NANOMATERIALS SCIENCE & ENGINEERING
Vol. 6, No. 1, pp. 27-37 (2024)

RESEARCH ARTICLE

https://doi.org/10.34624/nmse.v6i1.35515

Impurity and Vacancy analysis in Zig-Zag (8,0) carbon nanotubes

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Received 11 November 2023; accepted 18 April 2024; published online 6 May 2024

ABSTRACT

Nanoscience and nanotechnology have generated billions of dollars annually, generating jobs and new products. This is an area that involves the study and manipulation of nanoscale materials (nanomaterials, on the order of 10^{-9} m). One class of nanomaterials that has aroused significant interest in the scientific community are those carbon compounds (examples include graphene, carbon nanotubes and fullerenes), especially due to their potential applications in industry. In the present work, we carried out a study on defects (absence of carbon atoms) and Ni doping in the electronic properties of a zigzag carbon nanotube containing 32 carbon atoms. Our results indicated semiconductor behavior when two vacancies are present in the structure and also an increase in the energy level of the conduction band, valence band and Fermi level when the systems are doped with Ni. Finally, for systems doped with Ni, there was a greater probability of charge exchange occurring between the 2p orbitals of carbon and the 2p orbitals of carbon to the 3d orbitals of Nickel.

1. INTRODUCTION

Nanotechnology is an area that has always been shown to be very present in our lives, even without us realizing its presence. In recent decades, it has experienced rapid growth, impacting fields such as science, technology, and healthcare [1]. It is a technology that seeks to understand a system on a nanoscale, with precision from atom to atom, to create structures with a distinctive organization capable of exhibiting behaviors and properties different from commonly known materials [2]. There are various fields that benefit from the applications of nanotechnology products, including electronics, cosmetics, agriculture, medicine, among others. One of the several products derived from nanotechnology that is widely used are carbon nanotubes (CNTs). Some examples of applications include: Catalysis, photocatalysis and photoelectrocatalysis. For example, CNTs combined with titanium dioxide (TiO_2) have been used in photocatalysis to generate hydrogen from water [3]. According to Herbst, Macêdo, and Rocco, CNTs are formed from hexagonal arrangements of carbon that give rise to small cylinders [4]. Carbon nanotubes can be classified based on their structure and the arrangement of carbon atoms along the nanotube. Considering the structure, carbon nanotubes can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Figure 1). Single-walled carbon nanotubes consist of a single sheet of graphene rolled into a cylindrical shape. When nanotubes include other nanotubes, they are referred to as multi-walled carbon nanotubes.

When analyzing the arrangement of atoms, carbon nanotubes can be classified into three categories: armchair, zigzag, and chiral. We can characterize the structure of an SWCNT as a pair of indices (n, m) that describe the chiral vector and directly have an effect on electrical properties of

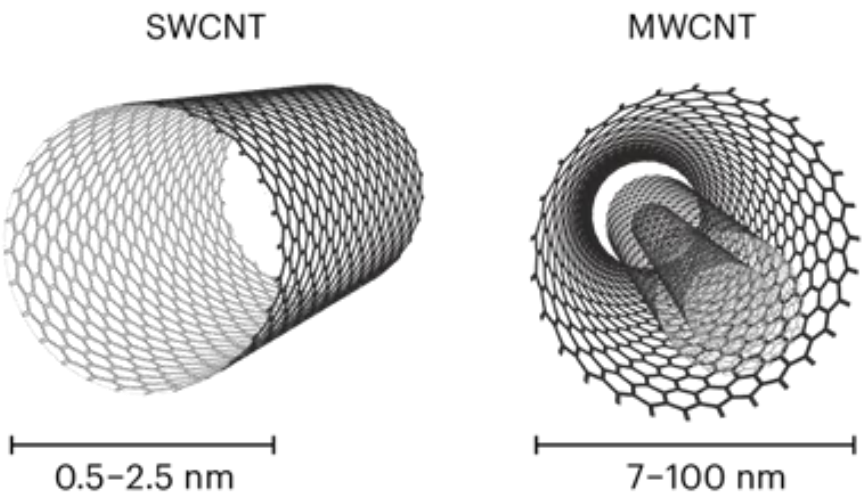

Figure 1. Single-walled nanotubes (left) and multi-walled nanotubes (right). Source: [5].

nanotubes. The number of unit vectors in the honeycomb crystal lattice of graphene along two directions is determined by the integers n and m. As a common opinion, when m = 0, the nanotubes are named zigzag nanotubes; when n = m, the nanotubes are named armchair nanotubes, and other state are called chiral [6] (Figure 2).

The properties exhibited by carbon nanotubes vary depending on the category in which they are classified: carbon nanotubes can “grow” in a different pattern. Although each tube has the same ingredient (carbon atoms arranged in a hexagonal lattice), the level of conductivity varies with chirality (the angle at which this carbon sheet is oriented relative to the tube axis). It ranges from metallic for “armchair” tubes to semiconductor in the case of “zigzag” or “chiral” tubes [5].

