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THEORY ON THE MECHANISMS OF NOVEL MAGNETISM IN STACKED NANOGRAPHITE

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Antiferromagnetism in stacked nanographite is investigated with using the Hubbard-type model. The A-B stacking is favorable for the hexagonal nanographite with zigzag edges, in order that magnetism appears. Next, we find that the open shell electronic structures can be origins of the decreasing magnetic moment with the decrease of the inter-graphene distance, as experiments on adsorption of molecules suggest.

Keywords: edge states; magnetism; nanographite; theory

INTRODUCTION

Nanographite systems, where graphene sheets of the orders of the nanometer size are stacked, show novel magnetic properties, such as, spin-glass like behaviors [1], and the change of ESR line widths while gas adsorptions [2]. Recently, it has been found [3] that magnetic moments decrease with the decrease of the interlayer distance while water molecules are attached physically.

In this paper, we consider the stacking effects in order to investigate mechanisms of antiferromagnetism using the Hubbard-type model with the interlayer hopping t_1 and the onsite repulsion U. We will show that the A-B stacking is favorable for the hexagonal nanographite with zigzag edges,

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in order that magnetism appears. Next, we show that the open shell electronic structures, coming from functional units and/or geometrical effects, can be origins of the decreasing magnetic moment with adsorption of molecules. Such the effects of edge states could be one of the origins of peculiar magnetisms observed in novel carbon compounds [4,5]. Details of the calculations will be reported elsewhere [6–8].

CLOSED SHELL ELECTRON SYSTEMS

First, we report the total magnetic moment per layer for the A-B stacked hexagonal nanographite shown in Figure 1 (a). The first and second layers are displayed by the thick and thin lines, respectively. In each layer, the nearest neighbor hopping t is considered. Each layer has closed shell electron systems when the layers do not interact mutually, because the number of electrons is equal to the number of sites. The interlayer hopping t_1 is assigned at the sites with closed circles. The model is solved with the unrestricted Hartree-Fock approximation, and antiferromagnetic solutions are obtained. Figure 1 (b) shows the absolute value of the total magnetic moment per layer as functions of t_1 and U. As increasing U, the magnitude of the magnetization increases. The magnetic moment is zero at the smaller t_1 region for $1.9\,t$ (open squares), $2.0\,t$ (closed circles), and $2.1\,t$ (open circles). The magnetic moment is zero only at $t_1 = 0$ for $U = 2.2\,t$ (closed triangles) and $2.3\,t$ (open triangles). We can understand the parabolic curves as a change due to the Heisenberg coupling proportional to t_1^2/U.

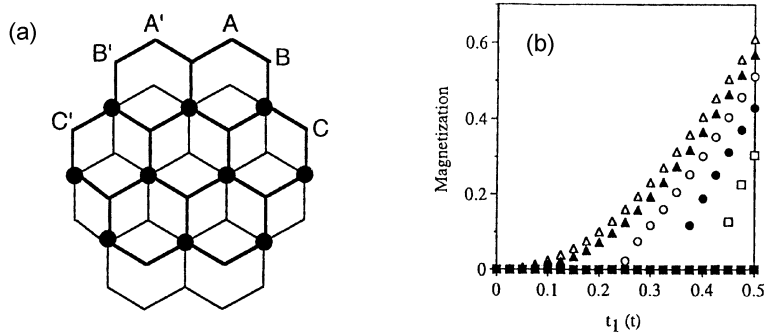

FIGURE 1 (a) A-B stacked hexagonal nanographite with zigzag edges. (b) The absolute magnitude of the total magnetic moment per layer as a function of t_1. The onsite interaction is varied within $1.8\,t$ (closed squares) $\leq U \leq 2.3\,t$ (open triangles). The interval of U between the series of the plots is $\Delta U = 0.1\,t$.

We have also calculated for the simple A-A stacking. We have not found any finite magnetization in this case. This is a remarkable difference between the A-A and A-B stackings, and is a new finding of this paper. The A-B stacking should exist in nanographite systems, because the exotic magnetisms have been observed in recent experiments [1–3]. The decrease of the interlayer distance while attachment of water molecules makes t_1 larger. However, it is known that the magnetism decreases while the attachment of molecules [3]. The calculation for the closed electron systems cannot explain the experiments even qualitatively.

OPEN SHELL ELECTRON SYSTEMS

Here, we consider the Hubbard-type model for systems which have open shell electronic structures when a nanographene layer is isolated. One case is the effects of additional charges coming from functional side groups. The next case is the roles of the standing magnetic moments due to the geometrical origin.

The active functional groups are simulated with introducing a site potential E_s [9] at edge sites. When $E_s > 0$, the site potential means the electron attractive groups. When $E_s < 0$, the electron donative groups are simulated because of the increase of the electron number at the site potentials. Here, we take $E_s = -2\,t$, and one additional electron per layer is taken account. Figure 2 displays the absolute values of total magnetic moment per layer. In Figure 2 (a), the site potentials locate at the site A in the first layer [Fig. 1 (a)], and at the symmetry equivalent site in the second layer. In Figure 2 (b), the site potential exists at the site B. The total magnetization is a decreasing function in both figures. The decrease is faster in Figure 2 (b) than in Figure 2 (a). The site B is neighboring to the site with the interaction t_1, and thus the localized character of the magnetic moment can be affected easily in this case. The decease of magnetization by the magnitude 30–40% with the water molecule attachment [3] may correspond to the case of Figure 2 (b).

