Electronic properties of FeCl₃-adsorbed single-wall carbon nanotubes

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The structural and electronic properties of FeCl₃ interacting with single-wall carbon nanotubes (SWNTs) were investigated by *ab initio* methods. By using first-principles spin-polarized calculations, we studied the structural and electronic behavior of FeCl₃ adsorbed on both semiconducting and metallic SWNTs. It was found that the FeCl₃ molecule behaves as an electron acceptor. The binding energy is very small, thus suggesting that the interaction is through a physisorption regime.

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I. INTRODUCTION

Nanostructured materials have been the focus of many research activities aiming to understand and tailor, specific and even unexpected physical-chemical properties. The discovery of carbon nanotubes by Iijima in the early 1990s was a great stimulus for nanoscience in general.[1] Single-wall carbon nanotubes (SWNTs) present striking properties regarding their electronic structure. These systems can be either semiconducting or metallic depending on their geometry which is defined by the chiral angle and the diameter.[2] Because of their low dimensionality, very high surface area, and the special electronic structure, nanotubes are promising for many applications in the next generation of electronics devices and sensors. The control and/or tuning of the electronic properties is a key point for transforming the potentiality of SWNTs into real-world technology. One way for achieving this type of control and/or tuning is by carrying out donor or acceptor doping experiments where either electrons or holes are added to the SWNTs through intercalation and functionalization processes.[3–10] By doing this in a controlled way, it is possible to assess how specific chemical species perturb the SWNT electronic properties. In addition, these modified systems also open up the opportunity for studying the basic properties of SWNTs.

In an analogy to the rich field of graphite intercalated compounds the doping of carbon nanotubes with electron donors and electron acceptors is a very active field and many efforts have been dedicated for understanding and controlling the electronic properties of SWNTs.[11,12] In particular, the properties of FeCl₃-intercalated SWNTs have been studied and the results demonstrate that the FeCl₃ acts as an electron acceptor in the presence of SWNTs.[7,13] This behavior is observed through the suppression of the optical transitions in the absorption spectra that are assigned to the depletion of states from the valence bands of SWNTs. The upshift in the Raman frequencies indicates the charge transfer effects upon FeCl₃ intercalation into SWNTs.[13] It was also shown that, similar to graphite, the FeCl₃ intercalation process in SWNTs

is completely reversible upon thermal annealing. Besides these experimental works on the FeCl₃-intercalated SWNTs, to best of our knowledge, there are no theoretical studies, reporting how the FeCl₃ doping affects the electronic properties of the SWNTs.

In this paper we report a study of the electronic properties of a semiconducting (8,0) and a metallic (5,5) SWNTs interacting with FeCl₃ by using *ab initio* simulations. We have found from our calculations that the FeCl₃ molecule interacts with the SWNTs through a physisorption regime. An analysis of charge transfers indicates that electrons flow from the nanotubes to the FeCl₃ molecule thus making FeCl₃-doped SWNTs a *p*-type material. Our calculations are in agreement with experimental results reported in the literature for FeCl₃-intercalated doped SWNTs.[4,9,14]

II. METHODOLOGY

The electronic and structural properties of SWNTs interacting with FeCl₃ (FeCl₃/SWNT) were calculated by using total energy *ab initio* calculations based on the density functional theory.[15] It was used with the SIESTA code, which performs full self-consistent calculations by solving the Kohn-Sham equations[16] and using numerical atomic orbitals as basis sets.[17] In all calculations the double zeta basis set plus the polarization function were used. For the exchange and correlation terms, the generalized gradient approximation is used as described by Perdew *et al.*[18] The interaction between ionic cores and valence electrons is described by norm conserving pseudopotentials.[19] A cutoff of 150 Ry for the grid integration was utilized to represent the charge density. The Brillouin zone is sampled with five *k* points along the Γ-*X* direction that represent the convergence of our systems.[20]

