Substrate-enhanced superconductivity in Li-decorated graphene

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Abstract – We investigate the role of the substrate for the strength of the electron-phonon coupling in Li-decorated graphene. We find that the interaction with a $h$-BN substrate leads to a significant enhancement from $\lambda_0 = 0.62$ to $\lambda_1 = 0.67$, which corresponds to a 25% increase of the transition temperature from $T_c = 10.33$ K to $T_{c1} = 12.98$ K. The superconducting gaps amount to 1.56 meV (suspended) and 1.98 meV (supported). These findings open up a new route to enhanced superconducting transition temperatures in graphene-based materials by substrate engineering.

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Introduction. – Recent observations in alkali-doped graphene have opened exciting venues to superconductivity accomplished by doping [1]. Most theoretical estimates of the electron-phonon coupling so far have assumed suspended graphene as a base, since this geometry makes calculations more direct and less computationally costly. However, most of the engineered superconducting graphene samples use a substrate. Hence, it is important to characterize the role of the substrate on the superconductivity in atomically thin graphene. We have performed a first-principles study of the role of the substrate on the phonon spectrum and the electron-phonon coupling and find not only that the interaction with the substrate is relevant but that in the case of a $h$-BN substrate the electron-phonon coupling can be enhanced by as much as 9% so that $T_c$ can be expected to reach 12.98 K, a 25% increase. This observation points to a new direction in the search for novel superconducting transition temperatures in graphene-based materials by substrate engineering.

Graphite intercalated compounds are characterized by a nearly free electron band, which upon increased doping crosses the Fermi energy ($E_F$). Empirically, there are intercalated compounds that exhibit superconductivity with a transition temperature of a few to about 10 K. An empirical correlation between the crossing of the chemical potential and the onset of superconductivity was first put forward in ref. [2] and subsequently was called the “Cambridge criterion” [3]. Superconductivity in Ca-intercalated bilayer graphene has been predicted with a sizable $T_c = 11.5$ K by analyzing this criterion in refs. [3,4]. Recently, the prediction has been verified experimentally for Ca-intercalated graphene on either the Si or the C face of a SiC substrate, finding $T_c = 7$ K [5]. Experimentally, it also has been observed that KC₈ graphite [6] and K-intercalated few-layer graphene on SiC are superconducting [7], where theoretical arguments for superconductivity in the latter material have been presented in ref. [8]. To complete the list of superconducting C allotropes we also mention that undoped single and multiwall nanotubes exhibit superconductivity with a sizable $T_c \sim$ 10 to 12 K [9,10]. Today, the highest value of $T_c = 38$ K is observed experimentally in Cs₃C₆₀ [11].

It was already pointed out that not all intercalants lead to an enhanced $T_c$ in graphite [2]. A high $T_c$ can be obtained when the distance between the intercalated atom and the graphene plane is small so that the deformation potential is large [12]. Our observations are

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consistent with this mechanism: The distance between the intercalant and the graphene plane is 2.62 Å, 2.47 Å, and 2.26 Å for non-superconducting BaC₆ [13], superconducting SrC₆ with $T_c = 1.65$ K [13], and superconducting CaC₆ with $T_c = 11.5$ K [14,15], respectively, see table 1.

In this paper we report a first-principles study of the electron-phonon coupling to estimate the values of $\lambda$ and $T_c$ for Li-decorated suspended graphene and Li-decorated graphene on a h-BN substrate. We show that the presence of the substrate enhances the electron-phonon coupling and superconducting transition temperature, which reflects a significant impact of the interaction of the electronic states with the substrate on the phonon-mediated superconductivity in doped graphene.

### Results and discussion

The unit cell of Li-decorated monolayer graphene comprises 6 C atoms and 1 Li atom in a $\sqrt{3} \times \sqrt{3} R30^\circ$ geometry, where the Li atom lies above the center of the C hexagon in a distance of 1.76 Å, slightly smaller than the value reported in ref. [1]. The possible reason for the latter is the inclusion of the van der Waals interaction in our calculations, which is expected to provide a correct interlayer spacing. The structural arrangements of Li-decorated graphene suspended and supported by a h-BN substrate are presented in figs. 1(a) and (b). The electronic band structures obtained for $\sqrt{3} \times \sqrt{3} R30^\circ$ suspended graphene without and with Li-decorations are shown in figs. 2(a) and (b). It is well known that the C $\pi$ and $\pi^*$ orbitals form a Dirac cone at the Fermi energy. Due to the Brillouin zone backfolding, the Dirac cone appears at the $\Gamma$-point and not at the K-point as in the case of the primitive unit cell of graphene.

