A defective graphene phase predicted to be a room temperature ferromagnetic semiconductor

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Abstract. Theoretical calculations, based on the hybrid exchange density functional theory, are used to show that in graphene, a periodic array of defects generates a ferromagnetic ground state at room temperature for unexpectedly large defect separations. This is demonstrated for defects that consist of a carbon vacancy in which two of the dangling bonds are saturated with H atoms. The magnetic coupling mechanism is analysed and found to be due to an instability in the π-electron system with respect to a long-range spin polarization characterized by alternation in the spin direction between adjacent carbon atoms. The disruption of the π-bonding opens a semiconducting gap at the Fermi edge. The size of the energy gap and the magnetic coupling strength are strong functions of the defect separation and can thus be controlled by varying the defect concentration. The position of the semiconducting energy gap and the electron effective mass are strongly spin-dependent and this is expected to result in a spin asymmetry in the transport properties of the system. A defective graphene sheet is, therefore, a very promising material with an in-built mechanism for tailoring the properties of future spintronic devices.

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The miniaturization of silicon devices has delivered exponentially growing performance for the past 50 years, but quantum limits are now being reached as transistor gate lengths approach 5 nm. Spintronics, which exploits the electron spin rather than the charge, will operate on a sub 1 nm length scale and thus facilitate another generation of devices [1].

The achievement of many of the promises of spintronics depends on the ready availability of a material that is a semiconductor, is ferromagnetic at room temperature and has a highly tunable band gap and magnetic coupling. The controlled synthesis of a robust room-temperature, ferromagnetic semiconductor on the nanoscale has yet to be achieved. Recent reports of high-temperature ferromagnetism in metal-free carbon materials have generated a great deal of interest [3]. Proton-bombardment of graphite [4] gives rise to a ferromagnetic phase which x-ray circular dichroism measurements [5] have shown to originate from carbon sp electrons. Pyrolytic treatment of organic compounds [6] also gives rise to a ferromagnetic material. In both cases, the magnetic phase appears to be a minority phase in a non-magnetic host. The detailed composition and structure of the minority phase have not yet been determined, but the concentrations of magnetic impurities have been measured sufficiently accurately to suggest that the magnetism is not the result of contamination [7].

The occurrence of high-temperature ferromagnetism in purely sp-bonded materials is a major challenge to current theoretical understanding of magnetic interaction mechanisms. A chemical or structural defect in a carbon-based material leads to the creation of local magnetic moments due to the presence of under- or over-coordinated atoms. The presence of local moments needs to be accompanied by strong long-range coupling between them for the ferromagnetic order to survive thermal fluctuations at room temperature. In extended graphene sheets, local moment formation at point defects is now well established [8]. A significant step forward in the study of the magnetic coupling between local defects has been the demonstration that the presence of spin moments at the edges of graphene ribbons can lead to an instability of the $\pi$-electron system, providing a mechanism for long range antiferromagnetic coupling which is robust with respect to competing instabilities involving charge ordering and geometric distortions [9]–[11]. More recently, Yazyev and Helm [12] have studied defective graphene using the density functional theory. They find a ferromagnetic ground state which they assume to be of the itinerant type due to the metallicity of their system. Vozmediano et al [13] studied the interaction between localized moments originating from lattice defects at large distances and concluded that the transition temperature to the ferromagnetic Ruderman–Kittel–Kasuya–Yosida (RKKY) state is far below room temperature. Dugaev et al [14] predicted that if the spin–orbit interaction is taken into account, an energy gap opens at the Fermi level and the
RKKY model is not applicable. A possible source of high-temperature ferromagnetism in carbon systems has been ascribed by Edwards and Katsnelson [15] to a limited screening of the interactions between itinerant electrons in impurity sp-bands. The expected suppression of the Stoner critical temperature (typical in the case of transition metal impurity d-bands) is considerably reduced due to a less effective screening of the electron interaction. In the present case, we show a completely different scenario, i.e. that high-temperature ferromagnetism in a carbon system can be entirely supported by an insulating state of the electronic structure. The present work demonstrates that local spin moments in defective graphene interact strongly over long distances and may therefore lead to a ferromagnetic semiconducting state at room temperature. The strong, long-range magnetic coupling necessary for magnetic ordering at room temperature in this semiconducting material is provided via a spin alternation mechanism that depends on the presence of partially filled π orbitals in the sp2-bonded, bipartite lattice of graphene. Moreover, it is shown that the spin-dependent band gap and magnetic coupling strength can be varied through control of the defect concentration, opening up the possibility of highly tunable graphene-based spintronics nanodevices. This study, therefore, reinforces the case, which has been growing stronger and stronger since the ground-breaking practical realization of isolated graphene sheets [2], for considering graphene amongst the most promising materials for building the electronic and spintronic devices of the future.

