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Cation dependence of the electronic structure of III–V nitrides

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Abstract. The *ab initio* pseudopotential method is used to study the effects of the cation potential on the electronic structure of two prototypical III–V nitrides, AlN and GaN. We examine both materials in the wurtzite and zinc-blende structures and compare these results with previous calculations for BN. Effects due to the s, p and d angular components of the Al and Ga potentials are studied. Because the charge densities of both AlN and GaN are dominated by N, the difference in the valence band charge density between these compounds is small. This is the reason that they have similar ground-state structural properties. Individual electronic levels at high-symmetry points, however, are altered by several electronvolts because of changes in the cation potential. This is the origin of the significant difference between the fundamental gaps of these compounds.

1. Introduction

The III–V nitrides have recently gained more attention primarily because of their possible use in devices such as short-wavelength diodes and lasers. Aluminum and gallium nitride in the wurtzite (WZ) structure are especially interesting because of the large difference between the band gaps ($E_g = 6.2$ eV for AlN, and 3.5 eV for GaN) but nearly identical lattice constants of these materials. The similarity in structure exists for all AlX/GaX (X= N, P, As, Sb) pairs, where the AlX gap is consistently about 1.5 times that of GaX. The nitride pair is the most dramatic because it has the largest difference ($\simeq 3$ eV) between the gaps. This suggests that it may be possible to fabricate a class of AlN/GaN alloys and superlattices [1] with widely tunable gaps. Experimental efforts have been directed at overcoming film growth problems [2–5] for the pure materials and show promise for growth of good-quality WZ as well as zinc-blende (ZB) films. The increasing number of theoretical studies of bulk AlN [6–9] and GaN [6, 9–15] and alloys and superlattices of these materials [16, 17] mirrors the growth in technological interest.

In general, to obtain a wide-band-gap III–V material, it is necessary to have deep atomic potentials and a small lattice constant. Compounds containing light elements with small atomic radii, such as boron and nitrogen, are therefore good candidates for these materials. The III–V B compounds—BN, BP, and BAs—were studied in detail by Wentzcovitch and coworkers [18, 19]. The trend in these compounds is from fairly ionic (BN) to covalent (BP) to almost a reversal of roles between the cation and anion (BAs or AsB). These properties were explained in terms of the ionic pseudopotentials acting on the valence electrons.

As an example, BN was found to be similar to typical III–V compounds in its charge distribution. Since both atoms lack p core states there is no repulsive p-pseudopotential and

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both potentials are strong and comparable to each other. The resulting charge density is therefore more similar to GaAs than to the more ionic III–V compounds such as AlN and GaN. In contrast, BP was found to have a charge distribution similar to diamond where there are two local maxima along the bond, of nearly equal heights. Since P is less electronegative than N, the B p potential in BP pulls charge from the anion site into the bond region. As a result, the valence bands in BP have a significant contribution from the p states of B as well as from the P atoms. The B compound with the largest lattice constant, BAs, could be more accurately described as arsenic boride based on its charge density. As in BP, there are two local maxima along the bond. In BAs, however, the slightly larger maximum is located near the B atom. A comparison between the self-consistent charge density and the superposition of the free atoms reveals a transfer of charge from the As atom to the B atom.

Band gaps in the B compounds decrease in going from BN to BAs. Within the local density approximation (LDA) [20], all three materials were found to be indirect, with calculated gaps of 4.2, 1.2, and 1.25 eV for BN, BP, and BAs, respectively. The LDA systematically underestimates band gaps [21] (the measured gaps [22] are around 6 eV for BN and 2 eV for BP); however the qualitative trend should be correct.

In addition to the B compounds, the III–V nitrides are also very good candidates for large-band-gap semiconductors. In the present study we focus on BN, AlN and GaN. As discussed above, BN is a typical III–V semiconductor with a large band gap and small lattice constant. Although AlN and GaN have similar structural properties, they have anomalously different band gaps. To investigate the physical similarities and differences of this pair, cation effects in AlN and GaN are discussed and comparison is made with previous studies of BN.

Table 1. Ionization potential, electronegativities, and sizes of atomic B, Al, and Ga.

	B	Al	Ga
Ionization potential (eV/atom)	8.30	5.98	5.98
X_{Garcia} [a]	1.92	1.62	1.67
X_{Pauling}	2.0	1.5	1.6
r_{Pauling} (Å)[b]	0.88	1.26	1.26
r_{ZC} (Å)[c]	0.254	0.479	0.492

[a] From first principles [23].
[b] Covalent radii derived from tetrahedrally coordinated solids [24].
[c] Zunger–Cohen atomic radii from [25].

Atomic characteristics of B, Al, and Ga are listed in table 1. While the ionization potentials, electronegativities, and radii of Al and Ga are very close, B is significantly smaller (due to its lack of core p states) and has a higher ionization potential and electronegativity than the heavier group III elements. From these simple considerations, one would expect that AlN and GaN would be more ionic and have larger lattice constants than BN.

In table 2 we give some structural data for the WZ phase, solid state ionicities, and the experimental band gap for WZ AlN and GaN. The structural properties of AlN and GaN are very similar, yet there is a large difference between their band gaps. Lattice parameters for AlN and GaN in both the WZ and ZB phases differ by at most a few percent. In contrast, their band gaps differ by almost 3 eV. Considering the similarities of Al and Ga shown in table 2, the large difference between the fundamental band gaps of WZ AlN and GaN is surprising. To explore this observation we consider an obvious difference between Al and Ga which is the lack of core d states in Al. In this paper an investigation of the roles of the

Table 2. Experimental[a] structural parameters (a, c/a, u) for the wurtzite (wz) phase, *ab initio* solid state ionicities, and the fundamental band gap in the wz structure for AlN and GaN.

