Magnetism of Nanometer-Scale Graphite with Edge or Topological Defects

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Abstract   Magnetic structure is studied for several π-networks of graphite-like structures with edge and/or topological defects using the tight-binding model (the Hückel model). Zigzag-edged graphite have edge states, which form a partly flat band at the Fermi energy. Short range repulsion (the Hubbard U) is enough to induce huge magnetic moments coming from spin polarization of localized electrons on the edge. While, introduction of azupyrene defect (two pentagons and two heptagons instead of four hexagons) in graphite modifies the band structure, some of which have a flat lowest excitation band. We propose a series of one-dimensional polymers with a flat band, which is exactly shown to be ferromagnetic for electron doping up to the half-filling of this band, so long as the system is well described by the Hubbard model.

INTRODUCTION

The discovery of fullerene molecules[1] and carbon nanotubes[2] renewed our knowledge of possible functions realized in carbon and its compounds. As well-known, intensive studies revealed that doped C_{60} exhibits superconductivity[3] and ferromagnetism.[4] Findings of nanotubes expand our scope of conceptions of carbon networks, too. Recently existence of defects in nanotubes becomes a central issue both experimentally and theoretically. For example, 5- or 7-membered rings were found in constricted parts of nanotubes[5] and coiled nanotubes.[6,7] While, tubes in a carpet-roll are suggested in several experiments.[8,9] The shape reminds us of edged graphite. Namely, next possible candidates may be i) edge in finite graphitic structures, and ii) polygonal defects other than hexagons in a honeycomb network. These defects, which cause change in morphology of a network, will affect electronic states on the network in turn. Thus we could expect that pure carbon clusters and networks can be a starting ground to search for materials with interesting electronic properties, such as spin-ferromagnetism.

Historically, network topology of carbon has been regarded as a key concept for design of high-spin organic molecules. The notion is called π-topology, on which numerous ideas are proposed and tested successfully. The oldest mile-stone may be the Longuett-Higgins rule[10] which gives a way of counting π non-bonding molecular orbitals (π-NBMO). Another strategy to design high-spin molecules was opened up by Ovchinnikov,[11] where one assumes a carbon network as a realization of a Heisenberg spin system. These considerations,[12] however, are mainly concerned finite alternant hydro-carbons, in which carbon atoms can be divided into a stared group and an un-stared one. In the graph theory, this type of network is called bipartite.

Here we would like to address a next question: Can we find novel magnetic networks which is out of the category of finite bipartite graphs? If we could find any example and extract a rule, our scope for design of high-spin organic molecules and polymers would be enlarged.

In this paper, we investigate magnetic structures of some π-networks, which may be relevant for graphite fragments or graphitic polymers. We pay attention to the next two possibilities.

1. Edge of a semi-infinite graphite sheet.

2. Topological defects (5- or 7-membered rings) in honeycomb networks.

As shown in the following sections, these structures can be an origin of highly degenerate single electron states. Then, we can expect a strong Fermi instability by relatively small electron-electron interaction, which may lead occurrence of magnetism. However, we must be careful concluding magnetism, because the degeneracy itself is not the sufficient condition for spin-polarization. Thus, in order to discuss spin structure, we should take the many-body effect into account explicitly.

The organization of the present paper is the followings. We first discuss graphite ribbon with edge. There have been several investigations on one-dimensional graphitic systems.[13-17] Here we pay attention to zigzag-edged graphite sheets, which have peculiar edge states at the Fermi energy, distinct to this type of edge. Using the unrestricted Hartree-Fock calculation, we can indeed show that weak short range repulsion is enough to induce huge magnetic moments on the zigzag edge.[17]

While, although armchair-edged graphite ribbons reproduces graphite band structure, introduction of azupyrene defect (two pentagons and two heptagons instead of four hexagons) modifies the band structure, some of which have a flat lowest excitation band.[18] We can construct the localized wavefunction on this band arising from an interference effect at the defects. We next propose a series of one-dimensional polymer with a flat band. Electron doping up to half-filling of this band causes ferromagnetism, which is exactly shown by applying the Mielke's theorem[19] for the

Hubbard model having a flat band,[19-22] which could be a general principle to design ferromagnetic networks.

