Structure and magnetism in carbon nanotubes including magnetic wire

Structure and magnetism in carbon nanotubes including magnetic wire

H. Shiroishi[1] T. Oda[1] H. Sakashita[1] and N. Fujima[2]

[1] Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan

[2] Faculty of Engineering, Shizuoka University, Hamamatsu 432-8561, Japan

Abstract. We have studied the electronic structure of the carbon nanotubes which include Fe atomic wire with using the density functional theory. As the stable geometries, we obtained the straight and zigzag wires, which have ferromagnetic and antiferromagnetic alignments, respectively. The antiferromagnets consists of the two ferromagnetic dimers which couple in antiparallel alignment. We presents the band dispersions and the density of states for the magnetic nanotubes. The electronic structure at the Fermi level consists of the Fe $3d$ and C $2p\pi$ states, which shows a strong hybridization between them.

1 Introduction

The carbon nanotube(CNT) may be a good candidate for new basic material due to its electronic flexibility and mechanical strength. It is well known that the CNT can contain various other molecules and clusters, for example, fullerenes, DNA, magnetic clusters and so on. Such substances may change the electronic state around the Fermi level. The CNTs are usually fabricated with the catalyst of magnetic materials. The effect of these on the electronic state may be interesting for understanding the microscopic mechanism of fabrication. In another point of view, to control electron transport properties in CNTs, it may be important to study the electronic structure in the complex of CNT with a molecule involved.

The CNT including magnetic material were theoretically studied by Yang *et al.*[1]. They predicted that the conduction electrons exhibit large spin polarization near

the Fermi level. The single magnetic atom on the CNT was studied by Fagan *et al.*[2]. They found that the site below the carbon-carbon bond center (the bridge site) had the lowest energy in the cage of CNT. In the previous work, Fujima *et al.* investigated magnetic structure of the Fe chain encapsulated in carbon nanocapsule[3]. The confinement of iron chain in a thin tubal capsule increases an antiferromagnetic coupling between the magnetic moments.

In this study, we investigated electronic structures of the CNT which includes the Fe atomic wire. The wire of magnetic atoms has an intermediate density of magnetic atoms, compared with the previous works[1,2]. This kind of wire configurations of magnetic atom in CNTs have never been observed explicitly, however the sophistication of wire calls us a nano-lead for electronic device and a nano spin-polarized devices for spintronics. We found a ferromagnetic zigzag wire as the lowest energy configuration. We will present the one dimensional band dispersions and the partial densities of states for the ferro- and antiferro-magnetic system of CNTs.

2 Calculation method and models

We have used the first-principles molecular dynamics[4] with ultrasoft pseudopotentials[5] and planewaves, which is based on the density functional theory[6]. The energy cutoffs are 24 Ry for planewave expansion of electron wave functions and 250 Ry for the augmented electron density[7]. With these energy cutoffs the total energy differences among stable states are well converged. The 16 sampling **k** points were used in calculating the self-consistent densities. The magnetic interaction among Fe atoms changes rapidly by the interatomic distance. Due to this property, noncollinear magnetic structures could appear in the optimization process of atomic and electronic configurations. Thus, we used the approach of noncollinear magnetism[8, 9] as well as the spin polarized (collinear) scheme. In our optimizations by noncollinear scheme, the low energy configurations have collinear configuration. We used the generalized gradient approximation for the exchange-correlation energy[10] and the Fermi level smearing of 0.002 Ry[11]. The magnetic moment on atoms is obtained by integrating the spin density within the atomic sphere having the radius of 0.90 Å for Fe and 0.74 Å for C.

