Crystals of covalently bonded carbon nanotubes: Energetics and electronic structures

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Structure and stability of hexagonally polymerized carbon nanotube solids are investigated using a generalized tight-binding molecular-dynamics scheme. The stable structures show internanotube connectivity via the $2+2$ and $2+4$ cycloaddition process. Calculated electronic density of states indicates that the studied materials have semiconducting or insulating properties depending on the type of internanotube connectivity in a system containing atoms with $sp^2$ and $sp^3$ bondings. We also predict the existence of a nanotube clathrate form.

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The discovery and large scale synthesis of single-wall carbon nanotubes (SWNT) have inspired tremendous interest in the interdisciplinary investigations of their properties.\(^1\)\(^-\)\(^4\) Very recently, molecular crystals of closely packed carbon tubes of nanometer diameter have been synthesized using special techniques.\(^5\) Investigations of van der Waals bonded nanotube bundles under high pressure, therefore, seem worthwhile and timely. The goal is to obtain phase transformation for SWNT in a manner similar to that reported for polymerized $C_{60}$ fullerites.\(^6\)\(^-\)\(^9\) Just as in the case of $C_{60}$ fullerenes, it was found that SWNT material also experienced reversible deformations at room temperature and at moderate pressure (up to 3 GPa). The forms of nanotubes were observed to change from circular into elliptical\(^10\) or polygonal\(^11\) shapes when subjected to pressure as predicted by Tersoff and Ruoff.\(^12\) Pressure investigation of SWNT’s up to 25.9 GPa using Raman spectra have shown no appreciable structural changes.\(^13\) However, recently Popov et al.\(^14\) have synthesized superhard materials of polymerized nanotubes (P-SWNT) under high-pressure treatment (up to 29 GPa). In a diamond anvil cell they applied shear deformation to a specimen obtained from Rice University.\(^3\) Thus, the question: “How SWNT’s may be polymerized?” still remains to be answered. Even though the possibility of joining of SWNT’s via covalent bonds have been considered in earlier works,\(^15\)\(^,\)!\(^16\) geometrical, and electronic characteristics of P-SWNT structures as well as their energetics have not been reported so far.

As shown in Ref. 12, polymerization should occur under $\approx 10$ GPa pressure for nanotubes of diameter $\approx 10$ Å. It can be speculated that nanotubes with diameters smaller than 10 Å and large curvature, in which significant deviation from $sp^2$ geometry is seen, will bond with each other under high-pressure and high-temperature treatment in a manner similar to that for the $C_{60}$ fullerenes.\(^6\)\(^-\)\(^9\),\(^26\)

In this Rapid Communication we focus on metallic SWNT molecular crystals as an example to illustrate changes in electronic properties after the formation of covalent bonds between nanotubes in this material. We address the problem of the stability and electronic properties of P-SWNT structures, consisting of “armchair” $(n,n)$ and “zigzag” $(n = 3q,0)$ nanotubes\(^3\) of diameter 1 nm (in real ropes the nanotube diameter\(^11\)\(^-\)\(^4\) fluctuates from 0.8 to 2 nm). To the best of our knowledge, we are aware of only one work where detailed calculations of stability and electronic spectra of SWNT molecular crystals were carried out using (6,6) nanotubes as an example.\(^17\) We, therefore, investigate P-SWNTs of this type first and pursue investigations of (9,0) and (12,0) P-SWNT crystals. It should be noted, however, that P-SWCNT structures can form from arbitrary $(n,m)$ nanotubes. For example, it has been shown that monoclinic P-SWNT structure can be created from (10,10) nanotubes.\(^18\)

