New Metallic Allotropes of Planar and Tubular Carbon

H. Terrones,[1,2,*] M. Terrones,[1,2] E. Hernández,[1,3] N. Grobert,[1] J-C. Charlier,[4] and P. M. Ajayan[5]

[1]*School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, BN1 9 QJ, United Kingdom*
[2]*Instituto de Física, UNAM, Laboratorio Juriquilla, Apartado Postal 1-1010, 76000 Querétaro, México*
[3]*Institut de Ciencia de Materials de Barcelona–CSIC, Campus de la Universitat Autonoma de Barcelona,*
08193 Bellaterra, Barcelona, Spain
[4]*Université Catholique de Louvain, Unite PCPM Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium*
[5]*Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180-3590*
(Received 3 September 1999)

We propose a new family of layered sp^2-like carbon crystals, incorporating five-, six-, and seven-membered rings in 2D Bravais lattices. These periodic sheets can be rolled so as to generate nanotubes of different diameter and chirality. We demonstrate that these sheets and tubes are metastable and more favorable than C_{60}, and it is also shown that their mechanical properties are similar to those of graphene. Density of states calculations of all structures revealed an intrinsic metallic behavior, independent of orientation, tube diameter, and chirality.

Carbon science has been revolutionized by the discovery and synthesis of fullerenes [1,2] and the subsequent identification of nanotubes [3]. These discoveries revealed that solid carbon, formally believed to be found only as graphite and diamond, was capable of forming novel structures with "nano" sizes [4]. This has led to a wealth of experimental and theoretical studies which has made this field of research one of the most exciting areas in materials science. Theoretical studies [5–7] predict that carbon nanotubes behave either as 1D conductors (quantum wires) or semiconductors, depending on the nanotube structure (radius and chirality). Recently, direct simultaneous measurements of the structure and of the density of states of individual single-wall nanotubes [8] have confirmed this prediction. The carbon bond in graphite is one of the strongest chemical bonds occurring in nature, and consequently nanotubes, which are seamless graphene cylinders, are extraordinarily stiff. Indeed the Young's modulus of nanotubes has been measured experimentally [9–11] and calculated theoretically [12] to be in the order of 1.2 TPa, the highest value known for any material. The combination of electronic and mechanical properties in nanotubes make them ideally suited for several future applications [13].

Both fullerenes and nanotubes incorporate six-membered carbon rings and in order to close these structures defects in the form of pentagons are necessary. The presence of other types of odd-membered rings, such as heptagons, has been indirectly established by electron microscopy observations of helicoidal and bent nanotubes [14] and giant spherical fullerenes [15]. Similarly bond rotational defects, known as Stone-Wales-type transformations, where four hexagons are converted into two sets of pentagon-heptagon pairs, are known to exist in graphite structures [16]. In this context, it is natural to ask the question "Is it possible to devise new structures, similar to graphite, but incorporating all three types of rings?" This is the question we address in this paper. There has been an earlier work proposing the stability of carbon layers made *entirely* of 5-7 rings (pentaheptites) [17]. We propose here a new family of layered carbon materials, which we term Haeckelites [18], consisting of ordered arrangements of pentagons, hexagons, and heptagons, and we study in detail their stability and their electronic and mechanical properties using theoretical methods. Surprisingly, the studied structures turn out to be more stable than C_{60} and can thus be regarded as energetically viable. All the structures are predicted to be metallic, exhibiting a high density of states at the Fermi energy, and to possess high stiffness like their conventional hexagonal graphite counterparts.

The flat covalent carbon crystals proposed here can be categorized as the following: (1) Rectangular ($R_{5,7}$), containing only heptagons and pentagons paired symmetrically within a flat surface (Fig. 1a). Its generation can be achieved by the creation of Stone-Wales-type defects on the graphene sheet, transforming pyrenelike rings into two pairs of heptagons and pentagons. This is similar to the structure proposed earlier [17]. (2) Hexagonal ($H_{5,6,7}$), which exhibits repetitive units of three agglomerated heptagons, surrounded by alternating pentagons and hexagons (Fig. 1b). (3) Oblique ($O_{5,6,7}$) containing pentalene and heptalene units bound together and surrounded by six-membered rings (Fig. 1c) [19]. Tubular structures can be constructed from these 2D arrays in exactly the same way as from graphene [13], namely, by folding the sheet into a seamless tube.

