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Citation: [Applied Physics Letters](#) **105**, 232406 (2014); doi: 10.1063/1.4903833

View online: <http://dx.doi.org/10.1063/1.4903833>

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## Oscillating magnetocaloric effect of a multilayer graphene

Z. Z. Alisultanov,<sup>1,2,3,a)</sup> L. S. Paixão,<sup>4</sup> and M. S. Reis<sup>4</sup>

<sup>1</sup>*Amirkhanov Institute of Physics, Russian Academy of Sciences, Dagestan Science Centre, Makhachkala, Russia*

<sup>2</sup>*Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia*

<sup>3</sup>*Dagestan State University, Makhachkala, Russia*

<sup>4</sup>*Instituto de Física, Universidade Federal Fluminense, Av. Gal. Milton Tavares de Souza s/n, 24210-346 Niterói, RJ, Brazil*

(Received 8 October 2014; accepted 28 November 2014; published online 9 December 2014)

The oscillating magnetocaloric effect of a multilayer graphene in Bernal and rhombohedral stacking is investigated to extend the previous knowledge of the effect on a single layer graphene. We started from results of a tight-binding model and obtained analytical expressions for the thermodynamic potential and for the entropy change. The last exhibits the same dependence on field and temperature observed for other diamagnetic systems; it oscillates with the inverse magnetic field and presents a maximum value at a given temperature. The amplitude of the oscillating entropy change decreases with the number of layers and the stacking sequence rules the magnetocaloric properties of the system. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4903833>]

Magnetocaloric effect (MCE) is a thermal response of magnetic materials to a magnetic field change  $\Delta B$ . The effect may be observed though an entropy change  $\Delta S$  (from an isothermal process), where the material exchanges heat with a thermal reservoir or through a temperature change  $\Delta T$  (from an adiabatic process). Thus, the effect is characterized by the quantities  $\Delta S$  and  $\Delta T$ . The main application for the MCE is in magnetic refrigeration, first suggested in the late 1920s with a process known as adiabatic demagnetization.

MCE is stronger in materials that present some magnetic order, particularly in the vicinity of a phase transition. Therefore, research of materials is specially focused on ferromagnets,<sup>1</sup> antiferromagnets,<sup>2</sup> and multiferroics.<sup>3</sup> Nevertheless, MCE in diamagnetic materials have been studied recently.<sup>4-7</sup> For these materials, both quantities  $\Delta S$  and  $\Delta T$  present an oscillating character as a function of the applied magnetic field and present a maximum value at a given temperature even though there is no critical temperature. The oscillatory behavior is related to the crossing of the Landau levels through the Fermi energy, analogously to the well known de Haas-van Alphen effect. The oscillating MCE was studied in 3D systems<sup>4,8</sup> (standard bulk diamagnets), and in systems of lower dimensionality, 2D<sup>5,6,9</sup> and 1D<sup>7</sup> diamagnets. It should be noted that the MCE in diamagnetic materials is much weaker than the effect observed in magnetically ordered materials. However, due to the oscillations, diamagnetic materials could work as highly sensitive magnetic field sensors.<sup>4,8,9</sup>

Among 2D systems, graphene has unique properties due to its linearity in the low energy part of the electronic spectrum. Comparing the MCE of 2D non-relativistic materials with graphene, the entropy change of the latter is 3 orders of magnitude larger. Besides, the temperature of maximum

entropy change is about 1 K for non-relativistic materials and 100 K for graphene under an applied field of 10 T.

Stacks of graphene layers also attract much attention and it is well known that the stacking configuration determines the electronic structure of the system.<sup>10,11</sup> Two of the most important stackings are Bernal (ababab...) and rhombohedral (abcabc...). While Bernal stacking shows a quadratic low energy spectrum, rhombohedral stacking shows a  $|p|^N$  dependence on its band structure. The aim of the present work is to study the dependence of MCE on the number of layers of a multilayer graphene as well as the importance of the stacking configuration.

The paper is organized as follows. In the following section, we briefly describe the tight-binding spectrum of multilayer graphene, and the quasi-classical quantization process used to introduce the magnetic field. In the following section, we use the energy spectrum to evaluate the grand canonical potential. Then, we obtain the entropy change to characterize the magnetocaloric effect. Finally, we briefly summarize and discuss our findings.

