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First principles calculations of the ground state properties and structural phase transformation in YN

Luis Mancera¹, Jairo A Rodríguez¹ and Noboru Takeuchi²

¹ Departamento de Física, Universidad Nacional de Colombia, Sede Bogotá, Colombia

² Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apartado Postal 2681, Ensenada, Baja California, 22800, México

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Abstract

We have studied the structural and electronic properties of YN in rock salt (sodium chloride), caesium chloride, zinc blende and wurtzite structures using first-principles total energy calculations. Rock salt is the calculated ground state structure with $a = 4.93 \text{ \AA}$, $B_0 = 157 \text{ GPa}$. The experimental lattice constant is $a = 4.877 \text{ \AA}$. There is an additional local minimum in the wurtzite structure with total energy $0.28 \text{ eV/unit cell}$ higher. At high pressure ($\sim 138 \text{ GPa}$), our calculations predict a phase transformation from a NaCl to a CsCl structure.

1. Introduction

Due to their excellent physical properties that include high hardness, mechanical strength and high melting point [1, 2], transition metal nitrides have a wide range of technological applications. These materials crystallize in the rock salt structure and they can be either metals or semiconductors. There has recently been interest in ScN, a transition metal nitride semiconductor. Early experiments [3] and first principles calculations based on the local density approximation [4] seemed to indicate that ScN was a semimetal with an almost zero indirect band-gap. However, recent experiments have shown that ScN is a semiconductor [5–8]. These results have been confirmed by calculations using techniques such as screened exchange (SX) and quasiparticle corrections [9, 10]. They have shown that ScN, YN, GdN and LaN are indirect semiconductors with gaps of $\sim 1\text{--}2 \text{ eV}$. Therefore, transition metal nitrides represent a novel and probably technologically important group of semiconductor materials. ScN has a very small lattice mismatch with GaN ($<2\%$) and therefore it has been thought to be useful to combine ScN with GaN as GaN/ScN heterostructures or ScGaN alloys. Very recently, smooth epitaxial growth of singly oriented ScN films was achieved [5–8, 11], showing the possibility of using ScN as an electronic material. In particular, Smith *et al* have reported the growth of ScN smooth films using radio frequency molecular beam epitaxy (RF-MBE) [11–13]. They have found that under N rich conditions, the growth in the (001) orientation is two-dimensional, and it results in atomically smooth surfaces with (1×1)

periodicity [11]. First principles calculations have shown that for N rich surfaces the most stable configuration corresponds to the ideal relaxed surface [14, 15]. However, for the Sc rich regime, the most stable configuration corresponds to N vacancies in the first layer, and the surface is metallic. ScN is not only stable at high temperature, but as shown by first principles calculations, ScN in its rock salt structure is also stable up to very high pressures [16]. In this paper, we examine the structural and electronic properties of YN, another transition metal semiconductor. In particular, we wanted to check the stability of YN in the rock salt structure with respect to the zinc blende and wurtzite structures. It is well known that the ground state configuration of group IIIA–V materials is wurtzite. However, depending on the substrate and growth conditions, a zinc blende phase can be formed [17]. Since many compounds that are stable in the rock salt structure show a phase transformation to a caesium chloride structure at high pressure, we were also interested in studying the high pressure behaviour of YN. Our calculations show that rock salt is indeed the ground state structure of YN. There is an additional local minimum in the wurtzite configuration, with total energy 0.28 eV/formula unit higher. This is quite a large energy difference, and therefore it will be difficult to stabilize a metastable wurtzite structure. However, the existence of a metastable wurtzite phase is important in the fabrication of ternary compounds with Ga or In, since the ground state configuration of GaN and InN is wurtzite. At ~ 138 GPa, our calculations predict a high pressure phase transformation to a CsCl structure.

