Ab initio Calculations of Electronic Band Structure and Charge Densities of Zinc Blende-type GaN, BN and Their Solid Solution $B_{0.5}Ga_{0.5}N$

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First principles calculations of the electronic band structures of zinc blende-type GaN and BN and their 1 : 1 mixture $B_{0.5}Ga_{0.5}N$ were carried out within DFT using the augmented plane wave method with both GGA and LDA approximations for the effects of exchange and correlation. Equilibrium lattice constants were determined from the total-energy minimization method. The results are compared with those of previous calculations and with experimental measurements. In agreement with these data, ZB-BN is an indirect ($\Gamma \rightarrow X$) wide-gap semiconductor (4.35 eV) while ZB-GaN has a direct gap of 1.9 eV at Γ. For ZB $B_{0.5}Ga_{0.5}N$ we predict a direct band gap of 3.35 eV. Electron charge densities are computed for the unit cell, and ionicity factors are derived for all systems.

Key words: DFT, GGA, Wide-gap Semiconductors, FP-LAPW

Introduction

The lack of blue luminescent semi-conducting materials is still a problem for opto-electronic applications. Many efforts have been made to produce a material likely to overcome this difficulty. Wide-gap semiconductors (GaN, AlN, and BN) and their mixtures are currently actively investigated in view of their promising potential for short-wavelength electroluminescence devices and high-temperature, high-power, and high-frequency electronics. These semiconductors are of great importance in micro-, and optoelectronics, and as such they have received considerable attention both experimentally and theoretically [1 – 10].

The major part of research on III-V nitrides was focused on the hexagonal wurtzite-type phases. Recently prepared gallium nitride films with a metastable cubic structure (of the zinc blende-type) have been widely investigated.

However, there has been less work on $B_xGa_{1-x}N$ solid solutions, and little information on their band structure exists. The investigation of electronic properties of solids using electronic charge densities is of increasing importance. So far, this work has been concerned with electronic charge densities, which were found to be useful for understanding the chemical bonding and the modification of the band structures by interstitial impurities [11, 12].

The solid solutions of group III nitrides were studied less, and few calculations have been reported on their charge densities. This has prompted us to perform such a calculation on zinc blende III-V semiconductors, particularly the $B_{0.5}Ga_{0.5}N$ solid solution.

The aim of this work is to prospect the electronic charge densities of zinc blende-type GaN, BN and their solutions. The calculations are based on the density-functional theory [13] in the local density approximation LDA for exchange and correlation. The self-consistent electronic structures are calculated by the full potential linearized augmented plane wave (FP-LAPW) method [14]. We also computed lattice constants, bulk moduli and their first derivatives by fitting the total energy *vs.* volume according to the Murnaghan's equation of state. We have mainly focused on the determination of the electronic states in such covalent solids and on how to assess their electron and energy levels as well as the charge densities, especially when mixtures are considered.

Method of Calculations

The foundation for modern electronic structure calculations for solids is the density-functional theory

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based on the work by Hohenberg and Kohn [15] and by Kohn and Sham [16]. Self-consistent calculations of total energies and the electronic structure based on the non-scalar-relativistic full potential 'linearized augmented plane wave' method were carried out using the WIEN2K code [14]. This is a very accurate and efficient scheme to solve the Kohn-Sham equations of density functional theory (DFT) in which exchange and correlation effects are treated, for example, by the GGA [17] which often leads to better energetic and equilibrium structures than the local density approximation (LDA) [13].

The electron density is obtained by summing up over all occupied Kohn-Sham orbitals and plays the key role in the formalism. For GaN we adopt the values of 1.8 and 1.6 Bohr (1 Bohr = 0.529 Å) for gallium and nitrogen, respectively, as the muffin tin (MT) radii of the tangent spheres. In the case of BN we use 1.32 and 1.45 Bohr for boron and nitrogen MTs, respectively.

For the $B_xGa_{1-x}N$ solid solutions, we have chosen the MT radii values of 1.7, 1.5 and 1.4 Bohr, respectively, for gallium, nitrogen and boron. In the linear APW (LAPW) method, the relevant convergence parameter is $R_{MT}K_{max}$, which is defined by the product of the smallest atomic sphere radius times the largest reciprocal lattice vector of the PW basis. We use $R_{MT}K_{max} = 8$ for GaN, BN and the ternary $B_xGa_{1-x}N$ system.

