

Polymorphism of carbon forms: Polyhedral morphology and electronic structures

Mitsutaka Fujita and Takahide Umeda

Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

Mitsuho Yoshida

Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi 441, Japan

(Received 29 December 1994)

We consider the morphology of fullerene families which have negative Gaussian curvature, formed by the introduction of seven- or eight-membered rings in a graphite sheet. The existence of seven- or eight-membered rings makes it possible to form a sponge-shaped periodic graphite network of carbon atoms in three-dimensional space. We first propose a construction method for the structures, which we will call spongy graphite, based on polyhedral geometry. Infinite spatial networks of equilateral triangles and hexagons can be obtained by space filling or open packing of regular icosahedra, octahedra, tetrahedra, and truncated octahedra which have triangular or hexagonal faces. We demonstrate the formation of various types of spongy graphite by decorating each face with honeycomb patches, by which we mean triangular or hexagonal fragments of a graphite sheet. Further, we study their electronic structures using a tight-binding model for the network of π electrons, and find that such networks show a variety of electronic states including metal, zero-gap semiconductor, and insulator, depending on the geometrical parameters.

Carbon is a unique element that bonds with itself through diamondlike sp^3 , graphitelike sp^2 , and even sp hybridization, and is quite different from silicon despite the fact that they have the same number of valence electrons. The resultant structures of regularly ordered allotropes of carbon are conventional diamond and graphite, and recently discovered fullerrite, i.e., C_{60} crystal in addition, while silicon forms only the crystal structure of diamond. It is apparent that this variety of carbon bonding leads to the existence of polymorphous forms in disordered carbon materials. We well know that some of them play an important role as activated carbons, carbon blacks, carbon fibers, etc. In spite of the usefulness, however, a microscopic understanding of the structures of these amorphous carbon (a -C) has not been well established yet. The structural complexity in a -C must go far beyond that in amorphous silicon.

The intrinsic features of the local structure in disordered carbon materials are the coexistence of two-, three- and fourfold coordinated carbon atoms, and the presence of five-, seven- and eight-membered rings in a graphitic network formed by threefold coordinated carbon atoms. The latter certainly comes from the fact that graphite, which is most thermodynamically stable at ambient temperatures and pressures, may contain some polygonal defects in the hexagonal network. Fullerenes are constructed from five-membered carbon rings in soot. A single pentagonal ring is introduced in a hexagonal network of carbon atoms, i.e., a graphite sheet forms a conical surface around it, and eventually the sheet can be closed totally with 12 pentagonal rings. Therefore, the fullerenes are considered as the latter structural disorder in a -C, although they are molecules.

The introduction of seven- and eight-membered rings results in more fascinating forms of fullerene families by

producing Gaussian negative curvature on a honeycomb network. Their appearance has already been suggested by the observation of morphologies of fullerene tubules via transmission electron microscopy.^{1,2} The possibilities of the forms with heptagonal and octagonal carbon rings were theoretically discussed for fullerene tubules,³ fullerene torus,⁴ and spongy graphites⁵⁻¹⁰ where the three-coordinated carbon networks spans periodically not in plane but in space.

The purpose of this paper is first to propose the polyhedral construction of carbon forms with negative curvature. Demonstrating various forms of spongy graphite with seven- or eight-membered rings, we show how our method is general comparing with others. Further, their electronic states are examined by means of the tight-binding method. The possible graphitic forms spreading in space around a seed of a sp^3 carbon atom are also mentioned.

Let us briefly review the geometry of fullerene molecules. In our previous work,^{11,12} we have proposed the use of a projection method based on a honeycomb lattice for describing the geometry of fullerenes consisting of hexagonal and pentagonal carbon rings, where an arbitrary fullerene is completely specified by the arrangement of 12 *pentagonal defects* on a honeycomb lattice. In other words, the structure of a fullerene can be regarded as a polyhedron with 12 vertices where the faces are decorated with a honeycomb pattern. The vertices of each polyhedral face are placed at the center of the honeycomb hexagons, and at each vertex the angular deficiency is 60° ; thereby, a pentagonal ring is produced at each vertex. In brief, the network of fullerenes can be produced by the patchwork of honeycomb pieces on the polyhedral faces.

