Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic and Transport Properties of Nanographites

Katsunori Wakabayashi [a] [b]

[a] Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto, 606-8502, JAPAN

[b] Institute of Materials Science, University of Tsukuba, Tsukuba, 305-8573, JAPAN

Version of record first published: 24 Sep 2006

To cite this article: Katsunori Wakabayashi (2000): Magnetic and Transport Properties of Nanographites, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 7-12

To link to this article: http://dx.doi.org/10.1080/10587250008025434

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 7-12
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic and Transport Properties of Nanographites

KATSUNORI WAKABAYASHI

Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606–8502, JAPAN, and Institute of Materials Science, University of Tsukuba, Tsukuba 305–8573, JAPAN

Magnetic and transport properties of nanographites are investigated in graphite ribbons with zigzag and armchair edges. One of the most remarkable features of these systems is the appearance of edge states, strongly localized states near zigzag edges. Because the edge states lead to a sharp peak of density of states at the Fermi level, the graphite ribbons with zigzag edges show Curie-like temperature dependence of the Pauli paramagnetic susceptibility. This paramagnetic contribution competes with the orbital diamagnetism, leading to a crossover from high-temperature diamagnetic behavior to low-temperature paramagnetic behavior in nanographite ribbons with zigzag edges. The edge states are also responsible for the low-energy electronic transport properties. Here we study the junctions connecting nanographite ribbons of different width by the Landauer approach. The conductance as a function of the chemical potential shows rich structure and a large number of dips of zero conductance. The perfect reflectivity originates from the formation of standing wave resonances in the junction region.

Keywords: nanographite; edge state; magnetic susceptibility; conductance

INTRODUCTION

After the discovery of fullerene molecules and carbon nanotubes, theoretical and experimental research has focused on various nanometer size carbon materials[1]. In this paper, we study nanometer-size graphite fragments, called "nanographites". In these systems, the edges and their shapes crucially affect the π electronic states, because the effect of the edges is not negligible in nanoscopic systems. There are two typical shapes for graphite

edges, armchair and zigzag. A simple and useful model to study the electronic states of nanographites is the graphite ribbon (see Fig.1). By using the tight binding model, Fujita and co-workers have found localized states near the zigzag edge ("edge states")[2]. Since the edge states introduce a sharp peak in the density of states at the Fermi level, the electronic states of nanographite are different from that of both aromatic molecules and a graphite sheet. We show that the edge states play an important role in the magnetic and transport properties of nanographites.

ELECTRONIC PROPERTIES OF NANOGRAPHITES

In this section, we introduce the electronic states of nanographites based on the tight binding model[2,3], in graphite ribbons with armchair and zigzag edges shown in Fig. 1. The ribbon width N is defined by the number of zigzag (dimer) lines for zigzag (armchair) ribbons. We call the A(B)-sublattice on the nth zigzag (dimer) line as the nA(nB) site. We assume edge sites are terminated by H-atoms. The energy bands were previously analyzed by both tight binding model and first-principle calculations[2-4].

The zigzag ribbons are metallic for all N. The energy band structure of $N = 20$ is shown in Fig. 2(a). One of the remarkable features is the appearance of partly flat bands at the Fermi level, where the electrons are strongly localized near zigzag edges. The analytic solution of the edge state for a semi-infinite graphite sheet with a zigzag edge (1A and 1B site shall be the edge sites and N is infinite in Fig. 1(a)) can be expressed as,

$$\phi_{nA} = D_k^{n-1}, \qquad \phi_{nB} = 0, \tag{1}$$

where ϕ_{nA} (ϕ_{nB}) means the amplitude of the edge states on nA (nB) site and $D_k = -2\cos(k/2)$. It is worth noting that the edge state has a non-zero amplitude only on one sublattice, i.e. non-bonding character. Because of the convergence condition of the edge states, the wave number k must be

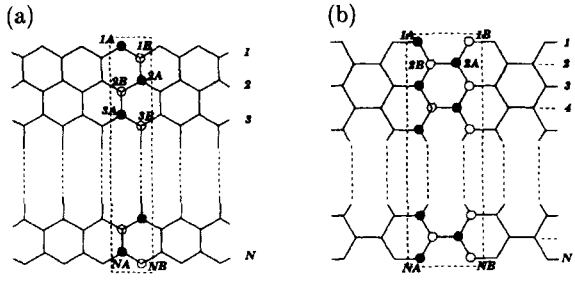

FIGURE 1 The structure of graphite ribbons with (a) zigzag edges (b) armchair edges. The rectangle with the dashed line is the unit cell.

