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# Band alignments and polarization properties of BN polymorphs

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## Abstract

Boron nitride can occur in the zincblende, wurtzite, and layered hexagonal phases. We use first-principles techniques based on hybrid density functional theory to study the electronic structure and polarization properties of these polymorphs. We find from the band structures that they have indirect band gaps. We report band offsets between the polymorphs and with respect to GaN and AlN; a very small conduction-band offset between wurtzite BN and AlN is found. The piezoelectric polarization coefficients of wurtzite BN have opposite sign to those in the other nitrides, and the magnitude of the spontaneous polarization is significantly larger.

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Boron nitride (BN) can occur in multiple polymorphs, including wurtzite (wz), zincblende (zb), and the two-dimensional, graphitic hexagonal (h) structure.<sup>1</sup> The large band gap of the h phase and the ability to synthesize single layers make it attractive for two-dimensional electronics and as a substrate for growth of graphene. The zb structure exhibits extreme hardness that can rival diamond. Recently, alloying BN into the traditional binary nitrides has been suggested as a way to tune the properties of barriers in wz nitride heterostructures.<sup>2</sup> While wz-BN by itself is not stable (though there are reports<sup>3-5</sup> that it can be stabilized under pressure), when BN is alloyed with wz-phase nitrides such as AlN or GaN, the resulting alloy is likely to occur in the wz structure (at least for modest B compositions), and predicting the properties of such alloys based on interpolation requires knowledge of the fundamental properties of BN in the wz phase.

There have been a number of theoretical studies of the electronic structure of the polymorphs. However, many of these studies used techniques based on traditional density functional technique (DFT) functionals, such as the local density approximation<sup>6,7</sup> and the generalized gradient approximation (GGA),<sup>7</sup> which are known to severely underestimate band gaps. To correct for this “band-gap problem,” the electronic structure has also been calculated with many-body perturbation theory based on the *GW* technique.<sup>8-11</sup> However, several important properties have not yet been explored. Band alignments were determined, using LDA, between zb-BN, diamond, and nickel,<sup>12,13</sup> but have not yet been reported for interfaces between different BN polymorphs, and with other III-nitrides. Knowledge of such offsets is essential for applications in electronics and optoelectronics. There has been only one theoretical study (using LDA) of the piezoelectric (pz) coefficients of wz-BN,<sup>14</sup> and no calculations of spontaneous polarization constants; these parameters are particularly important if BN is alloyed or integrated with other III-nitrides. Since wz-BN is not experimentally stable, computational studies are the only means of generating such numbers.

In this work, we use first-principles calculations based on DFT with a hybrid functional to explore the electronic and polarization properties of the different polymorphs of BN. The use of a hybrid functional has been shown to provide more accurate band structures as well as atomic structures than obtained with traditional functionals<sup>15</sup>; in particular, it allows overcoming the significant band-gap underestimation observed with LDA or GGA. We determine the indirect and direct band gaps of the BN polymorphs, band alignments between the polymorphs and with AlN and GaN, and the piezoelectric and spontaneous

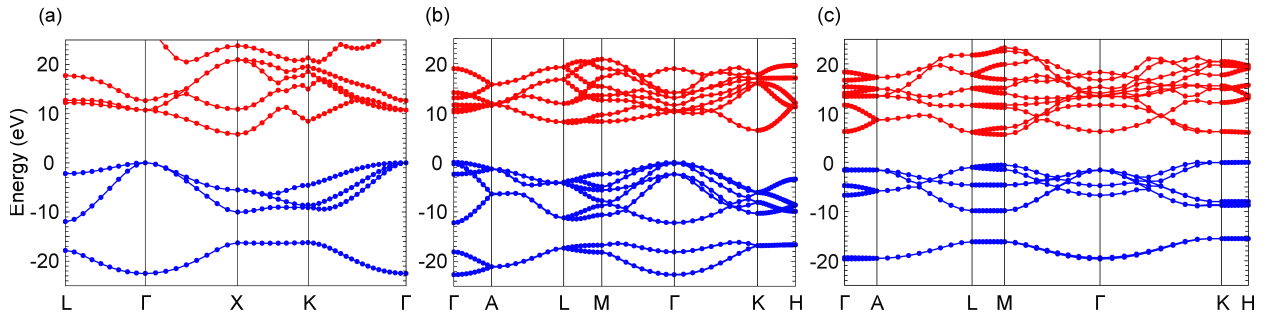


FIG. 1: Electronic band structure of (a) zb-BN, (b) wz-BN, and (c) h-BN calculated with DFT-HSE. The VBM is placed at zero on the energy scale.

polarization properties of wz-BN.

