First-principles calculations of the ground-state properties and stability of ScN

Noboru Takeuchi
Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apartado Postal 2681, Ensenada, Baja California, 22800, Mexico

(Received 19 June 2001; revised manuscript received 17 September 2001; published 3 January 2002)

Using first-principles total-energy calculations, we have studied the structural and electronic properties of ScN in the rocksalt (sodium chloride), cesium chloride, nickel arsenide, zinc-blende, and wurtzite structures. Rocksalt is the calculated ground-state structure with $a=4.54$ Å, $B_0=201$ GPa. Experimental values are $a=4.501$ Å, $B_0=182\pm40$ GPa. There is an additional local minimum in the wurtzite structure. Its total energy is 0.34 eV/(unit formula) higher than the energy of the rocksalt structure. Since other group IIIA nitrides crystallize in the wurtzite structure, this result is important in the possible fabrication of Sc-IIIA-N alloys. At very high pressure, our calculations show the possibility of a phase transition from the NaCl to a metallic CsCl structure.

DOI: 10.1103/PhysRevB.65.045204 PACS number(s): 71.20.Nr, 71.15.Nc

I. INTRODUCTION

Group III nitrides have been the subject of extensive research in the last decades.[1–7] This interest is partly motivated by the application of GaN, AlN, and InN in optical devices.[8] They are wide-band-gap semiconductors and they are used for short-wavelength electroluminescent devices. The ground-state configuration of these materials is wurtzite. However, depending on the substrate and growth conditions, a zinc-blende phase can be formed.[7] The difference in total energy between the zinc-blende and wurtzite structures is very small ($\sim$10 meV/atom), explaining why the two structures can be obtained experimentally. Although wurtzite and zinc blende are structurally similar [they differ only by the stacking in the (111) direction, and any atom coordination in either zinc blende or wurtzite is exactly the same through the second neighbor], electronic properties of the two phases can be very different.

Less is known about nitrides with group III transition metals. Very recently, it was achieved smooth epitaxial growth of singly oriented ScN films,[9–13] showing the possibility of using ScN as an electronic material. ScN is believed to be a narrow-gap semiconductor and since its lattice constant is very similar to GaN (a wide-gap semiconductor), combining the two semiconductors in the form of heterostructures could be of great interest in the fabrication of electronic devices. Whether ScN has a direct or indirect gap is still a matter of some controversy. Early theoretical work suggested that ScN was a semimetal.[14,15] Very recently, Lambrecht performed local density-functional calculations, complemented with estimated quasiparticle corrections of the optical response and found that ScN was a semiconductor with an indirect gap of $\sim$1 eV.[16] He also found a direct transition at the X point near 2.1 eV, in agreement with experiments that have shown a direct optical transition in the range of 2.1–2.4 eV.[9–12]

We have performed first-principles total-energy calculations to study the properties of ScN. In particular we were interested in knowing if besides the rocksalt structure there could be other stable or metastable phases of ScN. It was found that rocksalt is indeed the ground-state structure of ScN. We found an almost zero indirect band gap, in agreement with previous theoretical results. However, the calculations were performed using the density-functional theory (DFT), and it is well known that DFT always underestimate the magnitude of the energy gap. There is an additional local minimum in the wurtzite structure with total energy 0.34 eV/(unit cell) higher. In this structure ScN is a semiconductor with a band gap of $\sim$3 eV. Since the lattice constant of ScN in the wurtzite structure is similar to the lattice parameter of InN, this result is important for the possible fabrication of ScInN alloys. At 341 GPa, our calculations show the possibility of a high-pressure phase transition to a metallic CsCl structure.

