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Spin Wave Mode of Edge-Localized Magnetic States in Nanographite Zigzag Ribbons

Katsunori WAKABAYASHI, Manfred SIGRIST[1] and Mitsutaka FUJITA*

Institute of Materials Science, University of Tsukuba, Tsukuba 305
[1] *Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606-01*

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We consider the low-energy magnetic excitations of nanographite ribbons with zigzag edges. The zigzag ribbons possess almost flat bands at the Fermi level which cause a ferrimagnetic spin polarization localized at the edge sites. The spin wave mode of this magnetic state is investigated by a random phase approximation of the corresponding Hubbard model. This result is used to derive an effective Heisenberg model with ladder structure. Although this system has a spin gap (Haldane type), our analysis shows that the gap is small and the tendency towards ferrimagnetic correlation at the edges is strong.

KEYWORDS: nanographite, graphite ribbon, flat band, spin wave, Hubbard model, RPA

§1. Introduction

Nanographites are nanometer-sized graphite fragments which represent a new class of a mesoscopic system intermediate between aromatic molecules and extended graphite sheets. The characteristic feature of nanographites is that the edge region is not negligible, i.e., edge and bulk effects are comparable, and therefore, the existence of edge might affect the π electronic states which govern the electronic properties near the Fermi level.[1,2)] A useful and simple system to investigate the electronic states of nanographites is provided by ribbon-shaped graphite. By studying the electronic states of graphite ribbons based on the tight binding model, we found that the edge shape - we distinguish between *zigzag* and *armchair* edges - leads to a striking difference for the states near the Fermi level. In contrast to the electronic structure of ribbons with armchair edges, the ones with zigzag edges possess almost flat bands at the Fermi level associated with electronic states which are localized in the near vicinity of the edge. This localized state ("edge state") corresponds to the non-bonding molecular orbital (NBMO) as can be understood from the analytic solution for semi-infinite graphite with a zigzag edge.[1)]

While a graphite sheet behaves like a zero-gap semiconductor with vanishing DOS at the Fermi level, the flat bands of the zigzag ribbons introduce a sharp peak in the DOS at the Fermi level. Therefore, an instability could be induced by electron-phonon and/or electron-electron interactions. The study of the electron-phonon interaction based on the 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.[4)] On the other hand, the treatment of the Hubbard model within the unrestricted Hartree-Fock(HF) approximation showed that the electron-electron interaction causes a ferrimagnetic spin polarization at the zigzag edge even for very weak on-site Coulomb interaction.[1)]

The ferrimagnetic spin polarization obtained by HF approximation along the zigzag edges is of course interesting in view of the magnetic properties of nanographites. Nevertheless, the long-range order derived from this HF calculation is spurious, because no finite-momentum long-range spin order is expected in an one-dimensional system with full spin-rotation symmetry.[3)] Even we may argue that quasi-long-range order, similar to the spin-1/2 Heisenberg chain, is not realized in zigzag ribbons of any finite width for the following reason. The unit cell of the ribbons contains an even number of sites and the band is half-filled so that Haldane's conjecture applies, i.e. the system should exhibit a spin gap.[5)] This is very analogous to the case of the ladder systems with an even numbers of legs, which display a resonating valence bond (RVB) ground state, i.e., a short range correlated spin liquid state. With increasing width of the ribbon, however, the spin gap Δ_s should decrease exponentially due to the diminished overlap between two edges. In the limiting case of a semi-infinite graphite sheet, the state should, therefore, possess a gapless spin spectrum with quasi long range order. From this point of view, it is reasonable to study the low-lying spin excitations based on the HF result using the random phase approximation (RPA), which will give us in any case gapless spin wave modes. These modes lie below the charge gap induced by the electron-electron interaction for any width of the ribbon so that they remain always well-defined. We will use the RPA result to derive an effective Heisenberg spin model for the magnetic moments which emerge at the edges due to the electron-electron interaction.

