

Carbon foam: Spanning the phase space between graphite and diamond

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We study an unusual class of carbon structures, based on rigidly interconnected segments of graphite. The resulting foamlike systems cover the structural phase space extending from hexagonal diamond to graphite. Related to the most stable phases of carbon, these hybrid systems show an unusually high structural stability at low mass densities. Our density-functional calculations indicate that carbon foam is metallic, stable, and structurally rigid.

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With the apparently ever-expanding plethora of stable structures, including fullerenes and nanotubes,¹ elemental carbon continues to amaze the scientific community. In search of structural rigidity and toughness competing with that of diamond and graphite, hybrid structures containing sp^2 and sp^3 bonded carbon have been discussed in the literature.²⁻⁷ Here we study and theoretically characterize an unusual system which combines the shear rigidity of diamond with the open structure, low mass density, and an even higher stability of graphitic carbon.⁸ We also propose a way to synthesize the new carbon foam using self-assembly on stepped single-crystal surfaces as a template.

The structure studied, shown schematically in Fig. 1(a), is conceptually based on interconnected graphite strips. The resulting periodic three-dimensional (3D) network, depicted in Fig. 1(c), is structurally reminiscent of a foam. The long open channels are formed by terraces in the layered structure. These terraces are formed of graphitic strips that are interconnected in a seamless manner. The primitive orthorhombic conventional unit cell of a particular foam structure, containing 64 atoms, is depicted in Fig. 1(b). This figure also illustrates the use of three- and fourfold coordinated carbon atoms in the construction of carbon foam.

The rigidity of the foam structure depends on the area density of bonds in the c direction that connect the terraces in the ab plane. By construction, these bonds are formed by providing atoms within the graphitic ab layers with additional neighbors in the c direction, thus locally converting sp^2 to sp^3 hybridized carbon atoms. The unit cell in the b direction can be as short as 2.46 Å, the separation between the parallel sides of the graphitic hexagons. In this case, the structure contains chains aligned with the b axis, consisting of carbon atoms that are fourfold coordinated prior to relaxation. Increasing b yields a structure of interconnected graphite strips, wavy both in the a and b directions, that eventually becomes indistinguishable from graphite as $b \rightarrow \infty$.

Keeping b at its minimum value near 2.46 Å and reducing the terrace width in the a direction to zero, the structure reduces to a network of fourfold coordinated carbon atoms, namely that of hexagonal diamond or wurtzite. Increasing a , on the other hand, yields a structure which, in the $a \rightarrow \infty$ limit, is that of layered graphite.

The size of the unit cell is determined by the number of carbon atoms in the ab plane; the equilibrium value of c depends on the predominant type of hybridization and ranges between the interlayer spacings of diamond and graphite. In other words, with the flexibility of independently adjustable values of a and b , we have a system that continuously spans the structural phase space between diamond and graphite, the most stable phases of elemental carbon.

To describe the structural and electronic properties of carbon foam, we use the local-density approximation (LDA) within the framework of the density-functional theory.^{9,10} We adopt the Ceperley-Alder exchange-correlation potential in the LDA,¹¹ and use norm-conserving pseudopotentials¹² with the Kleinman-Bylander separable approximation.¹³ We use a plane-wave basis set with a cutoff energy of 50 Ry and eight special k -points to sample the full Brillouin zone of the foam. The geometry is optimized using the conjugate gradient approach.¹⁴

For the system depicted in Fig. 1, the optimized lattice parameters are $a_{opt} = 16.44$ Å, $b_{opt} = 9.58$ Å, and $c_{opt} = 3.28$ Å. We find the intralayer bond lengths to be close to the graphite value of 1.42 Å, and the interlayer distance to be only slightly smaller than the graphite value of 3.35 Å. During the optimization process, we observe an intriguing structure relaxation especially near the sites labeled sp^3 in Figs. 1(a) and (b). These atoms sacrifice one of their four neighbor bonds, characterizing an initial sp^3 hybridization, and bind strongly to only three neighbors with strong sp^2 bonds. Accordingly, the system of π electrons acquires a 3D metallic character, as will be discussed later.

Our total-energy calculations indicate that the foam is almost as stable as graphite and diamond, the most stable allotropes of carbon. We find the cohesive energy of the foam with 64 atoms per unit cell to be smaller by 0.13 eV/atom than that of graphite (or the equally stable diamond). The foam is more stable by 0.31 eV/atom than the isolated C₆₀ molecule, and similarly stable as carbon nanotubes. Consequently, we expect the new carbon foam to remain stable once it is synthesized.

