New type of antiferromagnetic state in stacked nanographite

Kikuo Harigaya

Physical Science Division, Electrotechnical Laboratory,
Umezono 1-1-4, Tsukuba 305-8568, Japan

National Institute of Materials and Chemical Research,
Higashi 1-1, Tsukuba 305-8565, Japan

Kanazawa Institute of Technology,
Ohgigaoka 7-1, Nonoichi 921-8501, Japan

Abstract

Nanographite systems, where graphene sheets of the orders of the nanometer size are stacked, show novel magnetic properties, such as, spin-glass like behaviors and the change of ESR line widths in the course of gas adsorptions. We theoretically investigate stacking effects in the zigzag nanographite sheets by using a tight binding model with the Hubbard-like onsite interactions. We find a remarkable difference in the magnetic properties between the simple A-A and A-B type stackings. For the simple stacking, there are not magnetic solutions. For the A-B stacking, we find antiferromagnetic solutions for strong onsite repulsions. The local magnetic moments tend to exist at the edge sites in each layer due to the large amplitude of wavefunctions at these sites. We study variations between the A-A and A-B stackings to find that the magnetism between the two stackings experiences the first order phase transition. The effect of the interlayer distance is also discussed.

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

*E-mail address: harigaya@etl.go.jp; URL: http://www.etl.go.jp/~harigaya/; Address after April 2001: National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305, Japan

†Corresponding address
I. 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 interlayer magnetic interactions increase with the decrease of the interlayer distance while water molecules are attached physically. The magnetic susceptibility decreases due to the enhanced magnetic coupling between layers. Here, the change of the inter-layer interactions has been anticipated experimentally, but theoretical studies have not been reported yet.

In this paper, we theoretically consider the stacking effects in the zigzag nanographite sheets [4-6] by using a tight binding model with the Hubbard-like onsite interactions $U$. In the papers [4-6], the one dimensional graphite ribbons have been investigated. In this paper, we assume that each graphite sheet has a hexagonal shape with zigzag edges. Such the shape geometry has been used in the semi-empirical study of fluorine doped graphite nanoclusters [7], too. The two stacking types, namely the A-A and A-B types, shown in Fig. 1 are of particular interests. The circles in Fig. 1 (a) (namely, nanographite a) show the sites where the interlayer distance between carbon atoms is shortest. The zigzag edge sites have very weak interactions with the neighboring layers. On the other hand, in Fig. 1 (b) (nanographite b), all of the adjacent carbon atoms interact within each layer and with neighboring layers.

In studying the magnetic properties of the stacked systems, it is interesting to look at the continuous change between the nanographites a and 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 [Fig. 1 (b)] to the A-B stacking [Fig. 1 (a)]. 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 main purpose of this paper is to investigate changes of magnetism in stacked nanographite systems. We also discuss
how magnetic properties change while interlayer distance $R$ varies.

The main finding of this paper is a remarkable difference in the magnetic properties between the simple A-A and A-B stackings. For the simple stacking, we have not found magnetic solutions, because the presence of local magnetic moments is suppressed at carbons. For the A-B stacking, we have found antiferromagnetic solutions for $U > 2t$, $t$ being the hopping integral in a layer. The local magnetic moments tend to exist at the edge sites in each layer due to the large amplitude of wavefunctions at these sites. Therefore, the A-B type stacking is favorable in order that the exotic magnetism is observed in nanographite systems.

We also study continuous changes between the A-A and A-B stackings. We will find that the magnetism between the two stackings experiences the first order phase transition. The interlayer magnetic coupling becomes stronger when the interlayer distance becomes shorter. Relations with experiments are discussed extensively.

In Sec II, we explain our model. Sections III and IV are devoted to the total magnetic moment per layer, and the local magnetic polarization per site, respectively. In Sec. V, we discuss the local density of states at the edge carbon atoms. This paper is closed with summary in Sec. VI.