We will also consider the stability of the local azupyrene defect applying the first-principles molecular dynamics method (FPMD) with constant-pressure condition,[23,24] which indicates the stability of this type of structure.

GRAPHITE WITH EDGE

As well known, graphite shows large diamagnetism in the bulk sample. However, if we consider a finite fragment of graphite, varieties of hidden properties would appear. Indeed, curious paramagnetic behavior is reported for a certain type of activated carbon fibers,[25] where carbon atoms at the edge seem to play a crucial role. We consider the effect of the edge in graphite sheets in this section.

Electronic State of Edged Graphite

There are several ways to make an edge. Here we pay attention to two typical edges, *i.e.*, those with armchair or zigzag peripheral shapes. By cutting a graphite sheet with two parallel lines, we obtain armchair and zigzag ribbons as shown in Fig. 1, where the dangling bonds at the edge is assumed to be terminated by hydrogen atoms. The tight-binding calculation for the π electron network reveals the following features of each edge.

1. The global band structure of the armchair ribbon can be interpreted as a projection of the 2D graphite band onto a plane perpendicular to Γ-M direction. The valence band top and the conduction band bottom are located at the Γ point. (For details, see ref. 17)

2. The zigzag edge has two almost dispersionless center bands within $2\pi/3 \leq |k| \leq \pi$ near the Fermi energy, in addition to other bands originated from the bulk-graphite bands. The system is metallic in a sense that two center bands touches always at $k = \pi$.
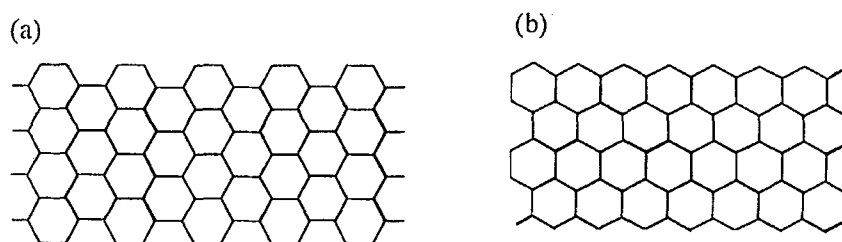
(a)   (b)

FIGURE 1 Graphite ribbons with (a) armchair and (b) zigzag edges.

These peculiar 'flat' bands for the zigzag edge are 'the edge states'. We can obtain an analytic form of the edge state for the semi-infinite sheet with the zigzag edge. (Fig. 2 (a)) The solution shows an exponential decay of amplitude inward the sheet. A state at $k = \pi$ is a non-bonding state, which is commonly seen in such a zigzag structure. Interestingly, the decay length increasing by changing the momentum k, and finally the edge state, coincides with an extended state of the graphite at the K point when $k = 2\pi/3$.

Magnetic Structure of The Zigzag Edged Graphite

The appearance of degenerate states at the Fermi energy for the zigzag edged graphite suggests that the system shows magnetic or structural instability by the electron-electron interaction or the electron-phonon interaction. Here we examine magnetic instability of the zigzag edged ribbon assuming that the system is well described by the Hubbard model. Using the unrestricted Hartree-Fock approximation, which can reproduce magnetic structure of the Hubbard model at the half-filling, we estimated magnetic texture. The mean-field Hamiltonian is given by,

$$
\begin{aligned}
H_{MF} = & -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^{\dagger} c_{j,\sigma} + h.c.) \\
& +U \sum_i \{ \langle n_{i,\downarrow} \rangle n_{i,\uparrow} + \langle n_{i,\uparrow} \rangle n_{i,\downarrow} - \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle \},
\end{aligned}
\tag{1}
$$

where t and U is the transfer energy and the Hubbard interaction.

The obtained local magnetization $m = \langle n_{i,\uparrow} \rangle - \langle n_{i,\downarrow} \rangle$ is shown using an arrow in Fig. 2 (b). We should notice that ferrimagnetic alignment of spins arises at the zigzag edge. The result suggests spontaneous magnetic order in a pure graphite fragment, although the net magnetization is zero for the ground state.

