Doped graphene: a prototype high-$T_c$ electron-phonon superconductor

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We show by first-principles calculations that $p$-doped graphene is a conventional superconductor with a critical temperature ($T_c$) above the boiling point of liquid nitrogen. The unique strength of the chemical bonds between carbon atoms and the large density of electronic states at the Fermi energy arising from the reduced dimensionality synergetically push $T_c$ above 90K, and give rise to large Kohn anomalies in the optical phonon dispersions. As evidence of graphene was recently reported, and doping of related materials such as graphene, diamond and carbon nanostructures is well established, superconducting graphene may be feasible.

The discovery of superconductors such as magnesium diboride$^1$ and iron pnictides$^2,3$ opened new horizons in the landscape of superconductivity research, fueling renewed interest in the quest for high-temperature superconductivity in materials other than the copper oxides$^4,5$. The critical temperature, $T_c$, reflects the energy scale of the quantum-mechanical interactions driving the electron condensation into the superconducting state$^6$. In high-$T_c$ copper oxides$^7$ the nature of the interaction leading to superconductivity is still under debate$^8$, yet it is generally accepted that Coulomb exchange and correlation effects, with energy scales around few hundred meVs, play an important role$^9,10$. In contrast, in conventional superconductors the pairing is known to be driven by the interaction between electrons and lattice vibrations, with an associated energy scale of only a few ten meVs$^{11}$. Due to the order-of-magnitude difference between such energy scales, it is generally assumed that conventional superconductors cannot exhibit $T_c$ as high as copper oxides$^4,5$. Here, we report first-principles calculations showing that $p$-doped graphene would make a conventional superconductor with $T_c$ well above the boiling point of liquid nitrogen.

The Bardeen-Cooper-Schrieffer (BCS) theory$^{11}$ defines the basic theoretical framework to understand conventional superconductivity. Its generalization, known as the Migdal-Eliashberg theory$^{12}$, incorporating the lattice dynamics, provides a predictive computational tool. Within BCS, $T_c$ is given by$^{11}:

$$k_BT_c = 1.14\hbar\omega_0 \exp \left(-\frac{1}{N_F V}\right)$$

(1)

where $k_B$ is the Boltzmann constant, $\hbar\omega_0$ a characteristic phonon energy, $N_F$ the electronic density of states (EDOS) at the Fermi Energy, $E_F$, $V$ an effective pairing potential resulting from the net balance between the attractive electron-phonon coupling (EPC) and the repulsive electron-electron interaction$^{11}$. Even though the original BCS formula for $T_c$ is now replaced by more refined expressions such as, e.g., the modified McMillan equation$^{13}$. Eq.(1) still proves useful for discussing trends. Eq.(1) indicates that one could maximize $T_c$ by increasing the materials parameters $\omega_0$, $N_F$, $V$. However, these are strongly intertwined, making such optimization complex$^{13,14}$. Here, we propose a simple procedure, based on Eq.(1) to design a high-$T_c$ superconductor.

Let us first consider the conventional superconductor with the highest $T_c$, MgB$_2$ ($T_c = 39K$)$^1$. For simplicity, we neglect multi-band and anisotropy effects, which were the object of detailed investigations$^{15–19}$. In MgB$_2$ the EPC contribution to $V$ is large ($\sim 1.4$eV, from $\lambda = N_F V$, using $N_F = 0.7$states/cell/eV, and $\lambda \sim 100$) because the states with energy close to $E_F$ (those which condense in the superconducting state$^{11}$) are of $\sigma$ character, i.e. derive from bonding combinations of planar B $sp^2$ hybrids localised around the middle of the B-B bonds$^{15–19}$. These electronic states are significantly affected by the B-B bond length variation associated with bond-stretching $E_{2g}$ phonons$^{16,20}$, resulting into a large EPC contribution to $V$. At the same time, the $E_{2g}$ phonon energy is large ($\sim 60$meV$^{16}$), due to the small B mass, leading to a large $\omega_0$ in Eq.(1). Furthermore, MgB$_2$ is a metal with a significant EDOS at $E_F(\sim 0.7$states/cell/eV$^{16}$). These three factors cooperate in Eq.(1) to establish a superconducting state with $T_c = 39K$$^{15–19}$. However, many attempts to improve upon MgB$_2$, by investigating related materials, only met limited success$^{21}$, with the experimental $T_c$ never higher than MgB$_2$.

