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Peculiar Localized State at Zigzag Graphite Edge

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We study the electronic states of graphite ribbons with edges of two typical shapes, armchair and zigzag, by performing tight binding band calculations, and find that the graphite ribbons show striking contrast in the electronic states depending on the edge shape. In particular, a zigzag ribbon shows a remarkably sharp peak of density of states at the Fermi level, which does not originate from infinite graphite. We find that the singular electronic states arise from the partly flat bands at the Fermi level, whose wave functions are mainly localized on the zigzag edge. We reveal the puzzle for the emergence of the peculiar edge state by deriving the analytic form in the case of semi-infinite graphite with a zigzag edge. Applying the Hubbard model within the mean-field approximation, we discuss the possible magnetic structure in nanometer-scale micrographite.

KEYWORDS: edge state, micrographite, nanometer scale, flat band, localized state, graphite edge

§1. Introduction

The discovery of fullerene molecules[1)] disclosed many artistic structures of carbon network based on three-coordinated sp^2 bonding. They form closed cages by introducing twelve pentagonal rings in the basis of a hexagonal network of carbon atoms. The subsequent discovery of carbon nanotubes[2)] shows that a graphite sheet can be rolled into a cylinder on a nanometer scale. They are of interest as defect-free materials, because we expect that the existence of any defect prevents the formation of such a perfect crystal.

The extension of structural variants of carbon leads to new members of the fullerene family such as carbon onions[3)] and coiled nanotubes,[4,5)] implying inexhaustible possibilities. In particular, the latter are thought to indicate the periodic alignment of heptagonal rings as well as pentagonal ones in a graphite sheet. There is considerable doubt, however, whether they are really formed by perfectly closed networks of sp^2 carbon atoms. Some recent experiments[6,7)] suggest the existence of defective nanotubes of carpet-roll or papier-mâché forms, which means that nanotubes might have some edge sites. Now we are faced with the presence of graphite edge in a microscopic view.

One of the interesting features of perfect cylindrical nanotubes is that the geometrical parameter which specifies the tubular circumference controls the electronic state to be metallic or insulating. For defective tubes the rule must be spoiled with discouragement. Here we emphasize, however, that attention should be focused upon the edge effect on the electronic state. In a bulk crystal the ratio of surface atoms is negligible, but if materials of a nanometer length have edges, quite a high proportion of atoms are on the surface.

There have been some theoretical studies on the electronic state of finite-sized graphite in a nanometer length including hundreds of carbon atoms as a molecule[8,9)] or in a unit cell of one-dimensionally periodic systems[9-12)] based on semi-empirical molecular orbital calculations. One of their important conclusions is that the finite size effect is critical in the electronic state of micrographites in a nanometer length, particularly in relation to the peripheral shapes. In this paper, we study the π electronic structure of one-dimensional (1D) graphite ribbons[9,10,12,13)] having edges of typical shapes from the viewpoint of energy band schemes, and show that the presence of edges gives rise to the critical difference in the electronic state from that of bulk graphite. The peculiar localized state which appears in the edge of a certain shape is discussed based on the analytic solutions derived in §3. Special emphasis will be placed on the significant edge effect on minute graphite systems of nanometer size.

§2. Energy Band of Graphite Ribbon

Cutting a graphite sheet along a straight line produces two typical kinds of peripheral shapes called armchair and zigzag, depending on the axial directions of 30° difference. If we then cut it along another parallel line, 1D ribbon-shaped graphite structures, i.e, armchair and zigzag ribbons, are obtained as shown in Figs. 1(a) and 1(b). Here we define the width N for each by the number of dimer lines for the armchair ribbon and by the number of zigzag lines for the zigzag ribbon. Since a graphite ribbon forms a bipartite lattice where the sites can be divided into A and B sublattices, we denote the index for the site in the N-th chain belonging to the A(B) sublattice as NA(NB) in the unit cell. 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.

