Ferromagnetic spin ordering on carbon nanotubes with topological line defects

Susumu Okada,1 Kyoko Nakada,2 Kei Kuwabara,2 Kota Daigoku,2 and Takazumi Kawai3

1Institute of Physics and Center for Computational Sciences, University of Tsukuba, Tennodai, Tsukuba 305-8571, Japan and CREST, Japan Science and Technology Agency, 4–1–8 Honcho, Kawaguchi, Saitama 332–0012, Japan
2Department of Chemistry and Biological Science, Aoyama Gakuin University, Fuchinobe, Sagamihara 229–8558, Japan
3Fundamental and Environmental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan

(Rceived 5 September 2006; published 29 September 2006)

We report first-principles total-energy electronic-structure calculations in the density functional theory performed for carbon nanotubes with a topological line defect consisting of pentagon and octagon rings. We find that the ground state of the nanotubes with the topological line defect is ferromagnetic with small but finite magnetic moment of about 0.04μB/Å. Detailed analyses of energy bands and spin densities unequivocally reveal the nature of the ferromagnetic spin ordering which is associated with the peculiar edge-localized states of graphite flakes.

DOI: 10.1103/PhysRevB.74.121412

Experimental observations of magnetism in polymeric fullerenes4 and graphite5,6 have stimulated a lot of attention to carbon allotropes as promising candidates for light and stiff magnetic materials which are expected to be applicable to a wide field of modern technology. Despite much theoretical effort, however, the magnetism of the carbon allotropes have not yet been elucidated. Vacancies,4,5 edges,6–11 and theoretical studies suggest that the network termination by introducing the vacancies or edges is essential to the magnetic behavior,6 along the edge of graphite ribbons having the so-called zigzag edges.6–11 It has been analytically shown that a delocalized electron state exists for carbon nanotubes6–8 whose characteristics is the same flat band state whose characteristics is the same as the edge states of the graphite ribbons. The nanotubes with the topological line defect are found to be thermally stable and are expected to be synthesized by implanting C2 clusters in nanotubes or by annealing atomistically defective nanotubes. Our finding is the first evidence of long-range spin ordering expected for the nanotubes of cylindrical shape consisting solely of threefold coordinated sp2 C atoms.

We perform first-principles electronic-structure calculations in the framework of the density functional theory (DFT) (Ref. 13 and 14) using the local spin density approximation (LSDA) to elucidate the electronic and geometric structures of the topological line defect. To express the exchange-correlation energy among interacting electrons, we use a functional form15 fitted to the Monte Carlo results16 for the homogeneous electron gas. Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction.17,18 In constructing the pseudopotentials, core radii adopted for C 2s and 2p states are both 1.5 Bohrs. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 50 Ry which is known to give enough convergence of total energy to discuss the relative stability of various carbon phases.17,19 We adopt a supercell model in which a nanotube is placed with its wall being separated by 8.0 Å from another wall of an adjacent nanotube. The conjugate-gradient minimization scheme is utilized both for the electronic-structure calculation and for the geometry optimization.20 Integration over one-dimensional Brillouin zone is carried out using four k points.21 We consider the armchair nanotubes with the topological line defect, denoted by (n,n)D, in which octagons and fused pentagons are alternately aligned in parallel to the tube axis [Fig. 1(a)]. The peculiar topological defect can be obtained by the implantation of C2 cluster in a hexagon per double periodicity of the nanotubes.

Figure 2 shows the spin densities (Δρ↑=ρ↑−ρ↓) of fully optimized geometries of (n,n)D nanotubes with n=4–10. Obviously, the nanotubes with the topological defect exhibit magnetic ordering: Along the circumference of the nanotube, the polarized electron spins are strongly localized to the atoms connected to the C2 clusters (Fig. 1), and the distribution...
of the spins rapidly decreases with increasing distance from the defect. In sharp contrast, along the tube axis direction, the polarized electron spins are aligned parallel with the direction, clearly exhibiting their ferromagnetic spin ordering. Thus, the armchair nanotubes with the topological line defect are ferromagnetic nanowires consisting solely of threefold-coordinated C atoms without carrier doping or network termination imposed by vacancies or edges.

Corresponding magnetic moments are listed in Table I. It is clear that finite magnetic moments do exist on the \((n,n)_D\) nanotubes and that the number of polarized electron spins is independent of the tube diameter. The ferromagnetic states of the nanotubes are slightly lower in total energy than the nonmagnetic ones. The energy gains are also shown in Table I. They clearly indicate that the ferromagnetic spin ordering takes place on the \((n,n)_D\) nanotubes below the Curie temperature of about a few tens K.

