Theoretical study of the relative stability of structural phases in group-III nitrides at high pressures

Jorge Serrano[*,†] and Angel Rubio
Departamento de Física Teórica, Universidad de Valladolid, Valladolid E-47011, Spain

Eduardo Hernández
*Institut de Ciència de Materials de Barcelona–CSIC, Campus de la Universitat Autònoma de Barcelona,
Bellaterra, Barcelona E-08193, Spain*

Alfonso Muñoz and Andrés Mujica
Departamento de Física Fundamental II, Universidad de La Laguna, La Laguna E-38205, Tenerife, Spain
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We present the results of a first-principles theoretical study of the relative stability of several structural phases of the group–III nitrides AlN, GaN, and InN that complements the picture of the behavior under pressure of these technologically important materials. Along with structures which have been previously considered in other theoretical studies of these materials (comprising those of the observed phases: wurtzite, zinc-blende, and rocksalt; and the d-β-Sn, NiAs, and CsCl structures) we have also assessed the stability of several novel structures, viz., the cinnabar structure, the $Cmcm$ structure, and the $sc16$ structure, which have been recently observed in high-pressure experiments on various related compounds (e.g., GaAs) and have also been reported to be either stable or close to stable in a certain range of pressures in other III-V and II-VI compounds on the basis of first-principles calculations. Our results indicate, however, that in AlN, GaN, and InN, the high-pressure rocksalt phase remains stable with respect to any other phase considered in this study up to the highest pressures investigated of ∼200 GPa, which agrees with the available experimental data. We have further considered the effect of the semicore d orbitals of GaN and InN on the phase diagram of these compounds.

I. INTRODUCTION

The experimental and theoretical study of the wide-band-gap semiconductors among the II-VI and III-V compounds has been strongly fostered during the past decade by the enticing potential of these materials in the development of optoelectronic devices operating in the high-frequency range. The family of group-III nitrides, in particular, has been successfully used in the construction of blue-light emitting and laser diodes by Nakamura and co-workers.[1,2] The direct band gap of these binary compounds and their alloys ranges from 2 to 6 eV,[3–5] which makes them especially well suited for applications in optoelectronics. As a consequence, a good deal of research has been done to characterize as accurately as possible not only their important optical and electronic properties, which are of primary interest,[1–3,6] but also their mechanical and structural response.[7] In this paper we focus on the structural response of the group-III nitrides AlN, GaN, and InN when subjected to extremely high pressures of up to several hundreds of GPa.

As a consequence of the very rapid improvement in both experimental and computational techniques, research on the physical properties of materials at high pressure has seen much activity in recent years. The higher accuracy that can now be achieved has led to several important discoveries, which in some cases has resulted in a complete reassessment of what seemed established before. In the case of the technologically important II-VI and III-V compounds, one of the remarkable aspects of the picture that has emerged from the results of the latest experimental and theoretical studies is that in certain ranges of pressures several *low-symmetry* phases (*low* compared with those previously considered) often seem to be favored by a number of different compounds belonging to these families.

The case of GaAs is an excellent example of this. It is now well established that as pressure is increased above ∼16 GPa, the low-pressure zinc-blende phase transforms to a stable orthorhombic phase with space group $Cmcm$ and four atoms (i.e., two formula units) in the primitive unit cell.[8,9] On reducing the pressure from this $Cmcm$ phase, two new (possibly metastable) phases have been observed. One of them has the same space group $P3_121$ as the structure of cinnabar (γ-HgS) but with such different values of the internal parameters that the six atoms in the primitive unit cell of the resulting structural phase have a completely different coordination and, as a matter of fact, the new phase could be better described either as having space group $P6_222$ or as being only slightly distorted from it.[9] Notwithstanding this, it is common practice to call this phase *cinnabar*. The other phase experimentally reported to date as having been formed upon decompression from the high-pressure $Cmcm$ phase is described by means of a simple-cubic cell containing 16 atoms which span the space group $Pa\bar{3}$, and is named $sc16$ (Ref. 10). The existence of such phases has been corroborated, when not previously predicted, on the basis of the results of several theoretical studies, which also show all three phases as stable or close to stability in some range of

pressures in several other III-V (Refs. 11–15) and II-VI compounds.[16] Our understanding of the high-pressure behavior of this material is, however, far from complete (for example, the post-*Cmcm* behavior is experimentally not sufficiently well established), a statement that can safely be extended to any compound of the family. In all certainty, many more new discoveries and subsequent further rationalizations of the present situation will occur in the near future.

In comparison to other III-V compounds, the high-pressure behavior experimentally reported to date for the group-III nitrides displays a rather reduced sequence of structural phase transitions. For all three compounds considered in this work, only a wurtzite→rocksalt transition has been experimentally observed and, within the range of pressures covered by the experimental studies, the rocksalt phase does not undergo any additional transformations.[17] However, in several other III-V compounds previously studied (e.g., InP and InAs), the observed rocksalt phase becomes unstable against a *Cmcm*-like distortion as pressure is further increased and the cinnabar and *sc*16 structures are at least competitive candidates in certain ranges of pressure.[12,15] With these facts in mind, it is important to complete the picture of the high-pressure behavior of the III-V compounds by establishing whether for the III nitrides one would be likely to observe, in some range of pressures, the kind of structural phases recently identified as being stable or nearly stable in other II-VI and III-V compounds.

In this paper, we show the results of a comprehensive total energy study of several structural phases of AlN, GaN, and InN, which comprise some previously studied structures, such as wurtzite (wur), zinc-blende (zb), rocksalt (NaCl), the diatomic analog of the β phase of tin (*d*-β-Sn), and the structure of NiAs; and also the new structural phases predicted or observed in other members of the III-V family: cinnabar (or rather the class of structures with the same space group $P3_121$ and set of Wyckoff positions as cinnabar, but with rather different structural parameters and structural features, which nonetheless we will refer to here collectively as cinnabar), *Cmcm*, and *sc*16. The main structural features of these phases have been described before and will not be repeated here,[18] but some further relevant structural discussion will be presented in Sec. III at the same time as our results on the relative stability of these phases are discussed.

The electronic and structural properties of the zero-pressure wurtzite phase have been the object of a number of theoretical works[19–22] and in addition some previous theoretical studies have also considered the relative stability among the wurtzite, zinc-blende, rocksalt, *d*-β-Sn, and NiAs structures up to pressures of ~200 GPa (Refs. 22–24). A very simple phase diagram consisting of the wurtzite (or zinc-blende) and rocksalt phases has been indicated by the authors of Ref. 23, who, however, did not check a large variety of high-pressure structures that turn out to be relevant in other III-V and II-VI semiconductors.[8–13,15,16] In addition, Christensen *et al.*[24] have predicted a transition from the rocksalt structure to the NiAs structure in AlN at a pressure of about 30 GPa, which, however, has not yet been confirmed experimentally. The assessment of the relative stability of the *Cmcm*, cinnabar, and *sc*16 structures has not been undertaken before.

The rest of the paper is organized as follows. In Sec. II,

we outline the theoretical framework within which all the calculations have been performed. In Sec. III, we present and discuss the results of our study concerning the structural properties of the compounds at zero pressure (Sec. III A), the local stability of the wurtzite phase (Sec. III B), the energy-volume curves and the calculated phase diagrams (Secs. III C–III E), the stability of the rocksalt phases against distortion (Sec. III F), and the pressure evolution of the energy gaps of the high-pressure rocksalt phases (Sec. III G). Finally, in Sec. IV we summarize our conclusions and make some remarks concerning the high-pressure behavior of the compounds studied.

