Mechanism of magnetism in stacked nanographite with open shell electrons

Kikuo Harigaya\textsuperscript{1,2,∗} and Toshiaki Enoki\textsuperscript{3}

\textsuperscript{1}National Institute of Advanced Industrial Science and Technology (AIST),
Umezono 1-1-1, Tsukuba 305-8568, Japan

\textsuperscript{2}Interactive Research Center of Science, Tokyo Institute of Technology,
Oh-okayama 2-12-1, Meguro-ku, Tokyo 152-8551, Japan

\textsuperscript{3}Department of Chemistry, Tokyo Institute of Technology,
Oh-okayama 2-12-1, Meguro-ku, Tokyo 152-8551, Japan

Abstract

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

PACS numbers: 75.30.-m, 75.70.Cn, 75.10.Lp, 75.40.Mg

\textsuperscript{∗}E-mail address: k.harigaya@aist.go.jp; URL: http://staff.aist.go.jp/k.harigaya/

\textsuperscript{†}Corresponding address
1. Introduction

Nanographite systems are composed of the structural units with stacking of graphene sheets of the nanometer size [1]. They show novel magnetic properties, such as, spin-glass like behaviors [2], and the change of ESR line widths while gas adsorptions [3]. Recently, it has been found [4,5] that magnetic moments decrease with the decrease of the interlayer distance while water molecules are attached physically.

In the previous papers [6,7], we have considered the stacking effects of hexagonal nanographite layers in order to investigate mechanisms of antiferromagnetism using the Hubbard-type model with the interlayer hopping integrals and the onsite repulsion $U$. We have taken account of the nanographite systems where the numbers of the sites and electrons in a layer are same, and therefore the electronic systems of the layer have closed shell structures. In the calculations, the finite magnetization develops, as the hopping interactions between layers increase in the case of the A-B stacking [6]. The same conclusion has been obtained when the system is near the A-B stacking and the interlayer distance becomes shorter [7]. 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 [4,5]. The calculation for the closed electron systems cannot explain the experiments even qualitatively.

The purpose of this paper is to extend the previous calculations to the systems with open shell electronic structures in the isolated nanographite layer. There are several candidates for the open shell of electronic structures. One of them is the electron number changes due to the presence of the active side groups. The electron or hole is donated from the side group. The effects can be modeled by a site potential in the idea of the model hamiltonians. This idea will be investigated in the present paper. The other origin of the open shell is a geometrical origin. The phenalenyl molecule $C_{13}$ with three hexagonal rings [8,9], and the triangulene $C_{22}$ with
six hexagons [10,11] are the examples of small graphene layers which have open shell electronic structures. The stacking effects of such kinds of molecules will be reported elsewhere [12].

We shall study with the two kinds of models which have been used in the papers [6,7]. Site potentials which simulate the additional side groups are introduced in the Hubbard-type hamiltonians. The change of the electron number is taken into account, too. We will show that the A-B stacking or the relative interlayer relation near the A-B stacking is favorable for the hexagonal nanographite with zigzag edges, in order that magnetism appears. We also find that the open shell electronic structure can be an origin of the decreasing magnetic moment with adsorption of molecules.

In the next section, we explain our models and review the method of the numerical calculations. In sections 3 and 4, the results of the two models are reported and discussed. The paper is closed with a summary in section 5.

2. Models

First, we will investigate with the model I [6],

\[
H = -t \sum_{\langle i,j \rangle: \text{intra-layer}} \sum_\sigma (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) \\
- t_1 \sum_{\langle i,j \rangle: \text{inter-layer}} \sum_\sigma (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) \\
+ U \sum_i n_{i,\uparrow} n_{i,\downarrow},
\]