	AlN	GaN
a (Å)	3.110	3.160
c/a	1.601	1.622
u	0.382	0.377
B_0(GPa)	202	195
g [b]	0.794	0.780
f_i [c]	0.449	0.500
E_g (eV)	6.2	3.5

[a] See references within [7] and [14].
[b] First-principles charge asymmetry coefficient from [26].
[c] Phillips ionicity [27].

different angular momentum components of the potentials in these compounds is given. In addition, we have studied the energy levels in both the ZB and WZ structures for AlN, GaN, and two materials having an Al–Ga hybrid potential and a N potential. Section 2 describes the calculational methods used, section 3 contains a discussion of the results, and section 4 gives some conclusions.

2. Calculational method

We use the standard *ab initio* pseudopotential method [28] to calculate the single-particle energy levels within the LDA. The exchange and correlation potential derived [29] from the Monte Carlo calculations of Ceperley and Alder [30] is used. Hamann–Schlüter–Chiang (HSC) [31] potentials are used for Ga and Al. A Troullier–Martins [32] soft pseudopotential is used for the stronger N core in order to achieve good convergence for the energy eigenvalues with a moderate-size basis set. The self-consistent calculation uses a plane-wave basis set with a cut-off energy of 40 Ryd. Increasing the cut-off to 80 Ryd showed no significant change in the relative energy levels.

Here we treat the Ga 3d electrons as part of the Ga core. Partial core corrections are used to model the core–valence exchange and correlation potentials [33]. This correction is important for computing the structural properties of Ga compounds [34], and has been shown [9] to give LDA band structures that compare very well with calculations [6] that include the d electrons as part of the valence complex.

How the Ga 3d electrons should be treated in calculations of structural and electronic properties of GaN, however, is currently an open question. A wide variety of theoretical methods have been used recently to study ZB and WZ GaN [6, 9–15], some of which include the 3D states in the valence complex and some where they are treated as band states. Among the published studies, there is fair agreement for the ZB and WZ lattice constants, excepting [13]. In contrast, bulk moduli and band gap values for cubic GaN vary by as much as 30–60% depending on the method and size of basis set used. Variations in calculated gap values for the WZ phase are similar.

It has been found [6, 12] that the Ga 3d electrons have a significant effect on the lower part of the valence band. Pseudopotential calculations for cubic GaN [10, 13] that put the 3d electrons in the Ga core give structural properties that agree well with those of [6] and [12]. In contrast, values for the gap calculated using these pseudopotential methods lie 0.6–0.7 eV higher than the all-electron values. Here we report a gap for cubic GaN 0.1–0.2 eV above

the all-electron values. Because the treatment of the Ga 3d electrons is an open question the values reported here may be in error by several tenths of an eV or more. This variation does not affect our comparison of the nitrides, however.

For this study, we use lattice constants for AlN and GaN from [7] and [14], respectively, which are well within the variation of reported theoretical values. Structural parameters for the ZB and WZ phases were not relaxed from these values.

3. Results and discussion

The s, p, and d components of the HSC potentials for Al and Ga are shown in figure 1. The minimum in the Ga p potential is slightly farther from the ion than that in Al, but the depth differs by only 1 eV. The physically relevant differences are found in the s and d potentials. The Ga s potential is more than 5 eV deeper than the Al s. This change can be explained by the underscreening by the core d electrons in Ga. For Al, the s and p core electrons lie close to the nucleus and effectively screen the core. The wavefunction for the Ga 3d electrons, however, reaches a maximum at a much larger radius. As a result, the valence s electrons feel a stronger potential in Ga than in Al. The energy difference between s-like states in AlN and GaN has been attributed to the sensitivity of these states to the depth of the potential well near the nucleus [6]. This is true, however the difference is due not simply to the fact that Ga has a larger Z than Al but to the presence of Ga d core states which do not effectively screen the larger core charge.

A more pronounced difference between the Al and Ga potentials is found in the shape of the d channel. The Ga d potential is repulsive [35] at the core and has a narrower and slightly deeper minimum than the Al d channel.

To separate the effects of the s, p, and d components of the Ga potential, we create three Al/Ga hybrid pseudo-atoms. Starting with the full Al potential we substitute *one* of the three channels with the corresponding Ga channel. These three hybrids are denoted by Al(Ga s), Al(Ga p), and Al(Ga d). The Al(Ga l) potentials provide a systematic way of examining the difference between the behaviours of the Al and Ga full potentials. We present electronic energy levels for the three hypothetical Al(Ga l)N compounds along with the results for AlN and GaN.

The theoretical lattice constant of pure AlN in the WZ [7] and ZB [9] structures is used for all five materials. Changes in the lattice constant have been shown [36] to significantly alter band gaps in group-IV semiconductors. The pressure dependence of the band gap of WZ GaN has been measured [37] and using the variation in the reported calculated lattice constants one could estimate the error in the calculated gap. Based on the structural similarities of AlN and GaN, however, we expect that the differences between the band structures of these compounds are mainly due to differences between the cation potentials. For this reason, we decouple the effects of volume and potential by studying all materials at a fixed volume. A similar study performed at slightly higher or lower volume would give qualitatively the same results. References to calculations for GaN in this paper will refer to GaN at the AlN lattice constant unless the GaN volume is explicitly specified.

