

# Energetics and Electronic Structures of Carbon Nanotube Solids

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On the basis of the density functional theory, we study energetics and electronic structure of solids consisting of single-wall carbon nanotubes, (6,0), (6,6), and (12,0). We find that mutual orientation angles of adjacent nanotubes are common in all the stable structures obtained. The characteristics of the intertube arrangement is similar to those of AB stacking in graphite. In the (n,n)-tube solid, it is found that the pseudogap due to symmetry breaking in the solid appears, and that this gap is enhanced by tiny rotation of tubes from the AB stacking arrangement.

Key words: carbon nanotube, solid, energetics, electronic structure

## 1. INTRODUCTION

Bundles of single-wall carbon-nanotubes are recently synthesized using laser ablation technique [1], and manifest themselves as a fascinating example of hierarchical solids. Solid C<sub>60</sub>[2] is another example of the hierarchical solid in which C<sub>60</sub> cluster states form solid-state energy bands as if atomic states form energy bands in ordinary solids [3]. In the case of solid C<sub>60</sub>, the inter fullerene interaction, which depends on the inter fullerene orientation and distance, plays an important role to determine the fascinating solid state properties. For instance, the superconducting transition temperature of alkali-atom doped solid C<sub>60</sub> depends on the inter-fullerene interaction [4]. Since the solid nanotube possesses the same hierarchy as the solid C<sub>60</sub>, the solid nanotube is expected to be a starting material for many compounds. Hence, it is important to clarify

the dependence of energetics of nanotubes solid on the intertube orientation and distance.

In the present work, we study the energetics and electronic structures of nanotube solids, i.e. hexagonally packed (6,0), (12,0), and (6,6) nanotubes, based on the total-energy calculations using the local density approximation (LDA) in the framework of the density-functional theory. In all the solids, the stable tube orientation is found to realize the AB stacking for adjacent nanotubes as in the case of graphite. In addition, in the (6,6) solid, the tiny rotation of tube from perfect AB stacking is found. We also find the AA stacking inter-tube arrangement is not stable in energy except (6,0) solid.

## 2. METHODS

In the present work, the electronic and geometric structure have been studied by using

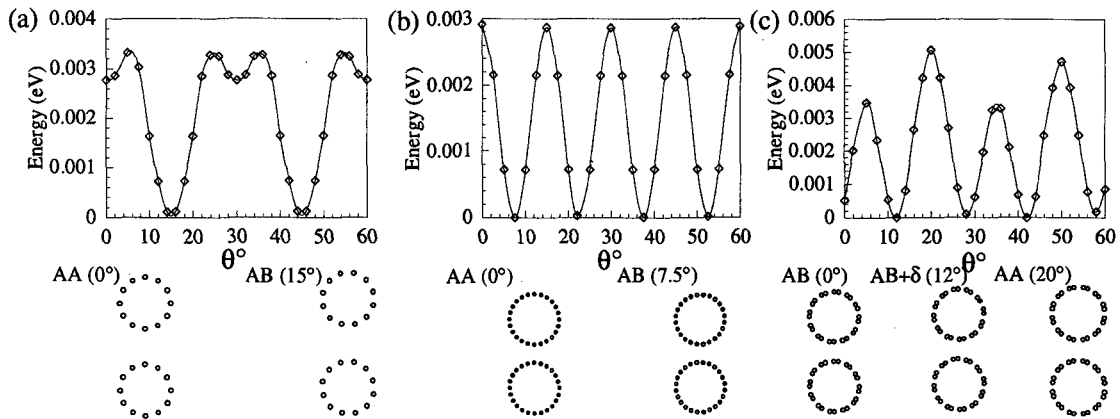


Figure 1: Dependence of the total energy of (a) (6,0), (b) (12,0), and (c) (6,6) solids on the mutual orientation angle  $\theta$ . AA and AB denote the tube arrangement being similar to AA and AB stacking of graphite. All energies are given per atom.

the local-density approximation (LDA) in the density-functional theory [5,6]. To express the exchange-correlation potential of electrons, we use a functional form fitted to the Ceperley-Alder result [7,8]. Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction [9,10]. 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 cut-off energy of 50 Ry which is known to give enough convergence of total energy to discuss the relative stability of various carbon phases [9]. We use 54  $k$ -points for the integration in  $k$  space. We adopt the conjugate-gradient minimization scheme both for the self-consistent electronic-structure calculation and for the geometric optimization [11].

### 3. RESULTS

The tubes which we explore are metallic, (6,6), or small-gap semiconducting, (6,0), (12,0), in their individual-tube phase [12,13]. We place the nanotubes in triangular lattice. Optimized lattice constant in the direction perpendicular to

the tube is 7.9 Å, 11.4 Å, and 12.6 Å for (6,0), (6,6), and (12,0) solids, respectively. In each case, nanotubes are placed in an arrangement where all atoms (bonds) in the nanotube possess a corresponding atom (bond) in the neighboring tube as in the case of the hexagonal AA-stacking graphite. In all cases, internal atomic coordinates in a cell are also fully optimized. The structural distortion of atoms from the perfect circumference, that is buckling, is rather small in (6,0) and (12,0) solids but significant buckling is observed in the (6,6) solid under the equilibrium lattice constant. The magnitude of buckling for the (6,0), (12,0), and (6,6) is 0.01 %, 0.03 %, and 0.36 %, respectively.

The calculated dependence of total energy on the mutual orientation angle  $\theta$  is shown in Fig. 1. Because of their chirality, (6,0), (6,6), and (12,0) with hexagonal lattice, we find the total energy to be periodic in  $\theta$  with a period  $\Delta\theta = 30^\circ$ ,  $\Delta\theta = 30^\circ$ , and  $\Delta\theta = 15^\circ$  for (6,0), (6,6), and (12,0) solids, respectively. In all cases, we find that the characteristics of the intertube arrangement is similar to those of AB stacking in graphite. In the (n,0) solids, the most stable orientations

are found to be  $\theta = 15^\circ$ ,  $\theta = 7.5^\circ$  for (6,0) and (12,0) solids, respectively. In both cases, under the optimum nanotube orientation, all the atoms on adjacent nanotubes are found to be kept as far away from each other as possible. In the (n,n)-tube solid, it is known that the pseudogap due to symmetry breaking appears at the Fermi level. This gap is enhanced by tiny rotation of tubes from the AB stacking arrangement, and the most stable rotation angle gives the widest pseudogap on the density of states. On the other hand, intertube arrangements of AA stacking is not preferable in energy for (6,6) and (12,0) solids. However, in the (6,0) solid, this arrangement corresponds to the local minimum in energy although the barrier against the global-minimum geometry (AB-stacking arrangement) is very small.

#### 4. SUMMARY

We have studied orientation effects on electronic and geometric structure of crystalline carbon nanotubes, (6,0), (12,0), and (6,6) by using the local density approximation. We found that the most stable orientation angle is AB-stacking arrangement as in the case of the graphite. However, AA-stacking arrangement is also metastable in the thin nanotube solid, (6,0)-solid. Furthermore, tiny rotation of tubes from perfect AB-stacking related to the presence of pseudogap is found in the (n,n) nanotube solid.

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