PHYSICAL REVIEW B **66**, 201203(R) (2002)

Properties of hexagonal ScN versus wurtzite GaN and InN

N. Farrer and L. Bellaiche
Physics Department, University of Arkansas, Fayetteville, Arkansas 72701

(Received 26 August 2002; revised manuscript received 1 October 2002; published 20 November 2002)

Local-density approximation calculations are performed to compare properties of hexagonal ScN with those of wurtzite GaN and InN. A nearly five-times coordinated hexagonal structure is found to be (meta)stable in ScN, unlike the wurtzite structure. Structural, dielectric, and optical properties of this stable hexagonal phase are predicted to be rather different from those of wurtzite GaN and InN. This implies that disordered hexagonal $Sc_{1-x}Ga_xN$ and $Sc_{1-x}In_xN$ alloys are very attractive both fundamentally and technologically.

DOI: 10.1103/PhysRevB.66.201203 PACS number(s): 61.50.Ah, 81.05.Zx, 77.84.Bw, 71.20.Nr

Interest in wurtzite nitride semiconductors—such as GaN, InN, AlN, and their alloys—has exploded in the past few years mainly because of their prospects in light-emitting device applications.[1,2] On the other hand, another nitride compound—that is, ScN—has attracted much less attention up to now, despite the fact that alloying ScN with GaN or InN could result in materials useful for band-gap engineering.[3,4]

Two kinds of recent studies conducted on ScN can be distinguished. First, theoretical and experimental investigations[5–7] mainly focused on the electronic band structure of ScN in its *rocksalt* ground state. All these works concluded that ScN is a semiconductor rather than a semimetal, as sometimes previously suggested.[8–10] Second, the pioneering study of Takeuchi[11] was aimed at investigating the stability of different phases *besides the rocksalt structure*. One particularly interesting prediction of Ref. 11 is the existence of a (meta)stable wurtzite structure in ScN. This finding can be important in light of growing technologically-promising $Sc_{1-x}Ga_xN$ and $Sc_{1-x}In_xN$ materials that would be true (hexagonal) *alloys* rather than an heterogeneous mixture between a rocksalt phase—ground state of ScN—and a wurtzite structure—ground states of both GaN and InN.

One aim of this Rapid Communication is to revisit the stability of the wurtzite phase in ScN. In particular, our calculations point out that the wurtzite structure is *unstable* in ScN. In contrast, we further predict that the hexagonal structure that has recently been found in MgO and which is nearly five-times coordinated,[12] is stable in ScN.

The second aim of this Rapid Communication is to show that the structural, dielectric, and optical properties of this hexagonal phase in ScN are rather different from those of wurtzite GaN and InN. Consequently, we expect that anomalous effects should occur in *hexagonal* $Sc_{1-x}Ga_xN$ and $Sc_{1-x}In_xN$ solid solutions when increasing the x composition. Examples of such effects are (1) a continuous evolution of the axial ratio from $\simeq 1.2$ to $\simeq 1.62$–1.63; (2) a change in the coordination number from $\simeq 5$ to $\simeq 4$; (3) a paraelectric-to-pyroelectric transition resulting in an enhancement of electromechanical responses; (4) a noticeable change in the cationic-averaged Born effective charge that is due to the fact that Sc is a transition-metal atom, unlike Ga or In; (5) a transition from an indirect to a direct band-gap semiconductor; and (6) the generation of materials with a wide range of band gap.

Here, we investigate the *class* of hexagonal phases for which the primitive lattice vectors of the direct Bravais lattice are,

$$\mathbf{a}_1 = a\left(\frac{1}{2}\mathbf{x} - \frac{\sqrt{3}}{2}\mathbf{y}\right),$$

$$\mathbf{a}_2 = a\left(\frac{1}{2}\mathbf{x} + \frac{\sqrt{3}}{2}\mathbf{y}\right),$$