2. 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 [18]. The exchange and correlation effects were treated using the generalized gradient approximation (GGA) [19, 20]. It should be noted that some of the calculated phases can be metallic. Therefore, a large number of integrating points over the irreducible Brillouin zone (BZ) was used: 72 k -points for the rocksalt, 56 for the CsCl structure, 60 for the wurtzite, and 116 for the zinc blende. We have used muffin-tin radii of $R_N = 1.6$ and $R_Y = 1.8$ au for the N and Y atoms respectively, angular momenta inside the muffin-tin sphere up to $l = 10$, and³ RKMAX = 8.

3. Structural properties

The total energy versus volume data for the rock salt, CsCl, zinc blende and wurtzite phases of YN are shown in figure 1. Energies and volumes are per single YN formula unit: there are two in a wurtzite cell and one in all the other cases. We have taken as the zero the sum of the energies of isolated neutral Y and N atoms. 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 1). In all cases, the fit is very good. To determine the most stable structure at finite pressure and temperature, the free energy $G = E + pV - TS$ should be used. Since the phase transformations reported for other NaCl \rightarrow CsCl phase transformations do not depend on the temperature, we neglect the last term and work with the enthalpy $H = E + pV$. We employ four crystal structures, and we cannot exclude the possible existence of other stable or metastable structures.

³ RKMAX determines the number of basis functions and it is equal to $R_{mt} \times K_{max}$, where $(K_{max})^2$ is the energy plane wave cut-off, and R_{mt} is the smallest of all atomic sphere radii.

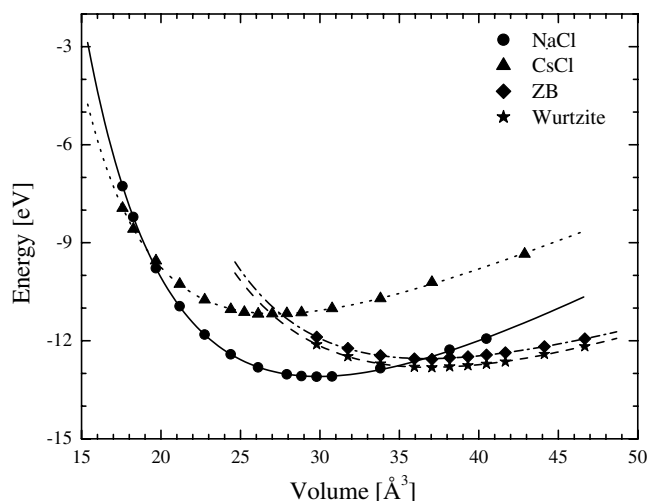


Figure 1. Total energy (in electronvolts/formula unit) versus the atomic volume (in \AA^3) for several structures of YN.

Table 1. Calculated structural properties of YN in the rock salt, caesium chloride, zinc blende and wurtzite structures. The value in parentheses corresponds to the experimental lattice constant of YN.

Structure	NaCl	CsCl	Zinblende	Wurtzite
a (\AA)	4.93 (4.877)	3.01	5.28	3.78
c/a				1.58
u				0.375
V (\AA^3)	29.89	27.27	36.74	36.93
B_0 (GPa)	157	136	110	115
B'_0	3.50	4.11	4.39	3.73
E_0 (eV)	-13.10	-11.18	-12.55	-12.82

The rock salt is the calculated ground state with $a = 4.93 \text{ \AA}$, and $B_0 = 157 \text{ GPa}$. The experimental lattice constant is $a = 4.88 \text{ \AA}$, indicating a good agreement between theory and experiment.

There is an additional local minimum in the wurtzite structure with total energy 0.28 eV higher. The existence of a metastable wurtzite phase is important in the fabrication of ternary compounds with Ga, or In, since the ground state configuration of GaN and InN is wurtzite. In figure 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. The common tangent between the NaCl and CsCl curves determines the transition path between the two structures. Because it is difficult to calculate accurate slopes from the common-tangent line, we have calculated $p(V) = -dE/dV$ to obtain the enthalpy $H = E + pV$ for the NaCl and CsCl phases as shown in figure 2. The transition pressure is obtained from the enthalpy curve crossings. We have then inverted the expression $p(V) = -dE/dV$ to obtain the respective volumes. We can predict the transition pressure to be $\sim 138 \text{ GPa}$. At this pressure the enthalpies of both structures are equal. Across the transition, there is a volume reduction of about 9% from 20.0 to 18.3 \AA^3 . Similar transitions, from NaCl to CsCl structures, have been observed experimentally and predicted theoretically in other compounds [21–25].

