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Isostructural phase transition in InN wurtzite

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Using the first-principles total-energy pseudopotential method, we study the behavior of wurtzite InN under hydrostatic pressure by relaxing all the structural parameters at all volumes considered. Our calculations point to the existence of a second order isostructural phase transition which occurs in the same pressure range as the wurtzite-NaCl first order phase transformation, and which completely changes the behavior of the structural parameters at higher pressures. We propose that this phase transition, which still awaits experimental observation, is induced by second-neighbor interactions between indium atoms and can be considered as a pretransitional effect inducing the reconstructive first order transition. [S0163-1829(96)01037-5]

In the past few years, the group III nitrides have been potential candidates for semiconductor devices, such as short wavelength emitters and detectors, and for high temperature electronics. However, only recently has the control of the material quality improved sufficiently to allow development of p-n junction devices.[1] In addition, many of their fundamental structural properties are still either not well established[2] or not interpreted, such as, e.g., the recent experimental evidence[3] that the axial ratio c/a of wurtzite InN rapidly decreases with increasing hydrostatic pressure, in contrast to the c/a of wurtzite GaN, which remains practically unchanged under pressure. The aim of the present paper, which is entirely focused on InN wurtzite, is to verify to which extent the behavior of the measured axial ratio corresponds to energy minima at $T=0$ K and to try to explain this somewhat unexpected behavior. For this purpose, we theoretically determine the $E(V)$ equation of state of the wurtzite modification, which has *all* its structural parameters, i.e., the axial ratio c/a and the internal parameter u, relaxed at *all* volumes V, in contrast to our previous paper,[4] where the structural parameters have been optimized at only *one* value of the lattice constant a and then kept constant, independent of the volume (at $c/a=1.6375$ and $u=0.3767$). We perform these calculations for the values of V corresponding to the pressures investigated in the experiments, and also above the pressure domain reached in Ref. 3. These calculations also reveal the evolution of the u parameter with pressure in InN wurtzite, which, so far, has been neither measured nor calculated at any pressure.[5]

Here we use the density-functional theory, in the local density approximation (LDA) (Ref. 6) and within the plane-wave pseudopotential scheme in momentum space,[7] for fixed ionic configurations, under very much the same conditions as in the previous paper:[4] we employ the norm-conserving pseudopotentials of Ref. 8, the Ceperley-Alder exchange and correlation[9] as parametrized by Perdew and Zunger.[10] The **k**-space summation is performed (with semiconductor sampling) using seven ''special points'' which, in the Monkhorst-Pack notation,[11] correspond to $(q_1, q_2, q_3) = (4,4,2)$. The nonlinearity of the exchange-correlation potential with respect to the core charge[12] is *not* taken into account and the indium $4d$ electrons are treated as core electrons, since the parallel calculations performed in Ref. 4 within an all-electron approach (FP-LMTO, or full potential linear muffin-tin orbital) suggested that there is no need for these corrections.

As a first step, we calculate the total energy for eight different volumes V of the unit cell ranging from 48 to 68 Å^3, with a kinetic energy cutoff of 40 Ry, and varying, for each volume, c/a and u until the Helmann-Feynman forces are smaller than 0.002 mdyn.

As a second step, we perform the self-consistent calculations for the eight structures just optimized above, by increasing the cutoff to 70 Ry. It turns out that these calculations (i) quite considerably decrease the equilibrium volume, by approximately 2.5%, but (ii) lead to an upper limit of the Hellmann-Feynman forces which remains very small: merely 0.005 mdyn. The former observation implies that a high cutoff is necessary to obtain an accurate $p(V)$ equation of state, whereas the latter suggests that the structural c/a and u parameters can be safely optimized already at 40 Ry. This will be instrumental in the third and last step of our calculations: once the correspondence between the volume and the pressure is known, as determined by the calculations with a 70 Ry cutoff, we perform one more series of calculations, with a kinetic energy cutoff of 40 Ry, to determine more accurately the structural parameters for nine volumes corresponding to pressures ranging from zero (equilibrium) to approximately 31 GPa; the experiments themselves were limited to about 15 GPa. For each of these nine volumes, we impose two rather severe requirements: first, the ratio c/a is optimized until its *absolute* uncertainty is smaller than $\pm 5\times10^{-4}$, and secondly the u parameter is varied until the Helmann-Feynman forces are smaller than 2×10^{-6} dyn.

The optimized calculated structural parameters at equilibrium are given in Table I. These results are compared with experiment[3,13,14] and with three other calculations,[15,2,16] which also allowed for relaxation of the structural parameters. In Ref. 15 the indium $4d$ electrons are frozen and treated as core electrons but the nonlinear core correction[12] is included. The other two works[2,16] treat the $4d$ as valence states.

