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Published in:
Nature Communications

DOI:
10.1038/ncomms3010

Published: 01/01/2013

Please cite the original version:
Dual origin of defect magnetism in graphene and its reversible switching by molecular doping

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Control of magnetism by applied voltage is desirable for spintronics applications. Finding a suitable material remains an elusive goal, with only a few candidates found so far. Graphene is one of them and attracts interest because of its weak spin-orbit interaction, the ability to control electronic properties by the electric field effect and the possibility to introduce paramagnetic centres such as vacancies and adatoms. Here we show that the magnetism of adatoms in graphene is itinerant and can be controlled by doping, so that magnetic moments are switched on and off. The much-discussed vacancy magnetism is found to have a dual origin, with two approximately equal contributions; one from itinerant magnetism and the other from dangling bonds. Our work suggests that graphene’s spin transport can be controlled by the field effect, similar to its electronic and optical properties, and that spin diffusion can be significantly enhanced above a certain carrier density.
Electric field control of magnetic properties has been the subject of considerable attention, with a few materials and hybrid magnetic systems found recently, where it is possible to control the magnetization direction and/or the Curie temperature. Electric field tunability is one of the fundamental properties of graphene and has been widely used to control its electronic, optical and other properties related to the electronic structure. On the other hand, graphene is believed to be an ideal material for spintronics because of the weak spin–orbit interaction and long spin relaxation lengths and the possibility to introduce paramagnetic centres via controlled introduction of defects, as recent experiments have shown that both vacancies and adatoms in graphene carry magnetic moments due to vacancies and adatoms in graphene but also the presence of the moments themselves which so far has not been possible in other materials.

In this contribution, we have employed Superconducting Quantum Interference Device (SQUID) magnetometry and molecular doping to investigate graphene’s paramagnetism. We have found that magnetic moments due to vacancies and adatoms can be switched off by shifting the Fermi energy $E_F$ above $\approx 0.45$ eV and then switched back on by returning to the neutral state or lower $E_F$. This proves the itinerant nature of magnetic moments in graphene, that is, π magnetism. The localization radius $r_L$ for the itinerant spins is estimated as $\approx 2.0$ nm. For the case of vacancies, we find them carrying two practically independent moments that are attributed to the π magnetism and an unpaired spin on broken bonds. Only half of vacancy magnetism can be switched off by doping. A profound implication of our findings is that π magnetism can be controlled by other means, notably by the electric field doping within realistically accessible carrier densities $n \approx 2 \times 10^{13}$ cm$^{-2}$. Furthermore, it is likely that the unexpectedly quick spin relaxation found in graphene devices and attributed to magnetic defects can be quenched by doping above the above threshold.

### Results

**Magnetic response of graphene with vacancies.** Our samples were graphene laminates that were shown to be a well-characterized, clean reference system, providing enough material (typically, several mg of graphene) for SQUID magnetometry. Our magnetometer (Quantum Design MPMS XL7) allowed measurements at temperatures $T$ between 300 and 1.8 K in fields $H$ up to 7 T. The samples were irradiated with 350 keV protons to achieve the desired density of single vacancies, $n_v$ (Methods). Irradiation resulted in a pronounced paramagnetic response arising from non-interacting moments. Typical magnetization curves are shown in Fig. 1. For all vacancy concentrations, such curves were accurately described by the Brillouin function with spin $S = 1/2$. The measured magnetic moment $M$ was found to be proportional to $n_v$, as $M \propto N_{\text{v}} \cdot \mu_B \cdot S \propto n_v$, where $\mu_B$ is the Bohr magneton and $N_{\text{v}}$ is the number of spins extracted from Brillouin function fits, in agreement with the earlier report.

**Control of carrier concentration in graphene laminates.** To probe the evolution of $M$ as the valence (conduction) band gets progressively filled up with holes (electrons), we varied the carrier concentration by using molecular doping: nitric acid (HNO$_3$) or NO$_2$ gas as hole dopants and aniline as an electron dopant. The properties of HNO$_3$ and NO$_2$ as acceptors were investigated both theoretically and experimentally, and both were shown to be very effective, with each physiosorbed molecule resulting in transfer of one electron. Aniline is reported as one of the best donors but the maximum doping it allowed was only $n \approx 5 \times 10^{12}$ cm$^{-2}$. Within the limited range of $n$ achievable for aniline, we have found no difference with respect to hole doping with HNO$_3$ and, therefore, focus below on the latter results.

