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Anomalous Low Temperature Specific heat in Graphene-On-Substrate in Ferromagnetic State: A Green's function approach

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Abstract. We report here a tight-binding model calculation taking into account of ferromagnetic order in graphene-on-substrate. The repulsive Coulomb interaction is considered within a mean-field model taking into account of the ferromagnetic moments at each sub-lattice of the honeycomb lattice. The sub-lattice magnetizations are calculated by Zubarev's Green function technique and are solved self-consistently.

Keywords: Graphene, Ferromagnetism , Electron specific heat, Tight binding model

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1. Introduction

The graphene is a 2-D crystal material which consists of carbon atoms with sp^2 hybridization. The graphene is not a magnetic by itself, that was theoretically easily predicted [1]. It has been manifestation that the ad-atoms in the graphene surface can simply form magnetic moments due to its different electronic properties such as low density of states [2]. The magnetic response is weaker in monolayer than in its bulk states. Graphene has very little ferromagnetic behavior at room temperature in pure form. Both vacancies and doping of external impurities can produce defects in pristine graphene. Few experimental works have been studied the presence of magnetism in carbon materials by electron or irradiation [3, 4, 5]. The first principle calculations and tight-binding model studies have been applied for magnetism in such systems [6, 7]. Adsorptions of atoms or molecules can lead to produce ferromagnetism. Yazyev et.al. [6] and Boukhvalov et.al. [8] have reported the magnetism produced by the adsorption of

hydrogen atoms in graphene. The recent increasing importance of the thermal properties of materials is explained both by practical needs and fundamental science. Removal of heat has became a crucial cause for continuing progress in the electronic industry to increase dissipation power. Hence the search for materials that conduct heat well has become essential for design for next generation integrated circuits and electronics. For understanding the origin of graphene's high thermal conductivity is challenging, because the theoretical model of two dimensional and nano scale physics are limited. The specific heat determines not only the thermal energy stored inside the body but also how quickly the body cools. Recently, Sahu et.al. [9, 10, 11] have reported the tight binding model calculation to explain the band gap opening in the non-magnetic state of graphene-on-substrate. More, recently Swain et.al. [12] have reported the existence of ferromagnetism in graphene in doped graphene-on-substrate. Using the same tight binding approach, we present here the microscopic theoretical study of the thermal properties of graphene in ferromagnetic state. The tight binding Hamiltonian is described in section 2 and calculation of specific heat in section 3. Finally the results are given in section 4 and conclusion in section 5. In present communication, we have investigated the effect of Coulomb interaction on electron entropy and hence the electron specific heat specific heat.

2. Tight-Binding Model Hamiltonian

The Hamiltonian consisting hopping of π-electrons up-to third nearest-neighbors is written as,

$$H_0 = \sum_{k,\sigma} \left[\varepsilon_{a,k} \; a^{\dagger}_{k,\sigma} a_{k,\sigma} + \varepsilon_{b,k} b^{\dagger}_{k,\sigma} b_{k,\sigma} \right] + \sum_{k,\sigma} \left[\varepsilon_{13}(k) \; a^{\dagger}_{k,\sigma} b_{k,\sigma} + \varepsilon^{*}_{13}(k) \; b^{\dagger}_{k,\sigma} a_{k,\sigma} \right] \quad (1)$$

where $\varepsilon_{a,k} = \varepsilon_a - \mu + \Delta + \varepsilon_{2k}$, $\varepsilon_{b,k} = \varepsilon_b - \mu - \Delta + \varepsilon_{2k}$ and $\varepsilon_{13}(k) = \varepsilon_{1k} + \varepsilon_{3k}$. The site energies ε_a and ε_b at A and B sub-lattices are modified by chemical potential (μ), substrate induced gap (Δ). Here $a^{\dagger}_{k,\sigma}$ $(a_{k,\sigma})$ and $b^{\dagger}_{k,\sigma}$ $(b_{k,\sigma})$ are respectively the creation (annihilation) electron operators at A and B sub-lattices having momentum $\vec{k}$ and spin σ. The electron-electron interaction for A and B sub-lattices is given by

$$H_U = \frac{U}{2}\left[\sum_{i,\sigma} a^{\dagger}_{i,\sigma} a_{i,\sigma} \; a^{\dagger}_{i,-\sigma} a_{i,-\sigma} + \sum_{i,\sigma} b^{\dagger}_{i,\sigma} b_{i,\sigma} \; b^{\dagger}_{i,-\sigma} b_{i,-\sigma}\right] \quad (2)$$

