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Explicit treatment of the gallium 3*d* electrons in GaN using the plane-wave pseudopotential method

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The plane-wave pseudopotential (PWPP) method has been used to calculate structural and electronic properties of wurtzite and zinc-blende GaN. In contrast to previous studies using the PWPP method, the gallium 3*d* electrons were treated as valence electrons. This yields larger lattice constants and smaller energy gaps as compared with previous PWPP results. For wurtzite, the three structure parameters were found to be $a=3.162$ Å, $c=5.142$ Å, and $u=0.377$. For zinc blende, the cubic lattice constant was found to be $a_0=4.460$ Å. The lattice constants are about 1% smaller than measured values and the cubic lattice constant is within about 0.2% of results from full-potential all-electron calculations. This study demonstrates that it is both possible and practical to treat gallium 3*d* electrons explicitly using the PWPP method.

I. INTRODUCTION

The III-V nitride semiconductors AlN, GaN, and InN have electronic properties that make them attractive candidates for fabricating optical devices.[1] They have direct energy gaps of 6.2, 3.4, and 1.9 eV, respectively, corresponding to the ultraviolet (AlN and GaN) and the visible (InN) regions of the spectrum. AlN, GaN, and their alloys are therefore suitable materials for making ultraviolet detectors sensitive to wavelengths below about 365 nm. Perhaps more important are the many possible applications in the visible region of the spectrum such as a blue light-emitting diode. There is tremendous need for such a device, yet it does not appear to be possible to make one using group-IV or other III-V materials (although wide band-gap II-VI semiconductors may be suitable materials).

In spite of their technological potential, relatively little is known about these compounds as compared, for example, to the P-, As-, and Sb-based III-V compounds. This is mainly due to the difficulty of producing high-quality samples.[1] There have also been problems in applying *ab initio* theoretical techniques to study the nitride compounds. These problems have been largely overcome, however, such that it is now practical to perform reliable studies using *ab initio* techniques. With this in mind, we have undertaken a comprehensive theoretical investigation of AlN, GaN, and InN, and their alloys. To begin, we have considered the (mainly) structural properties of GaN since it is the best characterized of these compounds.

The theoretical technique used in this study is the plane-wave pseudopotential (PWPP) method. This technique has several features that make it especially suitable for studying the nitride compounds. In particular, no assumptions are made about the shapes of the wave functions and the electron density. This is important since the bonding in GaN is a combination of covalent and ionic. In addition, it is easy to calculate atomic forces within the PWPP formalism because the basis functions (plane waves) are not attached to the atoms. This has allowed us, for example, to determine the three parameters which specify the wurtzite structure independently. Previous PWPP treatments of GaN have yielded unsatisfactory results due to neglect of hybridization between the gallium 3*d* states and the rest of the valence states. In contrast, this application of the PWPP method includes these effects, demonstrating that such a treatment is not only possible, but also practical.

The remainder of this paper is organized as follows. In Sec. II we summarize the results from experimental studies and categorize previous theoretical studies in terms of their treatment of the gallium 3*d* electrons. In Sec. III we describe the calculational procedure we have used and present results for the wurtzite and zinc-blende structures. These are compared with measurements and with previous calculations to determine the accuracy of the PWPP technique, and to illustrate the importance of treating the gallium 3*d* electrons explicitly. In Sec. IV we examine the inconsistency among previous pseudopotential calculations in which the frozen-core approximation was used for the gallium 3*d* electrons. We also show that explicit treatment of the gallium 3*d* electrons is important for GaP and GaAs. In Sec. V we briefly describe the effects of the gallium 3*d* electrons on the zinc-blende and wurtzite band structures, and we summarize our results in Sec. VI.

