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Electrocaloric effect on graphenes

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The present Letter explores the electrocaloric effect of graphene nano-ribbons, with a longitudinal electric field and transversal magnetic field. Special features of the effect can be ruled and tuned by the applied fields as, for instance, the unusual inverse effect, created by the Landau levels. These results open doors to enhance electrocaloric utility of materials. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4795863]

Caloric effects, such as magneto-, electro-, and barocaloric, have been extensively explored by the scientific community due to the increasing interest in renewable energy materials and devices.1–4 The electrocaloric effect (ECE) is the entropy and temperature change of a material subject to a change of electric field; being a function of both, temperature and electric field change \( \Delta E \). It has a significant technological importance, enabling the production of high-performance solid-state cooling devices for a broad range of applications, such as temperature regulation for sensors, electronic devices, and on-chip cooling devices.1,3 Furthermore, refrigeration based on the ECE has the promise to be more efficient and environmentally friendly compared to the conventional vapor compression cycle approach. In comparison to cooling devices based on the magnetocaloric effect (MCE), ECE-based ones offer several attractive features, such as light weight, compact device configurations, and easiness and cheapness in generating and manipulating electric fields.1,5 Although ECE has been studied for many decades, recent findings of large ECE in several ferroelectric materials revived the interest on this effect.5–9

Recently, the MCE on graphenes was studied,10 and oscillations were found, similarly to what was found to standard 3D diamagnetic materials.11 These oscillations come from the crossing of the Landau levels through the Fermi level of the system; and, for standard 3D diamagnetic materials, it occurs at \( \approx 1 \text{ K} \), while for graphenes, it occurs at c.a. \( 100 \text{ K} \), due to the huge Fermi velocity of these last materials. Very recently, this oscillatory MCE on graphenes was further studied, and the influence of a longitudinal electric field on the MCE properties was described.12

It is, therefore, straightforward to investigate the electrocaloric effect on graphenes under a transversal magnetic field, responsible thus for the existence of the Landau levels. Note we are describing the electrocaloric effect in a general context, as an entropy and temperature change due to an electric field change, even graphene being a conductor. This last fact can promote minor technical limitations, considering applications on cooling devices, as, for instance, Joule heating.2,13

The energy spectra for a nano-ribbon graphene sheet on \( x-y \) plan with \( \vec{E} = (-E,0,0) \) and \( \vec{B} = (0,0,B) \), i.e., electric field along the graphene plan and magnetic field perpendicular to graphene plan, are:14–16

\[
E_n = \hbar \omega \sqrt{n + \nu F b k_y}, \quad \text{where} \quad n = 0, 1, 2, \ldots, \hbar \omega = \sqrt{2 \hbar v_F \nu F (1 - \beta^2)^{1/4}},
\]

\[
b = \frac{E}{\nu F B} < 1, \quad (1)
\]

\( k_y = 2 \pi l / L_y \) \( (l = 0, \pm 1, \pm 2) \) is related to the size of the graphene along the \( y \) direction \( (L_y) \), and \( v_F = 10^6 \text{ m/s} \) stands for the Fermi velocity. From this energy spectra, the grand canonical potential per graphene area can be evaluated,15–20

\[
\Phi(T,B,E) = \Phi_0(T) + \Phi_{no}(B,E) + \Phi_{per}(T,B,E) + \Phi_{cos}(T,B,E),
\]

where \( \Phi_0(T) \) is a function that depends only on the temperature; \( \Phi_{no}(B,E) \) depends on both magnetic and electric fields in a non-oscillatory fashion and does not depend on the temperature; \( \Phi_{per}(T,B,E) \) and \( \Phi_{cos}(T,B,E) \) have, respectively, a periodic behavior and a cosine oscillatory character, and both depend on temperature, magnetic and electric fields.

Thus, the entropy of the system can be obtained from \( S(T,B,E) = -\partial \Phi(T,B,E) / \partial T \), and it is easy to see that \( S_{no} = 0 \) and \( S(T,B,E) = S_0(T) + S_{per}(T,B,E) + S_{cos}(T,B,E) \). As mentioned above, to characterize the electrocaloric effect, the entropy change must be considered.

\[
\Delta S(T,B,\Delta E) = S(T,B,E) - S(T,B,0), \quad (2)
\]

where \( E < E_{\text{max}} \).