§2. Spin Wave Mode in Graphite Ribbons

We use the following Hubbard model for the zigzag ribbons,

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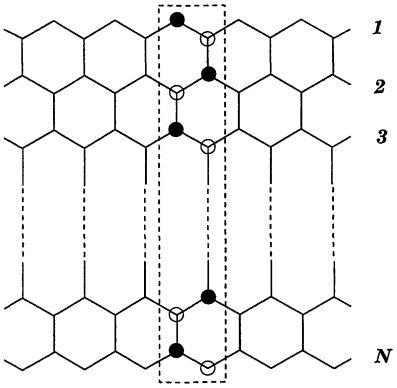

Fig. 1. The frame of zigzag ribbon, where closed(open) circles denote A(B)-sublattice. The rectangle with dashed line shows the unit cell.

$$H = -t \sum_{(\alpha,\alpha')} \sum_{(i,j),s} c^{\dagger}_{\alpha,s}(i) c_{\alpha',s}(j) + U \sum_{\alpha} \sum_{i} n_{\alpha,\uparrow}(i) n_{\alpha,\downarrow}(i), \tag{2.1}$$

where the operator $c^{\dagger}_{\alpha,s}(i)$ creates an electron with spin s on the site i of the unit cell α and $n_{\alpha,s}(i) = c^{\dagger}_{\alpha,s}(i) c_{\alpha,s}(i)$. Here (α, α') and (i, j) denote nearest neighbor unit cells and sites, respectively. The shape of the zigzag ribbon is shown in Fig. 1 with the definition of the ribbon width N and the unit cell. As a first step, we solve the unrestricted Hartree-Fock (HF) Hamiltonian, which is obtained by neglecting the fluctuation term after the substitution $n_{\alpha,s}(i) = \langle n_{\alpha,s}(i) \rangle + (n_{\alpha,s}(i) - \langle n_{\alpha,s}(i) \rangle)$ to eq. (2.1),

$$\begin{aligned} H = & -t \sum_{\langle \alpha,\alpha' \rangle} \sum_{\langle i,j \rangle,s} c^{\dagger}_{\alpha,s}(i) c_{\alpha',s}(j) \\ & + U \sum_{\alpha} \sum_{i} \left(\langle n_{\alpha,\downarrow}(i) \rangle n_{\alpha,\uparrow}(i) + \langle n_{\alpha,\uparrow}(i) \rangle n_{\alpha,\downarrow}(i) \right) \\ & - U \sum_{\alpha} \sum_{i} \langle n_{\alpha,\uparrow}(i) \rangle \langle n_{\alpha,\downarrow}(i) \rangle, \end{aligned} \tag{2.2}$$

where $\langle \cdots \rangle$ denotes the expectation value in the HF state. The self-consistence conditions are given by

$$\begin{aligned} m(i) &= \frac{1}{L} \sum_{k} \langle a^{\dagger}_{k\uparrow}(i) a_{k\uparrow}(i) - a^{\dagger}_{k\downarrow}(i) a_{k\downarrow}(i) \rangle \\ &= \frac{1}{L} \sum_{k} \sum_{l}^{occ.} \left\{ u^{*}_{k\uparrow}(i;l) u_{k\uparrow}(i;l) - u^{*}_{k\downarrow}(i;l) u_{k\downarrow}(i;l) \right\}, \end{aligned} \tag{2.3}$$

where $a^{\dagger}_{k,s}(i)$ is the Fourier transformed operator of $c^{\dagger}_{\alpha,s}(i)$,

$$c^{\dagger}_{\alpha,s}(i) = \frac{1}{\sqrt{L}} \sum_{k} e^{ikr_{\alpha}} a^{\dagger}_{k,s}(i), \tag{2.4}$$

and the sum $\sum_{l}^{occu.}$ is restricted for occupied states. The symbol $u_{k,s}(i;l)$ denotes the matrix element of the following canonical transformation

$$a^{\dagger}_{ks}(i) = \sum_{l} u^{*}_{ks}(i;l) \gamma^{\dagger}_{ks}(l) \tag{2.5}$$

in order to diagonalize the HF Hamiltonian with $\gamma^{\dagger}_{k,s}(i)$ as the new quasi-particle operators. Since the zigzag ribbons have a bipartite-lattice structure, we solve the self-consistent equations assuming that the basic correlation is antiferromagnetic (AF).

