Materials Physics and Mechanics 10 (2010) 72-81 Received: December 4, 2010

BAND STRUCTURE, DENSITY OF STATES AND SUPERCONDUCTIVITY OF ADSORBED TITANIUM CHAINS ON (8,8) and (14,0) CARBON NANOTUBES

C. Nirmala Louis[1*], Sr. Gerardin Jayam[1] and A. Amal Raj[2]

[1]Department of Physics, Holy Cross College, Nagercoil- 629 004, Tamil Nadu, India.

[2]Department of Chemistry, St. Jerome's College, Nagercoil- 629 201, Tamil Nadu, India.

e-mail: nirmala_louis@yahoo.co.in

Abstract. The electronic band structure and density of states of (8,8) armchair and (14,0) zigzag single walled carbon nanotubes (SWCNT) are investigated using densityfunctional calculations. The band structure of the pure (14,0) zigzag nanotube indicates that it is a semiconductor where as the band structure of pure (8,8) armchair tube exhibits metallic behavior. When a titanium chain is adsorbed on the carbon nanotube, the (14,0) zigzag tube changes from semiconductor to metal and the (8,8) armchair tube transforms from metal to semiconductor. In both the cases there is a net transfer of charge from the metal chain atom to the carbon atom. The delocalized 3d electrons from the titanium chain generate additional states in the band gap regions of the semiconducting tubes transforming them into metals. The band structures of Ti adsorbed nanotubes are completely different from that of pure nanotubes. The band structure results are used to study the superconducting behaviour of pure (8,8) armchair nanotube and the Ti adsorbed (14,0) zigzag nanotube. The superconducting transition temperatures, T_c, for the pure (8,8) nanotube and the Ti adsorbed (14,0) nanotube are computed for different values of Debye temperature. The electron-phonon interaction and superconducting transition temperature are small in (8,8) armchair tube and considerable in Ti adsorbed (14,0) zigzag tube. Based on this, we hint at room temperature superconductivity in carbon nanotube.

1. Introduction

Ever since the discovery of carbon nanotubes [1-3] there has been lot of interest in the study of electronic structure [4-8] , electrica1 [9] and therma1 [10,1l] conductivity of these tubes. Many recent experiments have given the evidence of titanium atoms deposited on a single-wall carbon nanotube (SWNT) are capable of forming continuous wires. In view of the unusually high thermal conductivity exhibited by the carbon nanotube, researchers were looking for superconductivity. Subsequently intrinsic superconductivity was discovered in carbon nanotube [12-17]. On the theoretical side only a few calculations are reported regarding the band structure and superconductivity of carbon nanotube. This motivated us to take up this investigation. Nanotubes coated with a Ti buffer layer also have a better chance of forming continuous wires made of other metals. A nanotube with adsorbed materials may also significantly changes its physical properties, providing useful means for manipulating electronic transport for nanoelectronic devices. Moreover, understanding the interaction between titanium and nanotube will be helpful in reducing the contact resistance between nanotubes and metal leads, which is the challenging problem in the nanoelectronic applications [18-24]. (14,0) zigzag and (8,8) armchair nanotubes are chosen to study the effect of curvature on the electron-phonon interaction; which are close to the experimentally

measured diameter of the well separated nanotubes for which superconductivity has been observed [8].