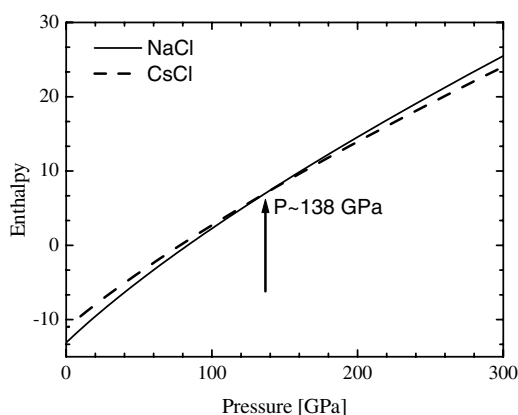


Figure 2. Enthalpy versus pressure for the NaCl and CsCl phases.

4. Electronic properties

Knowledge of the electronic properties is crucial to the understanding of the stability of the different structures at different volumes. Two different factors determine the response of YN to pressure: (a) changes in nearest-neighbour distances, and (b) changes in symmetry. These two factors are related to the band structure: the changes in nearest-neighbour bond-lengths affect the overlaps and bandwidths of the bands, while the changes in symmetry affect the p–d hybridization and band-repulsion. To see how these two factors affect the electronic properties, we present in figures 3(a)–(f) total and partial density of states (DOS) and in figures 4(a)–(f) band structures for YN at six different configurations or densities: (a) the rock salt phase at zero pressure, (b) the rock salt structure just before the phase transition (P_T), (c) the CsCl phase after the transition, (d) the CsCl phase at zero pressure, (e) the wurtzite phase at zero pressure, and (f) the zinc blende phase at zero pressure. Figure 3(a) shows total and partial DOS of YN in the rock salt structure at zero pressure. Three main regions can be observed in the total DOS: one below -10 eV and mainly due to nitrogen 2s electrons, another between -5 eV and the Fermi level due to nitrogen 2p electrons with a small contribution from Y 4d electrons, and the last one in the empty states region with the biggest contribution from Y 4d electrons and a smaller contribution from the other electrons. These results indicate that there is a strong hybridization between the N states and Y states: the partial DOS for the N and Y atoms are very similar in energy position and shape. Therefore, the bonding of this material has a covalent-like character as seen by the hybridization of N and Y states, but there is also an ionic component with a charge transfer from the Y atom to the more electronegative nitrogen atom.

Upon compression of the rock salt phase of YN (figure 3(b)), the bands broaden, indicating a stronger interaction between Y and N atoms. Some mixing between the valence and the conduction bands can be observed. With the rocksalt \rightarrow CsCl transition, the Y 4d states are heavily hybridized with the N 2p states (figure 3(c)). In the CsCl structure, YN is fully metallic. This result is observed not only at high pressure, but also at the equilibrium volume of the CsCl structure (figure 3(d)). We can observe that the different regions in the DOS are wider for the case of higher pressure, indicating more interaction between the Y and N atoms.