With 64 atoms in the unit cell, the above optimized unit-cell size translates into a mass density of only $\rho = 2.48$ g/cm³. This value is nearly as low as that of graphite,

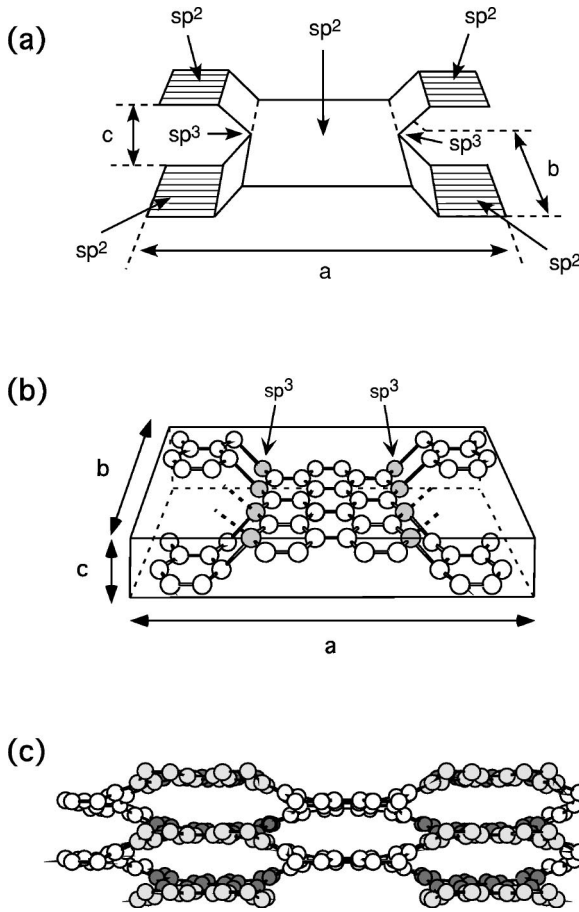


FIG. 1. Structural description of carbon foam. (a) Schematic illustrating the structural relationship between carbon foam and layered graphite. (b) Conventional orthorhombic unit cell of carbon foam, holding 64 atoms. Unit-cell variations are possible by changing the number of carbon atoms along the a and b axes. Initially fourfold coordinated sp^3 atoms are gray shaded, and the initial bond direction to their fourth neighbors is indicated by the dashed lines. (c) Perspective view of the 3D foam lattice structure, based on the above unit cell.

$\rho = 2.27 \text{ g/cm}^3$. In spite of its low density, the foam material shows an unusually high stiffness along all three axes.

Due to the structural similarity with graphite, we find the elastic stiffness of foam along the b axis $c_b = c_{22} = 9.42 \text{ Mbar}$ close to the very high in-layer stiffness of graphite, $c_{11} = 12.3 \text{ Mbar}$. This value also lies close to that of diamond, for which our elastic response calculations give $c_{11} = 11.29 \text{ Mbar}$, in close agreement with previously observed¹⁵ and calculated¹⁶ values. The reduced stiffness of carbon foam along the a direction, $c_a = c_{11} = 9.02 \text{ Mbar}$, is a consequence of the scissorslike instability in that direction.

As expected for a rigidly interconnected 3D lattice, the predicted value $c_c = c_{33} = 0.82 \text{ Mbar}$ in the foam is significantly higher than the graphite value $c_c = 0.34 \text{ Mbar}$. The predicted bulk modulus of carbon foam, with $B = 0.79 \text{ Mbar}$, lies in between the values $B = 0.33 \text{ Mbar}$ of graphite and $B = 4.69 \text{ Mbar}$ for diamond.

The structural rigidity of carbon foam results from strong covalent bonds along all spatial directions. In particular, the

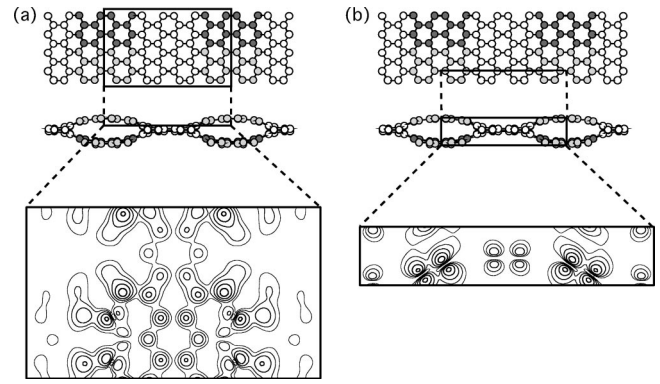


FIG. 2. Contour plot of the charge density associated with states close to the Fermi level. The plot covers a charge density range between $2.0 \times 10^{-4} \text{ electrons/a.u.}^3$ and $3.2 \times 10^{-3} \text{ electrons/a.u.}^3$, with contour lines representing twice the values at adjacent contours. The sp^2 character of covalent bonds is shown in (a) in the ac plane and in (b) in the ab plane, close to the terrace.

strong bonds in the c direction resemble the sp^2 intralayer bonds of graphite. The bonding integrity throughout the structure is reflected in delocalization of the charge density in the ab and ac plane, shown in Fig. 2.

