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Electronic and Magnetic Structure of Micro-Graphite

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Studying the π electronic structure of graphite ribbon with zigzag edges based on a tight binding model, we find that zigzag ribbon has almost flat bands at the Fermi level, which does not originate from infinite graphite. The wave functions of the almost flat bands are mainly localized on the zigzag edge. We solve the puzzle for the emergence of the peculiar Edge State by deriving the analytic form of the Edge state in a semi-infinite graphite with the zigzag edge. Applying the Hubbard model within the mean field approximation, we further discuss the possible magnetic structure in a nanometer scale micrographite.

1. Introduction

A certain type of activated carbon fibers (ACF), which has huge specific surface areas (SSA) ranging to $3000m^2/g$ and is believed to consist of an assembly of micrographite with a dimension of ca. 20Å×20Å, shows paramagnetic behavior near room temperature, although other ACFs with less SSA are diamagnetic as well as graphite[1]. Although the reason for the critical change in the magnetic behavior can not be clarified yet, it might suggest that the π electrons on a nanometer sized micro-graphite has the novel electronic which is different from that of a bulk graphite. In such an atomic network with a nanometer length, a large portion of atoms are placed on the edge sites, thus the existence of edges should crucially affect electronic states and magnetism as well. In order to Examine the edge effect on the π electronic state in a finite size graphite, we have investigated the π electronic states of one dimensional graphite ribbons based on the tight binding band calculations and find that graphite ribbon with zigzag edge (zigzag ribbon) has partly flat bands at the Fermi level, where electrons are mainly localized on the edge[2][3]. The purpose of the this paper is to exhibit the novel electronic and magnetic structure attributed to the zigzag graphite edge.

2. Electronic Structure of Graphite Ribbon

We show the zigzag graphite ribbon in Fig. 1(a). The width of the zigzag ribbon can be defined by the number of the zigzag line N. The rectangle with the broken line expresses the unit cell of the zigzag ribbon. Since we can divide the sites of a ribbon into two sublattices A and B, we specify the site on the A(B) sublattice of the n-*th* zigzag line in the unit cell as nA(nB). It should be noted that we assume the dangling bonds at the edge are all terminated by hydrogen atoms, and thus give no contribution to the electronic states near the Fermi level.

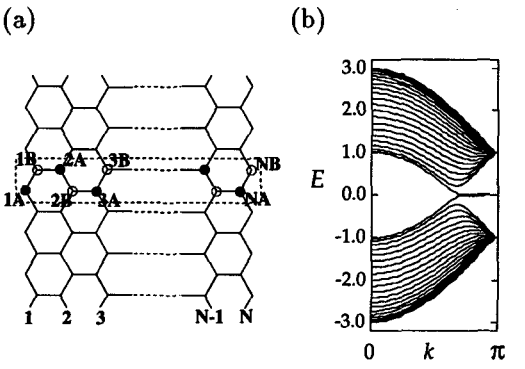

Figure 1: (a) One-dimensional graphite ribbon with zigzag edges for width N. The rectangle with broken line denotes the unit cell. (b) The enegy band structure of zigzag ribbon with $N=20$

In Fig. 1(b), we show the band structure of the zigzag ribbon with $N=20$ based on the tight

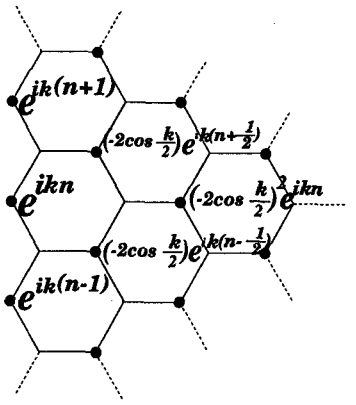

Figure 2: Analytic solution of partly flat band for a semi-infinite graphite.The wave function has the amplitude at the site indicated by closed circle.

binding model for the π electronics. It is found that the partly flat bands emerge at Fermi level, which do not originate from an infinite graphite sheet.

We can analytically represent the partly flat band as shown in Fig. 2. Since the neighboring edge sites has to keep the phase difference of e^{ik}, we set the wave function as $\ldots, e^{ik(n-1)}, e^{ikn}, e^{ik(n+1)}, \ldots$ at the successive sites. In order to be a solution of $E = 0$, the wave function must satisfy the mathematical requirement: the total sum of the components of the complex wave function over the nearest neighboring sites should vanish. As a result, exact solutions of $E=0$, the charge density is proportional to $\cos^{2n}\frac{k}{2}$ at the non-nodal site of n-th zigzag chain from the edge. Thus when $\frac{2\pi}{3} < k < \pi$ it shows the profile of an exponential decay. It turns out that the condition for convergence $|\cos\frac{k}{2}| \leq 1$ gives the exact region for the flat band in the semi-infinite graphite.

For some fixed wave number, we show the real part of the analytic solution in Fig. 3, where the amplitude is proportional to the radius, and the shading denotes the sign. The wave function has value on one of the sublattices which includes the edge sites. It is completely localized at the edge site when $k=\pi$, and starts to gradually penetrate into the inner sites as k deviates from π reaching the extend state at $k=2\pi/3$. Therefore, the electronic state in the partly flat bands of the zigzag ribbons is found to be characterized as the localized state near the zigzag edge.

