Crystals of covalently bonded carbon nanotubes: Energetics and electronic structures

Leonid Chernozatonskii*

Institute of Biochemical Physics, Russian Academy of Sciences, Moscow 117977, Russian Federation

Ernst Richter[†]

DaimlerChrysler AG FT3/SA, Wilhelm-Runge-Strasse 11, 89081 Ulm, Germany

Madhu Menon[‡]

Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055
and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045

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.

PACS number(s): 73.61.Wp, 71.20.Tx

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} fullerites, 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.[1] 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 ≈ 10 GPa pressure for nanotubes of diameter ≈ 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} fullerites.[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[1-4] 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 *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.[22] 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[23] that correctly reproduces the band gap for bulk carbon in the diamond structure.
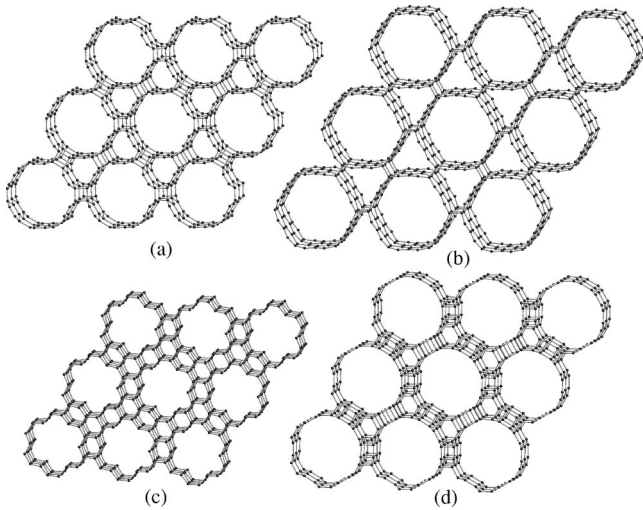
FIG. 1. Various polymeric solids formed from (a) (6,6), (b) (12,0), (c) (9,0) and, (d) another (6,6) carbon nanotube via $2+2$ and/or $2+4$ cycloadditions. While (a), (b), and (c) contain geometries with mixed sp^2- and sp^3-bonded atoms, the structure in (d) has all sp^3-bonded atoms and forms a nanotube clathrate.

We next describe a number of structures obtained from high-pressure–high-temperature treatment of SWNT bundles which, while retaining the SWNT rope structures, results in the formation of covalent bonding between them by means of cycloaddition process similar to that found in C_{60} fullerites.[6–9,24] It should be noted that a rope of identical metallic nanotubes without any covalent intertube bonding could be metallic [as was found in the case of a (6,6) nanotube crystal[17]]. In the case of semiconducting nanotubes the rope formation without covalent bonding may even lead to the closing of the gap as was found for a (10,0) nanotube bundle.[25]

In Fig. 1(a) we show a fully relaxed structure consisting of hexagonally packed (6,6) nanotubes with combinations of sp^2- and sp^3-hybridized atoms with an sp^2 to sp^3 ratio of 1:1. Each individual nanotube is connected to six neighbors by $2+2$ cycloaddition of bonds between each adjoining atom pair. This is analogous to the rhombohedral C_{60} solid reported.[8] The equilibrium energy of this structure is predicted to be higher than that of graphite by 0.52 eV/atom. The crystal of Fig. 1(a) belongs to the space group $P6/mmm$ with unit-cell parameters $a=9.918$ Å and $c=2.593$ Å. The two distinct C-atom positions are C1(sp^3)=(0.378, 0.088, 0.0) and C2(sp^2)=(0.297, 0.158, 0.5). The bonds linking the adjacent nanotubes each have a length of 1.520 Å. The crystal density $\rho=2.18$ g/cm^3 is more than that of its molecular crystal by 1.24 times. Note that the molecular crystal has unit cell parameters (in angstroms) $a=d+d_t=11.36$, $c=2.46$; $d_t=3.2$ Å, $d(6,6)=8.16$, where d is the tube diameter and d_t the intertube distance. In the polymerized structure the individual (6,6) tubes have three distinct bond lengths in the 1.36–1.53 Å range [see Fig. 1(a)].

The closed packing of (12,0) nanotubes can result in another polymeric solid form with internanotube connectivity via $2+2$ cycloaddition. The fully relaxed structure containing a mixture of sp^2 and sp^3 atoms is shown in Fig. 1(b).

