PHYSICAL REVIEW B **76**, 075205 (2007)

Bulk and nanoscale GaN: Role of Ga d states

Roby Cherian and Priya Mahadevan
S.N. Bose National Centre for Basic Sciences, JD-Block, Sector III, Salt Lake, Kolkata-700098, India

(Received 18 February 2007; revised manuscript received 21 May 2007; published 8 August 2007)

We have studied the role of Ga $3d$ states in determining the properties of bulk as well as nano-GaN using projected augmented wave potentials. A significant contribution of the Ga d states in the valence band is found to arise from interaction of Ga $4d$ states with the dominantly N p states making up the valence band. The errors in the calculated lattice constant arising from not treating the Ga $3d$ states as a part of the valence are found to be similar, ~1%, for bulk as well as for nanoclusters of GaN.

DOI: 10.1103/PhysRevB.76.075205 PACS number(s): 71.15.Mb, 71.55.Eq

I. INTRODUCTION

The semiconductor industry has used silicon as its basic building block since the beginning. Recently, the focus has shifted to other materials with the aim of harnessing their multifunctionality to construct alternative generation devices. An important class of materials that have received considerable attention in this context are the nitrides. The bulk nitrides formed with group III elements show interesting physical properties such as large piezoelectric response.[1] However, the dilute nitrides where one observes dramatic effects by the introduction of a small amount of nitrogen to replace the anion sites have received a lot of attention in recent times. Alloys of GaInNAs have been recognized as important materials for the development of long wavelength solid-state lasers emitting within the fibre-optic communication wavelength window (1.3–1.55 μm).[2] There are also theoretical predictions that exist which suggest that these materials could also be used to increase the efficiency of multijunctional solar cells.[3] In the case of GaNP alloys, the crossover from an indirect to a direct band gap induced by N incorporation[4] promises high radiative efficiency, whereas a N-induced reduction in the lattice constant offers a possibility of lattice matching between optically efficient III-V compounds and Si wafers, desirable for the integration of the two technologies.[5] GaInNAs semiconductor quantum dots with dilute amount of nitrogen substitutional impurities are promising candidates for the active region in the next generation of optoelectronic devices.[6] Transition metal doped GaN has been found to exhibit ferromagnetism at room temperature[7] which could make these materials useful in the emerging area of spintronics.

With recent advances in computational power, theory and specifically *ab initio* density functional theory have played an important role in the design of materials with tailor-made properties.[8] Calculations for the systems of interest in the context of the nitrides, dilute nitrides as well as quantum dots, are usually performed for periodic systems considering large and representative supercells. These are computationally demanding within an *ab initio* approach. It is therefore useful to have accurate and reasonable approximations which decrease the computational cost. In this context, it was shown that enormous saving in terms of computational time may be made if one used ultrasoft pseudopotentials developed by Vanderbilt.[9] Further improvements were made by Blöchl[10] who combined the ideas of soft pseudopotentials and all electron methods such as linearized augmented plane wave within an elegant framework called the projected augmented wave (PAW) method. In this work, we have examined the bulk electronic structure of GaN using PAW potentials. The results have been compared with those obtained using ultrasoft pseudopotentials. The calculated equilibrium lattice constants are within 0.3% of each other.

The role of the Ga $3d$ states in determining the physical properties of GaN has received considerable attention over the past two decades. Unlike in the case of other Ga-V semiconductors, one finds that in GaN the Ga $3d$ core states are not chemically inert. One finds a strong overlap in energy between the semicore Ga $3d$ states as well as the N $2s$ states. Fiorentini *et al.*[11] pointed out that ignoring this interaction would have consequences on both the cohesive energy as well as the equilibrium lattice constant deduced theoretically. According to the variational principle, neglect of any relaxation of the semicore levels would increase the total energy, an effect which would disappear in the limit of well separated atoms in the solid. Further, the overlap of the core states with the valence states on the same atom results in a nonlinear exchange interaction. Finally, the interaction of core states with core states on the neighboring atom results in the neglect of closed shell repulsion. This has the effect of an increase in the kinetic energy when the cores on neighboring atoms are made orthogonal. If this contribution is neglected, the cohesive energy comes out too large and the lattice constant too small. The net effect which they found was that the lattice constant when Ga $3d$ states were neglected was almost 4% smaller than that obtained with the Ga $3d$ states included within local density approximation (LDA). An additional effect of the neglect of the Ga $3d$ states is observed in the modification of the band gap. The Ga $3d$ states that split into states with t_2 and e symmetries in the tetrahedral crystal field of the N neighbors interact with the valence band derived levels with the same symmetry. This interaction pushes the valence band maximum to higher energies and therefore decreases the band gap of GaN in comparison with treatments in which Ga $3d$ states were a part of the core. Recent studies by Bouhafs *et al.*[12] on the GaN semiconductor, at a fixed lattice constant, also confirm that the band gap decreases in a treatment in which the Ga $3d$ states were included in the valence.

