



Interior edges induced half-metallic ferromagnetism in graphitic carbon nitride structures



Shih-Jye Sun*

Department of Applied Physics, National University of Kaohsiung, Kaohsiung 811, Taiwan

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ABSTRACT

We study the magnetic properties of graphitic carbon nitride, $g\text{-C}_4\text{N}_3$. A microscopic tight-binding model incorporated with the Hatree mean-field approach is adopted, showing that the $g\text{-C}_4\text{N}_3$ exhibits the significant ferromagnetism induced from the edge states. These edge states appearing on the zigzag boundaries not only deform the flat band but also upon proper hole doping provide the electrons with single polarized spin exciting to the Dirac linear bands and causes $g\text{-C}_4\text{N}_3$ half-metallic. The half-metallicity survives at room temperature and does not require strong Coulomb repulsion for induction. The ferromagnetism of these states yielding the half-metallicity refers to the broken or imperfectness of the honeycomb lattice structure; specifically, the ferromagnetic states are formed on the zigzag boundaries surrounding the vacancies in the imperfect (some lattice points being missed or removed) honeycomb lattice. We thus indicate that the half-metallicity should be generally reachable in materials of this kind of structure.

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1. Introduction

Spintronics [1,2] is considered to be superior to electronics in industrial applications because of the additional employed functionalities of spins, a quantum number of electrons or holes. The two physical researches, manipulating the degrees of freedom of spins and generating spin polarizations, have become inevitable concerns in designing spintronics devices. Particularly, significant attentions [3–5] have been drawn to the ferromagnetic semiconductors with high Curie temperatures [6–8] since those materials make the spin-polarized ferromagnetism created intrinsically. One of the origins, forming the ferromagnetism, is the incomplete filling of the electrons on a specific spin-dependent orbital (d orbital, for example), with causing the unbalanced fillings between the up and down spins. The ferromagnetism can also arise from some localized magnetic states in certain materials (for instance, the ferromagnetic edge state along a given zigzag edge of the graphene nanoribbon [9–12]). In addition, it is predicted that the carbon-based compounds yields intrinsic ferromagnetism from doping carbon atoms [20] in the carbon nitride polymer, C_3N_4 [13–16], which is a synthesized material to be applied on the photocatalysis and the photoelectrochemical energy [17–19].

Furthermore, it is proposed that the two-dimensional graphitic C_3N_4 ($g\text{-C}_3\text{N}_4$) polymer be a covalent-bonding semiconductor

[21,22], in which the double and single bonds alternatively interlacing between C and N atoms [see Fig. 1(a)]. There are no dangling bonds on the lattice sites, i.e., without out-of-plane π bonds that makes the graphene conductive. Nevertheless, another graphitic structure was recently proposed by Du et al. in Ref. [20] from the first-principle calculation, indicating that vacancies or holes will be induced by doping C atoms in $g\text{-C}_3\text{N}_4$ to replace some of the N atoms, as a result of yielding $g\text{-C}_4\text{N}_3$ compound. This compound renders ferromagnetism and exhibits a different (from $g\text{-C}_3\text{N}_4$) band structure that makes the $g\text{-C}_4\text{N}_3$ become a half-metallic conductor. However, there is no clear physical pictures beside the aspect of the band structure to explain the cause of the ferromagnetism and half-metallicity.

This paper attempts to provide an explicit physical interpretation on how the ferromagnetism and half-metallicity can be formed in $g\text{-C}_4\text{N}_3$. We follow Ref. [20] by further considering that the original un-doped $g\text{-C}_3\text{N}_4$ is deposited on a graphene layer. Due to the orbital coupling between these two layers, the doping of the carbon atoms in $g\text{-C}_3\text{N}_4$ will then eliminate the original double bonds and leave a dangling π bond on each lattice site, resulting in a conductive $g\text{-C}_4\text{N}_3$. Specifically, the adopted $g\text{-C}_4\text{N}_3$ here is similar to graphene except some atoms are currently missing [refer to Fig. 1(b)]. Focusing on the $g\text{-C}_4\text{N}_3$ layer, the zigzag boundaries or edges [dashed lines in Fig. 1(b)] surrounding the missing atoms are created. We find that those edges are at large density of states, i.e., forming the flat band, (Fig. 5) and play crucial roles in forming the ferromagnetism. Besides a significant flat band that possibly leads to the half-metallicity upon proper

* Tel.: +886 7 5919472; fax: +886 7 5919357.