II. EXPERIMENTAL AND THEORETICAL BACKGROUND

GaN was first synthesized by Johnson, Parsons, and Crew[2] in 1932 and Juza and Hahn reported the structure to be wurtzite in 1938.[3] This structure has space group designation $P6_3mc$ and consists of a hexagonal lattice with a four-atom basis. Two parameters a and c describe the hexagonal lattice and a third (internal) parameter u denotes the fractional separation of the gallium and nitrogen sublattices along the c axis. Measured values of the lattice constants span a range of about 1%. For the sake of comparison we refer to the values measured by Maruska and Tietjen,[4] $a=3.189$ Å and $c=5.185$ Å, as well as to

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their measured value for the energy gap $E_g = 3.39$ eV. For the internal parameter u we refer to the measured value of Schulz and Thiemann, 0.377.[5] There is also some disagreement as to the value of the bulk modulus. The estimates of Savastenko and Sheleg[6] (1.95 Mbar) and Xia, Xia, and Ruoff[8] (1.88 Mbar) are similar, but they differ from the values of Perlin *et al.*[7] (2.45 Mbar) and Ueno *et al.*[9] (2.37 Mbar).

There has been some success in growing the zinc-blende structure, mainly on cubic (001) substrates. However, the lattice constant and minimum energy gap are even less certain than for the wurtzite structure. For the sake of comparison, we refer to the values $a_0 = 4.52$ Å and $E_g = 3.3$ eV, which are in the middle of the ranges of measured values.[1] The resulting volume per GaN unit, however, is 1.1% larger than for wurtzite, which seems unreasonable given the similarities of the two structures. Sherwin and Drummond[10] estimated the bulk modulus for zinc-blende GaN from the elastic constants for wurtzite GaN calculated by Savastenko and Sheleg.[6] Their value, 1.90 Mbar, is close to the estimates of Savastenko and Sheleg[6] and Xia, Xia, and Ruoff[8] for the wurtzite structure.

Previous theoretical results for GaN should be considered with caution. In most of these studies, the gallium 3*d* electrons were treated as if they were inert core electrons.[11–16] However, recent studies indicate that this is not the case[17,18] and suggest that effects due to the gallium 3*d* electrons are important for GaN. Thus, we have categorized the previous theoretical studies in terms of the way the gallium 3*d* states were treated and have viewed their results accordingly. In the first category are the studies in which the gallium 3*d* electrons were treated explicitly. Most of these used the linear muffin-tin-orbitals (LMTO) method within the atomic-sphere approximation (ASA).[17,19–21] Recently, there has been a study of zinc-blende GaN using the full-potential (FP) version of the LMTO method[18] and a calculation of the zinc-blende lattice constants using the full-potential linear-augmented plane-wave (FP-LAPW) method.[22] The remainder of the previous theoretical studies belong to the second category, in which the gallium 3*d* electrons were treated as inert core electrons (the frozen-core approximation).[11–16] These studies all employed *ab initio* pseudopotentials. In addition, two of them used a mixed basis consisting of Gaussians and plane waves,[13,16] and the rest used a plane-wave basis.

III. DESCRIPTION OF THE TECHNIQUE AND RESULTS FOR ZINC-BLENDE AND WURTZITE GaN

We generated gallium and nitrogen pseudopotentials using the generalized norm-conserving pseudopotential (GNCPP) program developed by Hamann[23] including the nonlinear core correction of Louie, Froyen, and Cohen.[24] The nitrogen 2*s* and 2*p* electrons and the gallium 3*d*, 4*s*, and 4*p* electrons were treated as valence electrons and we used default values for the cutoff radii and energies[23] for all but the gallium *d* state. The default cutoff radius in this case, 0.21 a.u., yielded a *d* pseudopotential requiring a 400-Ry energy cutoff for the plane-wave expansion. Instead, we used a cutoff radius of 0.45 a.u., which yielded a *d* pseudopotential requiring no more than 240 Ry. The pseudopotentials were cast in the separable form of Kleinman and Bylander,[25] with the nitrogen *d* and gallium *f* pseudopotentials chosen to be the respective local potentials. Because this separation procedure can sometimes cause problems, we examined the logarithmic derivatives and verified the absence of "ghost states" using the criteria developed by Gonze, Stumpf, and Scheffler.[26]

The technique we used was based on the Kohn-Sham formulation[27] of density-functional theory[28] (DFT) together with the local-density approximation (LDA) for exchange and correlation. We used the Kohn-Sham form for the exchange energy[27] and the Perdew-Zunger form[29] for the correlation energy, which is based on the Monte Carlo simulations of Ceperley and Alder.[30] The Kohn-Sham functions were expanded in a plane-wave basis using an energy cutoff of 240 Ry, which corresponds to about 9400 plane waves per GaN unit. This large energy cutoff was necessary in order to describe the compact gallium 3*d* states adequately. To determine the self-consistent solutions, we used the Teter-Payne-Allan algorithm[31] along with seven and ten special **k** points,[32] respectively, to sample the wurtzite and zinc-blende Brillouin zones.

