Study of the structural and electronic properties of YC using DFT: The true ground state is a NiAs-like structure

G P Abdel-Rahim\textsuperscript{1,2}, J A Rodriguez\textsuperscript{2} and M G Moreno-Armenta\textsuperscript{3}

\textsuperscript{1} Grupo PERSEO, Universidad Antonio Nariño, Sede Bogotá, Colombia.
\textsuperscript{2} Grupo de Estudio de Materiales - GEMa, Departamento de Física, Universidad Nacional de Colombia, Sede Bogotá, Colombia.
\textsuperscript{3} Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, BC, México.

E-mail: pabdelrahim@gmail.com

Abstract. We study the structural and electronic properties of YC in volume using density functional theory (DFT) within the generalized gradient approximation (GGA), using the scheme of Wu-Cohen 2006 and Tran et al. 2007. Several crystal structures were considered: Nickel Arsenide (NiAs), Sodium Chloride (NaCl), Cesium Chloride (CsCl), and zincblende (ZB). A new fact that we present in this paper is the inclusion of the NiAs-like structure, which is the true ground state (GS) for YC. We calculated the density of states (DOS) and the band structure and found that YC is non-magnetic and its behavior is metallic-like. The lattice parameter $a_{\text{lat}}$ is 3.69 Å and the $c/a = 1.47$. Cohesion energy (Ecoh) is -12.90 eV, which is very close to Ecoh of the NaCl structure. Therefore, YC exists in these two structures. Our results with respect to $a_{\text{lat}}$, bulk modulus (B), Ecoh, and the main features of the electronic properties are in good agreement with those found by other researchers. Other researchers found a transition from NaCl to CsCl, but we found a new transition from NiAs to CsCl, where the volume diminishes ~10% and its transition pressure ($P_T \sim 79$ GPa) is very close to the 80 GPa of the former. The contraction can fracture the material if it is worked on near the transition. For pressures before and after the transition, YC maintains non-magnetic and metallic behaviors.

1. Introduction

The 4d-transition metal carbides (4d-TMC) are studied mainly due to their many industrial applications for mechanical parts and the fact that they are highly resistant materials. Additionally, 4d-TMC preserve various types of chemical bonds, such as the ionic, metallic and covalent ones. Other properties that increase the great number of industrial applications are their high degree of hardness, high melting point, and good electrical and thermal conductivity [1-5]. Pooja Soni [1] studied the structural properties in phases such as NaCl and CsCl using DFT with the exchange and correlation potential GGA of Perdew, Burke (GGA-PBE). They found a phase transition from NaCl to CsCl, at $P_T \sim 80$ GPa. The study by K. K. Korir [2] of the 4d-TMC and 4d-TM nitrides in phases NaCl, ZB, and wurtzite, using DFT with the Local Density Approximation (LDA) method and GGA-PBE, showed that the experimental values of Ecoh of the carbides or nitrides are close to those calculated with GGA-PBE. In Jemeson's study, the electronic, structural, and elastic properties of YC and ScC in the NaCl phase are shown, which were calculated using LDA and GGA-PBE96.
2. Method

Calculations were carried out using WIEN2k code [6], within the framework of DFT, with the GGA approximation of Perdew, Burke, and Emzerhof [7]. Because phases can exhibit a metallic behavior, a large number of k-points over the Irreducible Brillouin Zone (IBZ) were taken into account. We used about 135 k-points in IBZ. The muffin-tin radii were 1.99 and 1.77 a.u. Calculations were considered convergent if the difference of the total energy of successive iterations were consistent within a range of 10^-4 Ry. The base functions inside the muffin-tin spheres were expanded up to lmax = 10, on the basis of spherical harmonics, and the energy for the expansion of the wave function on the plane wave basis was limited by Rmt × Kmax = 7.0, where Rmt is the minimum muffin-tin radius. When it was necessary to optimize the c/a ratio and the volume, we used a recurrent process to optimize them, which included a minimizing of the forces in order to find the best atomic positions; the process was considered finished when the difference between the c/a and the volume of two successive calculations was less than 0.1 %.