2. Computational details

Spin localization at defects and long-range spin coupling are studied here using all-electron, two-dimensionally (2D) periodic, hybrid exchange density functional theory (B3LYP [16]–[18]), which significantly extends the reliability of the widely used local and gradient-corrected approximations to density functional theory in strongly interacting systems [19]–[21]. In the CRYSTAL package, used for this study, the crystalline wavefunctions are expanded as a linear combination of atom-centred Gaussian orbitals (LCAO) with s, p, d or f symmetry. The calculations reported here are all-electron, i.e. with no shape approximation to the ionic potential or electron charge density. Basis sets of double valence quality (6-21G* for C and 6-31G* for H) are used. A reciprocal space sampling on a Monkhorst–Pack grid of shrinking factor equal to 6 is adopted after finding it to be sufficient to converge the total energy to within 10−4 eV per unit cell.

In the present work, we consider three types of structures, characterized by different arrangements of defects. The first structure contains defects arranged in pairs within a rectangular unit cell that is 25 Å wide and of length 2L, which is convenient for studying interdefect coupling. The system under study is therefore infinitely periodic in the two dimensions parallel to the graphene plane and non-periodic in the direction perpendicular to the plane. In figure 3, the unit cell containing a pair of defects is shown. The defects are therefore arranged along parallel chains running along the horizontal direction and the chains are 25 Å part. The second structure is a hexagonal cell used to quantify interchain effects. The third structure is a triangular superlattice used for representing the band structure in a form compatible with that of graphene (figure 4). All the structures considered were initially relaxed using a force-field model (GULP [22]) in which the carbon–carbon and carbon–hydrogen interactions are described via the Brenner bond order potential [22]. In the case of the calculation of the stabilization energy ΔE (see below and figure 2), full quantum mechanical relaxation was carried out for the structure with L = 7.5 Å (see below) and resulted in a small increase in...
Figure 1. The structure of the defect considered in the present study.

ΔE (see figure 2) of 25 meV. As the additional relaxation is confined to the region of the defect, the energy shift is expected to depend weakly on the defect separation especially at large distances and thus full quantum mechanical relaxation was not required for larger structures. The magnetic stabilization energy reported in figure 2, and the transition temperature based on it, is therefore slightly underestimated. In the analysis of the electronic band structure shown in figure 4, where defects are displayed in a triangular lattice and are 20 Å apart, we performed a full quantum-mechanical optimization in order to quantify the magnitude and decay law of the semiconducting gap.

3. Results and discussion

A number of point defects are possible. Here we choose to study a simple carbon vacancy in which two of the three dangling carbon bonds are saturated with H atoms. This defect has been proposed previously, studied extensively [8] and is displayed in figure 1. Within a valence bond picture there are two unpaired electrons in the defect as the breaking of three π-bonds generates 1/3 of an unpaired electron on each of the C atoms neighbouring the vacancy and the breaking of the σ-bond also generates an unpaired electron. Hund’s rule coupling within the uncoordinated C atom and the spin-alternation rule operating between the π-electrons ensure that these spins are aligned and thus the overall magnetic moment on the defect is 2 μB (μB is the Bohr magneton)\(^5\).