2. Method of calculation

In the present work the band structure and density of states are obtained using a variant of zone folding method and Vienna *ab initio* simulation package VASP [1], a well known plane wave code uses density functional calculations. In the zone folding method we have chosen a unit cell which spirals along the length of the tube. Also we have used average density of states near the Fermi energy rather than density of states at the Fermi energy to take into account the role of van Hove like singularities which are unique for carbon nanotubes. The electron –phonon interaction is treated using McMillian's formula [25] in conjunction with the prescription by Gaspari and Gyorffy [26]. In most of the previous calculations [27-29] the electron-phonon interaction is treated using McMillian's theory and the effect of electron-electron interaction on pairing is taken into account assigning most probable values (0.1-0.2) to it. Therefore it is obvious that for systems like carbon nanotube we have followed the same treatment. We have used a unit cell which spirals up like a helix along the length of the tube. The allowed components of the k vectors due to confinement are obtained by projecting the k vectors along the circumferential direction. The binding energy between titanium atom and the nanotube is much greater than the case of Aluminium [20,30]. The 3d orbitals in titanium are rather delocalized and function as valence orbitals. The unfilled 3d shell of titanium leads to hybridization with 2p orbitals of carbon, results a stronger interaction between them. The tube radii for adsorbed titanium chains of (8,8) and (14,0) nanotube are 5.42 Å and 5.48 Å respectively. The metal-nanotube distance for adsorbed titanium chains of (8,8) and (14,0) nano tube are 2.11 Å and 2.24 Å respectively [7]. In the geometric structure of adsorbed titanium chains on (14,0) and (8,8) nanotube, along the tube axis each unit cell contains two titanium atoms for (14,0) tube and one Ti atom for (8,8) tube. Distances between the two neighboring titanium atoms in the titanium chain are 2.6 Å for (14,0) and 2.7 Å for (8,8) tubes [7,30].

3. Band structure

The band structures of pure and Ti adsorbed (14,0) zigzag and (8,8) armchair carbon nanotubes are given in Figs. 1-4. The characteristic features of these band structures are similar to that of the band structures reported previously [8,17]. The electronic structures of pure and Ti adsorbed (8,8) armchair and (14,0) zigzag carbon nanotubes are investigated by Chih-Kai Yang *et al.* [7]. The electronic structures of pure and Ni adsorbed carbon nanotubes and superconductivity of carbon nanotube coupled to Ni are investigated by Tit and Dharma-Wardana [17].

From the band structures (Figs. 1 and 2) it turns out that the pure (14,0) zigzag nanotube is a semiconductor where as the Ti adsorbed (14,0) zigzag nanotube is transformed into a metal. Even though in the atomic state 3d shell of Ti has two electrons, in the crystal state (carbon nanotube) there are more than two electrons in the 3d state leading to certain hybridization between this d orbital and the 2p orbital of carbon. Electron from carbon and titanium shells are delocalized and distributed among the four bands of Ti and carbon near the Fermi level and there is a net charge transfer from Ti to carbon (Table. 1) which causes the metallization. Similar feature is observed in the alkali metal intercalated SWCNT [20,30]. The above mentioned delocalization of conduction electrons of Ti and transfer of charge from Ti confirm effective contact between Ti and carbon nanotube. As pointed out by Chih-Kai Yang *et al.* [7] this observation might be helpful in reducing the contact resistance between carbon nanotube and metal leads [21,22].