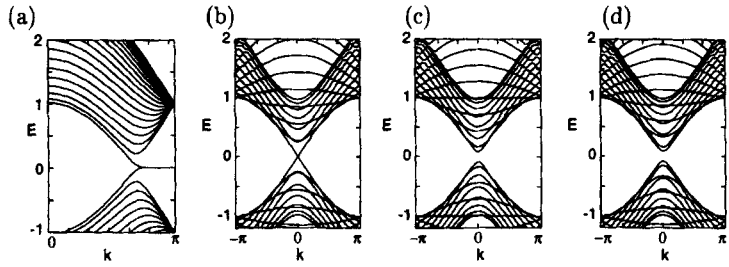

FIGURE 2 The energy band structure of graphite ribbons with zigzag edges ((a) N=20) and armchair edges ((b) N=20, (c) N=21, (d) N=22).

$2\pi/3 \leq k \leq \pi$, where $|D_k| \leq 1$. In this k-region, the edge states make a flat band at E=0 (Fermi energy). It should be noted that at $k = \pi$ the edge states are perfectly localized at the 1A sites, but at $k = 2\pi/3$ the edge states are completely delocalized. However, when we consider the zigzag ribbons, two edge states, which come from both sides, will overlap with each other and develop the bonding and anti-bonding configuration. The magnitude of the overlap becomes larger when the wave number approaches $2\pi/3$, because the penetration length of the edge states gets larger there. Therefore, the partly flat bands have a slight dispersion, which depends on the ribbon width N. The energy dispersion is given by,

$$E_k = -2tND_k^{N-1}\left(1 - \cos\left(\frac{k}{2}\right)\right). \tag{2}$$

From this equation, around $k = \pi$, the spectrum is approximated by $E \sim (\pi - k)^N$.

The DOS related to the edge states has the form,

$$\rho(\epsilon) = \frac{\partial k}{\partial \epsilon} \sim \frac{1}{N}\epsilon^{\alpha}, \qquad \text{for } \epsilon \ll \frac{t\pi}{N} \tag{3}$$

where $\alpha = \frac{1}{N} - 1$. It is found that the contribution of the edge states to the renormalized DOS gets smaller, if the ribbon width get larger. The energy band structure of armchair ribbons are shown in Fig. 2 (b)-(d) for $N = 20, 21, 22$. The armchair ribbons do not have edge states and become metallic for $N = 3m - 1$ and semiconducting for $N \neq 3m - 1$, where m is any integer.

MAGNETIC PROPERTIES OF NANOGRAPHITES

In this section we discuss the magnetic susceptibility of graphite ribbons[3]. There are two contributions to the observed magnetic susceptibility χ: the orbital diamagnetic contribution χ_{orb} due to the itinerant nature of the π

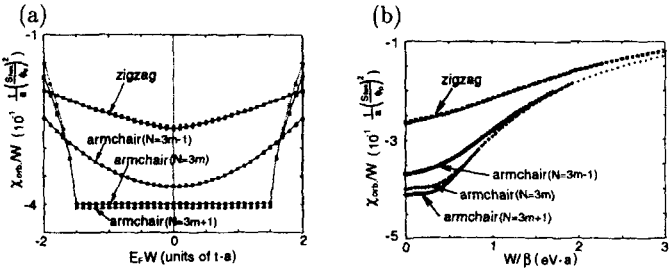

FIGURE 3 (a) The Fermi energy dependence of the orbital magnetic susceptibility χ_{orb} of graphite ribbons at $T = 0$. (b) The temperature dependence of the orbital magnetic susceptibility χ_{orb} of graphite ribbons.

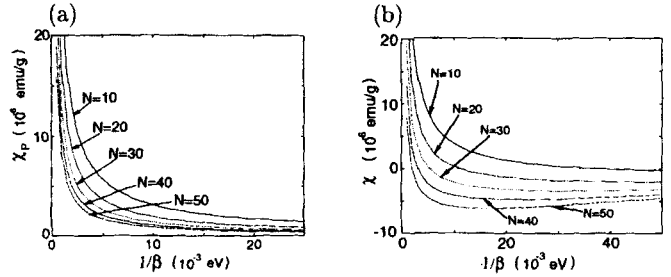

FIGURE 4 (a) The temperature dependence of χ_P of graphite ribbons. (b) The temperature dependence of total susceptibility $\chi = \chi_{orb.} + \chi_P$ of graphite ribbons.

electrons and the Pauli paramagnetic contribution χ_P due to the electron spin. The orbital magnetic susceptibility χ_{orb} of graphite ribbons is calculated in terms of the 2^{nd} derivative of the free energy with respect to the magnetic field.

In Fig 3(a) and (b), the Fermi energy dependence of χ_{orb} at T=0 and its temperature dependence are shown. In these figures, W means the ribbon width in units of the lattice constant and $\beta = 1/k_B T$. It is found that the χ_{orb} scales as a function of the Fermi energy, temperature and ribbon width. We can easily find that the edge effect becomes more important at lower temperature.

Next we show the Pauli susceptibility χ_P of zigzag ribbons up to room temperature in Fig. 4(a) for various values of N. Remarkably χ_P has a Curie-like temperature dependence. At very low temperature, χ_P has the form $\chi_P \sim \frac{1}{N} T^{\alpha}$, which originates from the DOS of the edge states (Eq.(2)).