The electronic band structure of Li-decorated graphene is found to be modified significantly as compared to that of pristine graphene. The nearly free electron Li $s$ band crosses the Fermi level, due to charge transfer from Li to C. As a consequence, the “Cambridge criterion” is satisfied and the system should be a superconductor. We will comment later on this phenomenon by analyzing the strength of the electron-phonon coupling. A gap of 0.38 eV opens 1.56 eV below the Fermi level, as to be expected [16,17]. In fig. 2(b) the partially occupied parabolic bands indicated by arrows are due to Li $s$ states, compare figs. 2(a) and (b). It has been reported that the carrier density in Li-decorated monolayer and Li-intercalated multilayer graphene with and without substrate can differ by a factor of 100 from that of pristine graphene [16].

| Compound   | Distance | $T_c$  |
|------------|----------|--------|
| BaC₆       | 2.62 Å   | 0 K    |
| SrC₆       | 2.47 Å   | 1.65 K |
| CaC₆       | 2.26 Å   | 11.5 K |

Table 1: Compound, perpendicular distance of the intercalated atom from the center of the C hexagon, and superconducting transition temperature.

For Li-decorated graphene on h-BN, see fig. 1(b), the separation between graphene and the substrate is found to be 3.39 Å, which is close to the values for superlattices of graphene and h-BN as well as graphene on a h-BN substrate. The perpendicular distance of the Li atom to the graphene plane is 1.77 Å. The lost sublattice symmetry (only each third C hexagon is occupied by a Li atom) is responsible for a band gap of 90 meV. This value agrees well with previous reports [18–20], which also applies to the fact that the B and N states appear far away from the Fermi level. The electronic band structure in fig. 2(d) clearly shows that a nearly free electron Li $s$ band crosses the Fermi level, satisfying the “Cambridge criterion” and thus pointing to superconductivity in the system. The nature and magnitude of the gap at the $\Gamma$-point just below the Fermi level are similar to fig. 2(b).

At this point we assume that the basic mechanism of the superconductivity in the suspended and supported cases is the same as in Ca-intercalated graphene, i.e., electron-phonon driven pairing [3]. It has been proposed that the dopant-induced soft phonon modes contribute substantially to the electron-phonon coupling [2,21] and it is known that the motion of the adatom is responsible for about half of the coupling, while the other half is due to the C atoms [22–24]. The presence of the Li $s$ states around the Fermi energy alone cannot be sufficient to give a large electron-phonon coupling [1], but the coupling to the out-of-plane C vibrations plays an important role due to transitions between the C $\pi^*$ and Li $s$ states. The Li $s$ band enhances the coupling [12] and, hence, the transition temperature. For this reason, we calculate the phonon dispersion, see fig. 3(a), and $\alpha^2 F(\omega)$, see fig. 3(b), and estimate the strength of the electron-phonon coupling $\lambda$ using eq. (2).
Fig. 2: (Colour on-line) Electronic band structure of (a) suspended C$_6$, (b) suspended C$_6$Li, (c) C$_6$ on h-BN, and (d) C$_6$Li on h-BN. Li s bands crossing the Fermi level are indicated by arrows.

Fig. 3: (Colour on-line) Electron-phonon dispersion of Li-decorated graphene (a) suspended and (c) supported by a h-BN substrate. (b), (d): corresponding Eliashberg functions.
For the phonon dispersion of Li-decorated suspended graphene we find that most modes between 300 cm$^{-1}$ and 500 cm$^{-1}$ are due to a mixture of Li and out-of-plane C vibrations. The pure out-of-plane modes appear from 500 cm$^{-1}$ to 900 cm$^{-1}$ and higher-energy C-C stretching modes from 900 cm$^{-1}$ to 1515 cm$^{-1}$. The modes from 300 cm$^{-1}$ to 500 cm$^{-1}$ are responsible for the electron-phonon coupling. This also can be seen from $\alpha^2 F(\omega)$ as addressed in fig. 3(b). Experimentally, for pristine graphene the frequency of the G-mode is 1580 cm$^{-1}$ [25], which softens to 1515 cm$^{-1}$ under Li decoration. The softening can be attributed to charge transfer from Li to graphene and the induced stronger electron-phonon coupling, in agreement with findings for the molecular/atomic charge transfer in graphene [26,27]. We obtain $(\omega)_{\log} = 316.8$ cm$^{-1}$, an electron-phonon coupling of $\lambda = 0.62$, and a superconducting transition temperature $T_c = 10.33$ K. This value is slightly higher than that of ref. [1], since we take into account the van der Waals interaction to achieve an accurate distance to the Li atom.