The GaN and BN binaries crystallize in the zinc blende-type structure, and the disordered solid solution at 50 % is modelled by using a supercell with 32 atoms in the primitive (P) structure. The k integration over the Brillouin zone is performed using the Monkhorst and Pack mesh [18]. A mesh of 10 and 8 special k points was taken in the irreducible wedge of the Brillouin zone for the binary and ternary systems, respectively.

The iteration process was repeated until the calculated total energy of the structure converged to less than 1 mRyd.

Calculations and Results

The structural properties in the strain-free case are obtained by a minimization of the total energy depending on the volume for GaN, BN and the $B_{0.5}Ga_{0.5}N$ solid solution in the zinc blende type (see Fig. 1). We compute the lattice constants, bulk modulus and its derivative by fitting the total energy *vs.* volume according to Murnaghan's equation of states [19] according

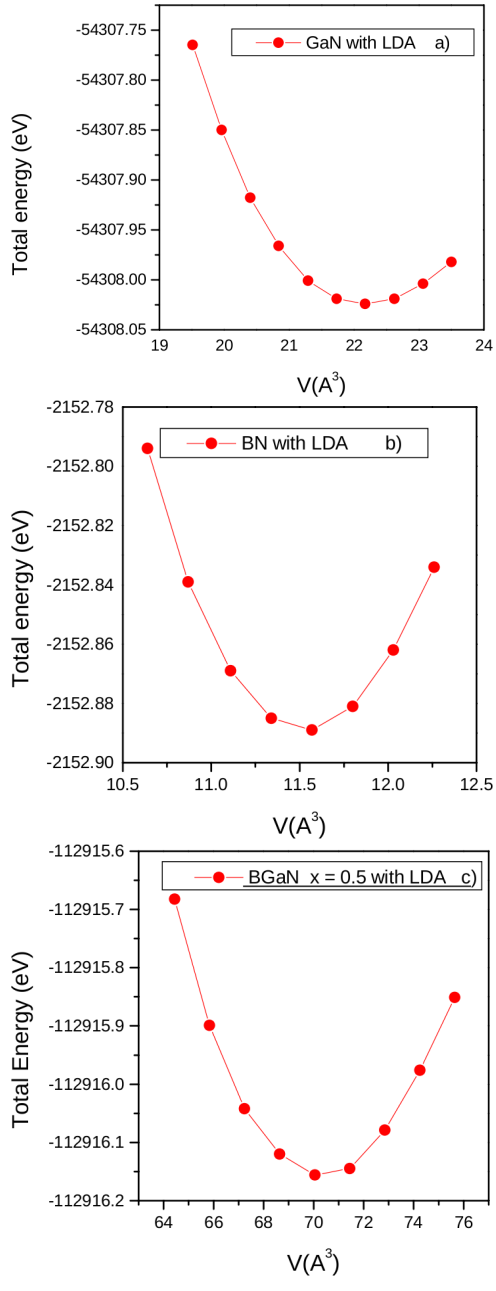

Fig. 1. Total energy as a function of the volume for zinc blende-type GaN a), BN b) and $B_{0.5}Ga_{0.5}N$ solid solution c) with LDA calculations.

to Eq. 1:

$$E(V) = E_0(V) + \frac{BV}{B(B-1)}\left[B\left(1-\frac{V_0}{V}\right) + \left(\frac{V_0}{V}\right)^B - 1\right] \quad (1)$$

Table 1. Equilibrium lattice constants, bulk moduli and their derivatives of zinc blende-type GaN, BN and $B_{0.5}Ga_{0.5}N$.

Composition		This work GGA	This work LDA	Other theoretical studies	Experimental data
GaN	a, Å	4.55	4.461	4.45; 4.461[a]	4.49[b]
	B, GPa	176	201	184; 202[a]	190[b]
	B', GPa	3.30	5.51	3.9; 4.32[a]	
BN	a, Å	3.630	3.585	3.584 – 3.623[c]	3.615[d]
	B, GPa	371	402	401.7 – 368[c]	
	B', GPa	3.70	3.57	3.661 – 3.32[c]	
$B_{0.5}Ga_{0.5}N$	a, Å	4.38	4.31		
	B, GPa	198	228		
	B', GPa	4.19	3.57		

[a] Refs. [19, 20]; [b] ref. [21]; [c] refs. [20 – 22]; [d] ref. [23].

Table 2. Zinc blende-type GaN and BN energies (in eV) at high-symmetry points in LDA and GGA approximations. All values refer to the top of the valence band.

