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Calculated structural phase transitions of aluminum nitride under pressure

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Total-energy calculations within the local-density approximation (LDA) to the density-functional theory are used to study the properties of AlN under pressure. The free energy (at zero temperature) is calculated as a function of pressure for AlN in the wurtzite, zinc-blende, rocksalt, nickel arsenide, anti-NiAs, and β-tin structures. According to the calculations the wurtzite structure is stable from zero pressure (P) up to ≈ 12.5 GPa, where AlN transforms into the rocksalt phase. The volume reduction is 19%. The volume change agrees with recent experiments, but the transition pressure is lower than observed, presumably due to the LDA. It is argued that the transition pressure in reality is close to 17 GPa. Another transformation is predicted at higher pressures, and the calculations suggest that this structure could be similar to that of NiAs, but with $c/a = 1.72$. The transition to the NiAs structure would occur between 30 and 40 GPa, and it is accompanied by a very small volume change. The internal parameters (c/a and u) of the hexagonal phases are optimized by total-energy minimization, and their variation with pressure is derived. At $P = 0$ the internal parameters of wurtzite-AlN are $(c/a, u) = (1.596, 0.3820)$. When P is increased c/a decreases monotonically, and u increases, but the interrelation between u and c/a differs from ideality (defined as the case where all bonds would have the same lengths).

I. INTRODUCTION

Among the III-V compound semiconductors the nitrides have attracted particular interest recently because they are characterized by large band gaps, high thermal conductivity, and large bulk moduli. These properties make the nitrides promising as materials for optoelectronic device applications. Aluminum nitride and gallium nitride have been studied in detail only within the last few years, mainly because it is difficult to obtain single crystals of high quality. A particular high-pressure growth technique,[1-3] however, allows the preparation of crystals with a quality that permits determination of optical properties. Single crystals, as well as powder material, have been used to examine the structural stability under pressure.[2,4-7]

Whereas several publications[2,4,8-11] report theoretical studies of GaN few results have been published for AlN. The pseudopotential calculation by Van Camp *et al.*,[12] predicts, in agreement with experiment and our linear muffin-tin-orbital (LMTO) calculation,[3,11] that AlN under pressure transforms from the wurtzite into the rocksalt structure. "Visual observation" suggested[3] that the transition pressure (P_t) should be in the range 16–17 GPa, and this agrees extremely well with the LMTO result, 16.6 GPa.[3] The pseudopotential calculation yields a lower transition pressure,[12] 12.9 GPa. This may still seem to be in fair agreement with experiment, but a very recent x-ray diffraction measurement[5] yields the hexagonal→cubic transition pressure to be 22.9 GPa. Although the value of P_t obtained in Ref. 6 is 16.5 GPa, this does not necessarily disagree with the experiment of Ref. 5, because the x-ray data were taken at room temperature and the quenching data refers[6] to high temperatures, 1400–1600 °C. As pointed out in Ref. 5, the phase boundary between the wurtzite and the rocksalt phases of AlN could have a negative slope as found for CdS and CdSe.[13-15] But it is stressed in Ref. 5 that indications of the phase transition are observed already at 17.5 GPa. The 22.9-GPa value thus rather represents an upper limit to the value of P_t, and no discrepancy would exist between these experiments and those of Ref. 3. In addition Ref. 5 identifies the new structure as being that of rocksalt, and the lattice dimensions were determined at a specified pressure. This, together with the measurement of the variation of c/a versus pressure in the wurtzite structure, allows a more detailed test of the theoretical calculations. We have therefore decided to perform more detailed calculations of the structural properties of AlN under pressure.

Our first LMTO calculations[3] were performed within the "atomic-spheres approximation"[16] (ASA), but it included the "combined corrections,"[16] and open structures were transformed into close-packed structures by introduction of "empty spheres." This minimizes LMTO-ASA errors, and according to our experience the method should be sufficiently accurate for the type of calculations considered. The wurtzite form of AlN does not assume structural parameters (for definition of u in the wurtzite and NiAs structures, see, for example, Ref. 17) identical to the ideal case, $c/a = \sqrt{8/3}$, and $u = 3/8$. We wish now to optimize these parameters and this requires that a full-potential method is applied. The ASA, which uses spherically symmetric potentials inside the spheres, cannot be expected to have the accuracy needed for calculations of minute total-energy changes associated with small atomic displacements. We therefore apply the full-potential LMTO (FP-LMTO) scheme, and the actual calculations were performed by means of the scheme implemented by Methfessel.[18-20] In cases where comparisons can be made (*s,p* materials) the accuracy of the FP-LMTO is at least as good as that of the pseudopotential method. As follows below, our present calculations agree extremely well with the results obtained by Van Camp *et al.*[12] This concerns the bulk modulus (wurtzite structure), the optimized values of c/a and u, and good agreement with experiment is found. Good agreement is also found for the pressure-volume relation and the volume reduction associated with the structural transition. In view of this it is interesting that we find the same transition pressure, $P_t = 12.5$ GPa, as in Ref. 12. In fact we shall show that the LMTO-ASA calculations agree even better with experiments than the FP-LMTO results as far as transition pressure and pressure-volume relations for the rocksalt and wurtzite phases are concerned.