The simplest way to describe the electronic structure of multilayer graphene is to use a tight-binding model which includes hopping between the  $\pi$  orbitals in carbon atoms, neglecting the remaining atomic orbitals which give rise to the  $\sigma$  bands. In multilayer graphene, the electronic structure depends on the stacking configuration (Fig. 1). Below, we describe Bernal and rhombohedral stacking orders.

The case of multilayer graphene with Bernal stacking (ababab...) was considered in Refs. 10 and 11. The energy spectrum can be written as

$$E = \sqrt{v_F^2 p^2 + \gamma_1^2 \cos^2\left(\frac{\pi}{N+1}\right)} - \gamma_1 \cos\left(\frac{\pi}{N+1}\right), \quad (1)$$

where  $N$  is number of layers,  $v_F = 10^8$  cm/s is the Fermi velocity, and  $\gamma_1$  is the hopping energy between nearest

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: [zaur0102@gmail.com](mailto:zaur0102@gmail.com)

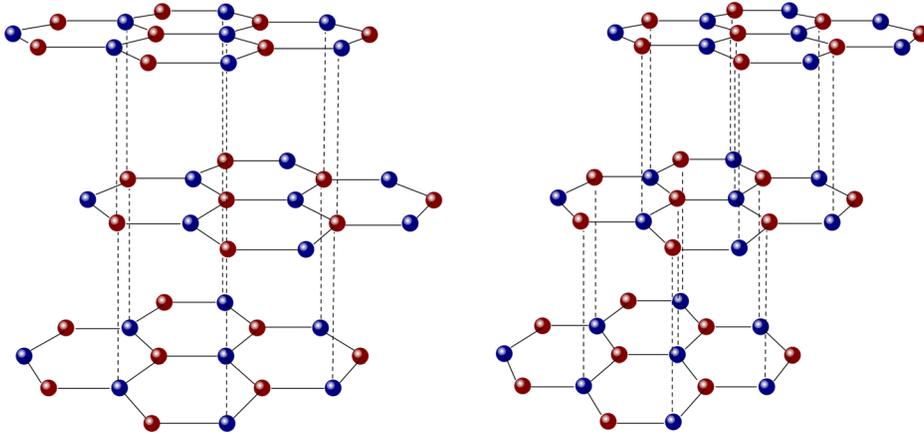


FIG. 1. Multilayer graphene: Bernal or aba stacking (left) and rhombohedral or abc stacking (right).

layers. We considered only low-energy electrons of conduction band.

For example, for single layer graphene ( $N=1$ ), we have  $E = v_F p$ , and for bilayer graphene ( $N=2$ ) we have  $E = \sqrt{v_F^2 p^2 + \gamma_1^2/4} - \gamma_1/2$ , etc., in full agreement with known works.<sup>12,13</sup>

Considering the rhombohedral stacking (abcabc...), the simplest effective Hamiltonian of multilayer graphene gives then the following energy spectrum:<sup>10</sup>

$$E = \sqrt{a_N^2 p^{2N} + \Delta^2}, \quad (2)$$

where  $p^2 = p_x^2 + p_y^2$ ,  $N$  is again the number of layers,  $\Delta$  is the band gap due to the breaking symmetry between layers, and  $a_N = \gamma_1 (v_F/\gamma_1)^N$ .

Equation (2) also recovers the Dirac spectrum for single layer graphene, and for bilayer graphene we have

$$E = \sqrt{v_F^4 p^4 / \gamma_1^2 + \Delta^2}, \text{ in accordance with Ref. 13.}$$

For the calculation, we will present below, the value of the nearest neighbor interlayer hopping energy is  $\gamma_1 = 0.4$  eV, following the references listed in Table I.

To go further, we will take advantage of the Lifshitz-Onsager quantization rule;<sup>21,22</sup> and this approach was already used in recent papers.<sup>23–26</sup> For a 2D electron gas, the area enclosed by the trajectory of an electron with energy  $\varepsilon = \varepsilon(p)$  (in the momentum space) reads as<sup>21,22</sup>

$$A_n(\varepsilon) = 2\pi\hbar e H(n + \gamma_\sigma), \quad (3)$$

where  $n = 0, 1, 2, \dots$  and  $\gamma_\sigma = \gamma + \sigma m^*(\mu)/2m$ . Furthermore,

$$m^*(\varepsilon) = \frac{1}{2\pi} \frac{dA_n(\varepsilon)}{d\varepsilon} \quad (4)$$

TABLE I. Values of the interlayer hopping energy  $\gamma_1$ , in eV, from a few references.