Previously we found that this HF Hamiltonian shows clear differences in the magnetic structure compared with the graphite sheet.[1] Since the latter is a zero gap semiconductor, where the DOS at the Fermi level is zero, the antiferromagnetic HF solution emerges only when U/t is larger than $U_c \sim 2t$, that is consistent with the fact that 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.[6]

Let us now turn to the collective mode associated with this peculiar magnetic structure of zigzag ribbons. We start with the following transverse dynamical susceptibility,[7]

$$\chi^{+-}_{i,j}(q,\omega) = i \int dt e^{i\omega t} \langle [S^{+}_{q}(i;t), S^{-}_{-q}(j;0)] \rangle, \tag{2.6}$$

where $S^{+}_{q}(i;t)$ is the Heisenberg representation of $S^{+}_{q}(i) = \sum_{k} a^{\dagger}_{k+q\uparrow}(i) a_{k\downarrow}(i)$. Using the canonical transformation eq. (2.5), the dynamical susceptibility $\chi^{0+-}_{ij}(q,\omega)$ for the mean field solution can be expressed in the Lehmann representation,

$$\chi^{0+-}_{ij}(q,\omega) = \sum_{k} \sum_{l}^{occ.} \sum_{m}^{unocc.} \left\{ -\frac{u^{*}_{k+q\uparrow}(i;l) u_{k\downarrow}(i;m) u^{*}_{k\downarrow}(j;m) u_{k\uparrow}(j;l)}{\omega - \epsilon_{k}(m) - \epsilon_{k}(l)} + \frac{u^{*}_{k+q\downarrow}(i;l) u_{k\uparrow}(i;m) u^{*}_{k\uparrow}(j;m) u_{k\downarrow}(j;l)}{\omega + \epsilon_{k}(m) - \epsilon_{k}(l)} \right\}, \tag{2.7}$$

where $\sum_{m}^{occu.}$ and $\sum_{l}^{unoccu.}$ are sums restricted to occupied and unoccupied states, respectively. In order to take into account the bipartite structure of the AF correlation, it is convenient to distinguish between "uniform" and "staggered" spins,