We use the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE)<sup>16</sup> as implemented in the VASP code.<sup>17</sup> The interactions between the valence electrons and the ionic cores are described using the projector-augmented wave method.<sup>18</sup> An  $8 \times 8 \times 6$  Monkhorst-Pack<sup>19</sup>  $k$  point mesh was used for the wz and h calculations and a  $8 \times 8 \times 8$  for the zb calculations. A plane wave energy cutoff of 500 eV was used for all calculations. We estimate that numerical convergence of energy differences between the polymorphs is within 20 meV per formula unit. We calculate polarization constants using the formalism of the Modern Theory of Polarization.<sup>20,21</sup> Proper piezoelectric constants are determined by finite differences, using the formulation of Bernardini *et al.*<sup>22</sup> Effective spontaneous polarizations are determined with respect to either zincblende (zb) or hexagonal (h) reference structures.

The band structures for all polymorphs of BN are displayed in Fig. 1. The zero of energy was chosen to coincide with the valence-band maximum (VBM) in each case. All of the polymorphs have indirect fundamental band gaps. The structural parameters, indirect band gaps, and smallest direct gaps of the three polymorphs, including information about the location of the VBM and conduction-band minimum (CBM), are listed in Table I along with previous calculated and experimental values where available.

We see from Table I that the structural parameters agree to within 1% with experimental parameters for the zb and wz structures. For the wz structure, we calculate an internal structural  $u$  parameter of 0.374. For the h polymorph, the  $a$  lattice parameter is consistent with experimental observations, but the  $c$  lattice parameter is larger by 3%, due to the fact that we do not include van der Waals interactions in our calculations. Our results agree with the observed relative stability of the three phases of BN: we calculate that h-BN is the

ground-state structure, zb-BN is 60 meV higher in energy per formula unit, and wz-BN is 90 meV higher in energy.

There is considerable spread in the experimental values for band gaps that have been obtained using optical<sup>23,24</sup> or x-ray<sup>25,27</sup> absorption/emission and electron energy loss spectroscopy.<sup>26</sup> As to calculations, LDA and GGA significantly underestimate the gaps. Our HSE-calculated indirect gaps for zb and h are within the experimental range. We note that electron-phonon interactions, which reduce band gaps, are not included in our study.<sup>28</sup> We have used 25 % exact exchange in the HSE functional. We tested the sensitivity of the band structure to this parameter by increasing it to 32 % mixing, finding that the indirect gap of wz-BN increases by 0.40 eV, and the direct gap by 0.56 eV. The resulting values still lie within the large range of reported band-gap values, and therefore comparison with experiment does not help in choosing a specific mixing parameter, as is frequently done in cases where the experimental gap is accurately known. Interestingly, our HSE gaps (with 25 % mixing) are 0.3–0.4 eV lower than the  $G_0W_0$  calculations of Gao<sup>8</sup> for wz- and zb-BN, while their selfconsistent  $GW$ <sup>8,9</sup> calculations result in gaps 1.1–1.6 eV larger than HSE. For h-BN, our calculated band gap lies within the range of band gaps reported selfconsistent  $GW$  studies.<sup>9–11</sup> Because of the uncertainty in the  $c$  lattice parameter of h-BN, we also calculated the band structure at the experimental lattice parameters. We obtained an indirect gap of 5.63 eV and a direct gap of 6.06 eV, with the band extrema occurring at the same points in the Brillouin zone as in the calculations at the theoretical lattice parameters, and only minor changes in the numerical values of the gaps.

