Magnetic Structure of Nano-Graphite Möbius Ribbon

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We consider the electronic and magnetic properties of nanographite ribbon with zigzag edges under the periodic or Möbius boundary conditions. The zigzag nano-graphite ribbons possess edge localized states at the Fermi level which cause a ferrimagnetic spin polarization localized at the edge sites even in the very weak Coulomb interaction. The imposition of the Möbius boundary condition makes the system non-AB-bipartite lattice, and depress the spin polarization, resulting in the formation of a magnetic domain wall. The width of the magnetic domain depends on the Coulomb interaction and narrows with increasing $U/t$.

KEYWORDS: nanographite, graphite ribbon, Möbius strip, Hubbard model

Carbon based nano-scale materials such as fullerenes and carbon nanotubes are attracting much attention due to their novel electronic properties.$^{1,2}$ In these systems, the geometry of $sp^2$ carbon networks crucially affects the electronic states near the Fermi level.$^3$ The electronic states of carbon nanotubes are classified by the chiral vector which assigns the diameter and chirality of the nanotubes. Besides the closed carbon molecules, systems with open boundaries also display unusual features connected with their shape.$^{4,5}$ Nanographite ribbons, one-dimensional graphite lattices with a finite width, have shown that ribbons with zigzag edges (zigzag ribbon) possess localized edge states near the Fermi level.$^{4,5}$ These edge states correspond to non-bonding molecular orbitals. Such states are completely absent for ribbons with armchair edges.

While a graphite sheet behaves like a zero-gap semiconductor with vanishing the density of states (DOS) at the Fermi level, the edge states of the zigzag ribbons introduce a sharp peak in the DOS at the same energy. Therefore, we expect that a strong Fermi instability might be induced by electron-phonon and/or electron-electron interactions. The study of the electron-phonon interaction based on the Su-Schrieffer-Heeger (SSH) model concluded that the lattice in-plane distortion does not occur in the zigzag ribbons, because of the non-bonding character of edge state.$^6$ On the other hand, by treating the Hubbard model within the unrestricted Hartree-Fock (HF) mean-field approximation, the electron-electron interaction causes the ferrimagnetic spin polarization at the zigzag edge even under a very weak on-site Coulomb interaction.$^4,7$}

Recently, a NbSe$_3$ Möbius strip has been fabricated.$^9$ It is quite intriguing that a crystalline ribbon forms this exotic topology. Such the novel experimental findings motivated us to study the electronic properties of nanographite ribbons with the Möbius boundary condition. The main purpose of this study is to clarify the following questions. 1) How does the Möbius boundary condition affect the peculiar ferri-magnetic states appeared along the nanographite zigzag edge? 2) Although there have been some theoretical works on the Möbius strip, these works have been based on the square lattice system.$^9,10$ If we make a nano-graphite ribbon the Möbius strip form, what will happen? In this letter, we tackle these naive questions through the study on the electronic and magnetic properties of nanographite Möbius ribbons.

Before we discuss the electronic structure of zigzag ribbon with Möbius boundary condition, we shall briefly review the electronic states of zigzag ribbon. The nanographite ribbon with zigzag edges is obtained by making the width $N$ finite and the length $L$ infinite, in Fig.1(a). Throughout this paper, we assume all edge sites are terminated by H-atoms, also all the $\pi$-electrons have the spherical $s$-orbit for simplicity. Let us employ the tight-binding model to study the electronic states of nanographite ribbons. The tight-binding Hamiltonian is defined by $H = \sum_{i,j} t_{i,j} c_i^\dagger c_j$, where $t_{i,j} = -t$ if $i$ and $j$ are nearest neighbors, otherwise 0, and $c_i^\dagger (c_i)$ is a creation (annihilation) operator on site $i$. The ribbon

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Fig. 1. (a)The schematic structure of the zigzag ribbon with finite length $L$. The length of the ribbon is defined by the number of carbon slices ($y$-direction), and the width of the ribbon is defined by the number of carbon atoms which form the each carbon slice. The 1st carbon slice and the $Lth$ one are connected in terms of the periodic or Möbius boundary condition. (b) The schematic figure of energy band dispersion of zigzag ribbons, where $N = 20$ and $L$ is infinite.
width $N$ is defined by the number of zigzag lines. As the graphite lattice is the bipartite, the A(B)-site on the $n$-th zigzag line is called nA(nB)-site. Fig. 1(b) is the energy band structure of zigzag ribbon for $N = 20$, where the momentum $k$ was introduced along the $y$-direction. The zigzag ribbons are metallic for all $N$. One of the remarkable features is the appearance of partly flat bands at the Fermi level ($E = 0$), where the electrons are strongly localized near zigzag edges.$^4$

$$\psi(0, y) = \psi(N + 1, y) = 0, \quad (1)$$
$$\psi(x, y + L) = \psi(-x, y). \quad (2)$$