High-symmetry points	GaN LDA	GaN GGA	BN LDA	BN GGA
$\Gamma_1{}^V$	−16.11	−15.71	−20.38	−20.11
$\Gamma_{15}{}^V$	0.02	0.00	0.00	−0.02
Γ_1^C	1.88	1.51	8.77	8.71
$\Gamma_{15}{}^C$	10.23	10.04	10.81	10.11
$X_1{}^V$	−11.45	−11.51	−14.56	−14.61
$X_3{}^V$	−6.39	−6.02	−9.07	−8.88
$X_5{}^V$	−2.9	−2.62	−5.06	−4.88
$X_1{}^C$	3.2	3.29	4.34	4.40
$X_3{}^C$	6.58	6.44	9.26	9.11
$X_3{}^C$	11.69	11.51	18.10	17.73
$L_1{}^V$	−11.95	−13.14	−16.04	−18.66
$L_1{}^V$	−7.37	−3.83	−10.96	−5.46
$L_3{}^V$	−1.04	−0.51	−2.00	−1.14
$L_1{}^C$	4.68	–	10.50	9.47
$L_3{}^C$	10.29	10.50	10.68	13.39
$L_1{}^C$	8.71	8.58	15.27	–

In Table 1 we compare the calculated with the experimental data and with results obtained from previous calculations. The LDA generally overestimates bulk moduli. The values obtained in our work are in agreement with theoretical [20, 21] and experimental data [22 – 24]. Compared to the experiment [21, 23], the LDA overestimates the bulk modulus, whereas GGA underestimates it. The LDA values are therefore in significantly better agreement with the experiment, and it appears that GGA does not bring about significant improvement over LDA for GaN and BN.

To provide a basis for understanding future energy gap device concepts and applications based on zinc blende III-V nitride semiconductors, we have computed the electronic band structure of a zinc blende $B_xGa_{1-x}N$ solid solution at $x = 0.5$. The energies calculated using the FP-LAPW method for zinc blende-type GaN and BN are listed in Table 2 for the high-symmetry points Γ, X and L in the Brillouin zone. All energies are with reference to the top of the valence band $\Gamma_{15}{}^V$. The band structures of GaN, BN and $B_xGa_{1-x}N$ are shown in Figs. 2 – 4.

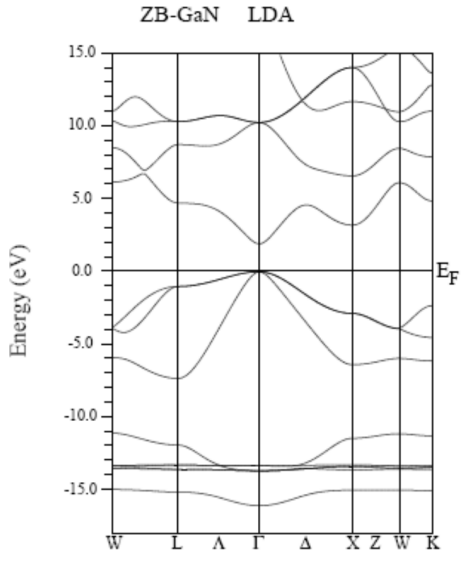

Fig. 2. Electronic band structures of zinc blende-type GaN.

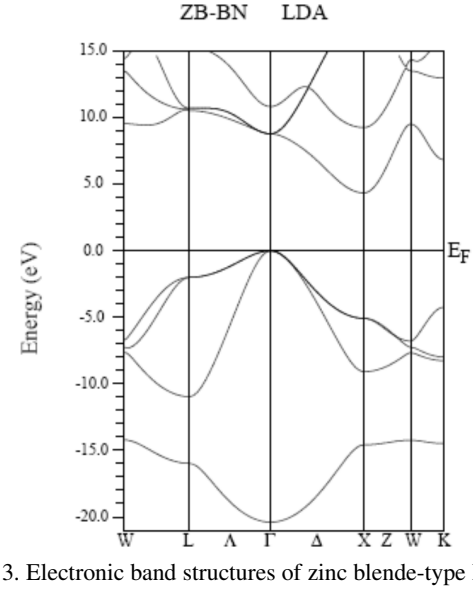

Fig. 3. Electronic band structures of zinc blende-type BN.