In our study we used the CNT(9,0) models with 72 carbon atoms, which contain 4 iron atoms. This cell corresponds to four unit cells in the empty CNT(9,0). The planewave method employs the periodic boundary condition(PBC). The dimension of cell along the tube axis, c, was fixed to be the value of 8.57 Å. This value is obtained from the geometrical optimization of the CNT(9,0). The PBC along the axis of tube also implies stresses in the wire. However, based on the fact that the compressibility along the tube axis in the empty CNT(9,0) is much smaller than that in an isolated Fe chain by about a factor of ten, the fixed cell-dimension used in our calculations is not supposed to raise any strong stress at the Fe wires in the CNT. The dimension of cell along the direction normal to the tube axis, a, was fixed to the value of 14.8 Å. The walls between the neighboring tubes are separated by
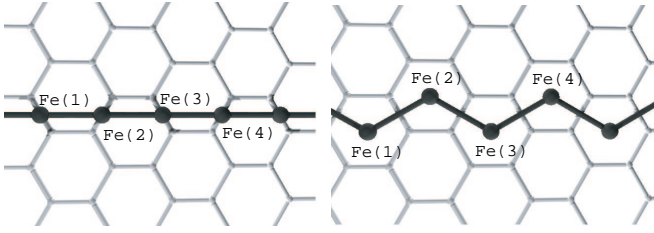
Fig. 1. Schematic presentations for the relation between the Fe wire and the nanotube wall; straight wire (left panel) and zigzag wire (right panel). The dark balls and sticks indicate the Fe wire and the gray honeycomb lattice indicates the cage of CNT. The horizontal direction of figure corresponds to axis of the CNT(9,0).

about 7.6 Å. This may be large enough for the artificial interaction with the image cells to be neglected[12].

3 Result and discussion

3.1 Atomic structures

The previous work by Fagan *et al.*[2] reported that the accommodation below the midpoint of C-C bonds (the bridge site) is lower in energy than that below the center of hexagon (the hexagon site) for the semiconductor of CNT(8,0). This was confirmed in our calculation for supporting the accuracy in our calculations. In the CNT(9,0) the energy of the hexagon site is much lower by 0.36 eV than that of the bridge site.

We have obtained the two kinds of stable geometries in the CNT(9,0). One has the Fe atoms with being straight wire and the other with being zigzag wire, as schematically drawn in Fig. 1. In both of geometries, the Fe wire is located on the wall and the distance of Fe-C resulted to about 2.2 Å. For straight and zigzag wires, we obtained

Table 1. Magnetic moments(MM) in μ_B and total energies(E_{tot}) in eV. In the column of atomic MM, different absolute values are provided only.

wire (magnetism)	total MM	atomic MM	E_{tot}
straight (AF)	0.0	2.13, 2.19	1.61
straight (F)	10.63	2.41	1.98
zigzag (AF)	0.06	2.76, 2.76, 2.73, 2.75	0.56
zigzag (F)	11.95	2.89, 2.63	0
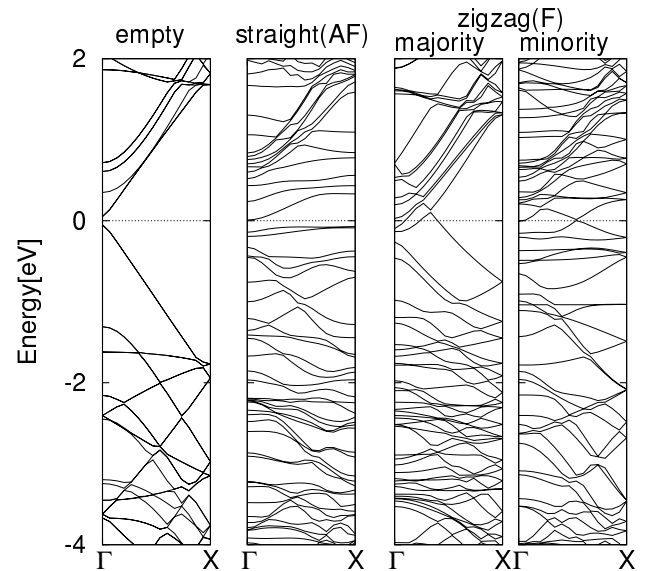
Fig. 2. Band dispersions in the empty CNT(9,0), the antiferromagnetic Fe-straight-wire@CNT(9,0), and the ferromagnetic Fe-zigzag-wire@CNT(9,0). The latter is presented in separation of spin-up and spin-down states. The horizontal lines at zero specify the Fermi level.

ferromagnetic and antiferromagnetic alignments, respectively. The magnetism of systems will be described later.