II. METHOD OF CALCULATION

All calculations were performed within the framework of the density-functional theory (DFT) (Ref. 29) with the local-density approximation (LDA) for which we used the Ceperley-Alder form of the exchange-correlation energy density of the homogeneous electron gas as parametrized by Perdew and Zunger.[30] $T=0$ K was assumed and the zero-point motion of the ions was not taken into consideration. This scheme is known to give an accurate enough description of the structural phase diagrams of group-IV, III-V, and II-VI semiconductors.

Only the outermost electrons of each atom were explicitly considered in the calculation, and the effect of the inner electrons and the nucleus (the *frozen core*) was described within a pseudopotential scheme.[31,32] We used the Troullier and Martins[34] scheme to generate the norm-conserving nonlocal pseudopotentials, which results in highly transferable and optimally smooth pseudopotentials; only in the case of Ga with d electrons in the core have we used the generation scheme of Hamann, Schlüter, and Chiang. Nonlinear core-valence exchange-correlation corrections (NLCC) were taken into account for the Ga and In pseudopotentials.[35,36]

A plane-wave basis set was used to solve the Kohn-Sham equations in the pseudopotential implementation of the DFT-LDA.[38] Even using smooth Troullier-Martins pseudopotentials, the hardness of the p component of the N pseudopotential and that of the d component of the Ga and In pseudopotentials (when their semicore d electrons are considered in the valence) requires the use of a rather large kinetic-energy cutoff in order to produce well-converged results, which along with the structural relaxation of several phases (see below) makes this study computationally challenging. We have found that a cutoff of 150 Ry (100 Ry) is enough to converge the total energy to an accuracy of about 1 mRy per formula unit (pfu) in the case of GaN (InN) with the d electrons in the valence; a cutoff of 90 Ry achieves a similar accuracy in the case of AlN and in the case of GaN and InN with frozen d orbitals in the core.[37] All the reciprocal-space integrations were performed using the Monkhorst-Pack scheme.[39] The **k**-point meshes[40] used for the semiconducting phases were $4\times4\times4$ for the NaCl, zb, and *sc*16 phases; $8\times8\times8$ for the cinnabar and *Cmcm* phase; and $6\times6\times3$ for the wur and NiAs phase. For the metallic *d*-β-Sn and CsCl phases, the mesh was increased to $20\times20\times20$. These samplings of the first Brillouin zone ensure an accuracy in the total energy of about 0.5 mRy pfu. A quasi-Newton method was employed in order to relax the

TABLE I. Structural parameters at zero pressure for the wurtzite (wur), zinc-blende (zb), and rocksalt (NaCl) structures of AlN, GaN, and InN. ΔE represents the difference in energy with respect to the zero-pressure wurtzite configuration (in meV pfu). Values in square brackets correspond to freezing the semicore d electrons of the cation. Experimental values for the different quantities are given in parentheses.

	Phase	B_0 (GPa)	B'	a (Å)	c/a	u	ΔE (meV)
AlN	wur	**209**	**3.7**	**3.061**	**1.600**	**0.382**	
		(207.9(6.3)[a], 201.7[b], 205.7[c])	(5.7–6.3[d])	(3.111[d])	(1.601[d])	(0.3821[e])	
	zb	**210**	**3.7**	**4.302**			**49**
				(4.37[d])			
	NaCl	**272**	**3.8**	**3.978**			**228**
		(221(5)[f], 295(17)[g])	(4.8(1.0)[f], 3.5(4)[g])	(4.045[h])			
GaN	wur	**196 [207]**	**4.3 [4.0]**	**3.180 [3.149]**	**1.632 [1.628]**	**0.376 [0.377]**	
		(237(31)[a], 245[i], 188[j])	(4.3(2.0)[a], 3.2[j])	(3.160–3.190[e])	(1.622–1.632[e])	(0.377[a,e,i])	
	zb	**196 [215]**	**4.2 [3.9]**	**4.497 [4.452]**			**10 [17]**
		(190[d])		(4.49–4.52[e])			
	NaCl	**240 [263]**	**4.5 [4.3]**	**4.225 [4.157]**			**908 [755]**
		(248[j], 323(27)[g])	(5.5[j]) (3.5(8)[g])				
InN	wur	**144 [136]**	**4.6 [3.9]**	**3.525 [3.477]**	**1.613 [1.614]**	**0.379 [0.379]**	
		(125.5(4.6)[a])	(12.7(1.4)[a])	(3.533[d])	(1.611[d])	(0.375[d])	
	zb	**147 [138]**	**4.4 [3.8]**	**4.968 [4.901]**			**20 [31]**
		(137[f])		(4.98[d])			
	NaCl	**191 [192]**	**4.6 [3.8]**	**4.636 [4.581]**			**372 [313]**
		(170(16)[g])	(5.0(9)[g])				

[a]M. Ueno *et al.*, Ref. 51.
[b]K. Tsubouchi *et al.*, Ref. 52.
[c]P. Boch *et al.*, Ref. 53.
[d]C. Stampfl and C.G. Van de Walle, Ref. 21 and references therein.
[e]Reference 54.

[f]Q. Xia *et al.*, Ref. 48.
[g]S. Uehara *et al.*, Ref. 17.
[h]H. Vollstädt *et al.*, Ref. 46.
[i]P. Perlin *et al.*, Ref. 49.
[j]H. Xia *et al.*, Ref. 50.

different structural parameters.[41] The E-V curves corresponding to the relaxed configurations for each phase were then fitted to the Birch-Murnaghan[42] equation of state and the pressure $p = -dE/dV$ and enthalpy $H = E + pV$ were evaluated from the fitted expression. The coexistence pressure of two phases is the pressure at which their enthalpies are equal.

Several phases of interest are structurally related in a very simple way (see, for example, Ref. 13 concerning *Cmcm*-NaCl and Ref. 15 concerning CsCl-NaCl-cinnabar) and can thus be represented using the same cell and basis vectors with, in each case, appropriate choices for the values of the internal and cell parameters. In these cases it is possible to perform a very accurate comparison of the total energies and relative stability of the phases at a certain volume, by varying the structural parameters in such a way as to deform one phase into the other. We have used this procedure to perform a detailed study of the relative stability of the structurally related phases.

III. RESULTS AND DISCUSSION

A. Structural properties at zero pressure

At normal conditions all three compounds AlN, GaN, and InN crystallize in the wurtzite structure, although it has proved possible to grow a zinc-blende modification using epitaxial techniques.[43,44] The zinc-blende structure is of technological interest as it can be doped more easily than the

wurtzite structure. Both structures have a semiconducting Kohn-Sham band structure. In the case of the wurtzite structure, the experimental energy-band gap is direct with values of 6.2 eV (AlN), 3.5 eV (GaN), and 1.90 eV (InN).[45] In Table I, we summarize the calculated structural properties at zero pressure for both the wur and zb structures, together with the high-pressure rocksalt structure.

At fixed volume, the hexagonal wurtzite structure (space group $P6_3mc$ with four atoms per unit cell) has two structural degrees of freedom, one internal parameter u and the axial ratio c/a. The wurtzite phase experimentally observed at low pressures in these and related compounds has $u \approx \frac{3}{8}$ and $c/a \approx 1.633$, which leads to very nearly tetrahedral coordination [at the *ideal* values $u_0 = \frac{3}{8}$ and $(c/a)_0 = \sqrt{8/3}$, all four nearest-neighbor distances are equal and all bond angles are ideal tetrahedral angles, $\sim 109.5°$]. In this case, the *local* (i.e., up to first neighbors) environment of each atom is very much the same as in the case of the zinc-blende phase and thus the resulting semiconducting structure is very close in energy to zinc-blende.[57] It is worth noting, however, that the ideal values of the structural parameters of this wurtzite configuration are *not* fixed by any symmetry consideration.