PAW potentials give us the freedom to toggle between using the Ga 3*d* in the valence and in the core and allow us to simultaneously examine the modifications in the electronic properties and more importantly the structural and cohesive properties. The implementation of PAW that we use allows for core-valence interaction within a frozen core approximation. We first review the existing understanding for bulk GaN using PAW potentials. The equilibrium lattice constant computed by us within pseudopotential calculations with and without Ga 3*d* in the valence differs by less than 0.3% using ultrasoft pseudopotentials. The deviations between the two approaches are similar when we use PAW potentials. All earlier studies have found that the lattice constant without Ga 3*d* in the valence is underestimated within the pseudopotential approach, and our results using ultrasoft pseudopotentials are consistent with this observation. The PAW approach gives us a different trend, however, and we attribute that to the treatment of core-valence exchange interaction. Changing the anion to P and then As, we find an overestimation of the lattice constant when Ga 3*d* states are not included as a part of the valence. The difference between the theoretical lattice constants, however, decreases as we go from GaN to GaAs. A considerable portion of the literature has commented on the Ga 3*d* admixture in the valence band of GaN. To explicitly examine this, we have plotted the Ga *d* partial density of states for both cases—with and without Ga 3*d* states in the valence. The Ga *d* contribution in the valence band arising from semicore-valence interaction accounts for 51% of the total *d* admixture. This ratio decreases as we move to GaP and GaAs.

Having studied the bulk limit of GaN, we examined small representative clusters of GaN. Quantum confinement effects modify the energy of the valence band maximum and conduction band bottom of the semiconductor nanoparticles, and should decrease the separation between the semicore Ga 3*d* states and the valence band maximum. This results in an increased interaction strength and therefore an enhanced 3*d* contribution in the valence band. Comparing the equilibrium lattice constant with and without Ga 3*d*, we find a difference of ~1% for clusters with an average diameter of ~10 Å.

II. METHODOLOGY

The electronic structure of bulk zinc-blende GaN, GaP, and GaAs was calculated using a plane wave pseudopotential implementation of density functional theory within VASP.[13] Ultrasoft pseudopotentials as well as PAW potentials[14] have been used. Calculations have been performed with and without Ga 3*d* states included in the valence band. GGA-PW91 approximation[15] has been used for the exchange. A dense *k*-points grid of $8\times8\times8$ within Monkhorst-Pack scheme has been used. The energy cutoffs used for the kinetic energy of the plane waves used in the basis were 500 eV for GaN, 337.5 eV for GaP, and 260.9 eV for GaAs. The calculations for GaP and GaAs which did not include the Ga 3*d* states as a part of the valence band had a cutoff of 353.4 eV. The convergence with respect to *k* points was tested by increasing the mesh density from $8\times8\times8$ to $10\times10\times10$. The total energies changed by 0.02 meV. The equilibrium lattice constant has been determined by fitting the energy variation with volume to the Murnaghan equation of state. An analysis of the electronic structure was performed using the density of states calculated using the tetrahedron method. The wave functions were projected onto atom-centered spherical harmonics that were integrated over spheres of radii 1.2 Å for Ga, P, and As in GaP, GaAs, and GaN and 0.95 Å for N in GaN for the evaluation of the density of states.

