

High-pressure phase of gallium nitride

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The recently found high-pressure phase of GaN is studied theoretically, using the density-functional theory. The $E(V)$ phase diagram set up from the calculated total energies shows that the crystal structure of this phase is rocksalt or NiAs, and the calculated energy bands indicate that both modifications are semiconducting.

Recent extended x-ray-absorption fine-structure measurements¹ on GaN evidenced a phase transition at hydrostatic pressure of order 50 GPa; the crystal structure of the new phase has remained, so far, unidentified. In the present paper we are attempting to characterize the unknown structure by *ab initio* calculations using the density-functional method. Besides the transition pressure, we also evaluate the transition volumes, energy difference, and the change in equilibrium volume consequent to the transition. Structural parameters and some electronic properties of the high-pressure phase are determined as well.

At zero pressure the stable modification of GaN has wurtzite structure, with mainly covalent, partly ionic tetrahedral bonding and a direct electronic gap of 3.5 eV at the Γ point.² The other structures we consider in this work are zinc blende, rocksalt, CsCl, β -Sn, and NiAs.³ Our goal is to evaluate the $E(V)$ equation of state for each of the structures and to compare the relative energies.

We apply the density-functional theory within the local-density approximation,⁴ in plane-wave basis, with norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter⁵ and Ceperley-Alder exchange correlation⁶ as parametrized by Perdew and Zunger.⁷ The convergence tests of static equilibrium performed on the zinc-blende modification of GaN revealed that a plane-wave cutoff E_{PW} of order 40–60 Ry is needed in order to obtain reliable results. The high values of the cutoff energies are consequence of the small radii and the deep potential of the nitrogen core; they are consistent with the cutoffs used by other authors on other III-V nitrides.^{8–12}

We first determined the $E(V)$ curves for several selected, plausible structures with E_{PW} of 40 Ry. In the wurtzite structure we assumed the experimental c/a ratio of 1.624 and obtained the theoretical lattice constant [the minimum of $E(V)$] at $a = 3.21$ Å, viz. 0.7% above its experimental value.² Comparison with the calculated equation of state in the zinc-blende modification showed that the $E(V)$ curve of wurtzite is only 15 meV/atom lower, so that in all subsequent calculations we treat the zinc blende instead of the wurtzite structure. We will see later that error in the transition pressure introduced by this

simplification does not exceed 2 GPa. The equation of state of the NiAs modification was first calculated at the “ideal” ratio of $c/a = 1.633$; by varying the unit-cell dimensions we then found the “optimized” value of c/a to be 1.68, which led to lowering the $E(V)$ curve by 40 meV/atom. We verified that the c/a ratio can be considered as constant in the entire range of volumes considered.¹³ These preliminary calculations led us to retain, as the most probable high-pressure phases, the rocksalt and the NiAs structures, and to eliminate the β -Sn and CsCl modifications because their energies turned out to be by about 1.5 eV/atom higher than in the NaCl structure.

The k -space summation in zinc-blende, wurtzite, rocksalt, NiAs, β -Sn, and CsCl phases was performed using, respectively, 10, 7, 10, 6, 2, and 10 “special points” which, in the Monkhorst-Pack¹⁴ notation, correspond to $q_1q_2q_3 = 444$ for zinc blende, NaCl, and CsCl, 442 for wurtzite and NiAs structures, and 224 for β -Sn. Also, completely filled bands were assumed (semiconductor), and we checked that the two most likely structures are, indeed, *not* metallic; in this checking procedure the corresponding band-structure calculations were based on the ground state constructed under the more general assumption of a metal—the Gaussian smearing technique^{15,16} for the k -space summation was employed to this end.

We then further refined the calculations by using more plane waves, and the results, obtained for the most important structures with the cutoff $E_{PW} = 70$ Ry (1500 plane waves in zinc blende, 1300 in rocksalt, and 2500 in the NiAs structure), are shown in Fig. 1. The dotted $E(V)$ curve for NiAs was calculated at 40 Ry, and only the position of its minimum, with respect to the rocksalt curve was verified at 70 Ry. The CsCl equation of state (not shown in the picture) is ~ 1.2 eV above the rocksalt one, with the minimum at $V_0 = 11$ Å³ and, similarly, we found the β -Sn curve ~ 1.0 eV above the rocksalt one, with minimum at $V_0 = 11.3$ Å³.