**Effect of doping on magnetization of irradiated graphene.** Figure 1 shows the evolution of $M(H)$ curves for one of the irradiated samples as it is doped from a nearly neutral state to $E_F \approx 0.5$ eV. It is clear that the doping has a strong effect on magnetization: $M$ reduces to half its initial value, even though all $M(H)$ curves look qualitatively the same and are accurately described by the Brillouin function with $S = 1/2$. This indicates a reduction in the number of magnetic moments for the same number of vacancies. It also shows that high $n$ do not lead to stronger interaction, as the vacancy magnetic moments remain non-interacting. This behaviour was found to be universal, even though $n_v$ varied for different samples by more than an order of magnitude, with the average separation between vacancies changing from $\sim 3$ to 10 nm. Figure 2 shows the evolution of the number of detected spins $N_{\text{D}}$ in two graphene samples with different $n_v$ as a function of $E_F$. Initially, $N_{\text{D}}$ is gradually decreasing with increasing the hole concentration, but at $E_F \approx 0.4$ eV, it falls sharply and seems to saturate to $N_{\text{D}} \approx N_{\text{D}}^{0}/2$ at the maximum doping, where $N_{\text{D}}^{0}$ is the number of spins before doping. As soon as the dopants were removed from graphene by mild annealing, $M$ recovered its initial value, that is, the effect is fully reversible (Fig. 2).
magnetic moments associated with a vacancy, and only one of 
shifted sufficiently away from the neutrality point. 

reconstruction and the associated Jan–Teller distortion that 
was measured for several samples with different vacancy 
reduction in magnetization signal at maximum doping, which 
after annealing cycles. To gain further insight, Fig. 3 plots the 

Hybridization between the 

Depending on the degree of hybridization, the magnetic moment 

We attribute this finding to the presence of two types of 
magnetic moments associated with a vacancy, and only one of 
them is being affected by such a shift in $E_F$. Indeed, let us recall 
the origin of defect-induced magnetism in graphene. It lies in the 
imbalance that the defects create between its two sublattices and 
the resulting appearance of localized $\pi$ states with energy close to 
the Dirac point\textsuperscript{12–21}. As long as these states are singly occupied, 
due to Coulomb repulsion, $U_C$, they give rise to magnetic moments $\mu = 1/2 \mu_B$. This simple picture is expected for adatoms, 
such as fluorine or hydrogen, whereas for vacancies the origin of 
magnetic moments is more complex. In addition to the above $\pi$ 
states, there are dangling $\sigma$ bonds that can have some role 
too\textsuperscript{10,14,16,18–21}. For example, vacancies in insulating boron nitride 
are expected to be magnetic\textsuperscript{27}. The relative contribution of $\sigma$ 
states to vacancy magnetism is unknown and a matter of 
debate\textsuperscript{18,20}. Because of high chemical reactivity of the dangling 
bonds, it is often assumed that they are saturated with, for 
example, hydrogen and therefore do not contribute to magnetism 
(see, for example, Palacios and Yndurain\textsuperscript{18} and Nanda \textit{et al.}\textsuperscript{21}). Then, the magnetic moment is purely due to itinerant 
(conduction) electrons. Another possible scenario is a vacancy 
reconstruction and the associated Jan–Teller distortion that 
results in hybridization between the $\pi$ and $\sigma$ states\textsuperscript{14,19–21}. 
Depending on the degree of hybridization, the magnetic moment 

$E_F \approx 0.54$ eV was the maximum doping that we were able to 
achieve with HNO\textsubscript{3}, in agreement with the calculated energy 
dependence of the density of states (DOS) for the NO\textsubscript{2} molecule 
adsorbed on graphene\textsuperscript{24}. The data scatter between different 
samples and doping levels does not allow us to follow the 
transition in Fig. 2 in more detail and confirm the apparent 
saturation to half magnetization above $E_F \approx 0.45$ eV. However, 
this behaviour was observed for many samples and repeatedly 
after annealing cycles. To gain further insight, Fig. 3 plots the 

for a vacancy has been predicted to be between $\sim 1.45$ and 2 $\mu_B$ 
(refs 14,16,19,21).

Our experiment suggests an intermediate scenario in which the 
dangling bonds remain unsaturated and the hybridization does not 
have a significant role. In this case, each vacancy is expected to 
provide two independent contributions, which come from the 
singly occupied localized $\pi$ state and the unsaturated $\sigma$ bond. At 
sufficiently large doping, such that $|E_F| \geq U_C$, the localized $\pi$ state 
becomes doubly occupied and the corresponding magnetic moment disappears, whereas the unpaired $\sigma$ electron remains 
unaffected by doping and provides the residual $M$. Because the 
two contributions appear to be nearly equal, hybridization 
between the two electronic states should be weak. This is also 
in agreement with the measured $S = 1/2$. Note that it would 
require unrealistically high doping to occupy the $\sigma$ state and fully 
suppress the vacancy magnetism.