During the manufacturing process of carbon nanotubes, defects may occur, such as the absence of atoms. Such defects may interfere with their chemical and physical properties. In general, defects can modify the properties of carbon nanotubes depending on the method used to generate them, their concentration, and the type of nanotubes. In some cases, defects can help increase the adhesion of carbon nanotubes to a

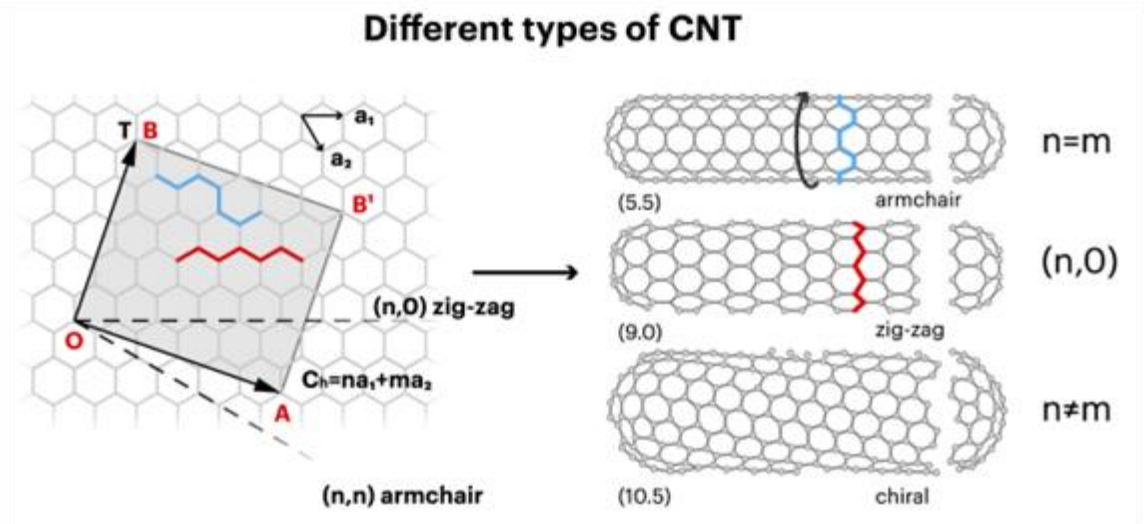

Figure 2. Different types of carbon nanotubes in terms of atom arrangement. Source: [5].

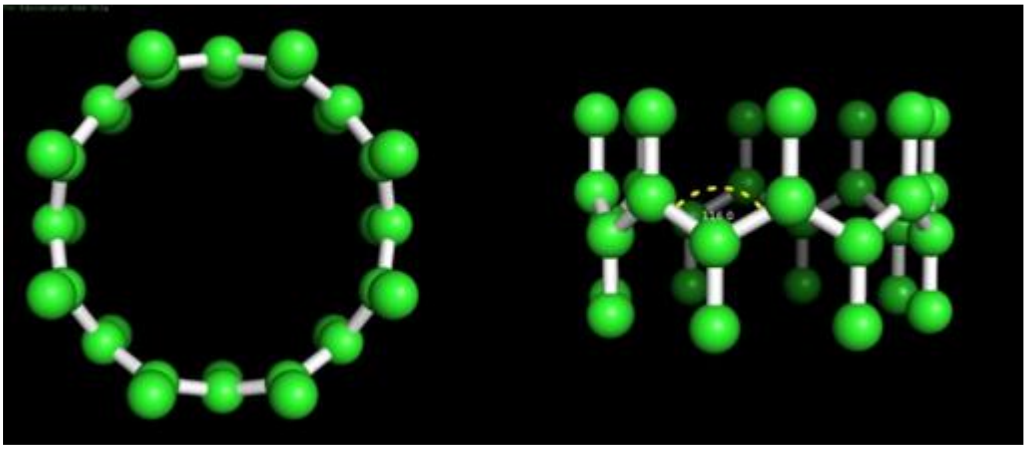

Figure 3. Defect free carbon nanotube.

polymer matrix, when mixing them to create a composite material. This could be beneficial to both the mechanical and electrical behavior of polymer nanocomposites that use CNT as fillers. Also, defects could improve the properties of carbon nanotube bundles by helping create defect-mediated covalent bonds between SWCNTs in bundles or between shells of MWCNTs. In carbon nanotubes, defects can be generated, for example, by irradiation or by chemical treatment [7].

As this is a quite common situation, the aim of this work is to conduct a study on defects in carbon nanotubes and additionally the effect of Nickel doping and how they can affect their properties.

2. METHODOLOGY

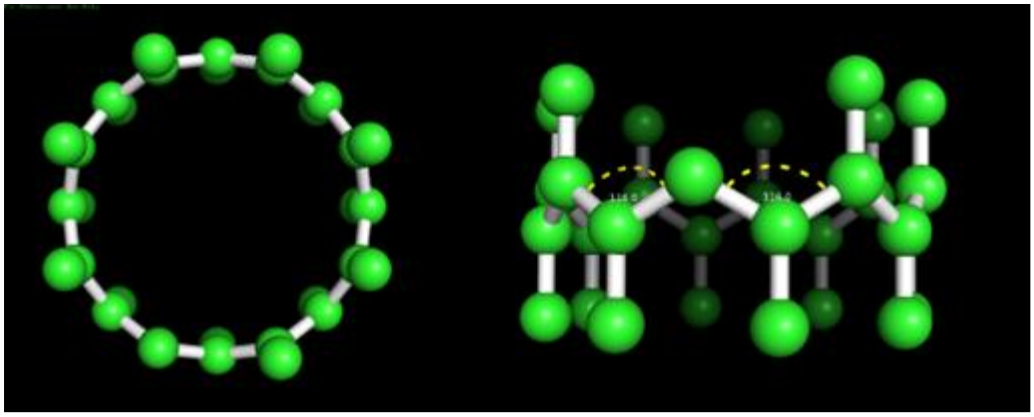

Figure 4. Carbon nanotube with one carbon vacancy.