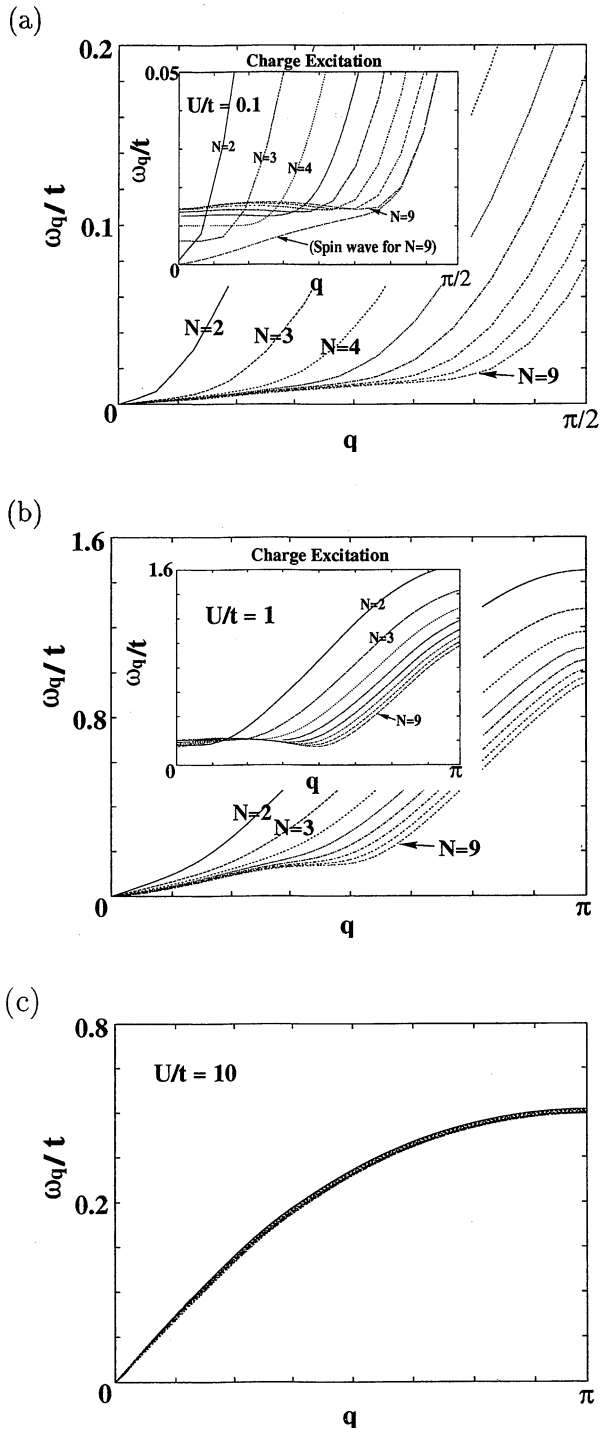

Fig. 2. Spin wave modes for various ribbon widths of $N = 2, 3, \cdots, 9$ when $U/t = 0.1$ (a), 1.0 (b) and 10.0 (c). The insets in (a) and (b) show the corresponding charge excitations. It should be noted that in (a) the spin wave dispersions are shown only up to $\pi/2$ to show the width dependence clearly.

$$\begin{aligned} \boldsymbol{S}_{iu;q} &= \sum_{\alpha} \boldsymbol{S}_{\alpha}(i) \mathrm{e}^{\mathrm{i}qr_{\alpha}}, \\ \boldsymbol{S}_{is;q} &= s(i) \sum_{\alpha} \boldsymbol{S}_{\alpha}(i) \mathrm{e}^{\mathrm{i}qr_{\alpha}}, \end{aligned} \tag{2.8}$$

where $s(i)$ is $+1$ (-1) if the site i belongs to the A (B)-sublattice. The spin operators are given by

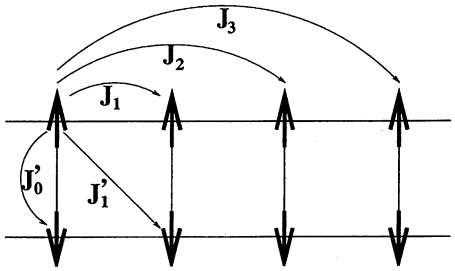

Fig. 3. The definition of effective Heisenberg interactions of the ladder model fitted for the spin modes of zigzag ribbons.

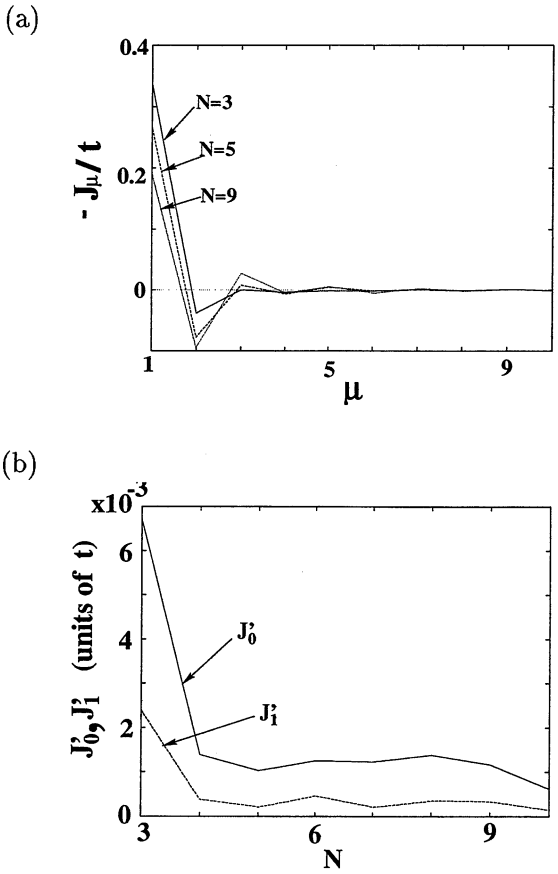

Fig. 4. (a) Site dependence of effective Heisenberg interactions $-J_{\mu}$ when $N = 3, 5$. (b) Ribbon width dependence of effective Heisenberg interactions J_0' and J_1' for interedge.

