Critical Temperature in Zigzag Graphene Nanoribbon: a First-principles Study

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Abstract. The critical (Néel) temperature in the zigzag graphene nanoribbon was calculated using the mean-field approximation within the generalized Bloch theorem. This calculation was carried out over the Brillouin zone of the magnon spectrum. We found a nearly flat magnon dispersion at the high energy in one-third of the Brillouin zone. Our calculation showed the critical temperature below room temperature, in good agreement with the prediction in the previous works. Our last work (Prayitno 2021 Physica E 129 114641) revealed that the critical temperature may be enhanced by increasing the ribbon width. In this brief report, we justified that the critical temperature becomes almost constant up to a certain ribbon width. This result indicates that the critical temperature in the graphene nanoribbon will never reach room temperature for any ribbon widths, thus it is likely difficult to apply pristine graphene nanoribbon in any practical devices working near room temperature.

Keywords: graphene nanoribbon, spin stiffness, critical temperature

1. Introduction
Recent studies on the zigzag graphene nanoribbon (ZGNR) and its area give rise to the interesting studies in magnetism due to localized edge states [1], which are responsible for the spintronic devices. Generally, the magnetism in materials can be found in the elements having either the d- or the f- electron shells. Compared to the d- or the f- elements, ZGNR has many benefits such as low density, high conductivity, and gap semiconductor. Son et al. predicted the half metallicity in the ZGNR under the electric field for the application of spin transport [2], see also Ref. [3] for similar cases. On the other side, controlling the magnetic order in ZGNR can also be realized by taking the carrier doping [4].

To utilize the ZGNR for the spintronic devices, the critical temperature $T_C$ should be higher or close to the room temperature. For the d-shell elements such as Fe, Co, and Ni, the $T_C$ is higher than the room temperature, thus indicating the d-elements-based practical devices can operate properly. However, the $T_C$ of the ZGNR is still unclear until now. Previously, Yazyev and Katsnelson predicted the critical temperature that reaches the room temperature in the ZGNR is possible when the spin correlation length in the order of few nanometers was taken into account [5]. In practical devices, such order of magnitudes is very subtle to produce at present, thus the ZGNR-based spintronic devices are only reliable at the low temperature. This prediction is also supported by Kunstmann et al. who justified the instability of the magnetic order in the ZGNR at room temperature [6]. They also claimed that the magnetic order can only be stabilized at a temperature below 10 K.
An optimistic hope is addressed to the spin stiffness $D$ in the ZGNR, which is much higher than those in the $d$-elements. This high value is believed to give information how to improve $T_C$ by controlling some parameters in the ZGNR [5]. The recent finding, which compared the experimental result with the Hubbard approach, showed the possibility of the stable magnetic order in the ZGNR even at room temperature, thus ZGNR-based devices should operate well [7]. They claimed that the possibility may occur when the magnetic order is controlled by the orientation of the edge. Therefore, it is still disputed whether if ZGNR-based devices can work or not at room temperature.

A suitable choice to investigate the $T_C$ is addressed to the spin-wave (magnon) excitations. Although previous studies explored the spin-wave excitations using the Hubbard model, there is no sufficient information, except Ref. [5], if the $T_C$ can reach the room temperature or not. You et al. focused on the feature of the relativistic magnon for ferromagnets and antiferromagnets [8] while Culchac et al. investigated the lifetime of the spin-waves [9]. At the same time, Rhim and Moon concentrated on the response of $D$ under external electric field [10]. The purpose of the present work is to investigate the $T_C$ and its relationship with the $D$ by using the generalized Bloch theorem (GBT) to calculate the magnon energy in the Brillouin zone. We suppose that this approach is very efficient since it only uses the primitive unit cell.

While Yazyev and Katsnelson [5] used the spin correlation as a parameter, and Kunstmann et al. [6] used the energy gap as a parameter to explain the low $T_C$ in the ZGNR, we use the magnon spectrum to explain why the $T_C$ in the ZGNR never reaches the room temperature. In our last work [11], increasing the ribbon width $N$ can increase the $T_C$, thus making a possibility to increase the $T_C$ through increasing $N$. Here, $N$ means the number of stripes along the ribbon width, as shown in Fig. 1. In this brief report, we demonstrate that increasing $N$ as large as possible leads to a constant $T_C$ below room temperature. This means that the $T_C$ of pristine ZGNR will never surpass the room temperature. We also show the dependence of $D$ and $T_C$ on $N$. We observe the same trend not only for $D$ but also for $T_C$ in all $N$.

