First-principles calculations of the superconducting properties in Li-decorated monolayer graphene within the anisotropic Migdal-Eliashberg formalism

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The \textit{ab initio} anisotropic Migdal-Eliashberg formalism has been used to examine the pairing mechanism and the nature of the superconducting gap in the recently discovered lithium-decorated monolayer graphene superconductor. Our results provide evidence that the superconducting transition in Li-decorated monolayer graphene can be explained within a standard phonon-mediated mechanism. We predict a single anisotropic superconducting gap and a critical temperature $T_c = 5.1\text{--}7.6\ K$, in very good agreement with the experimental results.

\section*{INTRODUCTION}

During the past decade graphene has revolutionized many areas of nanotechnology from organic electronics to photovoltaics, plasmonics, photonics, and energy storage \cite{1}. One notable application that was missing from this list was superconductivity, despite numerous theoretical predictions of either a conventional or an unconventional pairing mechanism \cite{2,3,4,5,6}. Very recently, a high-resolution angle-resolved photoemission spectroscopy (ARPES) study has presented evidence supporting the appearance of a superconducting phase in Li-decorated monolayer graphene (LiC$_6$) around $5.9\ K$ \cite{8}, within the standard phonon-mediated coupling mechanism. This work has been followed by two more studies that reported the observation of superconductivity in Ca-intercalated bilayer graphene \cite{9} and in Ca-intercalated graphene laminates \cite{10}.

In this article, we investigate from first principles the nature of the superconducting gap in LiC$_6$. To this end, we solve the fully anisotropic Migdal-Eliashberg equations \cite{11,12} to obtain the superconducting transition temperature ($T_c$) and the variation of the superconducting energy gap on the Fermi surface. While previous \textit{ab initio} calculations have shown that the electron-phonon coupling is sufficient to yield a critical temperature in $6.7\text{--}10.3\ K$ range using the Allen-Dynes formula \cite{3,13,14} or the isotropic Eliashberg formalism \cite{15}, the nature of the superconducting gap has not yet been addressed. We find that, similar to bulk CaC$_6$ \cite{15,16,17,18}, Li-decorated monolayer graphene exhibits a single anisotropic gap in agreement with the experimental work \cite{8}.

\section*{METHODOLOGY}

The calculations are performed within the local density approximation to density-functional theory \cite{19,20} using planewaves and norm-conserving pseudopotentials \cite{21,22}, as implemented in the \textit{Quantum-ESPRESSO} package \cite{23}. The planewaves kinetic energy cutoff is 100 Ry and the structural optimization is performed until the forces on atoms are less than 10 meV/Å. Li-decorated monolayer graphene is described in the $\sqrt{3} \times \sqrt{3} R30^\circ$ graphene supercell with one lithium atom per unit cell. The optimized lattice constant and the adatom-graphene distance are $a = 4.24\ \text{Å}$ and $h = 1.78\ \text{Å}$. A Brillouin-zone (BZ) $\Gamma$–centered k-point mesh of $24 \times 24$ and a Methfessel-Paxton smearing \cite{24} of 0.02 Ry are adopted for the electronic charge density calculations. The phonon modes are computed within density-functional perturbation theory \cite{25} on a $6 \times 6$ $\mathbf{q}$-mesh. We employ...
the EPW code [12, 20, 29] to obtain the superconductive gap. The calculation of the electronic wavefunctions required for the Wannier-Fourier interpolation [30, 31] in EPW is performed on a uniform unshifted BZ k-point grid of size 12×12. For the anisotropic Eliashberg equations, we use 120×120 and 60×60 k- and q-point grids. The Matsubara frequency cutoff is set to five times the largest phonon frequency (5×200 meV), and the Dirac delta functions are replaced by Lorentzians of widths 100 meV and 0.5 meV for electrons and phonons, respectively.