$\gamma_1$ (eV)	Reference
$0.378 \pm 0.005$	Experiment <sup>14</sup> (IR spec.)
$0.381 \pm 0.003$	Experiment <sup>15</sup> (IR spec.)
0.40	Experiment <sup>16</sup> (IR spec.)
0.30	Experiment <sup>17</sup> (Raman)
0.35	Experiment <sup>18</sup> (Raman)
0.34	<i>Ab initio</i> <sup>19</sup>
0.3963	<i>Ab initio</i> <sup>20</sup>

is the electron cyclotron mass,  $\sigma = \pm 1$  stands for the spin projection. For multilayer graphene, we have<sup>27</sup>  $\gamma = (N-1)/2$ . Also, for the present work, we are neglecting the Zeeman splitting, i.e., we are considering  $\gamma_\sigma = \gamma$ . Note the area in momentum space is  $\pi p^2$  and therefore the Landau levels for multilayer rhombohedral stacking reads as (Eq. (3) into Eq. (2))

$$\varepsilon_n = \sqrt{a_N^2 [2\hbar e H(n + \gamma)]^N + \Delta^2}, \quad (5)$$

while for Bernal stacking, it reads as (Eq. (3) into Eq. (1))

$$\varepsilon_n = \sqrt{2v_F^2 \hbar e H(n + \gamma) + \gamma_1^2 \cos^2\left(\frac{\pi}{N+1}\right)} - \gamma_1 \cos\left(\frac{\pi}{N+1}\right). \quad (6)$$

Reminding that  $A(\varepsilon(p)) = \pi p^2$ , it is possible to write useful relations: From Eq. (2),

$$A(\varepsilon) = \pi \left( \frac{\varepsilon^2 - \Delta^2}{a_N^2} \right)^{\frac{1}{N}}, \quad (7)$$

valid for rhombohedral stacking; and from Eq. (1),

$$A(\varepsilon) = \frac{\pi}{v_F^2} \left[ \varepsilon + \gamma_1 \cos\left(\frac{\pi}{N+1}\right) \right]^2 - \frac{\pi}{v_F^2} \gamma_1^2 \cos^2\left(\frac{\pi}{N+1}\right), \quad (8)$$

valid for Bernal stacking.

The general expression for the thermodynamic potential in the presence of a magnetic field has the form

$$\Omega = -\frac{2eHk_B T S_g}{\pi\hbar} \sum_n \ln \left[ 1 + \exp\left(\frac{\mu - \varepsilon_n}{k_B T}\right) \right], \quad (9)$$

where  $T$  is the temperature,  $k_B$  is the Boltzmann constant,  $\mu$  is the chemical potential, and  $S_g$  is the graphene area. We are considering the case of electron doping and therefore  $\mu > 0$ . Using the Poisson summation formula,

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x) dx + 2Re \sum_{k=1}^{\infty} \int_0^{\infty} f(x) e^{i2\pi k x} dx, \quad (10)$$

then integrating by parts and using Eq. (3), we obtain

$$\begin{aligned}\Omega(T, H) &= \Omega_0(T) + \Omega_H(T) \\ &= -\frac{S_g}{(\pi\hbar)^2} \int_0^\infty A(\varepsilon) f(\varepsilon - \mu) d\varepsilon - \frac{2eHS_g}{\pi^2\hbar} Re \\ &\quad \times \sum_{k=1}^{\infty} \frac{(-1)^{k(N-1)}}{ik} \int_0^\infty f(\varepsilon - \mu) \exp\left(\frac{ikA(\varepsilon)}{\hbar eH}\right) d\varepsilon,\end{aligned}\quad (11)$$

where  $f(\varepsilon - \mu) = 1/\{\exp[(\varepsilon - \mu)/k_B T] + 1\}$  is the Fermi-Dirac distribution function.

