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Electron-Phonon and Electron-Electron Interactions in Nanographite Ribbons

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Graphite fragments of nanometer size, called nanographite, have a different electronic structure than both bulk graphite and aromatic molecules. In particular, if they have zigzag edges, a sharp peak in the density of states at the Fermi level is generated, suggesting to cause Fermi instability. We have studied the lattice distortion and the possible magnetization based on the model of graphite ribbons with a nanometer width, by taking into account the electron-phonon and electron-electron interactions in the form of a tight binding model.

Keywords: nanographite, edge state, lattice distortion, magnetization

INTRODUCTION

Disordered carbon materials have been extensively used in a variety of electrochemical systems. Most of them are vaguely defined to embrace graphite related materials[1] such as activated carbons and carbon blacks. One of the most exciting current interests regarding the applications is as a practical medium for high-capacity lithium ion batteries. The porosity is said to play a key role in accommodating a large amount of Li ions; up to one Li ion for two carbon atoms, which is three times the Li ions contents in the first stage Li intercalated graphite. Because of the structural complexity at the atomic scale in disordered carbon materials, basic comprehension of the electronic functionality has not yet been well established.

For instance, as regards porous carbons, only a simple model pertaining an assembly of tiny graphite fragments has been proposed.

In the course of studying the electronic states of nanographites, which are a kind of minute graphite fragments of nanometer size, by using the graphite ribbon model[2], we found that the edge shape makes a crucial difference, in particular near the Fermi level. There are two prototype edge shapes, namely, armchair and zigzag edges. The two basic graphite ribbons, i.e., armchair and zigzag ribbons, can be constructed by confining a graphite sheet to a pair of parallel edges. We showed that the zigzag ribbons have almost flat bands at the Fermi level where the electronic states are strongly localized on the zigzag edge sites and nearby, which we call the edge state. The relative contribution of the edge state is the largest when the ribbon width is of a nanometer size[3], neither more nor less.

However, the sharp peak in the density of states (DOS) suggests the presence of some Fermi instabilities in the zigzag nanographite ribbons. In the present work, we have studied the lattice distortions and the possible magnetic structure in the graphite ribbons based on the SSH and the Hubbard models within the mean field approximations, respectively.

LATTICE DISTORTION IN NANOGRAPHITE RIBBONS

We present in Fig.1 the skeletons of zigzag and armchair ribbons. Special emphasis is placed on the emergence of almost flat bands at the Fermi level in the zigzag ribbons, which inevitably give a sharp peak in the DOS as seen in Fig.2. All dangling bonds at the edges are assumed to be terminated by hydrogen atoms.

The lattice distortion in the zigzag ribbons are examined in the framework of the extended SSH model, whose Hamiltonian is expressed as $H = \sum_{\langle i,j\rangle,\sigma}(-t_0 + \alpha y_{i,j})(c^{\dagger}_{i,\sigma}c_{j,\sigma} + h.c.) + K\sum_{\langle i,j\rangle} y^2_{i,j}/2$ with the self-consistent equation $\tilde{y}_{i,j}/\lambda = -<c^{\dagger}_{i,\sigma}c_{j,\sigma}> + (1/N_b)\sum_{\langle k,l\rangle,\sigma}<c^{\dagger}_{k,\sigma}c_{l,\sigma}>$, where N_b is the number of bond variables in the unit cell, t_0 is the hopping integral in the undistorted system, and α and K are the electron-phonon coupling and spring constants, respectively. The sum for $\langle i,j\rangle$ is taken over the nearest-neighbor pairs and $<\cdots>$ indicates the expectation value in the half-filling system. The bond variable $y_{i,j}$ expresses the deviation of

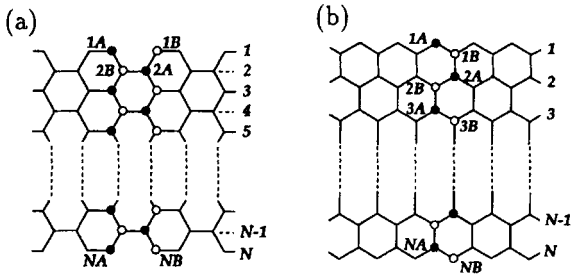

Fig.1 Skeletons of (a) armchair and (b) zigzag ribbons.

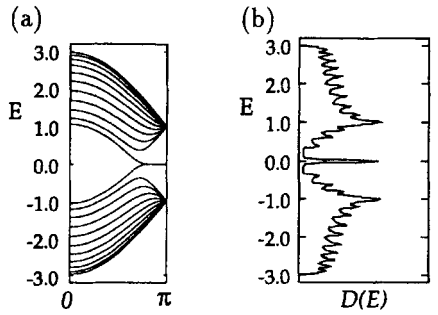

Fig.2 Band Structure (a) and DOS of the zigzag ribbon for N=11.

the bond length between the ith and jth sites due to lattice distortion. We can introduce the dimensionless electron-phonon coupling constant $\lambda = 2\alpha^2/Kt_0$ and the dimensionless bond variable $\tilde{y}_{i,j} = \alpha y_{i,j}/t_0$. As a set of realistic values for these parameters, we take t_0=2.5eV, α=6.31eV/Å and K=49.7eV/Å^2 which are successfully used to describe lattice distortions in fullerene-related materials of triply coordinated carbon atoms[4]. They give $\lambda \simeq 0.64$ as a realistic coupling constant for graphite ribbons.