The wurtzite structure is optimized at all volumes, and we shall show that c/a decreases and u increases with pressure. Among possible high-pressure structure candidates for AlN we consider the rocksalt, β-Sn, NiAs, anti-NiAs, and zinc-blende structures. It will be shown that although wurtzite AlN can transform into the rocksalt structure with application of pressure, this cannot remain to be the stable structure at very high pressures. The calculations suggest that the NiAs structure (with $c/a = 1.72$) has a lower free energy for P above ≈ 30 GPa.

The calculations have been carried out in most detail for the wurtzite structure, and these results are discussed in Sec. II. The results of total-energy calculations for different phases of AlN as well as the pressure-induced structural transformations are described in Sec. III, and summary and conclusions follow in Sec. IV.

II. AlN IN THE WURTZITE STRUCTURE

The total-energy calculations presented are all performed by means of the local (LDA) approximation to the density-functional theory. This means that the one-electron energy values cannot be directly related to spectroscopic measurements. In particular, the band gap as derived from the LDA is too small. Nevertheless, we show in Fig. 1 the calculated LDA band structure for AlN in the wurtzite structure. The calculated gap is 4.52 eV, indeed smaller than measured (6.2 eV).[21] We shall not calculate here the optical absorption spectra of AlN, and therefore no attempts are made to correct for the gap "error."[22] Rather we wish to examine how the gap responds to changes in the values of the structural parameters, c/a and u.

The experimental values of c/a and u are, at zero pressure, 1.601 and 0.3821, respectively.[23] The present total-energy minimization (see below) yields 1.596 and 0.3820, and these values were used in the calculation represented by Fig. 1. The splitting of the states at the valence band maximum (the singly and doubly degenerate $N-p$ levels just below 0 eV at Γ in Fig. 1) depends sensitively on the parameter values. Keeping u fixed (0.375), and reducing c/a from 1.633 to 1.596 alters this splitting by 144 meV, from 122 to 266 meV. The same structural change reduces the conduction band minimum at Γ by 27 meV. The variation of the direct gap (at Γ) of wurtzite AlN at zero pressure with c/a and u is illustrated in Figs. 2 and 3. The dash-dotted lines indicate parameter values corresponding to an "ideal" wurtzite structure. The LDA gap calculated for this structure is 4.73 eV, i.e., 0.21 eV larger than the value obtained after structure optimization. The difference between the gaps in the optimized and ideal structures increases when pressure is applied. At a volume that is reduced to 91.3% of the equilibrium volume the gaps are 5.56 (ideal) and 5.21 eV (optimized), respectively. This affects the deformation potential $\partial E_g/\partial \ln V$. Without optimization it is -9.1 eV, and if the structural parameters are optimized we get -7.6eV, i.e., a change by 20%.

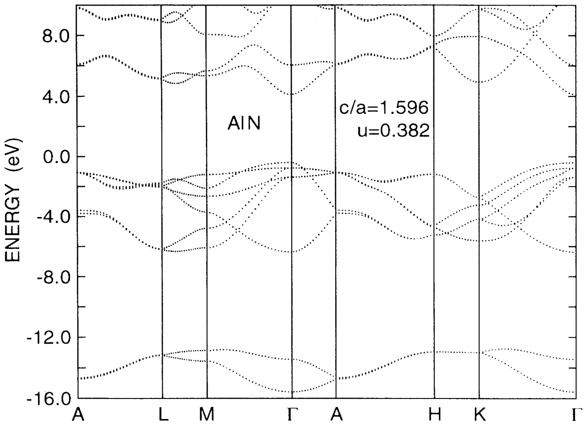

FIG. 1. Band structure (LDA) of wurtzite AlN at the (experimental) equilibrium volume. The values of c/a and u are obtained from total-energy minimization. The gap is direct and the valence-band maximum is at -0.43 eV (at Γ).

The structural optimization of the wurtzite phase of AlN was performed by calculating the total energy as function of the three variables c/a, u, and V/V_0 (V is the volume and V_0 its equilibrium value). Eight volumes were chosen and 120 pairs of $(c/a, u)$, i.e., 120 zero-

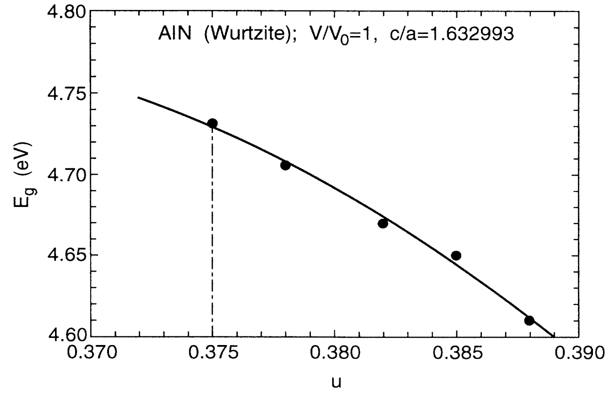

FIG. 2. Calculated variation of the (LDA) gap with u for wurtzite-AlN at fixed volume (experimental equilibrium) and fixed c/a ratio (the ideal, $\sqrt{8/3}$). The dash-dotted line indicates the ideal value of u.

