Prediction of a pure-carbon planar covalent metal

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Carbon is well-known as an insulator, a semimetal, a molecular solid, and a one-dimensional semiconductor or low-density-of-states metal. We propose a pure-carbon planar structure composed of pentagons and heptagons that is metallic with a density of states at the Fermi level of ~0.1 state per eV per atom. This structure, planar carbon pentaheptite, is metastable with a total energy per carbon atom comparable to that of C_{60}. The structure can be rolled into tubes in a manner similar to graphite. Possible synthetic pathways are discussed.

The discovery of fullerenes[1] and nanotubes[2] has induced a rennaisance in the study of carbon-based materials. Fullerenes, nanotubes, graphite, and diamond provide quasi-zero-, one-, two-, and three-dimensional insulators, semiconductors, and/or semimetals. The utility of pure-carbon materials would be enhanced if a higher density-of-states metallic allotrope could be found. We propose an ordered planar arrangement of pentagons and heptagons which is a good metal. A single sheet of planar carbon pentaheptite is a mechanically strong covalently bonded conductor.

An isolated graphite sheet is a semimetal with π and $\pi*$ bands touching at a pointlike Fermi surface. A reduction in symmetry below hexagonal can remove this degeneracy and eliminate semimetallic behavior. In this situation the strong carbon potential might be expected to open significant gaps near the Fermi level. However, a structure with a large number of atoms in a low-symmetry unit cell would favor a band-overlap metal. We provide an example of a pure-carbon planar metal composed of a periodic array of pentagons and heptagons.

Any structure with an equal number of pentagons and heptagons and threefold vertices has zero net curvature. Physically, if the pentagons and heptagons are nearly uniformly distributed, one might expect local flatness as well. Although there are an infinite number of ways of tiling a plane with equal numbers of heptagons and pentagons, a large subset of physically reasonable tilings can be generated by taking a graphite sheet, dividing it into diamonds of four adjacent hexagons, and rotating certain bonds by $\pi/2$ as shown in Fig. 1.[3] Each bond rotation of the interior bond on the diamond generates two pentagons and two heptagons. Clearly one can generate additional tilings outside the bond rotation algorithm, for example, by clustering pentagons or heptagons. However, bond rotation can produce patterns with minimal local curvature, or equivalently, minimal variation in bond length in a planar structure.

We choose to examine in detail the simplest possible way of tiling a plane with pentagons and heptagons, namely, a periodic network with one bond rotation per primitive cell. Although there are two distinct ways of decorating a graphite sheet with diamond-shaped primitive cells of four hexagons and then rotating the interior bonds of each diamond, both methods yield topologically equivalent structures with eight atoms per unit cell. As shown in Fig. 2, each pentagon is

adjacent to one pentagon and four heptagons. Each heptagon is adjacent to four pentagons and three heptagons. Two carbon atoms are shared by two pentagons and a heptagon, the other six carbon atoms being shared by one pentagon and two heptagons.

Nearest-neighbor curvature effects of pentagonal and heptagonal rings limit the number of plausible two-dimensional carbon networks. If a pentagon has only heptagonal neighbors, the incipient local negative curvature imposes a large energetic cost. If a pentagon has two or more pentagonal neighbors, the incipient local positive curvature imposes a similar large energetic cost. Bond length and bond angle variation in the planar structure is minimized when each pen-
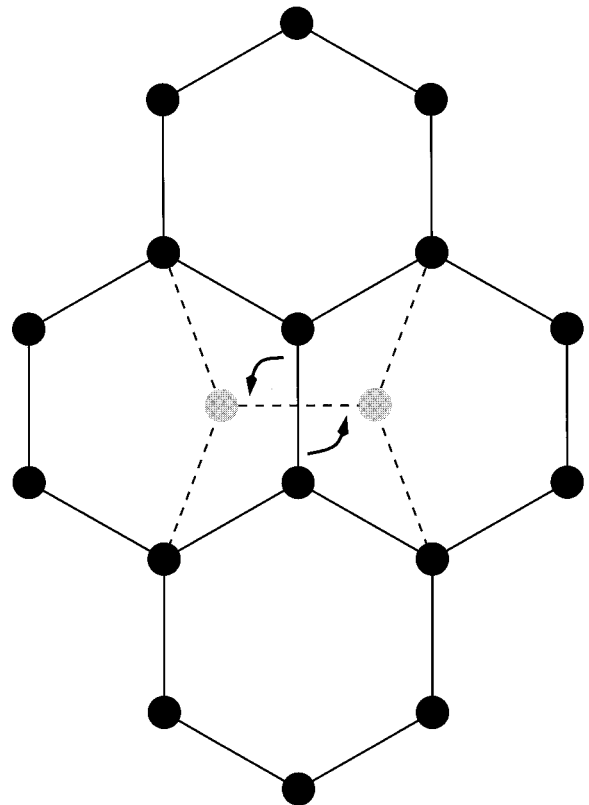