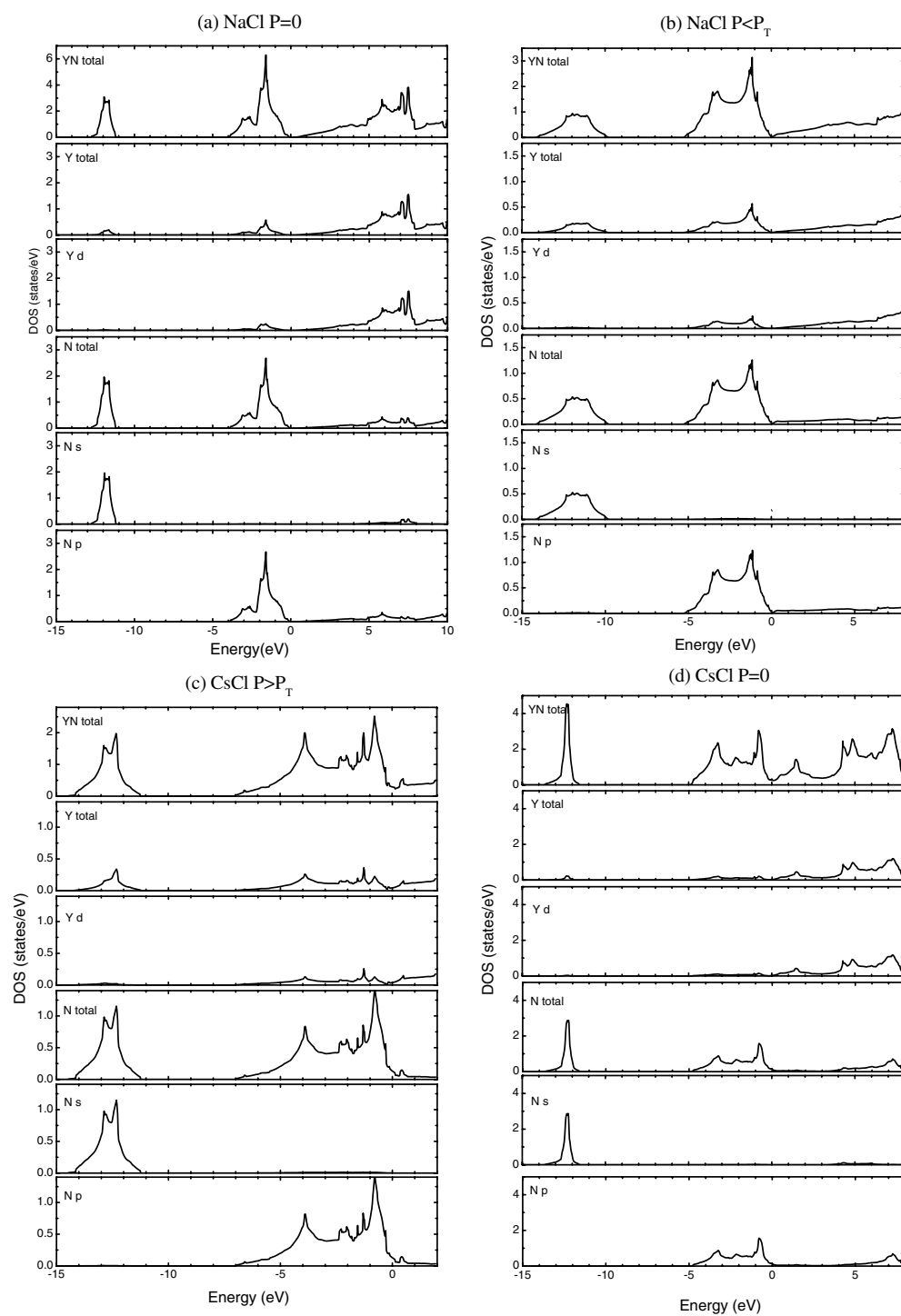


Figure 3. Total and partial DOS for YN in (a) the rock salt structure at $p = 0$, (b) the rock salt structure before the transition ($p < P_T$), (c) the caesium chloride phase after the transition ($p > P_T$), (d) the caesium chloride phase at $p = 0$, (e) the wurtzite structure at $p = 0$, and (f) the zinc blende structure at $p = 0$.