The values of u and c/a for the relaxed structures are close to their ideal values and are in excellent agreement with the experimental values, as shown in Table I. In this table we also show the calculated difference in energies between the wur and the zb structures at their respective equilibrium volumes $\Delta E_{zw} = E_{zb}^0 - E_{wur}^0$. In each of the three

compounds considered, the value of ΔE_{zw} is very small and positive, which is in line with the experimental observation of both phases at zero pressure, with the wurtzite phase being the more stable phase. Other previous theoretical studies reproduce this result (see, for example, Ref. 21 and references therein).

In Table I, comparison is made with several experimental values of the lattice constant, bulk modulus, and pressure derivative of the bulk modulus (all at zero pressure). Recently, a detailed study of the structural properties of the wurtzite phase at zero pressure has been presented by Stampfl and Van de Walle in Ref. 21. We refer the interested reader to the very careful comparisons between different experimental and theoretical works shown in Ref. 21 and the discussion therein for a fuller account of the structural properties of these compounds at zero pressure, which, however, are not our main concern here.

For each compound, our calculated values of the lattice constant, a_0, are within 1–2 % of the reported experimental value, which is the accuracy normally achieved within the LDA. For AlN, the agreement between the calculated and experimental values of a_0 is slightly worse than for GaN and InN. It has been reported in Ref. 21 that the use of a generalized-gradient approximation (GGA) in dealing with the exchange-correlation energy functional, instead of the LDA adopted in the present work, slightly improves these results for AlN; however, the use of a GGA does not result in any clear improvement in the cases of GaN and InN.

It is interesting to compare the results for GaN and InN obtained by treating the d electrons of the cation explicitly in the valence with those results obtained when the d electrons are assumed inert and included in the core. This comparison is also shown in Table I. For both compounds, the agreement with the available experimental data is better when the d electrons are included in the valence and allowed to relax. In particular, the calculated value of the lattice constant increases, which brings the calculated value closer to the experimental one. The bulk modulus at zero pressure is similarly reduced. The effect of the relaxation of the d electrons on the structural properties at zero pressure of GaN and InN has been considered before,[19,20] and our present results concerning the degree of improvement (compared with experimental values) by dealing with the d electrons explicitly among the valence electrons is similar to what has been found in previous studies. (A similar comparison concerning the energetics of different structural phases will be addressed in Sec. III D.)

B. The wurtzite phase at high pressure: Local stability, internal parameters, and isostructural transition

When the internal parameter u of the wurtzite structure takes the value $\frac{1}{2}$, the symmetry changes to space group $P\bar{6}m2$. Associated with this fact, the energy as a function of the internal parameter u has an extremal point at $u=\frac{1}{2}$. This configuration is best viewed as built up of graphitelike planes stacked in the (001) direction (each plane resulting from the coalescence of two hexagonal planes occupied by one of the two different atomic species, and where every atom in the graphitelike planes is surrounded by three unlike atoms). These planes are stacked one on top of the other in such a
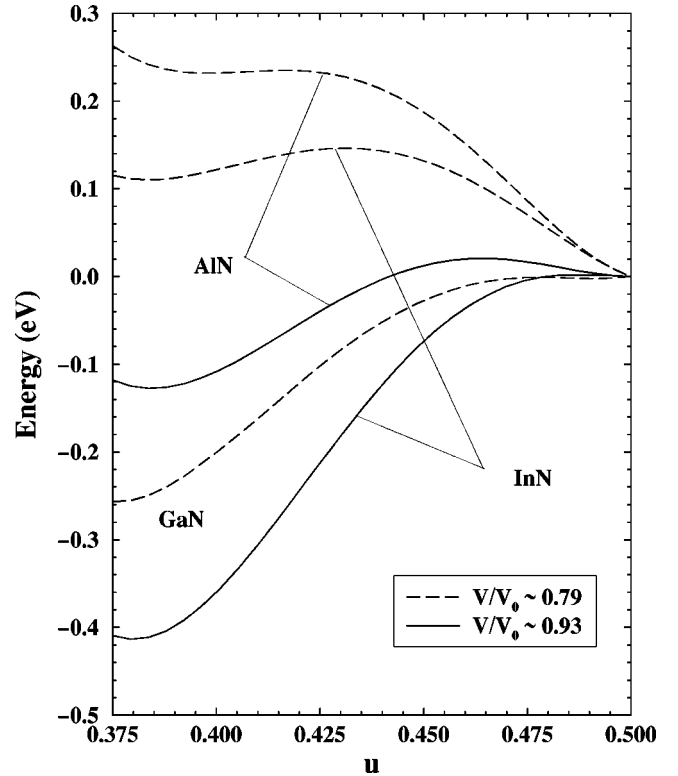

FIG. 1. The calculated energy of the wurtzite structure as a function of the internal parameter u at several different volumes; V_0 stands for the calculated wur zero-pressure volume (see Table I). At each volume the energy is given with respect to that for the configuration with $u=0.5$, which corresponds to a local minimum of the E-u curve.

way that the two atomic species alternate along a given atomic row in the c direction. The calculated optimal value of the axial ratio for this structure, which we will refer to as *hexagonal* (hex), is $c/a \approx 1.23$, which yields an irregular 3 +2 coordination. Interestingly, this structural configuration can be observed experimentally in BN, where it is stable at temperatures of ~1200–1800 K. The standard wurtzite structure has also been observed in this material, as well as the zinc-blende structure, which is thermodynamically stable under normal conditions.

In Fig. 1, we show the energy of the wurtzite phase (relative to the $u=0.5$ configuration) as a function of u for different volumes. As shown in this figure for AlN (InN), at pressures just above ~75 GPa (~65 GPa), which corresponds to a reduced volume of ~0.79, the configuration with $u\approx\frac{3}{8}$, which is observed at low pressures, becomes unstable with respect to the hexagonal configuration, which has $u=0.5$. In the case of GaN, the $u\approx\frac{3}{8}$ configuration remains stable with respect to any other configuration up to much higher pressures of ~200 GPa. However, at the high pressures at which the wur→hex instability is predicted in AlN and InN, the thermodynamically stable phase is rocksalt, and only if the wurtzite phase could exist as a metastable phase well above its calculated coexistence pressure with the rocksalt phase would it transform to this hexagonal structure. This is, however, not supported by the available experimental findings, which report the completion of the wur→NaCl transformation (see Sec. III C) and the extinction of the wur
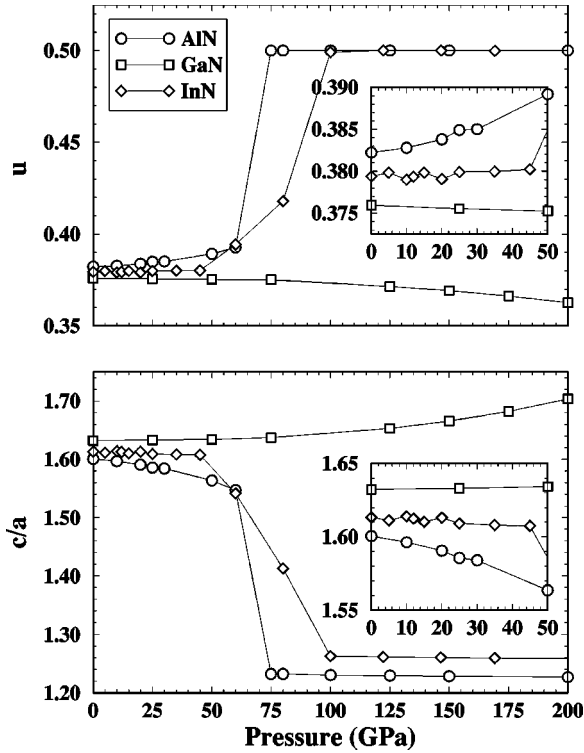
FIG. 2. Evolution of the u and c/a parameters of the wurtzite phase with pressure, for AlN (circles), GaN (squares), and InN (diamonds), with $u_0 = 0.375$.

phase in the range 20-30 GPa in AlN (Refs. 47 and 48) ($\sim$14 GPa in InN, Ref. 51). Regardless of this being the case in practice, the above pressures represent an upper bound to the local stability of the wurtzite phase in these compounds.