where \( n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma} \) for \( \sigma = \uparrow \) and \( \downarrow \); \( c_{i,\sigma} \) is an annihilation operator of an electron at the \( i \)th site with spin \( \sigma \); the sum of the first line is taken over the nearest neighbor pairs \( \langle i,j \rangle \) in a single layer of the nanographite; the sum of the second line is taken over sites where the distance between two positions of the neighboring layers is shortest; \( t_1 \) is the strength of the weak hopping interaction between neighboring layers; the positions of \( t_1 \) are shown by the filled circles in Fig. 1 (a); and the last term of the hamiltonian is the strong onsite repulsion with the strength \( U \). We will vary the strength in a reasonable range. The actual values of \( U \) for
carbon atoms are of the similar order of magnitudes as in this paper: for example, we have found $U = 4t$ for the neutral $C_{60}$ and $C_{70}$ [13] and $U = 2t$ for the doped $C_{60}$ and $C_{70}$ [14] in the theoretical characterizations of the optical absorption experiments.

Second, we will study with the **model II** [7],

$$H = -t \sum_{(i,j) \text{:intralayer}} \sum_{\sigma} (c_{i,\sigma}^{\dagger} c_{j,\sigma} + \text{h.c.})$$

$$\quad - \sum_{(i,j) \text{:interlayer}} \sum_{\sigma} \beta(r_{i,j}) (c_{i,\sigma}^{\dagger} c_{j,\sigma} + \text{h.c.})$$

$$\quad + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}, \quad (2)$$

where the sum of the second line is taken over pairs of the sites $(i, j)$ in neighboring layers with a cutoff for long distance as used in [15] of the calculation for multiwall carbon nanotubes; the function $\beta(r)$ is given by

$$\beta(r) = A \exp(-r/\zeta) \quad (3)$$

where $r$ is the distance between carbon atoms, $A = 5.21t$, and $\zeta = 0.86\text{Å}$. The magnitude, $\beta(r = 3.40\text{Å}) = 0.1t$, is a typical value for the interlayer interaction strength in the tight binding model for A-B stacked graphite layers [16]: the explicit value is about 0.35 - 0.39 eV, and $t \sim 3eV$ gives the interaction strength about 0.1$t$.

We investigate the systems which have open shell electronic structures when a nanographene layer is isolated. The effects of additional charges coming from functional side groups are simulated with introducing site potentials $E_s$ [17,18] at edge sites in the model I or II. The form of the site potentials is

$$H_{\text{site}} = E_s \sum_{i \in I} \sum_{\sigma} c_{i,\sigma}^{\dagger} c_{i,\sigma}, \quad (4)$$

where the sum of $i$ is taken over the set of the positions of site potentials $I$. When $E_s > 0$, the electron number decreases from the average value at the site $i$, and 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 $E_s = -2t$, and one additional electron per layer is taken account.
The finite size system, whose number of the stacking layers is similar to that of the samples with the nanometer size, is solved numerically with using the periodic boundary condition for the stacking direction, and we obtain two kinds of solutions. One of them is an antiferromagnetic solution, where the number of up spin electrons is larger than that of down spin electrons in the first layer, the number of down spin electrons is larger than that of the up spin electrons in the second layer, and so on. The other kind of solution is a nonmagnetic solution. The present author has discussed the antiferromagnetism in C\(_{60}\) polymers, too [19]. The same technique (unrestricted Hartree-Fock approximation) used in ref. [6,7,19] is effective for the open shell electronic systems of this paper. The number of unit cells in the stacking direction is 10, and therefore there are 20 layers in the system used for the numerical treatment.

In the model I, the parameters are changed within \(0 \leq t_1 \leq 0.5t\) and \(0 \leq U \leq 4t\). The realistic value of \(t_1\) is estimated to be about 0.1\(t\) at most [16], but we change this parameter for more extended regions in order to look at the behaviors of solutions in detail. In the antiferromagnetic solutions, the number of electrons is the same with the number of sites, and electronic states are half-filled. Because we assume the electron donative case \(E_s < 0\), the number of electrons per layer is larger than the site number. Here, we take the electron number per layer \(n_{el} = 25\) and the site number per layer \(n_{site} = 24\). All of the quantities of the energy dimension are reported using the unit \(t\) (\(~2.0 - 3.0\) eV).