We have performed tight binding (TB) calculations [20] in order to analyze the structural stability and the electronic and mechanical properties of both the planar crystals and the infinite nanotubes constructed from them. Although TB is not as accurate as first principles (FP) calculations, it allows the treatment of larger systems with a reduced computational effort. For the particular case of carbon-based systems there are TB models which are capable of
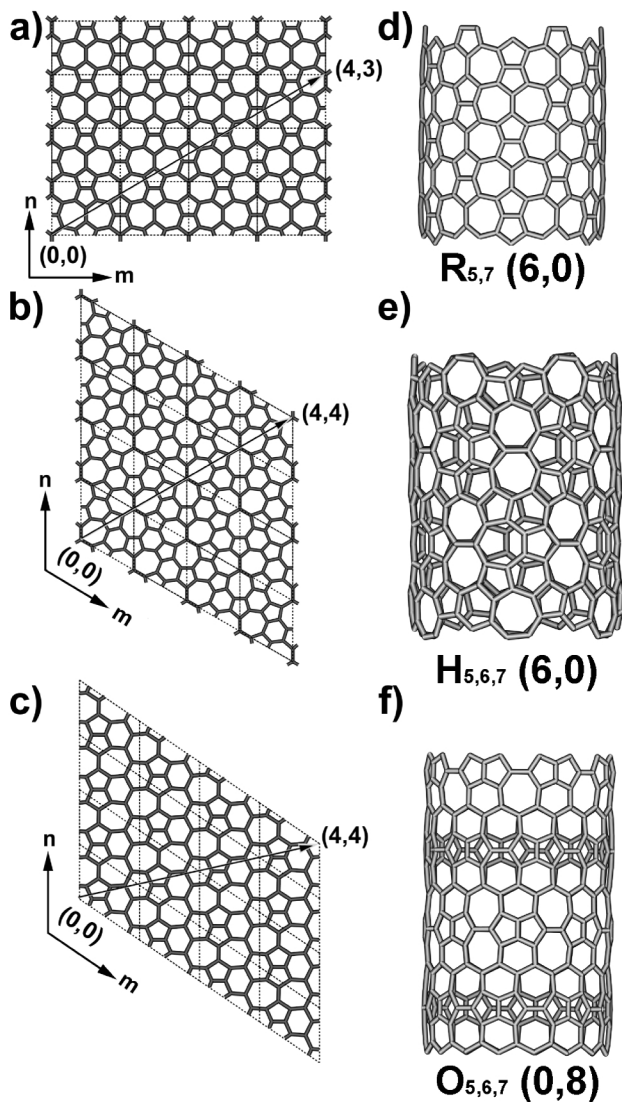
FIG. 1. Haeckelite sheets consisting of various units cells: (a) rectangular ($R_{5,7}$); (b) hexagonal ($H_{5,6,7}$), and (c) oblique ($O_{5,6,7}$). In order to generate nanotubes, we join atoms of cell $(0,0)$ with a given cell (m,n) by the vector $n\mathbf{a} + m\mathbf{b}$ (where $\mathbf{a}$ and $\mathbf{b}$ are the unit lattice vectors and m and n are integers. Nonchiral Haeckelite tubes of similar diameters (ca. 1.4 nm) have been created using the three types of layered crystals: (d) $R_{5,7}$ $(6,0)$, (e) $H_{5,6,7}$ $(6,0)$, and (f) $O_{5,6,7}$ $(0,8)$. [Note: Subindices $(5,6,7)$ of the above structures indicate the presence of pentagonal, hexagonal, and heptagonal rings, respectively.]

accuracy comparable to that of FP density-functional (DFT) based methods. In this work we have used two different TB models: (a) the model of Xu *et al.* [21], an orthogonal *s-p* TB model in which the Hamiltonian hopping integrals are fitted to *ab initio* results for various carbon phases and (b) the model of Porezag *et al.* [22], which includes explicitly the nonorthogonality of the *s-p* basis, and in which the hopping matrix elements are constructed directly from linear combination of atomic orbitals DFT calculations using the same basis set but

disregarding three-center contributions to the Hamiltonian. Young's modulus and Poisson ratio of all calculated structures were computed from the total energy and atomic positions of the relaxed structures as a function of the axial strain imposed on the system, using a calculation procedure which has been discussed elsewhere [12].