FIG. 1. The bond rotation algorithm which converts graphite to a sheet of interlinked pentagons and heptagons.
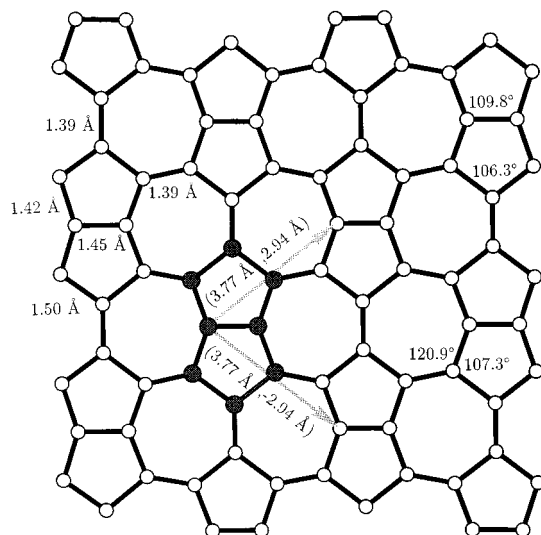
FIG. 2. The annealed equilibrium structure of single-sheet planar carbon pentaheptite, with unit cell, lattice vectors, and bond parameters marked.
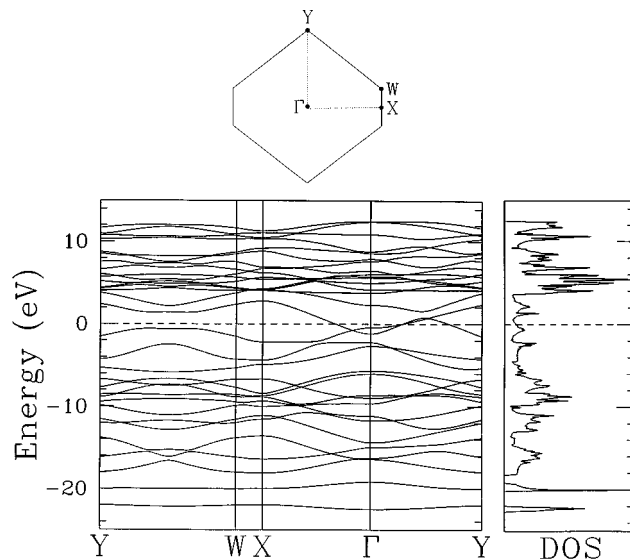

FIG. 3. Band structure and density of states for an infinite single sheet of planar carbon pentaheptite. The dashed line marks the Fermi energy, E_F. Bands are plotted along high-symmetry lines of the Brillouin zone, shown above. The reflection symmetry of the bands along the YW line is due to time-reversal invariance, $E(\vec{k}) = E(-\vec{k})$. The states nearest E_F have π character, and those farthest away are σ states.

tagon has one pentagonal neighbor. The requirement of a small unit cell then leads uniquely to the structure chosen for study.

Initial atomic coordinates were obtained from a crude bond rotation construction and subsequently annealed within tight-binding total energy molecular dynamics.[4] The anneal was performed on a finite 141-atom sheet. After initial local relaxation, the atomic positions were perturbed randomly by ~ 0.1 Å from equilibrium and the structure was annealed from 2500 K for 2.7 ps. Upon cooling the atoms returned to the essentially planar equilibrium positions. Unit cell coordinates were extracted from the atoms in the center of the sheet. Comparison across the interior atoms indicated that finite-size effects perturbed atomic positions by less than 0.01 Å. Bond lengths and angles are shown in Fig. 2.

It is instructive to compare bond lengths in planar carbon pentaheptite with those in pentalene, the molecule formed by terminating with hydrogens the dangling bonds of the penta-heptite unit cell highlighted in Fig. 2. The major difference is a lengthening of bonds to the apical carbons, from ~ 1.4 Å in D_{2h} pentalene[5] to 1.50 Å in pentaheptite. The carbon atoms making up these bonds in pentaheptite share 1.39-Å carbon-carbon bonds with atoms in the neighboring unit cells, in contrast with the weaker, but analogous C-H bonds in pentalene. In pentaheptite the increase in effective bond number for the intercell bonds is accompanied by a decrease in the effective bond number and consequent dilation of the intracell bonds to the apical carbons. We note that the dilation of the pentaheptite C-C bonds from graphitic bond lengths and the more open nature of the planar carbon pen-taheptite structure yield an areal atomic density of one carbon atom per 2.77 Å^2, 5% less than the graphitic density.

Electronic structure and total energy calculations were performed on the single-sheet periodic structure extracted from the finite sheet simulation. Within the tight-binding total energy scheme, the energy of a single infinite sheet of carbon pentaheptite is ~ 0.32 eV per atom above that of single-sheet graphite. By comparison, within the same