2. Computational Details

We carried out the self-consistent calculation using the GBT as implemented in the OpenMX code [12], a package exploiting the linear combination of pseudo-atomic orbital (LCPAO) as basis sets [13] as well as utilizing the norm-conserving pseudopotential [14]. The implementation of the spin spiral in this code was done by formulating the Kohn-Sham wavefunction as an LCPAO [11]

$$
\psi_{\nu k}(\mathbf{r}) = \frac{1}{\sqrt{N}} \left[ \sum_{n} e^{i(\mathbf{k} - \frac{\mathbf{q}}{2}) \cdot \mathbf{R}_n} \sum_{i\alpha} C_{\nu k, i\alpha} \phi_{i\alpha}(\mathbf{r} - \mathbf{r}_n) \left( \begin{array}{c} 1 \\ 0 \end{array} \right) \\
+ \sum_{n} e^{i(\mathbf{k} + \frac{\mathbf{q}}{2}) \cdot \mathbf{R}_n} \sum_{i\alpha} C_{\nu k, i\alpha} \phi_{i\alpha}(\mathbf{r} - \mathbf{r}_n) \left( \begin{array}{c} 0 \\ 1 \end{array} \right) \right],
$$

(1)

where the localized basis function $\phi_{i\alpha}$ is produced via a confinement method. Meanwhile, the magnetic moments of magnetic carbon atoms at the edges will be continuously rotated with respect to the azimuthal angle $\varphi$, which is given by

$$
\mathbf{M}_i = M_i (\cos[\varphi_0 + \mathbf{q} \cdot \mathbf{R}_i] \sin \theta_i + \sin[\varphi_0 + \mathbf{q} \cdot \mathbf{R}_i] \sin \theta_i + \cos \theta_i)
$$

(2)

Then, the magnon energy for each wavevector $\mathbf{q}$ was given by [15]

$$
\hbar \omega_{\mathbf{q}} = \frac{\mu_B}{M} \frac{E(\mathbf{q}, \theta) - E(0, \theta)}{\sin^2 \theta}.
$$

(3)
We used the conical spiral configuration (\( \theta = 10^\circ \)) instead of the flat spiral configuration (\( \theta = 90^\circ \)) for the magnetic carbon atoms at the edges in the antiferromagnetic order, which gives the most stable state, as shown in Fig. 1. Note that the antiferromagnetic order as a ground state also holds in the bilayer ZGNR [16]. Even though the calculation using the flat spiral configuration is more stable, in this case, it only fixes the magnetic moment close to \( \Gamma \) point [15]. Therefore, it cannot be used to evaluate the critical temperature since the calculation should be carried out over the Brillouin zone. The instability of the conical spiral configuration is due to the tendency of the system to go back to the ground state. For keeping the direction of magnetic moment, the penalty functional within the constraint method therefore was applied [17].

We used the lattice constant of 2.46 Å as the experimental lattice constant for graphite for the unit cell (\( x \)-axis) and took the vacuum length of 50 Å to create a non-periodic cell in \( y \) - and \( z \) -axes. To get the converged and reliable results, two \( s \) - and two \( p \) - primitive orbitals were assigned for the carbon atoms within the cutoff radius of 4.0 Bohr. At the same time, two \( s \) - and one \( p \) - orbitals were set to the hydrogen atoms within the cutoff radius of 6.0 Bohr. For the electron-electron interaction, the generalized gradient approximation (GGA) [18] was used for the self-consistent calculation with a \( k \)-point mesh of \( 90 \times 1 \times 1 \) and a cutoff energy of 150 Ryd.

3. Results and Discussions

Figure 2 shows the magnon spectra of ZGNR with \( N = 6, 10, 14, 18 \) over the Brillouin zone. It shows the nearly flat dispersion in one-third of the Brillouin zone, which gives the most contribution for the high \( T_C \). While the \( D \) is obtained by fitting the magnon energy \( \hbar \omega_q = Dq^2(1 - \beta q^2) \) near \( \Gamma \) point as shown in Fig. 3, the \( T_C \) is calculated by using the mean-field approximation (MFA) over the Brillouin zone [19]

\[
k_B T_C^{\text{MFA}} = \frac{M}{6\mu_B N_q} \sum_q \hbar \omega_q, \tag{4}
\]

where \( N_q \) is the number of \( q \). Therefore, the \( D \) and \( T_C \) originate from the contribution of the low magnon energy near the \( \Gamma \) point and all the magnon energies in the Brillouin zone, respectively.
Figure 2. (Color online) Spectra of magnon of ZGNR in the Brillouin zone.