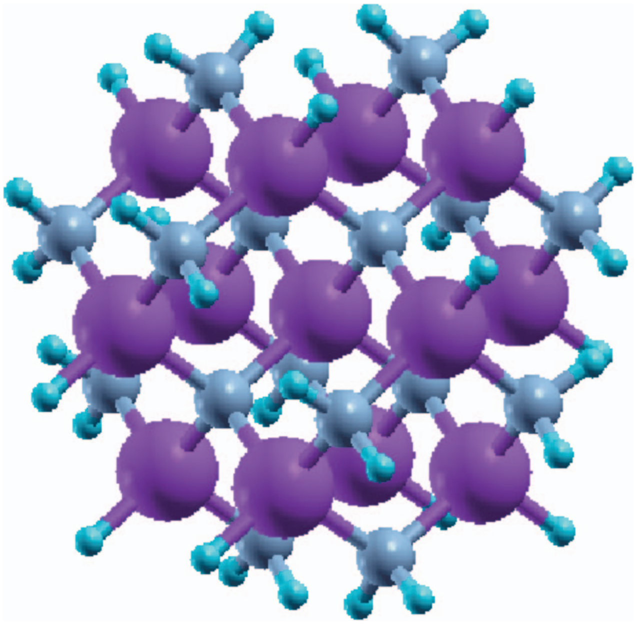

FIG. 1. (Color online) A ball and stick model for spherical nanocrystals ($n=3$) of GaN having an underlying zinc-blende geometry. The dark violet balls correspond to Ga atoms, the light gray balls correspond to N atoms, and the outer smaller blue balls denote the pseudohydrogen atoms.

We also examined the electronic structure of GaN nanocrystals in the cluster limit by considering representative clusters. We construct nanocrystals by cutting a spherical fragment of a bulk crystal, which has an underlying geometry of the zinc-blende structure. Now to define a spherical nanocrystal in this way, we need to specify the center and the radius. In our studies, the nanocrystal is centered on the Ga atom, and then the nanocrystals are generated by considering a spherical cutoff radius. These will have a T_d point group symmetry. The smallest cluster considered had four atoms around the central Ga atom, and since it had just one layer around the central atom for simplicity we denote this cluster as $n=1$ (where n stands for the number of layers around the central atom). The next size cluster which was considered in our study had three layers around the central atom ($n=3$), having in total 13 Ga and 16 N atoms (Fig. 1).

Calculating the equilibrium lattice constant of the cluster is a global optimization problem. Instead of allowing all degrees of freedom to be optimized simultaneously, we carried the optimization in parts. The cluster was expanded and contracted keeping the geometry fixed, i.e., *allowing for a volume dilation/contraction* about the bulk-like fragments. At each size, the convex hull formed by the surface atoms was

TABLE I. The lattice constant a_0 (Å) and bulk modulus B (GPa) variations in GaN with different potentials.

	PAW		USP	
	No Ga *d*	With Ga *d*	No Ga *d*	With Ga *d*
a_0	4.584	4.545	4.513	4.530
B	183.63	172.59	177.33	170.03

constructed and it was used to compute the volume. The equilibrium lattice constant was then calculated by fitting the energy variation with volume to the Murnaghan equation of state.[16] The clusters were then hydrogenated using pseudohydrogen atoms and the atom positions were optimized to reach minimum force positions. An average bond length was determined by averaging over all the nearest-neighbor bond lengths. This was then used to determine an average equilibrium lattice constant. Again as done in the case of the bulk, the equilibrium lattice constant with and without Ga 3*d* states in the valence was determined. Features of the electronic structure are examined by calculating the density of states broadening each eigenvalue with a Gaussian of full width at half maximum of 0.1 eV.