**ELECTRONIC AND VIBRATIONAL PROPERTIES**

In Figs. 1 (a)-(c), we show the crystal structure of Li-decorated monolayer graphene along with the corresponding decomposed electronic band structure and Fermi surface. Three bands cross the Fermi level around the Γ point, in agreement with previous reports [3, 13]. The inner and outer C π* bands, labeled as α and β (blue dots), are obtained by folding the π* states of graphene from K to Γ, following the superstructure induced by Li adsorption. The Li-derived band, labeled as IL (red dots), displays a nearly-free electron like dispersion upwards from about 0.56 eV below the Fermi energy. Similar weakly bound free-electron states have been observed in other layered materials [3, 32, 34] and nanotubes [35], and their rapid downshift under doping is due to the combined effects of quantum confinement and electrostatic response [3, 33, 35]. The corresponding Fermi surface of LiC₆ can be divided into two concentric regions centered around the Γ point. The inner region is characterized by a snowflake-like electron pocket intersecting a hexagonal electron pocket, which arises from the mixing of the inner C π* states with the Li s states. These Fermi sheets resemble the Γ-centered Fermi surface observed in Ca and Li intercalated bilayer graphene [17, 36]. The outer region also has a snowflake-like shape and originates on the outer C π* states and the Li s states.

We now focus on the vibrational properties and the electron-phonon coupling (EPC) in LiC₆. Similar to bulk CaC₆ [32] and bilayer Ca₆CaC₆ [17], one can clearly identify in Fig. 2(a) three regions in the phonon dispersion associated to (i) the Li-related modes (up to 50 meV, where above 37 meV are Li₂ modes mixed with carbon out-of-plane C₂ modes), (ii) the carbon out-of-plane Cₓₙ modes (50-100 meV), and (iii) the carbon in-plane Cₓᵧ modes (above 100 meV). The size of the symbols in Fig. 2(a) is proportional to the atomic displacements corresponding to Li and C in-plane and out-of-plane contributions.

The isotropic Eliashberg spectral function α²F(ω)

\[ \alpha^2 F(\omega) = \frac{1}{N_F N_k N_q} \sum_{k,k',\nu} |g_{kk'}|^2 \delta(\epsilon_k) \delta(\epsilon_{k'}) \delta(\omega - \omega_{q\nu}), \]

and the cumulative electron-phonon coupling strength λ(ω)

\[ \lambda(\omega) = 2 \int_0^\omega d\omega' \alpha^2 F(\omega')/\omega', \]

FIG. 2: (Color online) (a) Phonon frequency dispersion of LiC₆. The decomposition of the phonon spectrum with respect to C and Li atomic vibrations is indicated by: olive circle (Cπ), blue diamond (Cπy), red triangle up (Liπy), and green triangle down (Liπ). (b) Phonon density of states and (c) Eliashberg spectral function with cumulative electron-phonon coupling strength of LiC₆. The solid line is for α²F(ω), the dashed line is for λ(ω).
are shown in Figs. 2(b)-(c). In these expressions, \( N_F \) represents the density of electronic states per spin at the Fermi level, \( N_k \) and \( N_q \) are the total numbers of \( k \) and \( q \) points, \( \epsilon_k \) is the Kohn-Sham eigenvalue with respect to the Fermi level, and \( g^{\nu k' k} \) is the screened electron-phonon matrix element for the scattering between the electronic states \( k \) and \( k' \) through a phonon with wave vector \( q \) = \( k' - k \), frequency \( \omega_{q \nu} \) and branch index \( \nu \). Here \( k \) and \( k' \) indicate both the electron wavevector and the band index. We find that the low-energy phonons are key to achieving a high electron-phonon coupling in LiC\(_6\) as they account for 0.28 (51\%) of the total EPC (\( \lambda = 0.55 \)). On the other hand, the electron-phonon coupling strengths associated with the out-of-plane \( C_{z} \) and in-plane \( C_{xy} \) modes are 0.12 (22\%) and 0.15 (27\%), respectively. Such behavior has also been found in bilayer C\(_6\)CaC\(_6\), where the most significant contribution to the EPC comes from the low-energy phonon modes \([17]\). Overall, our calculated EPC \( \lambda = 0.55 \) is in good agreement with experimental value 0.58 ± 0.05 observed at the highest Li coverage \([8]\) and the values reported in previous theoretical studies \([3, 13]\).

To quantify the anisotropy in the electron-phonon coupling, we further evaluate the momentum-resolved EPC \( \lambda_k \) \([12]\), defined as:

\[
\lambda_k = \sum_{k', \nu} \delta(\epsilon_{k'}) |g^{\nu k' k}_{kk'}|^2 / \omega_{q \nu}.
\]