The ferromagnetism (FM) arises, when net magnetization in both the sub-lattices are in same direction and the average electron occupancy within the mean-field approach appears in general as, $\langle c_{i,\sigma}^{\dagger} c_{i,\sigma} \rangle = \left(\frac{n}{2} + \frac{\sigma m}{2}\right)$ where n and m are respectively the electron density and magnetization with σ taking $+1(-1)$ for up (down) spins.

3. Calculation of entropy and electron specific heat

The Green's functions for A and B site electron operator can be defined as,

$$A_1(k,\omega) = \ll a_{k,\sigma}; a_{k,\sigma}^{\dagger} \gg_{\omega} \; ; \; B_1(k,\omega) = \ll b_{k,\sigma}; b_{k,\sigma}^{\dagger} \gg_{\omega} \tag{3}$$

By using Zubarev's Green's function technique, the final expressions of the above Green's functions are

$$\mathrm{A_1(k,\omega)} = \frac{1}{2\pi} \frac{\left(\omega - \epsilon_{\mathrm{b},\sigma}(\mathrm{k})\right)}{|\mathrm{D}_{\sigma}(\omega)|}; \; \mathrm{B_1(k,\omega)} = \frac{1}{2\pi} \frac{\left(\omega - \epsilon_{\mathrm{a},\sigma}(\mathrm{k})\right)}{|\mathrm{D}_{\sigma}(\omega)|} \tag{4}$$

For $|\mathrm{D}_{\sigma}(\omega) = 0|$, we get two quasi-particle bands namely $\omega_{1\mathrm{k},\sigma}$ for valence band and $\omega_{2\mathrm{k},\sigma}$ for conduction band which are given by

$$\omega_{1\mathrm{k}\sigma} = \frac{\left(\epsilon_{\mathrm{a},\sigma,\mathrm{k}} + \epsilon_{\mathrm{b},\sigma,\mathrm{k}}\right) + \sqrt{(\epsilon_{\mathrm{a},\sigma,\mathrm{k}} - \epsilon_{\mathrm{b},\sigma,\mathrm{k}})^2 \; + \; 4|\, \epsilon_{13}\,|^2}}{2} \tag{5}$$

$$\omega_{2\mathrm{k}\sigma} = \frac{\left(\epsilon_{\mathrm{a},\sigma,\mathrm{k}} + \epsilon_{\mathrm{b},\sigma,\mathrm{k}}\right) - \sqrt{(\epsilon_{\mathrm{a},\sigma,\mathrm{k}} - \epsilon_{\mathrm{b},\sigma,\mathrm{k}})^2 \; + \; 4|\, \epsilon_{13}\,|^2}}{2} \tag{6}$$

In order to study the effect of Coulomb interaction, on the thermal properties of graphene, we write free energy for graphene in terms of the quasi-particle energies $\omega_{\alpha,\mathrm{k},\sigma}$ $(\alpha = 1,2)$ as

$$F = -k_B T \sum_{\alpha,k,\sigma} [\, \ln \{\, 1 + e^{-\beta(\omega_{\alpha,k,\sigma})} \,\}\,] \tag{7}$$

where $\mathrm{k_B}$ is the Boltzmann constant and $\beta = \frac{1}{\mathrm{k_B T}}$. The entropy of the system is defined as $\mathrm{S} = -\frac{1}{\mathrm{N}}(\frac{\partial \mathrm{F}}{\partial \mathrm{T}})_{\mathrm{V},\mu}$, where V and N are the constant volume and number of unit cells respectively and is given by

$$\frac{s}{k_B} = \frac{1}{N} \left[\; \sum_{\alpha,k,\sigma} \ln\{\, 1 + e^{-\beta\omega_{\alpha,k,\sigma}}\} + \frac{e^{-\beta\omega_{\alpha,k,\sigma}}}{1+e^{-\beta\omega_{\alpha,k,\sigma}}} \; \{\beta\omega_{\alpha,k,\sigma} - \; \omega'_{\alpha,k,\sigma}\} \right] \tag{8}$$

Further the temperature dependence specific heat is calculated numerically from entropy (S) from the relation

$$\bar{C}_V = \frac{C_V}{k_B} = \; (T \frac{\partial s}{\partial T})_{V,\mu} \tag{9}$$

The physical quantities are made dimensionless by NN hopping integral $t_1 = 2.78eV$. The parameters are: the Coulomb energy $= \frac{U}{t_1}$, substrate induced gap $d_1 = \frac{\Delta}{t_1}$ and temperature $t = \frac{k_B T}{t_1}$.