Table 1. Evaluated $D$ and $T_C$ for several $N$.

| $N$ | $D$ (meVÅ$^2$) | $T_C$ (K) |
|-----|----------------|-----------|
| 6   | 3345           | 102       |
| 10  | 3595           | 107       |
| 14  | 3801           | 108       |
| 18  | 3976           | 109       |

Note that the $T_C$ here refers to the Néel temperature since the ground state of the ZGNR system is antiferromagnetic.

We notice that the change of $D$ will be followed by the change of $T_C$, thus indicating a relationship between the $D$ and the $T_C$. It can also be found that the $D$ and $T_C$ increase as $N$ increases, as shown in table 1. For the large $N$, we predict that both the $D$ and $T_C$ will go to the constant values, exhibiting the critical $N$. This means that the $T_C$ in a pristine ZGNR will never gain room temperature although the $N$ increases. As a consequence, the magnetism in the ZGNR will be lost at room temperature. These results are consistent with those of previous works [5, 6].

From Eq. (4), we deduce that the $T_C$ is determined by the average of magnon energies $\bar{\hbar}\omega_q$ while the high $T_C$ contribution is given only in one-third of the Brillouin zone. According to Ref. [19], the Green function random phase approximation (GF-RPA) gives a better result as matched with the MFA. However, it needs much more $q$ in the Brillouin zone due to the harmonic average of magnon energies. As shown in Fig. 2, no strong fluctuations in the magnon spectra, so we claim that there is no large discrepancy of $T_C$ using those two approaches. The large discrepancy may happen in the case of strong fluctuations in the magnon spectra, as reported in Ref. [19].

Compared to the 3d ferromagnetic metals [19] or the oxide systems [20], the scale of magnon energy in the ZGNR is difficult to give the high $T_C$. From our point of view, this feature may be influenced by the dimensionality of a system when the spin-orbit interaction is very weak. When the dimensionality of systems is lowered, the $T_C$ tends to never reach the room temperature, for example in the case of two-dimensional metal dihalides [21]. This leads to the absence of magnetism at room temperature in the lower-dimensional materials, which has been stated by the Mermin-Wagner theorem [22]. One of the effective ways to preserve the magnetism in the lower-dimensional systems is to include the magnetic anisotropy. However, this way cannot be
Figure 3. (Color online) Spectra of magnon of ZGNR near Γ point for obtaining spin stiffness. Here, the boxes, triangles, diamond, and filled circles denote the calculated magnon energies while the solid line represents the fitting curve $\hbar \omega_q = Dq^2(1 - \beta q^2)$.

applied in the ZGNR due to the negligible spin-orbit interaction.

To discuss the change of $D$ as well as $T_C$ when $N$ increases, we consider the electron hopping from one edge magnetic carbon atom to the other one as an exchange magnetic interaction $J_{ij}$. Indeed, the strength of $J_{ij}$ is determined by the easiness of electron hopping. Based on the distance of separated edge magnetic carbon atoms, the largest $J_{ij}$ will be possessed by the smallest $N$ and vice versa. Therefore, the large $D$ is the implication of small $J_{ij}$ (large $N$), namely, the large $D$ is caused by the difficulty of an electron to hop. At the same time, when $N$ is so large, $J_{ij}$ remains unchanged, indicating that there is a critical $N$ due to the electron hopping. Therefore, the enhancement of $D$ and $T_C$ can only be performed up to a critical $N$. This means that $T_C$ in the ZGNR will never surpass the room temperature although $N$ increases as large as possible, as shown in table 1.