The possibility of metallic conduction along the graphitic strips in carbon foam had been suggested based on Hückel calculations.⁸ To investigate the degree of metallic behavior, we show the band dispersion along high-symmetry lines in the primitive orthorhombic unit cell in Fig. 3. We find the band dispersion within the ab plane, i.e., along the $\Gamma - X$ and $\Gamma - Y$ directions, to be large and comparable to the dispersion of a graphitic monolayer, reflecting the strong sp^2 bonding. Since our particular unit cell holds more carbon atoms in the a direction than in the b direction, the dispersion along $\Gamma - Y$ is larger than along $\Gamma - X$. The band dispersion along the $\Gamma - Z$ direction is somewhat larger than that of layered graphite, due to the rigid bonds in the c direction. Our 64-atom unit cell holds 256 valence electrons, and we find that the 128th and the 129th bands cross the Fermi level along the $\Gamma - Y$, $\Gamma - Z$, and the $Y - T$ lines.

The electronic density of states of carbon foam, displayed in the right panel of Fig. 3, is reminiscent of graphite, reflecting the structural similarity of the two structures. The system is metallic, with the nonvanishing value of the density of states at the Fermi level $N(E_F) = 1.0 \text{ states/eV/spin}$, similar to other previously discussed sp^2 lattices.⁴

A possible way to synthesize carbon foam may be achieved by directed assembly on a templated substrate. Recently, graphitic strips have been synthesized by hydrocarbon decomposition on stepped transition metal or metal carbide surfaces, such as Pt(557), Ni(557), or TiC(557).¹⁷ Whereas hydrocarbons such as benzene graphitize on the flat terraces, the more active step sites have been shown to break the graphitic bonds, thus separating the graphitic overcoating into disconnected strips. We postulate that under conditions where graphite layers still remain intact, such a separation into strips may be suppressed. Due to the stronger local bending of the still intact overlayer near the steps, the strained segments become more reactive. With more than

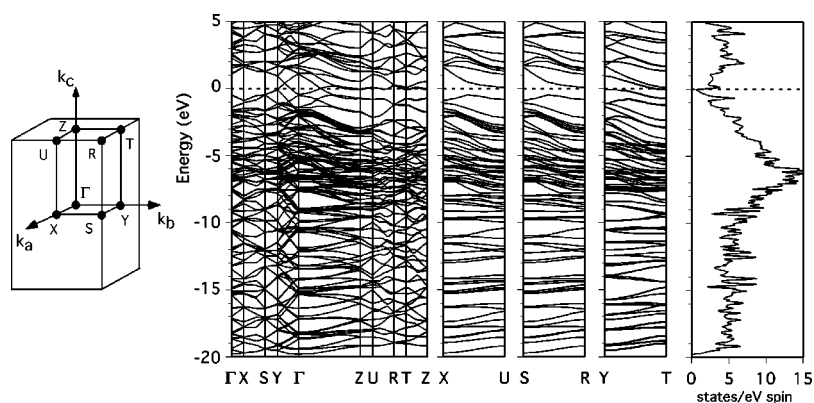


FIG. 3. Electronic band dispersion along high-symmetry lines in the Brillouin zone of the graphitic structure of Fig. 1. The schematic drawing of the Brillouin zone shows the labeling of high-symmetry points. The corresponding density of states is shown in the right panel. The energy reference is the Fermi level.

one graphitic overlayer, the initially layered structure, reminiscent of wavy graphite, may reconnect to a foamlike structure. Bonding arrangements, reminiscent of those illustrated in Fig. 1(c), also likely exist in defective graphite. In that case, however, the channels are likely to become very irregular, inducing significant strain to the lattice.

We would like to emphasize that the structural motif of the carbon foam introduced here is also easily extended to other layered systems, such as boron nitride. It is also conceivable to construct a hybrid foam material consisting of alternating graphite and BN layers. A decoration or substitution of the originally sp^3 sites by elements such as Si, with a different preferential bonding arrangement, may also be used to modify the interlayer spacing. In any case, the high porosity and accessibility of the foam structures suggests their potential for the absorption and storage of hydrogen or alkali metals for fuel cell or battery applications.

In summary, we studied an unusual class of structures, based on rigidly interconnected segments of graphitic carbon. The resulting foamlike systems cover the structural phase space extending from hexagonal diamond to graphite. Related to the most stable phases of carbon, these hybrid systems show an unusually high structural stability at low mass densities. Our density-functional calculations indicate that carbon foam should be metallic, stable, and structurally rigid.

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