The energies  $\varepsilon \sim \mu$  are important for the magnetic oscillations and therefore we expand the function  $A(\varepsilon)$  in the vicinity of  $\mu$

$$A(\varepsilon) \approx A(\mu) + 2\pi m^*(\mu)(\varepsilon - \mu). \quad (12)$$

Then, evaluating the right integral of Eq. (11) and considering  $k_B T \ll \mu \sim \varepsilon_F$ , we obtain the field dependent thermodynamic potential, with an oscillatory character

$$\Omega_H(T) = \frac{2eHk_B T S_g}{\pi\hbar} \sum_{k=1}^{\infty} \frac{(-1)^{k(N-1)}}{k} \frac{\cos(k\pi m)}{\sinh x_k}, \quad (13)$$

where

$$x_k = kx = k \frac{2\pi^2 k_B T m^*(\varepsilon_F)}{\hbar eH}, \quad m = \frac{\tilde{H}}{H} \quad \text{and} \quad \tilde{H} = \frac{A(\varepsilon_F)}{\hbar\pi e}. \quad (14)$$

On the other hand, the left integral of Eq. (11) gives the zero-field thermodynamic potential; and this contribution reads as

$$\Omega_0(T) = -\frac{S_g}{(\pi\hbar)^2} \left( \varepsilon_F A(\varepsilon_F) + \frac{\pi^3}{3} k_B^2 T^2 m^*(\varepsilon_F) \right). \quad (15)$$

The entropy is determined as

$$\mathcal{S}(T, H) = -\frac{\partial \Omega(T, H)}{\partial T} = \mathcal{S}_0(T) + \mathcal{S}_H(T). \quad (16)$$

From Eq. (15), the zero-field entropy is

$$\frac{\mathcal{S}_0(T)}{S_g k_B} \approx \frac{2\pi m^*(\varepsilon_F) k_B T}{3\hbar^2}. \quad (17)$$

Using the effective cyclotron mass for both rhombohedral and Bernal stacking with  $N = 1$ , the above expression recovers the entropy of single layer graphene.<sup>9</sup> To obtain Eq. (17), we used expansion (12), because the integrand in  $\partial \Omega_0 / \partial T$  is significantly different from zero only in the vicinity of  $\varepsilon = \varepsilon_F$ . Remember,  $S_g$  is the graphene area. Analogously to above, from Eq. (13), we obtain the field-dependent magnetic entropy, with an oscillatory character

$$\frac{\mathcal{S}_H(T)}{S_g k_B} = \frac{2A(\varepsilon_F)}{\hbar^2 \pi^2} \frac{1}{m} \sum_{k=1}^{\infty} \frac{1}{k} (-1)^{k(N-1)} \mathcal{T}(x_k) \cos(k\pi m), \quad (18)$$

where

$$\mathcal{T}(x_k) = \frac{x_k L(x_k)}{\sinh x_k} \quad (19)$$

and  $L(x_k) = \coth(x_k) - 1/x_k$  is the Langevin function.

However, the magnetic entropy change is given by  $\Delta \mathcal{S}(T, H) = \mathcal{S}(T, H) - \mathcal{S}(T, 0) = \mathcal{S}_0(T) + \mathcal{S}_H(T) - \mathcal{S}_0(T) = \mathcal{S}_H(T)$  and therefore the oscillating magnetic entropy change we are looking for is on Eq. (18).

Figure 2 presents the entropy change (Eq. (18)) for multilayer graphene as a function of temperature, and the number of layers varying up to  $N = 4$ . It is known that the stacking sequence affects the electronic properties, and here we can see that the stacking also rules the magnetocaloric effect.

Figure 3 presents the entropy change as a function of the inverse magnetic field and its oscillations. The amplitude of the entropy change becomes smaller when more layers are added, as we can also see in Figure 2.

In this paper, we applied a thermodynamic treatment to the electronic structure of multilayer graphene, obtained from a tight-binding model considering only one hopping energy, between carbon atoms in neighbor layers. We found the usual oscillating entropy change as a function of the inverse magnetic field; however, the amplitude of the entropy change decreases with the number of layers. Also, the entropy change presents a maximum value at a given temperature. This pair of features is characteristic of diamagnetic MCE. It is worth to notice that if we make  $N = 1$  on Eq. (18), i.e., considering a single layer graphene, the entropy change exactly matches our previous result in Ref. 6; as well as the case  $N = 2$  that also recovers our previous result considering a bilayer graphene, which was explored in detail in Ref. 13.