III. RESULTS AND DISCUSSION

As discussed earlier, the near resonance of the Ga 3*d* states with the N 2*s* states results in a strong deviation in calculated structural properties in treatments where Ga 3*d* states are not included as a part of the valence band. These considerations prompted us to carry out calculations using PAW potentials, allowing us to toggle between using Ga *d* in the valence, and merely as a part of the core. The results are given in Table I. For comparison, the results using ultrasoft potentials were also calculated (Table I). The error in the calculated lattice constant with and without *d* states in the valence was ~0.03–0.04 Å (around 1%). A smaller error in the calculated lattice constant is also found when one used ultrasoft potentials with and without Ga *d* in the valence. These results suggest that possibly the large deviations in the equilibrium lattice constant found earlier are specific to the choice of the method. The trends in the lattice constant with and without *d* are in opposite directions when we used ultrasoft potentials and when we use PAW potentials. As the treatment of the core electrons is meaningful in the PAW calculations, we examined these calculations in greater detail. The equilibrium lattice constant is predicted to be smaller when Ga *d* states are included in the valence. This is a surprising result at first as Ga *d* states interact primarily with the filled N *s* and N *p* states in the valence band. Hence, naively one does not expect there to be any energy gain as a result of the interaction. However, the valence and conduction band electrons feel the presence of the Ga 3*d* electrons in the semicore. Our recent analysis[17] has shown the manner in which the Ga *d* states interact with valence band states. By artificially moving the Ga *d* states to deeper energies using a U on the 3*d* states within the framework of LDA+U, we simulated the situations of having and/or not having chemically active Ga 3*d* states. Gradually moving the Ga 3*d* states to deeper energies, we find a redistribution of charge on Ga related levels. This in turn leads to a modification of the interaction between the anion *p* states and cation states. The altered interaction strengths can therefore explain why there should be any modification of the total energy and therefore the lattice constant of these systems with and without the inclusion of Ga 3*d* states in the valence.

TABLE II. Calculated structural properties for Ga*X*, *X*=N, P, and As. The lattice constant a_0 is in Å, and B is the bulk modulus in GPa.

	PAW			
	No Ga *d*		With Ga *d*	
	a_0	B	a_0	B
GaN	4.584	183.63	4.545	172.59
GaP	5.532	78.74	5.504	76.70
GaAs	5.759	62.47	5.746	61.28

Moving down the group V series of the Periodic Table to heavier anions instead of nitrogen, we find a similar trend. The theoretical lattice constant (Table II) calculated within the PAW method in the absence of 3*d* in the valence for Ga is consistently larger than when the 3*d* states are treated as a part of the valence. With increasing atomic number on the anion, the Ga 3*d* states are pushed deeper into the valence band, and hence their interaction with the anion *p* states making up the valence band is weaker. Hence, the deviation in the equilibrium lattice constant with the two choices of basis becomes smaller as we go from GaP to GaAs. While the deviations in the theoretical lattice constant are small, the errors in the theoretical bulk modulus are significant in the case of GaN, while they are small in the case of GaP and GaAs.

The significant interaction between the Ga 3*d* states with the N *p* states comprising the valence band is usually measured by plotting the Ga *d* admixture in the valence band. Our choice of basis, however, allows us to distinguish the 3*d* admixture from the 4*d* admixture, which one believes is not strongly affected by changing the basis and is largely additive. The total as well as the *s*,*p*,*d* contribution to the Ga and N partial density of states have been plotted (Fig. 2) for GaN with the 3*d* states on the Ga treated as a part of the core. The zero of the energy axis has been set to be the valence band maximum. The N *s* states contribute at around −11.5 eV while the N *p* states contribute between 0 and 6 eV. The band gap is calculated to be 1.47 eV within the present calculation. Ga *s* and *p* states are strongly intermixed in the conduction band. As is evident from the middle panel, there is a small admixture of the Ga 4*d* states within the states comprising the valence band (especially 0–3 eV below the valence band maximum).

