Influence of lithium doping on the thermodynamic properties of graphene based superconductors

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Abstract
The superconducting phase in graphene can be induced by doping its surface with lithium atoms. In this paper, it is shown that the critical temperature ($T_C$) for the LiC\textsubscript{6} and Li\textsubscript{2}C\textsubscript{6} compounds changes from 8.55 K to 21.83 K. The other thermodynamic parameters—the order parameter ($\Delta$), the specific heat for the superconducting ($C_S$) and the normal ($C_N$) state and the thermodynamic critical field ($H_C$)—differ from the predictions of the Bardeen–Cooper–Schrieffer theory. In particular, the ratio $R_{\Delta} \equiv 2\Delta(0)/k_B T_C$ is equal to $[3.72]_{\text{LiC}_6}$ and $[4.21]_{\text{Li}_2\text{C}_6}$. Additionally, the quantities $R_C \equiv \Delta C(T_C)/C_N(T_C)$ and $R_{HC} \equiv T_C C_N(T_C)/H_C^2(0)$ take the values $[1.47]_{\text{LiC}_6}$, $[1.79]_{\text{Li}_2\text{C}_6}$ and $[0.167]_{\text{LiC}_6}$, $[0.144]_{\text{Li}_2\text{C}_6}$. Finally, it is shown that the electron effective mass at $T_C$ is high and equals: $[1.61]_{\text{LiC}_6}$ and $[2.12]_{\text{Li}_2\text{C}_6}$.

Keywords: graphene, superconductivity, thermodynamic properties

(Some figures may appear in colour only in the online journal)

1. Introduction

At present, carbon allotropes constitute one of the most popular and promising research fields in condensed matter physics [1–3]. In particular, special attention is given to the two-dimensional one-atom-thick carbon structure known as graphene [4, 5]. The great interest in this material is driven by its numerous extraordinary electronic, thermal and mechanical properties [6–8]. As a consequence of these superior features, graphene is expected to have a variety of applications, particularly as a potential building block for future electronic devices [9, 10]. However, the usefulness of pristine graphene for electronics is somehow limited due to its semi-metallic character.

The semiconducting energy gap in graphene can be opened up by the structural or chemical modification of its pristine form [11, 12]. Structural modification or chemical doping can also enable the induction of the superconducting phase. We notice that the existence of the superconducting state in graphene is important since it may allow us to extend the available range of carbon-based nanoelectronics towards more efficient superconductor-quantum dot devices [13] or low-dimensional superconducting transistors [14].

Despite the semi-metallic character of pristine graphene (the low density of states at the Fermi level), there are two other reasons that make the induction of the superconducting state in this material difficult. First, the in-plane vibrations in graphene are very energetic. Second, there is no coupling between the in-plane $\pi$-type states and the out-of-plane vibrations [15]. In order to overcome these issues few solutions to this problem have been proposed.

Pioneering works predominantly concentrated on the existence of the Dirac points in the electron band energy function [16]. Another attempt concerned shifting the Fermi energy close to the van Hove singularity, in order to introduce mobile charge carriers above the Dirac points [17]. It should be noticed that this approach considered the unconventional pairing mechanism.
The preliminary investigations of the phonon-mediated superconducting state in graphene has been given in [18] and [19]. Similarly, as in [17], the investigations of the electron–phonon superconducting state has been made for energies above the Dirac point, though this time not close to the van Hove singularity. In particular, these papers discussed the valley structure of the order parameter and only suggested the possibility of inducing the superconducting state in graphene.

First quantitative predictions of the closely related graphene superconducting material known as graphane [20] has been proposed by Savini et al [21] on the basis of first-principles calculations. It has been shown that the p-doped graphane may lead to a superconducting transition temperature of a value above the boiling point of liquid nitrogen.

More progress on the conventional superconductivity in graphene has been made recently, when it was shown that the phonon-mediated superconducting state can be induced via deposition of lithium atoms on its surface [22]. In this study Profeta et al recalled the investigations on the graphite-intercalated compounds and showed that, due to the removal of quantum confinement, the lithium adatoms in graphene generate additional intra-layer states on the Fermi level, giving rise to the reasonably high electron–phonon coupling constant.

Although these findings are still not experimentally confirmed, recent experimental results show that the closely related lithium-intercalated bilayer graphene structures are stable [23]. Hence, the theoretical predictions given by Profeta et al can be considered as interesting and promising.

In the present paper, we have supplemented the results obtained in [22] by calculating the thermodynamic properties of LiC₆ and Li₂C₆ superconductors. Our analysis has been conducted within the framework of Eliashberg formalism [24], [25], which represents the strong-coupling generalization of the Bardeen–Cooper–Schrieffer theory (BCS) [26, 27].