E-mail address: sjs@nuk.edu.tw

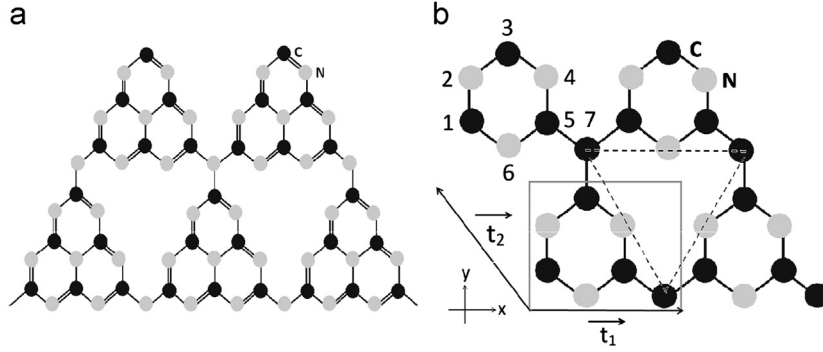


Fig. 1. Two different carbon nitride structures. The black and gray solid circles represent C and N atoms, respectively. (a) The structure of $g\text{-C}_3\text{N}_4$ with the double and single bonds alternatively interlacing between C and N atoms. (b) The structure of 2×2 $g\text{-C}_4\text{N}_3$ unit cell with the π orbit on each lattice sites. The gray square represents the unit cell with \vec{t}_1 and \vec{t}_2 being the translation vectors. The dash lines passing through the zigzag heads indicates the zigzag edges surrounding the vacancy (missing atoms of a honeycomb lattice). The lattice sites in a unit cell are labeled by 1, 2, ..., and 7.

hole doing, the flat band provides the electrons with single polarized spin exciting to the Dirac linear bands for conduction as predicted in Ref. [20]. However, it is surprising that such a simple level as the Hartree mean-field approach, and as adopted here, is enough to capture this half-metallicity. Upon the carrier conservation for each atomic π orbitals in the following calculations, the half-filling is assumed, i.e., the occupation number of electrons on each lattice site is one, while it must be noted that the fillings merely alter the chemical potentials but thus does not affect the arguments that the ferromagnetism and half-metallicity is induced by those edges and flat bands.

2. Theoretical description

We begin our calculation by considering the microscopic tight-binding model constituted of the unit-cell Hamiltonian,

$$H = \sum_{ij=1}^7 V_{ij} c_i^\dagger c_j + \sum_{i=1}^7 \left(E_i c_i^\dagger c_i + \frac{1}{2} \sum_{\sigma=\pm 1/2}^{+1/2} U_i n_{i,\sigma} n_{i,\bar{\sigma}} \right), \quad (1)$$

where c_i and (c_i^\dagger) is the annihilation (creation) operator for site $i = 1, 2, \dots, 7$ whose relative positions [refer to Fig. 1(b)] are $\vec{r}_1 = (0, 1/2\sqrt{3})$, $\vec{r}_2 = (0, \sqrt{3}/2)$, $\vec{r}_3 = (1/2, 2\sqrt{3}/3)$, $\vec{r}_4 = (1, \sqrt{3}/2)$, $\vec{r}_5 = (1, 1/2\sqrt{3})$, $\vec{r}_6 = (1/2, 0)$ and $\vec{r}_7 = (3/2, 0)$, respectively. The notation V_{ij} represents the nearest hopping between the i and j sites. Note that there are two kinds of atoms in the seven atoms comprising the unit cell of $g\text{-C}_4\text{N}_3$, namely, four C atoms with $i = 1, 3, 5$ and 7 and three N atoms with $i = 2, 4$, and 6 ; the $g\text{-C}_4\text{N}_3$ structure in Fig. 1(b) are of two types of hopping V_{ij} , the hopping between C and N atoms V_{CN} ($V_{1,2}$, for instance) and the hopping between C and C atoms V_{CC} ($V_{5,7}$, for instance). Two orbital energies, $E_i = E_C$ for i on the C atom sites and $E_i = E_N$ for i on the N atom sites in general can be different. The last term in Eq. (1), with $n_{i,\sigma}$ and $n_{i,\bar{\sigma}}$ being the particle number operators, accounts for the Coulomb repulsion on site i with strength $U_i > 0$ which gives the electrons on site i carrying spin $\sigma = \pm 1/2$ to exert repulsive forces to spin $\bar{\sigma} = -\sigma$. The whole system of infinite two-dimension is formed by the translation vectors, $\vec{t}_1 = (2, 0)$ and $\vec{t}_2 = (-1, \sqrt{3})$ [see Fig. 1(b)]; i.e., the total Hamiltonian is obtained by repeating the unit-cell Hamiltonian (1) with displacements $n\vec{t}_1 + m\vec{t}_2$, where n and m are integers. Based upon the tight-binding approximation calculated for the band structure we extend the unit cell to n and m integers being 3, respectively. Since the system is unit-cell translation invariant, the Hamiltonian can be represented in the momentum \vec{k} representation and the whole Hamiltonian on a basis of the crystal momentum \vec{k} is block diagonal. For brevity, in what follows, we will use $n_{i,\sigma}$ to notate