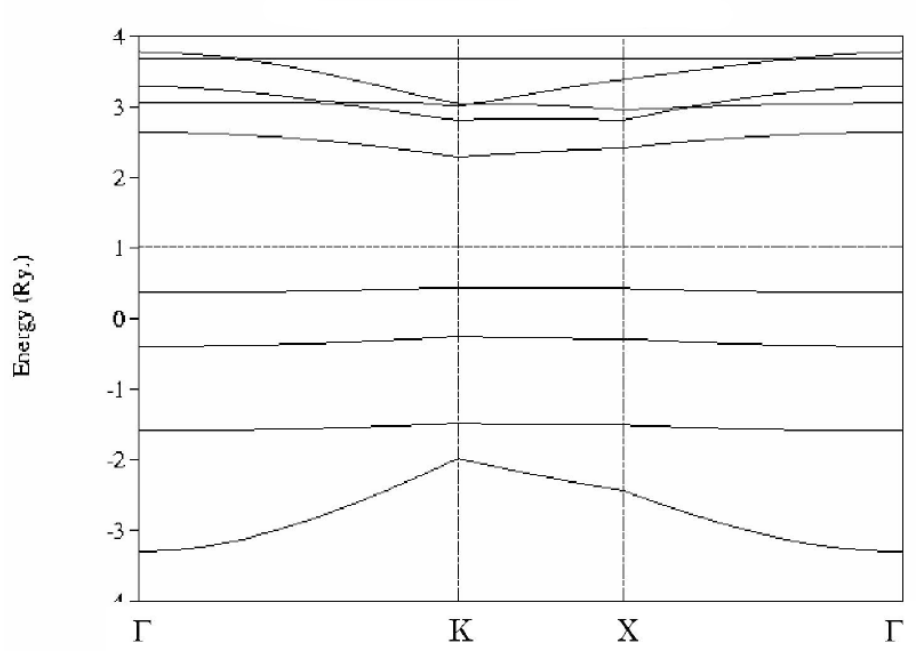

Fig. 1. Band structure of pure (14,0) CNT.

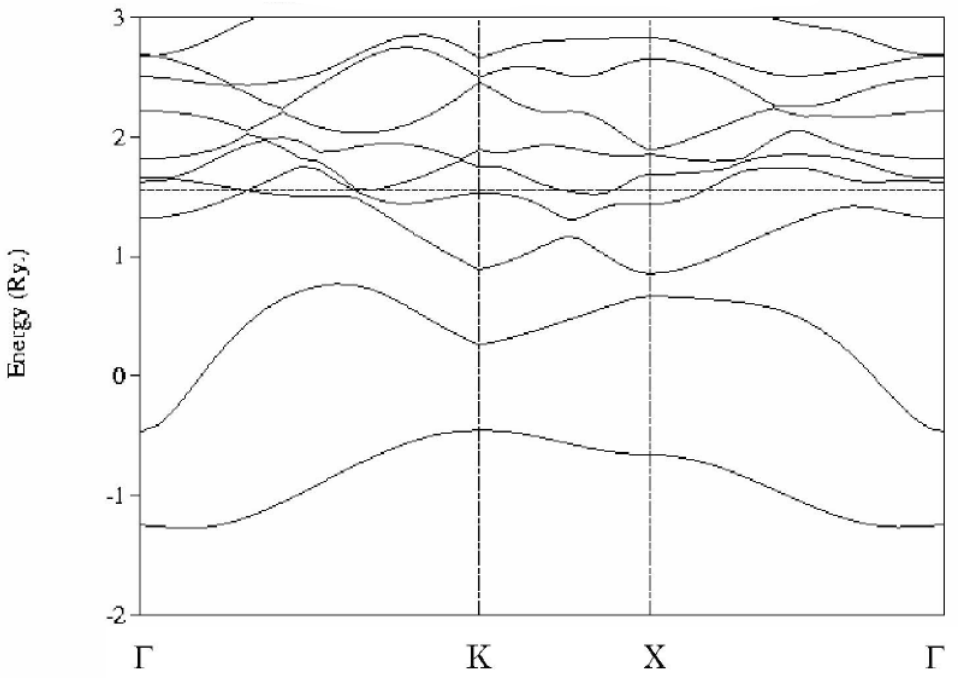

Fig. 2. Band structure of Ti-adsorbed (14,0) CNT.