Let us develop our argument to the honeycomb patch-

work in space. Since it is too general a problem, for a while we only considered the use of one kind of equilaterally triangular patch and sought three-dimensionally (3D) periodic structures. That is to say, the problem is reduced to find infinite periodic spatial structures exclusively composed of equilateral triangles, although it still sounds intricate. We find, however, that Pearce has exhibited various possibilities¹³ on the same problem. His basic idea was to consider open packings using three kinds of polyhedra: the tetrahedron, octahedron, and icosahedron, whose faces are equilateral triangles of a size. We exhibit two examples in Fig. 1, both of which form the diamond structure composed of all equilateral faces. In Fig. 1(a), we can find two octahedra at the nodal sites of the network, whose four of the eight faces are attached additional octahedra in the same directions as sp^3 hybridization serving as branches; while icosahedra sit at the nodal sites of diamond structure with branch octahedra in Fig. 1(b). We note that the latter has chirality, but the former does not. Hereafter, we call these structures formed by equilateral faces as frame A [Fig. 1(a)] and frame B [1(b)].

Once we get an infinite spatial network of equilateral triangles, fullerene structures expanding in space can be constructed by just decorating each of the faces with the triangular honeycomb patches displayed in Fig. 2. The triangular patches are assigned to the edge vectors $(m, n) = m\vec{p} + n\vec{q}$ where \vec{p} and \vec{q} are the primitive vectors of the honeycomb lattice given by $(a, 0)$ and $(a, a\sqrt{3})/2$ (a is the lattice constant). In Fig. 3, we show the resultant structures of spongy graphites by the decoration of the (2,0) patch for the frames A and B. Since at each vertex in both frames eight and seven triangular faces meet, an octagonal and a heptagonal ring appears at each as indicated by the shaded polyhedra. They have $32S_{m,n}$ and $56S_{m,n}$ carbon atoms in a unit cell for the sponges of the frame A and B, respectively. Here we should note that all of these spongy graphites are newcomers for the 3D periodic graphites with negative curvature except the network with the (1,1) patch on the frame B, which is found topologically equivalent to that by Vanderbilt and Tersoff.⁷

We examine the electronic states of these sponge structures, based on the simple tight-binding model with a constant transfer t_0 , under the knowledge that in the

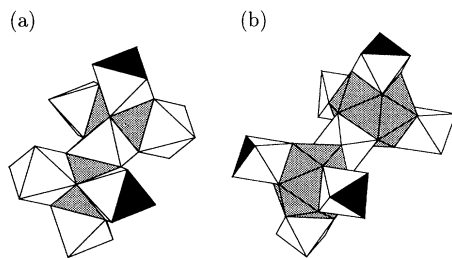


FIG. 1. Parts of polyhedral construction giving diamond structure. The nodal octahedra (a) and icosahedra (b) are lightly shaded. The darkly shaded faces on branch octahedra are attached to the next nodal polyhedra in the periodic frame.

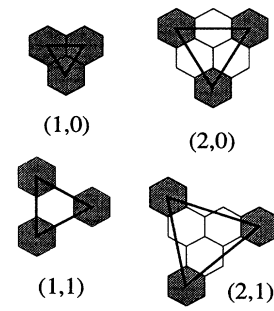


FIG. 2. Series of triangular honeycomb patches where (m, n) indicates the edge vector.