$$\mathbf{a}_3 = c\mathbf{z}, \tag{1}$$

where a and c are the two different lattice parameters, and where c/a is the axial ratio. $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ are the unit vectors along the Cartesian axes. The primitive unit cell contains four atoms: two atoms of type A (e.g., $A=\mathrm{Sc}$) located at $\mathbf{r}_1$ and $\mathbf{r}_2$, and two atoms of type B (e.g., $B=\mathrm{N}$) located at $\mathbf{r}_3$ and $\mathbf{r}_4$, with

$$\mathbf{r}_1 = \mathbf{0},$$

$$\mathbf{r}_2 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3,$$

$$\mathbf{r}_3 = u\mathbf{a}_3,$$

$$\mathbf{r}_4 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \left(\frac{1}{2} + u\right)\mathbf{a}_3, \tag{2}$$

where u is the dimensionless internal parameter. In the following, we will denote this class of hexagonal phases as h_c. Note that the wurtzite structure, which has a $6mm$ point group (in international notations) and for which $c/a=\sqrt{8/3}$ and $u=0.375$ in its ideal form, belongs to h_c. Similarly, the structure, which is stable in BN,[13] whose point group is $6/mmm$ and for which $c/a \simeq 2.60$ and $u=0.5$, is also contained in h_c.

We perform local-density approximation (LDA) (Ref. 14) calculations on the h_c class in ScN, using the Vanderbilt ultrasoft-pseudopotential scheme[15] with a plane-wave cutoff of 25 Ry. The $3s$, $3p$, $3d$, and $4s$ electrons of Sc, as well as the $2s$ and $2p$ electrons of N, are all included in the valence. As a result, the studied primitive unit cell exhibits 32 valence electrons per cell. We also use the Ceperley-Alder exchange

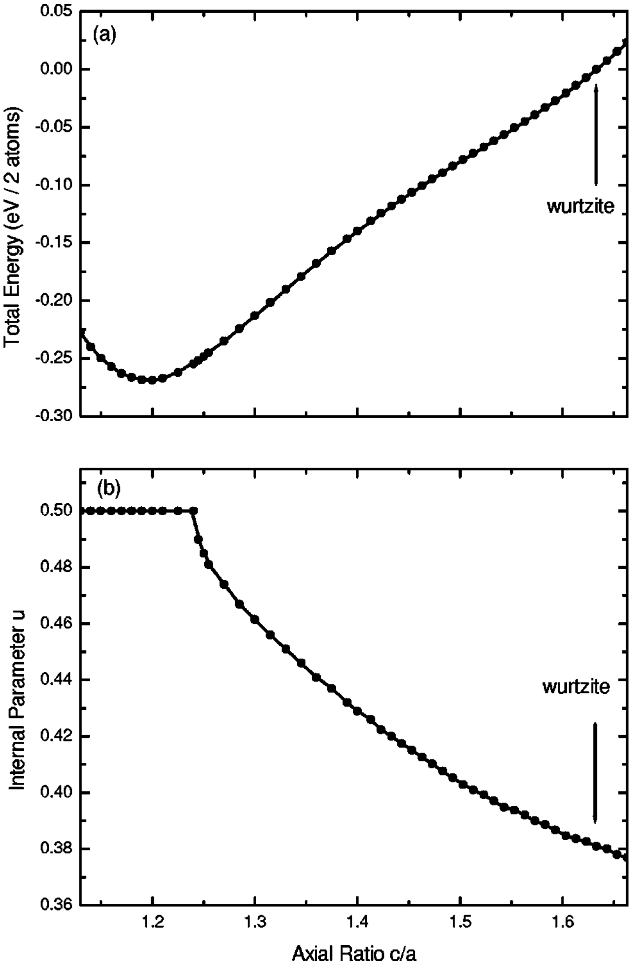

FIG. 1. (a): Total energy of the hexagonal phases belonging to h_c as a function of the c/a axial ratio, at the fixed volume of 55.3 Å^3. The zero of energy is chosen for the wurtzite structure ($c/a=1.633$ and $u=0.3815$), (b) Same as (a) but for the internal parameter u.

and correlation[16] as parametrized by Perdew and Zunger,[17] and a (6,6,4) Monkhorst-Pack mesh.[18]