scheme C_{60} is ~ 0.4 eV per atom above single-sheet graphite. A local density approximation *ab initio* pseudopotential calculation using the same atomic coordinates yields a 0.33 eV per atom energy difference between isolated sheets of pentaheptite and graphite. The bond rotation which generated the topology of pentaheptite also provides a kinetic pathway to graphite. Fixing the absolute angle of a single rotated bond in the center of the 141-atom sheet and annealing and relaxing atomic coordinates up to third nearest neighbors (including the bond length of the rotated bond) yields an energy barrier within tight-binding total energy of ~ 7 eV for the $\sim \pi/2$ rotation of a single nonsymmetry axis interheptagonal bond and local conversion of pentaheptite into graphite.[6] The breaking of two C-C bonds along this pathway explains the large energy barrier. Global conversion of single-sheet pentaheptite to graphite by simultaneous rotation of all relevant bonds is expected to have a comparable energetic barrier. More complex kinetic paths can be envisioned, but all require the breaking and reformation of two C-C bonds per bond rotation so that a large energetic barrier is likely for the isolated sheet. The rigidity of the nearly sp^2 carbon framework argues against the possibility of soft modes, a supposition supported by the stability of the penta-heptite framework under a 2500-K anneal. All evidence available suggests that an isolated sheet of carbon pentahep-tite is metastable towards conversion to lower energy carbon allotropes.

The tight-binding band structure[7] and density of states of a single sheet of carbon pentaheptite are shown in Fig. 3. The deviation from perfect sp^2 bond angles raises the σ bands. The lack of hexagonal symmetry then fills in the π-π^* pseudogap present at the Fermi level of single-sheet graphite, yielding a density of states at the Fermi level of ~ 0.1 state

per eV per atom. In comparison, the density of states for the smallest plausible metallic nanotube, the 5.3-Å diameter (4,4) tube,[8] is 0.07 state per eV per atom. For larger (n,n) metallic nanotubes the densities of states per atom drop inversely proportional to the tube radius, indicating that planar carbon pentaheptite is the largest density-of-states pure-carbon crystalline allotrope.

The planar pentaheptite stucture can be rolled into tubes indexed in a manner similar to graphite, wherein tubes are labelled (n,m), with n and m defining the circumferential periodicity in lattice coordinates. In contrast to graphite, the rhomboid structure of pentaheptite implies that we must consider tubes with $0 \leq |m| \leq n$ instead of simply $0 \leq m \leq n$. Unlike the graphite sheet, carbon pentaheptite has a large Fermi surface which surrounds the Γ point ($\mathbf{k}=\mathbf{0}$). Band-folding arguments[9] then predict all tubes to be metallic, independent of radius and helicity.

The nonzero Fermi level density of states of planar carbon pentaheptite motivates a brief discussion of superconductivity. Unlike curved C_{60} and the nanotubes,[10] we expect no enhancement in the electron-phonon coupling due to curvature-induced σ-π mixing. However, the deviation from perfect sp^2 bond angles in plane may increase the electron-phonon matrix elements above the values in graphite. T_c of undoped pentaheptite is likely to be small or moderate. Alkali doping to a stoichiometry of $\sim AC_4$, corresponding to one alkali atom per heptagon, should increase the density of states at the Fermi level and increase the superconducting T_c substantially.

Synthesis of planar carbon pentaheptite may be challenging. Formation of C_{60}, a carbon allotrope of comparable binding energy, is driven by the dangling bond energy of small carbon polymers in a carbon/helium plasma. Synthesis of planar pentaheptite requires a more subtle strategy since heptagons are strongly disfavored in a regime kinetically dominated by dangling bond energy. We entertain three possible synthetic strategies. First, it may be possible to form planar pentaheptite directly from graphite. Although the areal density of planar pentaheptite is 5% below that of graphite, the metallic nature of single-sheet pentaheptite suggests that the interplanar distance in the bulk material will be smaller than the interplanar distance in bulk graphite. Should the equilibrium atomic density of bulk pentaheptite exceed that of graphite, external pressure may favor planar carbon pentaheptite. A photochemical strategy using high-pressure graphite may induce the transformation to pentaheptite. Suitable use of intercalated catalysts may also increase the stability of pentaheptite relative to graphite. Polymer chemistry may provide another avenue for synthesis. Several different cyclic hydrocarbons containing a multiple of eight carbon atoms provide candidates for the monomer. The pentalene dianion is an obvious precursor on geometrical grounds, as are various cyclic structures with side branches. The base unit of the bond rotation algorithm of Fig. 1 provides a 16-atom precursor that may be arranged in two inequivalent orientations to produce the planar pentaheptite structure studied in this work. Azulene itself cannot tile a plane without introducing vacancies or hexagons. Chemically selective intermolecular bonding should be aided by local curvature since heptagons will tend to form preferentially near pentagons and vice versa (of course, hexagon formation must be avoided for the structure studied here). Epitaxial growth on a suitable substrate provides a third strategy. Although carbon-substrate interactions may be weak in the completed structure, the interaction between dangling bonds and the substrate in the growing material may modify the kinetic pathways enough to encourage epitaxial growth of the first layer. As regards synthesis, we note that $\sim \pi/2$ grain boundaries in pentaheptite involve little lattice distortion and should impose at most a minor energetic cost.

The incorporation of equal numbers of pentagons and heptagons into previously hexagonal planar carbon materials opens a new class of metallic carbon allotropes. The simplest form of planar carbon pentaheptite is a relatively good all-carbon covalently bonded planar metal. More complex structures with larger planar unit cells or tubular geometries can easily be envisioned.

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