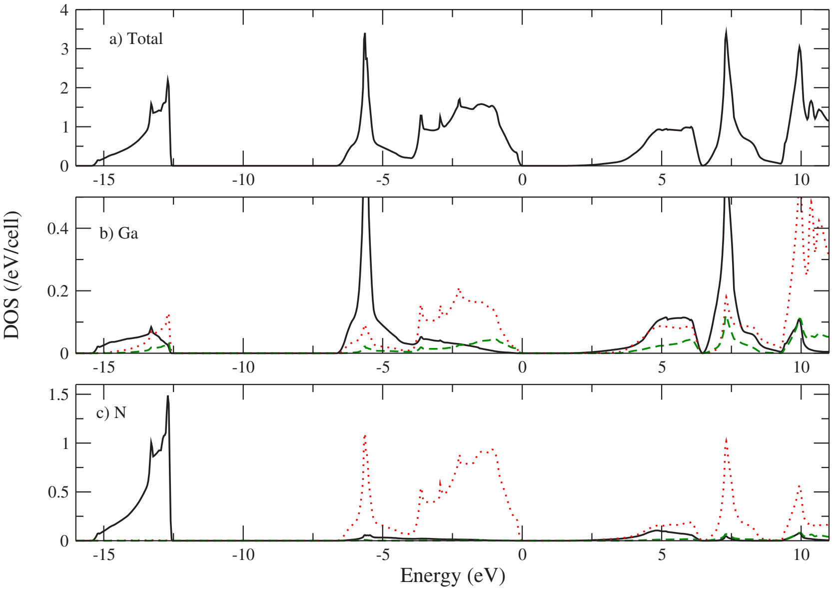

FIG. 2. (Color online) (a) The total density of states (DOS), (b) Ga *s* (black solid line), *p* (red dotted line), and *d* (dashed green line) projected density of states, and (c) N *s* (black solid line), *p* (red dotted line), and *d* (dashed green line) projected density of states for GaN using PAW potentials with no Ga *d*. The zero of energy corresponds to the valence band maximum.

A similar plot (Fig. 3) has been made from the calculations which include Ga 3*d* states in the valence. The gross features of the electronic structure remain unchanged. The Ga 3*d* states are found to lie at higher energies in these calculations than the N *s* states. Significant interaction is found to exist between the semicore N *s* and Ga *d* states because of their close proximity in energy. The Ga *d* states in the semicore also interact with the N *p* states. The band gap in the current calculation is found to be 1.56 eV, therefore increased by ~90 meV from the value obtained when the Ga 3*d* states were a part of the core. It should be noted that the density of states has been plotted at the theoretical equilibrium lattice constants given in Table I. Had we fixed the lattice constant in the two calculations, we would have seen a reduction in the band gap when the Ga 3*d* states were included in the basis as observed earlier.[12] Here we have the additional effect of a decreased lattice constant and so we find a larger band gap.

We have also examined the change in Ga *d* contribution in the valence and conduction bands with the two choices of basis. This is plotted in Fig. 4. Assuming that the Ga 4*d* admixture in the valence band is unchanged when Ga 3*d* states are included in the basis, the results are quite surprising. We find that the Ga 3*d* admixture in the valence band accounts for around 51% of the total Ga *d* component in the valence band. This is contrary to the belief that the Ga *d* contribution in the valence band is a measure of the semicore valence interaction. Similar results are plotted for GaP and GaAs in Figs. 5 and 6 at their theoretical equilibrium lattice constants (Table II). The *d* admixture gradually decreases as we go from GaN to GaP and finally to GaAs, and is mainly from interaction of the anion *p* states with the Ga 4*d* states in the conduction band. The Ga 3*d* admixture in the valence band accounts for around 42% and 23% of the total Ga *d* component in the valence band for GaP and GaAs, respectively.

