Proceedings of "Applications of Physics in Mechanical and Material Engineering" (APMME 2024)

The Superconducting State of the LiC_6 Compound: The Effective Triangular Lattice Model

R. Szczęśniak*

Division of Physics, Czestochowa University of Technology, al. Armii Krajowej 19, 42-200 Częstochowa, Poland

Doi: 10.12693/APhysPolA.147.236

*e-mail: radoslaw.szczesniak@pcz.pl

Thermodynamic parameters of the superconducting state of the LiC₆ compound were calculated. Based on experimental data and results obtained using the density functional theory, the following input parameters for the effective triangular lattice model were adopted: hopping integral t = 355 meV, chemical potential $\mu = -4.37t$, Coulomb pseudopotential $\mu^* = 0.01$, phonon energy $\omega_0 = 0.052t$, and electronphonon interaction energy $g_0 = 0.00931t$. Calculations allowed us to reproduce the experimental values of the electron-phonon coupling constant $\lambda = 0.58 \pm 0.05$ and critical temperature $T_C = 5.9$ K. The dimensionless thermodynamic ratios were as follows: $R_{\Delta} = 3.73$, $R_C = 1.71$, and $R_H = 0.16$. The obtained R_{Δ} , R_C , R_H values were compared with experimental data and density functional theory. It was shown that within the framework of the effective triangular lattice model, the thermodynamic properties of the superconducting phase of LiC₆ can be correctly reproduced. Additionally, the anisotropic structure of the electron-phonon coupling function and the anisotropic logarithmic phonon frequency function were discussed.

topics: LiC₆ compound, phonon-induced superconducting state, thermodynamic parameters

1. Introduction

In 2004, the existence of graphene — a twodimensional hexagonal structure of carbon — was experimentally confirmed [1, 2]. Extensive research has shown that it possesses unprecedented physical properties such as [3] low resistivity, high tensile strength, high elasticity, nearly 98% transparency, and high thermal conductivity. Graphene can also be used as a membrane that does not allow even helium atoms to pass through.

Theoretical calculations suggest that the electron-phonon coupling energy for graphene is relatively high ($g \sim 476 \text{ meV}$) [4], and the Debye frequency is also high ($\omega_{\rm D} \sim 192 \text{ meV}$) [5]. However, the electronic structure of pure graphene prevents the existence of a superconducting state due to the zero value of the electronic density of states at the Fermi level [6]. This fact can be explained by analyzing the energy spectrum of the effective Hamiltonian of the considered system, which has the structure of a two-dimensional Dirac Hamiltonian [3].

Undoubtedly, a significant achievement in the context of solid-state physics was the indication of the existence of a superconducting state in lithiumdoped graphene [7]. It was found that the critical temperature is 5.9 K, and the electron-phonon coupling constant ranges from 0.53 to 0.63 [8]. In the present work, based on experimental data and density functional theory (DFT) results, we estimate the input values of an effective model for the LiC_6 compound. Then, within the framework of this model, we calculate the basic thermodynamic parameters of the superconducting phase. It is worth noting that the effective triangular lattice (ETL) model is explicitly anisotropic, which potentially allows for a much more accurate characterization of the superconducting state than the isotropic formalism.

2. Model

The structure of electronic, phonon, and electron-phonon interactions for the LiC_6 compound can be described using the Fröhlich Hamiltonian [9]

$$H = \sum_{k} (\varepsilon_{k} - \mu) \Psi_{k}^{\dagger} \tau_{3} \Psi_{k} + \sum_{q} \omega_{q} b_{q}^{\dagger} b_{q} + \sum_{kq} g_{q} \Psi_{k+q}^{\dagger} \tau_{3} \Psi_{k} \phi_{q}, \qquad (1)$$

where $\Psi_{\mathbf{k}}^{\dagger}$ is the Hermitian conjugate Nambu spinor $\Psi_{\mathbf{k}}^{\dagger} = (c_{\mathbf{k}\uparrow}^{\dagger}, c_{-\mathbf{k}\downarrow})$. The creation operator of an electronic state with momentum \mathbf{k} and spin $\sigma \in \{\uparrow, \downarrow\}$ is denoted by $c_{\mathbf{k}\sigma}^{\dagger}$. Additionally, $\phi_{\mathbf{q}} = b_{\mathbf{q}} + b_{-\mathbf{q}}^{\dagger}$,



Fig. 1. (a) The electronic density of states function with the Fermi level. (b) The phonon density of states function and the rescaled Eliashberg function of the LiC_6 compound obtained using the DFT method [7]. (c) The electron-phonon density of states function.