3. Structural properties

![Energy vs. volume for the compound YC in several structures](image1)

![Enthalpy vs. pressure for NaCl and CsCl](image2)

**Figure 1.** Energy vs. volume for the compound YC in several structures.

**Figure 2.** Enthalpy vs. pressure for NaCl and CsCl.

**Table 1.** Structural parameters of YC. B is the bulk modulus and B’ its derivative with respect to pressure.

| Structural Parameter | Structural Phase |
|----------------------|------------------|
|                      | NaCl             | CsCl             | ZB                | NiAs             |
|                      | TW*              | TW*              | TW*              | TW*              |
| a_min [Å]            | 5.086^a, 5.01^b, 5.09^b | 5.11^c, 5.19^d   | 5.04            | 3.10^e           | 3.08            | 5.47^f           | 5.39            | 3.69            |
| c/a                  | ---              | ---              | ---              | ---              | ---              | ---              | ---              | ---              |
| B [GPa]              | 124.18^a, 124.3^b, 1262^c | 122.40           | 120^d            | 117.8            | 80.50^e           | 88.41           | 119.7           |
| B                    | 4.14^a, 4.451^c  | 4.04            | 4.12^a           | 3.50            | 11.53^b           | 3.36            | 3.15            |
| E_coh [eV]           | 12.03^a, 12.79^d  | -12.87          | -11.84           | -11.88           | -12.90           |

^a Reference 1, ^b Reference 2, ^c Reference 4 (experimental), ^d Reference 5, ^e Reference 3, ^ TW meaning this work.

Figure 1 shows the $E_{coh} = E_{comp} - E_{C} - E_{M}$ as a function of volume by unit formula. $E_{comp}$ is the total energy by unit formula, and $E_{C/M}$ the total energy of the carbon/metal free atoms. Other authors use $-E_{coh}$ instead of the above definition. The solid lines are the adjustment to Murnaghan's equation state [8]. One can conclude, from figure 1, that the GS is in the NiAs-like phase. The structural parameters are shown in Table 1, and a comparison with the results of other researchers can also be observed. The $E_{coh}$ in the structure NaCl is only 0.03 eV higher than for the NiAs-like structure. That difference is very small, and permits the material to exist simultaneously in the NaCl and NiAs phases. By contrast, the $E_{coh}$ of the structure ZB is ~1 eV higher than the value of NiAs-like phase. Therefore, the ZB phase is almost impossible to find spontaneously. A second conclusion from Figure 1 is that according to the behavior of the curves of the NiAs-like phase and that of the CsCl-like phase, there is a high-pressure
phase transition. Figure 2 shows that the pressure at which the transition occurs is \( P_T \approx 79 \) GPa. Based on table 1, one additional conclusion about the structural properties of YC is that the \( a_{\text{latt}} \) of the NaCl phase calculated with GGA-WC is under-estimated when compared with the results that one can find using GGA-PBE. Also, this fact is observed by means of comparison of the \( a_{\text{latt}} \) obtained by theoretical methods [1-3] and experimental ones [4] with those obtained using GGA-WC.