4. Results and Discussion

The free energy (F) of graphene-on-substrate in ferromagnetic state is written in eq.(7). The entropy 'S' and specific heat $\overline{C_v}$ given in eq.(8) and (9) are solved numerically from the self-consistent electron occupancies and are showed in fig.(1). Fig.1(a) shows the plot of temperature dependent electron specific heat for different Coulomb potentials in ferromagnetic state.

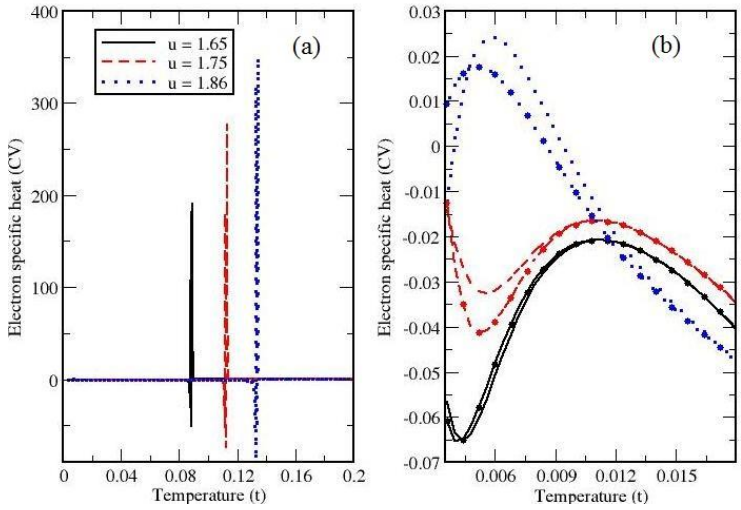

Fig. 1(a). The plot of electron specific heat ($\overline{C_v}$) vs. temperature (t) for different values of Coulomb potential $u = 1.65, 1.75, 1.86$ for fixed substrate induced gap $d_1 = 0.001$ and electron density ($n = 1$). **1(b)** The plot of electron specific heat ($\overline{C_v}$vs. temperature (t) for different values of Coulomb potential with solid, dash and dotted lines for A-sites and solid with circle, dash with circle and dot with circle for B-sites.

The specific heat shows large jump at the ferromagnetic critical temperature (Curie temperature (T_c)). The Curie temperature shifts to higher values with increase of Coulomb potential with corresponding increase in specific heat jump exhibiting a second order magnetic phase transition. For a given u, the specific heat jumps due to A-site and B-site magnetizations coincide. The magnified version of low temperature specific heat is shown in fig.1(b). It is observed that A-site magnetizations and B-site magnetizations have different values for a given u at low temperatures. For a given Coulomb potential $u = 1.86$, we get two

specific heats, i.e. one for A-site (dotted line) and B-site (dotted with circle line). For this, the specific heat increases with temperature, then attains its peak value and then decreases to zero at higher temperatures. This type of nature of specific heat appears for both sub-lattice sites. The specific heat becomes negative for lower Coulomb potentials ($\boldsymbol{u < 1.86}$). However, there exists a critical Coulomb potential ($\boldsymbol{u_c}$) i.e. $\boldsymbol{1.75 < u_c < 1.86}$ above which there exists ferromagnetic order on-substrate.

5. Conclusions

Our tight binding model calculation of specific heat shows that the electronic specific heats due to A and B sub-lattice magnetizations are same at higher temperatures for any given Coulomb potential and for very low substrate induced gap. However, the specific heats give different values for different sub-lattice magnetizations at very low temperatures (i.e. near room temperature). Further the ferromagnetic order exists in graphene-on-substrate at critical Coulomb potential, $\boldsymbol{1.75 < u_c < 1.86}$ in ferromagnetic state.

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