The temperature dependence of the total susceptibility $\chi = \chi_{orb.} + \chi_P$ is

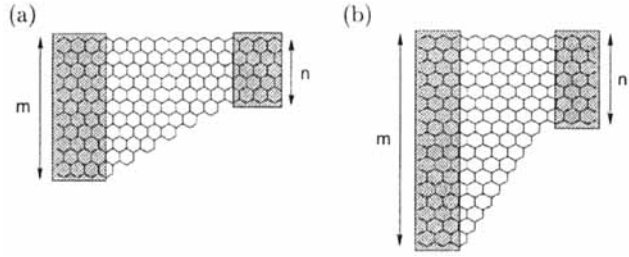

FIGURE 5 The structure of nanographite junctions with (a) an armchair edge and (b) zigzag edges in junction region.

shown in Fig. 4(b). The total susceptibility χ shows diamagnetic behavior for high temperature and paramagnetic behavior in the low-temperature regime. Note that both aromatic molecules and bulk graphite have diamagnetic behavior, while nanographites with zigzag edges have a remarkable paramagnetic behavior at low temperature due to the edge states. This behavior of magnetic susceptibility is found in experiments on graphitized nanodiamond and activated carbon fiber[5,6].

TRANSPORT PROPERTIES OF NANOGRAPHITES

Now let us study the electronic transport properties through junctions connecting zigzag ribbons of different width in order to clarify the influence of the edge states on the transport properties[8]. Since the edge states have non-bonding character, it seems that they are not responsible for the transport properties. However, in the graphite ribbons of finite width with two edge states which come from both sides overlap each other, make a slight dispersion, and provides so one channel for the electron transport.

In this paper we calculate the structure of the two nanographite junctions depicted in Fig.5. One has an armchair edge in the junction region, but the other zigzag edge. We define that the width of the left(right) hand side lead as n (m). We use Landauer formula, $G = \frac{e^2}{\pi\hbar}T$, to evaluate the conductance of the nanographite junctions, where T is transmission probability. The transmission probability is calculated by recursive Green function method based on the tight binding model[7].

In Fig. 6 the energy dependence of the conductance in units of $\frac{e^2}{\pi\hbar}$. Here we fixed m=50 and change $n = 10, 20, \cdots, 50$. When n decreases, the magnitude of the conductance gets smaller for both cases of junctions, because the length of the junction region becomes longer. When we focus on the low-energy region, we can easily find the striking difference in the conductance. While the conductance of junctions with an armchair edge introduce no pronounced dip structure and quite smooth energy dependence shown

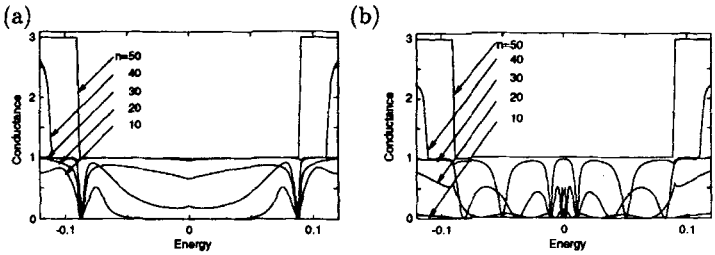

FIGURE 6 The energy conductance of nanographite junctions with (a) an armchair edge and (b) zigzag edges in junction region.

in Fig.6(a), the junctions with a zigzag edge has many zero-conductance points as dip-structures shown in Fig. 6(b). This perfect reflectivity originates from the formation of standing wave resonances in the junction region. Because these standing waves originate from the quantum interference effects, the magnetic field can easily remove the zero-conductance dips, so that a pronounced negative magneto resistance occurs[8].

Acknowledgments

This work is based on the collaboration with H. Ajiki, M. Igami, K. Kusakabe, K. Nakada, M. Sigrist and the late M. Fujita. I am grateful for support by Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, Japan, and the financial support of the Japan Society for the Promotion of Science for Young Scientist. Numerical calculations were performed in part on VPP500 in Institute for Solid State Physics, University of Tokyo and SX5 in Institute for Molecular Science.

References

[1] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, "Science of Fullerenes and Carbon Nanotubes", (Academic, San Diego, 1996); R. Saito, G. Dresselhaus, M. S. Dresselhaus, "Physical Properties of Carbon Nanotubes", (Imperial College, London, 1998).

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

[3] K. Wakabayashi et al, Phys. Rev. B., **59,** 8271, (1999).

[4] Y. Miyamoto, K. Nakada and M. Fujita, Phys. Rev. B., **59,** 9858, (1999).

[5] O. E. Andersson et al., Phys. Rev. B, **58,** 16387, (1998).

[6] A. Nakayama et al., Synth. Met. **55–57,** 3736, (1993).

[7] T. Ando, Phys. Rev. B, **44,** 8017, (1991).

[8] K. Wakabayashi and M. Sigrist, in preparation.