II. Model

We study the following model with hopping integrals between orbitals of carbon atoms and onsite strong repulsions of the Hubbard type:

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

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

$$+ U \sum_i n_{i,\uparrow} n_{i,\downarrow},$$

(1)

where $n_i = c_{i,\sigma}^\dagger c_{i,\sigma}$ 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 pairs of the sites \((i, j)\) in neighboring layers; the function \(\beta(r)\) is given by Eq. (2) (shown below); \(r_{i,j}\) indicates the distance between the \(i\)th and \(j\)th carbon atoms; and the last term of the hamiltonian is the strong onsite repulsion with the strength \(U\).

The interlayer interaction is taken into account with the functional form:

\[
\beta(r) = A \exp\left(-\frac{r}{\zeta}\right)
\]

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 [8]: the explicit value is about 0.35 - 0.39 eV, and \(t \sim 3eV\) gives the interaction strength about 0.1\(t\). The similar semi-empirical forms with the exponential dependence on the distance have been used for \(C_{60}\)-polymers [9], multi-wall carbon nanotubes [10], and many chains of conjugated polymers [11], in literatures. The interchain interactions in conjugated polymers are of the order 0.1\(t\) at most [11,12] also, and such the exponential dependence well describes the weak hopping interactions between the adjacent and nearer carbon atoms.

The finite size system is diagonalized numerically, and we obtain two kinds of solutions. One of them is a nonmagnetic solution where up and down spin electrons are not polarized in each layer. This kind of solutions can be found in weak \(U\) cases. The other kind of solutions 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. This kind of solution is realized in strong \(U\) regions. There will be cases of incommensurate spin density waves, but we have not obtained such kinds of solutions by choosing initial magnetic ordered states, which are commensurate with the one dimensional lattice in the stacking direction, at the first stage of the numerical iteration process. The present author has discussed the antiferromagnetism in \(C_{60}\) polymers [13]. The same technique used in Ref. [13] is effective in this paper, too.
The parameters are changed within $0 \leq d \leq 1.0a$ (a is the bond length in a layer), $3.0\text{Å} \leq R \leq 3.4\text{Å}$, and $0 \leq U \leq 3t$. All of the quantities of the energy dimension are reported using the unit $t$ ($\sim 3.0$ eV).

III. Magnetic moment per layer

In this section, we report the total magnetic moment in a layer. We discuss dependences on several model parameters: namely, the Coulomb interaction strength $U$, the relative shift between neighboring layers $d$, and the perpendicular distance between layers $R$.

First, we discuss the effects of the relative motion of one layer with respect to the neighboring one. Figure 2 shows the absolute value of the total magnetic moment per layer with changing $d$ and $U$. The interlayer distance is $R = 3.4\text{Å}$. See the figure caption for the parameter $U$. There is no magnetic moment for $0 \leq U \leq 2.1t$ for all the $d$. The finite magnetization appears with the antiferromagnetic ordering in the one dimensional direction for $U \geq 2.2t$ and $0.5a < d \leq 1.0a$. The appearance of the magnetization with respect to increasing $U$ is continuous, and this is the second order phase transition. The magnetic moment increases as a function of $U$. On the other hand, there is not any magnetic ordering for all the $U$ in the region $0 \leq d \leq 0.5a$. For larger $U$, the finite magnetization appears suddenly with the discontinuity at $d = 0.5a$. Therefore, the variation with respect to $d$ is the first order phase transition.

The remarkable difference on the magnetic properties between small and larger $d$ is mainly due to the change of the stacking properties. When $d \sim 0$, the system is near the A-A stacking. When $d \sim 1.0a$, it is near the A-B stacking. Such the difference will be discussed taking into account of the local magnetic polarization in the next section.