More interestingly, the local magnetization on the edge emerges by introduction of rather small U. (For the semi-infinite sheet, infinitesimal U is enough to induce non-zero m.) Besides, an effective interaction between two huge moments at opposite
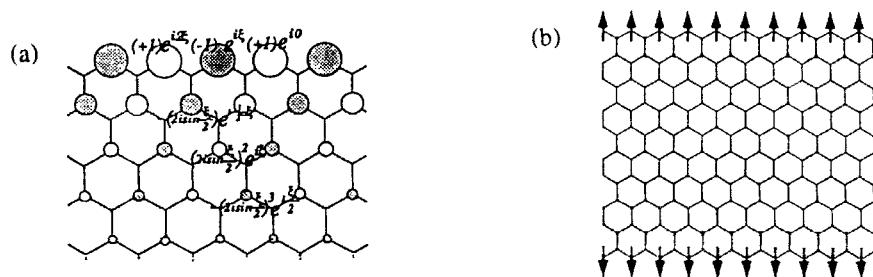

FIGURE 2 (a) Analytic solution of the edge state. A momentum ξ is defined as $\xi = k - \pi$, which gives a dumping factor $2i\sin\frac{\xi}{2}$ of the edge state. (b) Magnetic texture of the zigzag-edged graphite sheet.

edges is expected to be much smaller compared with the strong neighboring ferrimagnetic interaction at the edge. So, the system may behave as a ferrimagnetic spin chain at an intermediately low-temperature region.

GRAPHITE WITH TOPOLOGICAL DEFECTS

We next consider effect of topological defects in a honeycomb network. If we twist two atoms in a graphite sheet, we obtain the azupyrene structure as shown in Fig. 3 (a). By this transformation, four hexagons are changed into two pentagons and two heptagons. This is the simplest topological defect in a planar hexagonal network without changing the Euler characteristic of the structure.

Defective graphite with a flat band

In order to clarify the effect of azupyrene defects, we first studied the electronic band structure. We position defects periodically and obtained the tight-binding band structure assuming that each bond has a same transfer integral t. (Fig. 3 (b)) Here two lattice vectors $\vec{l}$ and $\vec{m}$ are defined on a honeycomb network with lattice vectors $\vec{a}$ and $\vec{b}$. Then we found that the band structure is classified into some classes determined by the shape of the unit cell. According to the relative position of defects, the system can be either a zero-gap semiconductor or a metal. (For detail, see Ref. 18)

For two types of special locations of defects, namely for $\vec{m} = (3,0)$ or $(1,1)$, and $\vec{l}$ satisfying the so-called Keklé rule, a dispersionless branch appears in the band structure. A typical structure of this flat band is shown in Fig. 4 (a). We can clearly see a dispersionless part of the LUMO band starting from the Γ point at zero energy. If we look at the wave function on this zero energy line, the amplitude is non-zero only in a cis-polyacetylene structure and defect sites. (Fig. 4 (b)) These facts motivate us to figure out a series of one-dimensional (1D) networks with a dispersionless band as discussed below.
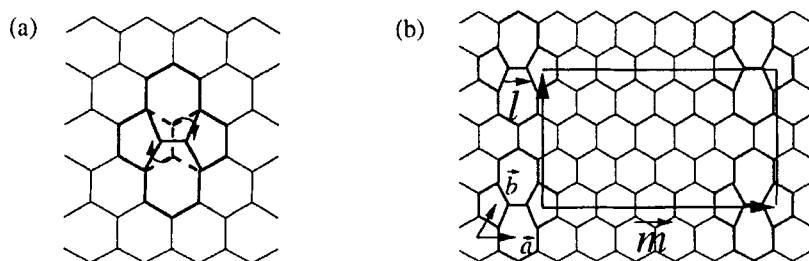