The quantized wave-numbers are $k_x = (\pi/N)n_x$ and $k_y = (2\pi/L)(1/2)[n_x + n_y]$, where $n_x = 1, 2, \cdots$ and $n_y = 0, \pm 1, \pm 2, \cdots$. The notation $[\alpha]_n$ represents $\alpha$ for $n =$even and 0 for $n =$odd. In the cylinder geometry, Eq.(2) should be replaced by $\psi(x, y + L) = \psi(x, y)$, and gives $k_y = (2\pi/L)n_y$. Thus, only the $n_x =$even eigenstates are affected by the switch from the conventional cylinder (periodic) boundary conditions to the Möbius ones. These are similar results as the square lattice system.$^9$ In Fig.2, we show the energy levels of nanographite ribbon with (a) the periodic boundary condition and (b) the Möbius boundary condition. Since the periodic boundary condition keeps the strip AB-bipartite lattice, the energy spectrum are symmetric. However, the zigzag Möbius strip shows the asymmetric energy spectrum at $E = 0$, because the Möbius boundary condition makes the strip non-AB-bipartite lattice system. It should be noted that, if the width $N$ is even (odd) integer, the length $L$ has to be even (odd) integer in order to exclude the polygonal defects such as four-, five-, and eight-membered rings.

The zigzag ribbon with an infinite length has the strong Fermi instability by the electron-electron interactions. However, instability by the electron-phonon interaction is weak due to the non-bonding character of the edge states. Here, we employ the mean field Hubbard model in order to study the magnetic structure in the nanographite ribbon with the Möbius boundary condition. The Hartree-Fock (HF) mean-field hamiltonian is written by

$$H = -t \sum_{\langle i,j \rangle, s} c_{i,s}^\dagger c_{j,s} + U \sum_{i,s} \langle n_{i,-s} \rangle - 1/2 n_{i,s} \quad (3)$$

where $s$ is spin index. In terms of the numerical calculation, we evaluate the electron density at each site, $\langle n_{i,-s} \rangle$, self-consistently. Also, the magnetization on each site, $M_i$, is defined by $M_i = \langle n_{i,\uparrow} \rangle - \langle n_{i,\downarrow} \rangle$.

Fig. 3. (a) The $U/t$ dependence of the magnetization in the zigzag ribbon with periodic boundary condition, where $N = 4$ and $L = 20$. (b) The schematic magnetic structure at $U/t = 0.1$, where black and white circles mean the up- and down-spin, respectively.

Previously, we found that this HF Hamiltonian shows clear differences in the magnetic structure compared with the graphite sheet.$^4$ Since the latter is a zero gap semiconductor, where the DOS at the Fermi level is zero, the
Fig. 4. (a) The $U/t$ dependence of the magnetization in the zigzag ribbon with Möbius boundary condition, where $N = 4$ and $L = 20$. (b) The schematic magnetic structure at $U/t = 0.1$.

Fig. 5. The site dependence of the magnetic moment along the upper and lower zigzag edges for (a) $U/t = 0.1$ and (b) $U/t = 1$, where $N = 4$ and $L = 40$.

antiferromagnetic HF solution emerges only when $U/t$ is larger than $U_c \sim 2t$, that is consistent with the fact that the graphite with a very weak Coulomb repulsion has no spontaneous magnetism. The graphite ribbons with zigzag edge, however, display a magnetic ground state, for any value $U/t > 0$. For $U/t \leq 2$, magnetic moments appear essentially only at the edge sites while in the center of the ribbon no magnetism can be found. Note that this behavior is consistent with the exact statement by Lieb for the half-filled Hubbard model. One of the present authors (K.H.) has discussed the stacking effects on the magnetic properties in nanographene planes with zigzag edges. It has been found that the A-B stackings and the open shell electronic structures in each graphene layer are necessary, in order to explain the decrease of the magnetic susceptibility in the course of adsorption of water molecules in activated carbon fiber materials. In the A-B type stackings, the edge sites do not interact with neighboring layers directly, and the local spin polarizations near edge sites remain against the interlayer hopping interactions. Therefore, the presence of edge sites exhibit an important role, and we can explain the novel magnetic properties of nanographites observed recently.

In Fig. 3, we show the $U/t$ dependence of the magnetization at each site in zigzag ribbon with the periodic boundary condition. Of course, the qualitative behavior shares with the results found in the zigzag ribbons with the infinite length. Here, the unit of the magnetization is the Bohr magneton. For the arbitrary $U/t$, the total magnetization is zero, which is consistent with the Lieb’s theorem, because the difference between A- and B-sublattice site numbers is zero. However, we find the non-zero solutions of the magnetization even if $U/t < 2$, where graphene sheet does not have the magnetic solutions. Since the system has a translational invariance along the $x$-axis, the magnetization is uniform along the this direction, as in the infinite zigzag ribbons. Most remarkable feature in this system is that the outermost edge sites have largest spin polarization, which form the ferrimagnetic spin alignment as shown in Fig. 3(b). The variation of the ribbon width and length does not change the results qualitatively.

