Electronic structure of heavily-doped graphene: the role of foreign atom states

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The discovery of superconductivity in CaC$_6$[1 2 3] demonstrates that superconducting critical temperatures (T$_c$s) as large as 15 K can be obtained in Graphite Intercalated Compounds (GICs). Recently, deposition of foreign atoms onto a graphene monolayer [4] has been achieved. This finding could considerably widen the number of GICs, since the constraints for deposition onto graphene are milder than those required for graphite intercalation. Consequently even larger T$_c$s could be discovered in these systems.

So far, the electronic structure of atoms deposited on graphene has been interpreted in terms of the pristine graphene band structure [5 6 7 8]. This is correct if the charge transfer to the graphene layer (doping) is weak. However, this is questionable for larger dopings, since foreign atom states could affect the band structure below the Fermi level ($\epsilon_f$). Indeed in GICs, an intercalant band crosses $\epsilon_f$ [9 10 11]. As far as K deposition on graphene is concerned, detailed Angular Resolved Photo Emission (ARPES) measurements [3 6 8] have shown that (i) the graphene band-structure below $\epsilon_f$ is weakly affected by the presence of K atoms, (ii) a marked kink occurs at 0.195 eV below $\epsilon_f$, an energy corresponding to the E$_{2g}$ graphene phonon frequency and (iii) the electron-phonon coupling extracted from ARPES measurements is 5.5 times larger than what could be expected on the basis of a rigid doping of the graphene bands [10 12]. In a very recent paper [13] deposition of Ca atoms on graphene at doping as large as that of CaC$_6$ was achieved and, most surprising, a massive enhancement of the electron-phonon coupling was reported. The apparent electron-phonon coupling has been shown to be very anisotropic with values ranging from 0.5 to 2.3, suggesting that an heavily-doped graphene monolayer could be superconducting with large critical temperatures and large anisotropic superconducting gap(s).

Such large and anisotropic values of the electron-phonon coupling were interpreted as due to many-body effects and to the occurrence of a Van hove singularity. However neither measurements nor calculations of the electronic density of states were performed.

In this work we use density functional theory calculations to interpret the huge and highly anisotropic electron-phonon coupling observed in heavily doped graphene by ARPES in terms of the CaC$_6$ monolayer band structure.

In ARPES the spectral weight is measured, namely, for a given band index,

$$ A(k, \epsilon) = \frac{-2|\Sigma''(k, \epsilon)|}{[\epsilon - \epsilon_k - \Sigma''_{\text{all}}(k, \epsilon)]^2 + [\Sigma''_{\text{all}}(k, \epsilon)]^2} $$

(1)

where $\Sigma''_{\text{all}}(k, \epsilon)$ and $\Sigma''_{\text{all}}(k, \epsilon)$ are the real and imaginary parts of the electron self-energy $\Sigma''_{\text{all}}(k, \epsilon)$, and $\epsilon_k$ are the single particle bands. The total electron self-energy includes contributions from all the interactions in the system. The electron-phonon coupling parameter is:

$$ \lambda_k = \left. \frac{\partial \Sigma''(k, \epsilon)}{\partial \epsilon} \right|_{\epsilon=\epsilon_f} $$

(2)

where $\Sigma(k, \epsilon)$ is the electron-phonon contribution to the electron self-energy and $\Sigma'(k, \epsilon)$ its real part. In what follows we assume that the dominant contribution to the electron self-energy is given by the electron-phonon coupling, $\Sigma''_{\text{all}}(k, \epsilon) \approx \Sigma(k, \epsilon)$.

The maximum position in the spectral weight is given by the relation $\epsilon_k^{\text{max}} - \epsilon_k - \Sigma'(k, \epsilon_k^{\text{max}}) = 0$. Linearizing $\Sigma'(k, \epsilon) \approx -\lambda_k \epsilon_k$ leads to $\lambda_k = \frac{\epsilon_k}{\epsilon_k^{\text{max}}} - 1$. If the bare bands behave linearly, namely $\epsilon_k = \hbar v_f k$, and if the renormalized can be linearized at $\epsilon_f$, $\epsilon_k^{\text{max}} = \hbar v_f k$, [12 14] then $\lambda_k$ and

$$ \lambda_k = \frac{\epsilon_0}{\epsilon_f} - 1 $$

(3)

where, $v_f$ is obtained from a linear fit to the maximum position in momentum distribution curves (MDCs) at energies close to $\epsilon_f$, while $\epsilon_0$ is obtained from a linear fit in
an appropriate energy window below the kink where the bare bands are linear. Note that if the bare bands are not linear then Eq. 3 is incorrect.