Here, we comment on our calculated $D$, which is quite higher than that in Ref. [5], which obtained $D=2100$ meV $\AA^2$. This large discrepancy may be caused by the different approaches. Although both of us employed the frozen magnon method to calculate the $D$, we use the GBT while the authors [5] used the supercell calculation. For the very small $q$ close to the Γ point, it is very difficult to calculate the $D$ in the supercell approach since the large number of cells with the orientation of magnetic moments of carbon atoms at the edges should be appropriately arranged. So, we think that they used the number of $q$ sufficiently far from the Γ point. Since the Stoner excitations may not be neglected in the $sp$- elements such as ZGNR [23], some magnon energies for the large $q$ should decay into the Stoner excitations. Therefore, we think that our approach should be more suitable.

Our findings show that the $T_C$ in the pristine ZGNR will never surpass the room temperature although the $D$ is quite high, in the opposite way with the opinion by Yazyev [5]. From the previous studies in Refs. [10, 24] who investigated the influence of $D$ in the ZGNR under external electric field $E$ along $N$ ($y$-axis), they found that the $D$ never surpasses that for the non-$E$ case, thus the $T_C$ has the same feature. Although some computational results show that this applied $E$ along $N$ is very useful to generate such as half-metallicity, this will not become feasible in this situation. Even for the hole-electron doping case, which can be realized by chemical doping, the $D$ never exceeds that for the non-doped case [15].

From table 1, we see that the increase of $D$ is followed by the increase of $T_C$ for all $N$. The situation can be different, in our case, when the electric field $E$ is taken into account along $x$-axis...
(periodic direction). As shown in Fig. 4, we observe the small enhancements of the $D$ as well as the $T_C$ up to the critical $E$ for all $N$ with the different tendency. Figure 4(a) shows the small increase of $D$ up to $E = 6$ V/nm for $N > 6$ and $E = 3$ V/nm for $N = 6$, a different tendency of $D$ for the small $N$. Meanwhile, the same tendency of $T_C$ occurs for all $N$, as shown in Fig. 4(b). For all $N$, the $T_C$ initially increases up to $E = 9$ V/nm and then tends to constant, thus never reaching the room temperature too. This tendency never occurs when the $E$ is employed along $y$-axis, i.e., both the $D$ and $T_C$ reduce as the $E$ increases for all $N$ as shown in our previous work [11].

Figure 4. (Color online) Dependence of $D$ and $T_C$ on applied $E$ along periodic direction ($x$-axis).

The different tendency between the $D$ and $T_C$ originates from the different contributions of the magnon energy, as previously mentioned. This means that the applied $E$ gives instability to the low magnon energy for the small $N$, i.e., the $D$ reduces with a different critical $E$. This reduction is addressed to the reduction of the magnon energy close to Γ point. It seems that this anomaly may be affected by the weaker $J_{ij}$ in the small $N$. On the contrary, this applied $E$ will not affect the magnon energy far from the Γ point, i.e., the tendency of $T_C$ is the same for all $N$.

In the previous report [6], Kunstmann et al. stated that the destruction of magnetism in the ZGNR at room temperature is caused by each small magnetic moment of two edge carbon atoms, which is close to $0.3 \mu_B$. We also obtain the magnetic moment close to $0.3 \mu_B$ for all $N$ both in the non-electric-field and in the electric field cases. This may be caused by the lost dangling bond when introducing the hydrogen atom to passivate the edges, as shown previously by Song et al. [27]. When the metal atom is included in the ZGNR [25, 26], the energy scale drastically increases due to the charge transfer from the metal atom to the magnetic carbon atoms, creating a strong bonding. This report is to support the previous work of Magda et al. [7] who included the Au atoms. This means that the stability of magnetism at room temperature
in the ZGNR is due to the strong bonding between the metal atom and the magnetic carbon atom, which enhances the magnetic moments of two edge carbon atoms.

4. Conclusions
By using the mean-field approximation (MFA), we show that the critical (Néel) temperature $T_C$ in the ZGNR never reaches room temperature even though the ribbon width $N$, which can increase the $T_C$, increases. This is due to a critical $N$ that gives a constant $T_C$ as well as the spin stiffness $D$. The main reason for this finding is the small magnetic moments of carbon atoms at the two separated edges. This implies that the magnetic feature can only maintain at low temperature.

Although introducing the electric field can also increase the $T_C$ for all $N$, it is still not possible to reach the room temperature. This is also due to a flat energy dispersion in one-third of the Brillouin zone around 300 meV. It is also supported by the small magnetic moments of two edge carbon atoms, thus destroying the magnetism at room temperature. Therefore, the ZGNR-based devices cannot be possible to operate well at room temperature.

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