3.1. The BN/AlN/GaN series

A summary of the calculated ionicity gaps between the lower and upper valence band complexes, and fundamental band gaps for AlN, Al(Ga s)N, Al(Ga p)N, Al(Ga d)N, and GaN in both the ZB and WZ phases, is given in table 3. Gaps for BN [18] are given for comparison. Although the GaN lattice constants were taken from [14], calculated

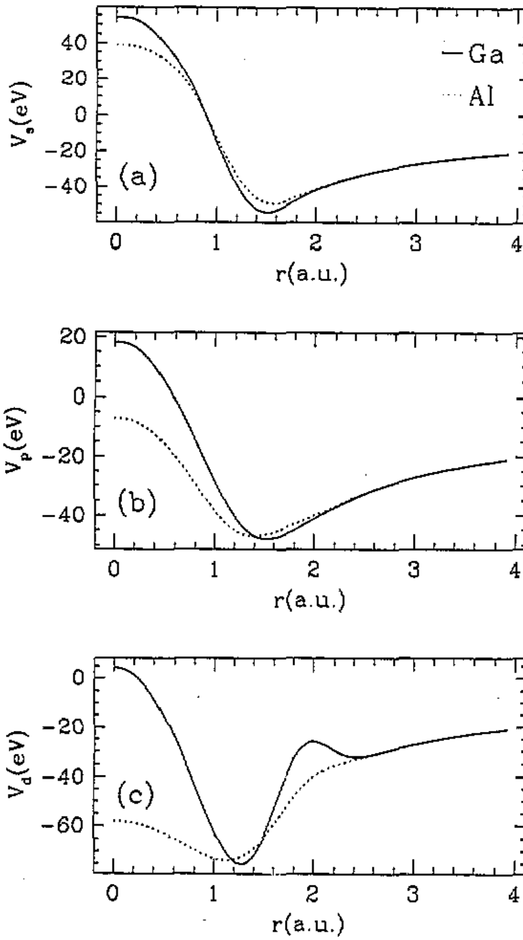

Figure 1. Al and Ga pseudopotentials generated using the HSC [31] method. The s, p and d components are shown in (a), (b), and (c), respectively.

fundamental gaps for both ZB and WZ GaN are 30–35% higher, and in better agreement with other reported theoretical values, than in that study. As expected, all fundamental gaps are small compared to experiment, due to our use of the LDA.

Table 3. Calculated ionicity gaps and band gaps in eV for AlN, Al(Ga s)N, Al(Ga p)N, Al(Ga d)N, and GaN in the WZ and ZB structures. Values for BN [18] are given for the ZB structure only. Both the direct and indirect gaps for the ZB structure are given. Gaps for GaN at its equilibrium lattice constant are shown in parentheses.

	BN	AlN	Al(Ga s)N	Al(Ga p)N	Al(Ga d)	GaN
Δ_{WZ}	—	6.38	6.05	6.45	5.91	5.65 (5.51)
Δ_{ZB}	3.6	6.23	5.87	6.25	5.77	5.30 (5.15)
$E_g^{\Gamma\Gamma}$(WZ)	—	3.91	3.47	3.93	2.92	2.40 (2.25)
$E_g^{\Gamma\Gamma}$(ZB)	8.6	4.22	3.77	4.25	3.04	2.54 (2.14)
$E_g^{\Gamma X}$(ZB)	4.2	3.17	3.34	3.16	3.11	3.27 (3.19)

BN follows the same trend in band gaps as found for AlN and GaN, where the direct gap in the ZB structure depends more strongly on the cation potential than the indirect $\Gamma \rightarrow X$ gap. However in contrast to AlN and GaN, the first conduction band state at Γ in BN is the Γ_{15}^{c}. The Γ_{1}^{c}, which is the lowest conduction band state in the Al and Ga compounds, lies several eV above the Γ_{15}^{c} in BN.

Although the B potential is much deeper than that for Al and Ga, the charge distributions for the heavier III–V nitrides have similar characteristics to the BN charge density. Here we examine the effect of d core states in Ga compared to Al to study the differences between AlN and GaN. A similar study of BN and AlN could be performed by focusing on the core p states.

3.2. *Wurtzite*

Since the equilibrium structure for both AlN and GaN is the WZ phase, we first examine the differences in electronic structure for this phase. Because of the similarities between WZ and ZB, this study provides a basis for understanding the differences in electronic structure between ZB AlN and GaN, and allows us to explore trends in the BN–AlN–GaN series.

Table 4. Electronic levels for AlN, Al(Ga s)N, Al(Ga p)N, Al(Ga d)N, and GaN in the WZ structure at the equilibrium volume for AlN. All levels are in eV and are referenced to the lowest Γ_{1}^{v} state in each compound.

	AlN	Al(Ga s)N	Al(Ga p)N	Al(Ga d)N	GaN
Γ_{1}^{v}	0.00	0.00	0.00	0.00	0.00
Γ_{3}^{v}	2.19	2.46	2.13	2.52	2.78
Γ_{3}^{v}	9.12	9.24	9.05	9.13	9.11
⋮					
Γ_{1}^{v}	15.21	15.62	15.19	16.19	16.63
Γ_{1}^{c}	19.12	19.09	19.12	19.11	19.03
X^{c} [38]	19.88	20.21	19.86	20.65	20.85

Selected energy levels for the five Al/GaN WZ compounds are given in table 4. All levels are given relative to the lowest valence band state at Γ. The charge density for pure AlN is given in figure 2 and differences between the charge densities of AlN and Al(Ga s)N, Al(Ga p)N, Al(Ga d)N, and GaN are given in figures 3–6. As expected, substitution of the Ga p potential causes only small changes—less than 1%—in each energy level when compared to pure AlN. Changes in the charge density are almost negligible compared to pure AlN, and are much smaller than changes seen in the compounds with altered s and d potentials.

Neglecting the p channel for now, we examine the trends within the other four compounds, XN, where X = Al, Al(Ga s), Al(Ga d), and Ga. As shown in table 3, the change in the gap for both structures is due to effects of the s and d potentials on an *equal* footing. The s channel accounts for 30% of the change while the d channel is responsible for 65–70% of the direct gap reduction from AlN to GaN.

We find that the energy difference between the bottom of the valence band and the bottom of the conduction band state at Γ remains constant whereas the top of the valence band rises with respect to these levels in going from AlN to GaN at constant volume.