Comparison with experiment should be done with caution: no reliable and precise experimental data exist on the lattice parameter of InN at ambient conditions since no x-ray diffraction has been performed on single crystals with controlled stoichiometry and purity (see legend of Table I). Nevertheless, if we assume the published experimental data to be representative of the actual values for bulk InN, our value for a is 1.7% smaller than the smallest experimental value, whereas the explicit inclusion of the $4d$ electrons, in the latest published work,[2] does not bring any significant improvement of the overall agreement with the experimental values of a and c. Whatever the effect of the $4d$ states may be, as long as the *variation* with pressure of the (relative) structural parameters is concerned $(a/a_0, c/c_0, \ldots)$, including the $4d$ electrons into the frozen core should cause *at most* 2nd order effects at pressures of the order of $\approx$10 GPa, as shown in Fig. 1. The origin of this ''insensitivity'' is most likely to be found in the considerable depth of the indium $4d$ level (-20 eV), so that the states are not much affected by pressures in the range of 10 to 20 GPa.

TABLE I. Measured and calculated structural parameters for the ground state of InN wurtzite.

	V(Å^3)	c(Å)	a(Å)	c/a	u
This work	59.76	5.715	3.475	1.6445	0.3749
Experiment[a]	62.20	5.718	3.544	1.613	
Experiment[b]	62.06	5.703	3.545	1.609	
Experiment[c]	61.77	5.705	3.536	1.613	
Theoretical[d]	61.82	5.709	3.536	1.615	0.380
Theoretical[e]	60.18	5.669	3.501	1.619	0.3784
Theoretical[f]	61.61	5.732	3.523	1.627	0.3770

[a] Reference 13: X-ray diffraction on sputtered InN films.

[b] Reference 14: X-ray diffraction on CVD films deposited from NCl$_3$.

[c] Reference 3: (Taken from Fig. 5 of this reference), data from industrial-grade material with oxygen impurities and unknown stoichiometry.

[d] Reference 15.

[e] Reference 2.

[f] Reference 16.

In Fig. 1, the vertical bars locate the region of phase coexistence, on the upstroke (Ref. 3): at 12 GPa, the wurtzite lattice is unstable since it starts transforming to the NaCl structure, and at 15.5 GPa, the transformation is completed. Up to that pressure, where the wurtzite phase can be observed, our calculated values of a/a_0 and c/c_0 are within 10^{-3} of experiment, and the equation of state, $V(p)/V_0$ is reproduced within 3×10^{-3}, which anyway is the precision of the x-ray diffraction method which was used in the experiments.[3] The pressure dependence of the c/a ratio is equally well accounted for, with a precision of 2×10^{-3}, including its remarkable nonlinear behavior between 10 and 15.5 GPa, which comes from a decrease in this region of the pressure coefficient of the a parameter and an increase of the coefficient of the c parameter. The latter is indicative of a second order pretransitional behavior.[17] Experiments done at 300 K cannot yield information on the behavior of wurtzite InN above 15.5 GPa, since it has totally transformed, but calculations can. Above that pressure, both a and c resume the expected pressure dependence for a stable structure and thus, so does c/a. The discontinuity in the *slope* of the parameters locates the second order phase transition line in the vicinity of 16 GPa. This is confirmed by the evolution of the internal coordinate u, which has not yet been measured, but which is shown by the present calculations to have also a sharp discontinuity in its pressure coefficient.

In order to ascertain that the change in the structural parameters with pressure is not an artifact of the calculations performed at 40 Ry, and taking account that, as the pressure increases, the number of plane waves decreases, so that it