In Fig. 2, we show the evolution with pressure of the internal parameters of the wurtzite structure, obtained upon structural relaxation as explained in Sec. II B. The instability of the low-pressure configuration of the wur structure shows up in the discontinuities apparent in both the u-p and the c/a-p curves. We also note the distinct nonlinear behavior of these curves immediately before the onset of the observed wur→NaCl transition (see Sec. III C) obtained by Bellaiche *et al.* for InN (Ref. 59). These authors relate such pretransitional effects in the evolution of u and c/a with p to an isostructural transition, and our calculations show that it is indeed connected to the existence of an equilibrium configuration with $u = 0.5$ and to the transition between the low-pressure configuration ($u \sim \frac{3}{8}$) and this high-pressure configuration.

C. Energetics and phase diagrams: The wur→NaCl transition

The energy-volume (E-V) curves corresponding to the different structures considered in the present work for the three compounds AlN, GaN, and InN are shown in Figs. 3, 4, and 5, respectively. The enthalpy-pressure (H-p) curves are similarly shown in Figs. 6, 7, and 8. The important case of the energetics of the *Cmcm* structure is not shown in these curves: it will be discussed independently in Sec. III F.

As it is seen in these figures, we obtain a very simple structural phase diagram for the three compounds considered here. At low pressures, the thermodynamically stable phase
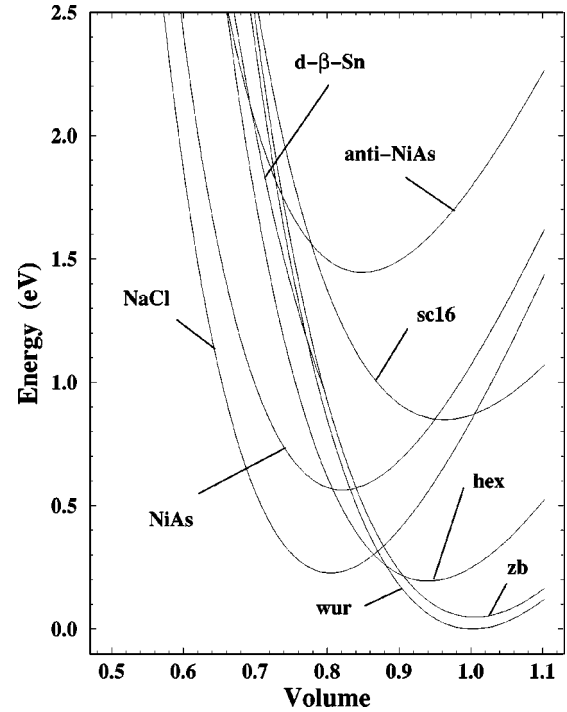

FIG. 3. Energy-volume curves for different structural phases of AlN. The volume is given normalized to the theoretical zero-pressure volume (or equilibrium volume) of the wurtzite phase, $V_{0,\text{wur}}^{\text{the}} = 9.934$ Å^3 pfu.

has the wurtzite structure, while above a certain coexistence pressure the rocksalt structure becomes favored over wurtzite. This is in perfect agreement with the experimental observations, which to date have only reported a wur→NaCl tran-
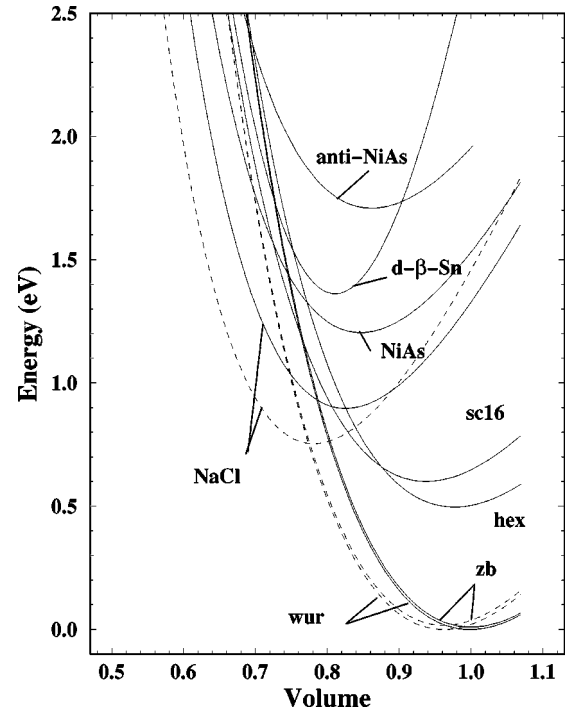

FIG. 4. Energy-volume curves for the different phases of GaN, $V_{0,\text{wur}}^{\text{the}} = 11.359$ Å^3 pfu. For the sake of comparison, the E-V curves for the wur and NaCl phases calculated with frozen $3d$ Ga electrons included in the core are also shown using dashed lines.
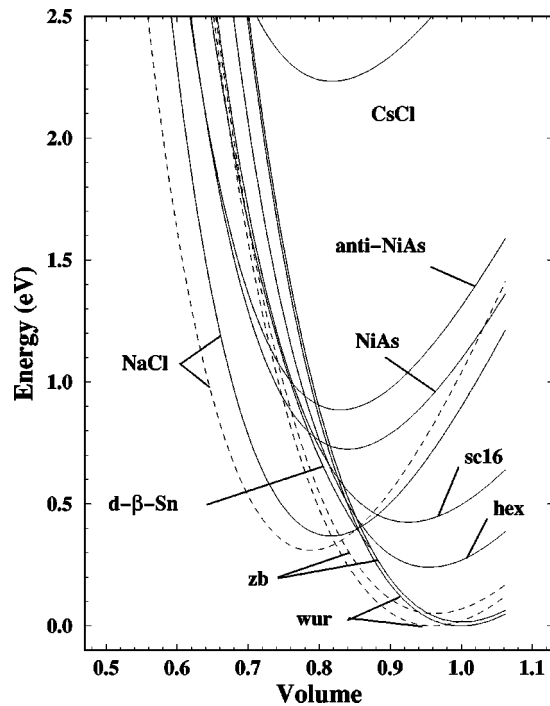
FIG. 5. Energy-volume curves for the different phases of InN, $V_{0,wur}^{the} = 15.296$ Å^3 pfu. Calculated E-V curves for the wur and NaCl phases with frozen In $4d$ electrons included in the core are shown using dashed lines.