We next focus on the electronic structures of the armchair nanotubes with the topological line defect. Figure 3(a) shows the dispersion relation of the \((10,10)_D\) nanotube. The electronic structure of the \((n,n)_D\) nanotubes exhibits different characteristics from that of the pristine armchair nanotubes. Although the \((n,n)_D\) nanotubes have no termination of bonding network, either by vacancies or by edges, we find a flat dispersion band around the \(\Gamma\) point near the Fermi level. Moreover, the flat band is split by 0.2 eV into the majority and minority spin bands resulting in the ferromagnetic spin ordering along the tube axis. Flat dispersion bands are usually concerned with the electron states of localized nature. However, this is not the case. As shown in Fig. 3(a), for all the \((n,n)_D\) nanotubes studied here, the flat dispersion band clearly loses its flatness at \(k=2\pi/3\) and exhibits a substantial dispersion around the zone boundary. The flat band, thus, results from a delicate balance of electron transfers among the \(\pi\) orbitals situated near the topological line defect.

The analysis of the wave function provides an insight into the flat band states. At the \(\Gamma\) point, the wave function of the flat band states is completely localized to the atoms connected to the \(C_2\) clusters, while it is extended along the tube axis [Fig. 3(b)]. The wave-function distribution is evidently different from that of the states near the flat band states as shown in Fig. 3(c) and 3(d): The electron states other than the flat band states are extended over the whole region of the nanotube. The calculated wave function, spin densities, and energy bands thus demonstrate that the flat-band ferromagnetism\(^{22-24}\) is realized in the \((n,n)_D\) nanotubes without magnetic elements and electron/hole doping.

The origin of the flat band states is explained by the simple tight-binding (TB) model. Our TB calculations within the nearest-neighbor approximation give an analytic expression for the flat band states of \((n,n)_D\) nanotubes. The \((n,n)_D\) nanotube with a large \(n\) has a single band which is flattened to be \(E=0\) within the region of \(0 \leq k < 2\pi/3\). The flat band exhibits the nature of the nonbonding orbital (NBO) essentially identical to the graphite ribbon’s NBOs found in the edge states:\(^6-11\) The NBOs, at \(k=0\), are completely localized to the atoms adjacent to the \(C_2\) clusters and then penetrate, in the region of \(0 < k < 2\pi/3\), to the sites along the tube cir-

![Image](121412-2.png)

FIG. 1. (Color) An optimized geometry of the \((10,10)\) nanotube with the topological line defect [the \((10,10)_D\) nanotube]. Red spheres denote the \(C_2\) clusters implanted in the perfect \((10,10)\) nanotube. Atoms on borders between hexagonal network and topological defect consisting of pentagon and octagon network are denoted by green spheres.

![Image](121412-2.png)

FIG. 2. (Color) Isosurfaces of the spin density distribution \((\Delta \rho=\rho_+\rho_-)\) for the nanotubes with the topological defect: (a) \((4,4)_D\), (b) \((5,5)_D\), (c) \((6,6)_D\), (d) \((7,7)_D\), (e) \((8,8)_D\), (f) \((9,9)_D\), and (g) \((10,10)_D\) nanotubes. Pink and cyan surfaces denote the surfaces corresponding to the positive and negative density of the electron spin.

### Table I. Magnetic Moments and Energy Gains

<table>
<thead>
<tr>
<th>((n,n)_D)</th>
<th>(\mu [\mu_B/\text{Å}^2])</th>
<th>(\Delta E [\text{meV}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>((4,4)_D)</td>
<td>0.058</td>
<td>4.8</td>
</tr>
<tr>
<td>((5,5)_D)</td>
<td>0.035</td>
<td>2.9</td>
</tr>
<tr>
<td>((6,6)_D)</td>
<td>0.053</td>
<td>6.3</td>
</tr>
<tr>
<td>((7,7)_D)</td>
<td>0.041</td>
<td>4.2</td>
</tr>
<tr>
<td>((8,8)_D)</td>
<td>0.037</td>
<td>3.9</td>
</tr>
<tr>
<td>((9,9)_D)</td>
<td>0.037</td>
<td>3.8</td>
</tr>
<tr>
<td>((10,10)_D)</td>
<td>0.045</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(\rho_+\) and \(\rho_-\) denote the positive and negative density of the electron spin.
enhances overlap between the wave function along the edges slightly extended nature of the edge state on the nanotube distribution of the edge state outside the nanotube. The curvature of the nanotubes; the curvature increases the net magnetic spin ordering. One factor leading to this discrepancy is unoccupied. In the LSDA calculation, however, the flat band situated just above the Fermi level so that the band is unoccupied. In the TB framework, the flat dispersion band is located just above the Fermi level so that the band is unoccupied.

The NBO character of the \((n,n)_{D}\) nanotubes stems from the topological structure of the tubes: The \((n,n)_{D}\) nanotube can be regarded as a zigzag graphite ribbon rolled up into a cylinder by adding an array of \(C_2\) clusters to glue the zigzag edge sites of the ribbon. The point to be noted is the fact that the wave function of the flat band states always vanishes at the \(C_2\) cluster. Being the nodal line of the wave function, the \(C_2\) clusters keep the NBOs of the edge state intact, if the NBOs on both sides of the \(C_2\) array are out-of-phase. Our TB analysis thus corroborate that the origin and nature of the flat band states of the \((n,n)_{D}\) nanotubes are the same as those of the edge states of the zigzag graphite ribbons, though the \((n,n)_{D}\) nanotubes have no real edge to terminate the network of \(sp^2\) C atoms.