Because we did not take into account the hopping inside the layers, the present result applied to a single layer

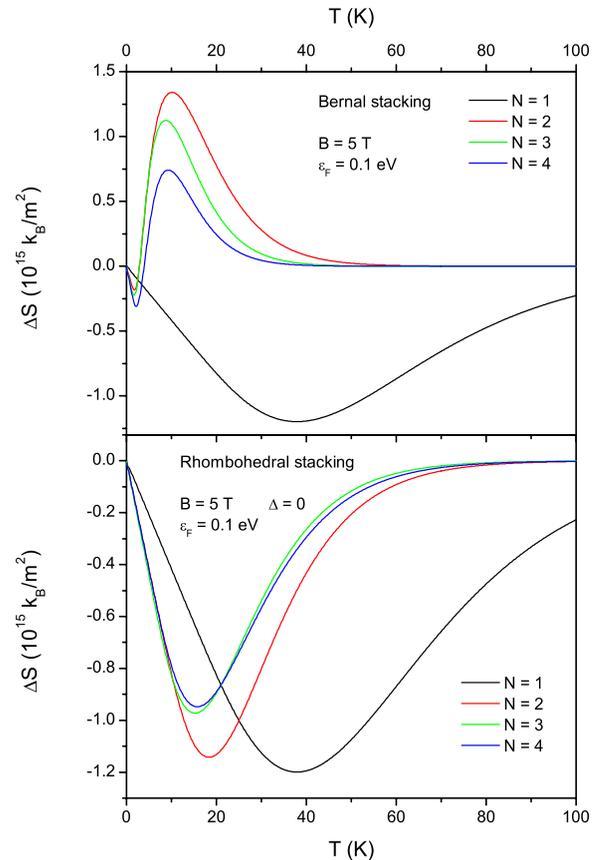


FIG. 2. Thermal evolution of the entropy change of multilayer graphene.

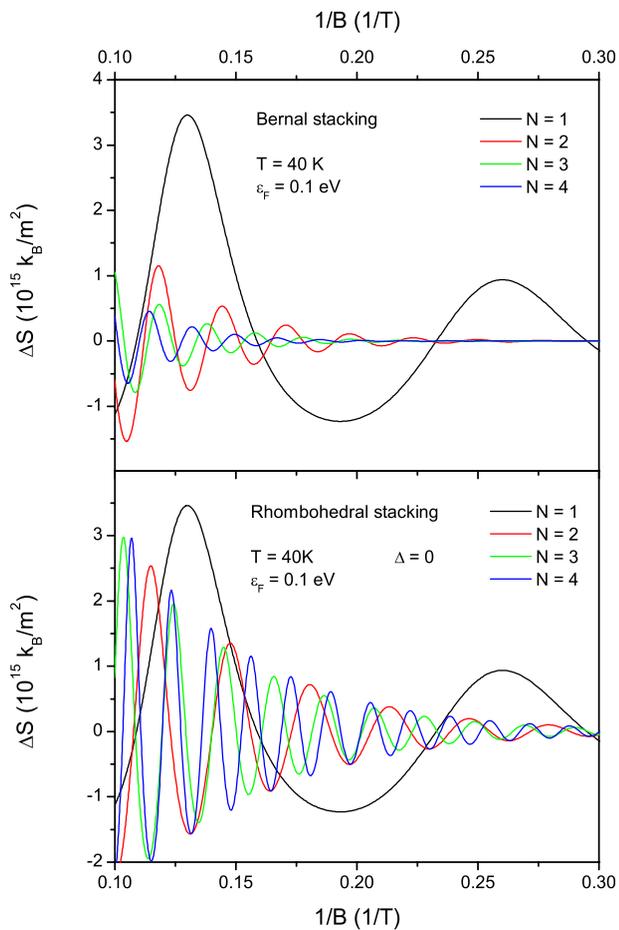


FIG. 3. Field dependence of the entropy change of multilayer graphene.

graphene matches our previous one, which considered a 2D electron gas. It is also interesting to notice that in the present work we used the quasi-classical approach to handle the magnetic field, which was not employed to single layer graphene. In general, since the electronic structure of multilayer graphene depends on the stacking sequence, the stacking also rules the magnetocaloric properties of the system.

Finally, we may say, that other physical interactions, such as dispersive or van der Waals interaction, will mainly affect the interlayer distance. It will then result in a change of the interlayer hopping parameter. Therefore, other

interactions would result in minor changes of the oscillating MCE, but no qualitative change is expected.

The reported study was partially supported by Project No. 3.1262.2014 of Ministry of Education and Science of Russia in scientific research and RFBR, Research Project No. 15-02-03311a. L.S.P. and M.S.R. thank Brazilian agencies CNPq, CAPES, FAPERJ, and PROPPi-UFF for the financial support.

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