We determined the equilibrium lattice constants for the wurtzite structure by calculating the total energy for a set of values of the unit cell volume and the c/a ratio. For each of these geometries, forces were calculated and the energy was minimized with respect to u. These results were fit to the equation

$$z = C_{00} + C_{10}x + C_{01}y + C_{20}x^2 + C_{11}xy + C_{02}y^2 + C_{30}x^3 + C_{21}x^2y + C_{12}xy^2 + C_{03}y^3 , \tag{1}$$

where z is the energy, x is the unit cell volume, y is c/a, and the C_{ij} are coefficients to be determined from the fit. From the fitted function, the equilibrium volume and c/a ratio were found to be 300.431 a.u. and 1.626 41, yielding lattice constants $a = 3.162$ Å and $c = 5.142$ Å. These values are about 0.8% smaller than measured values, which is a typical level of agreement for a technique based on DFT-LDA. The bulk modulus was found by fitting the computed energies at each volume to the equation

$$z = C_0 + C_1y + C_2y^2 , \tag{2}$$

where z is the energy, y is c/a, and the C_i are coefficients to be determined from the fit. The results were then fit to the Murnaghan equation[33] and the bulk modulus was found to be 2.02 Mbar. This is about 5% larger than the estimates of Savastenko and Sheleg[6] and Xia, Xia, and Ruoff,[8] but about 20% smaller than the estimates of Perlin *et al.*[7] and Ueno *et al.*[9] Our experience with DFT-LDA suggests that calculated bulk moduli are generally larger than measured values, which would tend to favor the results of Savastenko and Sheleg[6] and Xia, Xia, and Ruoff.[8]

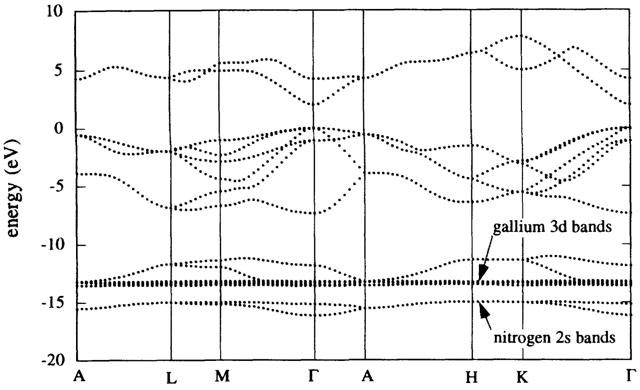

FIG. 1. Band structure for wurtzite including the gallium 3*d* electrons. The notations indicate the dominant characters of the lower bands. In fact, there is considerable hybridization between the nitrogen 2*s* and gallium 3*d* states.

From calculations at the equilibrium lattice constants, we found a value 0.377 for *u*, which is identical to the measured value. The band structure is shown in Fig. 1, and the energy gaps at the critical points are 2.04 eV at Γ, 4.29 eV at *A*, 4.92 eV at *M*, 4.33 eV at *L*, 4.99 eV at *K*, and 6.40 eV at *H*. The minimum energy gap corresponds to a direct transition at the Γ point with a value $E_g=2.04$ eV. The large discrepancy with the measured value is a well-known consequence of using the LDA.

For the zinc-blende structure, we calculated total energies for five values of the cubic lattice constant ranging from 8.10 to 8.70 a.u. From a fit to the Murnagahan equation,[33] we found an equilibrium lattice constant $a_0=4.460$ Å and a bulk modulus $B_0=1.87$ Mbar. The lattice constant is 1.3% smaller than the middle of the range of measured values (4.52 Å). However, the volume per GaN unit is within 0.4% of the value calculated for the wurtzite structure. This is not surprising given the similarity of the two structures, and suggests that when reliable, high-quality samples are available, the lattice constant will be somewhat lower than 4.52 Å. The bulk modulus is about 2% smaller than the estimated value of Sherwin and Drummond[10] and about 5% smaller than the value calculated for the wurtzite structure.