sition. All three compounds are difficult to grow and manipulate and this has limited the number of high-pressure structural studies, which are all fairly recent. There is some spread in the values of the reported experimental data concerning this transition, some of which have been collected along with our calculated results for each compound in Table
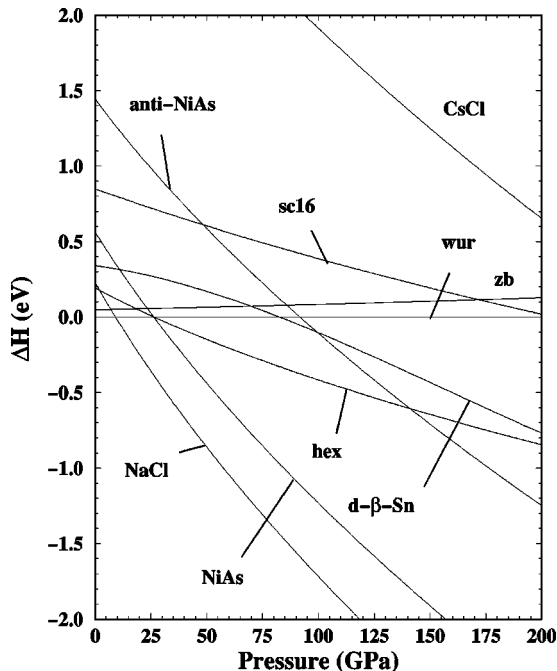

FIG. 6. Enthalpy-pressure curves for the different phases of AlN. At each pressure, the enthalpy is plotted with respect to that of the wurtzite phase at that pressure.
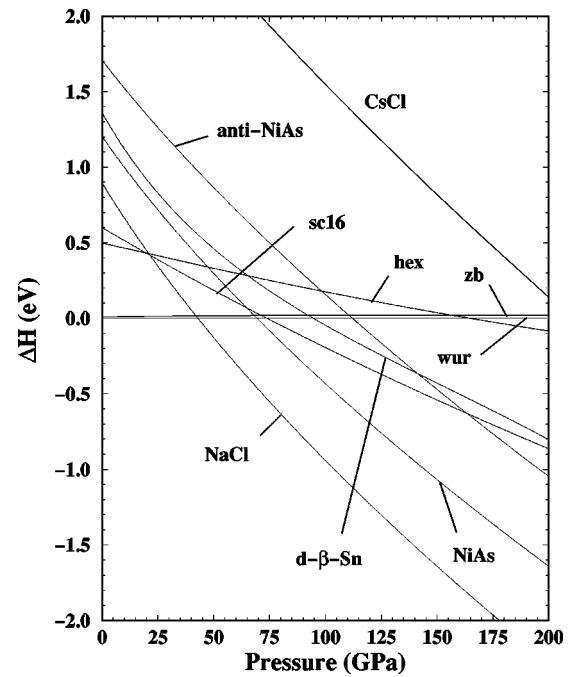

FIG. 7. Enthalpy-pressure curves for the different phases of GaN.

II. In this table, we also show the reduction in volume corresponding to the wur→NaCl transition. For specific details on the experimental values, we refer the reader to the results compiled and compared in Ref. 7 and to the original experimental articles. Some previous theoretical results concerning the theoretical wur-NaCl coexistence pressure are also shown in Table II.

Experimentally, the wur→NaCl transition in AlN has been reported to start at 22.9 GPa by Ueno et al.,[47] at 14 GPa by Xia et al.,[48] and more recently at 20.0 GPa by Uehara et al.[17] Upon releasing pressure from the NaCl phase, this
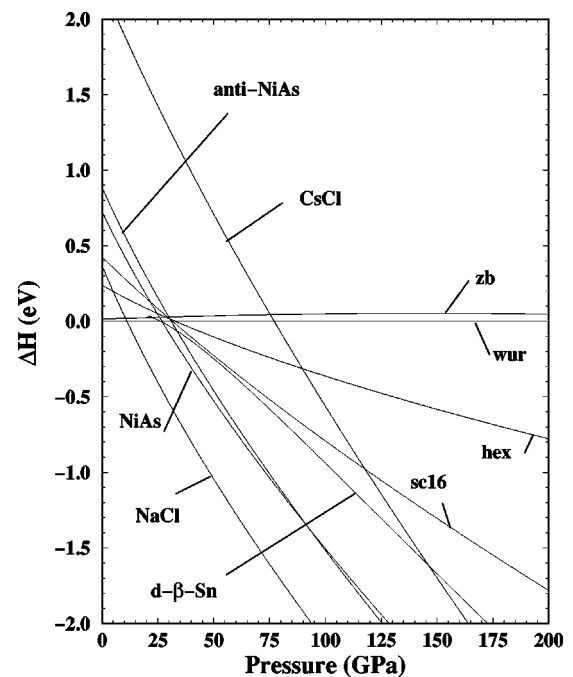

FIG. 8. Enthalpy-pressure curves for the different phases of InN.

TABLE II. Calculated coexistence pressure and transition volumes for wur→NaCl and zb→NaCl in AlN, GaN, and InN. Bracketed values were calculated by freezing the semicore d electrons in the core. Experimental values for the wur→NaCl transition are given in parentheses and calculated values from other theoretical studies are given between curly brackets.

	I→II	p_t (GPa)	ΔV_t (%)	V_I^t (Å^3)
AlN	wur→NaCl	**9.2**	**20.1**	**9.542**
	zb→NaCl	**7.1**	**20.4**	**9.652**
		(14–16.6[a], 22.9[b], 14–20[c])	(20.6[a], 17.9[b], 18.6[c])	
		{12.9[d], 16.6[e]}	{22.4[d], 18.3[e]}	
GaN	wur→NaCl	**42.9 [33.7]**	**15.0 [16.5]**	**9.78 [9.724]**
	zb→NaCl	**42.1 [32.8]**	**15.2 [16.6]**	**9.811 [9.757]**
		(47–50[f], 37[g], 52.2[3.0][h])	(15.1[f], 17.0[g], 17.9[h])	
		{51.8[e], 50[i], 35.4–51.9[j], 55[k], 65[l]}	{14.8[e], 13.4[i], 14[j], 17[k], 13[l]}	
InN	wur→NaCl	**11.1 [10.0]**	**17.4 [16.7]**	**14.350 [13.791]**
	zb→NaCl	**10.5 [8.2]**	**17.6 [17.2]**	**14.429 [13.983]**
		(12.1[2][h], 23.0[m], 10[n])	(17.6[h], 20[2][n])	
		{21.6[e], 4.93[o], 25.4[m]}	{15.3[e], 19.3[o]}	

[a]H. Vollstädt *et al.*, Ref. 46.
[b]M. Ueno *et al.*, Ref. 47.
[c]Q. Xia *et al.*, Ref. 48.
[d]P.E. Van Camp *et al.*, Ref. 26.
[e]N.E. Christensen *et al.*, Ref. 22.
[f]P. Perlin *et al.*, Ref. 49.
[g]H. Xia *et al.*, Ref. 50.
[h]M. Ueno *et al.*, Ref. 51.

[i]A. Muñoz *et al.*, Ref. 23.
[j]R. Pandey *et al.*, Ref. 27.
[k]P.E. Van Camp *et al.*, Ref. 28.
[l]P. Perlin *et al.*, Ref. 49.
[m]P. Perlin *et al.*, Ref. 55.
[n]Q. Xia *et al.*, Ref. 56.
[o]A. Muñoz *et al.*, Ref. 25.

structure persists down to atmospheric pressure.[48] The large hysteresis of the wur→NaCl transition does not permit a precise location of the coexistence pressure between the wur and NaCl phases, but we note that our calculated value of 9.2 GPa is plausibly close to the middle of the hysteresis cycle, ~7–11.5 GPa. The maximum pressure achieved in high-pressure experiments on AlN is 132 GPa (Ref. 17) and up to this pressure the NaCl structure does not undergo any further transitions.