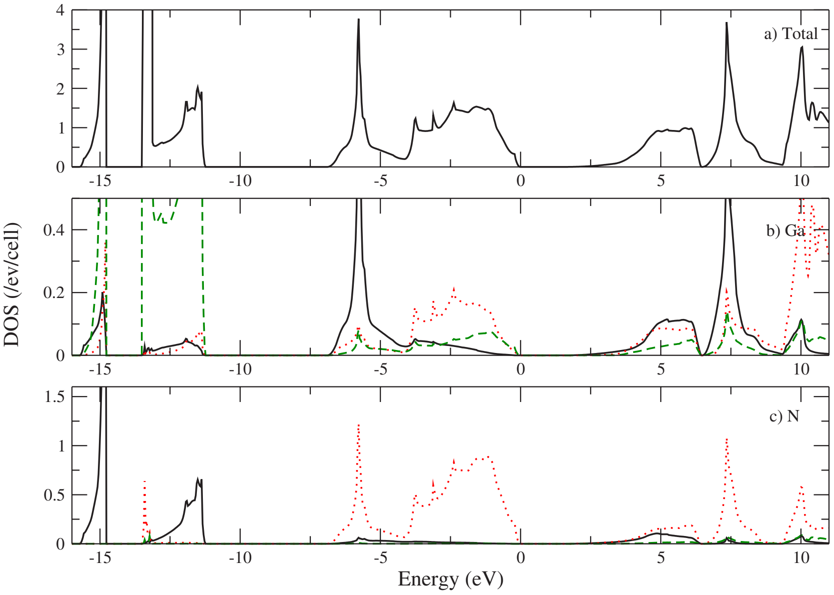

FIG. 3. (Color online) (a) The total DOS, (b) Ga *s* (black solid line), *p* (red dotted line), and *d* (dashed green line) projected densities of states, and (c) N *s* (black solid line), *p* (red dotted line), and *d* (dashed green line) projected densities of states for GaN using PAW potentials with Ga *d*. The zero of energy corresponds to the valence band maximum.

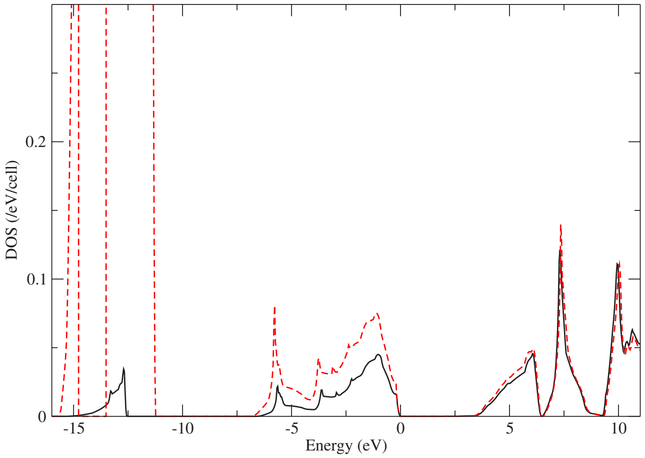

FIG. 4. (Color online) The Ga *d* projected density of states for GaN using PAW potentials with (red dotted line) and without (black solid line) Ga 3*d* as a part of the valence band. The zero of energy corresponds to the valence band maximum.

As GaN showed significant interaction between the Ga 3*d* states with the N *d* states, we examined the modifications in the interactions and consequent implications when one went down to the nanoregime. As is well known, quantum confinement effects modify the position of the levels which move from their positions in the bulk solid to deeper energies at a rate which is inversely proportional to the effective mass of the level. Since the *d* states would move more slowly than the states comprising the valence band maximum, with decreased cluster size, one expects the Ga *d*-N *p* separation to decrease, and hence interaction to increase. Indeed, the separation between the Ga 3*d* and N *p* states is found to decrease; we measure the enhancement in the *p*-*d* strength by the relative error that one finds in computed quantities such as the lattice constant. In Table III, we provide the optimized lattice constants for the two representative clusters. These are found to be smaller than that for the bulk GaN. As the size of the cluster decreases we find the relative position of the Ga 3*d* from the valence band maximum to decrease; for the smallest cluster ($n=1$) the separation is reduced by 2 eV and for the $n=3$ case it is reduced by 0.6 eV, with respect to the bulk separation value, resulting in the increased *p*-*d* interaction which modifies the lattice constant. With the two choices of basis, we also examined the changes in the Ga *d* and N *p* contributions in the valence and conduction bands. Around the conduction band region, the changes resulting from the two choices of basis were small. For the two nanocluster cases ($n=1$ and $n=3$), the density of states around the valence band region is shown in Fig. 7. The zero of the energy corresponds to the valence band maximum. Here, the Ga 3*d* admixture in the valence band accounts for around 53% for the $n=1$ case and 51% for the $n=3$ case of the total Ga *d* component in the valence band, which is almost the same as what we had observed for the bulk. Further, the presence and the absence of the semicore Ga 3*d* states modify the lattice constant in the same direction as the bulk calculations. The deviations are found to be of the same order as that observed for the bulk. At the theoretical calculated equilibrium lattice constant of these nanoclusters, we found band gaps of 5.45 and 5.46 eV within our calculations and the larger cluster had band gaps of 4.79 and 4.76 eV, for the cases with and without the inclusion of Ga 3*d* states in the basis.