From a calculation at the equilibrium lattice constant, we found that the energy was higher for zinc blende than for wurtzite by 22 meV per GaN unit. This agrees qualitatively with the results of all previous calculations except those of Min, Chan, and Ho,[13] who found zinc blende to be lower in energy than wurtzite. The electronic band structure is shown in Fig. 2, and the energy gaps at the critical points are 1.89 eV at Γ, 3.23 eV at *X*, 4.67 eV at *L*, and 4.91 eV at *K*. The minimum energy gap corresponds to a direct transition at the Γ point with a value $E_g=1.89$ eV. This is 0.15 eV smaller than the minimum energy gap calculated for the wurtzite structure. Further discussion of the band structures for both zinc-blende and wurtzite GaN will be provided in a subsequent paper, along with results for AlN and InN.

Our results are summarized in Table I and compared with results from theoretical studies in which the gallium 3*d* electrons were treated explicitly. Within this category, calculations for the wurtzite structure were carried out using the LMTO-ASA technique, although ideal values were assumed for c/a and u.[17,19,20] The lattice constants, bulk moduli, and minimum energy gaps from these LMTO-ASA studies disagree by as much as 2%, 10%, and 6%, respectively. While this disagreement is not as large as among the PWPP results (Table II), it nevertheless seems excessive. Our wurtzite lattice constants, bulk modulus, and minimum energy gap differ from the LMTO-ASA results by as much as 2%, 17%, and 25%, respectively. For the zinc-blende structure, the LMTO-ASA (Refs. 17 and 21) lattice constants, bulk moduli, and minimum energy gaps disagree by 2%, 50%, and 10%,

TABLE I. Results from previous theoretical studies in which the gallium 3*d* electrons were treated explicitly. Gorczyca and Christensen (Ref. 19), Lambrecht and Segall (Ref. 17), and Perlin *et al.* (Ref. 20) assumed the ideal c/a, so only one of the hexagonal lattice constants was determined independently. In addition, Lambrecht and Segall (Ref. 17) used the experimental c/a for their calculation of the energy gap.

Zinc blende	a_0 (Å)	B_0 (Mbar)	E_g (eV)
Lambrecht and Segall[a]	4.50	2.0	2.09
Wenchang, Kaiming, and Xide[b]	4.40	3.09	2.29
Fiorentini, Methfessel, and Scheffler[c]	4.47	1.98	2.00
Feibelman[d]	4.467	2.00	1.87
This work	4.460	1.87	1.89

Wurtzite	a (Å)	c (Å)	u	B_0 (Mbar)	E_g (eV)
Gorczyca and Christensen[e]	3.11	5.08		2.39	2.59
Lambrecht and Segall[a]	3.13	5.11		2.2	2.75
Perlin *et al.*[f]	3.16	5.16		2.39	
This work	3.162	5.142	0.377	2.02	2.04

[a] Reference 17.
[b] Reference 21.
[c] Reference 18.
[d] Reference 22.
[e] Reference 19.
[f] Reference 20.

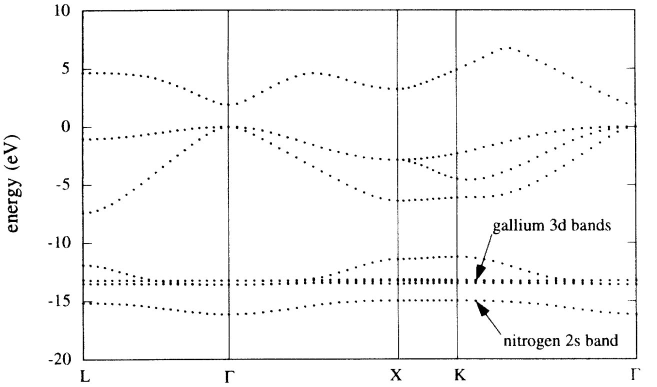

FIG. 2. Band structure for zinc blende including the gallium 3*d* electrons. The notations indicate the dominant characters of the lower bands. In fact, there is considerable hybridization between the nitrogen 2*s* and gallium 3*d* states.

respectively. (However, the results of Lamrecht and Segall[17] do agree quite well with ours and the other FP results.[18,22]) The agreement is much better, on the other hand, between ours and the other two FP studies;[18,22] 0.2% for the lattice constant, 5% for the bulk modulus, and 5% for the minimum energy gap.