For GaN, the wur→NaCl transition has been reported to occur at 37 GPa by the authors of Ref. 50, while Ueno *et al.*[51] find a NaCl phase above 52.2 GPa and Uehara *et al.*[17] find it above 53.6 GPa. An earlier experimental study[49] locates this transition at 47–50 GPa, and the reverse NaCl →wur transition on decreasing pressure as beginning at 30 GPa, indicating a rather large hysteresis. Our calculated value for the coexistence pressure between the wur and NaCl phases is 42.9 GPa, which is close to the above-quoted experimental values for the onset of the wur→NaCl transition and within the error bar associated with the hysteresis cycle measured by the authors of Ref. 49. The fact that the wur →NaCl coexistence pressure of GaN is much larger than for AlN and InN, on which both theoretical calculations and experiments agree, has been noted and discussed before.[23] The maximum pressure up to which experiments on GaN have been performed is 91 GPa[17] and there is no report of any further transition.

Experimental studies on InN have been reported up to a pressure of 72 GPa (Ref. 17). The experimental values for the onset of the wur→NaCl transition in InN are 12.1 GPa

(Ref. 51), 10 GPa (Ref. 56), and 14.4 GPa (Ref. 17). Our calculated value for the wur–NaCl coexistence pressure of 11.1 GPa agrees with these experimental values. The transition pressure of ~23 GPa obtained from direct observation by Perlin *et al.*[55] is, however, much larger than both our calculated value and other reported experimental values. No other transition has been reported on increasing pressure from the NaCl phase.

D. Effect of the semicore d electrons on the energetics of the phases

We have studied the effect of the semicore d electrons of GaN and InN on the relative stability of the phases by calculating E-V curves for the different structures while keeping these electrons frozen within the core as explained in Sec. II. These E-V curves are represented by means of dashed lines in Figs. 4 and 5, where only the relevant cases of the wur, zb, and NaCl structures are actually depicted for the sake of clarity.

As seen in Figs. 4 and 5, the main effect of *freezing* the d electrons is to shift the E-V curve corresponding to the rocksalt structure downwards in energy with respect to that for the wurtzite structure, which decreases the wur→NaCl transition pressure from 42.9 GPa to 33.7 GPa in the case of GaN and from 11.1 GPa to 10.0 GPa in the case of InN (see Table II). Once the effect of the core-valence overlap on the nonlinear exchange-correlation energy is properly taken into account in the case of frozen d electrons (NLCC, see Sec. II A), the main remaining effect of this freezing on the E-V

curves is due to the closed-shell repulsion arising from the overlap between core states (or core and valence states) in neighboring sites, as has been demonstrated by Fiorentini *et al.*[19] Neglecting this effect by including the d electrons in the core results in a reduction of the total energy. This reduction is stronger in the case of the rocksalt structure than in the case of the wurtzite structure on account of the larger coordination of the former structure. This accounts for the downward relative shift in energy of the E-V curve of the rocksalt structure with respect to that of the wur structure and the corresponding decrease in the coexistence pressure[61] when freezing the d electrons. (There is also a shift of the E-V curves downwards in volume, which is larger for the NaCl structure, and results in a reduction of the transition volumes when the d electrons are frozen.) This effect of the semicore d electrons is larger in GaN, where the resonance between the $3d$ orbitals of gallium and the $2s$ orbitals of nitrogen plays a key role in determining the structural properties of the solid, than in InN.

E. Further comments on the energetics of several structural phases

The important case of the *Cmcm* structure deserves special attention and will be considered separately in the next section.

We find that the $sc16$ structure is not thermodynamically stable in the whole range of pressures investigated and is not expected to be observed in high-pressure experiments. The $sc16$ structure has been experimentally observed in GaAs and has been predicted to occur in other III-V compounds on the basis of total-energy calculations similar to those presented here,[11,12] which find it either more stable than the rest of the structures considered or close enough to being stable in some range of high pressures to justify its possible formation as a metastable phase. However, the calculated coexistence pressure between the wurtzite (or zinc-blende) structure and the $sc16$ structure in the compounds studied here (e.g., 74 GPa in the case of GaN) is far beyond the limit of thermodynamical stability of the wurtzite phase (which in the case of GaN becomes less stable than the NaCl phase at a pressure of 42.9 GPa as per our calculations), and this structure does not seem to be close to thermodynamical stability at any pressure. For the three compounds considered, the $sc16$ phase has a semiconducting Kohn-Sham band structure, in agreement with previous studies in other III-V compounds.[11,12]

A similar state of affairs holds for the d-β-Sn structure, which is found in the present study not to be a favored phase at any pressure. The nonexistence of the d-β-Sn structure in II-VI and III-V semiconductors in experiments has been asserted by the authors of Ref. 58, who have critically considered all previously reported occurrences of this phase in III-V and II-VI binary compounds.

The case of the NiAs structure is of particular interest as for AlN the authors of Ref. 24 have theoretically predicted a transition from the rocksalt structure to the NiAs structure at a pressure of ~30–35 GPa. We note that all the calculations of Ref. 24 for the NiAs structure were performed at fixed values of the structural parameters, $u=0.25$ and $c/a=1.72$ (obtained upon relaxation at a single volume) and $u=0.25$

and $c/a \sim 1.633$ (ideal). In the present work, we have performed a full relaxation of the NiAs structure at each volume considered and have found that the c/a ratio varies from 1.717 to 1.722 in the relevant pressure range from ~20 GPa to ~50 GPa, which agrees with the results of Christensen *et al.* in Ref. 24 within the error bars of their quoted results. Within this range of pressures, the E-V and H-p curves of the NiAs structure for AlN are above those of the NaCl structure by a value approximately independent of volume of ~0.33 eV pfu (see Figs. 3 and 6). Therefore, we conclude that the NiAs structure *cannot* correspond to a stable high-pressure phase in the case of AlN. This is in agreement with the report of a recent experimental study,[17] which did not find any evidence of a NiAs phase up to the very high pressure of ~132 GPa. The origin of the discrepancy with the results of Christensen *et al.* in Ref. 24 is not clear. The difference in total energy is 6 meV/f.u. at 20 GPa between our fully relaxed calculation and one constrained relaxation, as done in Ref. 24 fixing the c/a ratio. The *ideal* NiAs configuration ($c/a=1.633$) is found to have a rather larger energy than the relaxed configuration ($c/a \approx 1.72$).[60] The anti-NiAs structure, which corresponds to interchanging the positions of the anion and the cation in the two inequivalent types of sites of the NiAs structures, with the anion occupying the simple hexagonal sublattice and the cation the hexagonal closed-packed sublattice,[18] is also unfavorable (1.38 eV larger in energy than the relaxed configuration at a volume $V/V_0=0.7$). Similarly to the case of AlN, the NiAs structure cannot correspond to a thermodynamically stable phase for either GaN or InN (see Figs. 4 and 5).

The CsCl structure, which is favored by strongly ionic compounds, is found not to be stable in the present cases in the whole range of pressures investigated. At zero pressure, the difference in enthalpies between the CsCl structure and the wur (NaCl) structure in, e.g., AlN is 3.56 eV per formula unit (3.32 eV pfu), which is considerably larger than in other III-V compounds [cf. the value of ~1.1 eV pfu in the case of AlAs (Ref. 12)]. We note the metallic character of this highly coordinated structure.