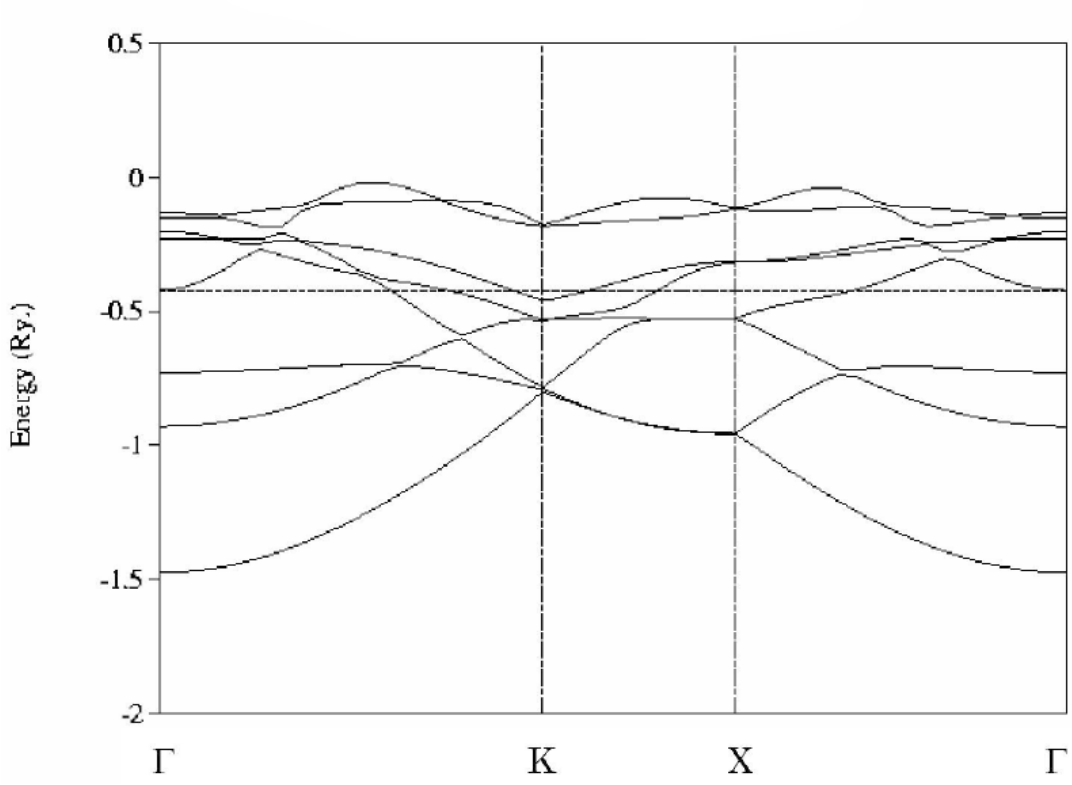

Fig. 3. Band structure of pure (8,8) CNT.

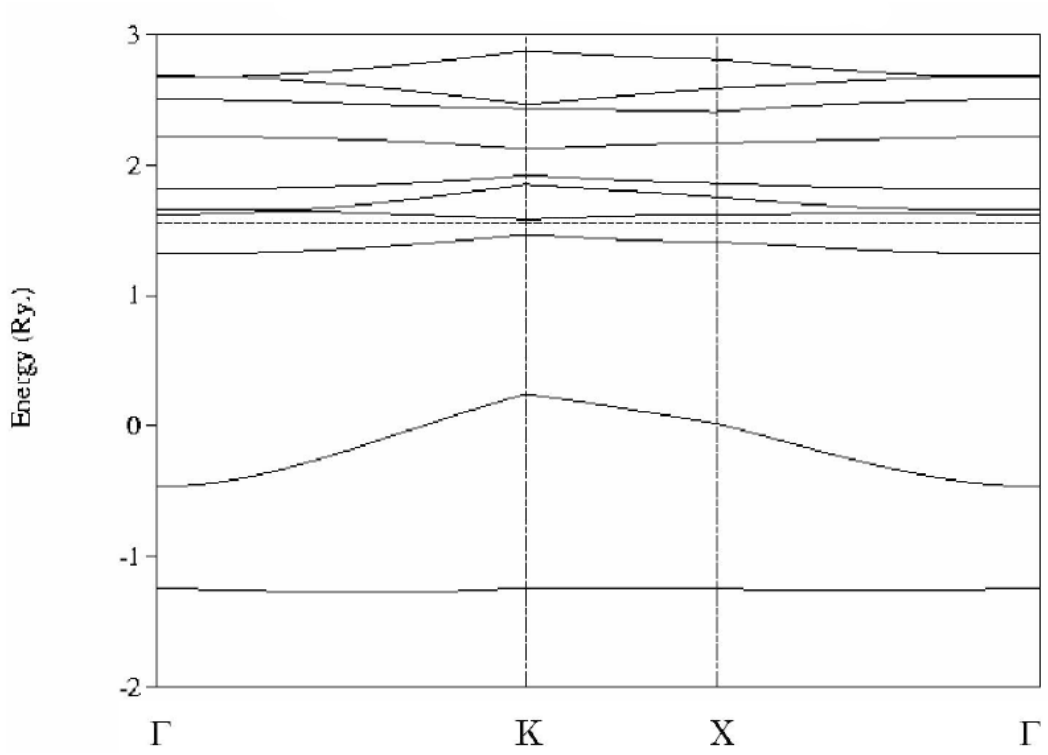

Fig. 4. Band structure of Ti-adsorbed (8,8) CNT.