Periodic boundary conditions and a supercell approximation with a lateral separation of 2.0 nm between tube centers are used to ensure that the SWNTs plus the molecule does not interact with their periodic images. The supercell used
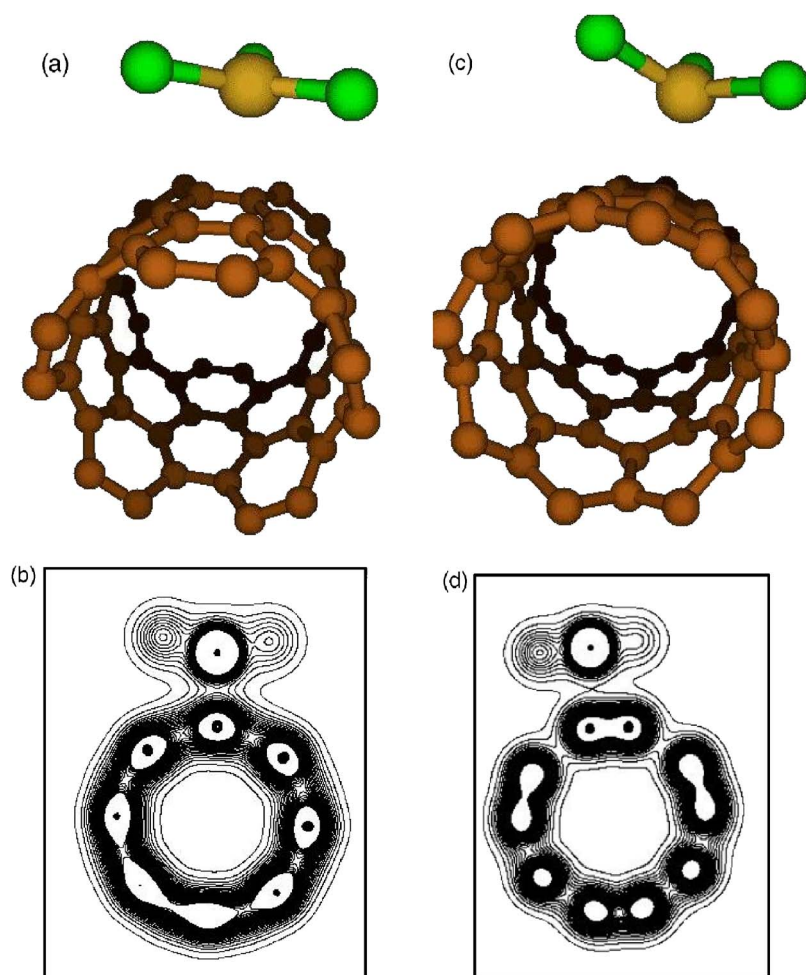
FIG. 1. (Color online) Schematic view of the $FeCl_3$ interacting with (a) the metallic (5,5) and (c) semiconducting (8,0) SWNT. (b) and (d) show the contour plots corresponding to the total charge densities for the $FeCl_3$ interacting with the (5,5) and (8,0) SWNT, respectively. The outermost and innermost contour lines correspond, respectively, to 0.0003 and $0.0099e$ Å^{-3}. The contour line spacing is $0.004e$ Å^{-3}.

has 60 (64) atoms for the armchair (5,5) [zig-zag (8,0)] carbon nanotube, with a total length of 0.737 nm (0.852 nm). The atomic positions of the structure are relaxed until all of the residual forces are smaller than 0.05 eV/Å.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(c) show the studied optimized structures of (5,5) and (8,0) SWNTs interacting with the $FeCl_3$ molecule, respectively. The minimum distance between the $FeCl_3$ molecule (Fe-C) for the (5,5) and (8,0) SWNT is 2.48 and 2.96 Å, respectively. The binding energy E_b calculated for the two systems are obtained through the sentence

$$E_b = E_{(FeCl_3/SWNT)} - E_{(SWNT)} - E_{(FeCl_3)}, \qquad (1)$$

where $E_{(FeCl_3/SWNT)}$ is the total energy for the $FeCl_3$/SWNT relaxed structure, $E_{(SWNT)}$ is the total energy of the pristine nanotube, and $E_{(FeCl_3)}$ is the total energy of the isolated $FeCl_3$ molecule. For the systems $FeCl_3/(5,5)$ and $FeCl_3/(8,0)$ nanotube the binding energies were calculated as being -0.48 and -0.42 eV, respectively. This result suggested that the interaction of $FeCl_3$ with the metallic (5,5) SWNT is slightly stronger than with the semiconductor (8,0) SWNT.

Figures 1(b) and 1(d) show the contour plots for the total charge densities of the structures showed in Figs. 1(a) and

1(c), respectively. It is possible to observe that, for both cases, the interaction is weak in agreement with the binding energies values. Furthermore, we can see that the contour line density indicates that the $FeCl_3$ interaction with (5,5) is stronger than with the (8,0) SWNT.

Figure 2 shows the calculated electronic band structure for the $FeCl_3$ interacting with the (5,5) nanotube. For comparison we plot in Fig. 2(a) the band structure for the pristine (5,5) SWNT. Figures 2(b) and 2(c) show the band structure for the majority (spin up) and minority (spin down) carriers. We can observe that the Fermi level of $FeCl_3/(5,5)$ SWNT is downshifted [Figs. 2(b) and 2(c)] compared with that of pristine (5,5) for both majority and minority electronic bands. By comparison with the pristine SWNT we can observe that the interaction with $FeCl_3$ introduces almost localized levels that weakly hybridize with the nanotube bands. These levels can be identified in the electronic band structure as the new bands below -0.5 eV (majority contributions) and above the Fermi level (minority contributions).