At negative pressures, we find a *cinnabar* structure which, upon relaxation, has internal parameters $u=v=0.5$ and $c/a \approx 2.444$ for AlN ($c/a \approx 2.349$ for GaN and $c/a \approx 2.390$ for InN). At these values of the internal parameters, the symmetry is increased and the resulting configuration is in fact fourfold coordinated (see the comments in Sec. I and Ref. 15). However, as pressure is increased, this configuration rapidly becomes unstable. This behavior is in line with previous studies of GaAs and other III-V compounds.[15] In the present cases, however, this particular configuration of the cinnabar structure is not thermodynamically stable or close to stability in any range of pressures of interest (see Fig. 10, where we show the variation of the energy corresponding to a path in the space of internal parameters u and v which links this configuration to the rocksalt structure). We have further checked that the NaCl phase is stable against a cinnabar-like distortion at all positive pressures considered. It is thus unlikely that any cinnabar phase could be formed as a metastable phase upon decrease of pressure from the high-pressure rocksalt phase.[62]
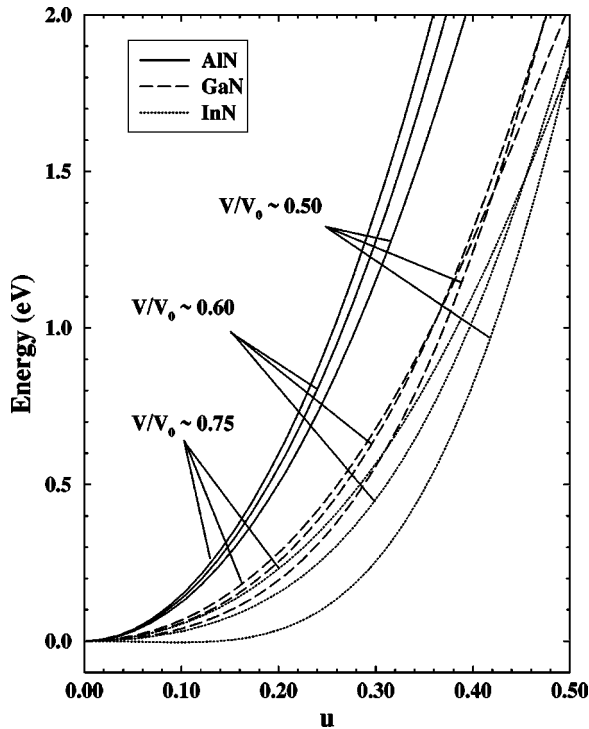
FIG. 9. Variation in the total energy when a shearing of alternate (100) planes in the [001] direction by a magnitude u (see text) is imposed on the NaCl phase, for different fixed volumes (given in units of the zero-pressure volume of the rocksalt phase). The energy is given in units of eV pfu and, at each volume, is measured with respect to the total energy of the rocksalt structure ($u=0$) at such volume. The magnitude of the shearing is given in units of the lattice constant a (see Refs. 12 and 13).

F. Local stability of the rocksalt phase

The kind of distortion of the NaCl phase leading to the structure known as *Cmcm* can be understood in terms of (a) a shearing of alternate (100) NaCl planes in the [001] direction, (b) a *puckering* of the [010] atomic rows of NaCl in the [001] direction, and (c) an orthorhombic adjustment of the axis.[12,13] This distortion has been recently found to occur in several III-V and II-VI compounds[7–10,12,13,16,58] and thus we have assessed its occurrence in the compounds considered here. Such a pattern of atomic displacements as appears in *Cmcm* (which in turn induces the orthorhombic deformation of the cell) corresponds in fact to a transverse-acoustic phonon of the NaCl structure at the X point, and the observed instability of the NaCl phase against a *Cmcm*-like distortion in the majority of the III-V and II-VI compounds can thus be related to this $TA(X)$ phonon softening, eventually becoming zero as pressure is increased. Ozoliņš and Zunger[63] have subsequently confirmed this result by calculating the full phonon spectrum of the NaCl phase in several III-V compounds: in their calculations, they obtain a negative $TA(X)$ mode Grüneisen parameter which eventually causes the instability of the structure. (These authors did not explicitly consider the compounds studied here.)

We have investigated the minimum-enthalpy configuration for a hypothetical phase with the *Cmcm* structure by using the relaxation procedure outlined in Sec. II B. *Cmcm* has two internal parameters, related to the shearing of planes and the puckering of atomic rows, and three different lattice
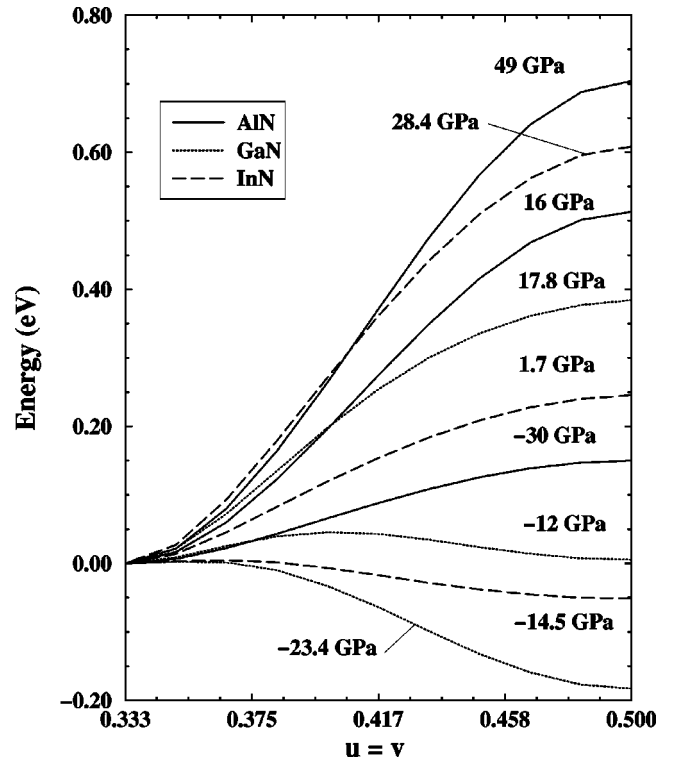

FIG. 10. Stability of the NaCl structure against a cinnabar-like distortion. The case $u=v=\frac{1}{3}$ corresponds to the NaCl structure.

constants.[13] The starting point of the minimization consisted of a distorted configuration, with nonzero shearing, puckering, and orthorhombic distortion: at all pressures investigated and for each different starting configuration considered, the relaxation procedure found only one minimum corresponding to the undistorted rocksalt structure, that is, zero shearing and puckering and all three lattice constants equal. We thus conclude that for the three compounds considered here, the orthorhombic *Cmcm* structure is *not* a favorable distortion of the high-pressure rocksalt phase, even at very large compressions of $V/V_0\sim0.60$ ($p>300$ GPa). This is unlike the rest of the III-V compounds and the II-VI compounds, for which the NaCl structure becomes unstable against a *Cmcm*-like distortion at only moderately high pressures.[12,13,16]