Along with the topological nature described within the TB framework, some other factors should be considered to explain the ferromagnetic spin ordering of the \((n,n)_{D}\) nanotubes. In the TB framework, the flat dispersion band is located just above the Fermi level so that the band is unoccupied. In the LSDA calculation, however, the flat band is partially occupied by electrons resulting in the ferromagnetic spin ordering. One factor leading to this discrepancy is the curvature of the nanotubes; the curvature increases the distribution of the edge state outside the nanotube. The slightly extended nature of the edge state on the nanotube enhances overlap between the wave function along the edges and results in small but substantial dispersion of the flat band. Owing to this small dispersion, the energy band of the edge state is partially occupied and results in the large density of states at the Fermi level inducing the Fermi level instability. Another factor leading to the difference between the TB and LSDA results is the dimensionality of the nanotube also plays an important role to induce the magnetic moment on the nanotubes. Our LSDA calculations show that the graphite sheet with the same topological line defect does not exhibit magnetic ordering. In this case, the width of the flat band is narrower by about 50 meV and they are unoccupied by electrons. Moreover, the extended character of the states around the \(X\) point results in another Fermi surface around the zone boundary of the two-dimensional BZ besides the surface located around \(k=2\pi/3\). Thus the magnetism on the nanotubes with the topological line defects results from the interesting interplay between the dimensionality and the curvature effects of the nanotubes.

In order to clarify the stability of the nanotubes with the topological defect, we discuss their energetics. Figure 4 shows total energies of the nanotube with the topological line defects as a function of the tube radius together with those of the perfect armchair nanotubes. The total energy of the nanotubes with the defect monotonically decreases with increasing the tube radius and is slightly higher by 40 meV/atom than the perfect nanotubes with the same radius. Hence, the nanotubes with the topological defect are energetically stable so that they keep their tubular structures under certain conditions. Indeed, our tight-binding molecular-dynamics (TBMD) simulations\(^{25}\) to check the thermal stability of \((3,3)_{D}\) nanotube including 260 atoms show that they are stable up to 3000 K for over 48 psec simulation time. Recently, Lee et al., discussed a transformation of pentagon-octagon defect into pentagon-heptagon defect on graphene sheet using the bond rotation, which occurs at 3800 K.\(^{26}\) The pentagon-octagon defect on \((3,3)_{D}\) nanotube, however, is not transformed into the pentagon-heptagon defect at even 4000 K before the destruction of tubular structure after 35 ps simulation time. The above results are also corroborated by...
DFT calculations with the constraint minimization scheme, where about 7 eV of fairly high activation barriers prevent such bond rotations. We consider that the linear arrangement of pentagon-octagon pair and the curvature effect stabilize the novel defect structure.

It is expected that the nanotubes with the topological line defect are synthesized by the implantation of C2 clusters in the perfect nanotubes. Indeed, our TBMD calculations show that reaction barriers of sequential implantation of the C2 clusters are 2 or less eV per cluster. Another possible pathway is the thermal annealing of the nanotubes with atomistic defects: We find that an array of atomic divacancies are easily transformed into the topological line defect within several ps/eV TBMD simulations at 1000 K.27 Thus, the formation of vacancy array is one of the valid processes for that of the topological line defect. Actually, Hashimoto et al., succeeded to form some vacancies intentionally on a graphene using electron beam irradiation,28 which may lead to the intentional formation of divacancies and a divacancy array on nanotubes. The scanning probe technique is another possible candidate, which is a promising tool to manipulate atoms on semiconductor surfaces. It was indeed demonstrated that H atoms on the H-covered Si (001) surfaces are removed along a Si dimer row in a controlled way.29,30 Thus, the magnetism on the nanotubes with the topological line defect is expected to take place by using the similar experimental technique.

In summary, our calculations based on the density functional theory have clarified that the armchair nanotubes with the topological line defect consisting of the pentagon and octagon rings exhibit ferromagnetic spin ordering without network edges, dangling bonds, or carrier doping. The polarized electron spins are localized at the edges of the topological line defect but ferromagnetically extended along the tube direction. Calculated magnetic moment is about 0.04 μB/Å. We give an analytic solution for a flat band state near the Fermi level, which induces the magnetic ordering. The results give a possibility of long-range spin ordering on the π electron networks consisting solely of threefold coordinated carbon atoms.

We would like to thank A. Oshiyama for providing the DFT program used in this work. This work was partly supported by CREST-JST, University of Tsukuba, NEDO, and MEXT. Computations were done at the SIPC, University of Tsukuba, YITP, Kyoto University, and RCCS, Okazaki National Institute.

21Convergence of the total energy, the energy gain of the ferromagnetic state, and the number of polarized electron spin with respect to the k points is examined on the (10,10)D nanotubes with six, eight, and ten k points. The total energy obtained with four k points is higher by 0.3 meV/atom than that obtained with the ten k-point calculation, while the energy gain with four k points is almost the same as that obtained with the ten k points (2 meV). The amount of magnetic moment with four k points is larger by 0.008 μB/Å.