We thus search for an alternative material having at least some of the desirable features of MgB$_2$, i.e.(i)$\sigma$ electrons at the Fermi surface,(ii)large bond-stretching phonon frequencies, and (iii)large EDOS at $E_F$. We note that the first two requirements are both met by B-doped diamond, a conventional BCS superconductor with $T_c = 4K$$^{22}$, where a small hole-like Fermi surface appears around the top of the valence band$^{22}$. The electronic states at $E_F$ have $\sigma$ character deriving from the bonding combination of tetrahedral C $sp^3$ hybrids, bearing some analogy to MgB$_2$. As these $\sigma$ states are localized in the middle of the C-C bonds, they couple considerably to bond-stretching phonons$^{23,24}$, resulting in a large EPC contribution to $V$, even superior to MgB$_2$ ($\sim 3$eV, from $\lambda = N_F V$, using $N_F = 0.1$states/cell/eV,$\hbar\omega_0 = 3$eV, $\lambda \sim 30$).
of the desirable features of MgB$_2$, its 3-dimensional (3d) nature implies that the EDOS in proximity of the valence band edge scales as $~E^{1/2}$ (with $E$ measured from the valence band edge)\cite{28}. Fig.1(a). Then, the number of carriers available for the superconducting state remains relatively small even for large doping. Superconducting diamond is thus a 3d analogue of MgB$_2$\cite{22, 24}.

This leads to the question of what would happen in a hypothetical B-doped diamond structure with reduced dimensionality, such as a thin film or a nanowire, where the EDOS can be significantly enhanced by quantum confinement. Indeed, the EDOS of a two-dimensional semiconductor goes as $~\theta(E)$ ($\theta$ being the step function)\cite{29}, hence the number of available carriers can be large, even at low doping. In order to estimate the expected EDOS increase in a diamond thin film it is helpful to consider a simple parabolic band model. For 2\% B doping, bulk diamond has $N_F=0.1$ states/eV/cell at $E_F$. A 0.5nm thick diamond film with the same doping would have $N_F=0.5$ states/eV/cell. Such an EDOS increase would significantly enhance $T_c$. Using the electron-phonon potential and the phonon frequency of bulk diamond, Eq.1 gives that a 0.5nm film would superconduct at $T_c \sim 80$K. However the question remains whether it is possible to synthesize an atomically thin diamond film.

Recent work on graphene and its derivatives points to a positive answer. Soon after the discovery of graphene\cite{30} several works considered how to functionalise and chemically modify this novel 2d material\cite{31–36}. In particular, it was proposed that fully hydrogenated graphene (graphane) would be stable\cite{37}. The main difference between graphene and graphane is that, while the former is fully $sp^2$ bonded, the latter is $sp^3$, as diamond\cite{37}. Recently, some experimental evidence of graphane was reported\cite{38}. Since graphene is the 2d counterpart of diamond, our scaling arguments immediately point to doped graphane as a potential high-$T_c$ superconductor. Doping could be achieved by gating, including using an electrolyte gate, or by charge-transfer, as done in graphene\cite{31, 32, 39, 40}. Substitutional doping of graphane was also reported, up to $\sim 10^{14}$ cm$^{-2}$\cite{35, 41}.

We thus perform density functional perturbation theory (DFPT) calculations of EPC and superconductivity in doped graphane within the framework of the Migdal-Eliashberg theory\cite{12} and the local density approximation (LDA)\cite{42, 43}. By analogy with B doped diamond, we consider $p$-doping. This is simulated using the rigid-band approximation\cite{44}. Fig.1(b) shows that the calculated EDOS in $p$-doped graphane close to the valence band maximum follows a step-like behavior, as expected for a 2d system. At 3\% doping the EDOS is 0.22 states/eV/cell, compared to 0.13 states/eV/cell in bulk diamond, with a factor 1.7 enhancement. Fig.1(c) indicates that the dispersions close to $E_F$ are essentially identical for a supercell containing B and for a rigid-band model of doped graphane. We expect this to hold also

\begin{align*}
\text{EDOS (states/eV/atom)} = \frac{N_F}{\sqrt{\frac{2\pi}{\hbar^2 g^2}}} \\
E_F &\approx -0.96 \text{eV (green line)}.
\end{align*}