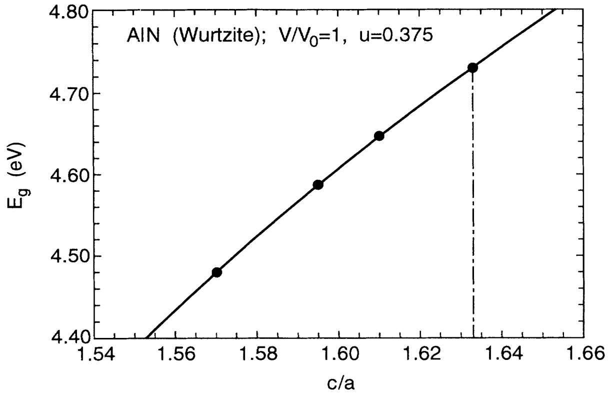

FIG. 3. Calculated variation of the (LDA) gap with c/a for wurtzite-AlN at fixed volume (experimental equilibrium) and fixed u (the ideal, $\frac{3}{8}$). The dash-dotted line indicates the ideal value of c/a.

temperature equations of state were calculated. The two-dimensional minimization of the total energy vs $(c/a,u)$ for a fixed volume requires that each of the self-consistent calculations is extremely well converged. In order to avoid that numerical noise affects the determination of the extremal parameter values it was necessary to ensure a convergence that is better than to 1 μRy. Examples of the optimization are shown in Figs. 4 and 5. Figure 6 shows the axial c/a ratio as a function of volume, and the variation of u is given in Fig. 7. The dashed curve labeled "ideal" in Fig. 7 is calculated from the optimized c/a values but assuming the two bond lengths to be equal:

$$u=\frac{1}{4}[1+\frac{4}{3}(c/a)^{-2}] .$$

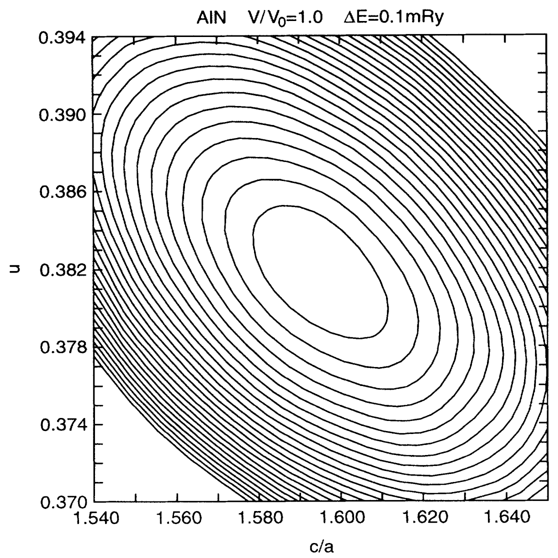

FIG. 4. Wurtzite-AlN at the equilibrium volume: Total-energy contours in the $(c/a,u)$ "plane" near the minimum (1.596, 0.3820). Energy separation between contours: 0.1 mRy.

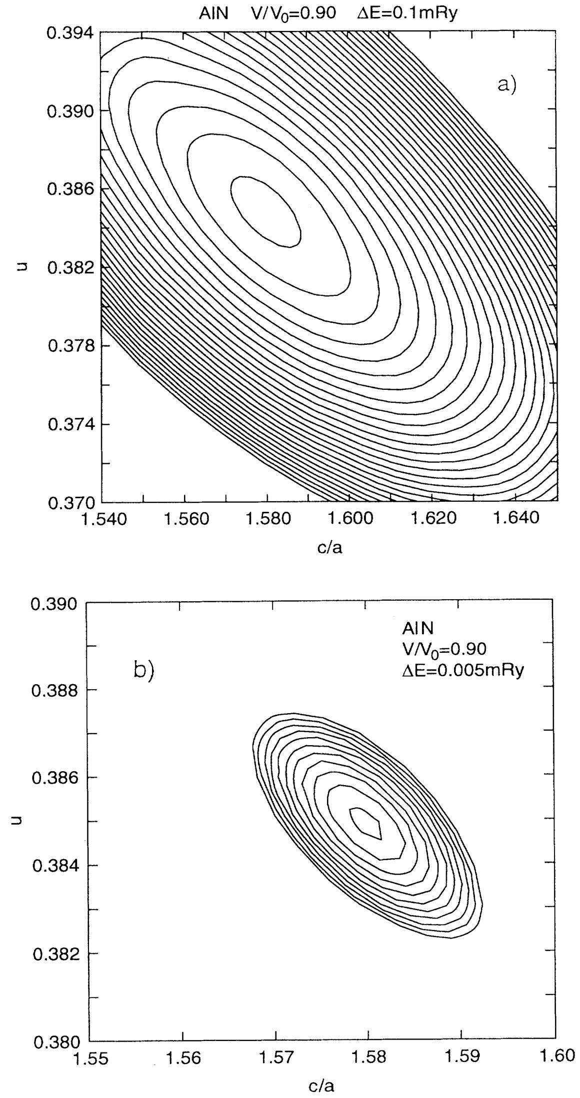

FIG. 5. (a) Similar to Fig. 4, but for a reduced volume $(0.90V_0)$. (b) The regime close to the minimum (at $c/a,u=1.578$, 0.3848), but with a contour separation of 5 μRy.

