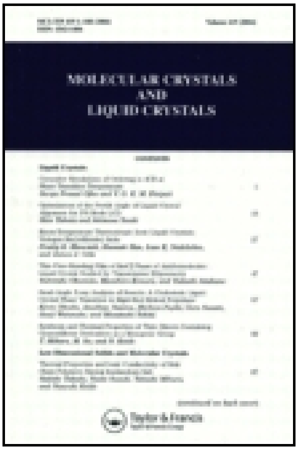

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ON POSSIBLE SURFACE MAGNETISM IN NANOGRAPHITE

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Magnetism of nanographite is examined by consideration based on known rigorous theorems for the Hubbard model. For a bearded nanographite ribbon with the zigzag edge on one side and Klein's decorated edge on the other side, the surface magnetization of $O(\mu_B)$ per a carbon atom is exactly shown to appear for the π-electron system described by the Hubbard model. The surface magnetism appears due to existence of the edge states, which are degenerate localized states specific to these edges of nanographite. The same magnetic mechanism holds for network structures called the hypergraphite, when edges are prepared so that completely degenerate edge states appear.

Keywords: nanographite; ferrimagnetism; surface magnetism

INTRODUCTION

Recently, graphite nanoparticles and graphitic nanostructures are attracting attention as a major target in carbon based materials [1,2]. In nanometer-scale graphite, namely nanographite, structure of the edge qualitatively affects electronic states around the Fermi level and physical properties of the system are modified according to shape of the edges. It has been recognized theoretically that the zigzag edge causes surface localized states, which were named the edge states [3].

The edge states are almost degenerate around the Fermi level and resulting enhancement of the local density of states could cause peculiar magnetic instability [3,4]. Similar localized states had been recognized to appear in another decorated edge by Klein [5].

Several works have been done to investigate possible magnetism within a mean-field approximation [3,6,7] and the first-principles calculation using the local-spin-density approximation [8]. The results suggest a

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ferrimagnetic spin structure on the zigzag edge, although the conclusion is not convincing enough because of the low-dimensionality of the system.

In this paper, we reinvestigate magnetism of nanographite based on rigorous knowledge on the ferrimagnetism appearing in the Hubbard model. By preparing proper edges, we can find that completely degenerate edge states appear at the Fermi level as noticed by several authors [9]. This complete degeneracy can be actually a basis of the so-called flat-band ferromagnetism and the Lieb theorem tells us that there appears finite magnetization and the system becomes ferrimagnetic [10,11].

However, an important point is that the magnetization appears only around the edges. We will show spatial distribution of local moments by considering a weak-coupling limit. In addition, by considering a limit of the infinite system size, we will derive a conclusion that a large magnetic moment is inevitably induced by the edge states. The surface magnetism due to the edge states is also shown to appear in a class of network structures called the hypergraphite networks [13,14]. The tight-binding electronic states on these networks intrinsically possess a nature which induce surface magnetization.

Edge States and Magnetic Mechanism on Flat Bands

Magnetism is crucially depends on structure of carbon network. For the nanographite, edge structure is a dominant factor. So far, two types of edges, *i.e.* the zigzag edge [3] and the bearded edge (Klein's edge) [5], are known to have special surface localized states. The surface states appearing at the zigzag (or bearded) edge is characterized by a non-bonding character and is called the edge states.

So far, magnetism is considered mainly for nanographite with zigzag edges [3]. Here we instead consider nanographite ribbon with the zigzag edge on one side and Klein's bearded edge on the other (Fig. 1(a)). Below we call this structure the bearded ribbon [9]. At the bearded edge, each single-coordinated atom is assumed to be terminated by 2 hydrogen atoms and to have a π orbital coupled to π-electron system in the bulk. At the zigzag edge, each carbon atom is terminated by a hydrogen atom, too.

We consider a tight-binding description of the π-electron system on nanographite ribbons. Introducing a short range repulsion, we obtain the Hubbard model on the nanographite. The Hamiltonian is given by,

$$H = -t \sum_{\langle i,j \rangle} \sum_{\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + \text{h.c.}) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}. \tag{1}$$

Here, $c^{\dagger}_{i,\sigma}$ (and $c_{i,\sigma}$) creates (annihilates) an electron with spin σ on the ith atom. $n_{i,\sigma}$ is the number operator. The electron transfer t have a same value

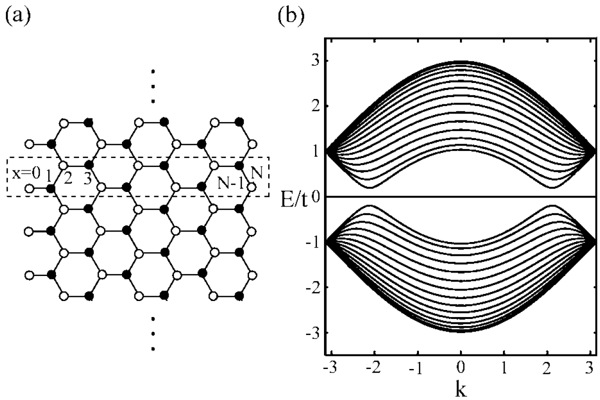

FIGURE 1 (a) The bearded nanographite ribbon. The right (left) edge is the zigzag (Klein's bearded) edge. The structure is assumed to be periodic in the vertical direction and the unit cell is indicated by the dotted line. Open and closed circles represent stared carbons (A-sites) and unstared ones (B-sites). (b) The tight-binding band-structure of the bearded ribbon. k is the wave vector along the vertical direction. The center band at zero energy consists from the degenerate edge states.

of $\sim$3.0 eV for each π-bond represented by $\langle i, j, \rangle$. We only consider a qualitative discussion around the Fermi level and thus the Hubbard U is regarded as a parameter.