The angular decomposition [39] of the lowest Γ_{1}^{v} and Γ_{1}^{c} states shows that they are s like on both the cation and anion and highly concentrated on N. These states move together

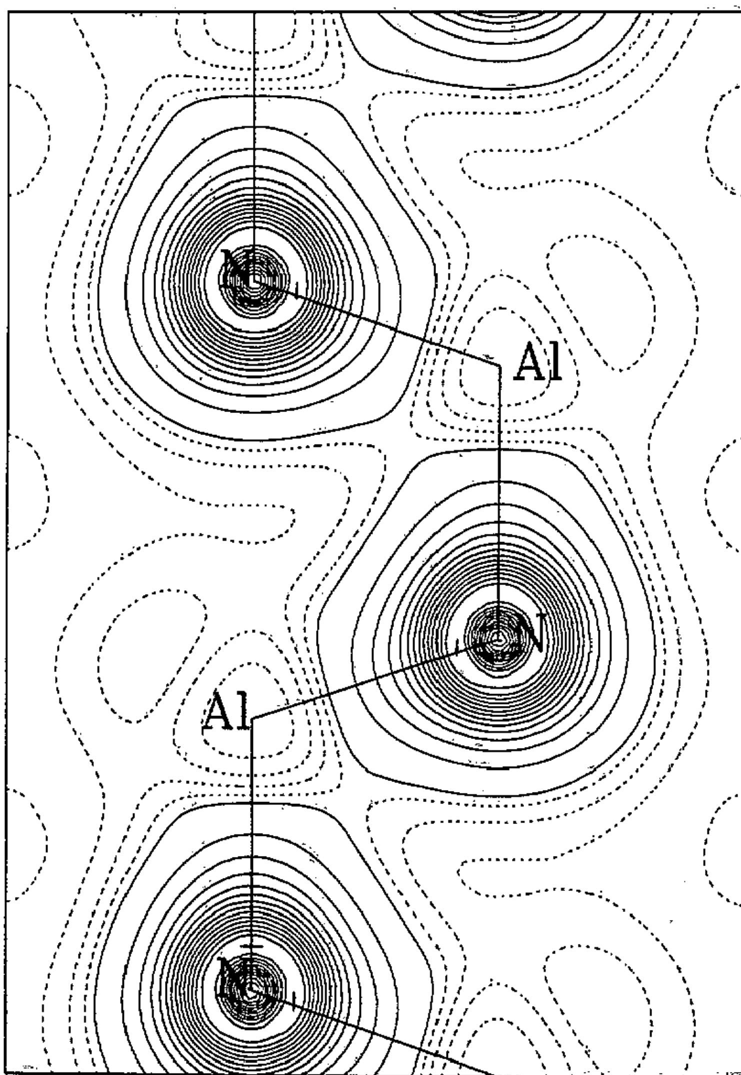

Figure 2. The valence band charge density in the [1$\bar{1}$0] plane for wz AlN is shown. Dotted contours correspond to 2, 4, 6, and 8 electrons/unit cell. Solid contours correspond to 10, 20, ..., 150 electrons/unit cell.

with changes in the cation potential simply because their charge densities are so similar. The top of the valence band Γ_1^v, however, has mostly p character on the anion, while the character on the cation changes from pd in AlN and Al(Ga s)N to mostly p in Al(Ga d)N and GaN.

Although our zero of energy is set at the lowest Γ_1^v, from our knowledge of the atomic potentials (see figure 1) it is more accurate to say that the increase in energy between the s-like and pd-like states is a combination of the decrease in energy of the s-like Γ_1^v and Γ_1^c levels in response to the stronger Ga s channel and the increase in energy of the pd-like Γ_1^v valence band maximum in response to the repulsive d channel. In this sense, our arbitrary energy reference can be misleading if taken as a true zero of energy but the quantitative discussion of cation effects is facilitated by making this choice.

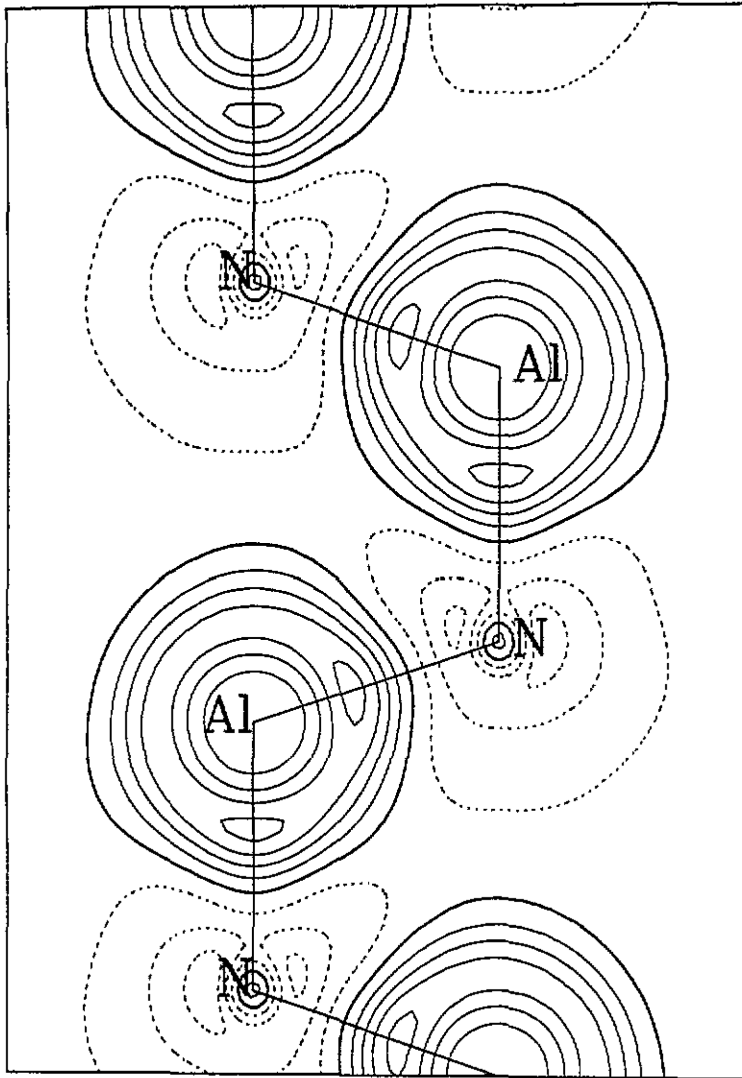

Figure 3. The difference in valence band charge density between wz Al(Ga s)N and AlN in the *[110] plane is shown. Contours are drawn for −0.6, −0.4, . . ., 0.8 electrons/unit cell. Negative* contours are dotted.

