FP-LAPW and pseudopotential calculations of the structural phase transformations of GaN under high-pressure

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Abstract

FP-LAPW and pseudopotential approaches have been used to investigate the structural phase transformations of GaN under high-pressure. In these calculations the local density and generalized gradient approximations (LDA and GGA) for the exchange-correlation potential have been used. Moreover, the electronic structure of the wurtzite (WZ), rocksalt (RS) and zinc-blende (ZB) phases of GaN have been calculated. The GGA result for the transition pressure of the WZ → RS transition is 42.3 GPa, which is in very good agreement with the X-ray absorption spectroscopy value of 47 GPa. The gradient corrections to the LDA, included via GGA, have small, but not negligible, effects on the properties studied. RS-GaN is predicted to be an indirect-band-gap semiconductor, with a band-gap of 1.7 eV.

Keywords: A. Semiconductors; D. Equation of state; D. Phase transitions; D. Electronic band structure

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GaN has recently attracted a lot of attention because of its use in optical devices operating in blue and ultraviolet wavelengths, and in high-temperature electronic devices [1]. At ambient pressure, GaN crystallizes in the wurtzite (WZ) structure. However, thin films of GaN can be successfully obtained by epitaxial growth, in both WZ and zinc-blende (ZB) structures, depending on the substrate [2]. The WZ-GaN is known to transform under high-pressure to the rocksalt (RS) structure. In spite of several experimental and theoretical investigations, the transition pressure, \( p_t \), of the WZ → RS transition is still a controversial issue (for a review see Ref. [3]), and so does the compressibility (or bulk modulus \( B_{eq} \)) of WZ-GaN. The main goal of this work is to contribute toward an accurate theoretical determination of \( p_t \) and \( B_{eq} \) of this system.

The first evidence of a transition of GaN under high-pressure to an unknown crystal structure was provided by the X-ray absorption spectroscopy (XAS) measurements of Perlin et al. [4,5], at about 47 GPa. Muñoz and Kunc [6] have predicted the unknown high-pressure structure to be the RS phase, using first-principles pseudopotential plane-wave (PP-PW) calculations. This prediction has been confirmed by the X-ray diffraction investigations of Xia et al. [7] and Ueno et al. [8], which gave values for \( p_t \) of 37 and 52.2 GPa, respectively. One should note that the above values for \( p_t \) were obtained upon pressure increase. The discrepancies between the above experimental results for \( p_t \) have been attributed to the sensitivity of the techniques used, as well as to the nature of the samples (powder [7,8] versus single crystal [4,5]). Moreover, there are also discrepancies in the obtained values for \( B_{eq} \) and the volume contraction, \( \Delta V/V_0 \), associated with the WZ → RS phase transition, obtained by the above experimental investigations: ranging from 188 [7] to 245 GPa [4,5] for \( B_{eq} \); 14 [4,5] to 17.9% [8] for \( \Delta V/V_0 \). The situation of the theoretical results for the above properties of GaN is not any better. The pseudopotential [6] (with the Ga 3d electrons treated as part of the frozen core) and LMTO-ASA (linear muffin-tin orbital, using the atomic-sphere-approximation) [9] results for \( p_t \) lie above the range of the experimental values. This is not consistent with the rational that the theoretical results must lie below the experimental values obtained upon pressure increase. On the other hand, full-potential (FP)-LMTO calculations [10] gave a value of 38.2 GPa, for the ZB → RS transition, in accord with the experimental result.
of Refs. [4,5]. However, it has been found [10,11] that the FP-LMTO results for \( p_t \) are sensitive to the computational ingredients used. The calculated values for \( B_{eq} \) and \( \Delta V/V_0 \) range between 176 and 240 GPa [3] and between 10 and 17.9% [8], respectively. Moreover, to the best of our knowledge, the electronic band structure of RS-GaN has not been studied before. Therefore, an accurate theoretical determination of \( p_t \), as well as the structural and electronic structure properties of GaN is in order.