Next, we look at the effects of the interlayer distance $R$. Figure 3 displays the absolute magnitude of the total magnetic moment per layer with changing $d$ and $R$. The strength of the Coulomb interaction is $U = 2.5t$. The values of $R$ are $R = 3.4\text{Å}$(filled squares), $3.2\text{Å}$(open squares), and $3.0\text{Å}$(filled circles), respectively. In the experiment [14], the change of the inter-
layer distance from 3.4Å to 3.8Å with desorption of the water molecules has been found. The chemical pressure from the adsorbed water becomes loose, and this gives rise to the change of the interlayer distance. This is an example of experiments which are related with the present calculation (even though the model parameter value is somewhat different and this is a minor problem). In decreasing $R$, the interlayer hopping interactions become stronger. This gives rise to the increase of the total magnetic moment per layer where the finite antiferromagnetic order is present. The change of magnetization between the small and larger $d$ is always discontinuous, and the first order phase transition occurs. The exponential dependence $\beta(r)$ could give change of the magnetic moment over several orders of magnitude in general. But, we have limited the change of $R$ in a certain region. Even though the parameter region is quite small, we can note that the magnetization increases by several times with only the slight decrease of the interlayer distance presumably by a static pressure or by some chemical pressure effects. Therefore, we conclude that the variation of magnetic properties by some modification of the stackings is a quite controllable one.

IV. Local magnetic polarization in a layer

Here, we report the magnetic moment per site in a layer, particularly paying attention to the edge sites.

Figure 4 shows the local magnetic moment at the edge sites A, B, and C (displayed in Fig. 1 (a)) with changing the relative motion $d$ between layers. These sites have weak interactions with neighboring layers when the system is near the A-B stacking $d \sim 1.0a$. In Fig. 4, the other parameters are $U = 2.5t$ and $R = 3.4Å$. The filled squares, open squares, and filled circles show the results at sites A, B, and C, respectively. All the plots within $0 \leq d \leq 0.5a$ overlap. The open squares and the filled circles overlap for $0.5a < d \leq 1.0a$. There are not local magnetic moments when the total magnetization in a layer is zero. This is the case of $0 \leq d \leq 0.5a$. In this region, all of the carbon atoms between layers interact strongly. The
hopping interactions tend to enhance the itinerancy of electrons in the direction perpendicular to the layers. This enhancement of the itinerancy suppresses the magnetic orderings. On the other hand, a certain magnitude of the local magnetic moments exist for larger $d$ (near the A-B stacking). The magnetic polarization is negative along the edge A-A’, and it is positive along the edges B-C and B’-C’ in the first layer of Fig. 1 (a). The value of the polarization at the inner atoms apart from the edges becomes smaller. The carbon atoms near the edges have weak interactions with the other atoms of neighboring layers. Such the property gives rise to the weak itinerant character of electrons, and this is the main origin of the appearance of the local magnetic polarization at the edge atoms. The first order phase transition between the small and large $d$ regions characterizes the qualitative difference of the magnetic properties.

In the band calculations of the stacked nanographite ribbons [15], the strong hybridization between edge states occurs in the A-A stacking case. Such the hybridization is weak in the A-B stacking case. The strong localization of wavefunctions at the edge carbon sites persists in the band calculations for systems with the A-B stacking [15], and this property agrees with the present result of the appearance of local magnetic polarization near the A-B stacking.

V. Density of states

In this section, we discuss the local density of states at the edge sites. The wavefunctions of electrons with up and down spins are projected on the edge sites which are labeled in Fig. 1 (a). The local density of states is reported together with the total density of states.

Figure 5 reports the density of states per layer while $d$ is varied: $d = 0$ for Fig. 5 (a), $d = 0.5a$ for Fig. 5 (b), and $d = 1.0a$ for Fig. 5 (c). The other parameters are taken constant: $U = 2.5t$ and $R = 3.4\text{Å}$. The bold line shows the density of states over 24 carbon atoms per layer and per spin. The thin and dashed lines indicate the density of states over the eight edge sites in a layer for the up and down spins, respectively. We note that the thin lines and the dashed lines accord with each other in Figs. 5 (a) and (b). This is related with the property
that magnetizations are not present. On the other hand, the up and down splitting typical to
the antiferromagnetism is seen in Fig. 5 (c). Because the number of edge sites is one third
of that of the total carbon atoms in the nanographite, the areas between the lines and the
horizontal axis have such the relative ratios. In one dimensional graphite ribbons [4-6], there
appears a strong peak due to the localized edge states at the Fermi energy. This is seen in
the non-interacting case. With interactions taken into account, such the edge states split into
bonding (occupied) and antibonding (unoccupied) states. This fact will be one of the reasons
why such the strong peak is not observed in Fig. 5. Also, in the present case, the edge sites
do not make a one dimensional lattice and each layer has a finite spatial dimension. Such the
difference will be the second reason of the absence of the strong peak.