For the straight wire the Fe atoms are at the bridge site and the zigzag wire at the hexagon site. The zigzag wire, thus, has a bond angle of about 120 degree. For the
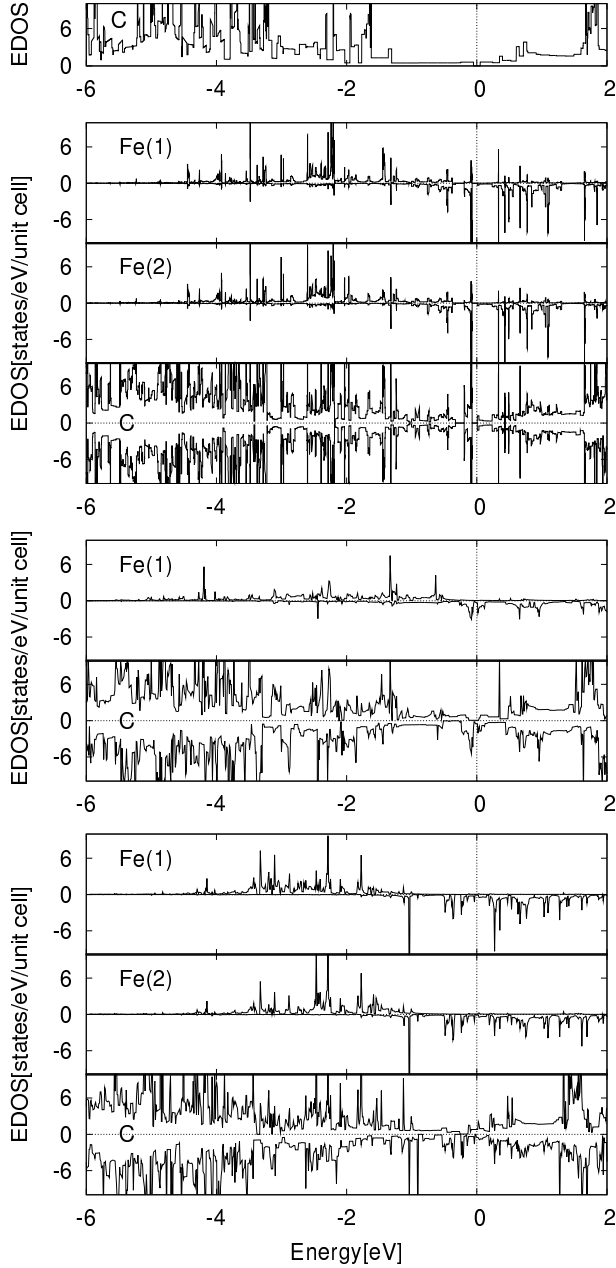
Fig. 3. Electronic densities of states in the empty CNT(9,0)(1st part), the antiferromagnetic Fe-straight-wire@CNT(9,0)(2nd part), the ferromagnetic Fe-straight-wire@CNT(9,0)(3rd part), and the ferromagnetic Fe-zigzag-wire@CNT(9,0)(4th part). The partial components of Fe 3d and C 2p are presented. The labels of Fe(1) and Fe(2) specify the respective atom in Fig. 1 and the densities of equivalent atoms are not shown. The panel of C 2p component in the 1st part presents in the unit of per-spin for comparison. The vertical lines indicate the Fermi level.

antiferromagnets, it is interesting that in both straight and zigzag there are alternative atomic distances, namely, short and long bond lengths; 2.06 and 2.22 Å for straight and 2.29 Å (average of 2.31 and 2.26 Å) and 2.70 Å (average of 2.66 and 2.74 Å) for zigzag. In the latter(zigzag) case, there are two short and two long bond lengths. In the ferromagnets, the Fe-Fe bonds have the equal distance; 2.14 Å for straight and 2.52 Å for zigzag. These atomic distances may be usual, compared with results of the previous cluster studies[3,13] except for 2.70 Å. This value is slightly longer, implying a localization of wavefunctions of electron.

3.2 Magnetism and energetics

The antiferromagnetic configuration is lower in energy than the ferromagnetic one within the straight wires, as shown in Table 1. The atomic magnetic moments has relatively small values of 2.13 and 2.19 μ_{B} and the alignment is the order of ↑↑↓↓. This novel antiferromagnet consists of the two ferromagnetic dimers which couple with an antiparallel alignment. The energy is lower by 0.37 eV than the ferromagnet of straight wire.

The zigzag geometry appears in the lowest energy state with the ferromagnetic configuration, namely, the ferromagnetic one is lower in energy by 0.56 eV than the antiferromagnetic one. This ferromagnet, as in Table 1, has the two values for atomic magnetic moment. These values are averaged to be 2.76 μ_{B}, which is larger than the averaged atomic magnetic moment of the other systems. This

indicates magnetic stability of the ferromagnetic zigzag wire.