The structures were first relaxed using the Tersoff potential [23] in order to obtain an initial-guess structure for the Haeckelite crystals and tubes, which were subsequently fully minimized according to the TB models using the conjugate gradient technique. Relaxation was carried out both with respect to the atomic positions and cell parameters. These calculations revealed that the layered Haeckelite structures are more stable than C_{60}, which, according to our calculations, has an energy of 0.419 eV/atom measured with respect to graphene (a value which is in very good agreement with both FP calculations [24] and with experimental measurements [25]). Structures $H_{5,6,7}$ and $R_{5,7}$ are predicted to be flat, while structure $O_{5,6,7}$ is corrugated. $H_{5,6,7}$ is found to be the most stable structure, possessing an energy of 0.304 eV/atom with respect to graphene. Structure $O_{5,6,7}$ is the least stable (0.408 eV/atom above graphene), whereas the stability of $R_{5,7}$ (0.307 eV/atom above graphene) nears that of $H_{5,6,7}$. These observations can be rationalized in terms of the recent findings of Albertazzi *et al.* [26], who, using a variety of computational methods, have established that the most favorable nonclassical fullerene clusters (i.e., those which may contain other types of rings, such as heptagons, as well as pentagons and hexagons) are those that minimize the number of pentagon-pentagon pairs and maximize the number of pentagon-heptagon pairs. The Haeckelite structures also adhere to these rules, since $H_{5,6,7}$, the most stable one, does not contain any pentagon-pentagon adjacencies. Both $R_{5,7}$ and $O_{5,6,7}$ possess a single pentagon-pentagon adjacency within the unit cell. However, $R_{5,7}$ has a larger number of pentagon-heptagon pairs and thus is more stable than $O_{5,6,7}$.

Our calculations reveal that Haeckelite tubular structures have a lower strain energy, relative to their corresponding flat sheets, when compared to conventional graphitic nanotubes (Fig. 2). This observation, combined with the fact that flat Haeckelites are comparatively stable (more stable than C_{60}), is a strong indication of the feasibility of Haeckelite nanotubes. It is noteworthy that boron nitride (BN) nanotubes were theoretically predicted on the basis of their lower strain energy compared to carbon nanotubes [27], which have indeed been synthesized (see Ref. [13], and references therein). We find that the strain energy of Haeckelite nanotubes follows the usual $1/D^2$ [where D is the tube diameter (Fig. 2)], which has also been reported for graphitic nanotubes [12].

Figure 3 shows the density of states (DOS) of all relaxed Haeckelite sheets, which exhibit a clear metallic behavior. Interestingly, $H_{5,6,7}$ displays a high intensity peak at the Fermi level, suggesting the possibility of
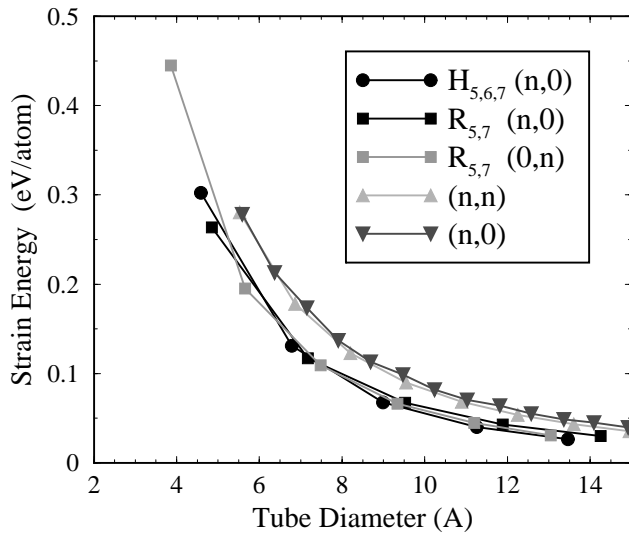
FIG. 2. Curvature strain energy as a function of the equilibrium tube diameter for the most stable Haeckelite tubes (measured with respect to the corresponding flat Haeckelite sheet). Strain energies of graphitic armchair and zigzag nanotubes are shown for comparison.

superconductivity. We also expect to observe enhanced electron-phonon coupling caused by the tubule curvature [28]. This would indicate the possibility of supercurrents within these Haeckelites at higher temperatures than those recently reported for single-wall carbon nanotubes (SWNT's) [29]. We also find that all Haeckelite nanotubes considered in this work are metallic, independently of chirality and diameter, in agreement with zone folding arguments [5,17], even though the details of the DOS vary slightly with changing chirality and diameter. Previous results [30] show that the presence of a single Stone-Wales defect in a semiconducting nanotube has the effect of narrowing the band gap at the Fermi level. Our calculations indicate that in systems containing a saturation of such Stone-Wales defects the band gap is completely closed and therefore the system is metallic. Furthermore, the caps of Haeckelite nanotubes, which in virtue of Euler's theorem require six additional pentagons, induce the presence of gap states, implying that these structures could be used in field emitting devices [31].