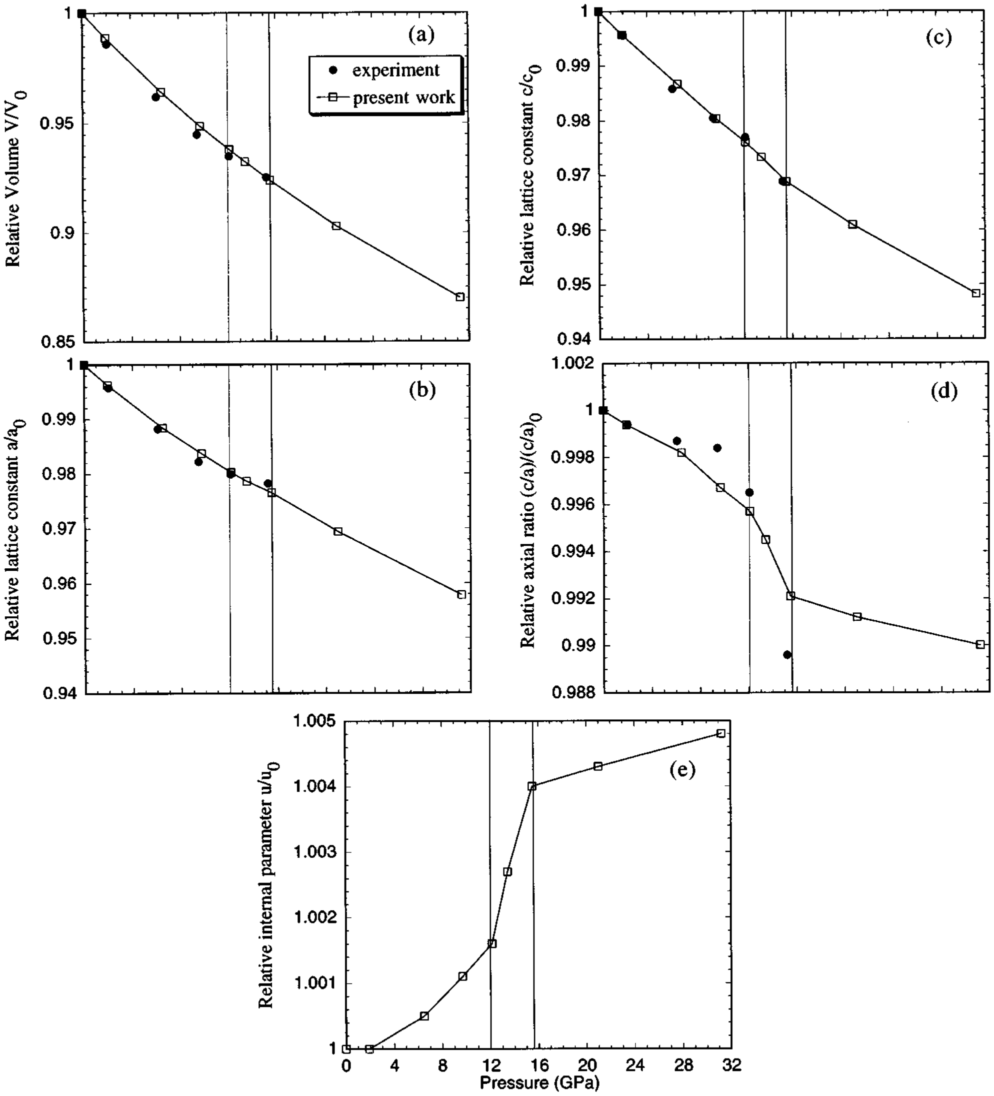

FIG. 1. Relative variation of the structural parameters of wurtzite InN with pressure: (a) volume V, (b) a axis, (c) c axis, (d) axial ratio c/a, and (e) internal parameter u. V_0, a_0, c_0, $(c/a)_0$, and u_0 stand for the equilibrium structural parameters . The solid line, and empty squares are our present calculations whereas the solid black circles are the experimental data (Ref. 3). The two vertical lines delimit the region extending from 12 to 15.5 GPa.

might become insufficient for giving accurate structural parameters at high pressures, we have also calculated the total energy as a function of c/a and u for the volume corresponding to one of the higher pressure (viz. 20 GPa) by using a kinetic energy cutoff of 70 Ry. These calculations correspond to 3000 plane waves and lead to exactly the same structural parameters as those performed with a kinetic energy cutoff of 40 Ry, which indicates, once again, that the structural parameters can be safely optimized at 40 Ry only, and which confirms the results shown in Fig. 1. Anyhow, the fact that our calculations do indeed reproduce the pressure behavior of the observed structural parameters below 15.5 GPa, validates their accuracy in the higher pressure region where experimental data are not available. The transition around 16 GPa is isostructural between two wurtzite networks and clearly is second order since it occurs without any discontinuity in the lattice parameters.[17] This point could not have been ascertained from the experimental data[3] alone which are not numerous enough [Fig. 1(d)] to exclude the existence of a discontinuity in the *slope* on the lattice parameters, or on the axial ratio between 12 and 15.5 GPa. Such a discontinuity in the slope, might, in addition, have been smeared out by sluggish kinetics in the transition process in the experiments. By contrast with experimental results, the calculations suffer neither from hysteresis, nor from slow kinetics and prove this transition to be second order.