Table II lists some results from theoretical studies in which the gallium 3*d* electrons were treated using the frozen-core approximation. The main feature to note is the significant disagreement in the results. The zinc-blende lattice constants, for example, differ by as much as 4%. In addition, the lattice constants are generally smaller than the value we found and the energy gaps are larger. These two features are actually related: the pressure dependence of the Γ-point energy gap is positive,[1] so the minimum energy gap increases with decreasing volume. To illustrate this, we performed a calculation for zinc blende using a lattice constant smaller than our equilibrium value; $a_0 = 4.32$ Å. The minimum energy gap was found to be $E_g = 2.51$ eV, which is about 0.6 eV larger than our equilibrium value. Overall then, it appears that explicit treatment of the gallium 3*d* electrons yields larger lattice constants than those found using the frozen-core approximation. This conclusion agrees with the LMTO-FP results of Fiorentini, Methfessel, and Scheffler.[8] However, Lambrecht and Segall[17] found just the opposite: using the LMTO-ASA technique, they found that not including the gallium 3*d* electrons among the valence electrons yielded a larger lattice constant.

IV. CONSEQUENCES OF USING THE FROZEN-CORE APPROXIMATION FOR THE GALLIUM 3*d* ELECTRONS

From the results listed in Table II, we concluded that treating the gallium 3*d* states as inert core electrons yields lattice constants that are too small and minimum energy gaps that are too large. However, there is also considerable inconsistency among these results. The zinc-blende lattice constants, for example, differ by as much as 4%. We decided to investigate this inconsistency and made two sets of gallium GNCPP (Ref. 23) in which the 3*d* electrons were treated as core electrons. Using these pseudopotentials we calculated lattice constants for zinc-blende GaN and compared them to the results listed in Table II. For consistency, we used the same nitrogen pseudopotentials as described in Sec. III.

First, we generated gallium pseudopotentials without the nonlinear core correction.[24] We used default core radii and energies for all of the states, and chose the *f* potential as the local potential for constructing the separable forms. An energy cutoff of 140 Ry and ten special **k**

TABLE II. Results from previous theoretical studies in which the gallium 3*d* electrons were treated using the frozen-core approximation. Muñoz and Kunc (Ref. 11) and Palummo *et al.* (Ref. 15) assumed the ideal *c*/*a*, so only one of the lattice constants was determined independently.

Zinc blende	a_0 (Å)	B_0 (Mbar)	E_g (eV)
Muñoz and Kunc[a]	≈4.50	1.79	
Van Camp, Van Doren, and Devreese[b]	4.419	1.73	1.48
Min, Chan, and Ho[c]	4.30	2.4	2.8
Yeh *et al.*[d]	4.364		
Palummo *et al.*[e]	4.45	1.76	2.65
Miwa and Fukumoto[f]	4.446	1.95	2.73

Wurtzite	*a* (Å)	*c* (Å)	*u*	B_0 (Mbar)	E_g (eV)
Muñoz and Kunc[a]	3.21	5.21			
Van Camp, Van Doren, and Devreese[b]	3.126	5.119	0.3767	1.90	1.63
Min, Chan, and Ho[c]	3.04	4.97	0.375	2.4	3.0
Yeh *et al.*[d]	3.095	5.000	0.378		
Palummo *et al.*[e]	3.15	5.14			2.76
Miwa and Fukumoto[f]	3.146	5.125	0.377	1.95	2.89

[a] Reference 11.
[b] Reference 12.
[c] Reference 13.
[d] Reference 14.
[e] Reference 15.
[f] Reference 16.

points[32] were adequate for convergence, and then we calculated the equilibrium lattice constant to be 4.131 Å. This is about 8% smaller than the measured value, which is very poor agreement for a technique based on DFT-LDA. Next, we generated an identical set of pseudopotentials except that we included the nonlinear core correction.[24] The lattice constant was found to be significantly larger, 4.318 Å, but still 4% smaller than the measured value. It should be noted, however, that the substantial increase in the lattice constant due to the nonlinear core correction indicates that the gallium 3*d* electrons play a considerable role in the bonding of GaN. In addition, these results support our conclusion that treating the gallium 3*d* electrons with the frozen-core approximation yields lattice constants that are too small.