In this work, a full-potential linearized augmented plane-wave (FP-LAPW) method is used to investigate the structural and electronic structure properties of the WZ, ZB and RS phases of GaN. The so-obtained equations of state are used to investigate its WZ → RS and ZB → RS phase transitions under high-pressure. In these calculations both the local density and generalized gradient approximations (LDA and GGA) have been used. Moreover, as a further check we also performed PP-PW calculations in which the Ga 3d electrons are treated as valence. Both methods have been successfully applied to study structural phase transitions of semiconductors under high-pressure.

The computational details of the FP-LAPW calculations are as follows. The calculations were performed by using the WIEN97 computer code [12]. The Ga 3d electrons were treated as valence. Atomic orbitals up to an angular momentum equal to ten were used to expand the wavefunctions inside the muffin-tin spheres. Whereas, in the interstitial regions they are expanded in terms of PWs. The wavefunctions and their derivatives are made continuous at the boundary of the spheres, and there are no shape approximations imposed on either the crystalline charge density or potential. The PWs cut-off was chosen from the highly recommended condition [12] \( R_{MT}K_{\text{max}} = 8.0 \) for LDA and \( R_{MT}K_{\text{max}} = 9.0 \) for GGA calculations, where \( K_{\text{max}} \) is the PW cut-off and \( R_{MT} \) is the muffin-tin radius. In order to use the same \( K_{\text{max}} \) for all the lattice constants studied, we kept constants the values for \( R_{MT} \). The values used were \( R_{MT}(\text{Ga}) = 1.95 \ a_0 \) and \( R_{MT}(\text{N}) = 1.65 \ a_0 \), for the three structures considered. Full relativistic effects were included for the core states, while scalar relativistic treatment was used for the valence ones. A sufficiently dense \( k \)-point grid was used to achieve a convergence of the total energy, \( E_{\text{tot}} \), to better than 0.1 mRy, namely a regular \( 8 \times 8 \times 8 \) Monkhorst–Pack (MP) [15] mesh for the ZB and RS forms, and a \( 8 \times 8 \times 4 \) mesh for the WZ phase.

The computational details of the PP-PW calculations are as follows. This approach has been used to study only the structural properties of the ZB and RS phases, and the ZB → RS phase transition. The Ga and N pseudopotentials were generated by using the Kerker scheme [16]. The valence atomic configuration used for Ga is 3d\(^{10}\)4s\(^{2}\)4p\(^{1}\), whereas for N we used 2s\(^{2}\)2p\(^{3}\) for the extraction of the s and p components and the ionic 2s\(^{2}\)2p\(^{1}\)7.52d\(^{0.25}\) for the d one. The core radii used for the s, p and d components are 1.675, 1.946 and 1.370 \( a_0 \) for Ga; 0.864, 1.289 and 2.022 \( a_0 \) for N, respectively. Then, the Ga d- and N p-components were optimized according to the Lin et al. [17] scheme. This is done by expanding the pseudo-wavefunctions, inside the core region, in terms of four Bessel’s functions. The expansion coefficients are then adjusted to minimize the kinetic energy beyond a chosen wave-vector cut-off, \( q_c \), which is assumed to be equal to \( q_4 \) (for the fourth order Bessel’s function). With the above values of core radii, the obtained values for \( q_4 \) are 104.8 and 94.3 Ry, respectively. Thus, the PW energy cut-off used was 120 Ry, which is found to give an excellent \( E_{\text{tot}} \) convergence. For the XC potential we have used the LDA data of Ceperley–Alder, as parametrized by Perdew and Zunger [18]. The integration over the first Brillouin zone was done by using a regular \( 4 \times 4 \times 4 \) MP mesh, which, in the PP-PW calculations, was found to give an excellent convergence [19].

The crystal structure of the ZB and RS phases can be fully defined by just the lattice parameter, \( a \). The WZ form is a hexagonal structure (with two formula units per unit cell), which can be described by three structure parameters: \( a \), \( c \) and an internal parameter, \( \alpha \). The optimal values of \( c/a \) ratio and \( u \), at a specific volume (\( V \)), were determined as follows. First, the \( E_{\text{tot}} \) is calculated at several values for the \( c/a \) ratio, at fixed \( V \) and a guessed value for \( u \). The obtained results are then fitted to a parabola to find \( (c/a)_{\text{eq}} \). Second, the optimal value of \( u \) is similarly determined, using the obtained \( (c/a)_{\text{eq}} \). Third, the first step is repeated to ensure that the \( (c/a)_{\text{eq}} \) determination was properly done. It has been found that the \( (c/a)_{\text{eq}} \) is \( V \)-independent. This finding is consistent with the experimental results of Ref. [8], which show that basically the \( c/a \) ratio does not change for GaN under hydrostatic compression. The LDA and GGA values are identical.