We notice that recently such an implementation of the Eliashberg theory has been successfully applied to a description of the thermodynamics of the strong-coupling solid Li superconductor [28]. From a physical point of view it is important to note that Li is the superconductor with the relatively high critical temperature of (T_C = 18.2 K) when under high pressure (p = 33 GPa).

2. Theoretical model

The thermodynamic properties of phonon-mediated superconductors can be derived from knowledge of the Eliashberg spectral function α²F (Ω), where α denotes the average electron–phonon coupling, F (Ω) represents the phonon density of states and Ω is the phonon frequency.

The α²F (Ω) function can be obtained by first-principles methods or by the analysis of tunneling data. In this paper, we have taken into consideration the α²F (Ω) functions for LiC₆ and Li₂C₆ compounds, which have been calculated in [22]. We notice that these functions have been obtained by using first-principles methods (QUANTUM ESPRESSO package [29, 30]).

The Eliashberg equations have been solved on the imaginary axis and in the mixed representation (simultaneously on the imaginary and real axis) using the iterative method presented in [31–33]. In our calculations, we have taken into consideration the 1100 Matsubara frequencies: \( \alpha_m = \frac{\pi}{\beta} (2m - 1) \), where the parameter \( \beta \) is given by \( \beta \equiv 1/k_B T \), with \( k_B \) denoting the Boltzmann constant and \( T \) the temperature.
3. Results and discussion

We begin our analysis with the calculation of the order parameter on the imaginary axis ($\Delta_m \equiv \Delta(i\omega_m)$).

In figure 1, we show the dependence of the maximum value of the order parameter ($\Delta_{m=1}$) on temperature. The above results have been obtained on the basis of the data plotted in the insets, where the order parameter as a function of $m$ is shown.

It can be observed that the value of $\Delta_{m=1}$ strongly decreases with the growth of temperature and the decrease of lithium doping. This fact can be exactly parameterized by using the simple formula:

$$\Delta_{m=1} = \Delta_{m=1}(0) \sqrt{1 - \left(\frac{T}{T_C}\right)^\Gamma},$$

where $\Delta_{m=1}(0) \equiv \Delta_{m=1}(T_0)$ is equal to 1.36 meV and to 3.87 meV for LiC$_6$ and Li$_2$C$_6$, respectively. In both cases: $\Gamma = 3.25$.

We notice that, in the first approximation, the $\Delta_{m=1}$ function allows us to determine the value of the energy gap at the Fermi level.

The value of the critical temperature ($T_C$) has been extracted on the basis of the equation: $[\Delta_{m=1}]_k = 0$. The obtained values of $T_C$ are equal to 8.55 K and to 21.83 K for LiC$_6$ and Li$_2$C$_6$ superconductors.

In contrast to the order parameter, the maximum value of the wave function renormalization factor (Z$_{m=1}$) grows with increasing temperature, as presented in figure 2. However, Z$_{m=1}$ also increases rapidly with the lithium doping.

Similarly to the case of the order parameter, the dependence of Z$_{m=1}$ on the temperature for considered lithium doping can be parameterized by the simple formula:

$$Z_{m=1} = \left[ Z_{m=1}(T_C) - Z_{m=1}(T_0) \right] \left( \frac{T}{T_C} \right)^\Gamma + Z_{m=1}(T_0),$$

where $Z_{m=1}(T_C)$ assumes the value 1.61 for LiC$_6$ and 2.12 for Li$_2$C$_6$. We should emphasize that $Z_{m=1}(T_C)$ can be calculated on the basis of the expression: $Z_{m=1}(T_C) = 1 + \lambda$. Additionally, $Z_{m=1}(T_0)$ is equal to 1.6 and to 2.01 for LiC$_6$ and Li$_2$C$_6$, respectively.

As in the case of the order parameter, the function Z$_{m=1}$ has an important physical interpretation. In particular, it allows us to calculate the dependence of the electron effective mass ($m^*_e$) on the temperature: $m^*_e \approx Z_{m=1} m_e$, where $m_e$ denotes the band electron mass.

On the basis of figure 2, it is easy to see that the ratio $m^*_e / m_e$ strongly increases with the growth of the lithium doping.

In order to determine the temperature dependence of the thermodynamic critical field and the specific heat, the free energy difference between the superconducting and normal state has been calculated:

$$\frac{\Delta F}{\rho(0)} = -\frac{2\pi}{\beta} \sum_{\omega_m} \left( \sqrt{\omega_m^2 + \Delta_m^2} - 1 - \omega_m \right) \left( Z_m^S - Z_m^N \frac{1}{\sqrt{\omega_m^2 + \Delta_m^2}} \right),$$

where the symbol $\rho(0)$ denotes the electron density of states at the Fermi level and $Z_m^S$ and $Z_m^N$ represent the wave function renormalization factor for the superconducting (S) and normal (N) state.