Next, we shall discuss the mean-field calculation results for the Möbius strip. In Fig. 4(a), we show the $U/t$ dependence of the magnetization at each site in zigzag ribbon with the Möbius boundary condition, where $N = 4$ and $L = 20$. Here we shall change the site index as follows, because the system is no longer an AB-bipartite lattice after the imposition of the Möbius boundary condition. The carbon site on the $l$-th zigzag line and $m$-th carbon slice is called $(l,m)$-site hereafter. There are also non-zero solutions of the magnetization when $U/t < 2$ even under the Möbius boundary condition. However, we easily find that the magnetization on some sites rapidly decreases around $U/t = 4$. These sites form the magnetic domain wall which crosses the strip as shown in Fig. 4(b). The appearance of the magnetic domain wall is somewhat intuitive, because the Möbius boundary condition forces to connect between same sublattices, resulting in the magnetic frustration in the ferrimagnetic alignment.
along a zigzag edge. Here, we should note that the position of the nodal site is arbitrary, because the Möbius strip is originally translational invariant under $U/t = 0$. In Fig.5, we show the site dependence of the magnetic moment along the two zigzag edges for the $U/t = 0.1$ and 1. We clearly observe that the width of the domain wall depends on the magnitude of the Coulomb interaction. Increasing $U/t$, the width of the domain wall is gradually narrowing. Here, we shall comment on the total magnetization of the nanographite Möbius strip system. We found that the total magnetization of the Möbius strip with even (odd) $N$ is zero (non-zero). In the original rectangle system without Möbius boundary condition, the difference between A- and B-sublattice site numbers is zero (non-zero) for the even (odd) $N$ system. Although the Möbius boundary condition makes the system a non-AB-bipartite, this fact reminds us that the argument of the Lieb’s theorem is still valid under the Möbius boundary condition.

Finally, we show the $U/t$ dependence of the energy spectrum for $N = 4$ and $L = 20$. In Fig.6, the solid lines indicate the variation of the energy spectrum under the periodic boundary condition, so that the Coulomb interaction produces the energy gap. However, under the Möbius boundary condition, new energy states appear inside the Hubbard gap. This is quite similar to the mid-gap states appeared in the doped polyacetylene systems due to the bond alternation, i.e. the soliton level.\(^{15}\)

In conclusion, we have studied the electronic and magnetic properties of the nanographite ribbon with zigzag edges under the periodic or Möbius boundary conditions. The zigzag nano-graphite ribbons possess edge localized states at the Fermi level which cause a ferrimagnetic spin polarization localized at the edge sites even in the very weak Coulomb interaction. The imposition of the Möbius boundary condition makes the system a non-AB-bipartite lattice, and depress the spin polarization at the boundary of the magnetic domain, resulting in the formation of a magnetic domain wall. The width of the magnetic domain depends on the Coulomb interaction and narrows with increasing $U/t$. However, there remain problems which have not been treated here. In this paper, we have assumed that each $\pi$-electron has the spherical s-orbital, however in reality $\pi$-electron has the $p$-orbital. The electronic states of the nanographite Möbius strip with the $p$-orbitals will be presented elsewhere. The effect on the electronic states by Bohm-Aharonov magnetic flux, passing through the Möbius strip, is also intriguing and will be presented elsewhere.

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1) M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullerene and Carbon Nanotubes, (Academic Press, San Diego, 1996).
2) R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Carbon Nanotubes, (Imperial College Press, London, 1998).
3) J. W. G. Wildöer et al., Nature 391, 59 (1998); T. W. Odom et al., Nature, 391, 62 (1998).
4) M. Fujita et al., J. Phys. Soc. Jpn. 65, 1920 (1996)
5) K. Wakabayashi et al., Phys. Rev. B59, 8271 (1998); Phys. Rev. Lett. 84, 3390 (2000); Phys. Rev. B 64, 125428 (2001); J. Phys. Soc. Jpn. 71, 2500 (2002).
6) M. Fujita et al., J. Phys. Soc. Jpn. 66, 1864 (1997).
7) K. Wakabayashi et al., J. Phys. Soc. Jpn. 67, 2089, (1998).
8) S. Tanda et al., Nature 417, 397 (2002).
9) K. Yakubo et al., cond-mat/0203366
10) M. Hayashi et al., J. Phys. Soc. Jpn. 70, 3495 (2002).
11) E. H. Lieb: Phys. Rev. Lett. 62 (1989) 1201 [Errata: 68 (1992) 1997]; Rev. Mod. Phys. 60, 1295 (2001); Chem. Phys. Lett. 340, 123 (2001).
12) K. Harigaya, J. Phys: Condens. Matter, 13 1295 (2001); Chem. Phys. Lett. 340, 123 (2001).
13) K. Harigaya and T. Enoki, Chem. Phys. Lett. 351, 128 (2002).
14) N. Kawatsu, Master Thesis, Tokyo Institute of Technology (2001); T. Enoki et al., Polyhedron 20, 1311 (2001); H. Sato et al., Solid State Commun. in press.
15) A. J. Heeger et al, Rev. Mod. Phys. 60, 781 (1988).