The volume of the phases belonging to h_c in ScN is first kept frozen at a value of 55.3 Å^3. We then relax the internal parameter u for different values of c/a by following the Hellmann-Feynman forces, the latter being smaller than 0.045 eV/Å at convergence. Figure 1(a) reports the resulting total energy as a function of the axial ratio, for c/a ranging between 1.13 and 1.663, while Fig. 1(b) shows the simultaneous evolution of u. Figures 1 clearly show that the wurtzite structure is unstable in ScN, and further indicate that the lowest-in-energy structure—among all hexagonal phases belonging to h_c—is characterized by $c/a \simeq 1.20$ and $u=0.5$. This structure will be denoted as h-ScN, is a layered hexagonal phase, and is displayed in Fig. 2. Interestingly, such structure has also recently been predicted to be (meta)stable in another material, namely, MgO.[12] This phase may thus exist in many other compounds. Surprisingly, our predictions are in disagreement with recent simulations[11] reporting a (meta)stable wurtzite phase in ScN. These simulations differ, in particular, from ours by the use of the generalized gradient approximation (GGA) (Ref. 19) and a larger k-points grid. To investigate the possibility that such differences are responsible for the discrepancy between the two studies, we performed our own GGA calculations[19] with a (9,9,6) Monkhorst-Pack mesh.[18] These "test" calculations confirm (i) that the h-ScN phase has a lower total energy than wurtzite-ScN [by 0.261 eV/2 atoms, to be compared with the value of 0.269 eV/2 atoms displayed in Fig. 1(a)], and (ii) that the wurtzite phase is unstable in ScN. The discrepancies between our calculations and those of Ref. 11 may thus be due to the neglect of fully relaxing c/a and u in the latter.

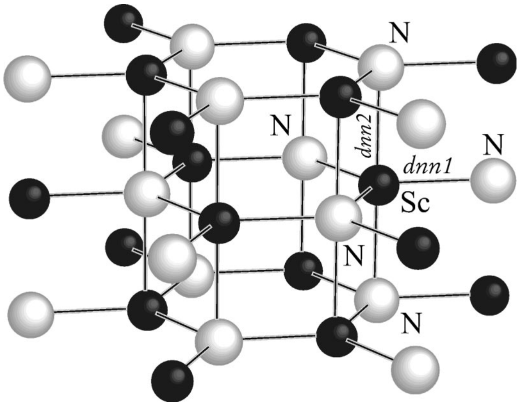

FIG. 2. Hexagonal h-ScN structure. d_{nn1} and d_{nn2} denote the nearest neighbors' distances.

We then determine the precise structural parameters of the h-ScN structure at its *equilibrium*, by relaxing *all* the degrees of freedom of Eqs. (1) and (2). Table I compares our predictions for the properties of this stable structure[20] with those derived from similar LDA calculations[21] for the (ground-state) wurtzite phase of both GaN and InN—to be denoted w-GaN and w-InN, respectively. One can see that the in-plane lattice constant is around 4% and 16% larger in h-ScN than in w-InN and w-GaN, respectively. On the other hand, the axial ratio decreases by as much as 26% when going from both w-GaN and w-InN to h-ScN. Consequently, the volume of the primitive cell of h-ScN is around 15% *larger* than the one in the wurtzite phase of GaN, but is $\simeq$17% *smaller* than the unit cell volume of w-InN. Conversely, Table I shows that the bulk modulus is smaller (larger) in h-ScN than in w-GaN (w-InN), as consistent with the fact that an increase in equilibrium volume usually leads to a decrease in bulk modulus.