In the experiments of nanographite, for example in [14], the stacking patterns have not been
observed directly. However, our theoretical results clearly show that the A-B type stacking is
favorable in nanometer size graphite systems in order that the exotic magnetic properties [1-3]
are to be observed experimentally.

VI. Summary

In summary, we have theoretically investigated the stacking effects in the zigzag nanographite
sheets. We have found a remarkable difference in the magnetic properties between the simple
A-A and A-B type stackings. For the simple stacking, there are not magnetic solutions. For
the A-B stacking, we have found the antiferromagnetic solutions for strong onsite repulsions.
The local magnetic moments tend to exist at the edge sites in each layer due to the large
amplitude of wavefunctions at these sites. We have studied the continuous changes between
the A-A and A-B stackings, and have found that the magnetism between the two stackings
experiences the first order phase transition. The effect of the interlayer distance has been
discussed. Therefore, the A-B type stacking is favorable in order that the exotic magnetism is
observed in nanographite systems.
Acknowledgements

The author is grateful for interesting discussion with T. Enoki, N. Kawatsu, T. Ohshima, Y. Miyamoto, K. Kusakabe, K. Nakada, K. Wakabayashi, and M. Igami. Useful discussion with the members of Condensed Matter Theory Group (http://www. etl.go.jp/~theory/), Electrotechnical Laboratory is acknowledged, too.
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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) (nanographite a), and it is the simple A-A type in (b) (nanographite 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 edge sites, A (B, C) and A’ (B’, C’), are symmetrically equivalent, respectively.

Fig. 2. The magnitude of the total magnetic moment per layer as a function of $d$ and $U$. The interlayer distance is $R = 3.4\text{Å}$. The values of $U$ are $U = 2.1t$ (filled squares), $2.2t$ (open squares), $2.3t$ (filled circles), $2.4t$ (open circles), $2.5t$ (filled triangles), and $2.6t$ (open triangles), respectively. All the plots within $0 \leq d \leq 0.5d$ overlap, so only the squares are seen.

Fig. 3. The magnitude of the total magnetic moment per layer as a function of $d$ and $R$. The strength of the Coulomb interaction is $U = 2.5t$. The values of $R$ are $R = 3.4\text{Å}$(filled squares), $3.2\text{Å}$(open squares), and $3.0\text{Å}$(filled circles), respectively. All the plots within $0 \leq d \leq 0.5d$ overlap, so only the filled squares are seen.

Fig. 4. Local magnetic moment at the edge sites A, B, and C, as a function of $d$. The parameters are $U = 2.5t$ and $R = 3.4\text{Å}$. The filled squares, open squares, and filled circles show the results at sites A, B, and C, respectively. All the plots within $0 \leq d \leq 0.5a$ overlap. The open squares and the filled circles overlap for $0.5a < d \leq 1.0a$. Therefore, the number of plots seems smaller.

Fig. 5. Density of states per layer while $d$ is varied: $d = 0$ for (a), $d = 0.5a$ for (b), and $d = 1.0a$ for (c). The other parameters are $U = 2.5t$ and $R = 3.4\text{Å}$. The bold line shows the density of states over 24 carbon atoms per layer and per spin. The thin and dashed lines indicate the
density of states over the eight edge sites in a layer for the up and down spins, respectively. We note that the thin lines and the dashed lines overlap in Figs. (a) and (b).