$\langle n_{i,\sigma} \rangle$, the quantum-thermal average number of the particle occupation. The block Hamiltonian for spin- σ subsystem is then of the form

$$H_\sigma = \begin{pmatrix} E_{C,\sigma} & M_{12} & 0 & 0 & 0 & M_{16} & M_{17} \\ M_{21} & E_{N,\sigma} & M_{23} & 0 & 0 & 0 & 0 \\ 0 & M_{23} & E_{C,\sigma} & M_{34} & 0 & 0 & M_{37} \\ 0 & 0 & M_{43} & E_{N,\sigma} & M_{45} & 0 & 0 \\ 0 & 0 & 0 & M_{54} & E_{C,\sigma} & M_{56} & M_{57} \\ M_{61} & 0 & 0 & 0 & M_{65} & E_{N,\sigma} & 0 \\ M_{71} & 0 & M_{73} & 0 & M_{75} & 0 & E_{C,\sigma} \end{pmatrix}, \quad (2)$$

with the matrix element $M_{ij} = \sum_l V_{ij} \exp(i\vec{k} \cdot \vec{T}_l)$, $\vec{T}_l = 0, \pm \vec{t}_1, \pm \vec{t}_2$, and $\pm \vec{t}_1 \pm \vec{t}_2$. The site energy $E_{C,\sigma} = E_C + U_{CN} n_{C,\bar{\sigma}}$ for the C atom sites ($E_{N,\sigma} = E_N + U_{NN} n_{N,\bar{\sigma}}$ for the N atom sites) takes into account the Hartree mean-field energy $U_{CN} n_{C,\bar{\sigma}}$ ($U_{NN} n_{N,\bar{\sigma}}$), which is induced by the spin- $\bar{\sigma}$ electrons. Note that \vec{k} is restricted within the first Brillouin zone (hexagonal in the present case) constructed in the reciprocal lattice formed by vectors, $\vec{b}_1 = 2\pi(1/6, (6\sqrt{3})^{-1})$ and $\vec{b}_2 = 2\pi(0, (3\sqrt{3})^{-1})$.

To determine the occupation $n_{i,\sigma}$, we consider minimizing the free energy, [25]

$$F = -\frac{1}{N} k_B T \sum_{\alpha, \vec{k}, \sigma} \ln(1 + e^{(\mu - E_{\alpha,\sigma})/k_B T}) - \frac{1}{2N} \sum_{i,\sigma} U_i n_{i,\sigma} n_{i,\bar{\sigma}}, \quad (3)$$

subject to the constrain of half-filling (i.e., occupation number on each atomic π orbit is one),

$$n_{i,\sigma} + n_{i,\bar{\sigma}} = 1.$$

Here $E_{\alpha,\sigma}$ is the α -th eigenvalues of the spin- σ Hamiltonian (2), μ is the chemical potential determined by

$$\sum_{i,\sigma} n_{i,\sigma} = 7 = \sum_{\alpha,\sigma} f_D(E_{\alpha,\sigma}), \quad (4)$$

with $f_D(e) = \{1 + \exp[(e - \mu)/(k_B T)]\}^{-1}$ being the Fermi-Dirac distribution function, μ the chemical potential, k_B the Boltzmann constant, and T the temperature. The minimization problem can be solved by adopting the Lagrange multiplier to find appropriate seven λ_i and fourteen $n_{i,\sigma}$ and $n_{i,\bar{\sigma}}$ that satisfy, fourteen ($i = 1, 2, \dots, 7$ and $\sigma = \pm 1/2$)

$$\nabla F = \sum_i \lambda_i \nabla g_i, \quad (5)$$

equations with $\nabla = \sum_{i=1}^7 \frac{\partial}{\partial n_{i,\sigma}} \hat{e}_{i,\sigma}$ and $\hat{e}_{i,\sigma}$ being the unit vector, and seven ($i = 1, 2, \dots, 7$)

$$g_i = (n_{i,\sigma} + n_{i,\bar{\sigma}} - 1) = 0. \quad (6)$$

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