The results obtained for the ratio $\Delta F/\rho(0)$ have been presented in the lower panel of figure 3(a). From the physical point of view, $\Delta F/\rho(0)$ determines the thermodynamic stability of the superconducting phase. Taking into account the data plotted in figure 3(a), it can be seen that the increasing lithium doping substantially strengthens the stability of the superconducting state in graphene.

The thermodynamic critical field is given by:

$$\frac{H_c}{\sqrt{\rho(0)}} = \sqrt{-8\pi [\Delta F/\rho(0)]}.$$  

In the upper panel of figure 3(a), we show the dependence of $H_c/\sqrt{\rho(0)}$ on temperature. The influence of the lithium doping on the critical field is also very big.
The difference between the specific heat of the superconducting ($C^S$) and normal ($C^N$) state can be calculated by using the expression:

$$\Delta C(T) = \frac{1}{k_B \rho(0)} \int \frac{d^3 [\Delta F / \rho(0)]}{dT^2} \frac{1}{\beta} d(k_BT)^2. \tag{5}$$

On the other hand, the normal-state specific heat is given as:

$$C^N(T) = \frac{\gamma}{\beta}, \tag{6}$$

where the Sommerfeld constant has the form:

$$\gamma = \frac{2}{3} \pi^2 (1 + \lambda).$$

In figures 3(b) and (c), the specific heat for the normal and superconducting state is presented. For both considered compounds, the characteristic specific heat jump at the critical temperature is marked by the vertical line.

The results obtained for the thermodynamic critical field and the specific heats allows us to estimate the values of the corresponding characteristic dimensionless ratios [26, 27]:

$$R_H \equiv \frac{T_c C^N(T_c)}{H^2(0)} \quad \text{and} \quad R_C \equiv \frac{\Delta C(T_c)}{C^N(T_c)}. \tag{7}$$

In particular, we have: $R_H=0.167$ and $R_C=1.47$ for Li$_2$C$_6$ and $R_H=0.144$ and $R_C=1.79$ for LiC$_6$. We notice that the BCS theory predicts: $R_H=0.168$ and $R_C=1.43$.

In the first part of this paper we presented our estimations of the energy gap on the basis of the Eliashberg solution on the imaginary axis. However, in order to determine the exact value of the order parameter, the solutions of the Eliashberg equations on the imaginary axis should be analytically continued on the real axis ($\omega$). For this purpose, we have numerically solved the Eliashberg equations in the mixed representation (see figure 4).

The obtained results allows us to estimate the physical value of the order parameter [24, 25]:

$$\Delta(T) = \text{Re} \{ \Delta(\omega = \Delta(T), T) \}. \tag{8}$$

In particular, the extracted values of the order parameter close to zero Kelvin are: $\Delta(0) = 1.37$ meV for LiC$_6$ and $\Delta(0) = 3.96$ meV for Li$_2$C$_6$.

The real-axis analysis allows us to additionally determine the dimensionless ratio: $R_\Delta \equiv 2\Delta(0)/k_BT_c$. In our case, the estimated values are: $R_\Delta = 3.72$ for LiC$_6$ and $R_\Delta = 4.21$ for Li$_2$C$_6$. The above results indicate that $R_\Delta$ for Li$_2$C$_6$ considerably exceeds the value predicted by the BCS theory ($[R_\Delta]_{\text{BCS}} = 3.53$) [26, 27].

### 4. Summary

In the present paper, we have calculated the thermodynamic properties of the lithium doped graphene superconductors LiC$_6$ and Li$_2$C$_6$.

Our analysis has predicted that the value of the critical temperature strongly rises together with the increase of the lithium doping. In particular, from 8.6 K for LiC$_6$ to 21.8 K for Li$_2$C$_6$.

The calculated values of the dimensionless parameters, which describe the zero-temperature energy gap to the critical temperature, the ratio of the specific heats, as well as the ratio connected with the zero-temperature thermodynamic critical field, exceed the predictions of the classical BCS theory (see table 1). The discrepancies between our results and the BCS estimates arise due to the occurrence of the retardation and strong-coupling effects in the LiC$_6$ and Li$_2$C$_6$ superconductors. We notice that these effects are completely omitted in the mean-field BCS theory and well described in the Eliashberg formalism by the parameter.


\[ r \equiv \frac{k_BT_c}{\omega_{ln}}, \text{ where } \omega_{ln} \text{ denotes the logarithmic phonon frequency: } \omega_{ln} \equiv \exp \left[ \frac{2}{\lambda} \int_{0}^{\Theta_{ln}} \frac{\alpha^2 F(\Omega)}{\Theta} \ln(\Theta) d\Omega \right] \quad [25]. \]

For the considered compounds, we have obtained: [\( r_{BCS} = 0.02 \) and \( r_{BCS} = 0.09 \)], but \( r \to 0 \) in the BCS limit.

To this end, the electron effective mass also increases together with the lithium doping.

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