The variation of the energy with respect to the shearing u of the alternate (100) planes of the NaCl structure is shown in Fig. 9 for several different volumes. As can be seen in this figure, the rocksalt configuration (corresponding to $u=0$) is the stable configuration at all compressions considered in the case of AlN and GaN. There is, however, a slight decrease in the slope of the E-u curves as the compression is increased, which would eventually lead to an instability of the NaCl structure. By extrapolation, this is expected to occur at extremely high pressures well above 300 GPa, which we have not explicitly studied and which are currently difficult to achieve experimentally. The E-u curves for InN show an incipient instability at $V/V_0\sim0.50$, which for this compound corresponds to a pressure above ~700 GPa. We can therefore conclude that, although there is a certain softening of the $TA(X)$ phonon as pressure is increased, the instability of this mode does not occur within the range of pressures of interest investigated in the case of the compounds considered in this study.
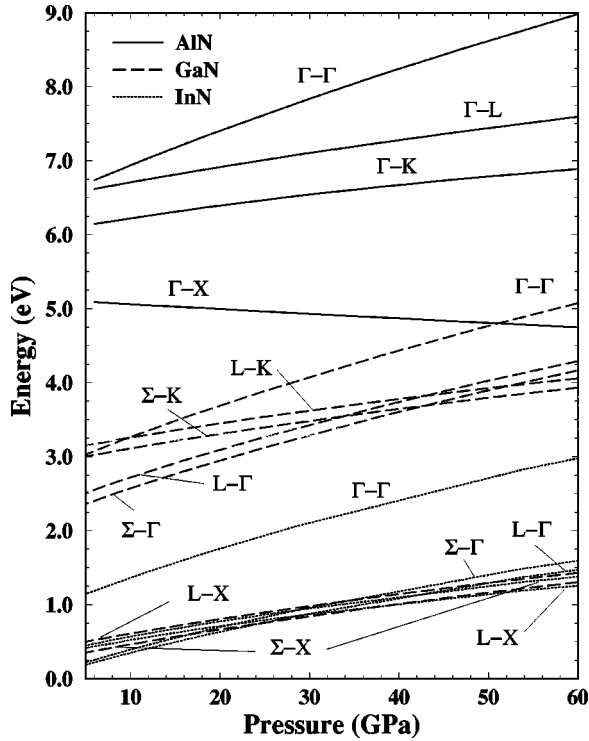
FIG. 11. Calculated evolution with pressure of the lowest-energy gaps of the NaCl phases of AlN, GaN, and InN. The lowest gap occurs between Γ-X, Σ-X, and L-Γ, for AlN (solid lines), GaN (dashed lines), and InN (dotted lines), respectively.

The stability of the NaCl phase with respect to a *Cmcm*-like distortion is related to the large ionicity of the group-III nitrides [0.794 (AlN), 0.780 (GaN), and 0.853 (InN) in the ionicity scale of Ref. 64; cf. the much smaller values for GaAs (0.316) or ZnSe (0.597), for which the *Cmcm* phase has experimentally been observed[7]]. It is expected that the instability of the shearing distortion of the NaCl structure decreases as the ionicity of the material is increased; in particular, a larger compression is required to produce an unstable mode on account of the larger Madelung energy, which has a positive contribution to the Grüneisen parameter.[63] Our results for the group-III nitrides support this picture.

G. Energy gaps of the rocksalt phases

For all three compounds studied here, the calculated Kohn-Sham band structure of the high-pressure rocksalt phase is semiconducting in the whole range of pressures investigated, with an indirect fundamental energy gap. This is shown in Fig. 11, where the pressure evolution of the lowest energy gaps is depicted.

It is well known that, although often taken as a starting point in quasiparticle calculations, the Kohn-Sham LDA band structure does not correspond exactly to the true quasiparticle spectrum of the solid. In particular, the band gap turns out to be underestimated. However, the results of a large body of calculations indicate that the pressure variation of the energy gaps obtained within the DFT-LDA are close to the experimental values. A precise description of the electronic and optical properties of these compounds requires a better treatment of many-body effects not properly ac-

counted for within the DFT-LDA. This can be done, for example, by calculating the quasiparticle spectrum using the so-called *GW* approximation, which yields electronic band gaps and excitation energies in much better agreement with experiment.[4,5] The study of the optical properties of these compounds at high pressures is beyond the scope of the present work and has not been undertaken here.

IV. SUMMARY AND CONCLUSIONS

We have presented a detailed study of the relative stability of several candidate structural phases of the group-III nitrides AlN, GaN, and InN which have been either observed experimentally as stable phases or proposed as likely candidates on account of their observation in other related III-V and II-VI compounds. This study complements the picture of the behavior of the technologically important group-III nitrides under pressure.

The materials considered in this work turn out to present a very simple phase diagram with only two stable phases: wurtzite at low and moderately high pressures and then rocksalt up to the highest pressure considered in this work of ~200 GPa. In addition, the zinc-blende structure has also been observed experimentally as a metastable phase at normal conditions and in the present study is found to be less stable than the wurtzite phase although lying very close to it in enthalpy. Our results also show that the NiAs phase is not thermodynamically stable within the whole range of pressures investigated, contrary to a previous theoretical study in AlN, which predicted it to be more stable than the rocksalt phase at pressures above ~30 GPa (Ref. 24), but in agreement with the present body of experimental evidence for this compound. From our results, the formation of such structural phases as *Cmcm*, cinnabar, or *sc*16 is not to be expected in these compounds.

The effect of the semicore (cation) *d* orbitals of GaN and InN on the phase diagram has been analyzed. In the case of GaN, these electrons play an important role in determining both its zero-pressure properties and its structural response under compression. Their effect in the case of InN is slightly smaller. We have also studied the local stability of the high-pressure rocksalt phase against *Cmcm*-like and cinnabar-like distortions, and that of the wurtzite structure against an isostructural wur→hex transition.

An important feature of the group-III nitrides is the absence of *p* electrons in the core of the nitrogen atoms. As a consequence, the *p* component of the N pseudopotential is rather deep, which favors the transfer of charge towards the nitrogen atoms and results in a larger ionicity than in the rest of the III-V compounds. This large ionicity is in particular responsible for the local dynamical stability of the high-pressure rocksalt phase in the group-III nitrides investigated.

It is commonly assumed that above a critical pressure most III-V semiconductors exhibit metallic behavior, which is connected with a structural transformation from the ground-state or zero-pressure phase to a phase having a more closely packed structure. This is not the case with the group-III nitrides within the range of pressures investigated, which also show a remarkably simple high-pressure phase diagram. It is arguable that once in a compressed metallic phase, energetic barriers between this phase and other metallic structural phases become less pronounced than in the case of a semiconducting structure, which would favor the formation

of different, more or less complex, structures. The absence of any accessible metallic structure within the interval of pressures so far investigated in the case of the nitrides is thus related to their simple structural-phase diagram in this range of pressures.

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*Present address: Max Planck Institute–FKF, Heisenbergstrasse 1, Stuttgart D-70569, Germany.

†Corresponding author. Email address: jserrano@kmr.mpi-stuttgart.mpg.de

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that of the all-electron wave function at a certain fixed radius in a range of energies around the eigenvalue of the reference configuration was also performed. The results of all these tests indicated excellent transferability of the pseudopotentials, which appears to be similar to that recently reported in the detailed study of the zero-pressure structural properties of these compounds given in Ref. 21.

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[60] As in the case of the wurtzite structure, this *ideal* configuration, which corresponds to a regular coordination with all nearest-neighbor distances equal, is not to be thought of as favored by any symmetry considerations. It does not in fact correspond to an equilibrium configuration.

[61] A further effect comes from the (small) relaxation of the *d* electrons, which reduces the total energy on account of the variational nature of the Kohn-Sham formalism. On its own, such relaxation (which is stronger in the case of the rocksalt structure than in the case of the wur structure) would lead, when freezing the *d* electrons, to an increase in energy of the relative positions of the *E-V* curve of the NaCl structure with respect to that of the wur structure, resulting in a slight increase of the coexistence pressure. This is, however, a very small effect (see Ref. 21).

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