The calculated \( \lambda_k \) displays a significant anisotropy with a distribution in the 0.42-0.78 range as shown in Fig. 3. This is in line with experimental ARPES measurements where a marked anisotropy in the electron-phonon coupling has been observed in the case of decorated graphene \([3, 37]\), intercalated bilayer graphene \([38]\), and intercalated graphite \([39, 40]\). An alternative way to look at the EPC anisotropy is presented in the inset of Fig. 3 where the variation of \( \lambda_k \) on the Fermi surface is shown. When compared with the Fermi surface plot in Fig. 1(c), one can clearly see that the largest value of \( \lambda_k \) is attained on the portions of the Fermi surface dominated by the Li states. Notably, in bulk CaC\(_6\), \( \lambda_k \) was also found to be larger for the states with Ca dominant orbital character on the Fermi surface \([16]\). An important implication of this finding is that the IL state and its associated interaction play a critical role in the superconducting paring of LiC\(_6\). A recent ARPES study has provided compelling evidence regarding the importance of the IL band in the pairing mechanism of bulk CaC\(_6\) \([41]\). Furthermore, the lack of any sign of superconductivity down to 3.5 K in few-layer graphene under large charge doping induced by electrochemical gating \([42]\) provides additional proof of the vital role of dopant atoms.

**SUPERCONDUCTING PROPERTIES**

The superconducting properties of LiC\(_6\) are obtained by solving self-consistently the fully anisotropic Migdal-Eliashberg equations along the imaginary axis at the fermion Matsubara frequencies \( \omega_n = (2n + 1)\pi T \) (with \( n \) an integer) for each temperature \( T \) \([4, 11, 12, 43]\):

\[
Z(k, i\omega_n) = 1 + \frac{\pi T}{N_F \omega_n} \sum_{k' \nu} \frac{\omega_{n'}}{\sqrt{\omega_{n'}^2 + \Delta^2(k', i\omega_n')}} \times \delta(\epsilon_{k'}) \lambda(k, k', n - n'),
\]

\[
Z(k, i\omega_n) \Delta(k, i\omega_n) = \frac{\pi T}{N_F} \sum_{k' \nu} \frac{\Delta(k', i\omega_n')}{\sqrt{\omega_{n'}^2 + \Delta^2(k', i\omega_n')}} \times \delta(\epsilon_{k'}) [\lambda(k, k', n - n') - \mu_c^*].
\]

\[
Z(k, i\omega_n) \Delta(k, i\omega_n) \lambda(k, k', n - n') \text{ is the superconducting gap function, } \lambda(k, k', n - n') \text{ is the momentum- and energy-dependent EPC, and } \mu_c^* \text{ is the semiempirical Coulomb parameter. The anisotropic } \lambda(k, k', n - n') \text{ to be used in the Eliashberg equations is given by:}
\]

\[
\lambda(k, k', n - n') = \frac{2 \omega_{q \nu}}{\omega_n - \omega_{n'}}^2 + \omega_{q \nu}^2 |g^{\nu k' k}_{kk'}|^2.
\]

Figure 4(a) shows the superconducting energy gap \( \Delta_k \) as a function of temperature, calculated for a screened Coulomb parameter \( \mu_c = 0.14 \), together with the average value of the gap (red squares). The superconducting gap \( \Delta_k \) on different parts of the Fermi surface at 0.5 K is shown in Fig. 4(b). We find that monolayer LiC\(_6\) displays a single anisotropic gap with an average value \( \Delta_0 = 0.89 \text{ meV} \) in the \( T = 0 \text{ K} \) limit, in very good agreement with the ARPES result of 0.9 ± 0.2 meV, measured at 3.5 K \([8]\). This situation is similar to bulk CaC\(_6\) where the multiple-sheet Fermi surface gives rise to a single gap structure with a sizable anisotropy \([16, 17]\), but unlike bilayer C\(_6\)CaC\(_6\) for which a two gap structure has been recently predicted \([17]\).
The superconducting $T_c$ is identified as the highest temperature at which the gap vanishes. From Fig. 4(a) we find $T_c = 5.9$ K and a ratio $2\Delta_0/k_BT_c = 3.50$, very close to the ideal BCS value of 3.53\cite{44}. The predicted superconducting critical temperature is in excellent agreement with the experimental estimation of 5.9 K based on measurements of the size of the superconducting gap\cite{8}. The temperature dependence of the superconducting gap can be well fitted with a BCS model, as obtained by solving numerically the BCS gap equation\cite{45} with $\Delta_0$ and $T_c$ from our first-principles calculations. This is shown by the blue dashed line in Fig. 4(a).