Several of the states at Γ can be thought of as fixed relative to the lowest Γ state. The second Γ_3^v and first Γ_1^c differ only about 1–1.5% each among the four XN. The first Γ_3^v and *the top of the valence band* Γ_1^v *rise with respect to the lowest state at* Γ. *For these states,* the change due to the full Ga potential can be seen to be a sum of the changes from the s and d potentials alone. For example, the first Γ_3^v state rises by 0.27 eV when the s potential from Ga is substituted for the Al s, 0.33 eV when the d potential is substituted, and a total of 0.59 eV for the full Ga potential. The top of the valence band Γ_1^v rises by 0.41, 0.98, and 1.42 eV for substitutions of the s channel, d channel, and full Ga potential, respectively.

Domination of the charge density by the N atom causes the total change arising from the replacement of Al by Ga to be the sum of the changes due to the difference in each angular component of the two atoms. In both AlN and GaN, a change in the cation potential

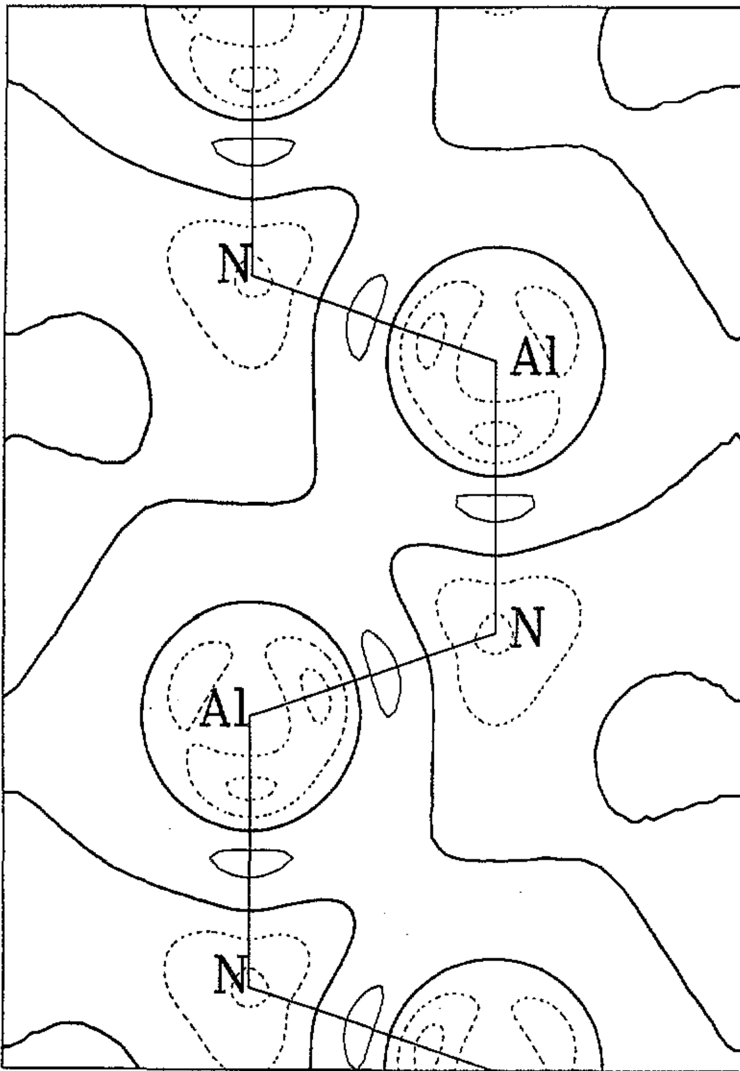

Figure 4. The difference in valence band charge density between wz Al(Ga p)N and AlN in the [110] plane is shown. Contours are drawn for −0.4, −0.2, 0.0, and 0.2 electrons/unit cell. Negative contours are dotted.

produces a very small perturbative change in the charge density and potential of the solid. A few individual levels may feel the change in cation potential and this is the origin of the changes in the relative energy levels. Hence, the energy gaps can vary on the order of several eV, but the basic charge distribution for the filled states remains relatively unchanged.

In the analogous system of AlAs/GaAs this will not be true [40]. The arsenides are much less ionic and there is a relatively more significant amount of charge on the cation than in the nitrides. For the less ionic case, the changes due to individual differences in the s and d channels of the potential will be too large to treat as perturbations and will cause a charge redistribution which will affect the band structure more significantly than in the nitrides.