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FIG. 1: (Color online)(a)EDOS per carbon atom of 1d (nanotube; diamond nanowire), 2d (graphene; graphane) and 3d (diamond) systems. With the exception of graphene, with linear dispersions, the EDOS is proportional to $E^{-1/2}$ in 1d, a step-like function in 2d, and $E^{-1/2}$ in 3d. The step-like EDOS in graphene implies that $N_F$ is large even at low doping. (b)EDOS of pristine (solid black line) and 12.5\% p-doped graphane (dashed red line). The top of the valence band is set as zero, and $E_F=0.96$eV (green line). The EDOS at $E_F$ is similar in the two models (0.26 states/eV/cell in rigid-band and 0.27 states/eV/cell in supercell). (c)Band structure of pristine (solid black line) and 12.5\% p-doped graphane (dashed red line). (inset) Ball-and-stick 2 $\times$ 2 supercell with one substitutional B (top and side views)
FIG. 2: (Color online) (a) Phonon dispersion of pristine (solid black line) and 1\% p-doped graphane (dashed blue lines). The C-H stretching modes have higher frequencies (2655-2711 cm\(^{-1}\)) and are not shown. (b) Optical modes around the zone centre, showing the Kohn Anomalies. The horizontal (green) arrows indicate the average Fermi surface diameter.

for lower doping, where the perturbation to the pristine dispersions is smaller. The similarity between these two models justifies our use of the rigid-band approximation. A supercell calculation with the B dopant explicitly included does not show impurity states inside the gap.

Fig. 2(a,b) report the phonon dispersions of pristine and p-doped graphane and Fig. 3(a) the corresponding phonon density of states (PDOS). Upon doping, the optical zone-centre modes with in-plane C-C stretching soften as a result of the inception of Kohn Anomalies.\[45\] The two degenerate TO modes, having planar C-C stretching and H atoms moving in-phase with the C atoms, downshift from 1185 to 715 cm\(^{-1}\) (147 to 89 meV). This is due to the large EPC of planar C-C stretching, which significantly affects the \(sp^3\)-like electronic states at the Fermi surface. The two degenerate zone-centre modes, having in-plane C-C stretching and H atoms moving out-of-phase with respect to the C atoms, downshift from 1348 to 1257 cm\(^{-1}\) (167 to 156 meV). The LO mode, with out-of-plane C-C stretching, does not couple to the electrons due to the different parity of potential and wavefunctions, resulting into a vanishing EPC. The two degenerate optical modes corresponding to the shear motion of the C and H planes (at \(\sim 1133\text{ cm}^{-1}\)) and the C-H stretching modes (2 modes at 2663 and 2711 cm\(^{-1}\)) do not undergo softening upon doping. This is consistent with the electronic states associated with the C-H bonds having little weight at \(E_F\), hence a small EPC.

The softening of modes with a large C-C stretching component is similar to that reported in B-doped diamond.\[24, 25\] In particular, the region of reciprocal space where the phonon softening is observed matches the diameter, \(2k_F\), of the hole Fermi surface.
the Brillouin zone is sampled with an electron grid up to doping, calculated using the standard DFPT formalism[51]:

FIG. 4: (Color online)(a)EPC of graphane as a function of doping, calculated using the modified McMillan formula[52]), and diamond (solid black line)[24]; triangles[25]. However, in B-doped diamond a rigid-band model provides a lower EPC and a lower bound to the EPCs[25, 28]. Nevertheless, such a large softening stands out as a qualitative effect.

where \( \lambda_{\nu q} \) is the EPC for a phonon mode \( \nu \) with momentum \( q \) and frequency \( \omega_{\nu q} \), and \( \delta \) is the Dirac delta (we used a Gaussian of width 2meV for this purpose). We get that the TO in-plane C-C bond-stretching phonons with C and H atoms moving in-phase (see Fig 3(b)) have the largest EPC, due to the \( \sigma \) character of the electronic states at \( E_F \) and the large C displacements associated with these modes. This is similar to B-doped bulk diamond[23–25, 28] and validates our hypothesis that p-doped graphene can be regarded as an atomically thin diamond film, exhibiting similar EPC and vibrational frequencies, but larger EDOS at \( E_F \). We note that the in-plane C-C bond-stretching phonons, with C and H atoms moving out-of-phase, do not contribute to the EPC. This happens because, upon softening, the four C-C planar stretching modes hybridize in such a way that those at \( 715cm^{-1} \) carry an increased weight on the C atoms, while the opposite happens for the two modes at \( 1257cm^{-1} \).

Figure 3(b) plots the Eliashberg spectral function[49], which shows the relative contribution of different modes to the superconducting pairing[49]:

\[
\alpha^2 F(\omega) = \frac{1}{2} \sum_{q\nu} \omega_{\nu q} \lambda_{\nu q} \delta(\omega - \omega_{\nu q}) \tag{2}
\]

around the \( \Gamma \) point, this being a typical signature of the Kohn effect[45]. The calculated phonon softening of the TO C-C stretching modes (\( \sim 58meV \) or\( \sim 470cm^{-1} \)) is significantly larger than in other materials, as typical Kohn anomalies range from \( \sim 5meV \) (graphite and graphene[46]) to\( \sim 10meV \) (TaC[47]). In the case of B-doped diamond the phonon softening takes place through the creation of a non-dispersive defect branch associated with the B dopant[25]. A similar effect could happen in B-doped graphene, but we expect the magnitude of the doping-induced softening to be reasonably well described within our rigid-band model. Also, more sophisticated calculations, taking B explicitly into account[25, 28] or with non-adiabatic corrections[48], may slightly revise the softening. Nevertheless, such a large softening stands out as a qualitative effect.