In experiments a finite resolution affects substantially the energy window close to $\epsilon_f$ so that the determination of $\nu_f$ is non-trivial [13]. The the following quantity is then computed:

$$\lambda_{\text{ARPES}} = \frac{\nu_0}{\nu_{\text{ARPES}}} - 1$$

where now $\nu_{\text{ARPES}}$ is obtained from a linear fit to the maximum position in MDCs in an energy window ranging from the kink energy up to the Fermi level. Clearly $\lambda_{\text{ARPES}} \approx \lambda$ only if $\nu_f \approx \nu_{\text{ARPES}}$. Consequently the energy window chosen to fit $\nu_{\text{ARPES}}$ is crucial. This has been demonstrated to be important in graphene at low electron-doping [12]. Indeed, in the case of rigid band doping of the graphene $\pi^*$ bands, where the electron-phonon coupling can be calculated analytically [10, 12], it has been found that $\lambda_{\text{ARPES}} \approx 2.5\lambda$. Thus, in this case, $\lambda_{\text{ARPES}}$ cannot provide a quantitative information of the electron-phonon coupling since $\nu_{\text{ARPES}}$ depends critically on the fit procedure.

When large dopings are considered, as in the case of a CaC$_6$ monolayer in ref. [13], the commonly accepted interpretation of the band structure in term of rigid doping of graphene $\pi^*$ states becomes questionable. For this reason we calculate the single particle band-structure of monolayer and bulk CaC$_6$ using density functional theory (DFT). We assume that the Ca deposition leads to an ordered $\sqrt{3} \times \sqrt{3}$ structure with axes rotated of $30^\circ$ respect to the standard C$_2$ crystal structure. Simulating a single layer requires very large cells to converge due to the finite electric dipole formed by the Ca donor and the graphene acceptor. The problem can be solved using a double slab geometry with two symmetric layers of CaC$_6$ separated by vacuum along the $z$ direction. This geometry has zero net electric dipole. The interstitial space between Ca atoms on different layers is 11 Å while that between the two Graphene layers is 10 Å. We optimize the in-plane graphene lattice parameter ($a$) and the distance ($z$) between the Ca atoms and the nearby graphene layer, obtaining $a = 2.47$ Å and $z = 2.315$ Å. Note that in bulk CaC$_6$ structural optimization leads to $a = 2.50$ Å and $z = 2.60$ Å [11]. Electronic structure calculations are performed using the espresso code [16] and the generalized gradient approximation [17]. We expand the wavefunctions and the charge density using a 35 Ry and a 600 Ry cutoffs, respectively. The electronic integration for the double slab geometry has been performed using a $8 \times 8 \times 8$ k-points mesh and a Gaussian smearing of 0.05 Ryd. For graphene we use a $30 \times 30 \times 2$ k-points mesh.

In fig. 1 we show the band structure of CaC$_6$ monolayer compared to that of graphene using the same in-plane lattice parameter, $a = 2.47$ Å. The energies of the Dirac point in the two structures have been aligned. In the CaC$_6$ monolayer Brillouin zone the Dirac point is refolded at $\Gamma$ due to the $\sqrt{3} \times \sqrt{3}R30^\circ$ surface deposition. Because of this superstructure, a small gap opens at the Dirac point in CaC$_6$ monolayer. The Fermi level is crossed by two Carbon $\pi^*$ bands and a third band mainly Ca in character. The steepest $\pi^*$ band (labeled $\pi_1^*$) is very similar to that of C$_2$, while the other $\pi^*$ (labeled $\pi_2^*$) is substantially affected by the Ca recovering. The most striking feature is, however, the occurrence of an additional band at $\epsilon_f$, having dominant Ca character. This band is the so called “intercalant” band in GICs [9, 10], descending to lower energies respect to its position in CaC$_6$ bulk. The bottom of the intercalant band is at $-1.15$ eV respect to $\epsilon_f$ in bulk CaC$_6$ and

![Fig. 1: (Color online) (a) Band structures of CaC$_6$ Monolayer (continuous line) and graphene (red-dashed) using the same in-plane lattice parameter, namely $a = 2.47$ Å (dashed). The size of the circles indicates the percentage of Ca character (see ref. [10]) in a given band. (b) Fermi surface of CaC$_6$ monolayer. The special points labels refer to the CaC$_6$ hexagonal Brillouin zone.](image-url)
is now at −1.65 eV in the monolayer. Correspondingly the graphene Dirac point is at \( \approx −2.04 \) eV in the bulk and at \( \approx 1.39 \) in the monolayer, in nice agreement with experiments [13]. This effect is well known; in alkaline-earths GICs, the intercalant band descends as the interlayer distance is reduced [9, 11, 18].