graphitic materials the π electrons mainly contribute to the electronic states near the Fermi level. The curvature, which must be one of the important structural factors, may give the effect of reduction for t_0 , in a qualitative stage of discussion; however, the simplified calculation is very useful to reveal the characteristic electronic states. We should note that for fullerene tubules the simple model of the π electron network explains the geometrical classification between the metallic and semiconducting tubules.¹⁴ The electronic states of sponges based on the frame B are classified into the insulating states for (1,1), (2,2), and (3,0) with gaps more than $t_0/3$, and the metallic states for (1,0), (2,0), and (2,1). Curious electronic states can be seen in the sponges of the frame A. Since they are composed of only even-membered rings, the energy band becomes symmetric within the simple model. The electronic structures in this series of structures are insulating for (1,1) [Fig. 4(a)], (3,0) and (2,2), and zero-gap semiconducting for (1,0) and (2,1) where the density of states (DOS) behaves as E^2 near E_F because they have linear dispersions around some Fermi points. Figure 4(b) shows the structure with (2,0), which is found to be metallic and further to have a flat band all over the Brillouin zone. Certainly although such a special feature is broken under more realistic calculation, the energy band with large degeneracy may remain near the Fermi level if this structure is achieved. For more fundamental interest, we note that this is an example that is a “Kekuléan” structure, but has a flat band.^{15,16}

The other way to create spongy graphites is to use

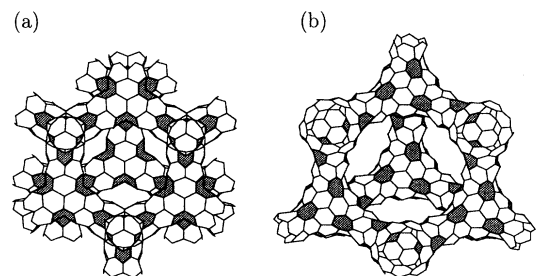


FIG. 3. Spongy graphites constructed by using the triangular patches (2,0) in Fig. 2 on the frames (a) A and (b) B in Fig. 1.

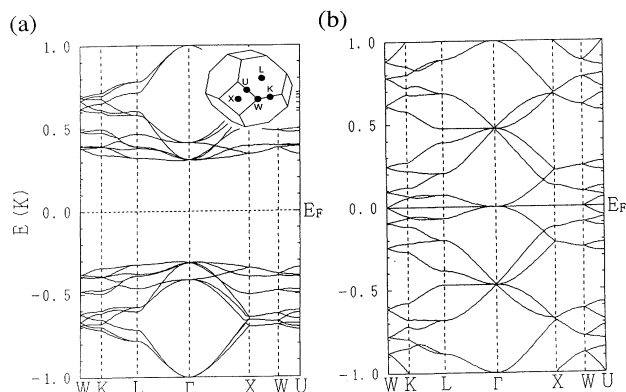


FIG. 4. Band structures for the spongy graphites (a) A(1,1) and (b) A(2,0) near the Fermi level. The Brillouin zone is depicted in the inset of (a).

the spatial network of hexagons. One of the examples is given by the spatial filling of truncated octahedra shown in Fig. 5(a). Considering only the connections of hexagonal faces, we see one of Coxeter's three regular sponges,¹⁷ which divide space into two equal parts. Now we can easily imagine that if the series of hexagonal patches are prepared, the other series of spongy graphite is constructed where the octagonal rings appears at each vertex because four hexagonal faces meet there. The electronic structures by the tight-binding model are found to be metallic for (0,1) and insulating for (1,1), (2,1), (3,0), and (3,1), and semiconducting with zero gap for (0,2) where the DOS behaves as $\sqrt{|E|}$ near E_F . The number of carbon atoms per unit cell is given by $48S_{m,n} (\equiv m^2 + mn + n^2)$. We should note that the network of (2,0) is topologically equivalent to the Mackay and Terrones's spongy graphite derived from the P surface,⁶ and (1,0) is one of O'Keeffe's polybenzenes.⁹ If you prepare the honeycomb patches so as that all the hexagonal corners sit not on the center of a hexagon in Fig. 2, but just on the vertices of a honeycomb lattice, i.e., the atomic sites, the resultant structures include the four coordinated carbon atoms at the place where the four hexagonal faces of truncated octahedra meet. One of the examples is displayed in Fig. 5(b). We

