Electronic structures and three-dimensional effects of boron-doped carbon nanotubes

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Abstract
We study boron-doped carbon nanotubes by first-principles methods based on the density functional theory. To discuss the possibility of superconductivity, we calculate the electronic band structure and the density of states (DOS) of boron-doped (10,0) nanotubes by changing the boron density. It is found that the Fermi level density of states \( D(\epsilon_F) \) increases upon lowering the boron density. This can be understood in terms of the rigid band picture where the one-dimensional van Hove singularity lies at the edge of the valence band in the DOS of the pristine nanotube. The effect of three-dimensionality is also considered by performing the calculations for bundled (10,0) nanotubes and boron-doped double-walled carbon nanotubes (10,0)@(19,0). From the calculation of the bundled nanotubes, it is found that interwall dispersion is sufficiently large to broaden the peaks of the van Hove singularity in the DOS. Thus, to achieve the high \( D(\epsilon_F) \) using the bundle of nanotubes with single chirality, we should take into account the distance from each nanotube. In the case of double-walled carbon nanotubes, we find that the holes introduced to the inner tube by boron doping spread also on the outer tube, while the band structure of each tube remains almost unchanged.

Keywords: boron doping, carbon nanotubes, superconductivity, density functional theory

1. Introduction
Carbon materials have high Debye frequency. Therefore their doping has been attempted in order to achieve high-transition-temperature superconductivity. In fact, several studies have revealed superconductivity in carrier-doped carbon materials, such as intercalated graphite compounds [1–3] and fullerene compounds [4–6], where carrier doping is realized via alkali-metal or alkaline-earth-metal doping. In the case of diamond, superconductivity has been realized by boron doping [7]. In these materials, superconductivity is considered to be the BCS-type (BCS refers to Bardeen–Cooper–Schrieffer) and the transition temperatures are roughly scaled using the value of the Fermi level density of states. In addition to these materials, recently, the sign of superconductivity in carbon nanotubes has been observed [8–11], and in some cases, carriers seem to be introduced by boron doping [10, 11].

The carbon nanotube, which is a rolled-up graphene sheet, is widely studied because of its various attractive features. For example, its electronic structure and transport properties (metallic or semiconducting) depend on the chirality, and there are divergences in the density of states because of the one-dimensional geometry. Concerning the boron doping of carbon nanotubes, there have been several experimental [12–21] and theoretical [22–24] studies. However, the relationship between the boron concentration and the conductivity is yet unclear. Thus, to clarify the possibility of superconductivity in carbon nanotubes, theoretical predictions are important, such as those of the doping rate dependence of the Fermi level density of states and the effect of three-dimensionality, which is essential to stabilize the superconductivity.

In this work, we study the boron-doped carbon nanotubes using the density functional theory. To discuss the possibility of superconductivity, we calculate the Fermi level density of...
states $D(\varepsilon_F)$ of boron-doped (10,0) nanotubes by changing the boron density. We also consider the two types of three-dimensional effects, that is, bundled and multiwall nanotubes. From the calculation of the bundled (10,0) nanotubes, we estimate the effect of the interwall interactions on the one-dimensional electronic structure. Furthermore, we compute the electronic structures of (10,0)@(19,0) boron-doped double-walled carbon nanotube (DWCNT) to clarify the effect of interwall interactions [25, 26]. We also discuss how the electronic structure of the B-doped DWCNT can be constituted by the electronic structures of the individual single-walled carbon nanotubes (SWCNTs).

2. Studied systems and computational methods

In the present work, we focus on the zigzag nanotube (10,0) as a typical semiconducting tube. There are 40 atoms in the unit cell of a (10,0) tube and we substitute one carbon atom with a boron atom, BC$_{39}$. We also study the cases of larger unit cells, such as BC$_{79}$, BC$_{119}$ and BC$_{159}$. Calculations are performed in the hexagonal unit cell with periodic boundary conditions. For the isolated nanotubes, we take a long lattice constant (supercell) so that the interwall distance between tubes is at least 7 Å, which should be long enough to neglect the effect of the intertube interactions on the electronic band structure.

To discuss the three-dimensional effects, we also consider a bundle of (10,0) nanotubes in the hexagonal unit cell and the DWCNT (10,0)@(19,0).