$$\boldsymbol{S}_{\alpha}(i) = \sum_{ss'} c^{\dagger}_{\alpha,s}(i)(\boldsymbol{\sigma})_{ss'} c_{\alpha,s'}(i). \tag{2.9}$$

It is natural to introduce the following transformation for the dynamical susceptibility,

$$\begin{aligned} \chi_{ij}^{0+-uu} &= \chi_{ij}^{0+-}, \quad \chi_{ij}^{0+-us} = s(j)\chi_{ij}^{0+-}, \\ \chi_{ij}^{0+-su} &= s(i)\chi_{ij}^{0+-}, \quad \chi_{ij}^{0+-ss} = s(i)s(j)\chi_{ij}^{0+-}. \end{aligned} \tag{2.10}$$

From this, we obtain the equations for the response to the oscillating fields, $h_{ju}^{+}(q,\omega)$ (uniform) and $h_{js}^{+}(q,\omega)$ (staggered), and the corresponding mean fields,[7]

$$\begin{aligned} \langle S_{iu;q}^{+} \rangle = &\sum_{j} \chi_{ij}^{0uu}(q,\omega) \left(h_{ju}^{+}(q,\omega) + I\langle S_{ju;q}^{+} \rangle \right) \\ &+ \sum_{j} \chi_{ij}^{0us}(q,\omega) \left(h_{js}^{+}(q,\omega) + I\langle S_{js;q}^{+} \rangle \right), \end{aligned} \tag{2.11}$$

$$\langle S^+_{is;q}\rangle = \sum_j \chi^{0su}_{ij}(q,\omega)\left(h^+_{ju}(q,\omega) + I\langle S^+_{ju;q}\rangle\right) + \sum_j \chi^{0ss}_{ij}(q,\omega)\left(h^+_{js}(q,\omega) + I\langle S^+_{js;q}\rangle\right). \quad (2.12)$$

The spectrum of the spin wave modes corresponds to the poles of the susceptibilities obtained from these equations.

The spin wave dispersions are shown in Fig. 2 for $U/t = 0.1$, 1.0 and 10, and various ribbon widths. Because the Hubbard gap is very small when $U/t = 0.1$, the spin wave dispersion of $U/t = 0.1$ is shown only up to $q = \pi/2$ to show the width dependence and the behavior around $q = 0$ clearly. Obviously, the spin wave spectrum is sensitive to both the interaction U and the width N. For all widths and all finite U the spin wave spectrum has a basic linear dispersion around $q = 0$ (and 2π) because the correlation is essentially antiferromagnetic. However, a strong quadratic dispersion is superposed due to the ferromagnetic character of the large moments appearing at each edge, as we can see clearly in Fig. 2(a) ($U = 0.1t$). This superposition completely disappear for $U = 10t(>U_c)$ in Fig. 2(c), where all sites generate a magnetic moment with well-developed Néel structure. In this case the dispersion very weakly depends on the width N and is entirely that of an AF system. The case of $U = t$ can be considered as intermediate, because for small N it is more similar to the small-U situation while for large N the low-energy spectrum resembles that of $U = 10t$. It is important to notice that the low-energy spectrum for all $U > 0$ lies below the continuum of the quasiparticle excitations described by the HF calculation (see insets in Figs. 2(a) and 2(b)). Therefore these spin waves represent well-defined undamped modes.

Now let us turn to the case of $U = 0.1t$ where only the outermost moments at the edges are well-developed and can be considered as localized spin degrees of freedom on a lattice with two leg ladder structure. We can derive the effective Heisenberg model for these spins by analyzing the RPA spin wave spectrum.