One striking difference between h-ScN and both w-GaN and w-InN is the number of nearest neighbors: w-GaN and w-InN are both nearly *four*-times coordinated, as consistent with the fact that their ground-state phase is close to the ideal wurtzite structure, while h-ScN is nearly *five*-times coordinated. A given Sc (N) atom forms short bonds $d_{nn1}=2.11$ Å with *three N* (Sc) atoms belonging to the same basal plane but also forms slightly longer bonds $d_{nn2}=2.21$ Å with *two* other *N* (Sc) atoms being in the c-planes below and above it, respectively (see Fig. 2).[22] Table I also indicates that the distance between nearest neighbors is quite similar in magnitude in h-ScN and w-InN. Another major difference between h-ScN and both w-GaN and w-InN is the

TABLE I. Comparison between the LDA-predicted properties of the *h*-ScN, *w*-GaN, and *w*-InN (see text). a, c/a, u, V, B_0 are the in-plane lattice constant, axial ratio, internal parameter, volume of the primitive cell, and bulk modulus, respectively. cn, d_{nn}, Z^*_{33}, and E_g denotes the coordination number, distance between nearest neighbors, effective charge, and band gap, respectively. ΔE_{HEX-RS} (ΔE_{HEX-ZB}) is the difference in total energy between the considered hexagonal phase and the rocksalt (zinc-blende) structure. The negative sign of the band gap in *w*-InN indicates that our calculations (erroneously) predict that the energy of the Γ_{1c} conduction state is below the energy of the Γ_{6v} valence state.

Property	*h*-ScN	*w*-GaN	*w*-InN
a (Å)	3.660	3.157	3.527
c/a	1.207	1.631	1.620
u	0.500	0.376	0.378
V (Å^3)	51.25	44.44	61.55
B_0 (GPa)	181	201	144
cn	3+2	$\simeq 4$	$\simeq 4$
d_{nn} (Å)	2.11–2.21	1.93–1.94	2.15–2.16
Point group	$6/mmm$	$6mm$	$6mm$
Polarity	Nonpolar	Polar	Polar
Z^*_{33} (a.u.)	4.49	2.70	3.05
Nature of the band gap	Indirect ($\Gamma \rightarrow K$)	Direct	Direct
E_g (eV)	0.25	2.09	-0.18
ΔE_{HEX-RS} (eV/2 atoms)	$+0.316$	-0.887	-0.346
ΔE_{HEX-ZB} (eV/2 atoms)	-0.504	-0.012	-0.020

point group and the related polarity. As a matter of fact, the point group of *h*-ScN is $6/mmm$ and thus contains the inversion among its 24 symmetry elements. As a result, *h*-ScN is *nonpolar*. On the other hand, the wurtzite phases of both GaN and InN are associated with a subgroup of $6/mmm$, namely, $6mm$. *w*-GaN and *w*-InN thus both exhibit an electrical polarization. Playing with the composition x in disordered hexagonal $Sc_{1-x}Ga_xN$ and/or $Sc_{1-x}In_xN$ alloys should thus result in a paraelectric-to-pyroelectric transition, in addition to continuously changing the coordination number from $\simeq 5$ to $\simeq 4$ and the axial ratio from $\simeq 1.2$ to $\simeq 1.62$–1.63 *within the* h_c *class*. This change of polarity can be useful for technological purposes because a small change in applied strain, stress, or electric field should yield a relatively large change in electrical polarization around this transition. Consequently, electromechanical responses should exhibit huge values around the paraelectric-to-pyroelectric transition.

Table I also reports some dielectric properties. More precisely, we have computed the dynamical effective charges $Z^*{}_{33}$—where the index "3" refers to the c axis—of the different atoms, by using the Berry phase approach.[23] In *h*-ScN, Z^*_{33} of Sc is found to be equal to $+4.49$ a. u., while the effective charge of N adopts an opposite value of -4.49 a.u.—in order to satisfy the acoustic sum rule $\Sigma_i Z^*_{33}(i)=0$, where i runs over all the atoms in the primitive cell. The magnitude of the effective charges in equilibrium *h*-ScN is thus anomalously large with respect to the ionic nominal value of 3. It is also enhanced with respect to the magnitude of Z^*_{33} of 2.70 and 3.05 in *w*-GaN and *w*-InN, respectively.[21] This enhancement has the same origin as in insulating perovskites, namely, a subtle hybridization between the *d* orbitals of the transition-metal cation (that is, Sc, in our case) and the *p* orbitals of the anion (i.e., N, in our case).[24] This enhancement should lead to an increase in piezoelectricity when inserting Sc in *w*-GaN and/or *w*-InN, since a larger Z^*_{33} effective charge implies larger e_{33} and e_{31} piezoelectric coefficients.[21]