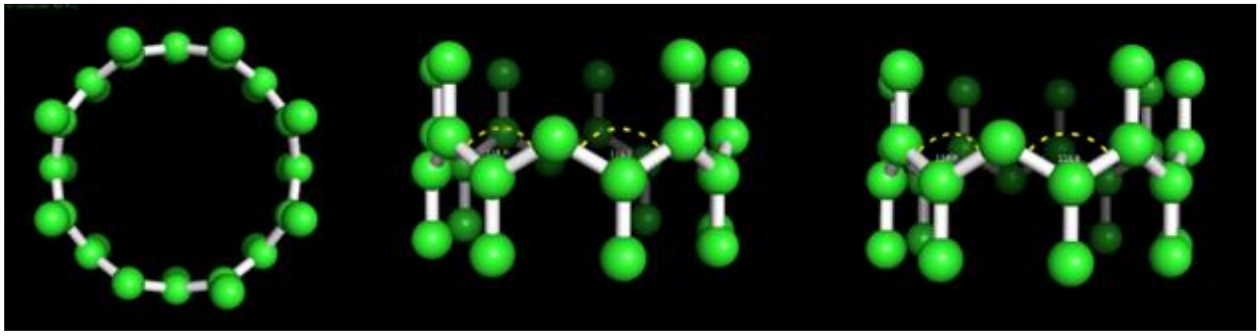

Figure 5. Carbon nanotube with two carbon vacancies. The middle figure shows one side where a carbon has been removed, and the figure on the right indicates the immediately opposite side.

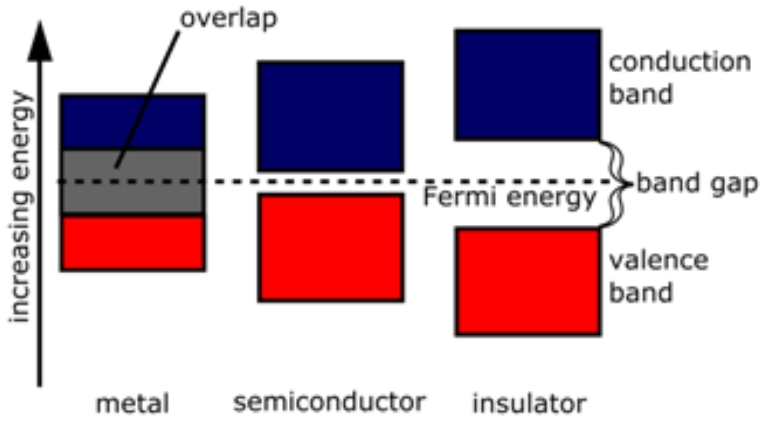

Figure 6. Illustration of the band gap. Source: Adapted from the reference [13].

In this work, a (8,0) zigzag-type carbon nanotube (CNT) composed of 32 carbon atoms was used to analyze the effects of carbon atom vacancies and Ni impurity on the electronic structure. The distance between carbon atoms (C-C) was between 141 Å and 1.42 Å, and the angle between three carbon atoms was 116º (Figure 3). Figures 3, 4 and 5 were generated by the pymol program [8]. The structure of the CNT, together with the input files for the Siesta program [9] used in this work, was obtained from Castillo's work [7]. The method employed in this work and implemented in Siesta was Density Functional Theory (DFT), and the exchange-correlation functional used was of the local density approximation (LDA) type with the CA parameterization. The carbon atom pseudopotential required for the calculations was obtained from the reference [10]. A thermodynamic correction was applied for a temperature of 300 K, with a kinetic energy cutoff for plane waves set at 300 Ry, and the following symmetry points were used to analyze the solid-state energy bands: G (0, 0, 0) and X (0, 0, 1). These points are in the unit cell constant with a value of 4.257 Å, considering a cubic unit cell with parameters a = b = c = 4.257 Å and α = β = γ = 90º. A relaxation of the structure coordinates was allowed through a geometry optimization using conjugate gradients with 200 steps and a force minimization criterion between atoms of 0.04 eV/Ang.