The differences between zb and wz band structures, including the location of the CBM for zb-BN (at  $X$ ) and wz-BN (between  $L$  and  $M$  points), follow the general trend for zb/wz polymorphs,<sup>29</sup> with the zb-BN indirect band gap being smaller than the wz-BN band gap. The zb/wz band-gap differences are also consistent with Ref. 30, in which the symmetry effects at the  $X$  point were proposed to explain the indirect behavior of zinc-blende compounds relative to wurtzite compounds. In h-BN, our calculated difference between direct and indirect band gaps is only 0.43 eV, in agreement with  $GW$  studies.<sup>11</sup> Experimentally, very strong photoluminescence has been observed in h-BN and has been interpreted as evidence of direct band-gap behavior.<sup>23</sup> However, other researchers have instead claimed that the strong emission was instead due to strong excitonic effects<sup>11</sup> (which are not included in this study).

TABLE I: Structural and band parameters of the polymorphs of BN calculated with DFT-HSE. Results from previous LDA and *GW* calculations are listed for comparison, as well as experimental values where available. For the band gaps, the nature of the transition (VBM  $\rightarrow$  CBM) is indicated.

Polymorph	Method	$a$ (Å)	$c$ (Å)	$E_{\text{gap}}^{\text{indirect}}$ (eV)	$E_{\text{gap}}^{\text{direct}}$ (eV)
zb	HSE	3.58		5.82 ( $\Gamma \rightarrow X$ )	10.72 ( $\Gamma$ )
	LDA <sup>7,8</sup>	3.57–3.63		4.20–5.18	8.70–8.80
	GGA <sup>7</sup>	3.66–3.58		4.45–5.43	
	$G_0W_0$ <sup>8</sup>			6.18	10.99
	GW <sup>8,9</sup>			7.13–7.28	11.79–12.04
	Exp.	3.62 <sup>3–5</sup>		5.5–6.9 <sup>25,27</sup>	
wz	HSE	2.52	4.17	6.46 ( $\Gamma \rightarrow K$ )	10.13 (near- $\Gamma$ )
	LDA	2.52–2.56 <sup>7,8</sup>	4.17–4.25 <sup>7</sup>	4.90–5.81 <sup>7,8</sup>	8.00–8.37 <sup>6,8</sup>
	GGA <sup>7</sup>	2.56	4.19–4.23	5.23–6.39	
	$G_0W_0$ <sup>8</sup>			6.86	10.43
	GW <sup>8</sup>			8.06	11.72
	Exp.	2.55 <sup>3–5</sup>	4.20–4.23 <sup>3–5</sup>		
h	HSE	2.50	6.85	5.65 ( $\sim H \rightarrow \sim M$ )	6.21 (M), 6.08 (K)
	LDA	2.47–2.52 <sup>7</sup>	6.39–6.66 <sup>7</sup>	3.81–4.10 <sup>7,8</sup>	(4.6–4.2), <sup>6,10</sup> (4.5–4.64) <sup>6,10</sup>
	GGA <sup>7</sup>	2.52	6.70–8.40		
	GW <sup>9–11</sup>			5.32–6.39	5.92–6.47, 6.33
	Exp.	2.50–2.52 <sup>31</sup>	6.65–6.68 <sup>31</sup>	3.8–5.9 <sup>23–27</sup>	5.2–5.97 <sup>23–27</sup>

To determine band alignments, we use the “universal alignment” proposed by Van de Walle and Neugebauer in Ref. 32. In Ref. 32 the (+/–) electronic transition level of interstitial hydrogen ( $H_i$ ) was found to act as a “charge neutrality level” and can be used to align the band structures of semiconductors and insulators. While other methods exist for calculating band alignments (e.g., surface calculations to align bands to the vacuum level,<sup>33</sup> or interface calculations between specific pairs of materials),<sup>34</sup> the hydrogen alignment technique involves no interfaces or surfaces and should reflect a natural band alignment, avoiding

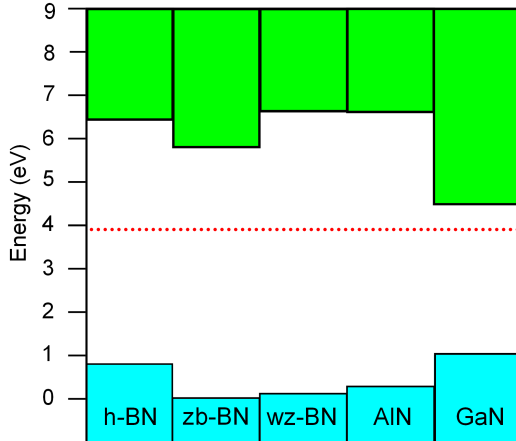


FIG. 2: Band alignments for the zb, wz, and h polymorphs of BN as well as AlN and GaN, calculated with DFT-HSE. The VBM of zb-BN was chosen as the zero of energy. Results for the nitrides are from Ref. 35. The dotted red line indicates the  $(+/-)$  electronic transition level for interstitial H.

complications due to dipoles, surface relaxation and reconstructions, and lattice mismatch. As shown in Ref. 32, offsets using this method agree with those obtained from interface calculations to within 0.3 eV. For alignments between similar materials, a higher accuracy can be expected.