Finally, in CaC\(_6\) monolayer there is a marked avoided crossing between the \( \pi^*_2 \) band and the Ca-band along \( \Gamma M \). In this direction, approaching the M-point, there is a large hybridization between the two bands, as it is evident from the change in the Ca character of the band. Most important, a large deviation from linearity occurs in the \( \pi^*_2 \) band at an energy of \( \approx 0.2 \) eV below the Fermi energy. This energy is very close to the \( E_{2g} \) phonon frequency [19] of undoped graphene at the \( \Gamma \) point, namely \( \omega_{E_{2g}} = 0.195 \) eV.

The Fermi surface of CaC\(_6\) monolayer is shown in Fig. 1 (b) in the CaC\(_6\) monolayer Brillouin zone and in Fig. 2 (b) in the C\(_2\) Brillouin zone. In Fig. 1 (b) the Fermi surface is composed of a 6-points star centered at \( \Gamma \) formed by the intersection of two triangular shapes. In addition there are 6 hole pockets centered around \( K \) and \( K' \). The hexagon within the star is due to the \( \pi^*_1 \) band, while the outer perimeter of the star is composed by the \( \pi^*_2 \) band hybridized with Ca states. Along \( \Gamma K \) the star has dominant C character, while along \( \Gamma M \) it has strongly hybridized Ca and C character. The hole pockets are mostly Ca. In Fig. 2 (b) one of the triangular shapes composing the star is compared with the Fermi surface determined by ARPES [13]. A very good agreement is found for the surface at the highest experimental doping.

In Fig. 2 the CaC\(_6\) monolayer and C\(_2\) bands are plotted in the C\(_2\) Brillouin zone. The aforementioned deviation from linearity in the \( \pi^*_2 \) bands, now occurring along \( MK \), results in an apparent kink. However this kink is not due to the electron-phonon interaction or to many body effects, but it is due to the non-linearity of the single particle bands. The change in slope is induced indirectly by the hybridization with the intercalant band.

In order to compare with experimental data, we estimate the “apparent” electron-phonon coupling \( \lambda_{\text{ARPES}} \) (Eq. 3) generated by the change in slope of the single particle band. We obtain \( \nu_0 \) and \( \nu_{\text{ARPES}} \) in Eq. 3 by linear fits to the \( \pi^*_2 \) band at several directions departing from the \( K \) point in the C\(_2\) Brillouin zone. The fits to obtain \( \nu_{\text{ARPES}} \) and \( \nu_0 \) are performed in the energy range \( −0.2 \) eV \( < \epsilon − \epsilon_f < 0 \) eV and \( −1.0 \) eV \( < \epsilon − \epsilon_f < −0.2 \) eV, respectively. A strong anisotropy in \( \lambda_{\text{ARPES}} \) is obtained as a result of the single-particle band-structure. Values as large as 2.5 are found along the \( K M \) direction. Along \( \Gamma K \), where no kink is present in the bare bands, a zero value is found.

To compare with experiments the contribution due to the electron-phonon coupling in the CaC\(_6\) monolayer should be added. In ARPES spectra in ref. [13] the only visible contribution is that due to the in-plane graphene phonons at \( \approx 0.2 \) eV. In bulk CaC\(_6\) this contribution is 0.11 [10]. As we have shown in ref. [12], the fitting procedure used in ref. [13] overestimates \( \lambda \) of a factor 2.5. Thus to the anisotropic bare band contribution we added an isotropic electron-phonon contribution of 0.275.

The results are illustrated as polar plots in Fig. 2 (b) and (c) and are compared to the experimental data of ref. [13] in Fig. 2 (c). We reproduce the strong anisotropy observed in ARPES experiment [13] and the huge values of \( \lambda_{\text{ARPES}} \) along the \( K M \) direction. In the \( K \Gamma \) direction, where the bare band contribution is zero, the value of \( \lambda_{\text{ARPES}} \) is given entirely by the electron-phonon contribution. In this direction the values of \( \lambda \) for bulk CaC\(_6\) underestimate the experimental one. This could
be due a larger density of states at the Fermi level in CaC₆ monolayer respect to bulk CaC₆. Indeed we found that the monolayer density of states at the Fermi level is 1.7 time larger than that in the bulk.

In this work we have studied the electronic structure of foreign atoms deposited on graphene. We have shown that as the charge transfer to graphene becomes significant, the band structure cannot anymore be interpreted in terms of the pristine graphene π* bands. When Ca is deposited on graphene at stoichiometry comparable with CaC₆, a Ca band occurs at the Fermi level. This band is the surface analogue of the intercalant band in superconducting graphite intercalated compounds [9, 10], that is crucial to understand the superconducting behavior of these compounds. The Ca bands strongly hybridize with the C π* states and induces a marked nonlinearity in one of the π* bands at energies comparable to ε_f − ω_{Eg}r. This non-linearity explains the large and strongly anisotropic values of \( \lambda_{\text{ARPES}} \) in CaC₆ monolayer. However, as shown in this work, these large and anisotropic values do not provide any information on the real electron-phonon coupling in the system.

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