To obtain the entropy change, only two grand canonical potentials must be known: \( \Phi_{cos}(T,B,E) \) and \( \Phi_{per}(T,B,E) \). The first one, per graphene area, is,15,16

\[
\Phi_{cos}(T,B,E) = \left( \frac{eB}{\pi \mu_0} \right)^2 \nu F (1 - \beta^2)^{1/4} \sum_{k=1}^\infty \frac{\cos(\pi km)}{(\pi k)^2} \frac{x_k^2}{\sin(\beta x_k)}, \quad (3)
\]

where \( \mu_0 = \hbar v_F \sqrt{N_0} \pi \) is the zero temperature and zero magnetic field chemical potential, i.e., the Fermi energy; and \( N_0 = 10^{16} \text{ m}^{-2} \) is the density of charge carriers.21,22 In addition,
In Eq. (6), the value used for $L_m$ is $[m^2 - 2m (2\sigma + 1) + 4\sigma(\sigma + 1)]$, which considers $\sigma = [m/2]$, where the brackets mean the integer part of the argument. The periodic behavior of $L_m$ can be seen in Ref. 12. It is important to note that for odd values of $m$, this function is $-1$ and, on the other hand, assumes $0$ for even values of $m$. In Eq. (6), the value used for $L_m$ is $10^{-8}$ m. 

Finally, the entropies can be obtained

\[
S_{\text{corr}}(T, B, E) = 2N_0/B \sum_{\ell=1}^{\infty} \frac{x_k}{\sinh(x_k)}
\]

and

\[
S_{\text{per}}(T, B, E) = 2\pi^2 k_B L_0 \beta A_m N_0 / m^2 \sqrt{N_0 \pi} T(x)
\]

where,

\[
T(z) = \frac{zL(z)}{\sinh(z)} \quad \text{and} \quad L(z) = \coth(z) - \frac{1}{z}
\]

is the Langevin function. As usually done for thermodynamic quantities of this kind, we considered only $k = 1$ term: the hyperbolic sine function at the denominator of Eq. (9) rapidly damping the summation. Note $x = \bar{x}_1$.

To evaluate Eq. (2), the $S(T, B, 0)$ terms must be calculated; i.e., the entropies for $\beta = 0$. Therefore, $S_{\text{per}}(T, B, 0) = 0$ and

\[
S_{\text{corr}}(T, B, 0) = 2k_B N_0 / m^2 \cos(\pi m) T(x)
\]

where $x = \bar{x}(\beta = 0)$. Thus, the entropy change per graphene area reads as: $\Delta S(T, B, \Delta E) = S_{\text{corr}}(T, B, E) + S_{\text{per}}(T, B, E) - S_{\text{corr}}(T, B, 0)$, where these terms are, respectively, on Eqs. (7), (8), and (10).

The temperature dependence of the entropy change, for some values of $m$ (inversely proportional to the magnetic field—see Eq. (4)), is presented in Figure 1. Note it is not the magnetocaloric effect, since we evaluated the entropy change due to an electric field change under a static magnetic field. The ECE was considered when the electric field changes from $0$ up to $10^6$ V/m (within the order of magnitude for bulk materials). Clearly, an applied magnetic field has a remarkable influence on the temperature dependence of the entropy change. Two characteristics of this thermal dependence must be emphasized and analyzed: (i) the temperature $T_{m}$ at which the entropy change is maximum—$T_{m}$ increases by increasing the applied magnetic field and this trend comes mainly due to $T(z)$ function (that peaks at $z = 1.6$), (ii) The value of this maximum—that comes mainly from the periodic behavior of the $S_{\text{per}}(T, B, E)$ contribution, following the trend of $A_m$ and being maximum near odd values of $m$ and minimum for even ones. Therefore, application of a constant magnetic field can be an interesting way to control important characteristics of the ECE on graphenes. Note the presented values of entropy change are comparable to the ones for standard magneto- and electro-caloric materials, and to obtain these values, we considered the accepted graphene density of $0.77$ mg/m$^2$.

Figure 2(a) represents the temperature dependence of the entropy change under a magnetic field of $20.6$ T ($m = 1$), for different values of electric field change. Similarly to the magnetic field dependence (see Figure 1), modification of the electric field change alters the value of the maximum entropy change and the temperature in which it occurs, enabling the tuning of these properties for a specific application. As $\Delta E$ increases, the maximum entropy change also increases, but $T_{m}$ decreases. Moreover, a quite interesting feature can be observed in Figure 2(a) for the highest electric field change used ($\Delta E = 20 \times 10^6$ V/m). For this value, the sign of $\Delta S$ changes with temperature, leading to the positive and negative ECE in the material. This behavior, i.e., normal and inverse ECE, is not usual and has been only recently studied.