Theoretical calculations are carried out as follows: We first use molecular mechanics MM+ method\(^19\) to obtain approximate P-SWNT structures. Some of the hexagonal P-SWNT structures thus obtained were first reported in Ref. 18. We then use the generalized tight-binding molecular-dynamic (GTBMD) scheme of Menon and Subbaswamy\(^20\) to obtain energetically stable P-SWNT configurations and their electronic structures. The GTBMD scheme makes explicit use of the nonorthogonality of the atomic orbitals and allows for full relaxation of covalent systems with no symmetry constraints. This scheme has been successfully used in obtaining geometries and vibrational properties of fullerenes and nanotube structures in agreement with both experiments and calculations based on \textit{ab initio} methods.\(^20\)\(^,\)!\(^21\) For the study of solid P-SWNT structures we use a $k$-space formalism incorporating a constant pressure (movable wall) ensemble.\(^25\) This allows for a simultaneous relaxation of lattice and basis degrees of freedom. A uniform grid consisting of 126 $k$ points was used in the calculation of forces. The electronic band structures of all the relaxed geometries were obtained using a $sp^3s^* $ tight-binding model\(^21\) that correctly reproduces the band gap for bulk carbon in the diamond structure.
The molecular crystal has unit cell parameters
\[ a = 9.883 \, \text{Å}, \quad c = 2.634 \, \text{Å} \]
and two distinct C-atom positions \[ C1(sp^3) = (0.377, 0.089, 0.0), \quad C2(sp^3) = (0.330, 0.182, 0.5). \]
The bonds linking adjacent nanotubes have lengths of 1.557 Å and 1.561 Å, confirming covalent nature of the bonding for carbon systems. The equilibrium energy of this structure is predicted to be higher than that for graphite by 1.26 eV/atom. Therefore, this structure is the least stable of all considered in this work. Its density, \( \rho = 2.16 \, \text{g/cm}^3 \), is not significantly different from the density of the structure in Fig. 1(a). We note that the densities of tetragonal diamondlike materials are usually 1.5 times larger than that of the structure in Fig. 1(d), indicating a high degree of porosity for this material when compared with diamond. This property should make doping with various elements relatively easy for many optical applications.

In Fig. 2, we show the electronic band structure for the P-SWNT (12,0) structure [Fig. 1(b)]. A line is along the \( k_z \) direction (symmetry axis of the nanotube). As the figure shows, the structure is predicted to be a semiconductor with a band gap of 1.3 eV. The polymerization of (6,6) tubes via

We next turn our attention to another structure in which individual (6,6) nanotubes are connected to six neighbors by “hexagon+hexagon” cycloaddition of bonds between each adjoining atom pair. This structure, thus, consists of all \( sp^3 \) atoms and forms a nanotube clathrate. The GTBMD relaxed geometry of the hexagonal cell is schematically shown in Fig. 1(d). We find that the relaxed structure preserves the space group \( P6_3/mmc \) and has unit cell parameters \[ a = 9.883 \, \text{Å}, \quad c = 2.634 \, \text{Å} \] and two distinct C atoms \[ C1(sp^3) = (0.377, 0.089, 0.0), \quad C2(sp^3) = (0.330, 0.182, 0.5). \] The bonds linking adjacent nanotubes have lengths of 1.557 Å and 1.561 Å, confirming covalent nature of the bonding for carbon systems. The equilibrium energy of this structure is predicted to be higher than that for graphite by 1.26 eV/atom. Therefore, this structure is the least stable of all considered in this work. Its density, \( \rho = 2.16 \, \text{g/cm}^3 \), is not significantly different from the density of the structure in Fig. 1(a). We note that the densities of tetragonal diamondlike materials are usually 1.5 times larger than that of the structure in Fig. 1(d), indicating a high degree of porosity for this material when compared with diamond. This property should make doping with various elements relatively easy for many optical applications.
states and translating properties. Its electronic band structure and density of polymers formed from values of 1.3 and 2.6 eV, respectively. Note that the nanotube $3$-hybridized atoms accompanied by a metal-insulator transition. This is further illustrated by the case of the all $sp$ nanotube clathrate structure of the semimetallic behavior of a molecular nanotube. $2 \times 2$ cycloaddition pairs, therefore, leads to a transformation of the semimetallic behavior of a molecular (6,6) nanotube crystal into a semiconducting one.

We have also carried out electronic band structure calculations for the geometries shown in Figs. 1(a) and 1(c) containing a mixture of $sp^2$ and $sp^3$ atoms and obtain band-gap values of 1.3 and 2.6 eV, respectively. Note that the nanotube polymers formed from (9,0) metallic tubes also show insulating properties. Its electronic band structure and density of states (DOS) are shown in Fig. 3. When subjected to high-temperature–high-pressure treatment, a molecular nanotube solid has the effect of opening a gap in initially semimetallic nanotubes. It is reasonable to expect that the presence of the $sp^2$-hybridized atoms with rigid bonds in structures shown in Figs. 1(a), 1(b), and 1(c) can result in a rather large value for the elastic modulus, suggesting the existence of hard materials of such solids similar to superhard C$_{60}$ fullerites reported.\textsuperscript{8,9} The electronic behavior of nanotube polymer should be contrasted with that of the C$_{60}$ polymer. While the C$_{60}$ molecular crystals have larger gap than the C$_{60}$ polymer phases ($\approx 2$ eV vs $\approx 1$ eV (Ref. 26)), molecular crystals of metallic nanotubes (diameter $\approx 1-1.5$ nm) may be metallic; semiconducting nanotubes may even close the gap when forming molecular crystals.\textsuperscript{25} Moreover, as we have shown using the (6,6) nanotube polymer as an example, nanotube polymers are rather large gap semiconductors.

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