Table I further displays some predictions about the electronic band-structure of *h*-ScN. In particular, we find that *h*-ScN is an *indirect* band-gap semiconductor with a valence-band maximum located at the Γ point and a conduction-band minimum indexed by the K point. This is in variance with *w*-GaN and *w*-InN, which are known to be materials with a *direct* band gap at Γ.[2] As a result, changing the composition in disordered hexagonal $Sc_{1-x}Ga_xN$ and/or $Sc_{1-x}In_xN$ solid solutions will yield a change from an indirect to a direct band-gap material, resulting from a change in the reciprocal-space location of the conduction-band-minimum. As shown in Table I, the value of the indirect band gap in *h*-ScN is predicted to be $\simeq 0.25$ eV.[25] However, this value should not be trusted because of the well-known LDA underestimation of the band gap (which is revealed when noticing that our calculations yield a band gap of 2.09 eV in *w*-GaN to be compared with the experimental value of 3.5 eV.[2]) Assuming that the LDA band gap of *h*-ScN should be increased by 1.3 eV—that is, the difference between the LDA (Ref. 5) and experimental[6] band gaps in the *rocksalt* phase of ScN—yields an indirect band gap around 1.55 eV in *h*-ScN. If this assumption is correct, hexagonal $Sc_{1-x}Ga_xN$ alloys would thus be technologically important in the sense that they will exhibit band gaps corresponding to a wide region of the visible light (e.g., orange, yellow, green, blue, and violet colors, depending on the x composition). Furthermore, diodes and lasers emitting and/or absorbing in the infrared region, as well as devices useful for optoelectronic communications and solar cells, may be made of hexagonal $Sc_{1-x}In_xN$ *if* the band gap of *h*-ScN is indeed around 1.55 eV and *if* the true band gap of *w*-InN is not 1.9 eV, as commonly believed,[2] but is rather around 0.8 eV, as recently claimed.[26,27]

As discussed above, *hexagonal* $Sc_{1-x}Ga_xN$ and $Sc_{1-x}In_xN$ alloys show great promise for technological purposes, as well as, for exhibiting fundamental anomalies. It is thus important to have an idea about the *energetics* of the hexagonal phases in these solid solutions. Consequently, Table I compares the total energy between the most stable phase among those belonging to the h_c class—that is, *h* in ScN *versus* the wurtzite structure in GaN and InN—and the rocksalt and zinc-blende phases in ScN, GaN, and InN.[28] One can notice that (1) the total energy of *h*-ScN is higher by 0.316 eV/2 atoms from the equilibrium rocksalt structure, which is the ground state of ScN;[6,11] (2) the rocksalt phase is relatively high in energy, with respect to the wurtzite structure, in both GaN and InN; (3) the zinc-blende phase is never predicted to be the ground state of the studied materials, and is quite far away in energy from the hexagonal phase in ScN. It is thus very likely that the ground state of $Sc_{1-x}Ga_xN$ and

$Sc_{1-x}In_xN$ alloys, with low and even intermediate composition of Sc, will belong to the hexagonal h_c class. On the other hand, Sc-rich $Sc_{1-x}Ga_xN$ and $Sc_{1-x}In_xN$ solid solutions should adopt a rocksalt structure as ground state, and would thus be hexagonal ''only'' when in a metastable state. Growing such hexagonal metastable phase would thus require strategic thinking, which may be the use of an hexagonal substrate to favor the emergence of an hexagonal phase rather than the rocksalt structure.

In summary, first-principles calculations were performed to investigate properties of hexagonal phases in ScN. It was found that the hexagonal phase, which is the lowest in energy among those belonging to the h_c class, is similar to the one recently found in MgO.[12] This phase exhibits properties that are quite different from those of the wurtzite phases of GaN and InN. Examples of such differences are the coordination number, point group, polarity, Born effective charge, and band gap. Changing the composition in disordered hexagonal $Sc_{1-x}Ga_xN$ and $Sc_{1-x}In_xN$ alloys (i) should thus lead to structural, dielectric, and optical anomalies, and (ii) should be technologically promising for creating new devices whose optimal functioning requires large electromechanical properties and/or band gap engineering. We thus hope that the present study will encourage the growth of such hexagonal alloys.