The primitive cell contains 48 atoms with three nonequivalent atoms given by C1(sp^3)=(0.434, 0, 0.177); C2(sp^2)=(0.331, 0.121, 0.349); C3(sp^2)=(0.226, 2.226, 0.169). The sp^2 to sp^3 ratio of atoms is 3:1. The density ρ of this structure is 1.94 g/cm^3. It, again, has $P6/mmm$ symmetry with cell parameters $a=11.53$ and $c=4.30$ Å. The structure is found to be very stable with cohesive energy only 0.18 eV/atom higher than that of graphite. Electronic structure analysis shows it to be semiconducting with a gap of 1.3 eV.

We have also performed calculations to determine the equilibrium geometry for (9,0) nanotube polymers which have the same diameter as C_{60}.[4] The cohesive energy of the GTBMD relaxed structure is predicted to be only 0.29 eV/atom higher than that for graphite. In Fig. 1(c) we show this structure of hexagonally packed tubes with a mixture of sp^2 and sp^3 hybridized atoms with a sp^2 to sp^3 ratio of 1:2. Each individual nanotube is connected to six neighbors via $2+4$ cycloaddition of bonds between each two adjoining atom pairs. The supercell used here consisted of 36 atoms. The crystal shown in Fig. 1(c) belongs to space group $P6_3/mcm$, has cell parameters (in hexagonal aspect) $a=8.613$ Å, $c=4.054$ Å, and two distinct C-atom positions C1(sp^2)=(0.355, 0.0, 0.332), C2(sp^3)=(0.332, 0.169, 0.186). The bonds linking the adjacent nanotubes each have a length of 1.525 Å. The crystal density, $\rho=2.77$ g/cm^3, is 1.49 times more than its molecular crystal density. Note that the molecular crystal has unit cell parameters (in angstroms) $a=d+d_t=10.26$, $c=4.26$; $d_t=3.2$, $d(9,0)=7.06$. The individual (9,0) tubes in the polymerized structure have three distinct bond lengths in the 1.36–1.53 Å range [see Fig. 1(c)].

We next turn our attention to another structure in which individual (6,6) nanotubes are connected to six neighbors by "hexagon+hexagon" cycloaddition[24] 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 $P6/mmm$ and has unit cell parameters $a=9.883$ Å, $c=2.634$ Å and two distinct C atoms C1(sp^3)=(0.377, 0.089, 0.0), 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, $\rho=2.16$ 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)]. ΓA 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
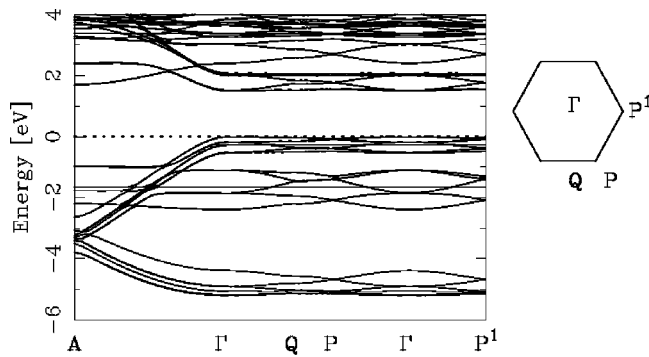
FIG. 2. The electronic band structure of the geometry shown in Fig. 1(b) showing semiconducting properties. The figure on the right shows the Brillouin zone in the (k_x, k_y) plane. ΓA line is along the k_z direction (symmetry axis of the nanotube).

FIG. 3. The electronic band structure and density of states (DOS) of the geometry shown in Fig. 1(c).

$2+2$ cycloaddition pairs, therefore, leads to a transformation of the semimetallic behavior of a molecular (6,6) nanotube crystal[17] 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 crystal may transform into a phase with maximal number of sp^3-hybridized atoms accompanied by a metal-insulator transition. This is further illustrated by the case of the all sp^3 nanotube clathrate structure [Fig. 1(c)]. This diamondlike tetragonal carbon crystal has an energy gap of 5.8 eV, similar to that of diamond.