The present energy calculations are sufficiently precise to distinguish between the $E(V)$ curves of the rocksalt and NiAs modifications. Nevertheless, as we are not taking into account any effect of temperature [calculating $E(V)$ instead of the free energy $F(V)$], one has to consider *both* structures as the probable high-pressure phases. We will

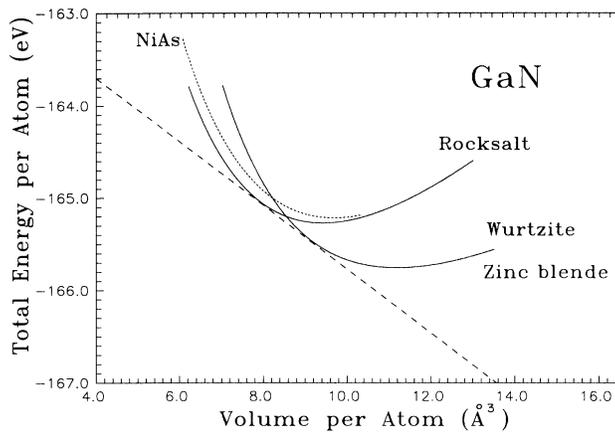


FIG. 1. The $E(V)$ equations of state for the energetically most favorable modifications of GaN. Solid lines represent the density-functional pseudopotential calculations with plane-wave cutoff $E_{PW} = 70$ Ry; the dotted line was obtained at 40 Ry and only its position above the rocksalt was determined in a 70-Ry calculation. The common tangent (dashed line) predicts the transition pressure from wurtzite to the rocksalt phase: 55 ± 4 GPa.

give below a few additional hints which might help to discern the two structures experimentally.

The common tangent of the equations of state for the wurtzite and rocksalt modifications, shown in Fig. 1 by the dashed line, yields the transition pressure $p = 55.0$ GPa. By comparing with the slope obtained in the 40-Ry calculation, we estimate the uncertainty of this result to be 4 GPa *at most*; on the other hand, an error of order -2 GPa is consequent to dealing with the zinc-blende rather than the wurtzite structure. The uncertainty of the corresponding experimental value is considerably larger, a consequence of the nearly always observed hysteresis: Ref. 1 situated the transition pressure at 50 (upstroke)

and 30 GPa (downstroke).

The calculated data in Fig. 1 provide further quantities of interest: The transition volumes turn out to be $V_t(\text{wurtzite})/V_0 = 0.82$ and $V_t(\text{NaCl})/V_0 = 0.71$, where $V_0 = 11.18 \text{ \AA}^3$ is the calculated equilibrium volume per atom in the wurtzite structure. The calculated equilibrium volume in the rocksalt structure is $V_0(\text{NaCl})/V_0 = 0.84$, in other words the transition wurtzite \rightarrow rocksalt makes the volume per atom (at ambient pressure) smaller by $\Delta V_0 \equiv V_0(\text{NaCl}) - V_0(\text{wurtzite}) = 1.77 \text{ \AA}^3$; the corresponding increase in energy, between the two minima of $E(V)$, is $\Delta E_0 = 484 \text{ meV/atom}$.

The static data on GaN in the rocksalt phase can be predicted as $a_0 = 4.22 \text{ \AA}$, and the bulk modulus $B_0 = 244$ GPa; the structure is semiconducting, with the (density-functional-)indirect gap Γ - X of 0.5 eV; for the direct gap at Γ one obtains 2.5 eV. The alternative high-pressure modification, the NiAs structure, is semiconducting as well, with a direct gap of 1.2 eV at Γ ; this structure is hexagonal, with $a_0 = 3.02 \text{ \AA}$.

Finally, some information was also obtained on the low-pressure ground state: from the $E(V)$ calculated in the "zinc-blende approximation" to wurtzite (see Fig. 1), the Murnaghan fit yields the bulk modulus $B_0 = 179$ GPa and its pressure derivative $B'_0 = 3.93$.

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