Turning now to the first order wurtzite-NaCl phase transition which occurs in the same pressure range, we note that, in III–V or II–VI semiconductors, second order processes may, on occasion, be associated with the first order phase transition between the low pressure blende or wurtzite structure with fourfold coordination to the high pressure structures with higher coordination number, sixfold as a rule. In that case, this association could involve shear instabilities in the [001] or [110] directions. A good example is the mercury chalcogenides[18] HgSe and HgTe where the first order transition from the zinc-blende structure to cinnabar is preceded by a strongly nonlinear behavior of the elastic constants, leading to their decrease under pressure just prior to the transition. In that case, the [110] displacement which is associated with the second order process has the adequate symmetry to induce the zinc-blende-cinnabar transition which follows from it.

In the present case, the nonlinear behavior occurs wholly in the pressure region (10 to 16 GPa) where the wurtzite lattice is known to be thermodynamically unstable against the NaCl structure, and the decrease of c/a and the increase of u, indicate that the In and N sublattices slide relative to each other until they reach a stable position around 16 GPa. We suggest that the isostructural phase transition occurring in wurtzite InN thus might be considered as a pretransitional effect inducing the reconstructive first order transition. Experiments using inelastic scattering of neutrons could confirm this assertion. On the other hand, the fact that the high pressure wurtzite structure becomes stable at $\simeq$16 GPa, i.e., precisely when the wurtzite-NaCl transition has been completed, should be regarded as a coincidence; the actual completion of a reconstructive first order transformation has no simple physical meaning: it is highly dependent on experimental artifacts, pressure inhomogeneity, shear components of stress and others.

The next question to ask is whether one particular interaction drives the isostructural transition occurring in InN. For that, we recall that in the wurtzite structure, the nitrogen atom, N(0), located on the origin has two kinds of indium first neighbors: one In(1), along the c axis, with the $(0,0,u)$ position in units of lattice vectors **a**, **b**, and **c**; the other In(2) with $(2/3,1/3,u-1/2)$ position in the same lattice vectors units. Converting our calculated c/a and u into the angle between N(0)-In(1) and N(0)-In(2) (Fig. 2), a rapid decrease of this angle is observed in the pressure range of 9 to 15.5 GPa. The decrease of this angle allows a possible interaction between the two indium atoms which could drive the isostructural phase transition we have found in InN.

In summary, we have performed *ab initio* calculations in order to study the behavior of wurtzite-InN under hydrostatic pressure. The calculations accurately reproduce the relative variations of all the structural parameters over all the pressures used in the experiments.[3] We find that a new second-order isostructural phase transition occurs in the same pressure range as the wurtzite-NaCl first order transition (viz. 12–15.5 GPa). The isostructural transition makes to decrease (increase) sharply the axial ratio c/a (the internal parameter u). We propose that this second-order isostructural phase (i) could be considered as a pretransitional effect inducing the reconstructive first order transition and (ii) could be driven by the second-neighbor interactions between indium atoms. Such effects are not unexpected and, indeed, have been proposed before,[19] in an attempt to explain the diffraction patterns in Si and InSb just prior to the high-pressure phase transition. But in that case, no direct observation of the expected softening of the lattice was reported. Since then, neither experimental nor theoretical studies brought any direct evidence for this type of behavior. In the present paper, we report direct observation of a lattice instability in InN *prior* to its transition to the high-pressure phase. Such pretransformational effects are perhaps present as well in other structures with fourfold coordination, prior to the first-order transition to the high-pressure sixfold coordinated lattice. Their intensity and the structural parameters they affect may be quite different, depending on the nature of the constituent atoms, as exemplified by the different behavior of GaN and InN (see Ref. 3). But in any case such investigations, which now become possible, should be extended to other members of the II–VI, III–V, and group IV semiconductors, both by experiment and by theory, since they certainly would bring significant clues on the precise mechanisms of this important class of phase transitions.

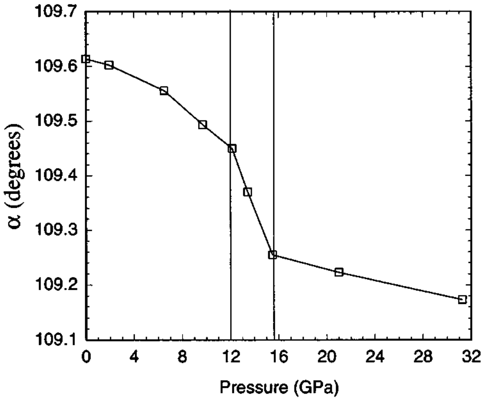

FIG. 2. Variation of the angle α, between N(0)-In(1) and N(0)-In(2) (defined in the text), with pressure. The two vertical lines delimit the region extending from 12 to 15.5 GPa.

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