4. Electronic properties

This section is devoted to the study of the electronic properties of YC in the GS. Figures 3 and 4 show the total and partial DOS at pressure \( P=0 \), i.e. at the minimum of the function \( E \) vs. \( V \) in Figure 1. The energy is referenced taking as the origin the Fermi level (EF). Although the calculations included spin, we only show only one spin component, because both DOS were identical. Therefore, YC is non-magnetic in its GS. In these figures, we see three regions: the first is a narrow peak below \(-6.4\) eV due mainly to the s-C orbital (see figure 3), plus a small contribution by the p-Y orbitals (see figure 4). The second region is located between EF and \( E \approx -4 \) eV, where we can see the upper valence band (VB), which is composed of 2p-like C orbitals (pz and px+py orbitals of C) and 3p-like Y and 3d-like Y orbitals. These orbitals are hybridized in this energy region. At EF, the DOS very quickly descends toward almost zero; this fact permits one to conclude that the material exhibits a metallic-like behavior. The last region is the conduction band (CB), which is linked to the valence band (VB) without an energy gap, and this region is formed mainly by d-like Y orbitals. Figure 5 shows the bands at the GS and the metallic-like behavior is evident. The bottom VB (\(-7\) eV to \(-10\) eV) is composed of two s-like C bands, and additionally there is a small component of a 3p-like Y orbital. There are two bands, because the NiAs phase has two lattice points in the Bravais lattice. Therefore, in figure 3, two small peaks are present in the DOS in this region. In this zone, the electron states show little dispersion, and they are localized in a narrow band of \(~3\) eV. In contrast, the upper VB and the bottom CB show great dispersion, which produces delocalized states.

![Figure 3. GS total and partial DOS due to C.](image1)

![Figure 4. GS total and partial DOS due to Y.](image2)

5. The features of the high pressure transition

In this section, we analyze the structural and electronic changes before and after the transition between the NiAs and CsCl phases. Understanding properties in different phases is important because in applications YC can suffer a phase transition because of increasing pressure or temperature. Changes in the electronic properties are determined by changes in the length of the bonds, the hybridizations, and the symmetries. As we mentioned above, the transition occurs at \( P_T \approx 79 \) GPa. There is a volume reduction of \(~10\)% from \(23.66\) Å\(^3\) to \(21.23\) Å\(^3\), and this compression can fracture the crystal; this is not desirable. Therefore, the material must be worked on at a pressure below \(79\) GPa. Figures 6 and 7 show the bands before and after the transition, respectively. In both phases it is non-magnetic and metallic. The bottom VB changes from two bands to only one. This modification is due to the different number of lattice points in the Bravais lattices. In the upper VB and in the CB, the hybridizations are similar to the hybridizations in the GS, but other changes of the bands are great and can be observed in the figures.
6. Conclusions
Calculations of structural and electronic properties of YC were carried out by means of DFT using the Wu-Cohen GGA approximation. Several phases were considered, and the GS is in the NiAs-like phase. YC, in the GS, is non-magnetic and metallic. \( a_{\text{lat}} = 3.69 \) Å for this phase and the \( c/a = 1.47 \). Its cohesion energy is about -12.90 eV. It is always possible that the YC exist simultaneously in two structures: NaCl and NiAs. A new phase transition (at PT~79 GPa) from NiAs to CsCl was found, where the volume reduces by about 10%; the pressure transition is very close to 80 GPa, which is the pressure for the change from NaCl to CsCl. During the transition, YC could fracture if it is worked on near transition. Before and after the transition, YC is non-magnetic and metallic.

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References
[1] Pooja Soni, Gitanjali Pagare, Sankar P Sanyal 2011 *Journal of physics and Chemistry of solid* 72 810-16
[2] K K Korir, G O Amolo, N W Makau and D P Joubert 2011 *Diamond Related Materials* 20-2 157-64
[3] Jameson Maibam, B Indrajit, Sharma, Ramendu Bhattacharjee, R K Thapa, R K Brojen Singh 2011 *Physica B* 406 4041-45
[4] P V Villars, L D Calvert 1985 *Pearson’s Handbook of Crystallographic Data for intermetallic Phases* (Ohio: ASM International, Materials Park)
[5] A F Guillermet, J Haglund, G Grimvall, M Smith 1192 *Phys. Rev. B* 45 11557
[6] P Blaha, K Schwarz and J Luitz 1999 *A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* (Austria: Techn Universität Wien)
[7] J P Perdew, K Burke, M Emzerhof 1196 *Phys. Rev. Lett.* 77 3865
[8] F D Murnaghan 1944 *Proc. Natl. Acad. Sci.* 30 5390