Transactions of the Materials Research Society of Japan 25 [3] 869-872 (2000)

A New Three-Dimensional π-electron Network With Edge States

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We propose a group of three-dimensional π-electron networks which have surface localized states with a non-bonding character (edge states). To test possibility that these networks is composed of carbon and hydrogen, we perform the total energy calculation for a typical structure by a first-principles method based on the local density approximation. The structure is optimized and the stability of the proposed materials is estimated.

Key words: edge states, polyacene, graphite, first-principles calculation

1. INTRODUCTION

It was predicted that special surface states appear in a π-electron system of the graphene with a zigzag edge theoretically[1, 2, 3, 4]. The surface states are named "edge states"[1], because the states localize at a zigzag edge of the graphene. Edge states are non-bonding orbitals (NBO). Besides, they form almost flat bands in a π-band structure at the Fermi energy and induce a sharp peak in density of states (DOS) at the Fermi energy. From the above reasons, the graphene with a zigzag edge is expected to show unusual magnetic properties[1, 5], *e.g.* spin polarization.

The peculiarity of edge states lead us to search for structures in which edge states appear. Recently, we showed a method to construct networks with edge states[6]. The method revealed that networks with edge states are constructed by linking AB bipartite networks which have an NBO as an eigen state.

In this paper, we propose a group of three-dimensional (3D) π-electron networks which are constructed by the method. As an example, we show that edge states appear in one of these networks by a numerical calculation. Besides, we discuss stability of the network composed of carbon and hydrogen by a first-principles calculation based on the local density approximation (LDA).

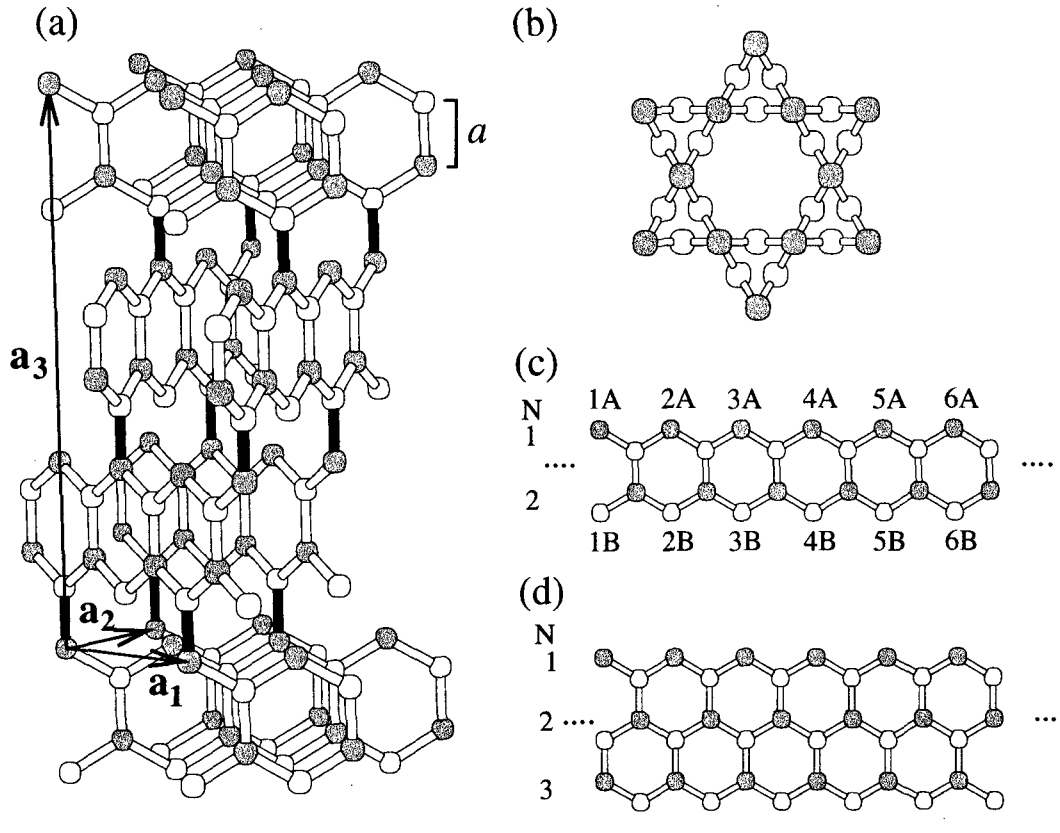

Fig.1 (a) A three-dimensional (3D) π-electron network. Closed circles and opened circles represent A-sites and B-sites, respectively. Each layer is linked by black bonds. $\mathbf{a_{1,2,3}}$ are primitive translation vectors, $\mathbf{a_1} = (\sqrt{3}a, 3a, 0)$, $\mathbf{a_2} = (\sqrt{3}a, -3a, 0)$, $\mathbf{a_3} = (0, 0, 9a)$, where a is the bond length. (b) A top view of the network shown in (a). (c) A unit to construct 3D π-electron networks. This is a zigzag ribbon with N=2. (d) Another unit to construct 3D π-electron networks. This is a zigzag ribbon with N=3.

2. NETWORKS AND BAND STRUCTURE

A proposed 3D π-electron network with edge states is illustrated in Fig.1(a). This network consists of layers of units shown in Fig.1(c). The unit is a zigzag ribbon with N=2. N represents a ribbon width. These units are linked by bonds which are parallel to the c axis in the network. The orientation of the units rotates by $\pi/3$ about the c axis from layer to layer. The primitive unit cell contains twenty-four sites. There are two important points when the network is constructed. 1) An AB bipartite network, which has a NBO as an eigen states, is used as a unit. 2) All bonds, which are parallel to the c axis, link A-sites in a unit to B-sites in the next unit.