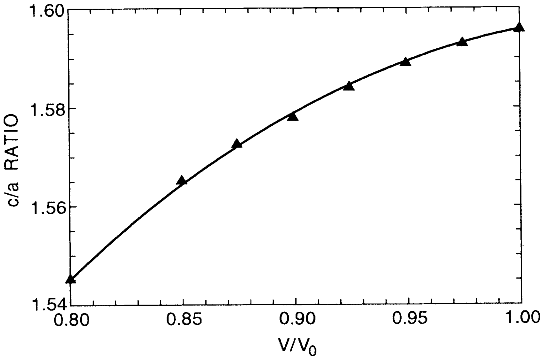

FIG. 6. Results of the optimization for wurtzite-AlN: c/a ratio as a function of volume.

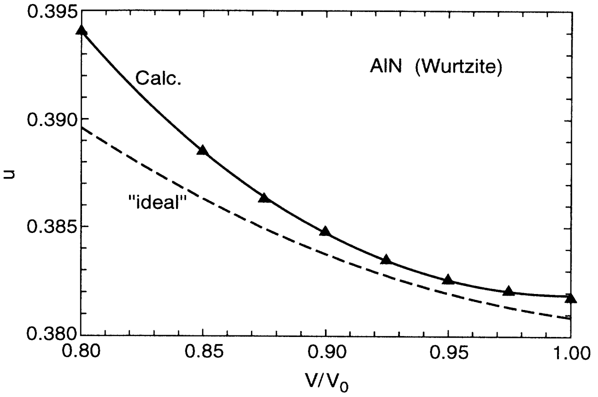

FIG. 7. Results of the optimization for wurtzite-AlN: parameter u as a function of volume. The dashes curve is calculated for an "ideal" case where all bond lengths are equal.

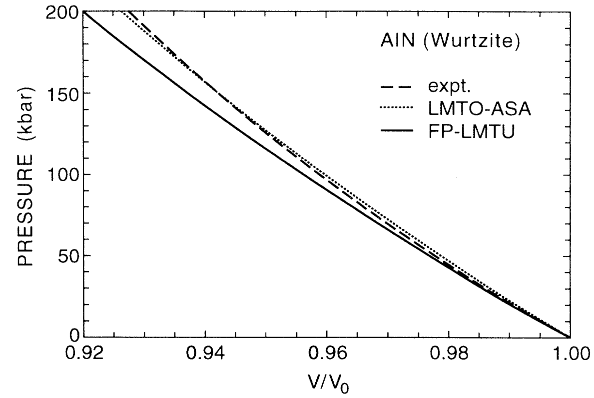

FIG. 9. Wurtzite-AlN: Calculated (FP-LMTO, solid line) pressure-volume relation (here V_0 is the theoretical equilibrium volume). Dashed curve: Murnaghan fit to experimental data (Ref. 5) with $B_0=2079$ kbars, $B_0'=6.3$. Dotted: Theoretical relation obtained with the LMTO-ASA.

For $c/a=\sqrt{8/3}$ this yields $u=3/8$. The deviation from "ideality" can also be examined by calculating (for a fixed volume) the values of u that minimize the total energy when c/a is varied. An example for $V/V_0=1$ is shown in Fig. 8. Again we show the "ideal" variation as a dashed curve, and the most ideal parameter set is indicated in the diagram. It is also seen that at this volume there is only a small difference between the "ideal" u value and the fully optimized value for $c/a=1.596$.

The equation of state at $T=0$ is obtained by calculating the derivative of the total energy vs volume (after optimization). In Fig. 9 we compare the theoretical P-V relation to the experiment of Ref. 5, or rather to a Murnaghan fit to the experimental data. The dashed curve used $B_0=207.9$ GPa and $B_0'=6.5$. Our calculation does yield lower pressures than the experiment,[5] but still, taking the volume where experiment and theory give 23 and 20 GPa, respectively, this difference is not sufficient to explain the different values of the transition pressure (22.9 and 12.5 GPa). The bulk modulus deduced from our calculation is 205 GPa, i.e., in excellent agreement with experiment [208 (Ref. 5) and 202 GPa (Ref. 6)] as well as other calculations, Ref. 24: 207 GPa, Ref. 12: 195 GPa. Our earlier LMTO-ASA calculation (not $c/a,u$ optimized) gave $B_0=221$ GPa.[3] We have included the P-V relation obtained from the LMTO-ASA calculation in Fig. 9. We note that this agrees almost perfectly with the experiment.