The ferromagnetic zigzag geometry is more stable by 1.61 eV than the antiferromagnetic straight one. The stability of the former is attributed to the stable accommodation at the hexagon site and the larger spin polarization of Fe atom.

3.3 Electronic structures of straight wire

The band dispersions and densities of states(DOS) are presented in Figs. 2 and 3. In these figures, the results of the empty CNT are also provided for comparison. The empty CNT(9,0) was considered to have a metallic feature[14]. The work by Hamada *et al.* reported a curvature effect of tubes as a narrow band gap at the zone center in wave number space[15]. Around the gap, the DOS has the constant value estimated from inverse of the derivative in the band dispersion. The electronic states of C $2p\pi$ extend from -4 to 4 eV.

In the antiferromagnetic system, as seen in Figs. 2 and 3, there is a narrow gap at the Fermi level, which is comparable with that in the empty CNT. Just below the Fermi level the bands isolated from the others, which show a strong hybridization between Fe $3d$ and C $2p\pi$, mainly consist of minority spin components. As in the other magnetic CNTs, the partial component of C $2p\pi$ increases around the Fermi level($-1 \sim 0.5$ eV) from the empty CNT to the magnetic CNTs.

In the ferromagnetic system, the minority spin states also appear just below the Fermi level (see the 3rd part of

Fig. 3). The shape in the DOS is slightly broadened from the antiferromagnetic counterpart.

3.4 Electronic structures of zigzag wire

For the zigzag wire, as seen from Fig. 3, the majority spin states of Fe $3d$ state are lowered from the straight wires. This results from the increase of effective exchange splitting in Fe atom, which appears in having a large atomic magnetic moment of Fe atom, as listed in Table 1. The large magnetic moment is related with the localization of wavefunctions and the decrease of hybridization with the neighboring Fe $3d$ and C $2p\pi$ orbitals. These changes in electronic structure come from the change of Fe position; from the bridge site to the hexagon site.

4 Summary

For Fe-wire@CNT(9,0), we have optimized the atomic structure and obtained two kinds of stable geometries; the one has a straight wire and the other a zigzag wire. The both types of structure emerged with the antiferromagnetic and ferromagnetic alignments. The geometry of ferromagnetic zigzag wire is the most stable in the magnetic CNTs studied. The antiferromagnetic Fe-wire@CNT(9,0) has the novel structure which consists of an anti-parallel alignment of two ferromagenetic dimers. The electronic states in vicinity of the Fermi level results from the strong hybridization between Fe $3d$ and C $2p\pi$, consisting of the minority spin states. The Fe site below the hexagon center

lowered the total energy and increased atomic magnetic moments.

References

1. C. K. Yang, J. Zhao and J. P. Lu, Phys. Rev. Lett. **90**, (2003) 257203.

2. S. B. Fagan, R. Mota, A J. R. da Silva, and A. Fazzio, Phys. Rev. B **67**, (2003) 205414.

3. N. Fujima and T. Oda, Phys. Rev. B **71**, (2005) 115412.

4. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, (1985) 2471.

5. D. Vanderbilt, Phys. Rev. B **41**, (1990) 7892.

6. P. Hohenberg and W. Kohn, Phys. Rev. **136B**, (1964) 864; W. Kohn, and L. J. Sham, Phys. Rev. **140A**, (1965) 1133.

7. A. Pasquarello, K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. Lett. **69**, (1992) 1982; K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, (1993) 10142.

8. T. Oda, A. Pasquarello, and R. Car, Phys. Rev. Lett. **80**, (1998) 3622.

9. T. Oda and A. Pasquarello, Phys. Rev. B **70**, (2004) 134402.

10. J. P. Perdew, J. H. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, and D. J. Singh, C. Fiolhais, Phys. Rev. B. **46**, (1992) 6671.

11. T. Oda, J. Phys. Soc. Jpn. **71**, (2002) 519.

12. For a larger value of $a = 16.9$ Å, the change in total energy was estimated to be a negligible value (~ 5 meV).

13. N. Fujima and T. Oda, Eur. Phys. J. D. **24**, (2003) 89.

14. R. Saito, G. Gresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London 1998) 59.

15. N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, (1992) 1579.