II. METHOD

The calculations were performed in the framework of density-functional theory. We have employed the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the wien97 code.[17] The exchange and correlation effects were treated using two different levels of ap-

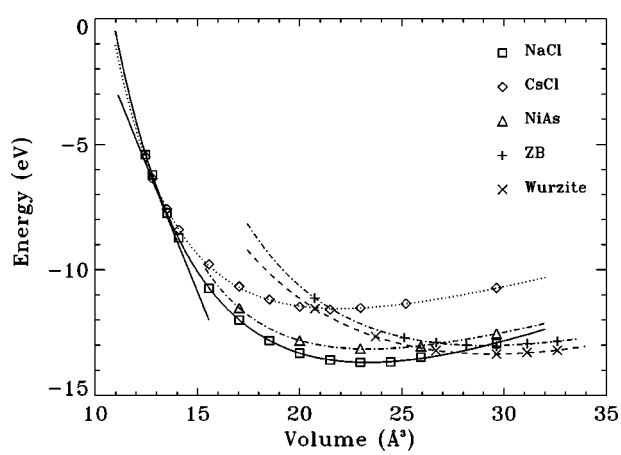

FIG. 1. Total energy (in eV per formula unit) versus the atomic volume (in Å^3) for five structures of ScN. Also shown is the common tangent between the NaCl and CsCl structures that determines the path of a possible phase transition.

 ©2002 The American Physical Society

TABLE I. Calculated structural properties of ScN in the rocksalt, cesium chloride, nickel arsenide, zinc-blende, and wurtzite structures.

Structure	NaCl	CsCl	NiAs	Zinc blende	Wurzite
a (Å)	4.54	2.81	3.10	4.88	3.49
c/a			1.8		1.6
u					0.38
V (Å^3)	23.4	22.15	23.35	29.09	29.41
B_0 (GPa)	201	170	171	153	156
B_0'	3.31	3.47	4.28	3.34	2.16
E_0 (eV)	-13.69	-11.58	-13.16	-13.03	-13.35

proximation: the standard local density-functional approach with the Ceperly-Alder data as reparametrized by Perdew and Wang,[18] and also the generalized gradient approximation (GGA).[19] Similar trends were found in both cases, and we present in this paper the results obtained using the GGA approximation. It should be noted that some of the calculated phases can be metallic. Therefore, a large number of integrating points over the Brillouin zone (BZ) is necessary. We have used 72, 84, 57, 91, and 70 k points in the irreducible part of the BZ for the rocksalt, cesium chloride, nickel-arsenide, zinc-blende, and wurtzite structures, respectively. A larger number of k points were used in selected calculations (in the rocksalt and CsCl phases around the high pressure transition), finding similar results.

III. STRUCTURAL PROPERTIES

Total energy versus volume data for the rocksalt, CsCl, NiAs, zinc-blende, and wurtzite phases of ScN are shown in Fig. 1. Energies and volumes are per single ScN formula unit: there are two in a wurtzite unit cell, and one in all the other cases. We have taken as the zero the sum of the energies of isolated neutral Sc and N atoms. Therefore, the absolute value of the energy at the minimum of each curve gives the cohesive energy of the corresponding ScN phase. The data is fitted to the Murnaghan equation of state for each phase. In this way, we can obtain the equilibrium lattice constant, the bulk modulus and other structural parameters (see Table I). In all cases, the fit is very good, indicating that a different choice of volume and/or a different equation of state would not alter the results. To determine the most stable structure at finite pressure and temperature, the free energy $G=E+pV-TS$ should be used. Since there is no known phase transition from 0 K to room temperature, we neglect the last term and work with the enthalpy $H=E+pV$. We employ five crystal structures, and we cannot exclude the possible existence of other stable or metastable structures.

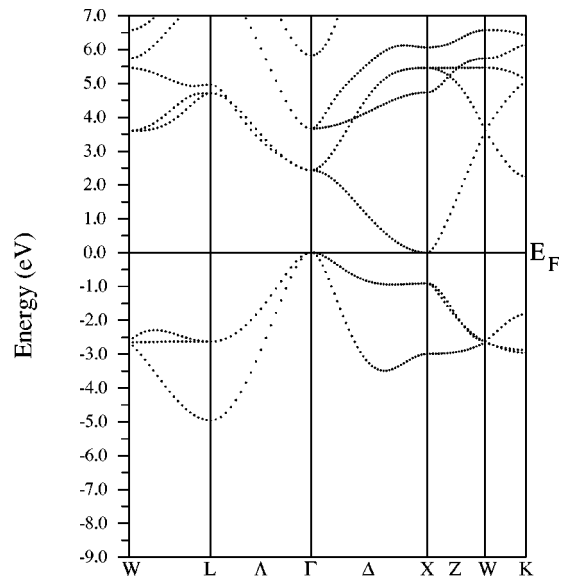

FIG. 2. Band structure for ScN in the rocksalt structure at the equilibrium volume.