In the model II, we investigate the continuous change between the A-B stacking [Fig. 1 (a)] and the A-A stacking [Fig. 1 (b)]. We will move the first layer of Fig. 1 (b) to the upper direction. When the relative shift \(d = 0\), the geometry is of Fig. 1 (b). As \(d\) becomes larger, the system changes from the A-A stacking to the A-B stacking. When \(d = a\) (\(a\) is the bond length in each layer), the system has the geometry of Fig. 1 (a). In increasing \(d\), the edge sites feel weaker interactions from neighboring layers. Such the changes will give rise to variations in magnetic properties. The magnetism of the model II will be discussed with varying \(d\) and \(R\) (\(R\) is the interlayer distance) in section 4.
3. Results of model I

Here, we consider the Hubbard-type model for systems which have open shell electronic structures when a nanographene layer is isolated. The effects of additional charges coming from functional side groups are considered using the model I whose form is given by eq. (1).

Figure 2 displays the absolute values of total magnetic moment per layer. Figures 2 (a), (b), and (c) are for the A-B stacking, and Fig. 2 (d) represents the case of the A-A stacking. The strengths of the Coulomb interaction $U$ are shown in the figure captions. In Fig. 2 (a), the site potentials locate at the site D in the first layer [Fig. 1 (a)], and at the symmetrically equivalent site D’ in the second layer. The site potentials exist at the sites E and E’ in Fig. 2 (b), and they are present at the sites F and F’ in Fig. 2 (c). The total magnetization is a decreasing function in these three figures. The decrease is faster in Figs. 2 (b) and (c) than in Fig. 2 (a). The sites E and F are neighboring to the site with the interaction $t_1$, and thus the localized character of the magnetic moment can be affected easily in these cases. The decrease of magnetization by the magnitude $30 - 40\%$ with the water molecule attachment [3] may correspond to the case of Fig. 2 (b) or Fig. 2 (c).

Next, we note that the magnetic ordering is not present for the A-A stacking case [shown in Fig. 1 (b)] whose numerical result is shown in Fig. 2 (d). This is owing to the fact that all the sites between the neighboring layers interact via the hopping integrals, and that the itinerant characters of the electrons are dominant strongly for the A-A stacking. The present results are in agreement with the calculations for the closed shell systems reported in the previous paper [6].

4. Results of model II

In this section, the effects of site potentials and additional charges are investigated with the model II taking into account of the continuous relative shift between layers. The model eq. (2) has been used in [7], and is reviewed in the section 2 of this paper.
Figure 3 shows the absolute magnitude of the total magnetic moment per layer as a function of the relative shift $d$. The site potentials with the strength $E_s = -2t$ are present at the sites D (E, and F) in the first layer, and at the sites D’ (E’, and F’) in the second layer, in Figs. 3 (a) [(b), and (c)], respectively. Here, the interlayer distance $R$ is fixed and the Coulomb strength $U$ is varied in the series of the plots. The system is with the A-A stacking at $d = 0$, and the stacking is of the A-B type at $d = a$. At $d = 0$ and in the smaller region of $d$, there is not finite magnetization due to the strong interlayer hopping interactions near the A-A stackings. This qualitative property agrees with that of the model I and also with the calculation of the closed shell electron system [7]. However, there appear the finite magnetic moments with the antiferromagnetic sign alternation in the stacking direction for the region $d > 0.5a$ and for $U$ larger than a critical value. The onset of the magnetic moment at $d = 0.5a$ might be due to the presence of a cutoff of the long distance interaction, which has been used in [15], also. The magnetic moment increases as $U$ becomes larger as expected for the increase of the localized characters of electrons. In contrast, the magnetic moment is a weak decreasing function with respect to $d$.