The 4.318-Å lattice constant we found using the latter set of pseudopotentials (gallium 3*d* electrons treated as core electrons together with the nonlinear core correction) is close to the 4.30 Å found by Min, Chan, and Ho.[13] The lattice constants found by Yeh *et al.*, 4.364 Å,[14] and Van Camp, Van Doren, and Devreese, 4.419 Å,[12] on the other hand, are noticeably larger. This is probably due to a lack of convergence with respect to their plane-wave bases. Using our frozen-core gallium pseudopotentials (with the nonlinear core correction) and the energy cutoffs used by Yeh *et al.*, 50 Ry, and Van Camp, Van Doren, and Devreese, 34 Ry, we found lattice constants almost identical to their values; 4.365 and 4.421 Å, respectively. Lack of convergence, however, does not account for the larger lattice constants calculated by Palummo *et al.*, 4.45 Å,[15] and Miwa and Fukumoto, 4.446 Å.[16] Palummo *et al.* used a plane-wave expansion with an energy cutoff of at least 100 Ry, so we expect that their results were probably well converged. However, they did not use the nonlinear core correction, which we found to be important. Miwa and Fukumoto used a mixed basis so their results were also probably converged. On the other hand, their lattice constant is over 3% larger than that of Min, Chan, and Ho[13] who also used a mixed basis.

The differences among results from converged calculations are especially disturbing. Our conclusion is that they are mainly due to differences in the pseudopotentials. One possible explanation is that there is a flaw in one or more of these pseudopotentials. Another is that treating the gallium 3*d* electrons using the frozen-core approximation tends to magnify what are normally small effects due to differences in pseudopotential generation procedures. To some extent, however, determining the exact causes for the inconsistency is unimportant. The results given in Sec. III demonstrate that it is both possible and practical to treat the gallium 3*d* electron explicitly within the pseudopotential formalism. On the other hand, it is worth emphasizing that *ab initio* pseudopotentials approximate the interactions of the valence electrons with the ionic cores. Comparison with FP all-electron results is the best way to test this approximation (see Ref. 34 for further discussion).

Before concluding this section, we note that treating the gallium 3*d* electrons explicitly also has an effect on GaP and GaAs. Using the frozen-core gallium pseudopotentials (with the nonlinear core correction) and phosphorous and arsenic pseudopotentials generated using the GNCPP program,[23] we calculated zinc-blende lattice constants of 5.364 Å for GaP and 5.549 Å for GaAs. Using the gallium pseudopotentials in which the gallium 3*d* electrons were treated explicitly, we calculated lattice constants of 5.404 and 5.632 Å, respectively. Thus, treating the gallium 3*d* electrons explicitly yields 0.7% and 1.5% increases in the lattice constants of GaP and GaAs.

V. ROLE OF THE GALLIUM 3*d* ELECTRONS IN GaN

In this section, we examine the effect of the gallium 3*d* electrons on the band structures of zinc-blende and wurtzite GaN. This discussion will be rather brief because these effects have already been noted by Fiorentini, Methfessel, and Scheffler[18] for zinc-blende GaN. In addition, similar effects were noted by Wei and Zunger[35] for the II-VI compounds ZnTe, CdTe, and HgTe.

One reason for the importance of the gallium 3*d* electrons in GaN is that their wave functions have nonnegligible overlap with the nitrogen 2*s* and 2*p* wave functions. This is illustrated in Fig. 3, where we show the radial atomic wave functions separated by the near-neighbor distance in GaN. As was pointed out by Fiorentini, Methfessel, and Scheffler,[18] this overlap is especially significant because the energies of the *d* states are close to those of the nitrogen *s* states (see Figs. 1 and 2). In particular, the gallium 3*d* bands are about 2 eV above the nitrogen 2*s* band. For comparison, the *d* bands in II-VI compounds are further above the anion *s* band (and closer to the upper valence bands) (see, for example, Refs. 18 and 35), while the *d* bands in germanium lie below the *s* band. The proximity of the gallium 3*d* and nitrogen 2*s* bands results in significant hybridization as can be seen in Figs. 1 and 2. This has the effect of narrowing the nitrogen 2*s* band as can be seen by comparing zinc-blende band structures from calculations with (Fig. 2) and without (Fig. 4) the 3*d* electrons.