Table 1. Electron distribution in various shells.

Nanotube	carbon			carbon or titanium		
	s	p	d	s	p	d
C-C (14,0)	0.745	2.424	0.832	0.745	2.424	0.832
C-Ti (14,0)	1.833	2.647	0.152	0.524	0.470	2.375
C-C (8,8)	1.084	2.565	0.351	1.084	2.565	0.351
C-Ti (8,8)	1.680	2.649	0.435	0.443	0.612	2.181

The band structures of pure and Ti adsorbed (8,8) nanotube are given in Figs. 3 and 4. The pure (8,8) nanotube is metallic where as the Ti adsorbed nanotube is semiconductor with a small gap but not a pseudo gap [8]. The band structure of Ti adsorbed carbon nanotube is very much modified compared to the band structure of pure (8,8) nanotube. The modified band structure of Ti adsorbed (8,8) nanotube is not simple superposition of those of individual nanotube and the titanium chain [8,17]. This modification in the band structure arises because of the charge transfer between carbon and titanium. Here also the net charge transfer is from Ti to carbon (Table 1). In the Fig. 4 one can see flat bands above and below the Fermi level indicating large effective mass for the conduction electrons in the Ti adsorbed nanotube. There is a small gap of about 0.54 eV introduced by the adsorbed Ti chain. We do not get the pseudo gap, similar to the one reported [8,22] (0.14 eV) .

Figs. 5-8 are the density of states (DOS) histograms of the pure and Ti adsorbed carbon nanotubes . In Figs. 5 and 6 one can see the significant changes introduced by the Ti chain in a (14,0) nanotube [8,17]. The original gap is closed and new states are created below and above the Fermi level. For (8,8) nanotube the changes are completely reversed. The states near the Fermi level (pure (8,8) tube) are pushed bellow and above the Fermi level opening a small gap (Ti adsorbed (8,8) tube). There is no pseudo gap. The density of states at the Fermi energy, which is playing a vital role here, needs a special treatment. The situation one faces here in the carbon nanotube, a pseudo gap in the density of state curve, is similar to the one encountered in a BCS superconductors [30]. In a BCS superconductor the normal state and the superconducting state are separated by a gap, at the Fermi energy E_F, and the new density of states has an energy gap centered around the Fermi energy.

4. Superconductivity

Ever since the report of superconductivity in single walled carbon nanotube [12,13] scientists are investigating [23,24] the possible superconducting mechanism in carbon nanotube. Park *et al.* [23], while investigating the possible phonon mechanism, also studied the enhancement of the electron-phonon interaction with decreasing diameter of carbon nanotube. As pointed out earlier, Tit and Wardana [17] have studied the superconductivity in carbon nanotube coupled to Ni atoms. They are of the opinion that superconductivity in carbon nanotube is basically due to the electron -phonon interaction. There is also another view that plasmon exchange mechanism may lead to superconductivity in carbon nanotube [14].