We show a π-band structure and DOS for a slab model of the 3D π-electron network. A surface of the slab model is composed of

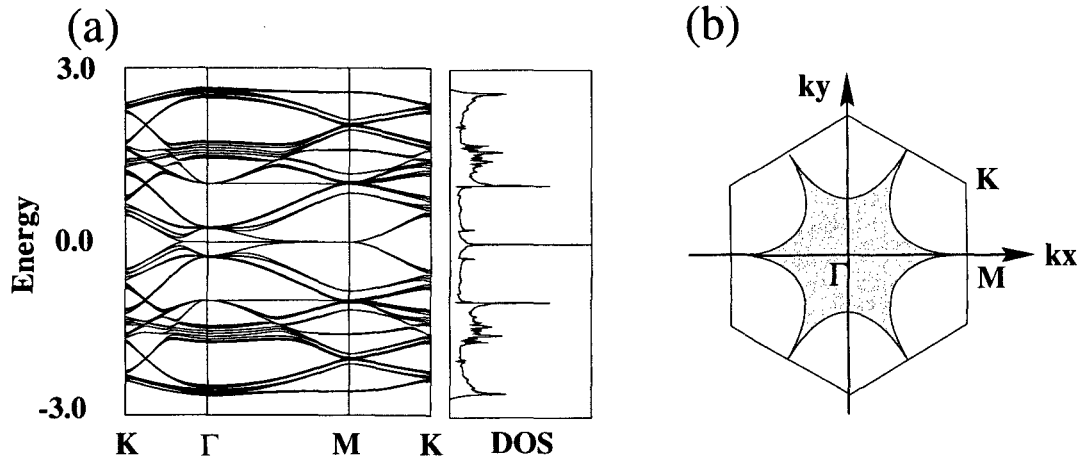

Fig.2 (a) A π-band structure and a density of states for a slab model of network shown in Fig.1(a). (b) The first Brillouin zone of it. Edge states emerge in the shadowed region.

the first-layer of units. This band structure is based on a single band tight-binding model. In this model, we assume that the on-site energy is equal to zero and a transfer integral between the nearest neighbor sites is equal to unity and the others are zero. Besides, it is assumed that one π-electron exists per each site. There is a pair of almost flat bands at the Fermi energy in the band structure. And, in DOS, the sharp peak exists at the Fermi energy. From the above facts, we recognize that edge states appear in the π-electron system of the network.

We can make many 3D networks with edge states by using a similar method. For example, one of these networks is created by linking $(4i+1)A$ of a unit shown in Fig.1(c) with $(4i+3)B$ of the next unit by extra bonds. ($i = 0, 1, \ldots$). Another examples are 3D networks constructed by the unit shown in Fig.1(d). The unit is a zigzag ribbon with N=3. We have confirmed that edge states appear in several networks which are constructed by zigzag ribbons with N=2 or 3. It is possible to make 3D networks with edge states from another unit, *i.e.* zigzag ribbon with N=i, ($i = 4, \cdots, n, \cdots$). We call these networks "Hyper Polyacene", because the structure shown in Fig.1(a) is regarded as stacking of polyacene-networks.

3. FIRST PRINCIPLES CALCULATION

Here, we assume that the network shown in Fig.1 is composed of carbon atoms and hydrogen atoms. Then carbon atoms are located in all three-fold or two-fold coordinated sites. All carbon atoms which are set in two-fold coordinated sites are terminated by a hydrogen atom. Thus, all of carbon atoms has sp^2-hybridized orbitals and one π-electron. A primitive unit cell contains twenty-four carbon atoms and six hydrogen atoms. In this structure, we assume that the carbon-carbon bond length is 1.42Å and the

carbon-hydrogen bond length is 1.10 Å.

We perform a first-principles calculation using LDA to research stability of the structure. In the calculation, we use the Troulier-Martins pseudopotential and the plane-wave basis sets to expand valence wave functions.

First we assume the shape of the unit cell. Using a cut off energy of 80 Ry, the structure is optimized, showing a local stability of the structure. Here, the k-point sampling is done with a uniform mesh having 64 k-points. We separately calculate a full optimization calculation varing the unit cell shape with energy cat off of 40 Ry and 27 k-mesh points. This calculation indicates that the assumed cell structure above is almost the same as optimized one.

4. SUMMARY

In this paper, we propose a group of 3D π-electron network with edge states and call these networks "Hyper polyacene". Moreover, we perform the LDA calculation for the structure which indicates that the structure is stable when it is realized as a hydro carbon material. If Hyper polyacenes are made, they will show interesting properties coming from edge states.

5. ACKNOWLEDGMENTS

We would like to thank Professor A. Oshiyama, Dr. M. Saito, Dr. O. Sugino and Dr. Y. Miyamoto for providing the program used in this work. Numerical calculation is performed on the Fujitsu VPP500 computer center at Institute for Solid State Physics, University of Tokyo and the NEC SX3 of computer center at Institute for Molecular Science, Okazaki National Institute. This work is supported by Grant-in-Aid for Scientific Research nos.10309003 and 11740392 from the Ministry of Education, Science and Culture, Japan.

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(Received December 17, 1999; Accepted March 30, 2000)