Figure 3(b) shows the Eliashberg spectral function[49], which shows the relative contribution of different modes to the superconducting pairing[49]:
\[ a_H = \epsilon/m^*a_0/2, \text{ } a_0 \text{ being the Bohr radius, } \epsilon \text{ the dielectric constant, and } m^* \text{ the effective mass}[55]. \text{ In diamond } a_H \sim 4\text{Å} \text{ and } n_c \sim 4 \cdot 20\text{cm}^{-3} [56], \text{ therefore the average separation between nearest neighbor B atoms is } \sim 15\text{Å}. \text{ In the case of graphane we use a similar criterion, replacing the } 3\text{d hydrogenic impurity with a } 2\text{d one. The ground-state hydrogenic wavefunction in } 2\text{d has a radius } 3d_H = \epsilon/m^*a_0/2[55]. \text{ Using the dielectric constant and hole effective mass of diamond } (\epsilon = 5.7; m^* = 0.74) \text{ we find } a_H^2 = a_H/2 \sim 2\text{Å}. \text{ Thus, the average separation between nearest neighbor B atoms at the MIT is } \sim 7.5\text{Å} \text{ and the corresponding doping can be estimated as } 5\% \text{ B (1 B every 20 C atoms) or } 2 \cdot 10^{14} \text{ holes-cm}^{-2}. \text{ This could be feasible, considering that substitutional doping in graphene was reported up to } 5\%[41]. \]

The calculated high-\( T_c \) for \( p \)-doped graphane bears consequences both for fundamental science and applications. One could envision hybrid superconducting-semiconducting circuits directly patterned through lithographic techniques, graphane-based Josephson junctions for nanoscale magnetic sensing, and ultimately an ideal workbench for exploring the physics of the superconducting state in two dimensions[55]. The superconducting phase transition in graphane could also be controlled by gating[34, 50]. A high-\( T_c \) superconductor with gate-controllable \( T_c \) could lead to novel switching mechanisms in nanoscale field-effect transistors. Furthermore, the discovery of an electron-phonon superconductor with \( T_c \) above liquid nitrogen would mean that (i) there are no fundamental reasons to believe that BCS superconductors cannot have \( T_c >40\text{K} \) (\( \text{MgB}_2 \)), and (ii) high-\( T_c \) superconductivity does not take place exclusively in the copper oxides. In particular, our calculations indicate that at least one material could exist where a very strong EPC leads to \( T_c \) in the copper oxide range without triggering a lattice instability. The superconducting phase transition in systems with reduced dimensionality has been the subject of numerous theoretical studies[64][61]. Quantum fluctuations could destroy the superconducting order in 2d[62]. However, recent experimental evidence suggests that this is not necessarily the case[55][55][63]. In particular, for thin Pb it was reported that the superconducting state is robust down to two atomic layers[55]. Since our proposed mechanism of superconductivity in doped graphene is BCS-like, as in Pb, there should be no fundamental limits to prevent the realization of high-\( T_c \) superconductivity in graphane.

It is immediate to extend the present study to diamond nanowires, which have been the subject of intense investigations in the past few years[64]. For a 1d system the EDOS near a band edge has a van Hove singularity going as \( E^{-1/2} \)[24]. We can assume phonon energies and EPC to be similar to bulk diamond and graphane. Then Eq.1 would yield \( T_c \) as high as \( 150\text{K} \) for a 1nm nanowire (see EDOS in Fig.1a). The possibility of achieving \( T_c \) higher than copper oxides by exploiting dimensionality deserves further investigation. Our work suggests that \( p \)-doped diamond nanostructures have an intriguing potential for high-\( T_c \) BCS-like superconductivity.

**Acknowledgments** Calculations were performed at HPCF (Cambridge) and the Research Center for Scientific Simulations of the University of Ioannina (Greece) using Quantum ESPRESSO[65]. ACF acknowledges funding from The Royal Society, the EU grant NANOPOTS and EPSRC grant EP/G042357/1; GS from JSPS and Grant-in-Aid for Scientific Research.

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