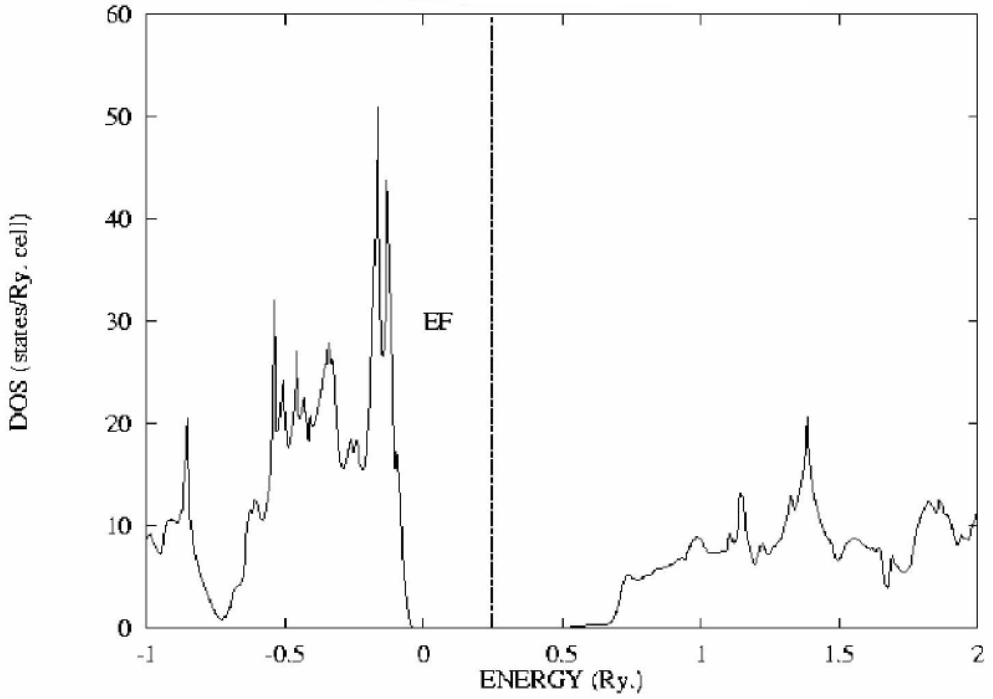

Fig. 5. Density of states of pure (14,0) CNT.

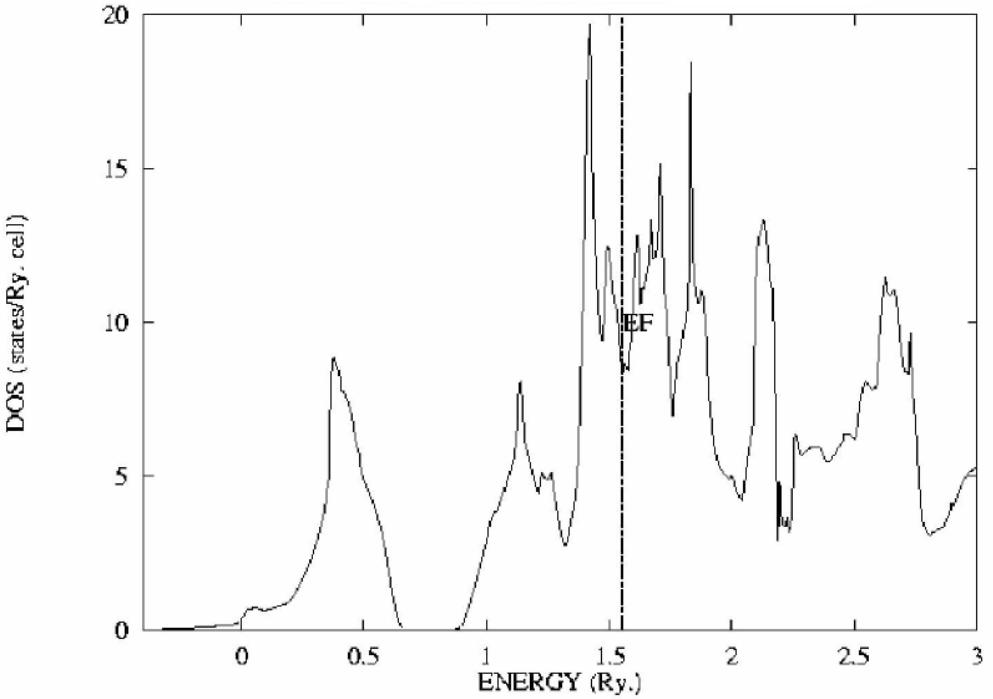

Fig. 6. Density of states of Ti-adsorbed (14,0) CNT.