In summary, we have carried out calculations on the structure, stability, and electronic properties of the hexagonal polymerized nanotube solids using GTBMD scheme. The P-SWNT solids are predicted to be less stable than free graphite and nanotube molecular materials. Our calculated electronic DOS 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. Our results indicate that
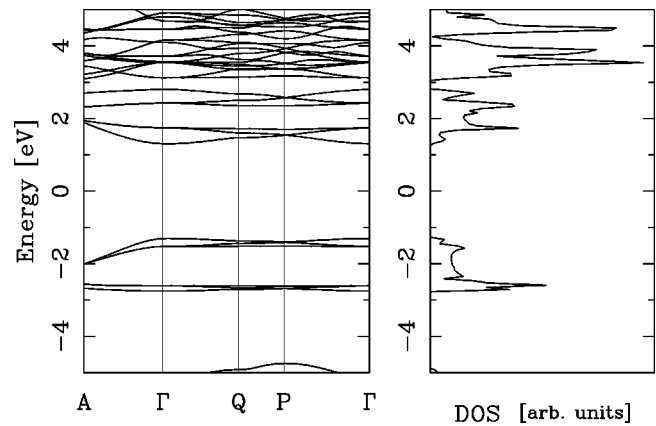
the value of the electronic gap increases with the number of sp^3 atoms in the P-SWNT structures of diameters ≈ 1 nm considered. The presence of the single bonds resulting from the $2+2$ and $2+4$ cycloaddition process in the P-SWNT solids has the effect of opening a gap in initially semimetallic nanotubes. 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.[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 [≈ 2 eV vs $\leqslant 1$ 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.[25] Moreover, as we have shown using the (6,6) nanotube polymer as an example, nanotube polymers are rather large gap semiconductors.

*Electronic address: cherno@sky.chph.ras.ru

†Electronic address: ernst.richter@daimlerchrysler.com

‡Electronic address: super250@pop.uky.edu

[1] A. Thess *et al.*, Science **273**, 483 (1996).

[2] H. Kataura, A. Kimura, Y. Ohtsuka, Y. Maniwa, T. Hanyu, and Y. Achiba, Jpn. J. Appl. Phys., Part 2 **37**, L616 (1998).

[3] P. Nikolaev, M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert, K.A. Smith, and R.E. Smalley, Chem. Phys. Lett. **299**, 314 (1999).

[4] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).

[5] R.R. Schluttler, J.W. Seo, J.K. Gimzewski, C. Dunkan, M.S.M. Saifullah, and M.E. Welland, Science **292**, 1136 (2001).

[6] Y. Iwasa *et al.*, Science **264**, 1570 (1994).

[7] M. Nuñez-Regueiro, L. Marques, and J.-L. Hodeau, Phys. Rev. Lett. **74**, 278 (1995).

[8] V.D. Blank, S.G. Buga, and N.R. Serebryanaya, Appl. Phys. A: Mater. Sci. Process. **A64**, 247 (1997).

[9] L. Chernozatonskii, N. Serebryanaya, and B. Mavrin, Chem. Phys. Lett. **297**, 257 (2000).

[10] S.A. Chesnokov, V.A. Nalimova, A.G. Rinzler, R.E. Smalley, and J.E. Fisher, Phys. Rev. Lett. **82**, 343 (1999).

[11] J. Tang, L.C. Qin, T. Sasaki, M. Yudasaka, A. Matsushita, and S. Iijima, Phys. Rev. Lett. **85**, 1887 (2000).

[12] J. Tersoff and R.S. Ruoff, Phys. Rev. Lett. **73**, 676 (1994).

[13] U.D. Venkateswaran, A.M. Rao, E. Richter, M. Menon, A. Rintzler, R.E. Smalley, and P.C. Eklund, Phys. Rev. B **59**,

10 928 (1999).

[14] M. Popov, M. Kyotani, Y. Koga, and R. J. Nemanich, Phys. Rev. B **65**, 033408 (2002).

[15] Z.Y. Kosakovskaya, L.C. Chernozatonskii, and E. Fedorov, JETP Lett. **56**, 26 (1992).

[16] L.A. Chernozatonskii, Mol. Mat. A **166**, 55 (1996).

[17] J.C. Charlier, X. Gonze, and J.P. Michenaud, Europhys. Lett. **29**, 43 (1994).

[18] L.A. Chernozatonskii, Chem. Phys. Lett. **297**, 257 (1998).

[19] *HyperChem Computational Chemistry* (Hypercube, Inc., Canada, 1996) p. 101.

[20] M. Menon, E. Richter, and K.R. Subbaswamy, J. Chem. Phys.

[21] M. Menon and D. Srivastava, Phys. Rev. Lett. **79**, 4453 (1997).

[22] H.C. Andersen, J. Chem. Phys. **72**, 2384 (1980).

[23] P. Vogl, H.P. Hjalmarson, and J.D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[24] M. O'Keeffe, Nature (London) **352**, 674 (1991).

[25] S. Reich, C. Tomsen, P. Ordejon, and D. Sanchez-Portal, *Program of XVIth International Winterschool on Electronic Properties of Novel Materials* (Kirchberg, Austria, 2002), p. 74.

[26] P. C. Eklund and A. M. Rao, *Fullerene Polymers and Fullerene Composites*, Springer Series in Material Science Vol. 38 (Springer, Berlin, 2000).

104, 5875 (1996).