FIGURE 3 Azupyrene defect in a graphite sheet (a) and the unit cell of the defective graphite (b).
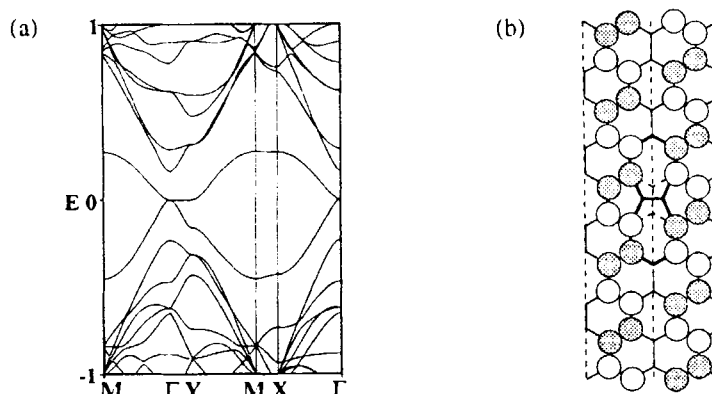
FIGURE 4 (a) Electronic band structure of a defective graphite sheet with azupyrene defects. ($\vec{m} = (3,0), \vec{l} = (-5,10)$) A dispersionless branch appears in the LUMO band. (b) The wave function in the flat-band at the Γ point.

One-dimensional polymers having a flat band

By cutting out a 1D structure from the above networks, we obtain a series of polymers. (Fig. 5 (a), (b)) As intended, the band structures of these polymers possess a flat band, which is the first un-occupied band at zero energy. (Fig. 5 (c), (d)) This band consists of localized wavefunctions, whose analytic form is easily obtained. (Fig. 5 (b)) Then we immediately notice that the localized wavefunction originates from interference effect occurring right at the azupyrene structure. The number of these localized states is the same as that of the defects in our polymers.

Ferromagnetism on the flat band

If we could dope electrons in this band, there may be large magnetic instability caused by the electron-electron interaction. The electron doping may be realized by stacking these polymers together with alkali metals as a donor. So, we consider here the effect of the short range interaction between electrons (the Hubbard U) provided that the background network structure remains stable.

Consider the case where the flat band of the azupyrene polymer is half-filled. Because the single particle energy is the same irrespective of the spin, there is large degeneracy of the one-body ground state when $U = 0$. This degeneracy is lifted by U. Such a situation is generally treated in the flat-band ferromagnetism. Here we note the Mielke theorem on general half-filled flat bands.[18] First we define a density matrix $\rho_{x,y} = (1/N)\langle\Psi|c^\dagger_{x\uparrow}c_{y\uparrow}|\Psi\rangle$ of the ferromagnetic ground state $|\Psi\rangle = \prod_l^{N_d} f^\dagger_{l\uparrow}|0\rangle$ on the flat band, where x (y) runs only on sites with non-zero amplitude of any localized wave function. Here $f^\dagger_{l\sigma}$ denotes an electron creation operator of l-th
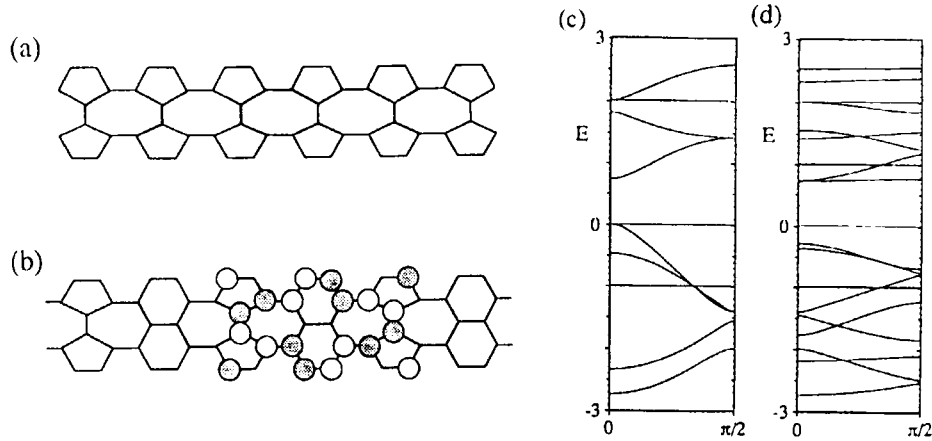
FIGURE 5   One-dimensional polymers having a flat-band. ((a), (b)) A localized wavefunction is also depicted with white (or dark) circles representing amplitude 1 (or -1) in (b). The band structure of the polymer (a) (or (b)) has a flat-band at the zero energy shown in (c) (or (d)).

localized orbital on the N_d-degenerate flat band. The theorem states that if the matrix $\rho_{x,y}$ is irreducible, the ground state is ferromagnetic for $U > 0$ for $N_e = N_d$, which half-fills the flat-band.