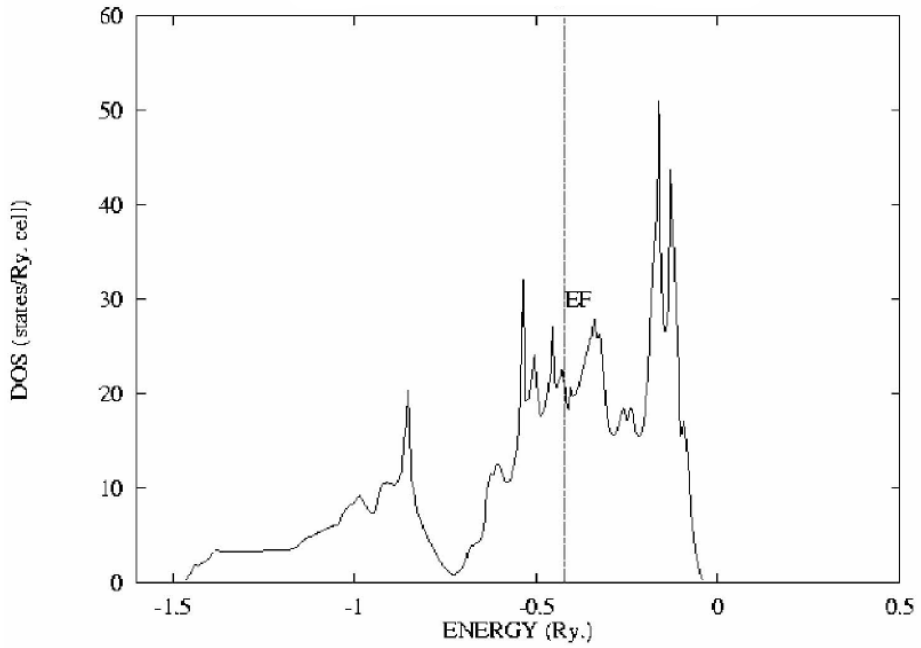

Fig. 7. Density of states of pure (8,8) CNT.

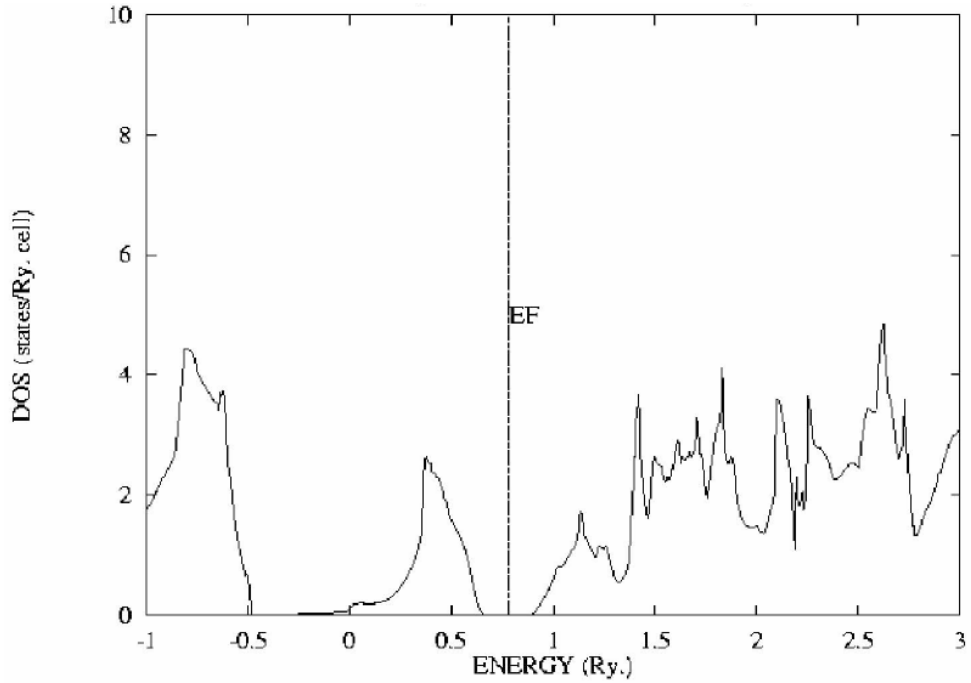

Fig. 8. Density of states of Ti-adsorbed (8,8) CNT.