where $b_{\boldsymbol{q}}^{\dagger}$ represents the creation operator of a phonon state with momentum \boldsymbol{q} . The energy μ is the chemical potential. The electronic dispersion relation for the triangular lattice is given by

$$\varepsilon_{\boldsymbol{k}} = -2t \left[\cos(k_x) + 2\cos\left(\frac{k_x}{2}\right)\cos\left(\frac{\sqrt{3}}{2}k_y\right) \right],\tag{2}$$

where the lattice constant is taken as unity. In this work, we consider electron hopping between nearest neighbors; t is the hopping energy. The phonon dispersion relation is

$$\omega_{\boldsymbol{q}} = \omega_0 \sqrt{3 - \cos\left(q_x\right) - 2\cos\left(\frac{q_x}{2}\right)\cos\left(\frac{\sqrt{3}}{2}q_y\right)},\tag{3}$$

where ω_0 denotes the phonon energy. The electronphonon interaction function explicitly depends on the phonon momentum [10]

$$g_{\boldsymbol{q}} = g_0 |\boldsymbol{q}| / \sqrt{\omega_{\boldsymbol{q}}},\tag{4}$$

where g_0 represents the electron-phonon interaction energy. Note that g_q possesses a structure predicted by Bloch [11]. The functions ε_k , ω_q , and g_q are symmetric. Considering their symmetry potentially simplifies numerical calculations performed at the level of anisotropic Eliashberg equations [12].

3. Input parameters of the model

The effective triangular lattice model has several input parameters that must be accurately determined based on experimental data or results obtained using the DFT method [13].

The values of the hopping integral t and the chemical potential μ were determined in the work [14]. Based on the DFT results [7], the values obtained were t = 355 meV and $\mu = -4.37 t$. In the considered case, the lower and upper bounds of the electronic band are, respectively, $W_d = -1.63 t$ and $W_u = 7.36 t$.

With these data, the electronic density of states function can be calculated. The formula used is $\rho(\varepsilon) = \frac{1}{N} \sum_{k} \delta(\varepsilon - \varepsilon_{k})$, where $\delta(x)$ represents

the Dirac distribution approximated by $\delta(x) = \frac{1}{\pi} \frac{a}{a2+x2}$. In numerical calculations, a = 0.005 t was adopted.

Figure 1a shows the electronic density of states for the LiC_6 compound and indicates the position of the Fermi level ($\varepsilon_{\rm F}$). It can be seen that the characteristic maximum of the function $\rho(\varepsilon)$ is far from $\varepsilon_{\rm F}$. As a result, the electronic density of states at the Fermi level is relatively low, namely $\rho(\varepsilon_{\rm F}) = 0.043 t^{-1}$. This fact is one of the reasons responsible for the relatively low critical temperature of the phase transition to the superconducting state in the LiC₆ compound , i.e., $T_C = 5.9$ K [8]. It should be noted that in the analyzed case the geometry of the crystal lattice of the analyzed system plays an important role. From the perspective of expectations related to high values of T_C , a square lattice geometry with a half-filled conduction band is significantly more advantageous. This situation occurs in cuprates [15], where critical temperatures at least an order of magnitude higher than those observed for the LiC_6 compound have been observed experimentally.

When determining the thermodynamic parameters of the superconducting state of the LiC₆ compound, it is necessary to know the value of the Coulomb pseudopotential (μ^*). This quantity characterizes the depairing electronic correlations [16]. To estimate it, the empirical formula given by Bennemann and Garland [17] was used, which is

$$\mu^{\star} = 0.26 \, \frac{\rho\left(\varepsilon_{\rm F}\right)}{1 + \rho\left(\varepsilon_{\rm F}\right)}.\tag{5}$$

Substituting the obtained value of the electronic density of states at the Fermi level, we get $\mu^* = 0.011$. This result indicates that the electronic correlations unfavorable to the formation of the superconducting phase in the LiC₆ compound are significantly weaker than it would result from the isotropic Eliashberg equations ($\mu^* = 0.114$) [18].

The next parameter that was estimated is the phonon energy ω_0 . In this case, ω_0 was chosen so that the maximum of the phonon density of states, $F(\omega) = \frac{1}{N} \sum_{\boldsymbol{q}} \delta(\omega - \omega_{\boldsymbol{q}})$, coincided with the dominant low-energy maximum of the Eliashberg function determined by the DFT method [7].



Fig. 2. Isotropic Eliashberg function for the LiC_6 superconductor determined within the ETL model.



Fig. 3. Anisotropic Eliashberg function for the LiC_6 superconductor determined within the ETL model ($\omega = 0.105 t$ was assumed).