The authors thank the financial assistance provided by the NSF Grants Nos. DMR-9988061, DMR-0102755, and DMR-0080054, and the NATO Grant Nos. PST.CLG.979025. The authors also acknowledge I. Kornev, W. F. Oliver, and S.-H. Wei for useful discussions, and are grateful to D. Vanderbilt for providing numerical codes.

---

[1] S. Nakamura, Adv. Mater. **8**, 689 (1996).

[2] *Properties, Processing and Applications of Gallium Nitride and Related Semiconductors*, edited by J. H. Edgar, S. Strite, I. Akasaki, H. Amano, and C. Wetzel, Emis Datareviews Series No. 23 (Inspec, London, 1999).

[3] J.P. Dismukes and T.D. Moustakas, *Proceedings of the III-V Nitride Materials and Processes Symposium*, ECS, **96-11**, 111 (1996).

[4] M.E. Little and M.E. Kordesch, Appl. Phys. Lett. **78**, 2891 (2001).

[5] W.R.L. Lambrecht, Phys. Rev. B **62**, 13 538 (2000).

[6] D. Gall, M. Stadele, K. Jarrendahl, I. Petrov, P. Desjardins, R.T. Haasch, T.-Y. Lee, and J.E. Greene, Phys. Rev. B **63**, 125119 (2001).

[7] C. Stampfl, W. Mannstadt, R. Asahi, and A.J. Freeman, Phys. Rev. B **63**, 155106 (2001).

[8] A. Neckel, P. Rast, R. Eibler, P. Weinberger, and K. Schwarz, J. Phys. C **9**, 579 (1976).

[9] R. Eibler, M. Dorrer, and A. Neckel, Theor. Chim. Acta **63**, 133 (1983).

[10] R. Monnier, J. Rhyner, T.M. Rice, and D.D. Koelling, Phys. Rev. B **31**, 5554 (1985).

[11] N. Takeuchi, Phys. Rev. B **65**, 045204 (2002).

[12] S. Limpijumnong and W.R.L. Lambrecht, Phys. Rev. B **63**, 104103 (2001).

[13] N. Ohba, K. Miwa, N. Nagasako, and A. Fukumoto, Phys. Rev. B **63**, 115207 (2001).

[14] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964); W. Kohn and L.J. Sham, *ibid.* **140**, A1133 (1965).

[15] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[16] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[17] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[19] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[20] We also checked the stability of the *h*-ScN phase versus the basal strain, considered in Ref. 12, that allows a transitional path from *h*-ScN to the rocksalt phase of ScN. This path is found to have an energy barrier of 38 meV/2 atoms.

[21] A. Al-Yacoub and L. Bellaiche, Appl. Phys. Lett. **79**, 2166 (2001); A. Al-Yacoub, L. Bellaiche, and S.-H. Wei, Phys. Rev. Lett. **89**, 057601 (2002).

[22] A coordination number exactly equal to five requires that $c/a = \sqrt{4/3}$ and $u = 0.50$ in Eqs. (1) and (2).

[23] R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).

[24] W. Zhong, R.D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).

[25] The direct band gap at Γ is $\simeq 2.26$ eV in *h*-ScN, according to our LDA calculations.

[26] J. Wu, W. Walukiewicz, K.M. Yu, J.W. Ager III, E.E. Haller, H. Lu, and W.J. Schaff, Appl. Phys. Lett. **80**, 4741 (2002).

[27] T. Matsuoka, H. Okamoto, M. Nakao, H. Harima, and E. Kurimoto, Appl. Phys. Lett. **81**, 1246 (2002).

[28] We chose to calculate the energetics of the rocksalt and zinc-blende phases because most octet binary compounds are known to adopt either one of these two structures as ground state [see, for instance, A. Garcia and M.L. Cohen, Phys. Rev. B **47**, 4215 (1993)].