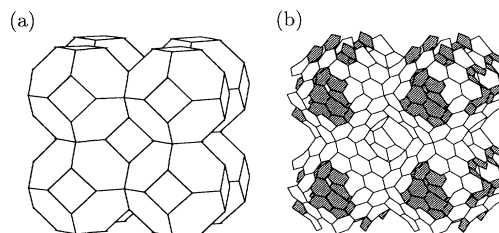


FIG. 5. (a) Space filling by truncated octahedra, and (b) another spongy graphite formed by the introduction of four coordinated carbon atoms in a graphite sheet.

have already mentioned the two intrinsic features of the local structure of a -C. Here we obtain the carbon networks with the mixture of sp^2 and sp^3 bondings, which also spread spacially. Now we should emphasize that our polyhedral construction is useful to consider the possible local structures of the carbon network.

We expect that the immense variety of polyhedral beauty must be hidden in disordered carbon materials. Moreover, our results suggest that if we can control the geometrical parameter, it means the electronic state becomes controllable. Here we introduce one of interesting trials to synthesize a carbon material with controlling the microscopic geometry. As is well known, zeolite has a polyhedrally constructed structure. If the porous space of zeolite is impregnated with a certain hydrocarbon, the carbonization is carried out by heat treatment; further, if the zeolite is removed with acid treatment, we may obtain a carbon network as a copy of the microscopic structure of the mother zeolite. Namely, zeolite plays a role of template.¹⁸ Other ideas might open a way to synthesize a carbon form.

The authors are grateful to E. Ōsawa, H. Aoki, K. Kusakabe, and K. Miyazaki for useful discussions. This work has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan and partly by Casio Science Promotion Foundation, Sumitomo Foundation, and The Japan Securities Scholarship Foundation (M.F.).

¹ S. Iijima, T. Ichibashi, and Y. Ando, *Nature* **356**, 776 (1992).

² S. Iijima, P. M. Ajayan, and T. Ichibashi, *Phys. Rev. Lett.* **69**, 3100 (1992).

³ B. I. Dunlap, *Phys. Rev. B* **46**, 1933 (1992).

⁴ S. Itoh, *Phys. Rev. B* **47**, 1703 (1993).

⁵ As a review, see, H. Terrones and A. L. Mackay, *Carbon* **30**, 1251 (1992).

⁶ A. L. Mackay and H. Terrones, *Nature* **352**, 762 (1991).

⁷ D. Vanderbilt and J. Tersoff, *Phys. Rev. Lett.* **68**, 511 (1992).

⁸ T. Lenosky *et al.*, *Nature* **355**, 333 (1992); M.-Z. Huang, W. Y. Ching, and T. Lenosky, *Phys. Rev. B* **47**, 1593 (1993).

⁹ M. O'Keeffe, G. B. Adams, and O. F. Sankey, *Phys. Rev. Lett.* **68**, 2325 (1992).

¹⁰ M. Fujita, M. Yoshida, and E. Ōsawa, *Fullerene Sci. Technol.* **3**, 93 (1995).

¹¹ M. Fujita, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **45**, 13834 (1992).

¹² M. Fujita, *Fullerene Sci. Technol.* **1**, 365 (1993).

¹³ P. Pearce, *Structure in Nature is a Strategy for Design* (MIT Press, Cambridge, MA, 1978); P. Pearce and S. Pearce, *Polyhedra Primer* (Van Nostrand Reinhold Ltd., New York, 1978).

¹⁴ R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **46**, 1804 (1992).

¹⁵ N. Shima and H. Aoki, *Phys. Rev. Lett.* **71**, 4389 (1993).

¹⁶ H. Hosoya, *Croatica Chem. Acta* **59**, 583 (1986).

¹⁷ W. W. R. Ball and H. S. M. Coxeter, *Mathematical Recreations and Essays* (Dover, New York, 1987), pp. 152–153.

¹⁸ T. Kyotani, T. Nagai, and T. Tomita (unpublished).