The applied procedure is illustrated in Fig. 1b. It should be noted that the remaining part of the Eliashberg function corresponds to much higher phonon energy values. This means that these areas do not contribute significantly to the electron-phonon coupling constant. This is because the constant is calculated using the integral of the ratio of the Eliashberg function to the phonon frequency. As a result of the analysis, $\omega_0 = 0.052t$ was obtained. Additionally, in the ETL model the Debye frequency value is $\omega_{\rm D} = 0.25t$.

The value of the parameter g_0 was chosen to reproduce the experimental value of the electronphonon coupling constant, which for LiC₆ is $\lambda = 0.58 \pm 0.05$ [8]. The obtained results are presented in Table I. It can be assumed that the correct value of the electron-phonon interaction energy is 0.00931 t, since the corresponding critical temperature, calculated based on the Allen-Dynes formula [19], accurately reproduces the experimentally observed critical temperature ($T_C = 5.9$ K [8]). The full electron-phonon density of states for the LiC₆ compound is shown in Fig. 1c. This quantity was calculated based on the formula $P(\omega) = \frac{1}{N} \sum_{q} \delta(\omega - g_q)$.

Spectral function of the electron-phonon interaction (Eliashberg function) $\alpha^2 F(\mathbf{k}, \mathbf{k}', \omega) = \rho(\varepsilon_{\rm F}) \sum_{\mathbf{q}} |g(\mathbf{q}, \mathbf{k}, \mathbf{k}')|^2 \,\delta(\omega - \omega_{\mathbf{q}})$ was calculated assuming $g(\mathbf{q}, \mathbf{k}, \mathbf{k}') \simeq g_{\mathbf{q}}$. To obtain the isotropic



Fig. 4. Anisotropic electron-phonon coupling function for the LiC_6 superconductor.

TABLE I

The electron-phonon interaction energy g_0 , the value of the electron-phonon coupling constant λ , and the critical temperature T_C .

$g_0 [t]$	λ	T_C [K]
0.00922	0.53	5.7
0.00931	0.545	5.9
0.01	0.63	7.8

Eliashberg function $(\alpha^2 F(\omega))$, the exact Eliashberg function needs to be averaged over the Fermi surface, thus $\alpha^2 F(\omega) = \frac{1}{N^2} \sum_{\mathbf{k},\mathbf{k}'} w_{\mathbf{k}} w_{\mathbf{k}'} F(\mathbf{k},\mathbf{k}',\omega)$, where $w_{\mathbf{k}} = \delta(\varepsilon_{\mathbf{k}})/\rho(\varepsilon_{\mathrm{F}})$. Calculations lead to the result

$$\alpha^{2}F(\omega) = \rho(\varepsilon_{\rm F})\sum_{\boldsymbol{q}} g_{\boldsymbol{q}}^{2}\delta(\omega - \omega_{\boldsymbol{q}}).$$
(6)

Equation (6) represents the Eliashberg function that can be used to calculate all important thermodynamic quantities characterizing the properties of the superconducting state in the isotropic approximation. This is because we know all the input parameters of the ETL model.

The function $\alpha^2 F(\omega)$ for the LiC₆ compound is plotted in Fig. 2. It can be seen that the dominant contribution to the electron-phonon coupling constant comes from the maximum located around the point $\omega = 0.105 t$.

The ETL model for the LiC₆ compound allows for the analysis of the superconducting state's properties beyond the standard isotropic approximation. The approach proposed in this work explicitly takes into account the dependence of the model parameters on the phonon momentum \boldsymbol{q} . In particular, we consider the anisotropic Eliashberg function given by $\alpha^2 F_{\boldsymbol{q}}(\omega) = \rho(\varepsilon_{\rm F}) g_{\boldsymbol{q}}^2 \delta(\omega - \omega_{\boldsymbol{q}})$, the form of which is shown in Fig. 3. Based on $\alpha^2 F_{\boldsymbol{q}}(\omega)$, one can determine the anisotropic electron-phonon coupling function (λ_q) and the anisotropic logarithmic frequency $(\omega_{\ln}^{(q)})$. These quantities are related to their isotropic counterparts, as follows $\lambda = \sum_q \lambda_q$ and $\ln(\omega_{\ln}) = \sum_q \omega_{\ln}^{(q)} / \lambda$, where

$$\lambda_{\boldsymbol{q}} = 2\rho\left(\varepsilon_{\mathrm{F}}\right)\frac{g_{\boldsymbol{q}}^2}{\omega_{\boldsymbol{q}}},\tag{7}$$

$$\omega_{\rm ln}^{(\boldsymbol{q})} = 2\rho\left(\varepsilon_{\rm F}\right) \frac{g_{\boldsymbol{q}}^2}{\omega_{\boldsymbol{q}\,\rm ln}} \left(\omega_{\boldsymbol{q}}\right). \tag{8}$$

It turns out that the extreme values of the functions $\lambda_{\boldsymbol{q}}$ and $\omega_{\ln}^{(\boldsymbol{q})}$ occur in the corners of the first Brillouin zone. This situation is illustrated in Fig. 4.