Fiorentini, Methfessel, and Scheffler reasoned that the interaction between the filled *s* and *d* bands accounts for

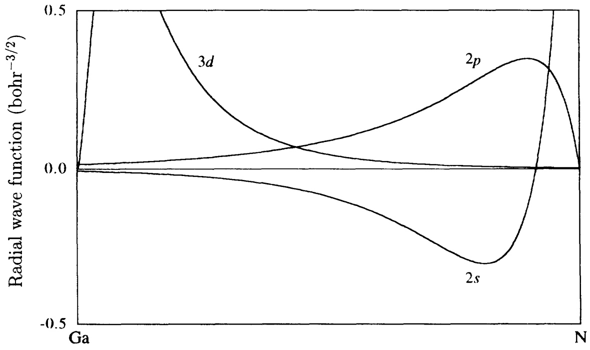

FIG. 3. Radial atomic wave functions for the gallium 3*d* states and the nitrogen 2*s* and 2*p* states. The origins for the two atoms have been offset by the near-neighbor separation in wurtzite GaN (1.94 Å).

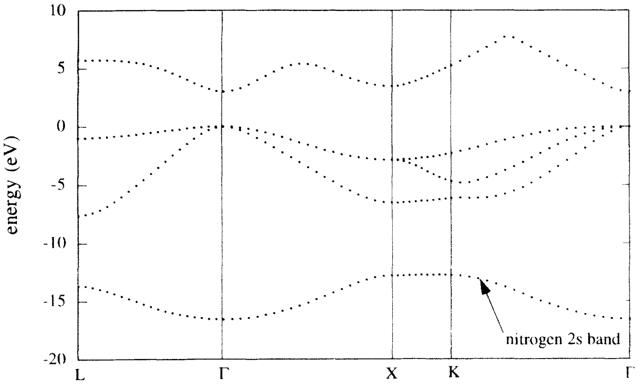

FIG. 4. Band structure for zinc blende using the latter set of pseudopotentials described in Sec. IV and treating the gallium 3*d* electrons within the frozen-core approximation.

the increase in the zinc-blende lattice constant. They noted three components of this interaction: (1) relaxation of the core states, (2) on-site nonlinear exchange-correlation interactions, and (3) core repulsion. Their explanation is plausible and we would only add that the interaction between the *d* electrons and the upper valence band may also play a role in setting the lattice constant. This was the conclusion reached by Wei and Zunger[35] for the II-VI compounds: the cation *d* states were about 4 eV above the anion *s* states, yet there was still a sizable increase in the lattice constant due to treating the cation *d* states explicitly. The rationale for this effect is that hybridization between the *d* states and the *p*-like states at the top of the valence band yields an antibonding *d* component at the top of the valence band. This tends to weaken the bonding resulting in an expansion of the lattice. For the II-VI compounds studied by Wei and Zunger,[35] the *d* bands were about 7 eV below the valence-band maximum, yet the lattice constants were found to be 0.43–0.87 Å larger when the *d* electrons were treated explicitly. For the II-VI compound ZnS, the *d* states are also about 7 eV below the valence-band maximum, and Fiorentini, Methfessel, and Scheffler[18] found a 0.33-Å increase in the lattice constant. For GaN, the separation between the *d* states and the top of the valence band is about twice as large and the increase in the lattice constant due to explicit treatment of the 3*d* electrons is smaller—on the order of 0.15 Å for the zinc-blende structure.

VI. SUMMARY AND CONCLUSION

We have performed DFT-LDA calculations for zinc-blende and wurtzite GaN using the PWPP method and treating the gallium 3*d* electrons as valence electrons. For zinc blende, the cubic lattice constant was found to be 4.460 Å and the minimum energy gap was found to correspond to a direct transition at the Γ point with a value 1.89 eV. For the wurtzite structure, all three structural parameters were determined independently. The lattice constants were found to be $a=3.162$ Å and $c=5.142$ Å, and the internal parameter was found to be $u=0.377$. The minimum energy gap for wurtzite was found to be 2.04 eV corresponding to a direct transition at the Γ point. These results are in excellent agreement with results from other FP calculations in which the gallium 3*d* electrons were treated explicitly.

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