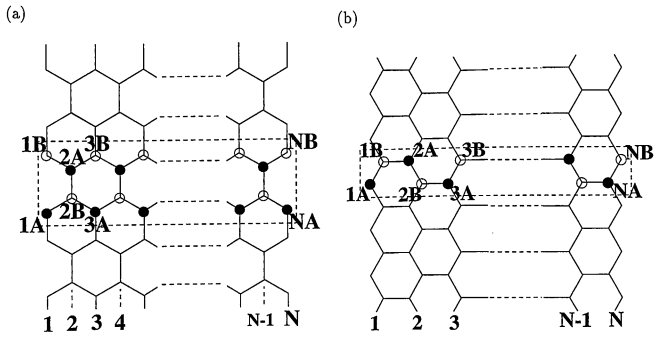

Fig. 1. One-dimensional graphite ribbon with (a) armchair and (b) zigzag edges for width N. The rectangle drawn with a broken line denotes the unit cell.

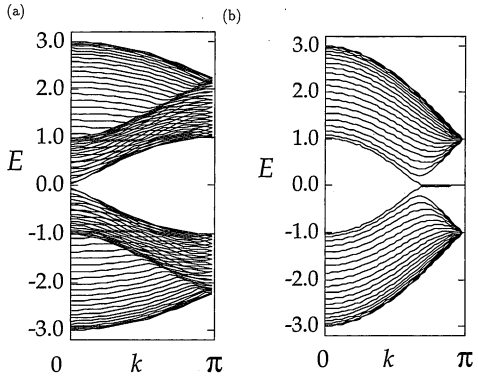

Fig. 2. Band structure of (a) armchair and (b) zigzag ribbons with width $N=20$.

We calculate the energy band structure for both systems based on the tight binding model for the π electron network. Transfer integrals are set at t between all the nearest neighbor sites for simplicity, because here we aim to reveal the intrinsic difference in the electronic states originating from the topological nature of each system. Before showing the results, let us make a conjecture concerning the band structure of each 1D graphite ribbon with a sufficiently large width based on that of a two-dimensional (2D) graphite sheet. A graphite sheet is a zero-gap semiconductor where the upper and lower bands are in point contact with each other at the K point having a linear dispersion in the hexagonal first Brillouin zone (BZ). The global band structure of each 1D graphite ribbon can be surmised by projecting the 2D graphite band onto the corresponding axis; the axial direction of armchair ribbons turns to the M point between the neighboring K points in the first BZ of a graphite sheet, while that of zigzag ribbons turns to the K point. As a result the K point is mapped to $k=0$ and $k=\pm 2\pi/3$ for the armchair and zigzag ribbons, respectively, where the unit is normalized on each periodicity. We expect that the states in the vicinity of those points are related to the Fermi level states of the 2D graphite.

An example of the energy band is depicted in Fig. 2 for each system, where the Fermi level is at $E=0$. For the armchair ribbon (Fig. 2(a)), both the valence band top and the conduction band bottom are located at the Γ point as expected. It is interesting to note that the state at the Γ point can be analytically determined because the problem is equivalent to a system whose Hamiltonian is $H=-t\sum_{j=1}^{N}\{\sum_{\mu=1}^{2}(a_{j,\mu}^{\dagger}a_{j+1,\mu}+\text{h.c.})+a_{j,1}^{\dagger}a_{j,2}+\text{h.c.}\}$, i.e., the tight binding model for the ladder system with two legs having N rungs.[14,15] The site indices (j,1) and (j,2) correspond to the jA(B) and jB(A) sites, respectively, when j is even(odd). The eigenvalues are evaluated as $\epsilon^{\pm}=-2t\cos n\pi/(N+1)\pm t$ $(n=1,\,2,\,\cdots,\,N)$ which is found to be zero, meaning the system is metallic, when N=3M-1, because ϵ^{+} and ϵ^{-} become zero for $n=M$ and $2M$, respectively. The direct energy gap in the insulating case tends to vanish with increasing width.

For the zigzag ribbon (Fig. 2(b)), a remarkable discrepancy arises in the energy band structure. First of all, since the system is always metallic, according to the above conjecture we expect that the degeneracy between the valence and conduction bands should appear only at the points of $k=\pm 2\pi/3$ in the zigzag system. Nevertheless the center two bands always show the degeneracy at $k=\pi$ which does not originate from the energy band structure of the 2D graphite. In addition we find that almost flat bands sit steadily at the Fermi level and become flatter for a wider ribbon within the region of $2\pi/3\le|k|\le\pi$. The agreement with the conjecture is that the dip of the upper band and the dump of the lower one sandwiching the flat bands approach each other as the width increases so as to generate the electronic state around the K point.