We have investigated the superconducting properties of pure (8,8) and Ti adsorbed (14,0) carbon nanotubes using the band structure results obtained for them. Assuming that the electron-phonon interaction causes superconductivity in single walled carbon nanotube, we have estimated the superconducting transition temperature T_C using McMillan formula [25] in conjunction with the theory of Gaspari and Gyorffy [26]. The various steps involved in the estimation of T_C is detailed in Ref. 27. Here we give only the results and discussion.

In the above calculation θ_D, the Debye temperature, which is directly related to the phonon frequency, plays an important role in deciding the T_C value. The Debye temperature reported for carbon in its various phases ranges from 50 to 2500K [28]. We have estimated the T_C values for different values of θ_D. The T_C values estimated for the pure (8,8) carbon nanotube and for the Ti adsorbed (14,0) carbon nanotube are given in Table 2. With the increase of θ_D the T_C value increases and reaches 270K corresponding to θ_D = 2500K. Tang *et al.* [2] have observed superconductivity in a 4 Å SWCNT around (<) 15K. We get this value (14.25K) corresponding to θ_D = 125K. In the case of Ti adsorbed (14,0) nanotube, the T_C value goes on increasing with increase of θ_D , but the rate of increase is less than the rate of increase in the case of (8,8) nanotube. Tit and Wardana [17] have found the T_C value of carbon nanotube - Ni wire coupled system to be in the range 10-50K. The computed values of T_C in the case of transition metal adsorbed carbon nanotube once again confirms the observation, "A nanotube with adsorbed materials may also significantly change its physical properties, providing useful means for manipulating electronic transport for nanoelectronic devices", by Chih-Kai Yang *et al.* [7].

Table 2. Superconducting transition temperature *(T_C)* as a function of θ_D

Debye Temperature θ_D, K	Superconducting transition temperature T_C	
	C-C (8,8)	C-Ti (14,0)
50	0.71	0.05
75	2.80	0.29
100	8.84	1.71
125	14.25	3.27
150	24.02	14.67
400	84.87	49.11
700	140.7	78.23
1000	184.6	107.3
1500	223.0	120.7
1750	228.6	135.8
2000	245.1	162.9
2500	270.4	178.3

The carbon nanotube being 1D electronic system, the quantum fluctuations inevitably reduce all classical transition temperatures. This is applicable to McMillan formulation of superconductivity [27]. Our results set an upper bound to the superconducting temperature and are compatible with the previous theoretical estimates and the experimental situation. Tang *et al.* [8] measured the superconducting transition temperature of well separated carbon nanotubes in a zeolite matrix as 15K. The diameter of the tubes are around 4 Å. Also they observed Meissner effect. The (8,8) tube, which we have studied, with diameter 10.8 Å may be the tube present in the zeolite matrix. This T_C value could be further improved to get closer to the experimental value by proper choice of electron-electron interaction parameter μ^* such that it is large enough to suppress the phase transition and maintain superconductivity.

5. Conclusion

Our band structure calculation has brought out all the characteristic features of the electronic structure of pure and Ti adsorbed single walled (8,8) and (14,0) carbon nanotubes. The band structure of the pure (14,0) zigzag nanotube indicates that it is a semiconductor where as the band structure of pure (8,8) armchair tube exhibits metallic behavior. When a titanium chain is adsorbed on the carbon nanotube, the (14,0) zigzag tube changes from semiconductor to metal and the (8,8) armchair tube transforms from metal to semiconductor. In both the cases there is a net transfer of charge from the metal chain atom to the carbon atom. The superconducting transition temperature calculation using the band structure results is capable of explaining the experimental observation and it also hints at possible room temperature superconductivity in single walled carbon nanotube [14,29].

Acknowledgments

The financial support from the UGC minor research project No:MRP-2987/09 (UGC-SERO) dated 31.3.2009 is greatly acknowledged with thanks.

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