For ZB-GaN, the magnitude of the gap and the correct ordering of the valence band at Γ can immediately be noticed. From Fig. 3, in the energy range −15 to −10 eV, the d bands (Ga-d) are seen to be strongly

Composition		This work GGA	This work LDA	Other theoretical studies	Experimental data
GaN	$E_g(\Gamma_{15}^{v} \rightarrow \Gamma_1^{c})$	1.51	1.9	1.9, 1.9[a]	3.2[b]
	$E_g(\Gamma_{15}^{v} \rightarrow X_1^{c})$	3.3	3.2	3.2, 3.2[a]	
	Total valence bandwidth	14.8	16.0	16.3, 15.7[a]	
BN	$E_g(\Gamma_{15}^{v} \rightarrow \Gamma_1^{c})$	8.71	8.77	8.61, 8.79[c]	
	$E_g(\Gamma_{15}^{v} \rightarrow X_1^{c})$	4.40	4.35	4.19, 4.45[c]	6.0[d]
	Total valence bandwidth	14.31	20.3	20.6, 20.35[c]	22.0[d]
$B_{0.5}Ga_{0.5}N$	$E_g(\Gamma_{15}^{v} \rightarrow \Gamma_1^{c})$	3.23	3.35		
	$E_g(\Gamma_{15}^{v} \rightarrow X_1^{c})$	3.94	4.03		
	Total valence bandwidth	16.06	15.95		

Table 3. Calculated LDA and GGA band gaps, and valence bandwidths, of GaN, BN and $B_{0.5}Ga_{0.5}N$ in the zinc blende structure compared to results of other theoretical calculations and of experiments.

[a] Refs. [27, 28]; [b] ref. [31]; [c] refs. [22, 34]; [d] ref. [35].

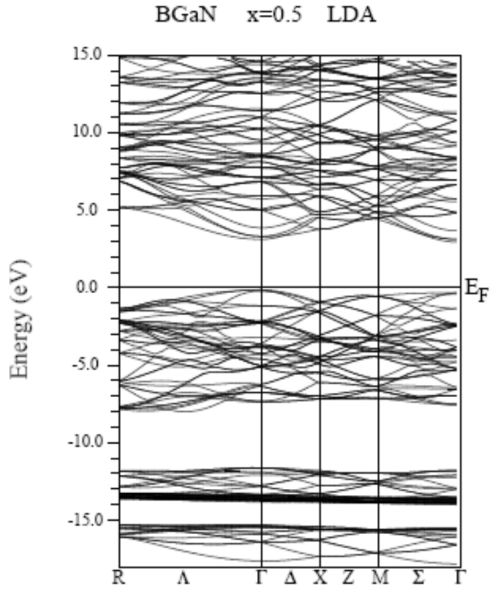

Fig. 4. The band structure of zinc blende-type $B_{0.5}Ga_{0.5}N$.

hybridized with the bottom *s*-like valence bands of nitrogen (N-2*s*). Also the hybridization of the N *p*-like states with those of Ga *d* reduces the energy gap compared to BN (Fig. 2). The interaction between the N *p* and occupied Ga *d* states result in a level repulsion, moving the VBM upwards.

It is known that cation *d*- and anion *p*-coupling reduces the band gaps in nitride compounds [25 – 27]. The *p*-*d* coupling increases with small *p*-*d* energy differences and large overlap between the *p*-*d* orbitals.

In ZB-GaN we obtain direct band gaps of 1.90 eV, in agreement with other LDA results (see Table 3 for comparison). The band gap of GaN is underestimated in the LDA, when compared to the experimental data [30 – 31] (Table 3), which are 40 % smaller than the experimental values, and this is an intrinsic feature of the DFT-LDA.

The Ga 3*d* bands in both crystal structures overlap in energy with the N 2*s* band. The N 2*s* band is split thereby into two bands. This is an additional shortcoming of LDA calculations. This result is in disagreement with the experiment and can be overcome by SIC calculations [20].

It is widely accepted that the LDA electronic band structures are qualitatively in good agreement with the experiments in what is concerning the ordering of the energy levels and the shape of the bands. In many cases it is even possible to superimpose LDA electronic bands to the GW or the experimental ones simply with an upwards shift of the theoretical conduction bands [28].

For cubic BN, previous calculations used plane-wave-Gaussian (PWG) [31] or non-local empirical pseudo-potential (EPM) methods [32]. A direct gap at Γ was reported with the conduction state at this point being ${\Gamma_{15}}^{c}$.

In a more recent work we used augmented spherical waves within LDA, and an indirect gap has been reported in agreement with the experiments [33 – 34].