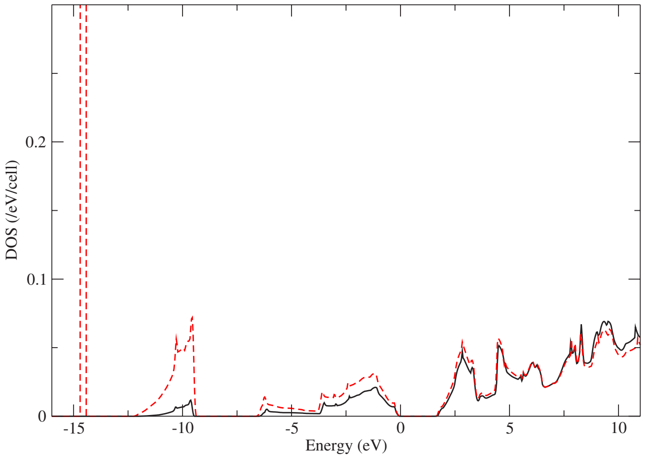

FIG. 5. (Color online) The Ga *d* projected density of states for GaP using PAW potentials with (red dotted line) and without (black solid line) Ga 3*d* as a part of the valence band. The zero of energy corresponds to the valence band maximum.

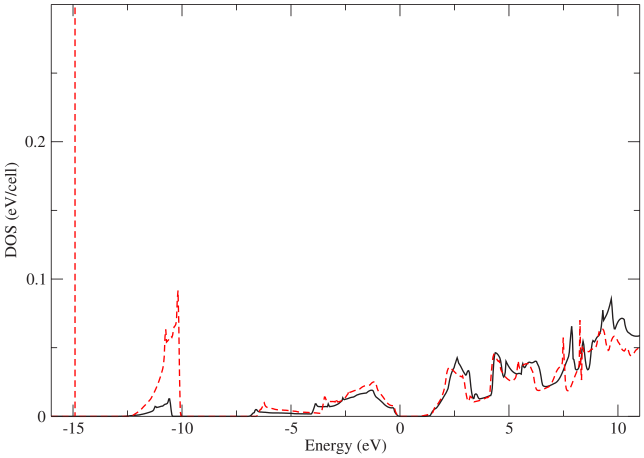

FIG. 6. (Color online) The Ga *d* projected density of states for GaAs using PAW potentials with (red dotted line) and without (black solid line) Ga 3*d* as a part of the valence band. The zero of energy corresponds to the valence band maximum.

IV. CONCLUSION

Hence, we have studied the modification of the equilibrium properties for GaN, with and without treating the Ga 3*d*

TABLE III. Optimized lattice constant in Å for Ga centered clusters.

Cluster size (n)	PAW	
	No Ga *d*	With Ga *d*
1	4.521	4.483
3	4.550	4.509

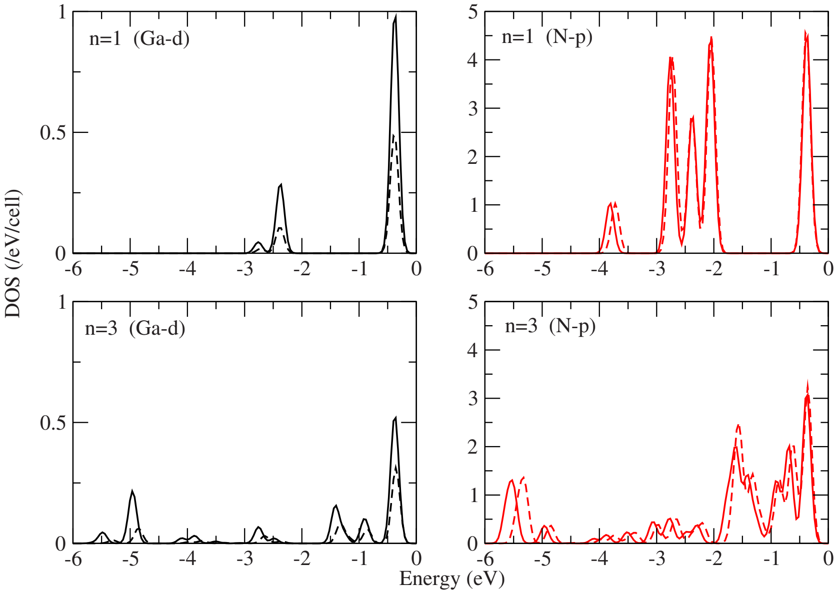

FIG. 7. (Color online) The Ga d projected density of states (left panels) using PAW potentials with (black solid line) and without (black dashed line) Ga $3d$ as a part of the valence band, and the N p projected density of states (right panels) using PAW potentials with (red solid line) and without (red dashed line) Ga $3d$ as a part of the valence band for the two cluster sizes $n=1$ (top panels) and $n=3$ (bottom panels) considered have been shown. The zero of energy corresponds to the valence band maximum.