All calculations are carried out within the local-density approximation (LDA) in the framework of the density functional theory. We use norm-conserving pseudopotentials [27], the Ceperley–Alder exchange-correlation energy functional [28] parametrized by Perdew and Zunger [29] and a plane-wave basis with a cutoff energy of 50 Ryd. We take $1 \times 1 \times 6k$ points in the first Brillouin zone for the isolated tubes and $3 \times 3 \times 4k$ points for the bundled tubes. In all calculations, the geometries are fully optimized.

Figure 1. Doping rate dependence of the Fermi level density of states. Each point corresponds to BC$_{19}$, BC$_{79}$, BC$_{119}$ and BC$_{159}$. The broken curve is a guide for the eye. Inset shows the density of states of BC$_{159}$. The Fermi level is set to zero.

3. Results and discussion

3.1. Electronic structures of isolated tubes

We first discuss the Fermi level density of states per atom $D(\varepsilon_F)$ of the isolated single-walled nanotubes. Figure 1 shows the $D(\varepsilon_F)$ of B-doped (10,0) nanotubes with boron densities of 0.625 at.% to 2.50 at.%.

Figure 2. Density of states of bundled and isolated pristine (10,0) nanotubes.

3.2. Bundle effects

To discuss the bundle effects, we calculate the density of states of a bundle of pristine (10,0) nanotubes. The interwall distance is 3.24 Å which is determined by geometry optimization. Figure 2 shows the comparison of the densities of states between isolated and bundled pristine (10,0) nanotubes. At the optimized interwall distance, it is found that peaks at the van Hove singularity of a one-dimensional system are highly suppressed because of the intertube dispersion of $\sim$0.5 eV. The gap of the bundled tube collapses and the density of states appears similar to that of graphite or graphene. Thus, to achieve the large $D(\varepsilon_F)$ and to realize superconductivity in the uniform-chirality crystalline carbon nanotubes, we should introduce a large amount of carriers. For this purpose, boron doping might not be promising because substitutional boron doping requires positive formation energy [24], and only a small amount of boron can be doped experimentally [17], except for the formation of BC$_3$ domains [16]. Alkali-metal or alkaline-earth-metal doping, as in the graphite or fullerene compounds, might
be more appropriate, though superconductivity has not yet been discovered [31]. Note that the broadening of the van Hove peaks owing to the interwall interaction is commonly observed in optical measurements [32].

If we can tune the interwall distance, the one-dimensional van Hove singularity will be recovered by pulling apart each nanotube. To observe the influence of interwall distance, we plot in figure 3 the peak values of the density of states around the edge of the valence band top.

3.3. DWCNT

To discuss the three-dimensional effect further, we also consider the DWCNT (10,0)@(19,0). We substitute a carbon atom of the inner tube with a boron atom as BC_{19}@C_{76} because boron should be more easily doped in the inner tube [24]. The electronic band structure and the density of states are shown in figure 4. There are three bands at the Fermi level. From the characteristics of the wave functions, we find that two bands at the top of the valence band are from the inner B-doped (10,0) tube and the third band is from the outer (19,0) tube. The mixing of wave functions between the inner and outer tubes is small. In fact, the band structure of this B-doped DWCNT is well reproduced as a sum of the band structures of a B-doped (10,0) tube and a pristine (19,0) tube, if we consider the vacuum level properly. These results indicate that holes originally introduced in the inner tube upon boron doping also spread to the outer tube without changing the shapes of the band structures of each nanotube, and that this charge transfer only affects the work functions of each nanotube. We hypothesize that the electronic structures of general B-doped multiwalled carbon nanotubes (MWCNTs) behave similarly and that we can predict the band structures and density of states of MWCNTs from the electronic structures and work functions of the individual tubes, as in the case of pristine MWCNTs [33].

4. Summary

We have studied the effect of boron doping in the isolated and bundled SWCNTs and the DWCNT by LDA calculations. To discuss the possibility of superconductivity, we calculated the doping rate dependences of the Fermi level density of states $D(\epsilon_F)$ in the isolated SWCNT and found that $D(\epsilon_F)$ can be large even with low carrier concentrations because of the one-dimensional van Hove singularity. We observed how the divergence of the one-dimensional van Hove singularity is suppressed by the bundling. In addition, we obtained the electronic structure of the B-doped DWCNT (10,0)@(19,0) and found that the electronic structure of the DWCNT and the possibility of charge transfer can be discussed from the electronic structures of the individual SWCNTs. According to these results, it is possible to predict $D(\epsilon_F)$ in various situations, which is useful in designing preferable materials for superconductivity.

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