Likewise, in this work we obtain an indirect gap (${\Gamma_{15}}^{V} \rightarrow {X_1}^{C}$) of 4.35 eV and a direct gap (${\Gamma_{15}}^{V} \rightarrow {\Gamma_{15}}^{C}$) of 8.77 eV. The total valence bandwidth is equal to 20.38 eV and compares well with experiments [36]. The electronic band structure calculated for *c*-BN at the equilibrium lattice constant is shown in Fig. 3.

Zinc blende-type $B_xGa_{1-x}N$ alloys should, therefore, have an direct gap. The calculated energy gaps of GaN ${E_g}^{\Gamma}$ and BN ${E_g}^{\Gamma}$ of 1.90 and 4.35 eV, respectively, are in good agreement with the theoretical values [28 – 35] as listed in Table 3.

In comparison, the LDA underestimates the energy band gap. As yet, in the literature, there is a lack of data on zinc blende-type $B_{0.5}Ga_{0.5}N$ with a complex superstructure regarding the band structures. To our knowl-

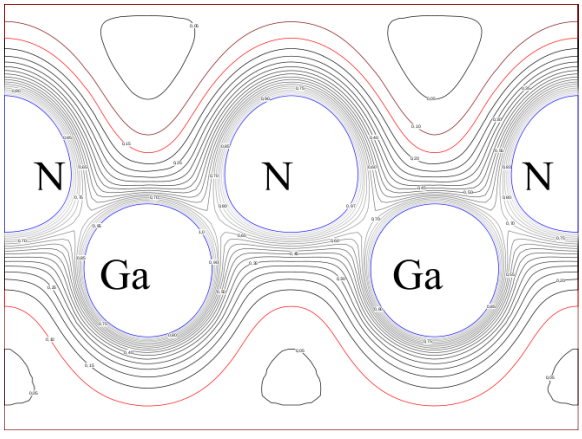

Fig. 5. (color online) Total valence charge densities in GaN in the (110) plane calculated with LDA.

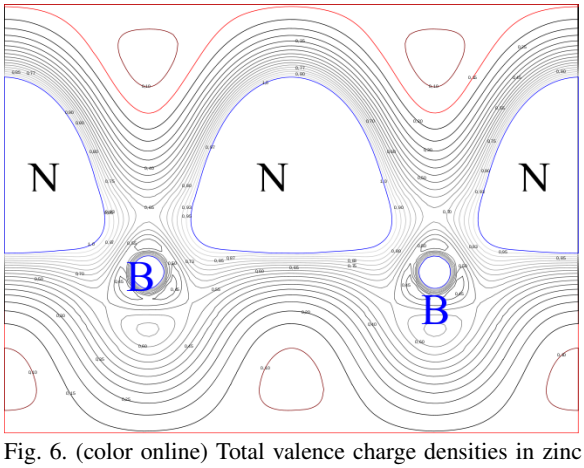

Fig. 6. (color online) Total valence charge densities in zinc blende BN in the plane (110) calculated with LDA.

edge no theoretical studies have been carried out by other authors for a direct comparison.

The calculated band gaps exhibit strong composition dependence. The strongest contribution to the gap is probably due to a structural effect, *i. e.* the composition-induced disorder in the bond lengths. The fundamental gap for $B_xGa_{1-x}N$ ranges from 1.90 eV (x = 0) to 2.73 eV (x = 0.25) to 3.26 eV (x = 0.5) to 3.67 eV (x = 0.75) to 4.35 eV (x = 1).

Total charge densities

To visualize the nature of the bond character and to explain the charge transfer and the bonding properties of GaN, BN and their solution at x = 0.5 ($B_{0.5}Ga_{0.5}N$), the total valence charge densities were calculated.

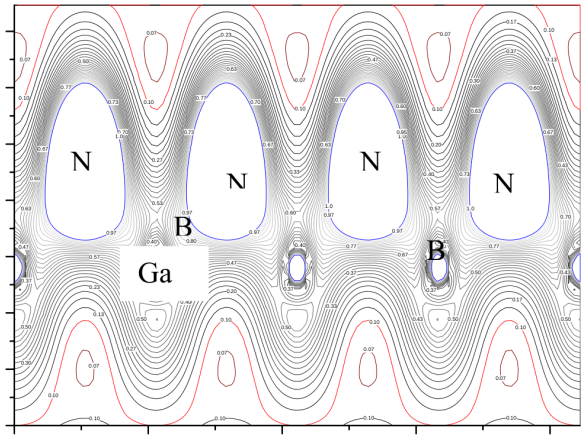

Fig. 7. (color online) Total valence charge densities in zinc blende-type $B_{0.5}Ga_{0.5}N$ in the (110) plane calculated with LDA.