We can check the irreducibility of $\rho_{x,y}$ for the flat band of azupyrene polymers. Naively, the irreducibility is ensured if neighboring two localized orbitals have a common site with a finite amplitude and all of them are connected in this sense. This property is clearly seen for our polymers. Thus the theorem is applicable to show ferromagnetism.

Stability of the azupyrene structure and its magnetism

To derive the above result, we assume that i) the local azupyrene structure is a metastable structure and ii) a tight binding parameter is t for any pair of neighboring carbons. We now consider about validity of these assumptions.

The local azupyrene structure is indeed confirmed to be stable by a more realistic calculation, i.e. the first-principles LDA calculation. Our FPMD scheme allows the shape of the unit cell to vary. This process is realized by using the internal stress calculated at each step of MD.[23,24] Thus we can optimize all of the structural parameters for periodic systems in principle at any pressure. Here we adopted the plane-wave expansion to describe the electronic state with a cut-off energy of 40Ry using the Troullier-Martins pseudo-potential.

As an example, we show the optimized structure of a defective graphite ($\vec{m} = (3,0), \vec{l} = (-2,4)$) with electron charge density in Fig. 6. At the azupyrene defects,
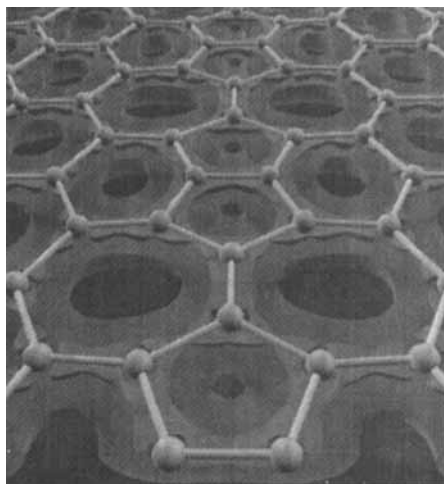
FIGURE 6 A defective graphite sheet with azupyrene structures optimized by the FPMD method at ambient pressure. Electronic charge density is shown by two surfaces around carbon atoms (white spheres).

we can see a concentration of charge. This characteristics is consistent with the result of the tight-binding model, where states near the Fermi level form a local density of state at the defects.

The result indicates that the bond length in this network varies from that of pure graphite. Electron doping on this structure may also cause additional deformation of the structure. However, it has been shown in several examples that the flat-band ferromagnetism remains stable even when lattice (or network structure) is changed so that the flat band becomes slightly dispersive.[22] The amount of U to produce ferromagnetism becomes larger for more wider band width. But the critical U remains finite around the flat-band limit where the band width $W = 0$. (Fig. 7) As a result, we can hopefully expect a possibility of ferromagnetism in the polymer with azupyrene structure as well.

CONCLUSION

We proposed two types of nanometer-scale graphitic structures, which might show new classes of organic magnetism. There localized orbitals, which are complete but not orthogonal having "a finite overlap" with neighboring orbital, are a basis to provoke ferromagnetic spin alignment.

Owing to many intensive experimental studies, we get conscious of various possible morphology in carbon networks. Interestingly, the new types of shape reveal
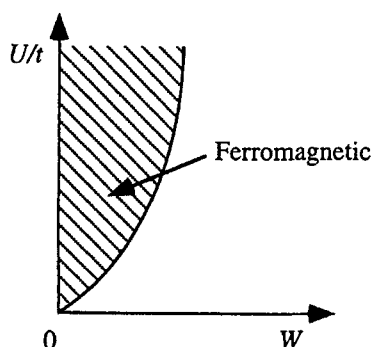
FIGURE 7 A schematic phase diagram for the flat-band ferromagnetism. Ferromagnetism appears above a critical U_c (solid curve), which is infinitesimal when the band width W is zero. For a dispersive band, ferromagnetism survives around the flat-band limit ($W = 0$).

not only existence of unconventional structures but also possibility of novel electronic states, which might revise our view to design new functionality in carbon technology.

ACKNOWLEDGMENT

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