These results provide support for a conventional phonon-mediated mechanism as the superconducting origin in Li-decorated graphene. For completeness, we also explore the sensitivity of the calculated superconducting energy gap and critical temperature to the choice of the Coulomb parameter $\mu^*$, as shown in Figs. 4(c)-(d). For $\mu^* = 0.12$ and 0.16, we obtain $\Delta_0 = 1.10$ meV and 0.69 meV and $T_c = 7.6$ and 5.1 K, respectively.

Finally, using the $\alpha$-model\cite{45, 46}, we obtain the temperature dependence of the reduced electronic specific heat in the superconducting state. Within this model, the ratio $\alpha = \Delta_0/k_BT_c$ is an adjustable parameter and the normalized superconducting state electronic entropy $S_{es}$ and heat capacity $C_{es}$ are expressed in terms of $\gamma_n T_c$ as:

$$\frac{S_{es}(t)}{\gamma_n T_c} = -\frac{6\alpha}{\pi^2} \int_0^\infty [f \ln(f) + (1-f) \ln(1-f)] d\bar{\varepsilon}, \quad (7)$$

$$\frac{C_{es}(t)}{\gamma_n T_c} = t \frac{d(S_{es}/\gamma_n T_c)}{dt}, \quad (8)$$

where $f = \left[\exp(\alpha \bar{\varepsilon}/t) + 1\right]^{-1}$ is the Fermi-Dirac distribution function, $t = T/T_c$ is the reduced temperature, and $\gamma_n = (2/3)\pi^2 k_B^2 N_F$ is the Sommerfeld coefficient. The reduced quasi-particle energy is defined as

![FIG. 4: (Color online) (a) Energy distribution of the anisotropic superconducting gap $\Delta_k$ of LiC$_6$ as a function of temperature. The gap was calculated using a Coulomb pseudopotential $\mu^*$ of 0.14. The red squares represent the average value of the gap which vanishes at the critical temperature $T_c = 5.9$ K. The blue dashed line is the BCS fit to the calculated data. (b) Momentum-resolved superconducting gap $\Delta_k$ (in meV) on the Fermi surface at 0.5 K. The data points correspond to electrons within ±150 meV from the Fermi energy. (c) Calculated superconducting gap at the Fermi level in the $T = 0$ K limit as a function of the Coulomb parameter $\mu^*$. (d) Calculated superconducting critical temperature as a function of the Coulomb parameter $\mu^*$. (e) Normalized specific heat as a function of temperature for $\alpha = 1.75$ in the superconducting state (solid line) and normal state (dashed line). The specific heat difference between the normal and superconducting state versus reduced temperature is shown in the inset.](image)
\[ \tilde{E} = \sqrt{\tilde{\varepsilon}^2 + \delta^2(t)}, \] 
where \( \tilde{\varepsilon} = \varepsilon / \Delta_0 \) is the reduced normal state single-particle energy relative to the Fermi level and \( \delta(t) = \Delta(T) / \Delta_0 \) is the reduced gap function. The upper limit in the integral in Eq. 7 is set to 500 \( \gg 1 \).

Figure 1(a) shows the calculated \( C_{es} / \gamma_n T_c \) for \( \alpha = 1.75 \). The temperature dependence of the normalized gap \( \delta(t) \) is assumed to be the same as in the BCS theory [42, 46]. We checked the numerical results by comparing the data for \( \alpha_{BCS} = 1.764 \) with Tables II–IV in Ref. 46 and by verifying that the entropy at the critical temperature is equal to that of the normal state. The shape of the calculated specific heat curve is consistent with a one-gap BCS model and undergoes a discontinuous jump at the critical temperature. The specific heat jump at \( T_c \) is found to be \( \Delta C_c(T_c) / \gamma_n T_c = 1.385 \) [shown in the inset of Fig. 1(a)], close to the weak limit BCS value of 1.426 [44]. Furthermore, this result is comparable to the experimental and theoretical values reported for the normalized specific heat jump in bulk CaC\(_6\) [14, 47].

CONCLUSIONS

In conclusion, we have studied the superconducting properties in Li-decorated monolayer graphene within the \textit{ab initio} anisotropic Migdal-Eliashberg theory. Our results provide support for a standard phonon-mediated mechanism at the origin of the superconducting transition. Most of the electron-phonon coupling originates from the low-energy modes dominated by the motion of Li atoms similar to bilayer C\(_6\)CaC\(_6\). We find a sizable anisotropy in the electron-phonon coupling which yields a single anisotropic gap over the Fermi surface. Further enhancement in the critical temperature of LiC\(_6\) is expected in the presence of a substrate [13] or under applied strain [38].

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