Figure 4 shows the same quantity as a function of $d$. In these plots, the Coulomb interactions are taken constant as a representative strength $U = 1.2t$, and the interlayer distance $R$ is varied. The interlayer distance becomes smaller from the filled squares, through the open squares, to the filled circles. In the regions of $d$ where the finite magnetization is present, the magnetic moment decreases strongly while the interlayer distance becomes shorter. The total hopping interactions become larger as $R$ decreases. This effect enhances the itinerant characters of electrons in the stacking direction. Therefore, the magnetic moment becomes smaller with respect to the decrease of the interlayer distance. Such the qualitative behavior of the open shell electron system is in contrast with that of the closed shell electron system reported in the paper [7]. The present calculation is in qualitative agreement with that of the experiment which reports the decrease of the magnetization in the course of the adsorption of molecules [4,5]. In fact, the decrease of the interlayer distance about 0.4 Å while the adsorption of water
molecules has been reported [20].

The magnetic moment decreases easily for the site potentials at E and E’ [Figs. 3 (b) and 4 (b)], and also for the site potentials at F and F’s [Figs. 3 (c) and 4 (c)]. It does not vary so much in the case of the site potentials at D and D’ [Figs. 3 (a) and 4 (a)]. Such the quantitative difference comes from the contrast whether the site potentials are far from the sites with strong interlayer hopping interactions or not. The difference of the effects of the site potentials at D (D’) from those of the potentials at E (E’) or F (F’) agrees qualitatively with the result of the model I reported in the previous section.

To conclude, the two calculations of models I and II of this paper agree with the experiments, qualitatively. The case of the site potential at E or F agrees with experiments, even quantitatively. We can explain the decrease of magnetism of 30 – 40 % in the process of adsorption of molecules [4,5]. Therefore, the open shell electronic structure due to the active side groups is a good candidate which could explain the exotic magnetisms. The exotic magnetism is related with the edge states which have large amplitudes at the zigzag edge atoms of the each graphene layer. The important roles of the edge states have been discussed intensively for the nanographite ribbon systems recently [21-23].

5. Summary

Antiferromagnetism in stacked nanographite has been investigated with the Hubbard-type models. The A-B stacking or the relative interlayer relation near the A-B stacking is favorable for the hexagonal nanographite with zigzag edges, in order that magnetism appears. We have also found that the open shell electronic structure can be an origin of the decreasing magnetic moment with adsorption of molecules.

Acknowledgements

The authors are grateful for interesting discussion with N. Kawatsu, H. Sato, K. Takai, T.
Ohshima, Y. Miyamoto, K. Kusakabe, K. Nakada, K. Wakabayashi, and M. Igami. Useful discussion with the members of Nanomaterials Theory Group, Nanotechnology Research Institute, AIST is acknowledged, too.
References

[1] M. S. Dresselhaus, "Supercarbon: Synthesis, Properties and Applications", eds. S. Yoshimura and R. P. H. Chang, (Springer Verlag, Berlin, 1998), Part II.

[2] Y. Shibayama, H. Sato, T. Enoki, and M. Endo, Phys. Rev. Lett. 84, 1744 (2000).

[3] N. Kobayashi, T. Enoki, C. Ishii, K. Kaneko, and M. Endo, J. Chem. Phys. 109, 1983 (1998).

[4] N. Kawatsu, H. Sato, T. Enoki, M. Endo, R. Kobori, S. Maruyama, and K. Kaneko, Meeting Abstracts of the Physical Society of Japan 55 Issue 1, 717 (2000).

[5] N. Kawatsu, H. Sato, T. Enoki, M. Endo, R. Kobori, S. Maruyama, and K. Kaneko, preprint.

[6] K. Harigaya, J. Phys.: Condens. Matter 13, 1295 (2001).

[7] K. Harigaya, Chem. Phys. Lett. 340, 123 (2001).

[8] K. Fukui et al, Synth. Metals 103, 2257 (1999).

[9] K. Fukui et al, Mol. Cryst. Liq. Cryst. 334, 49 (1999).

[10] G. Allinson, R. J. Bushby, and J. L. Paillaud, J. Am. Chem. Soc. 115, 2062 (1993).

