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Ab initio study of magnetic and electronic properties of Fe-filled single-walled carbon nanotubes

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Abstract

We investigate the electronic and magnetic properties of a metallic (3, 3) single-walled carbon nanotube (SWCNT) filled with a linear Fe nanowire, based on the *ab initio* spin-polarized density functional theory. We find that in the stable structure the Fe-filled (3, 3), (5, 0) SWCNTs exhibit semiconducting properties, and the Fe nanowires lose their magnetic moment, while the (4, 4), (5, 5), (6, 6), (6, 0) SWCNTs having larger radius with linear Fe nanowires are metallic, and show magnetic moments.

1. Introduction

Carbon nanotubes (CNTs) have fascinating properties that make them potentially useful in nanoscale electronic and mechanical applications. They have found applications [1, 2] in the fabrication of various devices, e.g., scanning probes, electronic transistors, and field emitting devices, exhibiting unusual strength, unique electrical, and extremely efficient heat conducting properties. Nanotubes can absorb materials such as biological molecules, raising the possibility of applications in biotechnology [3]. Magnetic metal nanoparticles (such as Fe, Co, Ni) also have a wide variety of useful applications such as for high-density magnetic data storage. CNTs filled with ferromagnets should be promising in providing the required magnetic properties, low dimensionality, and small volume for future nanoscale devices. Fe-filled multi-walled carbon nanotubes (MWCNTs) have been synthesized by chemical vapour deposition (CVD) using ferrocene as precursor, and showed pronounced magnetic anisotropy [4]. Fe-filled MWCNTs of the diameter of 10–20 nm and the length of 100–800 nm have also been synthesized by pyrolysis of ferrocene along with acetylene [5].

In this study, we investigate the electronic and magnetic properties of structurally stable Fe-filled single-walled carbon nanotubes (SWCNTs) within the density functional theory. We find that the Fe-filled SWCNTs (3, 3), (5, 0) do not exhibit spin polarization, and become

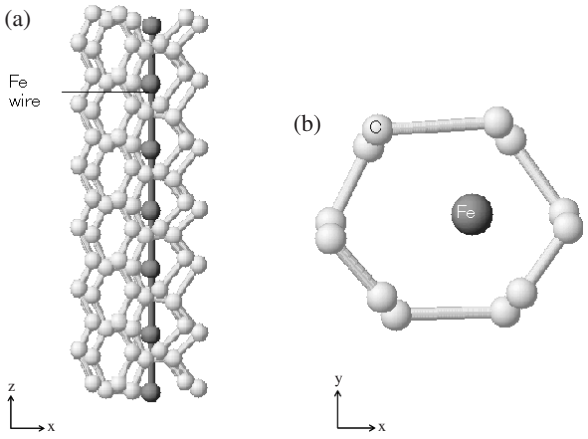

Figure 1. The side view (a) and the cross sectional view (b) of our model system for an Fe-filled (3, 3) SWCNT. The black and white balls express Fe and C atoms respectively.

semiconducting, while the (4, 4), (5, 5), (6, 6), (6, 0) SWCNTs having larger radius with linear Fe nanowires are metallic, and show magnetic moments. In the following, we give a detailed report based on the calculated band structure, local density of states (LDOS), and charge density distribution.

2. Model and calculations

The calculations for single-walled carbon nanotubes (SWCNTs) filled with linear Fe nanowires are based on *ab initio* spin-polarized density functional theory, using the generalized gradient approximation (GGA) for the exchange–correlation energy. We perform calculations with plane waves and pseudopotentials [6]. The electron–ion interaction is described by optimized ultrasoft pseudopotentials, using a cut-off energy of 35 Ryd to limit the plane-wave basis set. The one-dimensional Brillouin zone is sampled by 51 k-points. All numerical results are obtained by the spin-polarized GGA calculations with an initial magnetic moment of 2.4 μ_B for Fe.

To understand the magnetism and conductivity due to constructions of Fe–C bonds, we consider the (3, 3) SWCNT as one of the SWCNTs described in this paper, which has metallic characteristics. In the super-cell approximation with periodic boundary conditions, we have 12 C atoms and one Fe atom with a cell length in the growth direction of 2.48 Å. We set the periodicity of the SWCNT along the SWCNT axis direction, and a 10 Å vacuum region perpendicular to the SWCNT axis direction in order to avoid interaction between SWCNTs. We performed structural optimizations by minimizing the total energy until the residual forces became smaller than 0.05 eV Å^{-1}. We also calculated in the super-cell approximation with periodic-boundary conditions, where we have 24 C and two Fe atoms with a cell length in the growth direction of 4.96 Å. In this case we considered a linear Fe nanowire initially with both ferromagnetic and antiferromagnetic states.

3. Result and discussion

The stable (3, 3) SWCNT structure with a linear Fe nanowire, after optimization, is shown in figure 1. The distance between the Fe atom and its nearest C atom is about 1.9 Å. In both cases of a linear Fe nanowire with an initial ferromagnetic state and an initial antiferromagnetic state, in the stable structure, neither the Fe atom nor C atoms exhibit spin polarization. The energy band of the stable structure is shown in figure 2(b), and exhibits a bandgap of about 1 eV. In contrast, (4, 4), (5, 5), (6, 6), (6, 0) SWCNTs filled with linear Fe nanowires which have larger