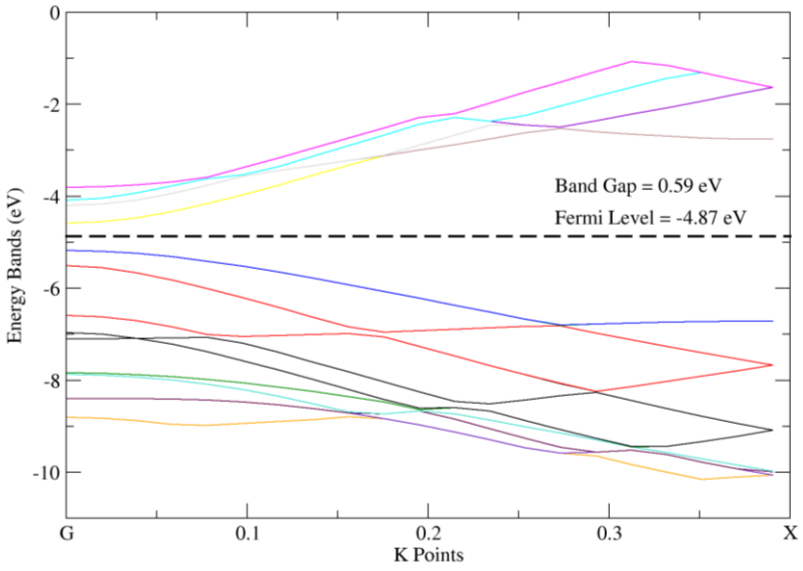

Figure 7. Energy band diagram of a nanotube without carbon vacancies. Source: Adapted from the reference [7].

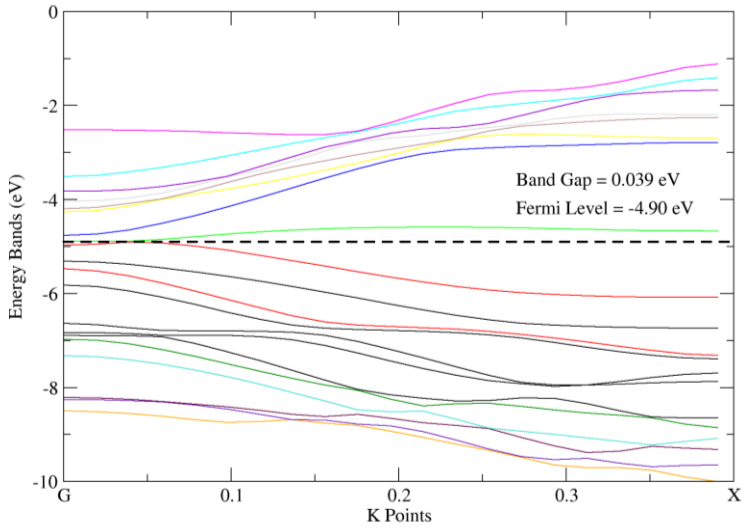

Figure 8. Energy band diagram of a nanotube with the vacancy of one carbon. Source: Adapted from the reference [7].

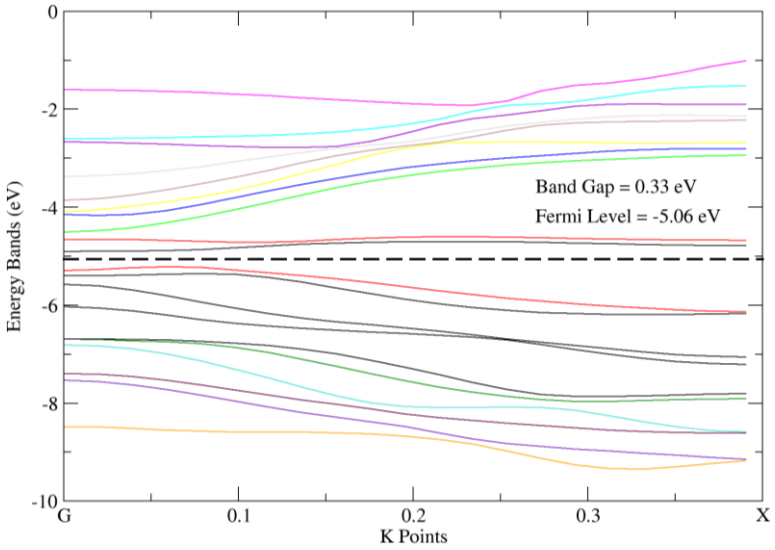

Figure 9. Energy band diagram of a nanotube with the vacancy of two carbons. Source: present work.

We use a supplementary program in Mathematica [11] and the Siesta utility programs to format the output data from the Siesta program into a format that can be recognized by GRACE [12]. With the data organized, we constructed the energy bands and density of states for each nanotube.

3. RESULTS AND DISCUSSION

After the calculations were performed, it was possible to calculate the band gap value of each nanotube. The "band gap" (E_g) consists of the separation between the valence band and the conduction band of the solid (Figure 6).

Insulating materials have $E_g > 4$ eV, semiconducting materials have $E_g < 4$ eV, and metallic materials have $E_g \approx 0$.

In Figures 7 (defect-free), 8 (one carbon vacancy), and 9 (two carbon vacancies), we present the energy band graphs of the CNT as a function of the k-points and also the Fermi energy and the value of E_g.