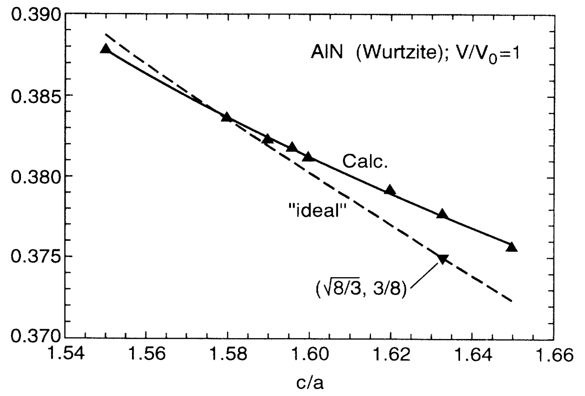

FIG. 8. Wurtzite-AlN: Total-energy optimized values of u (triangles connected with solid line curve) for varying c/a at fixed volume (equilibrium). The dashed curve represents the "ideal" model with equal bond lengths.

It is interesting that Ueno *et al.*[5] were able to measure the c/a ratio of AlN as a function of pressure. As also calculated, a decrease is found when P is increased. It seems as if the reduction in c/a with pressure is somewhat smaller than calculated, but quantitative comparison is difficult due to the scatter in the experimental data points (Fig. 4 of Ref. 5).

III. CALCULATED STRUCTURAL PHASE TRANSITIONS

The total-energy variations with volume have been determined for AlN in the wurtzite, zinc-blende ("ZB"), nickel-arsenide ("NiAs"), rocksalt, anti-NiAs, and beta-tin ("β-Sn") structures. They are displayed in Fig. 10. In this graph the wurtzite structure is optimized, whereas this is not the case for the two other hexagonal structures. For these the ideal values, $c/a=1.633, u=0.25$, were chosen. It follows from Fig. 10 that pressure-induced transitions are predicted from wurtzite to rocksalt, and further from rocksalt to a NiAs structure. Obviously, none of the other structures can be high-pressure phases of AlN in the pressure range considered here. But the NiAs structure must be examined more in detail. A structural optimization like the one performed for wurtzite-AlN is required.

The determination of the optimal c/a and u values is simpler for NiAs than wurtzite AlN because we find that u tends to keep its ideal value, 0.25. This follows from Fig. 11, where the total energy as a function of the displacement δ (in percent of a) of the Al and N layers is shown. The value $\delta=0$ corresponds to $u=0.25$, and this

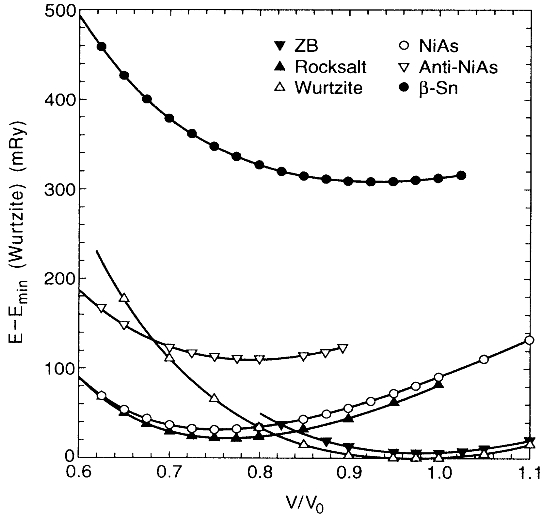

FIG. 10. Total energies of AlN in wurtzite (optimized), zincblende (ZB), rocksalt (Rock), NiAs ($c/a=1.633$, $u=0.25$), anti-NiAs ($c/a=1.633$, $u=0.25$), and β-Sn (ideal c/a ratio) structures.

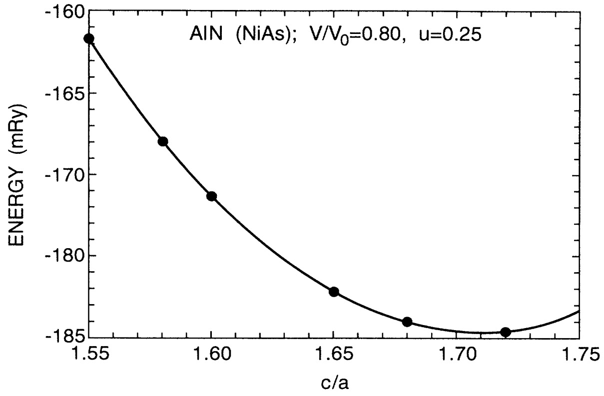

FIG. 12. NiAs-AlN: Total energy as a function of c/a for fixed u (0.25) and volume ($V/V_0=0.80$).

is clearly the optimum. In Figs. 12 and 13 we show the total energy as functions of c/a for two volumes, $V/V_0=0.80$ and 0.65, respectively. A slight increase in c/a is found when pressure is applied. The volume $0.65V_0$ is close to the rocksalt→NiAs transition (see below), and we therefore calculate the entire energy-volume curve for $c/a=1.72$, the optimum value from Fig. 13.

The total-energy variations are shown on a finer energy scale in Fig. 14, and now the one for NiAs-AlN with $c/a=1.72$ is included. The wurtzite→rocksalt transition is accompanied by a volume reduction of ≈19%, i.e., close to the experimental value, ≈18%.[5] The second transition is characterized by a much smaller volume change, ≈2%.