To support the above interpretation, a neat experiment would 
be to compare the effect of doping on vacancy magnetism with 
that for adatoms, where there are no dangling bonds and only 
localized $\pi$ states are expected\textsuperscript{13–15}. However, it has proven 
difficult experimentally to introduce adatoms without their 
significant clustering. The latter locally opens a band gap, 
quenches nearest-neighbour magnetic moments and so on, so 
that the system can no longer be considered as graphene but 
becomes its chemical derivative\textsuperscript{8}. We have circumvented this 
problem by exploiting the experimental fact that if graphene is 
heated at $\gtrsim 350$ °C, it results in the appearance of so-called 
resonant scatterers\textsuperscript{28–31}. They reduce graphene’s electronic 
quality and result in the D peak in Raman spectra. The scatterers are attributed to some organic residue that is always 
present on graphene and strongly (sp\textsuperscript{3}) bonds to it at high $T$\textsuperscript{28}.

Resonant scatterers is another name for the localized $\pi$ states near 
the Dirac point in the context of electron transport. With these 
early studies in mind, we annealed several samples of pristine 
(nonirradiated) graphene laminates at $350$ °C in Ar–H\textsubscript{2} 
atmosphere. This induced notable paramagnetism with $N_S^0 \approx 3 \times 10^{18}$ g\textsuperscript{−1}. The observed $M(H)$ curves were practically identical to those of irradiated laminates and, again, are 
accurately described by the Brillouin function with $S = 1/2$. The 
found $N_S^0$ corresponds to 2–3 sp\textsuperscript{3} bonds induced by annealing per 
each graphene crystallite in the laminates.
but is in agreement with the experiment. The reason for a finite
hybridization strength (that is, determination of $N$)
as soon as HNO$_3$ molecules were removed by mild annealing
in the case of vacancies, the switching effect is also fully reversible:
for $|a|$ and the switching effect is also fully reversible:
as soon as HNO$_3$ molecules were removed by mild annealing
at ~100 °C, the paramagnetic signal recovered its initial value $N_0$.

Discussion

The magnetic moment due to sp$^3$ impurities and its variation
with doping can be calculated analytically using the expression:

$$N(E) = \frac{d^2|E|}{[E(1 - a\ln|E/E_a|) + E_a]^2 + (|a^2E|)^2}$$

which describes the DOS in graphene due to resonant scatterers such as sp$^3$ adsorbates (see Supplementary Note 1). Here, $E_a$ is the states' energy position and $a$ the hybridization parameter, both in units of the half width $W$ of graphene's energy band ($t$ is the nearest-neighbour hopping parameter). For sp$^3$ impurities relevant to our experiment (monovalent organic groups or hydrogen adatoms), $E_a = 0.02$ and $a = 2/3$ (that is, hybridization strength $\approx 2t$)$^{31}$. The magnetic moment (number of spins) is given by the fraction of singly occupied impurity states, which is determined by the Hubbard energy $U$ and can be found by integrating equation (1) over the occupied states:

$$N_0(E_F) = \int_{E_F - U}^{E_F} dE N(E)$$

Using equation (2), we obtained the $N_0(E_F)$ shown in Fig. 4, which effectively has only one fitting parameter, $U$, because the dependence is found to be qualitatively insensitive to $E_d$ and $a$ over a wide range of the parameters (the best-fitting value of $U$ as in Fig. 4 is $U = 0.5$ eV). $N_0$ drops sharply at $E_F \approx U$ as expected, exhibiting a cusp-like dependence $1/\ln|E_F - U|$. Note that the cut off does not lead to zero magnetization, which seems surprising but is in agreement with the experiment. The reason for a finite remaining $N_0$ on the theoretical curve is that the DOS deviates significantly from the standard Lorentzian peak. This arises due to the linear increase in the DOS of conduction electrons in graphene and a renormalization of the positions of impurity states because of hybridization. As a result, $N(E)$ decays as $1/|E\ln|E||$ at large $E$, much slower than the standard $1/E^2$ dependence for the Lorentz distribution. This means that the magnetic states become totally doubly occupied only for $E_F \gg U$ and, therefore, $N_0$ exhibits a long tail at higher $E_F$ such as in Fig. 4.