§3. Edge State of Zigzag Ribbon

The electronic state in the almost flat bands of the zigzag ribbons is found to be characterized as the localized state near the zigzag edge by examining the charge density distribution.[12,13] Here we show that the puzzle of the emergence of the edge state can be solved by considering a semi-infinite graphite sheet having a zigzag edge, where we derive the analytic solution for the flat band state. We note that Klein[11] studied the graphite ribbons where an additional methylene group is placed at every edge site of the zigzag ribbon and showed the existence of a kind of edge state giving the asymptotic description mathematically. We will mention later that the different feature of Klein's edge state can also be clarified by constructing the analytic solution in a semi-infinite system.

In the semi-infinite graphite sheet, a perfectly flat band can be constructed within $2\pi/3\le|k|\le\pi$. Before showing the analytic form, we show the real part of the wave function in the flat band states for some wave numbers in Fig. 3, where the amplitude is proportional to the radius, and the shading denotes the sign. The wave function takes values on one of the sublattices which includes the edge sites. It is completely localized at the edge sites when $k=\pi$, and starts to gradually penetrate into the inner sites as k deviates from π, reaching the extended state at $k=2\pi/3$.

We can represent the flat band analytically as shown in Fig. 4. Since the neighboring edge sites must keep the phase difference of e^{ik}, we set the wave function as $\cdots$, $e^{ik(n-1)}$, e^{ikn}, $e^{ik(n+1)}$, $\cdots$ at successive sites. In order

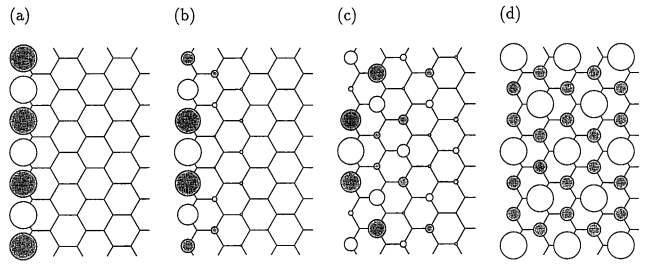

Fig. 3. Schematic figures of the real part of analytic solutions for the edge state in semi-infinite graphite, when (a) $k=\pi$, (b) $8\pi/9$, (c) $7\pi/9$ and (d) $2\pi/3$.

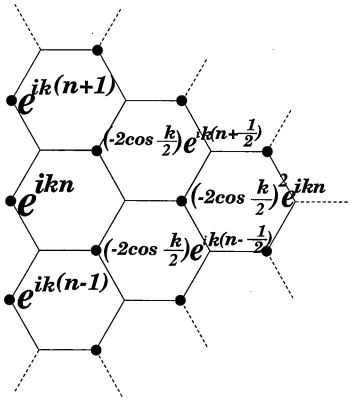

Fig. 4. Analytic solution of the sdge state for semi-infinite graphite. The wave function has the amplitude at the sites indicated by closed circles.

to be a solution of $E=0$, the wave function must satisfy the mathematical requirement that the sum of the components of the complex wave function over the nearest neighboring sites should vanish. In the resultant exact solutions of $E=0$, the charge density is proportional to $\cos^{2m}\frac{k}{2}$ at the non-nodal site of the m-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 $|2\cos\frac{k}{2}|\leq 1$ gives the exact region for the flat band in the semi-infinite graphite.

In Klein's ribbon,[11] assuming a semi-infinite system the penetration of the edge state is analytically derived as $\cos^{-2m}(\frac{k}{2})$. It gives the region for the flat band in $0<k<\frac{2\pi}{3}$. Since there is no state localized only at the edge site such as that of $k=\pi$ in the zigzag ribbon, Klein's ribbons always have an energy gap, suggesting less Fermi instability in comparison with the zigzag ribbon discussed below.