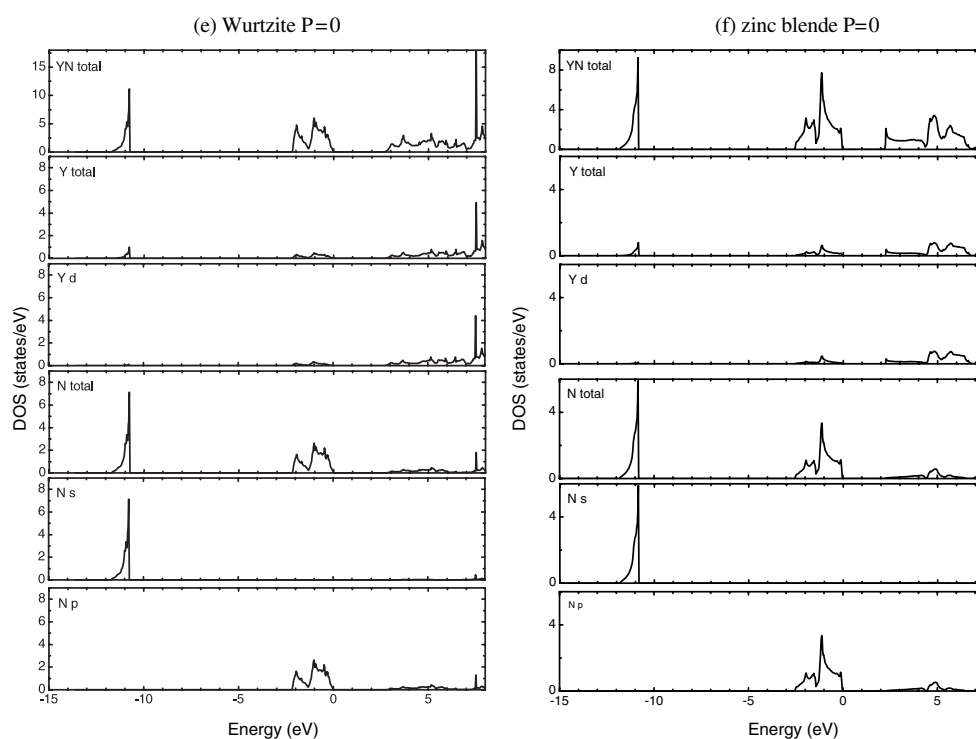


Figure 3. (Continued.)

In figure 3(e), we show the total DOS of the wurtzite phase at zero pressure. As in the rock salt structure at zero pressure, three regions dominated by N 2s, N 2p and Y 4d states can be observed. A large band-gap indicates semiconductor behaviour. Similar results are found for the zinc blende phase (figure 3(f)). The positions and widths of the peaks are similar to those of the wurtzite phase. These results are not surprising, since 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 neighbour). This similar behaviour has been observed in other nitrides [26].

The band structures provide more information on the electronic properties. Figure 4(a) shows the band structure of YN in the rock salt structure at zero pressure. It is very similar to the band structure of ScN. It shows a small 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 Stampfl *et al*, SX corrections result in a fundamental indirect band-gap of ~ 0.85 eV. Figure 4(b) shows the band structure of YN in the rock salt structure before the phase transition. As in the total DOS, there is a broadening of the upper Y 4d and N 2p bands, with some intermixing between them. As a result, YN becomes metallic. Figure 4(c) shows the band structure of YN in the CsCl structure after the high pressure phase transition. It shows a metallic behaviour and the Y 4d and N 2p states are completely hybridized and cannot be disentangled. A similar result is found for the YN in the CsCl structure at zero pressure (figure 4(d)). The structure shows a metallic behaviour, but now the bands are narrower. This is an indication that Y and N are interacting less, due to the larger distance between them. In figures 4(e) and (f) we show the band structures