The band structure can be analyzed in more detail by looking at the projected density of electronic states (PDOS) onto the Fe and Cl atoms. In Fig. 3 we show the PDOS onto Cl $3p$ orbitals [3(a)] and Fe $3d$ orbitals [3(b)] for the system $FeCl_3/(5,5)$ SWNT for the majority (labeled up) and minority (labeled down) states. The levels coming from Cl $3p$ orbitals atoms are all occupied for the majority states and
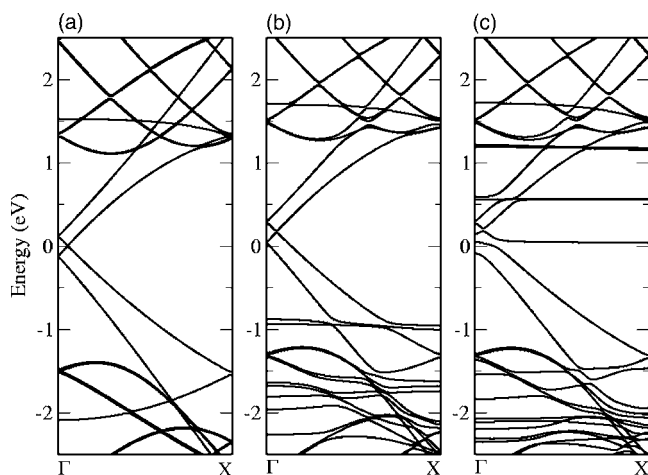
FIG. 2. Calculated electronic band structure for (a) (5,5) pristine, (b) spin up, and (c) spin down levels for the $FeCl_3/(5,5)$ SWNT. The Fermi energy is located at 0.0 eV.

partially occupied for the minority states. In the case of minority states there is a small contribution of two peaks at about 0.5 and 1.1 eV whose origin comes from the hybridization of levels located about the Fermi energy in Figs. 2(a) and 2(b). We can observe that the majority levels related with the Fe $3d$ orbitals are all occupied. These states are identified in the electronic band structure as the slightly dispersive bands in Fig. 2(b). In contrast the minority states are almost all empty and the main contribution is located above the Fermi level at 0.2, 0.6, and 1.3 eV. We should emphasize that $FeCl_3/(5,5)$ SWNT has occupied levels crossing the Fermi level thus keeping the system metallic.
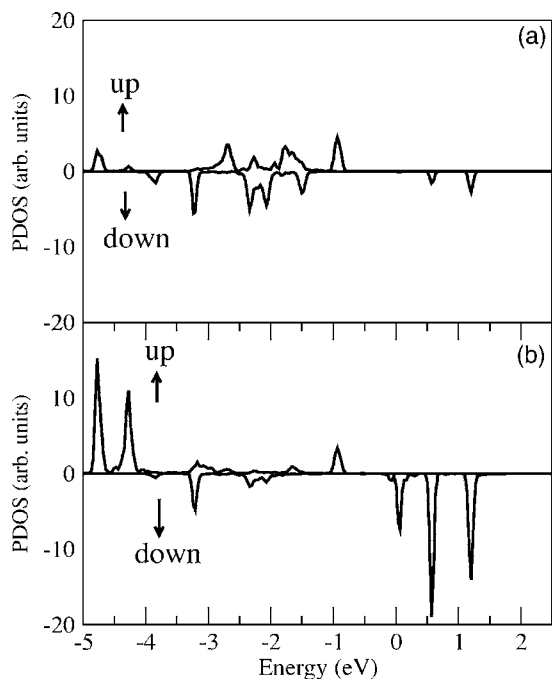

FIG. 3. Projected density of electronic states onto the Cl $3p$ orbitals (a) and Fe $3d$ orbitals (b) atoms for the $FeCl_3/(5,5)$ SWNT system. The curve labeled up and down stand for majority and minority carriers, respectively. The Fermi level is located at 0.0 eV.
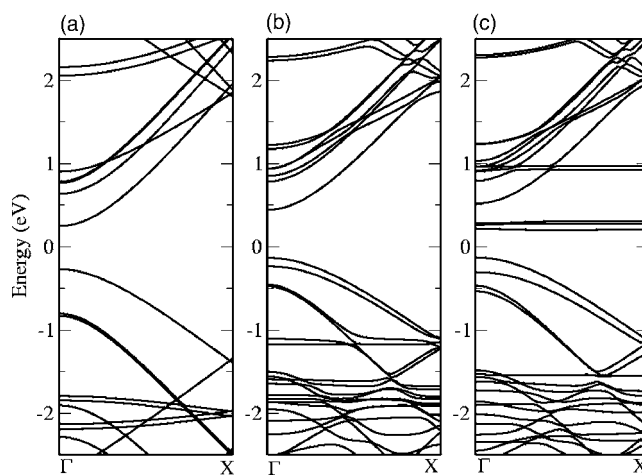

FIG. 4. Calculated electronic band structure for (a) (8,0) pristine, (b) spin up, and (c) spin down levels for the $FeCl_3/(8,0)$ SWNT. The Fermi energy is located at 0.0 eV.