In Fig. 2 the band alignments between the polymorphs of BN as well as AlN and GaN are plotted, based on calculations of the electronic behavior of  $H_i$ . For wz-BN the atomic structure of  $H_i$  is similar as in AlN and GaN, with  $H_i^+$  occupying an antibonding configuration and bonding closely with one N atom, and  $H_i^-$  occupying an octahedral interstitial position. In zb-BN,  $H_i^-$  also occupies a tetrahedral position, while  $H_i^+$  occupies a bond-center position where it forms a close bond with one N atom. In h-BN,  $H_i^+$  binds out-of-plane to an N atom, forming a N-H bond with a length of 1.01 Å, and  $H_i^-$  binds out-of-plane to a B atom, forming a B-H bond with a length of 1.15 Å.

Regarding the alignment between the BN polymorphs, we find that the VBM of wz-BN is slightly higher than that of zb-BN (by 0.14 eV), similar to what was reported for zb/wz-GaN.<sup>36</sup> The VBM of h-BN lies above that of both zb and wz, presumably due to it being comprised of  $sp^2$  rather than  $sp^3$  bonding states. While the band gap of wz-BN is larger than that of AlN, we find the conduction-band offset to be very small (0.04 eV, higher on the wz-BN side), which could limit the applicability of BN as a barrier layer in AlN-based

TABLE II: Calculated polarization constants for wurtzite BN. All values are in C/m<sup>2</sup>.

	This work	Previous calculations <sup>14</sup>
$e_{33}$	-1.068	-0.85
$e_{31}$	0.282	0.27
$P_{\text{sp}}$ (zb reference)	-0.012	
$P_{\text{sp}}$ (h reference)	-2.174	

devices.

Finally, we have calculated the polarization constants for wz-BN. This is relevant in light of integrating BN with wurtzite-phase nitrides such as AlN and GaN. For wurtzite films, polarization is in the crystallographic  $c$  direction,  $P_3$ , is given by the sum of the spontaneous (sp) polarization,  $P_{\text{sp}}$ , and the  $z$  component of the piezoelectric (pz) polarization (in Voigt notation)<sup>37</sup>:

$$P_3 = P_{\text{sp}} + (\varepsilon_1 + \varepsilon_2)e_{31} + \varepsilon_3e_{33}, \quad (1)$$

where  $\varepsilon_i$  ( $i=1,2,3$ ) is the strain in the  $i$  direction and  $e_{3i}$  are the corresponding piezoelectric constants.

Our calculated polarization constants for wz-BN are given in Table II, along with previous LDA calculations reported in Ref.14. The magnitude of our values are larger for both constants due to the difference in functional used. We also calculate the spontaneous polarization coefficients using both the zb and h structures as a reference.

The polarization properties of wz-BN are significantly different than those of the other III-nitrides. The signs of the pz coefficients for BN is opposite to that in the other III-nitrides.<sup>22</sup> Also the magnitude of the spontaneous polarization with respect to the h reference is significantly larger.<sup>38</sup> The sp polarization difference between wz-BN and zb-BN is significantly less than between wz-BN and h-BN. The small difference between wz and zb is consistent with the fact that the  $u$  parameter of wz-BN is very similar to the ideal value of 0.375.

In summary, using hybrid density functional calculations we have investigated the electronic structure and polarization constants of polymorphs of BN. We find that all of the polymorphs have indirect gaps. We have determined band alignments between the polymorphs, and with respect to AlN and GaN. For polarization constants of wz-BN, we find



that the piezoelectric coefficients have opposite sign to those in the other nitrides, and the magnitude of the spontaneous polarization is significantly larger.

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