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Fig. 1. Energy versus volume curves of the WZ (solid lines), ZB (dashed–dotted lines) and RS (dashed lines) phases of GaN.
and equal to 1.625. This value is in an excellent agreement with the experimental values of 1.626 [8] and 1.627 [20]. The optimal value for $u_{eq}$ is $0.377$, which is identical to the experimental results of Ref. [20], and it is also $V$-independent.

The $E_{tot}$ versus $V$ curves of the three structures considered for GaN are determined by calculating $E_{tot}$ at seven or eight different volumes, and fitting the results obtained to the Murnaghan equation of state. For WZ-GaN, the values for $(c/a)_{eq}$ and $u_{eq}$ have been determined for each of the values of $V$ considered, as described above. Fig. 1 shows the fitted $E_{tot}$ versus $V$ curves of the three phases of GaN considered, calculated by using the FP-LAPW approach and both LDA and GGA. The important features to note from this figure are as follows. (i) The WZ phase is the ground state structure, in agreement with nature. (ii) The difference between the equilibrium $E_{tot}$ of the WZ and ZB phases is very small (the LDA and GGA results are of 0.0056 and 0.0098 eV, respectively). This is expected, since the ZB and WZ phases have local tetrahedral bonding and they only differ in the second-nearest neighbors. This also explains the epitaxial growth of GaN in the WZ or ZB forms, depending on the substrate [2]. (iii) The changes in the relative stability of the considered structures by going from LDA to GGA are quite small, but not negligible: the GGA results for the ground state $E_{tot}$ of the ZB and RS phases, relative to that of WZ, are 0.0098 and 0.4728 eV/atom, respectively. Whereas, according to the LDA calculations they are of 0.0056 and 0.4232 eV/atom, respectively. (iv) The GGA curves are shifted to the right with respect to those of the LDA.

Our calculated structural parameters of the phases of GaN considered are listed in Table 1, together with some theoretical results (because of space limitations, for an extensive review see Ref. [21]) and the available experimental data. All of the theoretical results reported in Table 1 were

<table>
<thead>
<tr>
<th>Approach</th>
<th>$a_{eq}$ (Å)</th>
<th>$c_{eq}$ (Å)</th>
<th>$B_{eq}$ (GPa)</th>
<th>$B_{0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WZ-GaN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FP-LAPW: LDA 8</td>
<td>3.163</td>
<td>5.140</td>
<td>208.3</td>
<td>5.79</td>
</tr>
<tr>
<td>FP-LAPW: GGA 8</td>
<td>3.226</td>
<td>5.243</td>
<td>172.4</td>
<td>4.86</td>
</tr>
<tr>
<td>PP-PW: LDA [22]</td>
<td>3.162</td>
<td>5.142</td>
<td>202.0</td>
<td>–</td>
</tr>
<tr>
<td>PP-PW: GGA [21]</td>
<td>3.245</td>
<td>5.296</td>
<td>172</td>
<td>5.11</td>
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<tr>
<td><strong>ZB-GaN</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FP-LAPW: LDA 8</td>
<td>4.466</td>
<td>–</td>
<td>208.1</td>
<td>4.64</td>
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<tr>
<td>FP-LAPW: GGA 8</td>
<td>4.554</td>
<td>–</td>
<td>175.4</td>
<td>5.30</td>
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<tr>
<td>PP-PW: LDA 8</td>
<td>4.512</td>
<td>–</td>
<td>193.7</td>
<td>4.29</td>
</tr>
<tr>
<td>Experiment [24,25]</td>
<td>4.50</td>
<td>–</td>
<td>190</td>
<td>–</td>
</tr>
<tr>
<td><strong>RS-GaN</strong></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>FP-LAPW: LDA 8</td>
<td>4.185</td>
<td>–</td>
<td>251.8</td>
<td>4.49</td>
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<tr>
<td>FP-LAPW: GGA 8</td>
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<td>–</td>
<td>211.6</td>
<td>4.50</td>
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<tr>
<td>PP-PW: LDA 8</td>
<td>4.240</td>
<td>–</td>
<td>235.4</td>
<td>4.71</td>
</tr>
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</table>

* Present work.