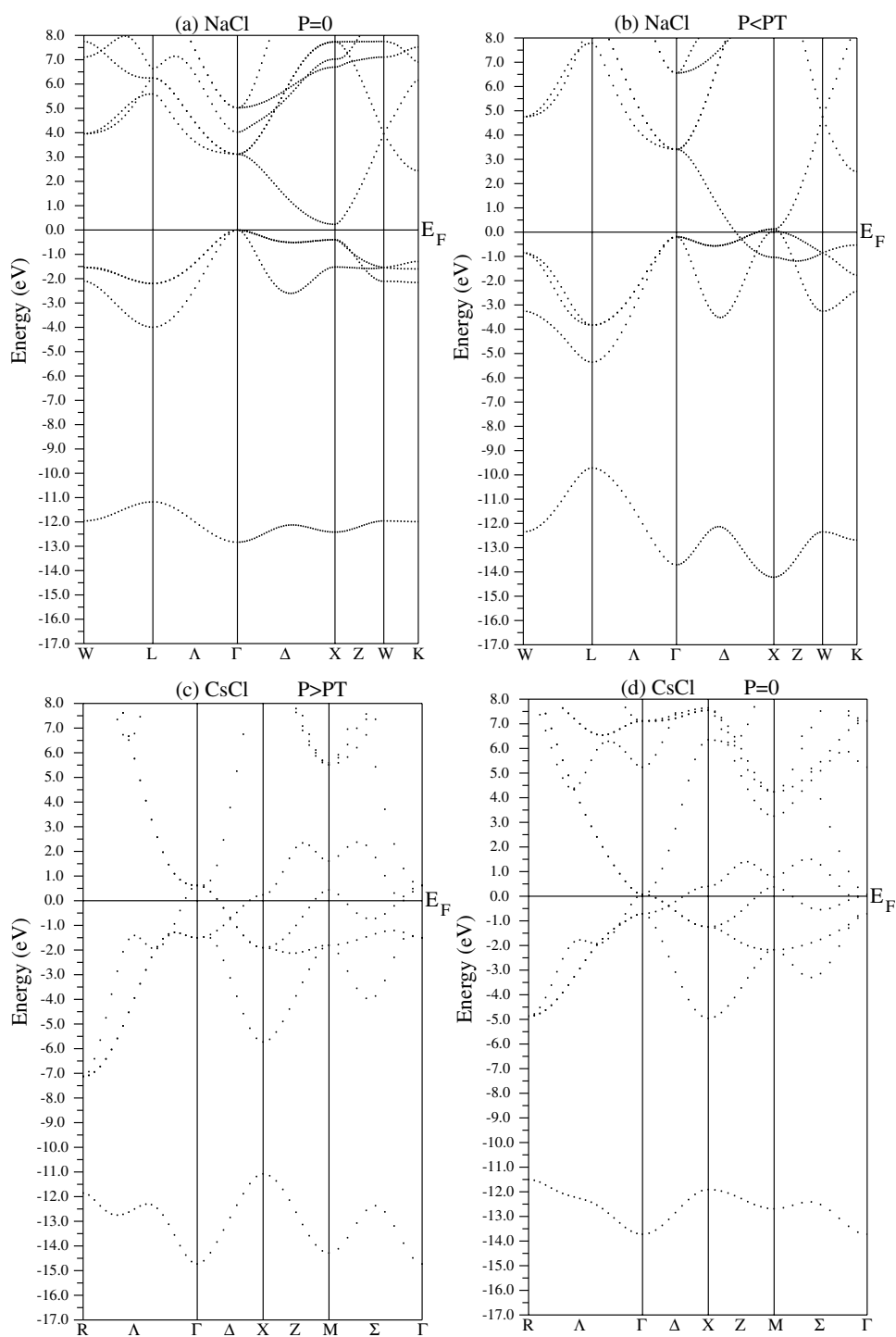


Figure 4. Band structure for YN in (a) the rock salt structure at $p = 0$, (b) the rock salt structure before the transition ($p < P_T$), (c) the caesium chloride phase after the transition ($p > P_T$), (d) the caesium chloride phase at $p = 0$, (e) the wurtzite structure at $p = 0$, and (f) the zinc blende structure at $p = 0$.

