Relative phase and physical properties of CrN/AlN multilayer: A DFT study

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Abstract. Using first principles total-energy calculations within the framework of density functional theory, we studied the relative stability and the structural and electronic properties of multilayer CrN/AlN in the sodium chloride (NaCl), cesium chloride (CsCl), nickel arsenide (NiAs), zinc-blende, and wurtzite structures. The calculations were carried out using the method based on pseudopotentials, employed exactly as implemented in Quantum-ESPRESSO code. Based on total energy minimization, we found that the minimum global energy of CrN/AlN is obtained for the zincblende structure. Additionally, at high pressure our calculations show the possibility of a phase transition from the zincblende to NaCl structure. For the zincblende phase, the density of states analysis reveals that the multilayer exhibits a half-metallic behavior with a magnetic moment of 3.0µβ/Cr-atom. These properties come essentially from the polarization of Cr-d and N-p states that cross the Fermi level. Due to these properties, the multilayer can potentially be used in the field of spintronics or spin injectors.

1. Introduction
The group III nitrides, such as aluminum nitride (AlN), have been the subject of many intense investigations during the last few years. This interest is partially motivated by their promising applications in the field of optical devices in the violet region [1]. They are also used as electronic packaging material and are applied to optical disks as well as lithographic photo masks [2-4]. AlN stabilizes in the wurtzite structure in bulk form, but can also be grown in the zincblende structure under appropriate conditions [5, 6]. On the other hand, chromium nitride stabilizes in the zincblende structure [7]. This material has excellent properties, such as a high degree of hardness, brittleness, a high melting temperature, good electrical-thermal conductivity and superconductivity, which makes it suitable for many important technological applications, for example hard coatings, cutting tools, and punching machines [8-13]. Additionally, over the last few years there has been a great deal of interest in developing new and improved ultrahard materials using the group III nitrides and a metal transition ion. Experimental studies show that these superhard compounds can be grown; for example, a TiN/GaN multilayer was grown via reactive pulsed laser deposition [14, 15], while an AlN/VN multilayer was grown via reactive sputtering [16]. Additionally, the combination of the semiconductor properties of AlN and the magnetic properties of the transition metal ions is currently of great interest because of its potential applications in diluted magnetic semiconductors (DMS) [17, 18]. For this reason, in this paper we report a detailed theoretical calculation of the structural and electronic properties of CrN/AlN in order to determine the energetically most favorable structure. We present the results of the calculated structural and magnetic properties in the zincblende, wurtzite, rock-salt, CsCl,
and NiAs structures, and finally, we present a study of the electronic properties of the most favorable phase, the zincblende structure.

2. Computational method

The calculations were performed within the DFT framework using the Quantum Espresso package [19]. The correlation and exchange effects of the electrons were dealt with using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [20]. Electron-ion interactions were studied using the pseudopotential method [21, 22]. The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40 Ry. For the charge density, a kinetic energy cutoff of 400 Ry was used. The calculations were performed taking into account the spin polarization due to the presence of the Cr atom. To calculate the lattice constant, the bulk modulus, and the total energy of each studied superlattice, the calculated data were fit to the Murnaghan equation of state [23]. The CrN/AlN multilayer was modeled according to the special quasirandom structures approach [24], and the disorder aspects were ignored.

To determine the structural properties in the ground state, such as the lattice constant ($a_0$), bulk modulus ($B_0$) and total energy ($E_0$) of the CrN/AlN multilayer in the CsCl, NaCl, NiAs, zincblende, and wurtzite structures, the total energy was calculated as a function of the volume and the results were fit to the Murnaghan equation of state, Equation (1).

$$E(V) = E_0 + \frac{B_0 V}{B_0 - 1} \left[ \left( \frac{V_0}{V} \right)^{\frac{B_0}{B_0 - 1}} - 1 \right] - \frac{B_0 V_0}{B_0 - 1}$$

where $B_0$ is the bulk modulus, and its first derivative is $B'_0$.

3. Results and discussions

3.1. Structural properties

Figure 1 shows the energy-volume curves for the CrN/AlN multilayer. It can be noted that the five structures considered in this study are metastable, because for each of the energy-volume curves there is a minimum energy value. In Figure 1, we can clearly see that the zincblende phase is the energetically most favorable structure, because it has the lowest minimum energy value. Additionally, we can see that the curve corresponding to the zincblende phase crosses the curve of the NaCl structure of smallest equilibrium volume. This indicates a high-pressure phase transition from the zincblende to the NaCl structure. In order to analyze the phase transformation under high pressure, the Gibbs free energy equation $G=E+PV-TS$ can be used. Since the calculations are for the ground state ($T=0^\circ K$), the last term of the Gibbs energy equation can be neglected, and by working with the enthalpy, the Gibbs free energy equation reduces to $H=E+PV$ [25, 26]. We use this equation for the five crystal structures considered in this paper; however, we cannot exclude the possible existence of other stable or metastable structures for the CrN/AlN multilayer.