Table 2

<table>
<thead>
<tr>
<th>Approach</th>
<th>$p_t$ (GPa)</th>
<th>$\Delta V/V_0$ (%)</th>
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</thead>
<tbody>
<tr>
<td><strong>ZB → RS transition</strong></td>
<td></td>
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<tr>
<td>FP-LAPW: LDA 8</td>
<td>38.15</td>
<td>14.32</td>
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<tr>
<td>FP-LAPW: GGA 8</td>
<td>40.80</td>
<td>14.10</td>
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<tr>
<td>PP-PW: LDA 8</td>
<td>42.60</td>
<td>12.80</td>
</tr>
<tr>
<td>PP-PW: LDA [10]</td>
<td>53.80</td>
<td>18</td>
</tr>
<tr>
<td>FP-LMTO: LDA [10]</td>
<td>38.21</td>
<td>13.4</td>
</tr>
<tr>
<td><strong>WZ → RS transition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FP-LAPW: LDA 8</td>
<td>38.10</td>
<td>14.96</td>
</tr>
<tr>
<td>FP-LAPW: GGA 8</td>
<td>42.30</td>
<td>13.62</td>
</tr>
<tr>
<td>ASA-LMTO: LDA [9]</td>
<td>51.8</td>
<td>12</td>
</tr>
<tr>
<td>PP-PW: LDA [10]</td>
<td>56</td>
<td>18.4</td>
</tr>
<tr>
<td>XAS [4,5]</td>
<td>47</td>
<td>14</td>
</tr>
<tr>
<td>X-ray diffraction [7]</td>
<td>37</td>
<td>17</td>
</tr>
<tr>
<td>X-ray diffraction [8]</td>
<td>52</td>
<td>17.9</td>
</tr>
</tbody>
</table>

* Present work.
enthalpy. The results for were determined from the constraint of equal static lattice
experimental value for the WZ phase of 207 \[26\].

obtained by high-resolution X-ray diffraction measurements
for the obtained by using non-optimized pseudopotentials, except
almost identical with the PP-PW:LDA results of Ref. \[22\],
FP-LAPW:LDA results for the WZ and ZB phases are
remarkable features to note are as follows. (i) Our
obtained by treating the Ga 3d electrons as valence. The
band, and the lowest and upper valence bands are shown.
For the WZ phase, only the GGA results for the lowest conduction
prepared by using LDA (solid lines) and GGA (dashed lines).

The other features to note are as follows. (i) Our
FP-LAPW:LDA results for the WZ and ZB phases are
almost identical with the PP-PW:LDA results of Ref. \[22\],
except for the \(B_{eq}\) of the ZB phase. Whereas, our PP-PW:LDA
results (obtained by using optimized pseudopotentials) are
almost identical to the similarly obtained results by Stampfl
and Van de Walle \[21\]. (ii) The pseudopotential optimization
leads to softer materials. (iii) The same effect is
observed when our GGA results and those of Ref. \[21\] are
compared with the corresponding LDA ones, which is
already a well-established trend. (iv) The experimental
values of the lattice parameters of the WZ and ZB phases
lie between our LDA and GGA results obtained using the
FP-LAPW approach. Thus, one expects that the true value
of \(B_{eq}\) also does so. This is the case of the most accurate
experimental value for the WZ phase of 207 \(\pm 3\) GPa,
obtained by high-resolution X-ray diffraction measurements
\[26\].

The \(p_t\) of the WZ \(\rightarrow\) RS and ZB \(\rightarrow\) RS transitions of GaN
were determined from the constraint of equal static lattice
enthalpy. The results for \(p_t\) obtained from both the FP-
LAPW and PP-PW calculations are listed in Table 2,
compared with other available theoretical results and experimental data. The important features to note here are as
follows.