Next, we look at the magnetism of stacked "triangulenes". The "triangulene" has the geometry displayed in Figure 3 (a), and there are six hexagonal rings [10]. The Lieb's theorem [11,12] says that the total spin $S_{\rm tot}$ of the repulsive Hubbard model of the A-B bipartite lattice is $S_{\rm tot} = (1/2)|N_A - N_B|$, where N_A and N_B are the numbers of A and B sites. We find $S_{\rm tot} = 1$ for the single triangulene. Figure 3 (b) displays the absolute magnitude of the total magnetic moment per layer for the A-B stacking with the vertical shift [Fig. 3 (a)]. The total magnetic moment is a decreasing function with respect to t_1. As we discuss in detail [6–8], there appear strong local magnetic moments at the zigzag edge sites, and they

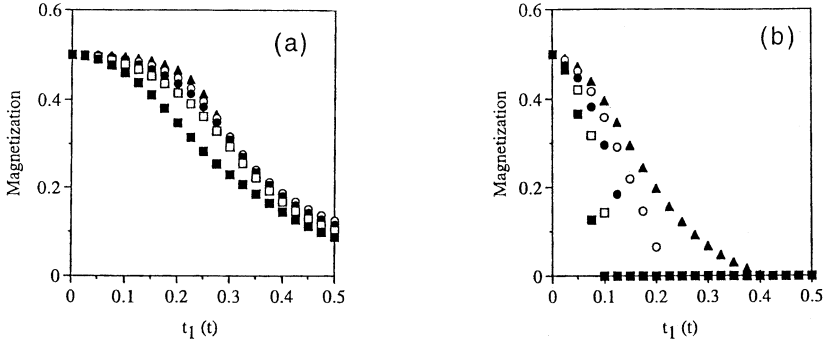

FIGURE 2 The absolute magnitude of the total magnetic moment per layer as a function of t_1 for the system with a site potential $E_s = -2t$, (a) at the site A and (b) at the site B. The site positions are displayed in Figure 1 (a). In (a), the onsite interaction is varied within $0.6\,t$ (closed squares) $\leq U \leq 1.8\,t$ (closed triangles). The interval of U between the series of the plots is $\Delta U = 0.3\,t$. In (b), it is varied within $1.0\,t$ (closed squares) $\leq U \leq 2.0\,t$ (closed triangles). The interval of U between the series of the plots is $\Delta U = 0.25\,t$.

give rise dominant contributions to the magnetism of each layer. In the triangulene case, most of the edge sites are neighboring to the sites with the interaction t_1 in Figure 3 (a). The interactions of the edge sites with the neighboring layers are strong, and the itinerant characters of electrons become larger as increasing t_1. Therefore, the magnetic moment is a decreasing function in Figure 3 (b).

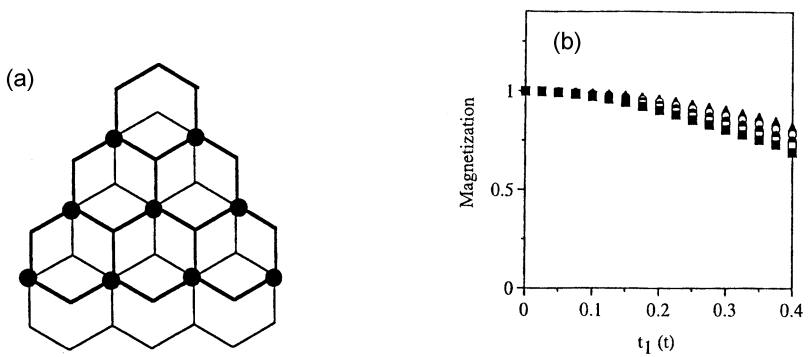

FIGURE 3 (a) A-B stacked triangulene with vertical shift. (b) The absolute magnitude of the total magnetic moment per layer as a function of t_1. The onsite interaction is varied within $0.4\,t$ (closed squares) $\leq U \leq 2.0\,t$ (closed triangles). The interval of U between the series of the plots is $\Delta U = 0.4\,t$.

The present two calculations agree with the experiments, qualitatively. We can explain the decrease of magnetism in the process of adsorption of molecules [3]. Thus, the open shell electronic structures due to the active side groups and/or the geometrical origin are candidates which could explain the exotic magnetisms.

SUMMARY

Antiferromagnetism in stacked nanographite has been investigated with the Hubbard-type model. The A-B stacking is favorable for the hexagonal nanographite with zigzag edges, in order that magnetism appears. Next, we have found that the open shell electronic structures can be origins of the decreasing magnetic moment with adsorption of molecules.

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