to those of typical III-V compound semiconductors.

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