In the present study, this defect is used as an example of the many possible structures at which electron localization might occur in a graphene sheet. The conclusions drawn below depend on the arrangement of defects and on their ability to generate a local magnetic moment through an instability of the electronic system, but are not expected to depend on the structural and chemical details of the defects.

The interaction of the localized moments is quantified by computing the quantity ΔE (stabilization energy), which is defined as the difference between the total electronic energy of the antialigned and aligned arrangements of the defects’ spins. The decay of the stabilization energy with L is approximately \(ΔE = 4208L^{-1.43}\) meV and it is shown

\(^5\) We note that the discrepancy with the value of 1.2 μB obtained in [8] for the same defect is due to a higher degree of electron localization induced by a hybrid functional.
Figure 2. The dependance of the magnetic stabilization energy $\Delta E$ on the distance between defects $L$.

The calculated coupling energy can be related to the Curie temperature ($T_c$), at which the ferromagnetic order is lost due to thermal fluctuations, through an effective Heisenberg model with an interaction $J = \Delta E/2$ per pair of spins. According to the Mermin–Wagner theorem [23], a 2D isotropic Heisenberg ferromagnet is unstable with respect to thermal fluctuations at any finite temperature and therefore does not support long range order. However such effects are seen to reduce significantly when a small coupling along the third direction is introduced. Recent quantum Monte Carlo (QMC) studies on quasi-2D Heisenberg ferromagnets [24, 25] have shown that the introduction of an interlayer coupling 0.1% of that in-plane is enough to restore a finite value of $T_c$. In particular, for a square lattice of spin-1, $T_c = J S(S + 1)0.44/K_B$ (see figure 3 in [25]) which, compared to a mean-field expression $T_c = JS(S + 1)z/3K_B$ ($z$ is the coordinaton number), differs by a factor of about 3. On the right-hand side of the graph in figure 2, the transition temperature $T_c$ for a square lattice arrangement of defects within the QMC formula above is shown for different interdefect distances. For this arrangement of the defects, the ferromagnetic state is lower in energy over the whole range of distances considered and is predicted to be stable at room temperature up to very large defect separations (figure 2).

The present system should be considered as a model system for the study of more complex and realistic cases such as defective graphite [4] or multilayer defective graphene or defective graphene on a substrate where a small but non-zero exchange interaction in the third direction is usually found. The ferromagnetic long-range order at room temperature is in agreement with recent experiments on bombarded graphite where a room temperature ferromagnetic ground state is found and the average interdefect distance was determined to be about 1 nm [26].

Effects due to interchain interaction expected at distances $L$ close to the interchain fixed distance of 25 Å are seen not to change the picture qualitatively. To confirm this, we independently considered a series of calculations of $\Delta E$ for a strictly 2D arrangement of defects (a hexagonal superlattice of defects) for which the qualitative nature of the long-ranged interaction is unchanged and the power of the decay law is found to be 1.7.
Figure 3. Isovalue surfaces of the spin density of the graphene sheet with a defect separation of 20 Å. The red (at $0.021 \mu_B \text{Å}^{-1}$) and blue (at $-0.021 \mu_B \text{Å}^{-1}$) isosurfaces represent the majority and minority spin densities, respectively. The majority spin density within the defect is concentrated on the unsaturated carbon atoms and their second neighbours. The operation of the spin alternation rule in the spin-polarized lattice is clearly visible.