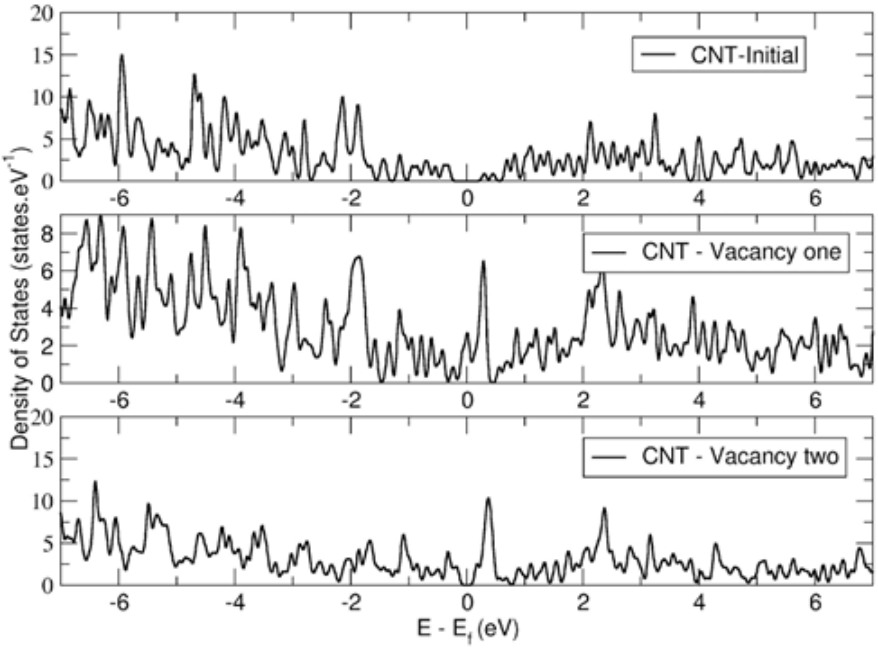

Figure 10. Density of states for three cases studied this work. Source: present work.

Removing a carbon atom causes an overlap of the valence and conduction bands, causing it to transition from a semiconductor state (E_g = 0.5898 eV) to a metallic one (E_g = 0.039 eV) [7]. When two carbon atoms are removed, the nanotube reverts back to exhibiting semiconductor properties (E_g = 0.326 eV). We attempted to replicate these defects in different positions/another carbon atoms, the results didn't change. These results are in agreement with those obtained by Orellana and Fuentealba [14] who carried out studies with (10,0) and (14,0) zigzag CNT using computational methods similar to those used in the present work.

Figure 10 displays the density of states (DOS) for the three cases mentioned above. The Fermi level is located at the origin of the abscissa axis and one can clearly see an absence of separation of density of states at the Fermi level, indicating a metallic character for the graph with one vacancy. With two vacancies, a slight separation of the density of states at the Fermi level is observed, indicating semiconductor behavior like the primitive CNT in agreement with the literature.

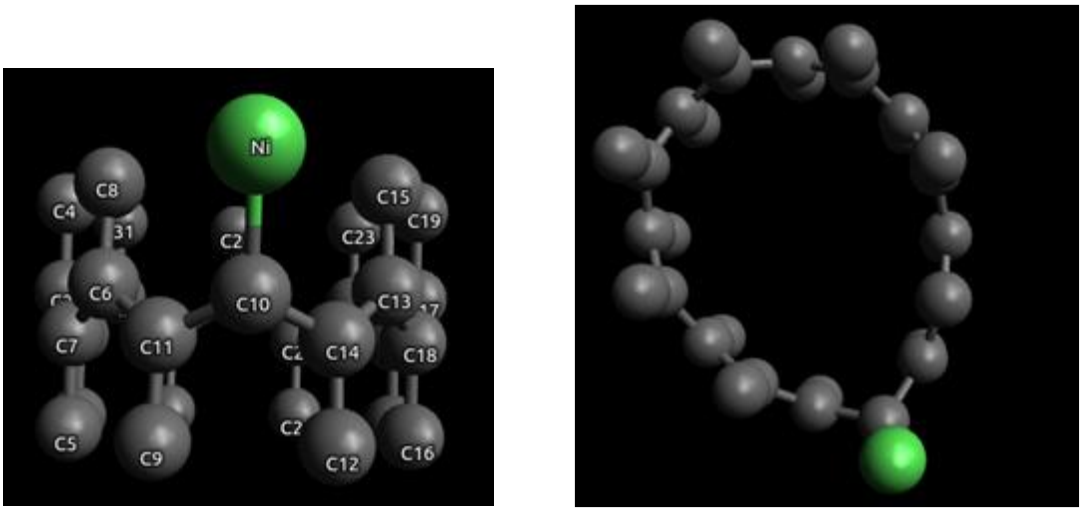

Figure 11. CNT doped with Ni. Source: present work.