This is shown in Figs. 5 – 7 along the ⟨110⟩ direction for each material.

The calculated electron charge distribution indicates that there is a strong ionic character as can be seen along the Ga–N and B–N bonds.

The areas around the nitrogen atoms are larger than for the gallium atoms for both cases. The driving force behind the displacement of the bonding charge is the greater ability of N to attract electrons towards it due to the difference in the electronegativity of Ga and N and of B and N.

Because of the large mixing of the wave functions for $B_{0.5}Ga_{0.5}N$, this solution has a charge density whose characteristic is intermediate between those of GaN and BN.

The ionicity factor

Three different approaches have been used to calculate the ionicity factor for GaN and BN:

(i) the model of Zaoui *et al.* based on valence charge density calculations [37],

(ii) the Pauling definition based on electronegativity values of the elements [38] and the

(iii) Garcia-Cohen approach based on valence charge density calculation [39].

The Zaoui ionicity factor is defined as follows [37] (Eq. 2):

$$f_I = [S_A/(S_A + \lambda S_C)]^{\lambda} \qquad (2)$$

Table 4. The calculated ionicity factor f_i of GaN and BN.

Nitride	f_i (calculated)	f_i (ref. [38])	f_i (ref. [39])
GaN	0.48	0.50	0.78
BN	0.38	0.25	0.48

where S_A is the area of the anion charge density, S_C the area of the cation charge density and $\lambda = -1$ for compounds IV-IV and III-V.

Using the Pauling definition [38] of the ionicity of a single bond and the Philips electro-negativity values for N and Ga, a rough estimation of the ionicity factor is obtained by using the Pauling equation (Eq. 3).

$$f_i^P = 1 - \exp[(\chi_A - \chi_B)]^2/4 \quad (3)$$

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

The scaling law by Garcia and Cohen was successful in predicting the f_i behavior for a wide variety of semiconductors. However, these authors calculated the charge densities using the total-energy pseudo potential method, and the deduced ionicity factors exhibited a large discrepancy with the Phillips ionicity scale for all the group-III nitrides. The Garcia-Cohen ionicity factor is defined according to Eq. 4

$$f_I = (S_s/S_a)^{1/2} \quad (4)$$

where S_s and S_a are the measures of the strength of the symmetric and asymmetric components of the charge density, respectively, and are defined as in Eq. 5 [39]:

$$S_{s/a} = (1/V_0) \int_{V0} \rho^2{}_{s/a} d^3 dr \quad (5)$$

The calculated ionicity values for GaN and BN are given in Table 4. We notice that the value of f_i for a same compound is different following the used method of calculation. The calculated values of 0.53 for GaN and 0.46 for BN are close to those given by Philips [39], but are very different from those found by Garcia and Cohen [40].

Conclusion

We have presented a study of the electronic band structures of GaN, BN and $B_{0.5}Ga_{0.5}N$. The results of the FP-LAPW calculations have been confirmed by a comparison with experimental data and theoretical results. GaN and $B_{0.5}Ga_{0.5}N$ were found to have a direct gap, while zinc blende-type BN is an indirect gap semiconductor from our calculations. We found that for GaN and BN these bandgaps are about 0.39 eV ($\sim 20\,\%$) and 0.06 eV (0.68 %) smaller for GGA than for LDA. This, as mentioned earlier, can be primarily attributed to the larger GGA lattice constant. We provide information about the electron charge densities, which allows us to evaluate the charge transfer in the two binary compounds.

The ionicity factors for GaN and BN zinc blende structures were calculated with three approaches.

From the investigation of the valence charge density, it has been found that in the GaN and BN zinc blende structure there is a strong ionic character along the Ga–N and B–N bonds. The nitrogen ions are larger than the gallium and boron ions.

We have concluded also that the explicit treatment of Ga 3*d* electrons as valence states is essential to have an accurate description of the electronic properties of the title materials compared to other non-nitride III-V compounds.

The calculated ionicity shows that GaN is largely an ionic compound while BN is more covalent. In conclusion, we hope that this analysis has contributed to clarify many physical aspects of these interesting materials.

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