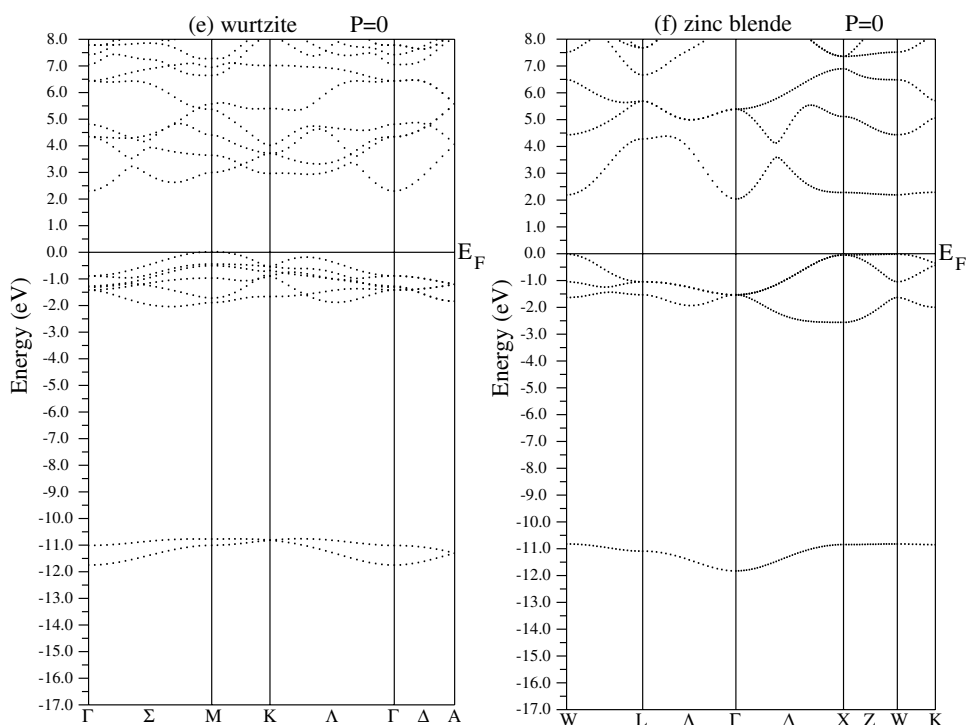


Figure 4. (Continued.)

of YN in the wurtzite and zinc blende structures respectively (at the equilibrium volume or zero pressure). The results are similar for both structures and they show a large indirect band-gap $\gtrsim 2$ eV. We again have to remember that the Kohn–Sham eigenvalues underestimate band-gaps in semiconductors. So we expect a larger band-gap, similar to the one of GaN [26]. YN could replace GaN in GaInN alloys used in the search of materials with intermediate band-gaps. From figures 4(e) and (f), we can observe narrow valence bands, indicating a weak bonding in the wurtzite and zinc blende structures.

To understand the stability of YN in the NaCl structure we follow the Harrison and Straub description in [27]. The five d levels on each Y atom interact with the three p levels on each neighbouring N atom forming p–d σ bonds and p–d π bonds. This coupling yields two non-bonding bands, three bonding and three anti-bonding bands. Thus, rocksalt YN, with six valence electrons (excluding the N 2s states), fills all the available bonding states while leaving the remaining non-bonding and anti-bonding states completely unoccupied as shown in figure 3(a). This filling of states results in a strong and stable structure.

5. Summary

In summary, we have performed first principles total energy calculations of YN in the rock salt, caesium chloride, zinc blende and wurtzite structures. The rock salt is the ground state configuration, but a second local minimum in a wurtzite structure is found with total energy 0.28 eV higher. The calculated lattice constant of 4.93 Å is in very good agreement with experimental results. Our calculations show the possibility of a phase transformation to a

caesium chloride structure at ~ 138 GPa. Although the predicted transition pressure is high, we hope these calculations stimulate experimental work with YN at high pressures.

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