[11] M. J. Bearpark, M. A. Robb, F. Bernardi, and M. Olivucci, Chem. Phys. Lett. 217, 513 (1994).

[12] K. Harigaya, N. Kawatsu, and T. Enoki, "Nanonetwork Materials: Fullerenes, Nanotubes, and Related Systems", ed. S. Saito, (AIP, New York, 2001), in press.

[13] K. Harigaya and S. Abe, Phys. Rev. B 49, 16746 (1994).

[14] K. Harigaya, Phys. Rev. B 50, 17606 (1994).

[15] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, J. Appl. Phys. 73, 494 (1993).

[16] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. 30, 139 (1981).

[17] K. Harigaya, A. Terai, Y. Wada, and K. Fesser, Phys. Rev. B 43, 4141 (1991).

[18] K. Harigaya, J. Phys.: Condens. Matter 3, 4841 (1991).

[19] K. Harigaya, Phys. Rev. B 53, R4197 (1996).

[20] T. Suzuki and K. Kaneko, Carbon 26, 743 (1988).

[21] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. 65, 1920.
(1996).

[22] M. Fujita, M. Igami, and K. Nakada, J. Phys. Soc. Jpn. 66, 1864 (1997).

[23] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B 54, 17954 (1996).
Figure Captions

Fig. 1. Stacked nanographite with zigzag edges. The bold and thin lines show the first and second layers, respectively. The stacking is the A-B type in (a), and it is the simple A-A type in (b). There are 24 carbon atoms in one layer. The circles in (a) show sites where the interlayer distance between carbon atoms is shortest. The sites, A, B, ..., and F, are edge sites of the first layer, and the sites, A’, B’, ..., and F’, are edge sites of the second layer. When there is a site potential at D (E or F) of the first layer, another site potential is present at D’ (E’ or F’) of the second layer.

Fig. 2. The absolute magnitude of the total magnetic moment per layer of the model I as a function of $t_1$. The stacking is the AB-type in (a), (b), and (c), and it is the AA-type in (d). There is a site potential $E_s = -2t$, (a) at the site D, (b) at the site E, and (c) at the site F. The site positions are displayed in Fig. 1 (a). In (a), the onsite interaction is varied within $0.6t$ (closed squares) $\leq U \leq 1.8t$ (closed triangles). The interval of $U$ between the series of the plots is $\Delta U = 0.3t$. In (b), it is varied within $1.0t$ (closed squares) $\leq U \leq 2.0t$ (closed triangles). The interval of $U$ between the series of the plots is $\Delta U = 0.25t$. In (c), it is varied within $0.6t$ (closed squares) $\leq U \leq 1.8t$ (closed triangles). The interval of $U$ between the series of the plots is $\Delta U = 0.3t$. Finally, in (d), we display that there is no magnetization for the AA-stacking with a site potential at the D, E, or F.

Fig. 3. The magnitude of the total magnetic moment per layer of the model II as a function of $d$ and $U$. There is a site potential $E_s = -2t$, (a) at the site D, (b) at the site E, and (c) at the site F. The site positions are displayed in Fig. 1 (a). The interlayer distance is $R = 3.4\AA$. The values of $U$ are $U = 0.4t$ (filled squares), $0.8t$ (open squares), $1.2t$ (filled circles), $1.6t$ (open circles), $2.0t$ (filled triangles), respectively.
Fig. 4. The magnitude of the total magnetic moment per layer of the model II as a function of $d$ and $R$. There is a site potential $E_s = -2t$, (a) at the site D, (b) at the site E, and (c) at the site F. The site positions are displayed in Fig. 1 (a). The strength of the Coulomb interaction is $U = 1.2t$. The values of $R$ are $R = 3.4\text{Å}(\text{filled squares})$, $3.2\text{Å}(\text{open squares})$, and $3.0\text{Å}(\text{filled circles})$, respectively. All the plots within $0 \leq d \leq 0.5a$ overlap, so only the filled squares are seen.