The theoretical transition pressures are derived from the enthalpies calculated as functions of pressure, Figs. 15, 16, and 17. From Fig. 15, where the enthalpy of wurtzite-AlN is used as reference, we see that the calculated pressure of the wurtzite→rocksalt transition is 125 kbars (12.5 GPa). As mentioned earlier, the LMTO-ASA calculation yields $P_t=16.6$ GPa, a result that also follows from Fig. 16. In Fig. 17 the enthalpy of the rocksalt phase is taken as reference, and it is seen that the $B1$→NiAs transition is predicted to occur at ≈300 kbars (30 GPa). The publication by Ueno *et al.*[5] does not discuss results for P above 30 GPa. But up to this pressure, their data clearly indicate the cubic structure, and this is not in contradiction with our results.

In Table I we summarize some of the zero-pressure properties of the phases of AlN examined in the calculations. We note that the equilibrium volume is ≈4% smaller than observed. This tendency to overbinding in the LDA is well known, but it is absent in many LMTO-ASA calculations[25] for compound semiconductors. Indeed, the LMTO-ASA also yields a better equilibrium

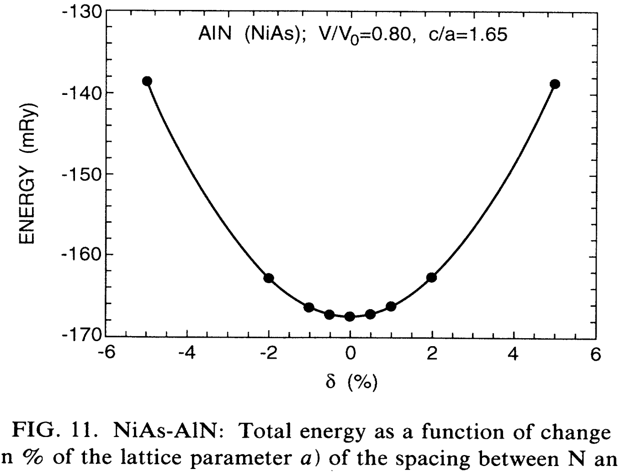

FIG. 11. NiAs-AlN: Total energy as a function of change δ (in % of the lattice parameter a) of the spacing between N and Al layers. The value $\delta=0$ corresponds to $u=0.25$ (the ideal value). The c/a ratio is kept fixed (1.65), and the volume is 80% of the (experimental) wurtzite-phase volume. The curve is a parabolic least-squares fit.

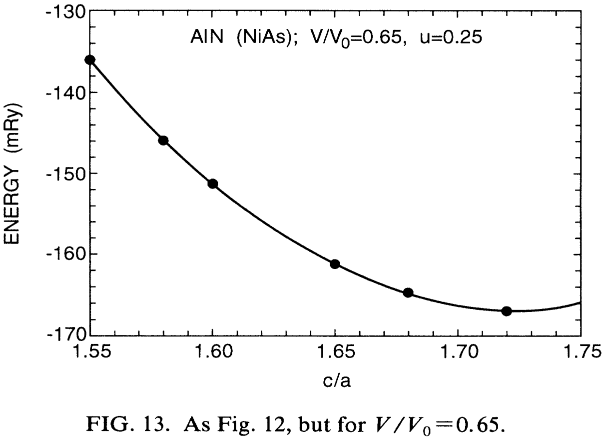

FIG. 13. As Fig. 12, but for $V/V_0=0.65$.

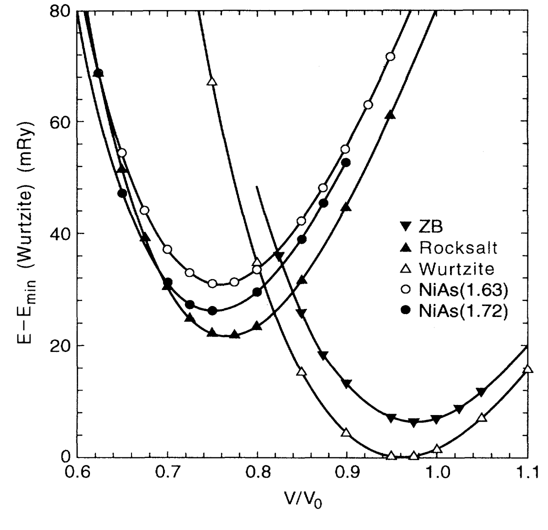

FIG. 14. Volume variation of the total energies of the lowest-lying AlN phases. This figure includes the calculation for the optimized NiAs structure ($c/a=1.720$).