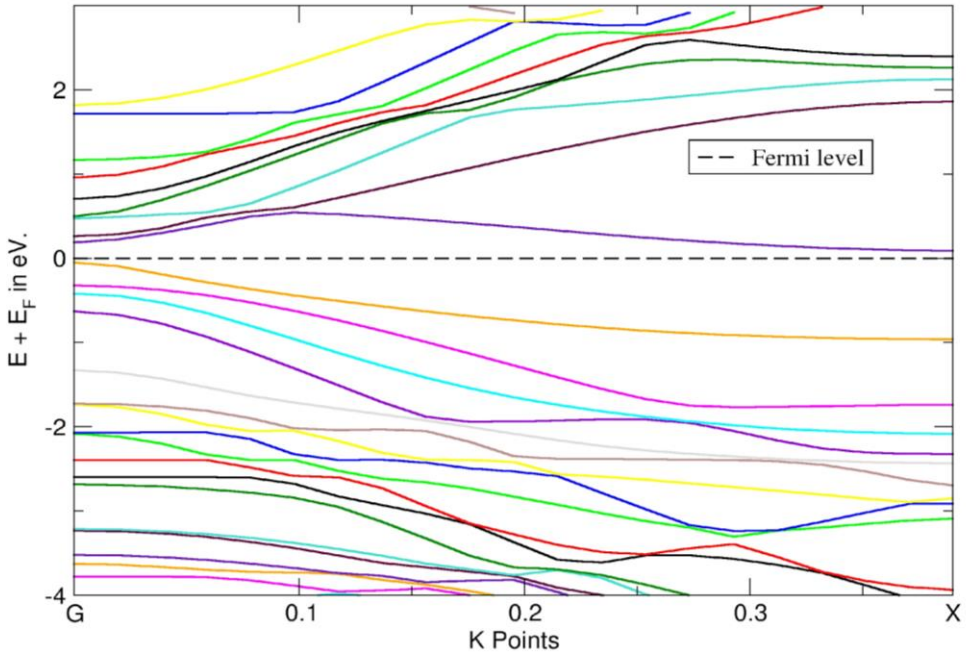

Figure 12. Energy band diagram of a nanotube doped with one Ni. Source: present work.

The inclusion of impurities composed of transition elements from the periodic table in CNT has indicated important applications in energy storage. For example, Yang and collaborators [15] carried out doping (by replacing a carbon atom) of an armchair CNT with chiral indices (6,6) with the following transition metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn and investigated quantum capacitance and electronic structure. The results indicated that doping with transition elements improves the quantum capacitance of carbon nanotube electrodes. The highest quantum capacitance was obtained with Ni doping [15]. Azevedo and collaborators [16] carried out the doping (by adding an impurity inside the carbon nanotube) of ziz-zag type CNT containing 64

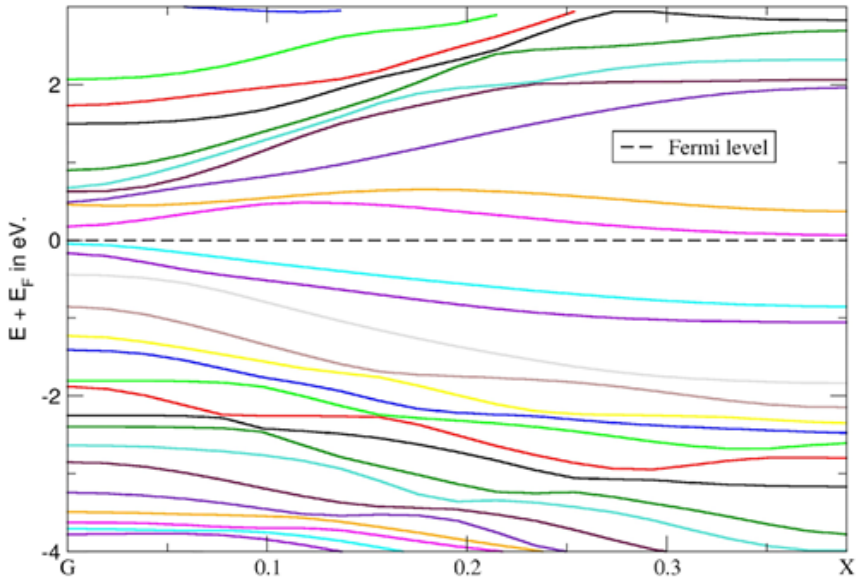

Figure 13. Energy band diagram of a nanotube with one vacancia doped with Ni. Source: present work.

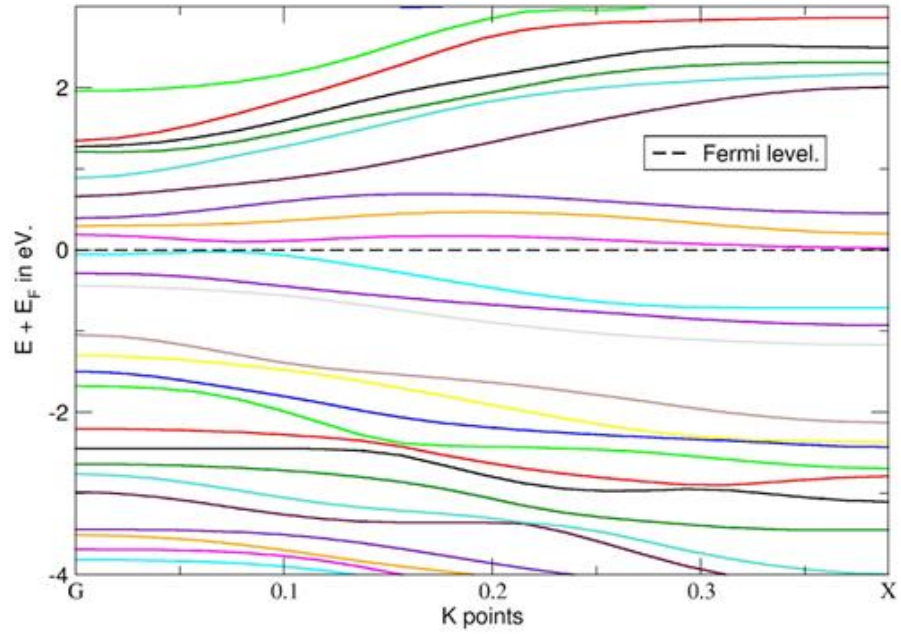

Figure 14. Energy band diagram of a nanotube with two vacancies doped with Ni. Source: present work.

carbon atoms with the Fe, Ni and Mn transition metals. They investigated the diameter's effect on stability and electronic properties. Some of the results indicated that the magnetization depends on the radius of curvature and increases with Mn impurities and decreases with Fe and Ni impurities. With the aim of contributing to the understanding of the behavior of impurities of transition elements in CNT in the present work we also investigated the behavior of the three cases discussed previously after doping with Ni atoms. We randomly replace a carbon atom by a Ni atom.