We also have analyzed the interaction of $FeCl_3$ with an (8,0) semiconducting SWNT. The calculated electronic band structure for the $FeCl_3/(8,0)$ SWNT is shown in Fig. 4. Similar to the case of a metallic nanotube, the interaction with $FeCl_3$ moves the Fermi energy towards valence bands thus indicating that the $FeCl_3$ is acting as an electron acceptor. However, the band structure for the minority states shows that levels coming mainly from Fe d orbitals are localized in the conduction bands above the Fermi level. These states are identified in Fig. 4(c) as the flat bands around 0.25 eV. These levels are located at about 0.21, 0.26, and 0.28 eV above Fermi level, respectively. Apart from this, the nanotube band structure remains almost unaltered, thus preserving its semiconducting behavior and the energy band gap of 0.57 eV.

From an analysis of the Mülliken population we have determined that $FeCl_3$ behaves as an electron acceptor when interacting with both semiconductor and metallic SWNTs. An effective charge transfer of 0.38 [0.34] electrons from the (5,5) ([8,0]) SWNTs was determined.

In order to give support to our theoretical predictions, we now discuss our results in comparison with the experiments reported in the literature. Kukovecz and co-workers[14] have reported Raman scattering results for $FeCl_3$-intercalated SWNTs bundles in the resonant window of metallic and semiconducting SWNTs. It was shown that the Briet-Wigner-Fano shape of the G band for metallic SWNTs disappears gradually as the amount of $FeCl_3$ intercalant increases. The total intensity of the G band is quenched when the adsorption of $FeCl_3$ saturates, thus indicating that the first van Hove singularity in the valence band was completely depleted. This result indicates that the electrons are removed from the tube thus depleting the uppermost valence bands of the metallic tubes. Our electronic band structure calculations for $FeCl_3$ interacting with a metallic tube is in qualitative agreement with the experimental results reported in Ref. 14. In the case of semiconducting nanotubes a quench in the Raman intensity upon $FeCl_3$ was also observed, thus also indicating the depletion of the filled states. We should point out that the

results reported in the literature are for bundled SWNTs where a large number of $FeCl_3$ molecules are intercalated and they are responsible for removing charge from the tubes up to the first van Hove singularity for metallic SWNTs. It has been experimentally estimated that $0.12e^-$ per carbon atom are transferred from the SWNTs to the $FeCl_3$ molecule. Our predictions can be compared only qualitatively with the experiments. The *ab initio* approach is not appropriate for studying a system like many $FeCl_3$ molecules intercalated into a bundle of SWNTs because of computational time. However, some comparison connecting experiments and modeling can be performed as we will discuss next.

The calculated shift in the Fermi level is low (0.1 eV) compared with what that was observed in the experiments (1.0 eV).[13] This small shift is expected since we have only one $FeCl_3$ molecule. However, our calculations are in agreement with the experiments in the following sense. The 0.1 eV shift in the Fermi level corresponds to the removal of 0.006 electrons per carbon atom from the nanotube. This value is 20 times lower than the estimated charge transfer estimated in the experiments (0.12 electrons per carbon atom).[13] By shifting the Fermi level by a factor of 10, the charge transfer per carbon atom would be $0.006 \times 10 \times 2 \approx 0.1$ electrons per carbon atom. The factor 2 is due to spin up and spin down configurations. This value is in agreement with 0.12 electrons per carbon atom estimated in the experiments.

Finally, we discuss the magnetic properties of the system. The total magnetic moment for the isolated $FeCl_3$ is $5.00\mu_B$. When interacting with the (8,0) nanotube the total magnetic moment is $4.83\mu_B$. This value is larger than for the system (5,5) SWNT whose value is $4.35\mu_B$. This result can be understood in terms of the delocalization of Fe $3d$ orbitals. When interacting with the semiconducting SWNT, the d levels are more localized than in the case of metallic SWNT which implies that the total magnetic moment is closer to the that of the free molecule.

IV. CONCLUSIONS

Summarizing, we have reported an *ab initio* study of the interaction of $FeCl_3$ with semiconducting and metallic SWNTs. We have found that the $FeCl_3$ molecule behaves as an electron acceptor. For both metallic and semiconducting SWNTs the binding energy is very small, thus suggesting that the interaction is through a physisorption process. This is in agreement with the experiments which revealed that the $FeCl_3$ intercalation is completely reversible upon a thermal annealing. Therefore, our modeling is supported by the experimental results previously reported regarding both charge transfer effects and the physisorption regime.

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