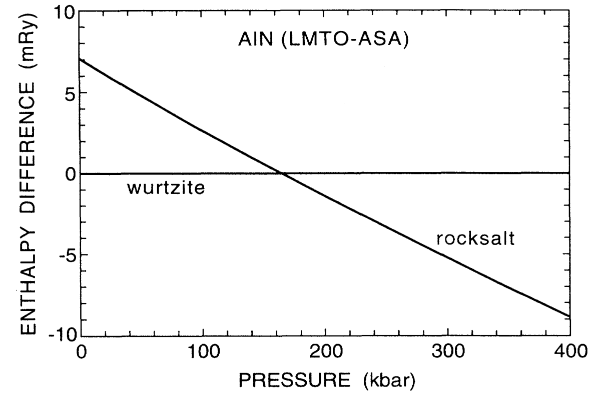

FIG. 16. LMTO-ASA calculation of the wurtzite- and rocksalt-phase enthalpies (that of wurtzite-AlN is reference) vs pressure. The transition pressure is 16.6 GPa.

volume for wurtzite AlN, $V/V_0=0.994$, than the FP-LMTO.

A 4% volume error does correspond to an error in pressure of 8 GPa for a material with a bulk modulus of 200 GPa; but this does not imply that the FP-LMTO calculations of the transition pressures are in error by that amount. The LDA overbinding is also affecting the rocksalt calculations, and if we, as a first approximation, increase artificially all the volume values used in the total-energy calculations by 4% the transition pressure is still 12.5 GPa. But, the errors might be different at different volumes. We did (Fig. 9) compare experimental and theoretical P-V relations for wurtzite-AlN. It is important to do that also for the rocksalt phase. Figure 18 shows the calculated pressures versus the cubic lattice constant, a. The solid line curve is obtained from the FP-LMTO calculation, whereas the LMTO-ASA result is represented by the dashed curve. Only one experimental point is known (indicated by a dot in Fig. 18), the lattice constant $a=3.938$ Å at 30.0±0.8 GPa from Ref. 5. The value of a at 30 GPa obtained from the FP-LMTO is 3.874 Å, corresponding to an error in volume of 5%. This is still the order of magnitude that is usually found in accurate LDA calculations, but the overbinding is a bit more pronounced than at the zero-pressure volume. The bulk modulus of rocksalt-AlN is ≈400 GPa at the volume where $P=30$ GPa. Again, it is interesting to observe that the LMTO-ASA yields a P-V relation that passes through the experimental point (Fig. 18).

IV. DISCUSSION

We have performed theoretical calculations, using the density functional theory, of AlN in various crystal structures. The hexagonal wurtzite and NiAs structures have been total-energy optimized in the sense that the internal parameters, c/a and u, have varied until the energy is minimal. The structural parameters deduced for

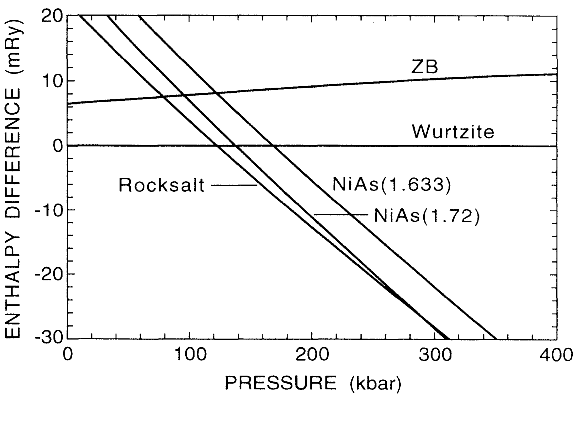

FIG. 15. Calculated (FP-LMTO) enthalpies of AlN in the NiAs ($c/a=1.633$ and 1.720), zinc-blende (ZB), rocksalt, and wurtzite structures. The latter is taken as reference.

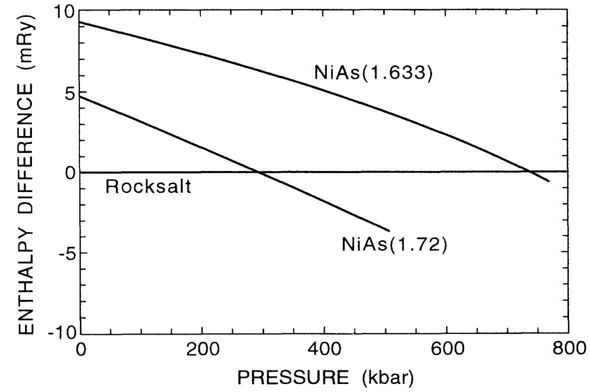

FIG. 17. Rocksalt→NiAs transition in AlN. The figure shows the enthalpies of the NiAs structures with $c/a=1.633$ and 1.720, as functions of pressure. The calculated enthalpy of the rocksalt phase has been subtracted.

TABLE I. AlN. Zero-pressure properties. V_0 is the experimental equilibrium volume per formula unit of the wurtzite phase. It corresponds to lattice constant $a = 3.110$ Å and $c = 4.980$ Å (Ref. 23). The table lists the equilibrium volumes V, bulk moduli B_0, the axial ratios c/a, and internal parameters u, where relevant. The bulk moduli are calculated at the theoretical equilibrium volumes. E_0 is the minimum total energy (in mRy per formula unit) with the wurtzite structure as reference. Calc. refers to the present FP-LMTO calculation. The c/a ratios were not optimized for the anti-NiAs and β-Sn structures.