Figure 3 shows the texture of the lattice distortions for the armchairs with N=12, 13 and 14, where the shortened (stretched) bonds are represented by solid (broken) lines, each line width indicating the length variation relative to the undistorted system. We can see the large distortion near the edges, basically forming the Kekulé pattern. We should mention that the Kekulé pattern distortion starting from the both edges interfere with each other showing triple periodicity for the ribbon width, although

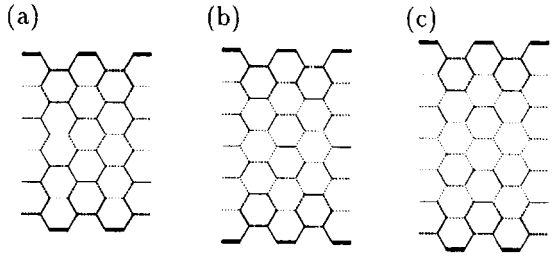

Fig.3 Texture of the lattice distortions in armchair ribbons with N=12(a), 13(b) and 14(c).

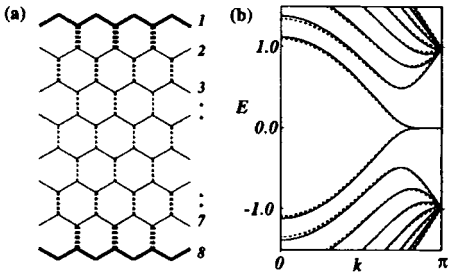

Fig. 4. (a) Texture of the lattice distortion in the zigzag ribbon when N=8. (b) Band structure near the Fermi level. The broken lines denote that of the undistorted ribbon.

the lattice distortion decreases in the inner region of the ribbons.

On the other hand, our calculation for the zigzag ribbons shows that they do not undergo a distortion which destroys the edge state below $\lambda_c \simeq 0.8$. We show the lattice distortion and the band structure near the Fermi level when N=8 and λ=0.64 in Fig.4 (a) and (b), respectively. Among each zigzag bond-chain parallel to the edge, no bond alternation occurs except that the bonds parallel to the ribbon axis become a little shorter and the rung bonds between them expand a little. Since such a texture respects the condition of forming the edge state, the flatness of the center bands remains.

The reason why the zigzag ribbons possess less Peierls instability de-

spite the fact that they are one-dimensional metals can be demonstrated by deriving the analytic solution for polyacene, namely, the smallest zigzag ribbon of N=2. If we assume the bond alternation along the peripheral bonds as $-1\pm\delta$, we can easily get the analytic forms of the two occupied bands. Integrating the two bands in $|k| \leq \pi$ and taking into account the harmonic energy loss by the distortion, we obtain the total energy. In the expansion of δ, we find that the coefficient of the δ^2 term changes sign from plus to minus at λ_c=0.86. A plus sign in the weak coupling region indicates that $\partial E/\partial\delta$=0 only at δ=0 showing no bond alternation[5], which is obviously different from trans-polyacetylene where the term $\delta^2 \ln \delta$ guarantees the non zero solution even for an infinitesimal λ.

Even for the wider zigzag ribbons, the story is essentially the same. In the edge state of the flat band region, the wave functions are constructed by forming so-called non-bonding orbitals (NBO), where the NBO network is torn into pieces because the nodes always sit on one of the two sublattices. They are not responsible for the bond deformation between the nearest neighbor sites. The less energy gain by opening the gap turns out not to compensate the loss by the distortion, thus the zigzag ribbons can experience a the distortion in an anomalously large electron-phonon coupling. We should mention that the second nearest neighbor and higher hoppings may induce the instability in the weak coupling region, which ought to give a slight change.

MAGNETIZATION AND DISCUSSION

We have also examined the effect of the electron-electron interaction for the zigzag ribbons by using the Hubbard model within the mean field approximation, which is expressed as $H_{MF} = -t\sum_{n,\sigma}(c^{\dagger}_{n,\sigma}c_{n+1,\sigma} + c.c.) + U\sum_n\{\langle n_{n\downarrow}\rangle n_{n\uparrow} + \langle n_{n\uparrow}\rangle n_{n\downarrow} - \langle n_{n\downarrow}\rangle\langle n_{n\uparrow}\rangle\}$ where $n_{n\sigma} = c^{\dagger}_{n,\sigma}c_{n,\sigma}$, and U is the on-site Coulomb repulsion which may be less than 0.1 in the present system. Seeking the self-consistent solutions within the unrestricted Hartree-Fock approximation, we find that, while nothing happens in the armchair ribbons, the interesting magnetic solution[2] where the ferromagnetic spin alignment stands at both edge sites occurs even under small $U(\approx 0.1)$, as shown in Fig.5. This magnetic solution opens a gap in

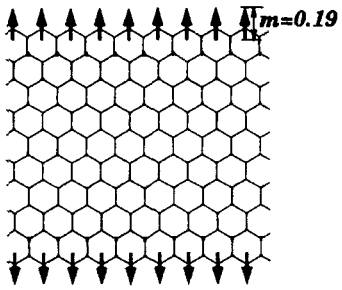

Fig. 5. Magnetic structure of the zigzag ribbon N=10 when U=0.1.

the flat bands because the NBO character of the edge state is responsive to the on-site instability. It is noted that the total magnetization is zero.

We cannot fully understand the useful functionalities of nanographite related materials, unless the π electronic structures to cause the functionalities are throughly revealed. One of which might be the singular edge state which is formed in the zigzag edges. This may even open the possibility of magnetization in the nanographite system. By controlling the size and edge shape of graphite, we expect that a new class of carbon material can be artificially produced in the near future.

Acknowledgements

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