Our central result is that an enhancement of the superconductivity in Li-decorated graphene can be achieved by the application of a h-BN substrate. The phonon modes between 100 cm$^{-1}$ and 300 cm$^{-1}$ at the $\Gamma$-point are attributed to the Li vibrations, out-of-plane C vibrations, and h-BN substrate, see fig. 3(c). There are also substrate modes around 850 cm$^{-1}$ as well as higher-energy modes between 900 cm$^{-1}$ and 1430 cm$^{-1}$, which are due to both the substrate and C-C stretching. The softening of the modes as compared to the suspended system is due to the interaction with the substrate, as observed experimentally, for example, in graphite supported by Ni(111) [28]. The modes in the range from 100 cm$^{-1}$ to 300 cm$^{-1}$ are responsible for a shift in $\alpha^2 F(\omega)$ see fig. 3(d), and enhancement of $\lambda$ and $T_c$. We obtain $(\omega)_{\log} = 330.5$ cm$^{-1}$, $\lambda = 0.67$, and thus $T_c = 12.98$ K, which is a 25% increase with respect to the suspended system. This clearly indicates that one can take full advantage of the substrate to boost $T_c$. Similarly, it has been observed experimentally in the FeSe$_{0.5}$Te$_{0.5}$ superconductor that $T_c$ is enhanced by 15% if the material is supported [29], while the details of the band structure are very different in the present material. The most likely reason for the obtained enhancement of $T_c$ by the application of a h-BN substrate are stronger spin fluctuations due to the lattice mismatch of 1.4%. Finally, we estimate the superconducting gap $\Delta_c$ by the relation $1.75k_BT_c = \Delta_c$ [30], where $k_B$ is the Boltzmann constant. We obtain for Li-decorated suspended and supported graphene, respectively, values of 1.56 meV and 1.98 meV.

**Conclusion.** – In conclusion, using density functional theory we have investigated the role of the substrate for the electron-phonon coupling in Li-decorated suspended and supported graphene. We find that the interaction with a h-BN substrate significantly enhances the electron-phonon coupling to $\lambda = 0.67$ as compared to $\lambda = 0.62$ in the suspended case. The transition temperature thus is enhanced by 25% to 12.98 K. The superconducting gap for the suspended and supported systems is found to be 1.56 meV and 1.98 meV, respectively. Our results show that graphene-based nanomaterials can be tailored by properly choosing the substrate to robustly increase the superconducting transition temperature.

**Appendix.** –

**Computational details.** All the results are obtained from density functional theory in the local density approximation. The van der Waals interaction is taken into account via Grimme’s scheme [31]. We use the Quantum ESPRESSO code [32] with norm-conserving pseudopotentials and a plane-wave cutoff energy of 70 Ryd. A Monkhorst-Pack $32 \times 32 \times 1$-k-mesh is employed for the optimization of the lattice parameters and the ionic relaxation and a $48 \times 48 \times 1$-k-mesh for refining the electronic structure. We achieve an energy convergence of $10^{-7}$ eV and a force convergence of 0.002 eV/Å. Li-decorated monolayer graphene is modeled by a $\sqrt{3}\times\sqrt{3}$R30° supercell with $a = b = 2.26$ to that a Li atom is added on each third hollow site. Phonon frequencies are determined by density functional perturbation theory for evaluating the effects of the adatoms and substrate on the phonon spectrum, using the scheme described in ref. [33]. The phonon dispersion is calculated with a $24 \times 24 \times 1$ grid. We study the effect of the substrate on the strength of the electron-phonon coupling and the transition temperature for a supercell with Li-decorated monolayer graphene on top of h-BN with $a = b = 4.32$ Å and $c = 15$ Å (to avoid artificial interaction due to the periodicity). Note that graphene on h-BN can be synthesized due to the small lattice mismatch of only 1.4% and interacts only weakly with the substrate [34–36]. By construction of the supercell of the suspended system, with 6 C atoms and 1 Li atom, there are 21 phonon modes, whereas we have 39 modes for the supported system.

**Superconducting transition temperature.** The Allen-Dynes formula [37,38], which is a modification of McMillan’s formula [39], is used to calculate

$$T_c = \frac{\langle \omega \rangle_{\log}}{1.29} \exp \left( -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right). \quad (A.1)$$

The terms $\langle \omega \rangle_{\log}$, $\lambda$, and $\mu^*$ are the logarithmic frequency average, electron-phonon coupling constant, and effective Coulomb repulsion, respectively. Moreover, the dimensionless parameter

$$\lambda = 2 \int_0^{\infty} \frac{d\omega \alpha^2 F(\omega)}{\omega} \quad (A.2)$$
measures the strength of the Eliashberg function
\[ \alpha^2 F(\omega) = N_f(0) \sum_{kk'} |M_{kk'}|^2 \delta(\omega - \omega_q) \delta(E_k) \delta(E_{k'}) \]
where \( k \) and \( q \) represent the electron band index and phonon wave number, respectively. In addition, \( N_f(0) \) is the single-spin density of states at the Fermi surface and \( M_{kk'} \) is the matrix element for electron-phonon coupling. The effective Coulomb repulsion (also called Coulomb pseudopotential) is given by \[ 1/\mu^* = 1/\mu + \ln \left( \frac{\omega_{pl}}{\omega_0} \right), \]
where \( \omega_{pl} \) is the plasma frequency and \( \omega_0 \) the frequency cutoff in \( \alpha^2 F(\omega) \). The Coulomb coupling \( \mu \) is given by the product of the density of states at the Fermi surface and the matrix element of the screened Coulomb interaction averaged over the Fermi surface. We use \( \mu^* = 0.115 \) in agreement with the experimental observation of the critical temperature for bulk CaC$_4$.[14].

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