In contrast to the cases discussed above, the changes for the first X^c state do not follow

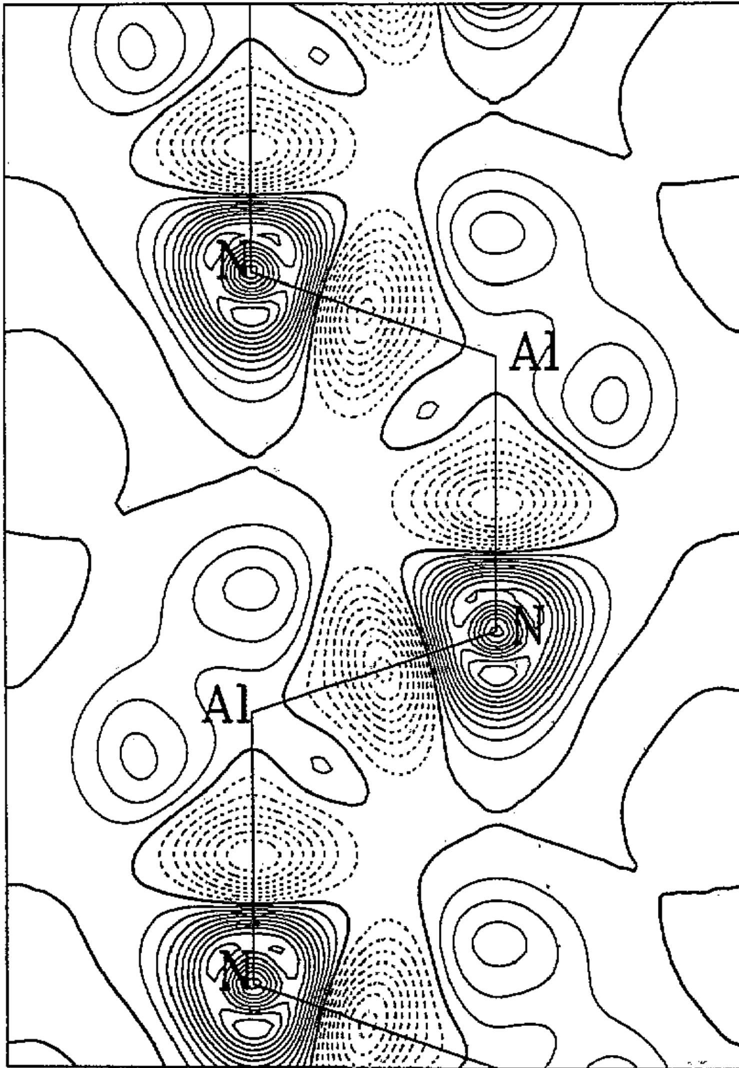

Figure 5. The difference in valence band charge density between wz Al(Ga d)N and AlN in the [110] plane is shown. Contours are drawn for −1.6, −1.4, ..., 2.0 electrons/unit cell. Negative contours are dotted.

this rule of addition. Angular decomposition of the X^c reveals that contributions from the s, p, $d_{xy,yz,zx}$, and $d_{x^2-y^2,3z^2-r^2}$ components are of the same order of magnitude. This is in contrast to the decomposition of the Γ states, which are dominated by no more than two components for each atomic site. For the X state, the interactions between added charge from a deeper s potential and redistribution of charge by the d potential cannot be ignored.

3.3. *Zinc blende*

The situation for the ZB structure is almost completely analogous to the findings for WZ. We predict, however, a change from an indirect gap to a direct gap material in going from AlN to GaN. This change can basically be attributed to the higher symmetry of the X^c state in ZB than in WZ [6].

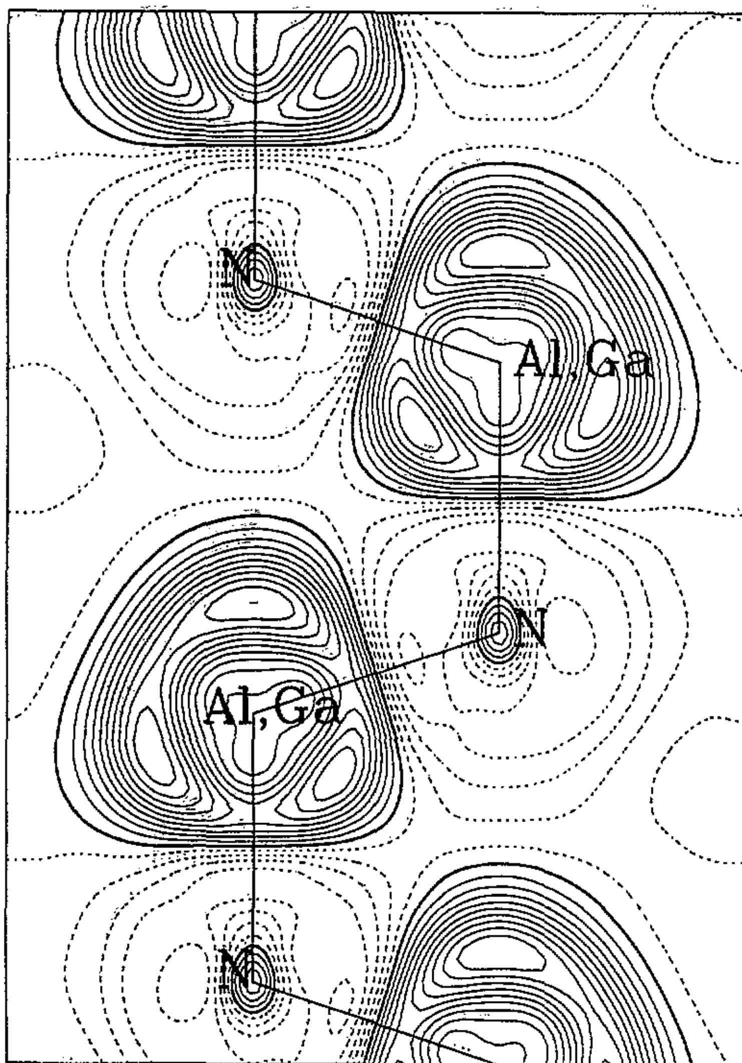

Figure 6. The difference in valence band charge density between wz GaN (at a_0 for AlN) and AlN in the [110] plane is shown. Contours are drawn for −1.2, −1.0, ..., 2.0 electrons/unit cell. Negative contours are dotted.