Finally, let us add several comments. First, the found value of the Coulomb energy $U = 0.5$ eV allows us to estimate the spatial localization $r_L$ of the $\pi$ states as $r_L \approx 2.0$ nm (using the known effective Coulomb interactions in graphene$^{2,3}$), that is, the $\pi$ state is localized over several benzene rings, in agreement with theory$^{13,14,16}$. Second, comparing the nearly constant $N_0$ at $E_F < 0.3$ eV for sp$^3$ impurities in Fig. 4 (both theory and experiment) with gradually decreasing $N_0$ for vacancies indicates that the magnetic moment is sensitive to the shape of the DOS peak: the latter is much broader for vacancies$^{14}$ resulting in a more gradual decrease of $N_0$ in equation (2), in agreement with experiment. Third, an alternative mechanism for quenching of the magnetic moments at high $\pi$ could be the Kondo effect$^{17,20}$. However, the observed cumulative contribution from localized and itinerant moments and their $T$ dependence (Supplementary Figs S3 and S4) do not support this scenario (see Supplementary Note 2). Fourth, the discussed threshold doping is achievable in field-effect devices with high-quality gate dielectrics such as boron nitride. This should allow strong suppression of the rapid spin relaxation, characteristic to the existing graphene devices, so that spin currents can be efficiently switched on and off by gate voltage as required for a spin transistor operation.

Methods

Preparation of irradiated graphene laminates. Our graphene samples were prepared as described in Nair et al.$^8$ In brief, we used ultrasonic cleavage of highly oriented pyrolytic graphite in an organic solvent, N-methylpyrrolidone, following the procedure described in Sepioni et al.$^{33}$ The resulting laminates consist of predominantly 50–50 nm crystallites, aligned parallel to each other and
dependent. Proton irradiation under such conditions produces
predominantly single vacancies$^{12}$; their number for each sample was estimated
on the basis of the corresponding fluence, surface area and the number of defects
created by each proton as obtained from computer simulations (SRIM software package). Further details can be found in Nair et al.$^8$ We note that impacts of energetic protons on graphene may also give rise to a finite concentration of other defects, such as divacancies and carbon adatoms, but their effect on magnetism is negligible, as the former do not possess magnetic
moment and the latter are mobile at room temperature and tend to cluster
with the loss of magnetism$^{34}$.

In our SQUID measurements, the field was usually applied parallel to the
lamination direction to avoid diamagnetism that is strong in the perpendicular
field$^5$. A small remnant diamagnetic background due to some misalignment was
linear with $H$ up to $7T$ at all $T$ and subtracted for clarity from the plotted data.

Molecular doping and determination of carrier concentrations. Molecular
doping has been shown to be an effective way of changing carrier concentration in
graphene, with water, NO$_2$ gas and HNO$_3$ identified as acceptors (hole dopants)
and ammonia, anisole, aniline and N,N,N’,N’-tetramethyl-p-phenylenediamine (TMDP)
as donors (electron dopants)$^{23,25,26,35–39}$. After testing the above
molecules on graphene laminates, HNO$_3$ was found to be the only molecule
providing sufficiently high carrier concentrations, $n$ (up to $n \approx 2 \times 10^{13}$ cm$^{-2}$),
with $n$ remaining same for several weeks and uniform distribution (as manifested in same $n$ measured in different locations on the graphene laminates). To achieve gradual changes in $n$, the laminates were exposed

\[ N(E) = \frac{d^2|E|}{[E(1 - a\ln|E/E_a|) + E_a]^2 + (|a^2E|)^2} \]

\[ N_0(E_F) = \int_{E_F - U}^{E_F} dE N(E) \]
to HNO₃, diluted with water at different molar concentrations of 0.1–15 M.

The maximum doping level that we could achieve corresponded to n ≅ 2 × 10¹⁵ cm⁻² cm⁻³. Importantly, once exposed to HNO₃, the carrier concentration remained stable for many days at room T, in agreement with relatively high adsorption energy for this molecule but recovered the initial value under mild annealing in argon.

Gaseous NO₂ produced qualitatively similar results (in terms of both measured n and the effect on magnetization), but the doping level was difficult to control and showed significant nonuniformity. Ammonia did not produce any agreement with relatively high adsorption energy for this molecule but recovered changes in HNO₃ concentration.

**References**

Acknowledgements
This work was supported by the UK Engineering and Physical Sciences Research Council. A.H.C.N. acknowledges support from NRF-CRP (R-144-000-295-281). A.V.K., O.L. and J.K. acknowledge support from the Academy of Finland through projects 218545 and 263416.

Author contributions
I.V.G. directed the project. I.V.G. and R.R.N. designed the experiments. R.R.N., I.-L.T. and M.S. performed the experiments. O.L., J.K. and A.V.K. performed proton irradiation and analysed defect structures. M.I.K. and A.H.C.N. provided theory. I.V.G. and A.K.G. wrote the paper. All authors contributed to discussions of the results.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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