First, our results for \(p_t\) of the ZB \(\rightarrow\) RS and WZ \(\rightarrow\) RS
transitions calculated by using both the FP-LAPW and
PP-PW methods, and the LDA and GGA, lie within a
narrow pressure range, of 4.5 GPa. This is expected
from the use of highly accurate approaches, and the
close similarity between the WZ and ZB phases. On
the other hand, this also shows that the gradient corrections
to the LDA (included via GGA) have very small effects on \(p_t\)
of GaN.

Second, our results agree very well with those of
FP-LMTO \[10\], for both \(p_t\) and \(\Delta V/V_0\). Whereas, this is
not the case with the results of the LMTO-ASA \[9\] and
previous PP-PW \[6\] calculations. These discrepancies can
be understood in the former case as due to the use of ASA,
while in the latter case as due to the inaccuracy of the calcu-
lations of Ref. \[6\] and their treatment of the Ga 3d electrons
as part of the frozen core.

Third, the present results agree very well with the XAS
results \[4,5\], for both \(p_t\) and \(\Delta V/V_0\). The difference between
the XAS result and our GGA value for \(p_t\) of the WZ \(\rightarrow\) RS
transition is of 4.7 GPa. Whereas, it has been found \[7\] that
this transition is not reversible, with a difference in the
obtained value for \(p_t\) upon pressure increase and decrease
of 7 GPa. As noted by Ueno et al. \[8\], the 5 GPa difference
between their X-ray diffraction result and that of XAS is
reasonable, in spite of the enhanced sensitivity of the latter
approach. The difference between XAS result and that of
the other X-ray diffraction measurements can be understood as
due to the samples used (powder \[7\] versus single crystal
\[4,5\]), since grains with very small radii may cause surface
related effects which reduces the measured value of \(p_t\).
These arguments and the excellent agreement between our
results for \(\Delta V/V_0\) and that of Ref. \[4,5\], enhances further the
reliability of our results and the experimental results
obtained by using XAS.

The band structures of the WZ, ZB and RS phases of
GaN, calculated by using the FP-LAPW approach and
both LDA and GGA, are shown in Fig. 2. This figure
shows that both the WZ and ZB phases are direct-band-
gap semiconductors, at the \(\Gamma\)-point, while the RS form is
an indirect-band-gap semiconductor (with the valence band
maximum at the \(L\)-point and the conduction band minimum
along the \(X-W\) direction). There are two main deficiencies
in the LDA band structures of such compounds. (1) The
band-gaps are underestimated. The LDA band-gap of
WZ-GaN is of 2.08 eV (1.22 eV smaller than the experi-
mental value, of 3.3 eV). (2) The position of the Ga 3d
bands are overestimated, by about 2.3 eV (13.4 compared
to the experimental result \[27\] of 15.7). As expected, the use
of GGA does not solve these problems. In the contrary,
the GGA band-gaps are smaller than those of the LDA by 0.4,
0.4 and 0.2 eV for the WZ, ZB and RS phases, respectively.
Moreover, the use of GGA has negligible effects on the
position of the Ga 3d bands. However, the upper-valence
band width is improved by the use of GGA (the
LDA and GGA values for WZ-GaN are 7.35 and 6.89 eV,
respectively, compared to the experimental result of 6.5 eV
\[27\]).

The other features to note from Fig. 2 are as follows. (1)
The very close similarity between the electronic structures
of the ZB and WZ phases. This is expected, because of the
similarity of these two phases. (2) By assuming that the
underestimation of the band-gap of RS-GaN is similar to
that of the WZ phase, the indirect band-gap of RS-GaN is expected to be about 1.7 eV.

In a summary, the results of the present FP-LAPW and PP-PW investigations (in which the Ga 3d electrons were treated as valence) for the $p_t$ of the WZ $\rightarrow$ RS phase transition of GaN under high-pressure and the associated volume contraction agree very well with the XAS results, and the FP-LMTO calculations. The $c/\alpha$ ratio and the internal parameter $u$ are found to be volume-independent, and their values are in excellent agreement with the experimental data. The use of GGA is found to have small, but not negligible, effects on the calculated structural and electronic structure properties, and on $p_t$ of the above phase transition. The RS-GaN is predicted to be an indirect-band-gap semiconductor with a band-gap of about 1.7 eV.

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References