The rocksalt is the calculated ground state with $a=4.54$ Å, $B_0=201$ GPa, and cohesive energy $E_0\sim1.00$ Ry. Values obtained with LDA are $a=4.44$ Å, $B_0=220$ GPa, and $E_0\sim1.12$ Ry. Experimental values are $a=4.501$ Å and $B_0=182\pm40$ GPa for the lattice constant and bulk modulus, respectively.[11] The agreement between theory and experiment is very good. Our results show the usual trends of LDA and GGA: LDA cohesive energy is too large and the lattice constant is slightly small, while GGA corrects the cohesive

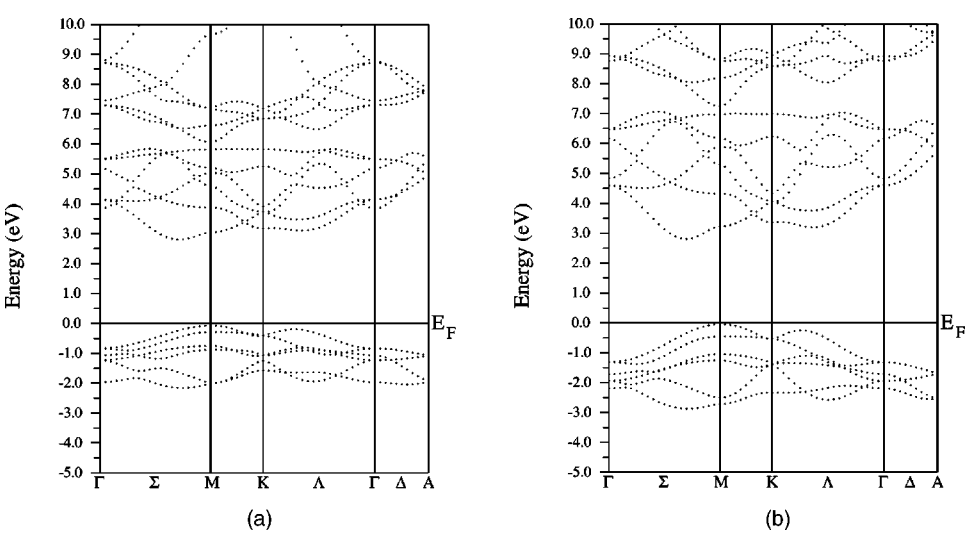

FIG. 3. Band structure for ScN in the wurtzite structure (a) at the equilibrium volume, (b) at the equilibrium volume in the rocksalt structure.

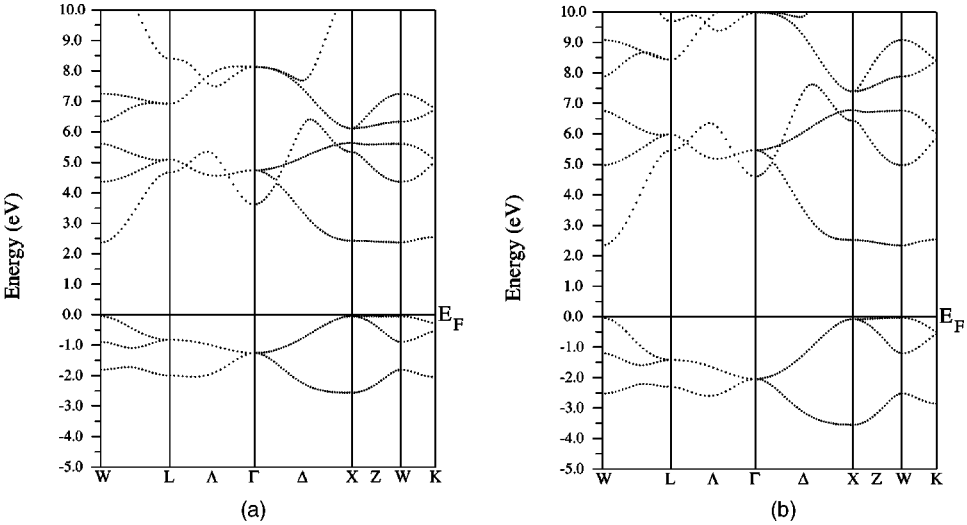

FIG. 4. Band structure for ScN in the zinc-blende structure (a) at the equilibrium volume, (b) at the equilibrium volume in the rocksalt structure.

energy but overcorrects the lattice constant.