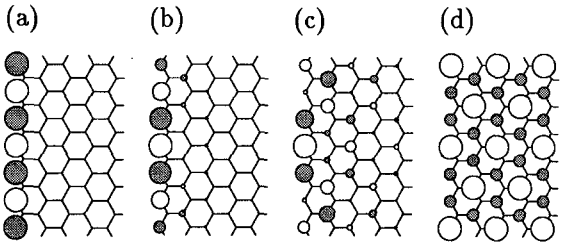

Figure 3: The real part of analytic solutions when (a)$k=\pi$, (b)$8\pi/9$, (c)$7\pi/9$ and (d)$2\pi/3$.

3. Magnetic Structure of Graphite Ribbon

The presence of the almost flat bands in the zigzag ribbon should induce the lattice distortion by the electron-phonon interaction and/or the magnetic polarization by the electron-electron interaction. Here we examine the effect of the electron-electron interaction utilizing the Hubbard model in order to show a peculiar feature of the zigzag edge. We can indeed display a possibility of spontaneous magnetic ordering peculiar to the nanometer scale fragments of graphite, which is known to show diamagnetism in the bulk sample. In order to analyze the magnetic structure, we investigate the Hubbard model on the zigzag ribbon with unrestricted Hartree-Fock approximation. This method is known to reproduce an outline of the magnetic structure. Quantum fluctuation, which is not taken into account by the mean-field approach, is expected only to reduce magnetic moment here. The mean field Hamiltonian is described as $H_{MF} = -t\sum_{n,\sigma}(c^{\dagger}_{n,\sigma}c_{n+1,\sigma} + c.c.) + U\sum_n\{\langle n_{n\downarrow}\rangle n_{n\uparrow} + \langle n_{n\uparrow}\rangle n_{n\downarrow} - \langle n_{n\downarrow}\rangle\langle n_{n\uparrow}\rangle\}$, where $n_{ns} = c^{\dagger}_{n,s}c_{n,s}$, and U is the on-site Coulomb repulsion. The expectation value for the number operator is denoted as $\langle n_{n,s}\rangle$. Starting from an initial spin configuration with Néel order, we solve the mean-field equations self-consistently by means of iteration method. By this way, we can estimate local magnetization m, which is given by $\langle n_{\uparrow}\rangle - \langle n_{\downarrow}\rangle$, at each site of the zigzag ribbon, where we take μ_B as unity.

We show the U dependence of magnetization m at the sites 1A, 2A and 5A for the zigzag ribbon of

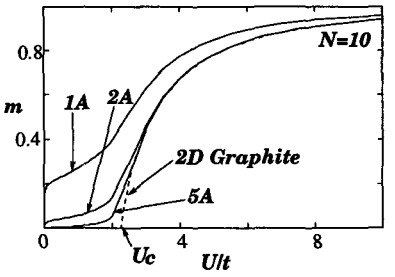

Figure 4: U dependence of m at 1A, 2A and 5A sites for the zigzag ribbon with $N=10$. That of a graphite sheet is also shown by the broken line.

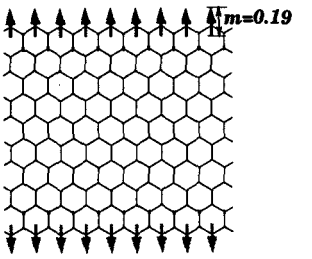

Figure 5: Magnetic texture of zigzag ribbon when $N=10$ and $U/t=0.1$.

$N = 10$ in Fig. 4, together with the magnetic solution for a 2D graphite sheet(broken line). First, we can clearly see a peculiar feature for the ribbon, *i.e.*, large magnetic moment emerge on the edge carbons even for the weak U, which is easily explained as follows. Since the 2D graphite is a zero-gap semiconductor whose density of states (DOS) is zero at the Fermi level, the broken line stands up at a finite value $U(=U_C)$. This is consistent with the fact that graphite is non-magnetic, where U is expected to be much smaller than t. On the other hand, the zigzag ribbon has a large density of states at the Fermi level originated from the localized states. Thus non-zero magnetic solution can emerge for infinitesimally small U region as indicated in the present mean field result. However, special emphasis should be put on the behavior of the magnetization at the edge site 1A. As shown in Fig. 4, the magnetization at the site $1A$ rapidly rises up and reach as much as about 0.2 even at small $U(\approx 0.1)$, when the width of ribbon is increased. We note that the armchair ribbon does not show such singular magnetic behavior.

Next, we note the exsitence of local ferrimagnetic structure for the zigzag ribbon. We show the magnetic texture of the ribbon with $N = 10$ at $U/t = 0.1$ in Fig. 5, where spin alignment are visualized at both edge sites. Origin of this structure is also explained from the nature of the edge states, which are responsible to the magnetization. Since the amplitude of the edge state is non-zero only on one of the two sublattices at an edge and dumps inwards, the magnetic moment selectively grows on this sublattice forming local ferrimagnetic spin configuration, which is getting smaller promptly on inner sites. The opposite edge sites, however, belong to the different sublattices, the total magnetization of the zigzag graphite ribbon is zero, although this vanishing total spin for the ground state is consistent with exact statement of the half-filled Hubbard model.

In conclusion, the spontaneous magnetization is possible for a graphite fragment in a nanometer scale. It is sure that the competition with the lattice distortion induced by the electron-phonon interaction is critical for the emergence of the magnetic order. We will discuss it in the next step, as well as effect from quantum fluctuation in order to go beyond the mean field treatment.

References

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