Haeckelite tubules are considerably stiff exhibiting high Young's modulus values [ca. 1 TPa (see Table I)]. Although this value is somewhat lower than that measured experimentally [9–11] and predicted theoretically [12] for both multiwall and SWNT's, it is still higher than that predicted for heteroatomic structures such as BN nanotubes (ca. 0.8 TPa), and certainly much higher than that of other prototype hard materials (SiC nanorods have a Young's modulus of ca. 0.6 TPa) [10].

From our discussion above it should be clear that Haeckelites, if synthesized, would have a range of remarkable electronic and mechanical properties that could make them useful in many practical applications. The question
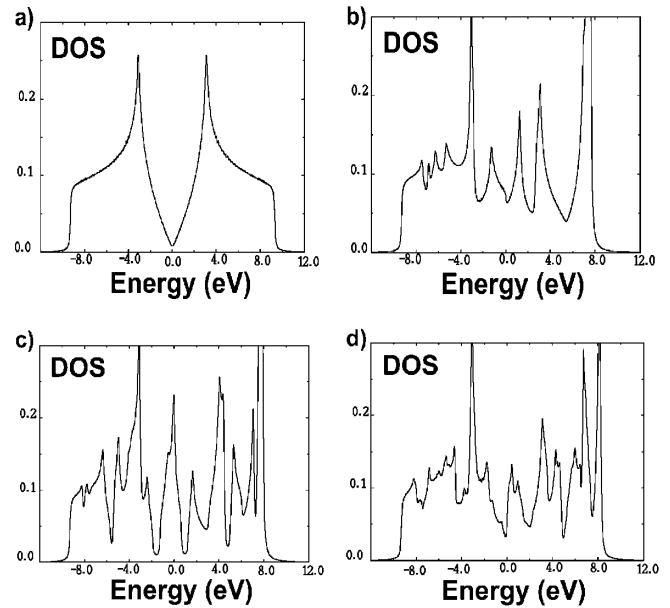
FIG. 3. Electronic density of states (Fermi level positioned at zero energy) for (a) a graphene sheet exhibiting semimetallic behavior and for Haeckelites (b),(c),(d), showing populated DOS at the Fermi level indicating a metallic behavior. (b) The $R_{5,7}$ sheet; (c) $H_{5,6,7}$ flatlayer; (d) the $O_{5,6,7}$ sheet. In all the plots the units of the density of states are *states per eV.*

then is how these structures could be produced. It has already been shown that electron irradiation of carbon SW nanotubes results in lattice reconstructions leading to the formation of five- and seven-membered rings [32]. Similar experiments using other radiation sources, coupled with mechanical compression/stretching (which can also initiate Stone-Wales transformations [33]) may also lead to Haeckelites. An alternative route could be chemical surface reconstruction processes using strong acids or halogens, which could produce defects saturated with functional groups; subsequent annealing in inert gases would be needed to achieve covalently bonded systems

TABLE I. Structural and elastic properties of selected Haeckelite nanotubes obtained from our TB calculations. The result for graphite along the basal plane is shown for comparison. σ is the Poisson ratio.

Structure	Diameter (nm)	Young's modulus (TPa)	σ
Graphite		1.10	
$R_{5,7}$ (0, 4)	0.75	1.28	0.26
$R_{5,7}$ (0, 6)	1.20	0.99	0.25
$R_{5,7}$ (0, 8)	1.49	1.02	0.27
$R_{5,7}$ (4, 0)	0.95	0.93	0.28
$R_{5,7}$ (6, 0)	1.42	0.95	0.27
$H_{5,6,7}$ (4, 0)	0.90	1.00	0.26
$H_{5,6,7}$ (6, 0)	1.35	1.03	0.24
$O_{5,6,7}$ (0, 4)	0.71	0.94	0.26
$O_{5,6,7}$ (0, 6)	1.05	0.89	0.21

containing pentagons, hexagons, and heptagons. In connection with this we note that arc-discharge, pyrolysis, and laser-ablation synthesis methods may lead to highly defective tubular structures, which must contain pentagons and heptagons in order to explain the high level of corrugation experimentally observed [32]. While we do not claim that these highly defective tubes are Haeckelites, we may say that Haeckelites can serve as a first-order model for these structures. If this is so, irrespective of the high concentration of defects, these tubes should be metallic and have a high Young's modulus, a fact that to our knowledge has not yet been experimentally corroborated.