There is an additional local minimum in the wurtzite structure with total energy 0.34 eV/(unit cell) higher. This is a quite large energy difference, and it is probably difficult to stabilize a metastable wurtzite structure as it occurs in MnTe (its ground state has a NiAs structure, but a metastable zinc-blende structure can be stabilized during growth[20,21]). However, the existence of a metastable wurtzite structure is important in the possible fabrication of Sc–group-IIIA–N alloys, in particular, $Sc_{1-x}In_xN$ alloys, since the lattice constants of ScN and InN in the wurtzite structure are very close.

In Fig. 1 we can see that the curve corresponding to the NaCl crosses the curve of the CsCl structure, indicating a high-pressure phase transition from the NaCl to the CsCl structure. At these volumes, the difference in the total energy of the two phases is very small, and they are probably beyond the accuracy of the calculation. If such transition occurs, the common tangent between the NaCl and CsCl curves determines the transition path between the two structures. From its slope we can predict the transition pressure to be 341 GPa. At this pressure the enthalpies of both structures are equal. Across the transition, there is a volume reduction of about 5% from 13.5 $Å^3$ to 12.8 $Å^3$. Similar transitions, from NaCl to CsCl structures, have been observed experimentally and predicted theoretically in other compounds.[21–23]

IV. ELECTRONIC PROPERTIES

We have calculated the band structure for ScN at different structures and volumes: (i) the NaCl phase at its ground state volume, (ii) the wurtzite structure at its minimum energy and at a volume similar to the rocksalt, (iii) the zinc-blende structure at its minimum energy and at a volume similar to the rocksalt, and (iv) the CsCl phase after the high-pressure phase transition. In Fig. 2 we show the band structure of ScN in the rocksalt structure. It is very similar to the results reported by Lambrecht using LDA.[16] It shows an almost zero indirect fundamental gap, and a small direct transition at the *X* point. We have to remember that the Kohn-Sham eigenvalues are known to underestimate band gaps in semiconductors, and as shown by Lambrecht, quasiparticle corrections result in a fundamental indirect band gap of ~1 eV.

In Fig. 3(a) we show the band structure of ScN in the wurtzite structure at its equilibrium volume (zero pressure). In this phase, a large indirect band gap of ~3 eV is found. The magnitude of this gap is larger than the one of InN (~2 eV) and, therefore, different concentrations of In and Sc atoms in ScInN alloys could be used to fabricate material with intermediate band gaps. From Fig. 3(a), we can observe a narrow valence bandwidth. This is an indication of a weak bonding in the wurtzite structure. Since GaN and AlN have smaller lattice constants (~3.19 and 3.11 Å, respectively), we present in Fig. 3(b) the band structure of ScN at a lower lattice constant ~3.2 Å (giving a volume similar to the rocksalt). Now the valence band is wider, indicating a stronger bond. On the other hand, the band gap hardly changes. Since AlN has a very large band gap (~6 eV), variations of Sc and Al concentrations in ScAlN alloys could lead to materi-

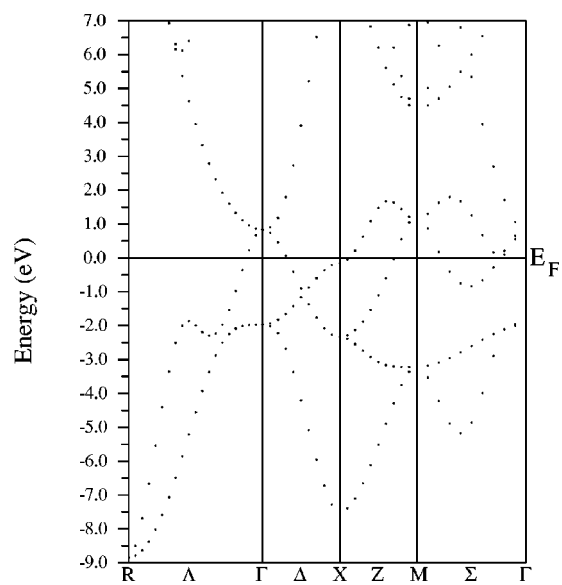

FIG. 5. Band structure for ScN in the cesium chloride structure at the transition pressure.

als with interesting properties.