Selected energy levels for the five Al/GaN ZB compounds are given in table 5. As in the WZ structure, substituting the p channel of Ga for the Al-p does not change the electronic energy levels at the high-symmetry points.

For the other four XN compounds, the first conduction band state at Γ again moves rigidly with the lowest valence band Γ state as the potential is changed. The bottom of the conduction band stays constant to within 0.3%. The top of the valence band Γ^v_{15} rises with changes in the s and d channels as in the WZ structure.

Energy changes due to the change in s and d potentials are again additive. For example, the Γ^v_{15} state rises by 0.43 and 1.17 eV with respect to the lowest Γ state when the s and d channels, respectively, are changed from Al to Ga. The total change from AlN to GaN is 1.62 eV $\simeq$ 0.43 + 1.17 eV.

Table 5. Electronic levels for AlN, Al(Ga s)N, Al(Ga p)N, Al(Ga d)N, and GaN in the ZB structure at the equilibrium volume for AlN. All levels are in eV and are referenced to the lowest Γ_1^v state in each compound.

	AlN	Al(Ga s)N	Al(Ga p)N	Al(Ga d)N	GaN
Γ_1^v	0.00	0.00	0.00	0.00	0.00
Γ_{15}^v	15.09	15.52	15.06	16.26	16.71
Γ_1^c	19.31	19.29	19.31	19.30	19.25
X_1^c	18.26	18.86	18.22	19.37	19.98

Here, the X_1^c state has a higher symmetry (pd on the cation, sd on N) than in the WZ structure and the changes from the s and d potentials decouple. The total change due to the substitution of Ga for Al is simply the sum of the s- and d-induced changes ($0.60 + 1.11 \simeq 1.72$ eV).

3.4. Structural properties and ionicity

Since the electronic levels are affected by the change in cation potential, one may ask why the structural properties of AlN and GaN remain so similar. The charge in all five compounds (see figures 2–6) is heavily concentrated on the N site. As discussed with reference to the WZ structure, changes in the energy of several states at high-symmetry points are small compared to the domination of the charge distribution by the N atom. The largest change in charge density arising from our potential substitutions, in the Al(Ga-d)N and GaN compounds, is only 1% of the maximum $\rho(r)$ in AlN. Hence, bonding properties, bulk moduli, lattice constants, phonon modes, and other structural and ground state properties are expected to be similar in AlN and GaN.

The case of ionicity is interesting since it can be related both to properties of the charge density on the whole and to features in the band structure. The solid state ionicity can be derived from first principles [26] by evaluating the strength of the symmetric and antisymmetric parts of the bond charge. Since the bond charge on the cation increases very slightly in going from AlN to GaN, the solid state ionicity decreases from 0.794 to 0.780 (see table 1). Another measure of the ionicity [41] is the difference in energy between the lowest s-derived valence bands and the p-derived complex directly above them, called the ionicity gap. Table 3 lists the ionicity gaps for the four compounds studied in both the WZ and ZB structures. In comparison to the ionicity gap in BN, we see that the Al and Ga compounds are relatively similar, while the trend agrees with the *ab initio* ionicity scale based on the bond charge.

In addition to the large band gap differences, another surprising difference between AlN and GaN is the transition pressure from the WZ to the rocksalt phase. It is almost three times higher for GaN than for AlN; AlN transforms from WZ to rocksalt at pressures around 15 GPa [42] while the transition for GaN is around 40 GPa [43]. This discrepancy is most likely related to the lack of core d states in Al. Similar differences are found for the pressure-induced structural transitions [44] and pressure dependences of Raman modes [45] for Si and Ge. Since the WZ phase favours sp^3 bonding over contributions from d-like states, the transition from WZ to rocksalt will most likely increase the d character of the charge density. The repulsive d potential of Ga reduces the effective volume available for these d states, causing the increase in d character to be energetically costly. The transition pressure from WZ to rocksalt for GaN is expected therefore to be somewhat higher than the transition pressure for AlN.

4. Conclusions

This study yields information about the origins of the similarities and differences of the structural and electronic properties of the III–V nitrides. The variation in the band gaps for the series BN–AlN–GaN is studied. For BN, which behaves like a typical III–V compound with deep atomic potentials and a small lattice constant, a large energy gap results. For the heavier III–V nitrides, AlN and GaN, although they have similar structural properties, their band gaps differ by several eV. Since the AlX gap is consistently a factor of 1.5–2 larger than the GaX gap for the arsenides and antimonides as well as the nitrides, this study may prove useful in explaining the gap differences for the series of AlX/GaX pairs.

Since Ga has core d electrons, Ga has a repulsive d pseudopotential. The d potential in Al, however, is fairly attractive around the core. A comparison of the s channels for Al and Ga shows that the Ga s is deeper than the Al s due to underscreening by the core d electrons in Ga. Differences in the atomic potentials of Al and Ga cause individual electronic levels at high-symmetry k points to shift by several eV relative to the bulk of the band structure in going from AlN to GaN. Although the charge density remains essentially unchanged, a large change in the fundamental band gap results. The detailed study of AlN, Al(Ga s)N, Al(Ga p)N, Al(Ga d)N, and GaN presented here separates and quantifies the effects of the s and d channels of the potentials. The change in s potential from AlN to GaN accounts for 30% of the total band gap reduction while the d potential is responsible for 65–70%.

It is predicted that the differences between AlAs and GaAs are more complicated, since the arsenides are much less ionic. Differences between the Al and Ga potentials will have a much larger affect for these compounds than they do for the nitrides.