$$H = \sum_{i,j} J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j, \quad (2.13)$$

where J_{ij} is the effective spin-spin interaction not restricted to nearest neighbors as shown in Fig. 3. By means of the Holstein-Primakoff transformation, the spin wave spectrum derived from the ordered state with parallel alignments of the spin along the edges and antiparallel between the edges is given by

$$\omega_q = \sqrt{\left(-4\sum_\mu J_\mu \sin^2\mu q + 2\sum_\mu J'_\mu - J'_0\right)^2 - \left(2\sum_\mu J'_\mu \cos 2\mu q - J'_0\right)^2} \quad (2.14)$$

where J_μ and J'_μ denote intra- and interedge interactions, respectively. Here μ is equal to the distance between two spins, $|i-j|$. We use the least square fit method in order to determine J_μ and J'_0 from the RPA spectra ($\mu = 1,\ldots,10$). Figures 4(a) and 4(b) show that J_μ decreases fast with distance along the ribbon ($|J_\mu| \propto \mu^{-\alpha}$, $\alpha_{N=3} = 3.2$, $\alpha_{N=9} = 2.2$), but weakly with N. On the other hand, J'_0 and J'_1 drop sharply with increasing N, where the results for $N > 5$ are limited by the numerical accuracy. One important result in this context is the fact that the interedge interaction is almost two orders of magnitude smaller even in the case of $N = 3$. This suggests that the magnetic states of both edges are almost independent. Consequently, the ferromagnetic correlation of the large moments should lead to an enhancement of the paramagnetic signal in the uniform susceptibility.

The spin system is eq. (2.9) has a spin gap for finite J'_0 and J'_1. The small value of J'_0 suggests a rather small value of the spin gap, $\Delta_s \sim J'_0$.[5] The accurate values are difficult to estimate, however, even with exact diagonalization due to severe finite size effects for weakly coupled spin chains.

§3. Conclusions

We have analyzed the spin wave modes arising from the ferrimagnetic state in nanographite ribbons. The spin wave spectrum shows a linear dispersion for small q reflecting the basically antiferromagnetic correlation. However, a strong quadratic component occurs in addition to this linear dispersion as a consequence of the ferromagnetic alignment of the basically localized spins at the edge. The HF approximation which is the basis of our spin wave analysis overestimates usually the tendency towards to magnetic order. Nevertheless, the basic magnetic correlations are given correctly. From this point of view, the spin wave discussion allows us to analyze the stiffness of the magnetic state. If we concentrate on the dominant magnetic moments appearing in the HF approximation and interpret them as localized spins (edge spins), then we may describe the basic magnetic properties by an effective Heisenberg model of these spins on a lattice with ladder structure. This model incorporates the features mentioned in the introduction, i.e. we encounter here in a real (Haldane type) spin gap system. However, our analysis shows also that this spin gap must be rather small. Therefore, the spin wave discussion shows that the strong tendency towards a ferrimagnetic state is real and should have strong influence on the magnetic properties of this type system. This is particularly interesting from point of view of recent experimental developments in related nanographite structures where we believe that edge states as described here are highly relevant.

Some graphite-related materials consisting of nanographites, *e.g.,* activated carbon fibers (ACF), amorphous carbons, carbon blacks, defective carbon nanotubes etc., show actually anomalous behaviors in the magnetic susceptibility. While bulk graphite has a large diamagnetic and anisotropic susceptibility, a certain type of ACF with a huge specific surface area (SSA) up to

3000 m^2/g (believed to consist of an assembly of minute graphite fragments with a dimension of 20 Å × 20 Å) exhibits an isotropic paramagnetic response at room temperature and a strong Curie-like behavior in low temperature.[8] This kind of anomalous behavior of the susceptibility is also observed in many amorphous carbons and defective carpet-rolled carbon nanotubes.[9]

The sample production of graphite-related materials has still insufficient influence on size and edge shapes, which makes it difficult to identify of the origin of magnetic properties. There are some recent experimental attempts, however, to synthesize nanographite systems and controlling the size and edge shapes. One is "graphitization" of diamond powder with grain sizes 40–50 Å by annealing in argon atmosphere. Another method to produce nanographites is epitaxial growth on substrates with step edges.[10] Depending on the morphology of step edges, *e.g.*, terrace structure of a vicinal surface, ribbons with well-defined edge properties may be grown. Other types of nanographites with well-defined edges might be obtained by lithographic techniques or by STM. Therefore we expect that in near future the magnetic properties of edge states will be observable so that their influence can be tested in a controlled way.

Acknowledgments

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