In conclusion, we have described a new family of layered allotropic carbon forms, named Haeckelites, which consist of equal numbers of pentagons and heptagons, in addition to any number of hexagons. Three specific examples with different symmetries have been studied in detail, and we have shown that in all three cases the Haeckelite structure is energetically more stable than C_{60}, although metastable with respect to graphite. Among the structures considered, we find that the most stable is the most symmetric, possessing pentagons surrounded by hexagons and heptagons only, thus indicating that the isolated pentagon rule frequently invoked in the case of fullerenes also plays a key role in the relative stability of Haeckelites. All the sheets and nanotubes investigated are metallic, exhibiting a high density of states at the Fermi level. The strain energy for these tubules follows a similar behavior to that of conventional graphitic nanotubes, and, furthermore, their mechanical properties are also found to be similar. Interestingly, it is more energetically viable to roll up Haeckelite sheets into tubes, rather than creating conventional SWNT from ordinary graphene sheets. Because of the intrinsic metallic behavior of the Haeckelite sheets, all the tubes with any chirality and diameter will be metallic—unlike classical nanotubes. The unusual high DOS peak at the Fermi energy presented by the hexagonal system and its nanotubes might be indicative of superconductivity, which can be enhanced by increasing the curvature.

*Corresponding author.
Email address: terrones@fenix.ifisicacu.unam.mx

[1] H. W. Kroto et al., Nature (London) **318**, 162 (1985).

[2] W. Krätschmer et al., Nature (London) **347**, 354 (1990).

[3] S. Iijima, Nature (London) **56**, 354 (1991).

[4] T. W. Ebbesen and P. M. Ajayan, Nature (London) **358**, 220 (1992).

[5] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[6] R. Saito et al., Phys. Rev. B **46**, 1804 (1992); J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).

[7] X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).

[8] J. W. G. Wildöer et al., Nature (London) **391**, 59 (1998); T. W. Odom et al., Nature (London) **391**, 62 (1998).

[9] M. M. J. Treacy, T. W. Ebbesen, and M. J. Gibson, Nature (London) **381**, 678 (1996).

[10] E. W. Wong, P. E. Sheehan, and C. M. Lieber, Science **277**, 1971 (1997).

[11] A. Krishnan et al., Phys. Rev. B **58**, 14 013 (1998).

[12] E. Hernández et al., Phys. Rev. Lett. **80**, 4502 (1998).

[13] M. Terrones et al., Top. Curr. Chem. **199**, 189 (1999).

[14] S. Amelinckx et al., Science **265**, 635 (1994); M. Terrones et al., Philos. Trans. R. Soc. London A **354**, 2055 (1996).

[15] S. Iijima, J. Cryst. Growth **5**, 675 (1980); D. Ugarte, Nature (London) **359**, 707 (1992); F. Banhart and P. M. Ajayan, Nature (London) **382**, 433 (1996).

[16] M. Terrones and H. Terrones, Full. Sci. Tech. **4**, 517 (1996).

[17] V. H. Crespi et al., Phys. Rev. B **53**, 13 303 (1996).

[18] The name Haeckelites is chosen for their architectures, because they resemble (locally) the radiolaria drawings of Ernst Haeckel, in *Report on the Scientific Results of the Voyage of the H.M.S. Challenger during the Years 1873–1876,* Zoology Vol. 18 (Her Majesty's Stationery Office, London, 1887), Pts. 1–2; E. Haeckel, in *Art Forms in Nature* (Prestel-Verlag, Munich, 1998).

[19] Fractional coordinates for these structures are available from the authors upon request.

[20] C. M. Goringe, D. R. Bowler, and E. Hernández, Rep. Prog. Phys. **60**, 1447 (1997).

[21] C. H. Xu et al., J. Phys. Condens. Matter **4**, 6047 (1992).

[22] D. Porezag et al., Phys. Rev. B **51**, 12 947 (1995).

[23] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).

[24] M. S. C. Mazzoni et al., Phys. Rev. B **60**, 2208 (1999).

[25] H. S. Chen et al., Appl. Phys. Lett. **59**, 2956 (1991).

[26] E. Albertazzi et al., Phys. Chem. Chem. Phys. **1**, 2913 (1999).

[27] X. Blase et al., Europhys. Lett. **28**, 335 (1994).

[28] Y. Miyamoto et al., Phys. Rev. Lett. **74**, 2993 (1995).

[29] A. Y. Kasumov et al., Science **284**, 1508 (1999).

[30] V. H. Crespi, M. L. Cohen, and A. Rubio, Phys. Rev. Lett. **79**, 2093 (1997).

[31] W. A. de Heer, A. Châtelain, and D. Ugarte, Science **270**, 1179 (1995).

[32] P. M. Ajayan, V. Ravikumar, and J-C. Charlier, Phys. Rev. Lett. **81**, 1437 (1998).

[33] M. Buongiorno Nardelli, B. I. Yakobson, and J. Bernholc, Phys. Rev. B **57**, R4277 (1998).