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References

[1] Sitar Z, Paisley M J, Yan B, Ruan J, Choyke W J and Davis R F 1990 *J. Vac. Sci. Technol.* B **8** 316
Sitar Z, Paisley M J, Yan B, Davis R F, Ruan J and Choyke J W 1991 *Thin Solid Films* **200** 311

[2] Lei T, Moustakas T D, Graham R J, He Y and Berkowitz S J 1992 *J. Appl. Phys.* **71** 4933
Lei T, Fanciulli M, Molnar R J, Moustakas T D, Graham R J and Scanlon J 1992 *Appl. Phys. Lett.* **59** 944
Eddy C R, Moustakas T D and Scanlon J 1993 *J. Appl. Phys.* **73** 448

[3] Paisley M J, Sitar Z, Posthill J B and Davis R F 1989 *J. Vac. Sci. Technol.* A **7** 701
Sitar Z, Paisley M J, Ruan J, Choyke J W and Davis R F 1991 *J. Mater. Sci. Lett.* **11** 261

[4] Ross J and Rubin M 1991 *Mat. Lett.* **12** 215

[5] Amano H, Sawaki H, Akasaki I and Toyoda Y 1986 *Appl. Phys. Lett.* **48** 353
Hiramatsu K, Detchprohm T and Akasaki I 1992 *Japan. J. Appl. Phys.* **32** 1528

[6] Lambrecht W R L and Segall B 1992 *Mat. Res. Soc. Symp. Proc.* vol 242 (Pittsburgh, PA: Materials Research Society) p 367

[7] Van Camp P E, Van Doren V E and Devreese J T 1991 *Phys. Rev.* B **44** 9056

[8] Ching W Y and Harmon B N 1986 *Phys. Rev.* B **34** 5305
[9] Rubio A, Corkill J L, Cohen M L, Shirley E L and Louie S G 1993 *Phys. Rev.* B **48** 11810
[10] Palummo M, Bertoni C M, Reining L and Finocchi F 1993 *Physica* B **185** 404
[11] Wenchang L, Kaiming Z and Xide X 1993 *J. Phys.: Condens. Matter* **5** 875
[12] Fiorentini V, Methfessel M and Scheffler M 1991 *Phys. Rev.* B **47** 13353
[13] Min B J, Chan C T and Ho K M 1991 *Phys. Rev.* B **45** 1159
[14] Van Camp P E, Van Doren V E and Devreese J T 1992 *Solid State Commun.* **81** 23
[15] Muñoz A and Kunc K 1991 *Phys. Rev.* B **44** 10372
[16] Nelson J S, Fong C Y, Hemstreet L A and Moll N 1993 *Bull. Am. Phys. Soc.* **38** 622
[17] Rubio A, Corkill J L and Cohen, M L *Phys. Rev.* B at press
[18] Wentzcovitch R M, Chang K J and Cohen M L 1986 *Phys. Rev.* B **34** 1071
[19] Wentzcovitch R M and Cohen M L 1986 *J. Phys. C: Solid State Phys.* **19** 6791
[20] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J1965 *Phys. Rev.* **140** A1133
[21] See the discussion given by Louie S G 1985 *Electronic Structure Dynamics and Quantum Structural Properties of Condensed Matter* ed J Devreese and P van Camp (New York: Plenum) p 335
[22] Surh M P, Louie S G and Cohen M L 1991 *Phys. Rev.* B **43** 9126
[23] García A and Cohen M L 1993 *Phys. Rev.* B **47** 4221
[24] Pauling L 1960 *The Nature of the Chemical Bond* 3rd edn (Ithaca, NY: Cornell University Press)
[25] Zhang S B, Cohen M L and Phillips J C 1987 *Phys. Rev.* B **36** 5861
Zunger A and Cohen M L 1978 *Phys. Rev.* B **18** 5449; 1979 *Phys. Rev.* B **20** 4082
Zunger A 1980 *Phys. Rev.* B **22** 5839
[26] García A and Cohen M L 1993 *Phys. Rev.* B **47** 4215
[27] Phillips J C 1970 *Rev. Mod. Phys.* **42** 317; 1973 *Bonds and Bands in Semiconductors* (New York: Academic)
[28] Ihm J, Zunger A and Cohen M L 1979 *J. Phys. C: Solid State Phys.* **12** 4409
Cohen M L 1982 *Phys. Scr.* **T 1** 5
Pickett W E 1989 *Comp. Phys. Rep.* **9** 115
[29] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[30] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 565
[31] Hamann D R, Schlüter M and Chiang C 1979 *Phys. Rev. Lett.* **43** 1494
[32] Troullier N and Martins J L 1990 *Solid State Commun.* **74** 613; 1991 *Phys. Rev.* B **43** 1993
[33] Louie S G, Froyen S and Cohen M L 1982 *Phys. Rev.* B **26** 1738
[34] García A and Cohen M L 1993 *Phys. Rev.* B **47** 6751
[35] Phillips J C and Kleinman L 1959 *Phys. Rev.* **116** 287
[36] Corkill J L and Cohen M L 1993 *Phys. Rev.* B **47** 10304
[37] Perlin P, Gorczyca I, Christensen N E, Grzegory I, Teisseyre H and Suski T 1992 *Phys. Rev.* B **45** 13307
[38] For an ideal c/a ratio, the position of the X point in the wz structure is in the M–L direction, two-thirds of the distance away from M.
[39] Shirley E L private communication
[40] Corkill J L, Rubio A and Cohen M L *Mater. Sci. Eng.* at press
[41] Grobman W D, Eastman D E and Cohen M L 1973 *Phys. Lett.* **43A** 49
[42] Vollstädt H, Ito E, Akaishi M, Akimoto S and Fukunaga O 1990 *Proc. Japan Acad.* B **66** 7
[43] Xia H, Xia Q and Ruoff A L 1993 *Phys. Rev.* B **47** 12925
[44] Chang K J and Cohen M L 1986 *Phys. Rev.* B **34** 8581
[45] Lewis S P and Cohen M L 1993 *Phys. Rev.* B **48** 3646