Figure 11 displays the molecular geometry after Ni inclusion and structure optimization. Regarding

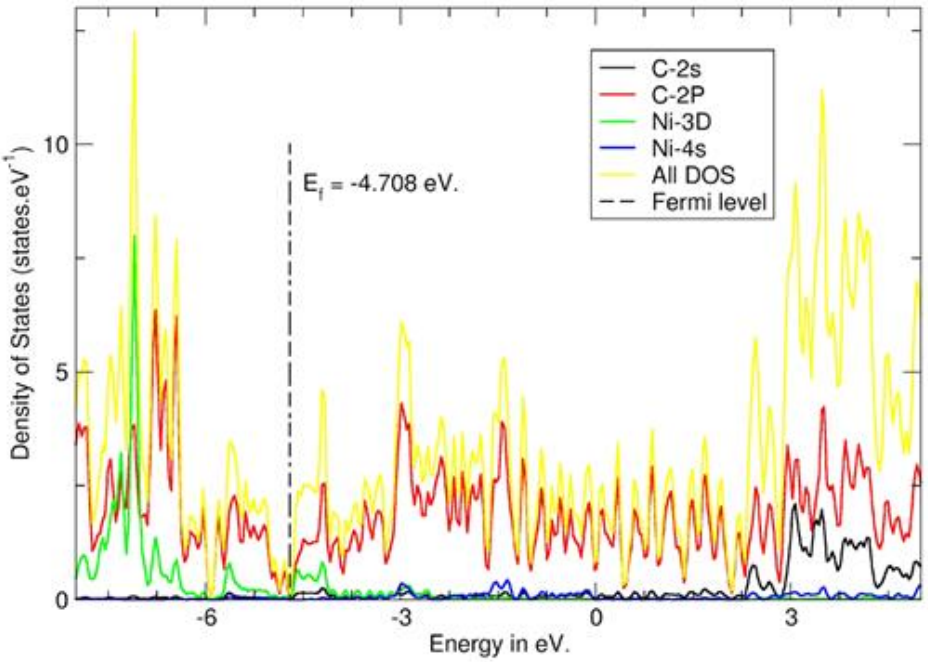

Figure 15. Partial and total density of states of the initial Structure doped with one Ni impurity (C31Ni).

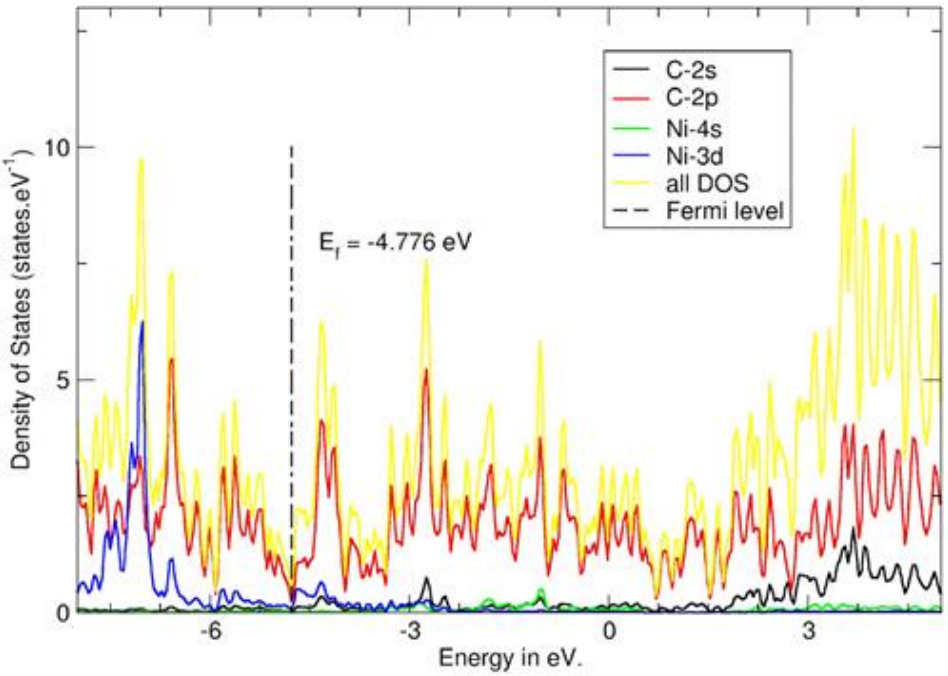

Figure 16. Partial and total density of states of the initial Structure doped with one Ni impurity and with one vacancy (C30Ni).

the bond length, the most abrupt changes occurred in the bonds between C10 - Ni (from 142 Å to 1.82 Å), C11 - C10 and C14 - C10 (from 141 Å to 1.49 Å). For the angular dimension, the most abrupt