Figures 4(a) and 4(b) show the band structure of ScN in the zinc blende structure at the same two volumes. They are similar to the results in the wurtzite structures. Magnitudes of band gaps and valence bandwidths are almost the same, and they follow similar trends: band gaps do not change at smaller volumes, but valence bandwidths increase at smaller volumes.

Figure 5 shows the band structure of ScN in CsCl after the high-pressure phase transition. In this case, the structure is clearly metallic.

V. SUMMARY

In this paper we have performed first-principles total-energy calculations of ScN in the rocksalt, cesium chloride, nickel arsenide, zinc-blende, and wurtzite structures. The rocksalt is the ground-state configuration. The calculated lattice constant and bulk modulus are in very good agreement with experimental results. In this structure, an almost zero indirect band gap is obtained. A second local minimum in a wurtzite structure is also found. At high pressure, the calculations show the possibility of a phase transition to a metallic cesium chloride structure.

ACKNOWLEDGMENTS

We acknowledge support from DGAPA Project No. IN111600, CONACYT project 33587 E. We thank Art Smith and Sergio E. Ulloa for useful discussions.

[1] W. M. Yim and R. J. Paff, J. Appl. Phys. **45**, 1456 (1974).
[2] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, Phys. Rev. B **44**, 9056 (1991).
[3] V. A. Tyagi, A. M. Evstigneev, A. N. Krasiko, A. F. Malakhov, and V. Ya, Fiz. Tekh. Poluprovodn. **11**, 2142 (1997)[Sov. Phys. Semicond. **11**, 1257 (1977)].
[4] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, Solid State Commun. **81**, 23 (1992).
[5] A. Munoz and K. Kunc, Phys. Rev. B **44**, 10 372 (1991).
[6] B.J. Min, C. T. Chan, and K. M. Ho, Phys. Rev. B **45**, 1159 (1992).
[7] C.-Y Yeh, Z. W. Lu, S. Froyen, and A. Zunger, Phys. Rev. B **46**, 10 086 (1992).
[8] S. Nakamura, Solid State Commun. **102**, 237 (1997).
[9] P. Dismukes, W. M. Yim, and V. S. Ban, J. Cryst. Growth **13/14**, 365 (1972).
[10] D. Gall, I. Petrov, L. D. Madsen, J.-E. Sundgren, and J. E. Geene, J. Vac. Sci. Technol. A **16**, 2411 (1998).
[11] D. Gall, I. Petrov, N. Hellgren, L. Hulman, J.-E. Sundgren, and J. E. Geene, J. Appl. Phys. **84**, 6034 (1998).
[12] T. D. Moustakas, R. J. Molna, and J. P. Dismukes, Electrochem. Soc. Proc. **96-11**, 197 (1996).
[13] H. A. Al-Brithen and A. R. Smith, Appl. Phys. Lett. **77**, 2485 (2000).
[14] R. Monnier, J. Rhyner, T.M. Rice, and D.D. Koelling, Phys. Rev. B **31**, 5554 (1985).
[15] R. Eibler, M. Dorrer, and A. Neckel, Theor. Chim. Acta **63**, 133 (1983).
[16] W. R. L. Lambrecht, Phys. Rev. B **62**, 13 538 (2000).
[17] P. Blaha, K. Schwarz, and J. Luitz, *WIEN97: A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Austria, 1999).
[18] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[20] S. H. Wei and A. Zunger, Phys. Rev. Lett. **56**, 2391 (1986).
[21] T. Li, H. Luo, R. G. Greene, A. L. Ruoff, S. S. Trail, and F. J. DiSalvo, Phys. Rev. Lett. **74**, 5232 (1995).
[22] H. Luo, R. G. Greene, K. Ghandehari, T. Li, and A. L. Ruoff, Phys. Rev. B **50**, 16 232 (1994).
[23] J. E. Jaffe, J. A. Snyder, Z. Lin, and A. C. Hess, Phys. Rev. B **62**, 1660 (2000).