	V/V_0	B_0 (GPa)	c/a	u	E_0 (mRy)	
Wurtzite	0.961	205	1.596	0.3820	0.000	Calc.
	1.00[a] 0.987[b]	207.9[c]	1.601	0.3821		Expt.
Zinc blende	0.976	216			6.364	Calc.
Rocksalt	0.767	270			21.580	Calc.
β-Sn	0.926	170	0.5264		308.480	Calc.
NiAs	0.752	251	1.720	0.250	26.213	Calc.
Anti-NiAs	0.793	226	1.633	0.250	110.826	Calc.

[a] Reference 23.
[b] Reference 17.
[c] Reference 5.

wurtzite-AlN at zero pressure agree well with experiments and with pseudopotential calculations. Also the bulk modulus agrees with experiments. The wurtzite→rocksalt transition is found to occur at 12.5 GPa. This again agrees with the pseudopotential result, 12.9 GPa.[12] It is slightly lower than found in the experiment of Ref. 3, 16–17 GPa, and substantially lower than 22.9-GPa value derived from the x-ray diffraction experiments by Ueno *et al.*[5] If, however, we assume that the transition in fact should be attributed to the first indication of a structural change at the 17.5-GPa value, then the two experiments agree well. We do calculate pressures that are somewhat lower than measured (see Fig. 9), but this difference is not sufficient to explain the difference between the values of P_t. From Fig. 3 of Ref. 5 we estimate that the smallest volume at which the wurtzite structure can be stable is $0.92V_0$. The calculated smallest volume is 94.5% of the *theoretical* equilibrium volume. This again agrees with the calculation of Van Camp *et al.*[12] This tends to exclude that there are errors in our calculation due to a different accuracy of the total-energy calculations for the rocksalt and wurtzite structures. We did pay attention, though, to this possibility. The FP-LMTO scheme uses the concept of "muffin-tin" spheres to define the basis set, and in the procedure of fitting the nonspherical charge density.[18] For this reason we minimized errors by including "empty spheres" in the wurtzite, zinc-blende, as well as the rocksalt structures (but no orbitals are centered on the "empty-sphere" sites). In order to bring our value of P_t in agreement with the 22.9-GPa value as observed,[5] we would need to increase the rocksalt-wurtzite energy separation by ≈ 8 mRy, and such an error is unlikely.

We thus conclude that P_t should be lower than the 22.9-GPa value, but we also believe that the calculated 12.5 GPa is an underestimate. The consistency with other full-potential results[12] suggests that the discrepancy is caused by the local-density approximation. The LDA does yield an equilibrium volume that is slightly too small, $0.961V_0$ (with V_0 from Ref. 23) or $0.974V_0$ (V_0 from Ref. 17) for the wurtzite structure (Table I). In all our volume related graphs we give volumes in fractions of V_0, the experimental equilibrium volume (from Ref. 23), except for the P-V relation in Fig. 9. There the theory is normalized to the theoretical and experiment to the experimental equilibrium volumes, respectively. Since the tendency to overbinding in the LDA is likely to be similar in the wurtzite and the cubic structures it could be expected that such errors would tend to cancel. But, comparison to the experimental lattice constant[5] of the rocksalt structure at 30 GPa shows that the error in fact is larger at this small volume than at the equilibrium volume of the wurtzite phase. This, together with the very large bulk modulus of compressed rocksalt-AlN is sufficient to explain the difference. Accidentally, the atomic-sphere approximation introduces small corrections that cancel the LDA errors in this case. The P-V relations calculated within the LMTO-ASA agree for the rocksalt as well as the wurtzite structures perfectly with the experiments. Since this calculation simultaneously yields $P_t = 16.6$ GPa, we believe that this is very close to the "real" value.

The calculation certainly supports the observation that

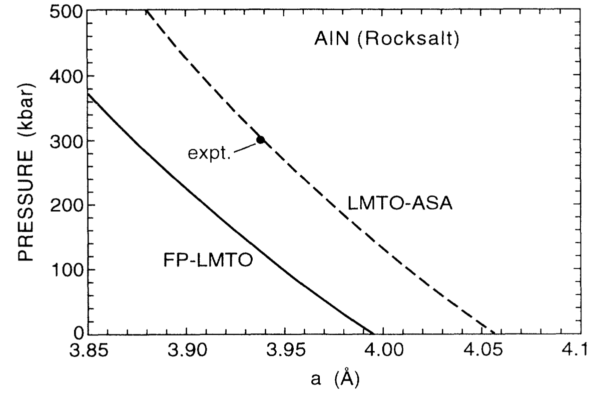

FIG. 18. Rocksalt-AlN: Pressure as function of lattice constant. The solid line represents the FP-LMTO calculation ("best LDA"), the dashed curve is the result obtained with LMTO-ASA, and a single experimental point (Ref. 5) has been marked by a dot.

wurtzite AlN transforms into the rocksalt structure. Further, it would be interesting if the experiments could be extended to higher pressures, where we predict that the rocksalt phase would become instable. We suggest that the AlN could assume the NiAs structure at pressures above ≈30–35 GPa.

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