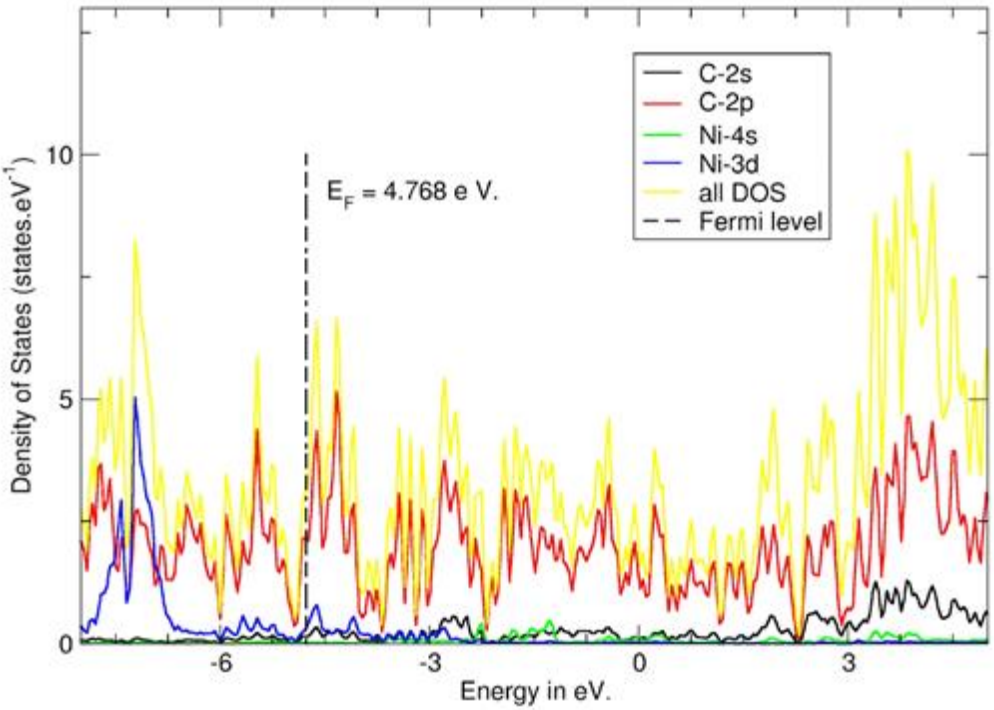

Figure 17. Partial and total density of states of the initial Structure doped with one Ni impurity and with two vacancy (C29Ni).

Table 1. Properties of nanotubes calculated in the present work.

Nanotube	valence band energy (in eV)	conduction band energy (in eV)	Fermi level (in eV)	Band gap (in eV)	behavior
C32	-5.18	-4.59	-4.87	0.59	semicondutor
C31	-4.92	-4.89	-4.90	0.04	metallic
C30	-5.23	-4.90	-5.06	0.33	semicondutor
C31Ni	-4.76	-4.62	-4.71	0.14	semicondutor
C30Ni	-4.82	-4.71	-4.78	0.11	semicondutor
C29Ni	-4.89	-4.58	-4.74	0.15	semicondutor

changes occurred for the angles between C6-C11-C10 and C10-C14-C13 (from 116º to 127º).

Figures 12, 13 and 14 show the energy bands with the Fermi level centred at the origin. The Fermi level was - 4.71 eV, - 4.78 eV and 4.74 eV and the band gaps were 0.14 eV, 0.11 eV and 0.15 eV for C31Ni (without vacancy), C30Ni (one vacancy), and C29Ni (two vacancy), respectively. The inclusion of Ni led to semiconducting behaviour in all three cases.

Figures 15, 16 and 17 show the density of states for the three cases C31Ni, C30Ni and C29Ni respectively:

For the three cases, we can observe, analyzing the densities of states, a greater probability of charge exchange occurring, between the valence and conduction bands, from the 2p orbitals to the 2p orbitals of carbon and from the 2p orbitals of carbon to the 3d orbitals of Nickel. In the present work, we do not consider the effect of spin polarization in our calculations.

Table 1 displays all the values of the properties calculated in the present work. We rounded to two decimal places.

It can be seen in table 1 that the presence of Ni increases the energy levels of the valence and conduction bands as well as the Fermi level, therefore explaining the change from metallic behavior (C31) to semiconductor (C30Ni) after doping with Ni.

4. CONCLUSIONS

In the present work, we present a study of the effect of carbon vacancies and Ni impurities on the electronic properties of zigzag-type CNT with chiral indices (8.0) and with 32 carbon atoms. Analyzes of energy bands and density of states were carried out in the absence of one and two carbon atoms and also analysis of these systems doped with Ni. Analysis of the results led to the following conclusions:

1 – Regardless of the position from which a carbon atom is removed, CNT behaves like a metallic material.

2 – Regardless of the position from which two carbon atoms are removed, the CNT once again behaves like a semiconductor material.

3 - For systems doped with Ni, it was found that the greatest probability of charge exchange occurring is from the 2p orbitals to the 2p orbitals of carbon and from the 2p orbitals of carbon to the 3d orbitals of Nickel.

4 – The presence of Ni increases the energy levels of the valence and conduction bands, as well as the Fermi level, therefore explaining the change from the metallic behavior of C31 CNT to the semiconductor behavior of 30Ni CNT after doping with Ni.

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