in the valence, in both the bulk and the cluster limit. The effects of the lattice constant modification are found to be small and of the order of 1% at both limits. Hence, we conclude that a treatment using PAW potentials where Ga $3d$ states are treated as a part of the core is adequate to describe the properties of the GaN.

---

[1] *Properties of Group III Nitrides*, EMIS Datareviews Vol. 11, edited by J. H. Edgar (INSPEC, London, 1994).

[2] M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, Jpn. J. Appl. Phys., Part 2 **33**, L1056 (1994); J. S. Harris, Semicond. Sci. Technol. **17**, 880 (2002); H. Riechert, A. Ramakrishnan, and G. Steinle, *ibid.* **17**, 892 (2002).

[3] D. J. Firedman, J. F. Geisz, S. R. Kurtz, and J. M. Olson, J. Cryst. Growth **195**, 409 (1998); J. F. Geisz and D. J. Firedman, Semicond. Sci. Technol. **17**, 769 (2002).

[4] L. Bellaiche, S. H. Wei, and A. Zunger, Phys. Rev. B **56**, 10233 (1997); H. P. Xin, C. W. Tu, Y. Zhang, and A. Mascarenhas, Appl. Phys. Lett. **76**, 1267 (2000); W. Shan, W. Walukiewicz, K. M. Yu, J. Wu, J. W. Ager III, E. E. Haller, H. P. Xin, and C. W. Tu, *ibid.* **76**, 3251 (2000); I. A. Buyanova, G. Pozina, J. P. Bergman, W. M. Chen, H. P. Xin, and C. W. Tu, *ibid.* **81**, 52 (2002).

[5] K. Momose, H. Yonezu, Y. Fujimoto, Y. Furukawa, Y. Motomura, and K. Aiki, Appl. Phys. Lett. **79**, 4151 (2001); H. Yonezu, Semicond. Sci. Technol. **17**, 762 (2002).

[6] C. Y. Liu, S. F. Yoon, Z. Z. Sun, and K. C. Yew, Appl. Phys. Lett. **88**, 081105 (2006); C. Y. Liu, S. F. Yoon, Q. Cao, C. Z. Tong, and Z. Z. Sun, Nanotechnology **17**, 5627 (2006); Q. Gao, M. Buda, H. H. Tan, and C. Jagadish, Electrochem. Solid-State Lett. **8**, G57 (2005); Z. Z. Sun, S. F. Yoon, K. C. Yew, B. X. Bo, D. A. Yan, and T. C. Hang, Appl. Phys. Lett. **85**, 1469 (2004); S. Makino, T. Miyamoto, T. Kageyama, N. Nishiyama, F. Koyama, and K. Iga, J. Cryst. Growth **221**, 561 (2000).

[7] M. L. Reed, N. A. El-Masry, H. H. Stadelmaier, M. K. Ritums, M. J. Reed, C. A. Parker, J. C. Roberts, and S. M. Bedair, Appl. Phys. Lett. **79**, 3473 (2001); S. E. Park, H. Lee, Y. C. Cho, and S. Jeong, *ibid.* **80**, 4187 (2002).

[8] See Mater. Res. Bull. **31**(9) (2006) for a recent collection of reviews.

[9] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[10] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[11] V. Fiorentini, M. Methfessel, and M. Scheffler, Phys. Rev. B **47**, 13353 (1993).

[12] B. Bouhafs, F. Litimein, Z. Dridi, and P. Ruterana, Phys. Status Solidi B **236**, 61 (2003).

[13] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); Comput. Mater. Sci. **6**, 15 (1996).

[14] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[15] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[16] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[17] R. Cherian, P. Mahadevan, and C. Persson (unpublished).