4. Thermodynamic parameters of the superconducting state

The critical temperature within the Migdal– Eliashberg model, due to the low value of the electron–phonon coupling constant ($\lambda = 2 \int_0^{\omega_{\rm D}} d\omega \ \alpha^2 F(\omega)/\omega = 0.545$), can be estimated using the Allen–Dynes formula [19]

$$k_{\rm B} T_C^{\rm AD} = f_1 f_2 \, \frac{\omega_{\rm ln}}{1.2} \exp\left(\frac{-1.04\,(1+\lambda)}{\lambda - \mu^\star \,(1+0.62\lambda)}\right). \tag{9}$$

The correction functions f_1 and f_2 are given by

$$f_1 = \sqrt[3]{1 + \left(\frac{\lambda}{\Lambda_1}\right)^{\frac{3}{2}}},$$

$$f_2 = 1 + \frac{\lambda^2}{\lambda^2 + \Lambda_2^2} \left(\frac{\sqrt{\omega_2}}{\omega_{\ln}} - 1\right),$$
(10)

where $\Lambda_1 = 2.46 (1 + 3.8\mu^*)$ and $\Lambda_2 = 1.82 (1 + 6.3\mu^*) \sqrt{\omega_2}/\omega_{\rm ln}$. The logarithmic phonon frequency and the second moment of the normalized weight function are respectively $\omega_{\rm ln} = \exp\left[\frac{2}{\lambda}\int_0^{\omega_{\rm D}} \mathrm{d}\omega \ln(\omega)\alpha^2 F(\omega)/\omega\right] = 0.034 t$ and $\omega_2 = \frac{2}{\lambda}\int_0^{\omega_{\rm D}} \mathrm{d}\omega \omega \alpha^2 F(\omega) = 0.008 t^2$. As a result, we have $k_{\rm B}T_C = 0.00143 t$. Assuming t = 355 meV, we get $T_C = 5.9$ K. We can also calculate the dimensionless coefficients of the superconducting state

$$R_{\Delta} = \frac{2\Delta(0)}{k_{\rm B}T_C},\tag{11}$$

$$R_C = \frac{\Delta C \left(T_C\right)}{C^N \left(T_C\right)},\tag{12}$$

$$R_H = \frac{T_C C^N (T_C)}{H_C^2 (0)},$$
(13)

where $\Delta(0)$ denotes the value of the order parameter at zero Kelvin, $\Delta C(T_C)$ is the value of the specific heat jump at the critical temperature, $C^N(T_C)$ represents the value of the normal state heat capacity at the critical temperature, and $H_C(0)$ is the value of the thermodynamic critical field at zero Kelvin. In Bardeen–Cooper–Schrieffer (BCS) theory, the parameters R_{Δ} , R_C , and R_H have universal values of 3.53, 1.43, and 0.168, respectively [20, 21]. This is not necessarily the case in the Migdal–Eliashberg theory. Therefore, these quantities should be calculated using the formulas [22]

$$R_{\Delta} = 3.53 \left[1 + 12.5 \left(\frac{T_C}{\omega_{\ln}} \right)^2 \ln \left(\frac{\omega_{\ln}}{2T_C} \right) \right], \qquad (14)$$

$$R_C = 1.43 \left[1 + 53 \left(\frac{T_C}{\omega_{\ln}} \right)^2 \ln \left(\frac{\omega_{\ln}}{3T_C} \right) \right], \qquad (15)$$

$$R_H = 0.168 \left[1 - 12.2 \left(\frac{T_C}{\omega_{\ln}} \right)^2 \ln \left(\frac{\omega_{\ln}}{3T_C} \right) \right].$$
(16)