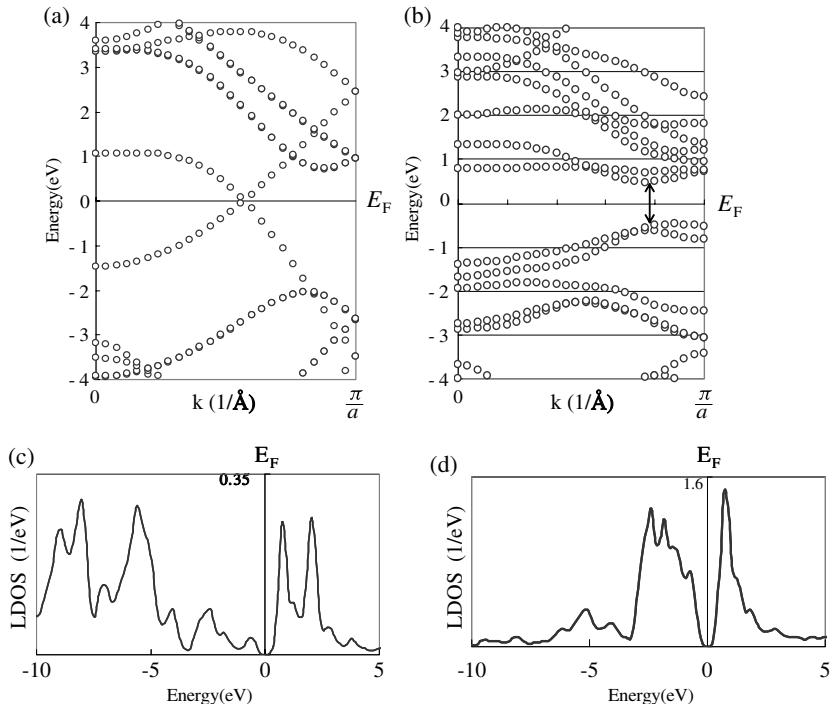

Figure 2. Energy band for pristine (3, 3) SWCNT and Fe-filled (3, 3) SWCNT shown in (a) and (b). Local density of states (LDOS) for the C atom near the Fe atom (c), and for Fe atom (d). E_F is the Fermi level.

radius than (3, 3), (5, 0) SWCNTs are metallic, and exhibit spin polarization. For example, in the case of an Fe-filled (4, 4) SWCNT the distance between the Fe atom and its nearest C atom is about 2.1 Å and it exhibits ferromagnetic metal characteristics with 2.6 μ_B/atom [7]. Because of the weak Fe–C bond, the Fe wire character remains.

Pristine (3, 3) SWCNT has metal characteristics since π bands exist at the Fermi energy (figure 2(a)). The Fe-filled (3, 3) SWCNT is a semiconductor exhibiting no spin polarization, and the bonding state of the Fe and C atoms can account for this. The electron charge density between Fe and its near C atoms is 0.6–0.8 electron Å^{-3} (figure 3), and it is thought that σ bonds are formed between Fe and C atoms. Since one Fe atom forms σ bonds with four (or six) C atoms, it is divided into bonding and anti-bonding orbitals. At this time, C atoms form a sp^3 hybrid-like orbital. Consequently, the Fe-filled (3, 3) SWCNT becomes a semiconductor, and the magnetic moment of the Fe atom disappears. Moreover, it also turns out that the magnetic moments of Fe atoms disappear as the density of states at the Fermi energy is zero (figure 2).

4. Conclusions

We have investigated the electronic and magnetic properties of a metallic (3, 3) SWCNT filled with a linear Fe nanowire, based on *ab initio* spin-polarized density functional theory. Because σ bonds between Fe atom and C atoms are formed, (3, 3), (5, 0) SWCNTs with linear Fe nanowires exhibit semiconducting characteristics and no spin polarization, while the (4, 4), (5, 5), (6, 6), (6, 0) SWCNTs having larger radius with linear Fe nanowires are metallic, and show magnetic moments [7].

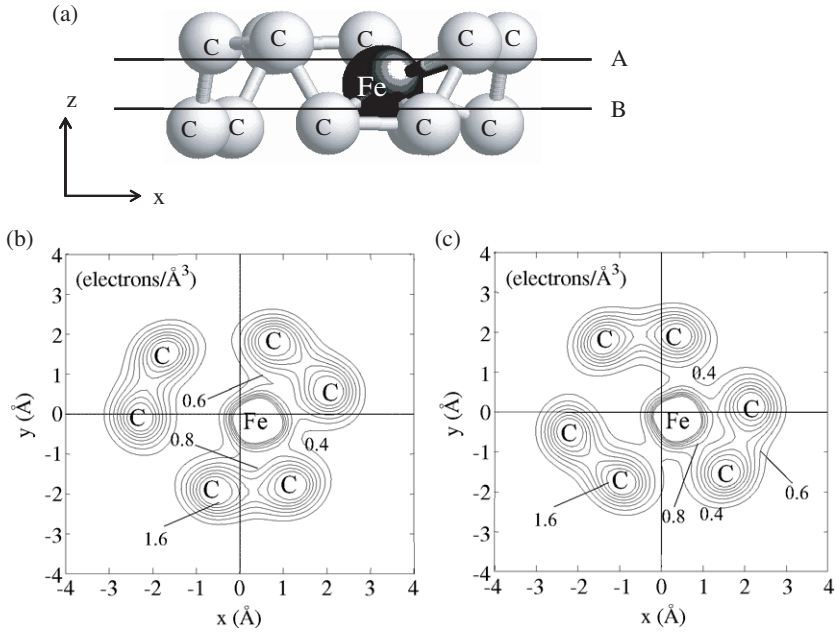

Figure 3. (a) Side view for one unit cell. (b), (c) The corresponding contour lines displaying the electron charge density distribution in cross sections A and B of (a).

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