§4. Magnetic Structure of Graphite Ribbon

The presence of the almost flat bands in the zigzag ribbon should induce lattice distortion due to the electron-phonon interaction and/or magnetic polarization due to 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 find a possibility of spontaneous magnetic ordering peculiar to nanometer-scale fragments of graphite, which is known to show diamagnetism in bulk samples. In order to analyze the magnetic structure, we investigate the Hubbard model for the zigzag ribbon with unrestricted Hartree-Fock approximation. This method is known to reveal the overall magnetic structure. Quantum fluctuation, which is not taken into account in 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 an iteration method. By this means, 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 with $N=10$ in Fig. 5, together with the magnetic solution for a 2D graphite sheet (broken line). We can clearly see a peculiar feature of the ribbon, i.e., a large magnetic moment emerges on the edge carbons even for 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 nonmagnetic, 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 which originates from the localized states. Thus a nonzero magnetic solution can emerge for infinitesimally small U as indicated by the present mean field result. However, special attention should be paid to the behavior of the magnetization at the edge site $1A$. As shown in Fig. 5, the magnetization at the site $1A$ rapidly increases and reaches as much as about 0.2 even at small $U(\approx 0.1)$, when the width of the ribbon is increased. We note that the armchair ribbon does not show such singular magnetic behavior.

Next, we note the existence 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. 6, where spin alignments are visualized at both edge sites. The origin of this structure is also explained in terms of the nature of the edge states, which are responsible for the magnetization. Since the amplitude of the edge state is nonzero only on one of the two sublattices at an edge

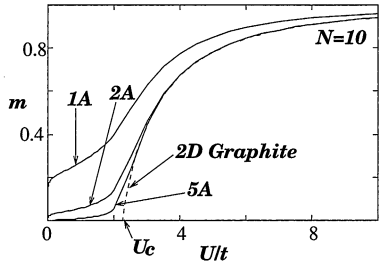

Fig. 5. U dependence of m at 1A, 2A and 5A sites for the zigzag ribbon with $N=10$. That of a graphite sheet is also shown by the broken line.

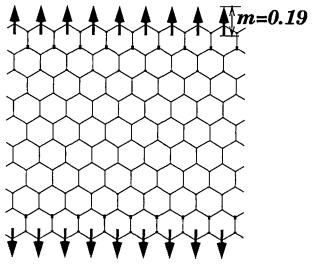

Fig. 6. Magnetic texture of zigzag ribbon when $N=10$ and $U/t=0.1$.

and dumps inwards, the magnetic moment selectively increases on this sublattice forming a local ferrimagnetic spin configuration, which is getting smaller promptly on inner sites. The opposite edge sites, however, belong to the different sublattices, and the total magnetization of the zigzag graphite ribbon is zero; this vanishing total spin for the ground state is consistent with the exact statement of the half-filled Hubbard model.[16]

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

§5. Discussion

Throughout the long history of human being associating with carbon materials, which probably begin with soot, one point of interest has been how to control their macro-, meso- and microscopic structure. For example, by controlling the degree and type of porosity of activated carbons we obtain a specific adsorption capacity. In spite of the remarkable utility of carbon materials, their functionality has not been investigated from micro- and mesoscopic points of view, but only by means of macroscopic measurement on a micron scale.

We should emphasize, however, that if we control the size of a graphite sheet on a nanometer scale, we have to pay attention to the existence of edges, which should affect the overall electronic state of a graphite fragment. We demonstrated that a graphite ribbon with the zigzag edge intrinsically possesses the edge state which does not appear in an armchair ribbon. The peculiar edge state shows the localization of the electron near the edge and a sharp peak in the DOS at the Fermi level. In addition we should take notice of the behavior of the edge state that with increasing the ribbon width the height of the peak in the normalized DOS reaches the maximum when the ribbon is dozens of atomic layers in width, and diminishes rapidly with increasing width. This tells us that there is an edge state if we find the zigzag edge, but the global effect on the electronic properties is negligible when the system is large. The edge state is conspicuous when the system consists of minute graphite with a nanometer-order length. The electronic properties may be very different from that of graphite, in particular, at the Fermi level, if you mince a graphite sheet very hard.

Finally we mention a noteworthy magnetic measurement for disordered carbon materials. Nakayama *et al.*[17] found that a certain type of activated carbon fibers (ACF), which has huge specific surface area (SSA) ranging to 3000 m^2/g and is believed to consist of an assembly of micrographite with a dimension of ca. 20 Å×20 Å, shows paramagnetic behavior near room temperature, although graphite and other ACFs with lower SSA are diamagnetic. This may suggest that an amount of mysterious DOS exists near the Fermi level, which might be related to the edge states above. Disordered carbon materials are presently of exceptional interest in physics, because they are exceptionally dirty materials.

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