After performing numerical calculations, we obtain $R_{\Delta} = 3.73$, $R_C = 1.71$, and $R_H = 0.160$. It turns out that the obtained results closely correspond to the results obtained using the Eliashberg function derived from experimental data [8], namely $[R_{\Delta}]_{\text{Exp.}} = 3.58$, $[R_C]_{\text{Exp.}} = 1.51$, and $[R_H]_{\text{Exp.}} = 0.166$. Similar results can also be obtained by taking as a starting point the Eliashberg function calculated using the DFT method [7], i.e., $[R_{\Delta}]_{\text{DFT}} = 3.60, [R_C]_{\text{DFT}} = 1.54, \text{ and } [R_H]_{\text{DFT}} =$ 0.165. However, in the considered case the critical temperature is slightly overestimated T_C = 8.1 K [7]. Self-consistent calculations performed at the level of the Eliashberg equations gave similar results [23], namely $[R_{\Delta}]_{\text{DFT}} = 3.72 \ ([R_{\Delta}]_{\text{Exp.}} = 3.71),$ $[R_C]_{\text{DFT}} = 1.47$, and $[R_H]_{\text{DFT}} = 0.167$. Selected properties of the superconducting state of the compound LiC_6 were also analyzed within the isotropic Eliashberg formalism, which included vertex corrections to the electron-phonon interaction. In the considered approach, the following result was obtained [18]: $[R_{\Delta}]_{\text{DFT}} = 4.57 \ ([R_{\Delta}]_{\text{Exp.}} = 4.37).$

5. Conclusions

In this work, using an effective model based on a triangular lattice, we calculated the basic thermodynamic parameters of the superconducting state induced in the LiC_6 compound. The obtained results were compared with experimental data and DFT theory results. We demonstrated that within the framework of the considered model, it is possible to correctly reproduce the properties of the superconducting phase in the LiC_6 compound.

It is worth noting that due to its relative simplicity, the ETL model allows for a full anisotropic analysis of the superconducting state. For this purpose, it is necessary to numerically solve the appropriate Eliashberg equations. This issue was analyzed by us for the case of a square lattice in the work [12]. Currently, we are working on solving the anisotropic Eliashberg equations for the LiC₆ compound.

References

- K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* 306, 666 (2004).
- [2] C. Berger, Z. Song, T. Li et al., J. Phys. Chem. B 108, 19912 (2004).
- [3] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, *Rev. Mod. Phys.* 81, 109 (2009).
- [4] C.-H. Park, F. Giustino, M.L. Cohen, S.G. Louie, *Phys. Rev. Lett.* **99**, 086804 (2007).
- [5] D.K. Efetov, Ph.D. Thesis, Columbia University 2014.
- [6] P.R. Wallace, *Phys. Rev.* **71**, 622 (1947).
- [7] G. Profeta, M. Calandra, F. Mauri, *Nat. Phys.* 8, 131 (2012).
- [8] B.M. Ludbrook, G. Levy, P. Nigge et al., *Proc. Natl. Acad. Sci.* **112**, 11795 (2015).
- [9] H. Fröhlich, Proc. R. Soc. Lond. A 215, 291 (1952).
- [10] M.P. Allan, M.H. Fischer, O. Ostojic, A. Andringa, *SciPost Phys.* 3, 010 (2017).
- [11] F.Z. Bloch, Z. Phys. 52, 555 (1928).
- [12] K.A. Szewczyk, M.W. Jarosik, A.P. Durajski, R. Szczęśniak, *Phys. B Condens. Matter* 600, 412613 (2021).

- [13] R.G. Parr, W. Yang, *Density-functional Theory of Atoms and Molecules*, Oxford University Press, Oxford 1989.
- [14] K.A. Krok, M.M. Adamczyk, A.P. Durajski, R. Szczęśniak, *Phys. Rev. B* 108, 054512 (2023).
- [15] J.G. Bednorz, K.A. Müller, *Rev. Mod. Phys.* **60**, 585 (1988).
- [16] P. Morel, P.W. Anderson, *Phys. Rev.* 125, 1263 (1963).
- K.H. Bennemann, J.W. Garland, in: Superconductivity in d- and f-Band Metals, Ed. D.H. Doughlas, AIP, New York 1972.
- [18] D. Szczęśniak, R. Szczęśniak, *Phys. Rev. B* 99, 224512 (2019).
- [19] P.B. Allen, R.C. Dynes, *Phys. Rev. B* 12, 905 (1975).
- [20] J. Bardeen, L.N. Cooper, J.R. Schrieffer, *Phys. Rev.* **106**, 162 (1957).
- [21] J. Bardeen, L.N. Cooper, J.R. Schrieffer, *Phys. Rev.* 108, 1175 (1957).
- [22] J.P. Carbotte, Rev. Mod. Phys. 62, 1027 (1990).
- [23] D. Szczęśniak, A.P. Durajski, R. Szczęśniak, J. Phys. Condens. Matter 26, 255701 (2014).