The entropy change was also evaluated as a function of the electric field change at constant temperature ($T = 300$ K) and $m = 1$ (inset of Figure 2(b)). The change of $\Delta S(T, B, \Delta E)$ sign occurs above a certain $\Delta E$ value, which is temperature dependent. In order to understand the physical origin of this sign change, all of the contributions $S_{\text{corr}}(T, B, E)$, $S_{\text{corr}}(T, B, 0)$, and $S_{\text{per}}(T, B, E)$ to the entropy change $\Delta S(T, B, \Delta E)$ are presented in Figure 2(b), as a function of temperature, for the case $\Delta E = 20 \times 10^6$ V/m and $m = 1$. 

FIG. 1. Entropy change as a function of temperature, for $\Delta E = 10^6$ V/m, under different values of applied magnetic field ($m$ is inversely proportional to $B$—see Eq. (4)).
Scos is quite different and exotic, combining both periodic behaviors inversely proportional to the magnetic field. It is important to remember different entropy contributions $S_{\cos}(T, B, E)$, $S_{\operatorname{per}}(T, B, E)$, and $S_{\operatorname{cor}}(T, B, 0)$ for $\Delta E = 2 \times 10^6$ V/m. Inset: Entropy change as a function of electric field change, emphasizing the normal and inverse effects.

From this figure, the importance of the $S_{\cos}(T, B, 0)$ contribution is clear. As temperature increases, the other contributions go to zero, leading to $\Delta S(T, B, \Delta E) = -S_{\cos}(T, B, 0)$. This phenomena of inverse ECE comes, therefore, simply from the existence of the Landau levels due to the applied magnetic field. Thus, the possibility of changing the sign of ECE is due to the applied magnetic field, and this inverse effect can be efficiently controlled by both, the values of $\Delta E$ and $m$. This is a very interesting result that can open new ways to tune and enhance electrocaloric properties of materials for future application.

Finally, in order to illustrate the strong modifications of the ECE coming from the application of a static transverse magnetic field, and consequently the appearance of Landau levels, the behavior of $\Delta S(T, B, \Delta E)$, for $\Delta E = 10^6$ V/m and 10 K, is presented in Figure 3, as a function of $m$ (inversely proportional to the magnetic field). It is important to remember that a maximum value for $m$ exists, deduced from Eqs. (1) and (4). The behavior of $\Delta S(T, B, \Delta E)$ as a function of $m$ is quite different and exotic, combining both periodic behavior of $S_{\operatorname{per}}(T, B, E)$ and oscillatory fashion of $S_{\cos}(T, B, E)$ and $S_{\operatorname{cor}}(T, B, 0)$. For the lowest values of magnetic field (higher values of $m$), an oscillatory behavior of $\Delta S(T, B, \Delta E)$ is found. Furthermore, the entropy change vanishes for half-integer $m$ values, but reaches local maximum for integer $m$ values—due to the $S_{\operatorname{cor}}(T, B, 0)$ contribution. A similar behavior was found for higher $B$ value (smaller $m$ values); however, with a difference that $\Delta S(T, B, \Delta E)$ nearly vanishes for even $m$ values and reaches local maximum for the subsequent odd values—due to the $S_{\operatorname{per}}(T, B, E)$ contribution. This property could be used like a on/off switch of the ECE of the material.

Summarizing, we have described the influence of an applied magnetic field on the electrocaloric properties of graphenes. A magnetic field promotes Landau levels and, consequently, two contributions on the entropy change: one with a periodic behavior and other with an oscillating fashion. Three important features of the ECE were observed. First, the presence of a magnetic field allows modifying the maximum of the entropy change value, as well as the temperature at which this maximum occurs. Second, by applying a magnetic field, the sign of ECE can be tuned, i.e., by either normal or inverse. Finally, changing the static magnetic field value can be a way to nearly switch off the ECE. Therefore, applying a constant magnetic field can be a very interesting way to control and tune important characteristics of the ECE, opening new ways to enhance electrocaloric utility in applications. The authors are convinced that these efforts can encourage studies of the influence of magnetic field in conventional and advanced electrocaloric materials.

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1M. Valant, Prog. Mater. Sci. 57, 980 (2012).