The bipartite nature of the lattice and the presence of the partially filled π system of electrons in the sp² network of atoms are essential for establishing the strong, long-range coupling mechanism that gives magnetic ordering at high temperature. This mechanism is the result of local exchange repulsion, which ensures that the partially filled π orbital of each carbon atom is coupled in an antiparallel fashion to that on its nearest neighbour. The operation of this mechanism to produce a long-range spin polarization within the sheet is evident in the spin density displayed in figure 3 and has been observed previously in π-bonded carbon networks [27]. It is notable that this mechanism extends the validity of Lieb’s theorem beyond a nearest neighbour model [28]. The predicted ferromagnetic nature of the overall interaction is also entirely consistent with previous studies of interactions between extended defects in graphene ribbons [9, 10]. It is clear from the spin alternation mechanism that the ferromagnetic coupling between the localized spin moments depends on the defects being arranged on the same sublattice of the graphene sheet. A regular arrangement on opposite sublattices would lead to antiferromagnetic coupling, as seen by Yazyev and Helm [12] at short separation, and a random arrangement of defects would be expected to lead to a ground state of smaller spontaneous magnetization, while retaining the strong local coupling. This prediction agrees with the current experimental observation by Esquinazi et al [4, 27] (i.e. high transition temperature and small total magnetization), where the defect density is controlled, to an extent, via the defect implantation technique, but the defects are most probably distributed randomly. The production of a graphene sheet and control of its defect density is not unrealistic using current techniques [2, 4], but methods for controlling the defect arrangement have not yet been established.

To analyse the semiconducting properties of the electronic structure of the system considered in the present study, the electronic band structure is shown in figure 4 for the ferromagnetic state of a triangular array of defects at a separation of 20 Å. This choice of array facilitates comparison with the electronic structure of perfect graphene. The previously analysed
The electronic energy bands of the majority (a) and minority (b) spin states of the ferromagnetic ground state in a defective graphene sheet with a defect separation of 20Å plotted with respect to the Fermi energy ($E_F$). The rather flat impurity bands near the Fermi energy, which are associated with the states localized at the defect, are indicated in red.

The presence of the defects and the magnetic ordering break the symmetry of the graphene $\pi$ system, opening band gaps of 0.51 and 0.55 eV in the majority and minority spin band structures, respectively. The energy gap of the majority states is shifted upwards by about 0.20 eV with respect to the energy gap of the minority states, and the shape of the bands around the Fermi energy is markedly spin-dependent. A strong spin asymmetry in the conductivity of the sheet is therefore to be expected. The size of the band gap is reduced to 0.1 eV when adopting the generalized gradient approximation proposed by Perdew, Burke and Ernzerhof (PBE) [31].

Calculations at a variety of defect separations establish that the band gap scales as $L^{-2}$. This decay law is consistent with that recently calculated for graphene ribbons where the edges are line defects at which the spin moments localize and the band gap scales as $L^{-1}$ with the ribbon width.

Recently, Yazyev and Helm [12] reported generalized gradient approximation (GGA) calculations that produced ferromagnetism in graphene induced by the presence of defects, but the magnetic coupling mechanism proposed differs strongly from that described in the present study. In [12], a metallic state is obtained and the ferromagnetic order is therefore assumed to be supported by itinerant electrons. In the present study, the ground state is semiconducting and the magnetic coupling is clearly not due to itinerant electrons. For this reason, we adopt an effective Heisenberg model in order to assess the temperature-related properties of the system rather than the Stoner model of [12]. The explanation for this different behaviour does not reside in the morphology or in the concentration of defects nor in the treatment of electronic exchange and correlation (the band gap is still present when using the gradient-corrected functional PBE as adopted in [12]) but is due to the arrangement of defects. In [29], the authors studied the same H-chemisorption defect as in [12], but considered a different arrangement of defects.

![Figure 4](http://www.njp.org/)
(specifically, the unit cell in [29] has zigzag borders, whereas armchair borders are used in [12]). This results in a semiconducting ground state as found here. In [29], the magnetic coupling between defects was not analysed and this is the aim of the present study.

The opening of a gap obtained in this study is an effect of much larger magnitude than the opening due to spin–orbit coupling described in [15]. The effect of the spin–orbit coupling is not included in our study since it is expected to be negligible in carbon systems (see for example [30]).

4. Conclusions

In conclusion, the ground state of a 2D graphene sheet containing a periodic array of point defects has been shown to be both ferromagnetic at room temperature and semiconducting for defect separations up to 20 Å and thus for defect concentrations as low as $10^{13}$ cm$^{-2}$. The energy gap and magnetic coupling depend strongly on defect concentration. We conclude that a doped or defective graphene sheet is a very promising material with an in-built mechanism for tailoring properties for a variety of spintronics applications.

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