Each π-orbital is occupied by an electron on the average, which is called the half filling. Since the nanographite structure is bipartite, the Lieb theorem [10] is applicable to determine the total spin moment S of the system. In the bearded ribbon, since the number of A-sites N_A is larger than the number of B-sites N_B by one per a unit cell, $S = |N_A - N_B|/2$ is finite. Besides, the ferrimagnetic order has been proved for the model with $|N_A - N_B| > 0$ at zero temperature [11]. However, these theorems do not tell spatial distribution of magnetic moments.

Appearance of Magnetization on Edges

Let us consider the weak coupling limit $U/t \sim 0$. Then we can show that only the center band of the tight-binding model at $U = 0$ becomes spin polarized, since there is a gap between the higher (or the lower) bands and the flat band (Fig. 1(b)). The distribution of magnetic moments is thus evaluated by the wave functions on the flat band. Figure 2 shows the profile of magnetization $M(x)$ in the unit cell. Here, the g-value is assumed to be $g = 2.0$. We can see prominent enhancement of $M(x) = O(\mu_B)$ at both edges.

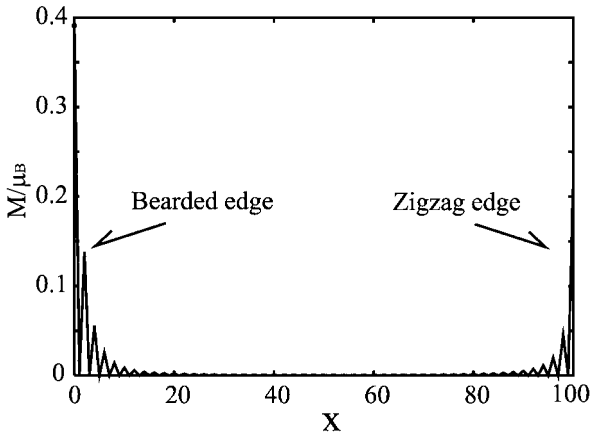

FIGURE 2 Magnetization M of the bearded ribbon. The width of the ribbon is $N = 100$. The right edge is the zigzag edge, while the left edge is the bearded edge. At both edges, M has a finite value of $O(\mu_B)$.

Such surface magnetization is not always expected even if we have a flat band by letting $|N_A - N_B| > 0$. A counter example is a ribbon of the square lattice having an bearded edge and a zigzag edge just like the bearded nanographite ribbon. In this system, local magnetization can be only $O(\mu_B/N)$ everywhere. Here N is the width of the ribbon. Difference in the surface magnetism is determined by existence or non-existence of the edge states. In the latter system, degenerate states at zero energy are not dumping waves. In nanographite ribbon, however, we have the edge states which are non-bonding dumping waves.

Next we consider to make width of the bearded ribbon N large. As far as the system is finite, the Lieb theorem is applicable. An interesting point is that, even if we let $N \to \infty$, the value of the surface magnetization remains finite.

Discussion

It has been recognized that ferrimagnetic spin structure appears at the zigzag edge and the bearded edge of nanographite [3,5]. If both of edges are zigzag edges, or if they are Klein's edges, edge magnetizations couples antiferromagnetically. However, they are ferromagnetically coupled for the bearded ribbon with a zigzag edge and a Klein's bearded edge.

If the picture that two surface magnetizations on nanographite edges interact with each other by an exponentially weak coupling mediated by the graphite bulk is correct as discussed by Wakabayashi-Sigrist-Fujita [12], the magnetization profile determined exactly in this paper confirms existence of edge magnetization.

Difference in surface magnetization between nanographite structure and finite square lattice is attributed to existence or non-existence of degenerate non-bonding dumping waves. The determination equation of the dumping factor D is a regular function of D and k. For the nanographite ribbon, the function satisfy the Weierstrass condition, which confirms existence of degenerate edge states. While the condition is not satisfied for the case of ribbons of the square lattice having zigzag (and/or bearded) edges and there is only one surface state at the zigzag edge.

The above discussion indicates that enhanced magnetization around edges is a special character of the graphite network. Two important conditions for the edge magnetism is 1) the network satisfies $|N_A - N_B| > 0$ and 2) appearance of the edge states which form a center flat band. If these conditions are satisfied, the surface magnetism appears in other networks, too. Actually, we know several examples of networks called the hypergraphite which possess these characteristics [14].

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