Figure 2 shows the enthalpy as a function of pressure for the zincblende and NaCl phases. We note that the compound will transform from a zincblende structure to NaCl at a transition pressure of $P_T=2.5\text{GPa}$. Note that before the transition ($0<P<P_T$), the lowest values of enthalpy correspond to the zincblende phase. This shows the relative stability of the zincblende phase within this pressure range, while for higher values of the transition pressure ($P>P_T$), the NaCl phase has the lowest values of enthalpy. Therefore, within this pressure range, NaCl is the most stable phase. At this transition pressure, the enthalpies of both structures are equal. Across the transition, there is a volume reduction of about 17.75%, from 42.899\AA$^3$ to 35.284\AA$^3$. A similar transition phase was reported by Casiano et al. in their study of the relative stability of the CrN compound [27].
Figure 1. Total energy as a function of the volume of the CrN/AlN multilayer in the FM states.

Figure 2. Enthalpy as a function of pressure in the NaCl and zincblende phases of CrN/AlN multilayer.

Table 1 shows the structural parameters of CrN/AlN, calculated for the phases CsCl, NaCl, NiAs, wurtzite, and zincblende.

Table 1. Structural parameters lattice constant (a₀), bulk modulus (B₀), and total energy (E₀) of the superlattices.

| Phase    | a₀ (Å) | c/a | V₀ (Å³) | B₀ (GPa) | E₀ (eV) | μ (μβ) |
|----------|--------|-----|---------|----------|---------|--------|
| CsCl     | 2.5401 | -   | 32.733  | 266.082  | -3078.917 | -2.8   |
| NaCl     | 2.9240 | 1.414| 35.284  | 188.988  | -3082.645 | -3.0   |
| NiAs     | 4.4146 | -   | 42.899  | 177.491  | -3082.554 | -3.0   |
| Zincblende| 2.8753 | 1.696| 34.924  | 230.821  | -3083.117 | -4.1   |
| Wurtzite | 3.1561 | 1.613| 43.927  | 172.011  | -3082.774 | -3.0   |
We can see that the phase with the lowest value of energy corresponds to the zincblende structure. Additionally, we can see that the value of the bulk module (230.821 GPa) of the CrN/AlN multilayer in the zincblende phase is higher than the bulk modules of CrN (204.5 GPa) [27] and AlN (191.85 GPa) [28], which confirms that they are quite rigid, making them good candidates for possible applications in devices operated at high temperature and high power, as well as in hard coatings.

3.2. Electronic properties
Figure 3(a) shows the total and partial spin-polarized density of states of the CrN/AlN multilayer in the zincblende phase. Figure 3 shows that they are half-metallic and ferromagnetic. This result occurs because in the valence band close to the Fermi level, the majority spins (spin-up) are metallic, and the minority spins (spin-down) are semiconductors. These compounds have a spin polarization of 100% of the conduction carriers in the ground state, which is a requirement for spin injectors [29, 30].

This finding suggests that this compound can be efficiently used for spin injectors. Figure 3(a) shows that in the valence band near the Fermi level, the spin-up density of the majority spins (up) is mainly dominated by the Cr-3d states, and to a lesser extent by the N-2p states, which cross the Fermi level. The magnetic properties essentially come from the chromium atom, and can be attributed to the Cr$^{3+}$ configuration, because the Cr atom in the superlattice donates three electrons, and the Cr atom retains two valence electrons (the electronic configurations Cr$^{3+}$=[Ar]3d$^3$). These valence electrons couple ferromagnetically, and as a result the three electrons produce a total magnetic moment of 3μ$_B$/atom-Cr. Figure 3(b) shows the electronic band structure for up and down spin. The band structure confirms that the multilayer has a half-metallic character, because the minority spin down (dn) states preserve a band gap, but in the majority spin (up) states there is a penetration toward the prohibited energy zone of the 3d-Cr states in a greater proportion and the 2p-N and 2p-Al states in a lesser proportion.

![Figure 3](image)

*Figure 3.* (a) Total and partial density of state (b) Electronic band energy for the CrN/AlN multilayer.

4. Conclusions
We reported first-principles calculations to determine the structural, electronic, and magnetic properties of a AlN/GaN multilayer for the CsCl, NaCl, NiAs, zinc-blende, and wurtzite structures, within the framework of density functional theory using the approach of the generalized gradient approximation (GGA). From the computation of the total energy versus unit-cell volume, the zincblende structure was found to be favored. We found that the transition pressure for the zincblende to the NaCl phase was about 2.5 GPa. The calculated values of the bulk modules are quite high; therefore, the multilayers are quite rigid, which makes them attractive for potential applications at high temperatures and for hard coatings. On the basis of the density of states for the zincblende phase, we
found that the multilayer exhibits a half-metallic behavior with a magnetic moment of 3\(\mu_B\)/Cr-atom. The ground-state ferromagnetic behavior comes from the polarization of the C-3d and N-2p orbitals, which cross the Fermi level. These compounds are good candidates for potential applications in spintronics and can be used as spin injectors.

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