Defective Graphene Phase Predicted to be a Room Temperature Ferromaapetic Semiconductor

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Theoretical calculations based on 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 a defect separation up to 25 A. This is demonstrated for defects which consist of a carbon vacancy in which two 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 polarisation characterised 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 pro a very promising material with an in-built mechanism for tailoring the properties of the spintronic devices of the future.

PACS numbers: pars

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

The achievement of many of the promises of spintronics depends on the ready availability of a material that is a semiconductor, ferromagnetic at room temperature, and with a highly tunable band gap and magnetic coupling. The controlled synthesis of a robust room temperature, ferromagnetic semiconductor on a nanoscale has yet to be achieved. Recent reports of high temperature ferromagnetism in metal-free carbon materials have generated a great deal of interest'. The ferromagnetic phase, produced by the proton-bombardment of graphite or the pyrolytic treatment of organic compounds 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 contaminations.

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. 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 π-electron system, providing a mechanism for long, range antiferromagnetic coupling which is robust with respect to competing instabilities

involving charge ordering and geometric distortions. More recently, Yazyev and Helm have studied defective graphene using 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 studied the interaction between localised moments originating from lattice defects at large distances and concluded that the transition temperature to the ferromagnetic RKKY state is far below room temperature. Dugaev et al. 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.

In the current work it is demonstrated that local spin moments in defective graphene interact strongly over a long distance, up to 25 A, and lead to a ferromagnetic semiconducting state at room temperature. This defective graphene sheet, therefore, displays all of the desirable properties for spintronics applications. 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 realisation of isolated graphene sheets', for considering graphene amongst the most promising materials for building the electronic and spintronic devices of the future.

Spin localisation at defects and long range spin coupling are studied here using all electron, two-dimensionally periodic, hybrid exchange density functional theory (B3LYP) which significantly extends the reliability of the widely used local and gradient corrected approximations to density functional theory in strongly interacting systems. 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 structure, characterised by different arrangements of defects. The first contains defects arranged in pairs within a rectangular unit cell that is 25 A wide and of length 2L, which is convenient for studying inter-defect coupling. In Fig. 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 distant 25 A . The second is an hexagonal cell used to quantify inter-chain effects. The third is a triangular superlattice used for representing the band structure in a form compatible with that of graphene (Fig. 4). All of the structures considered were initially relaxed using a force-field model (GULP") in which the carbon-carbon and carbon-hydrogen interactions are described via the Brenner bond order potential". In the case of the calculation of the stabilisation energy AE (see below and Fig. 2), full quantum mechanical relaxation was carried out for the structure with L=7.5A (see below) and resulted in a small increase in AE (see Fig. 2) of 25 meV. As the additional relaxation is confined to the region of the defect, the energy shift is independent of the defect separation and thus full quantum mechanical relaxation was not performed for larger structures. In the analysis of the electronic band structure shown in Fig. 4, where defects are displayed in a triangular lattice and are 20 A apart, we performed a full quantum-mechanical optimisation in order to quantify exactly the magnitude and decay law of the semiconducting gap. 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, and is displayed in Fig. 1.

FIG. 1: The structure of the defect considered in the present study.

Within a valence bond picture there are two unpaired electrons in the defect as the breaking of three 7-bonds generates 1/3 of an unpaired electron on each of the C-atoms neighbouring the vacancy and the breaking of the a-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 ensures that these spins are aligned and thus the overall magnetic moment on the defect is 2pB (μ_B is the Bohr magneton). (We note that the discrepancy with the value obtained in Ref. 7 for the same defect is due to a higher degree of electron localisation induced by a hybrid functional.) In the current study this defect is used as an example of the many possible structures at which electron localisation 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 localised moments is quantified by computing the quantity AE (stabilization energy) which is defined as the difference between the total electronic energy of the antialigned and aligned arrangements of the defects spins. The calculated coupling energy can be related to the Curie temperature (T_c), at which the ferromagnetic order is lost due to thermal fluctuations. Here an effective Heisenberg model within a mean-field approximation is used which expresses the critical temperature as $T_c=[S(S+1)/3K_B]\Delta E$, where the spin, S, localised at each defect is 1 and K_B is the Boltzmann constant. On the right-hand side of the graph, T_c is expressed in Kelvin. The decay of the stablisation energy with L is approximately $\Delta E=4208L^{-1.43}$ meV (Fig. 2).

FIG.2:The dependance of the magnetic stabilization energy ΔE on the distance between defects L.

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 a defect separation of 25 A (Fig. 2). The Mermin-Wagner theorem states that a strictly two dimensional Heisenberg ferromagnet will be unstable with respect to thermal fluctuations but here such fluctuations are likely to be strongly suppressed by the large spatial anisotropy of the graphene sheet in any physical realisation.

Effects due to interchain interaction expected at distances L close to the interchain fixed distance of 25 A are seen not to change the picture qualitatively. To confirm this, we independently considered a series of calculation of ΔE for a strictly 2-dimensional 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. It is interesting that the decay law depend quantitatively on the arrangement of defects but that is not the main point of this study which is concerned with the interaction between moments and the semiconducting nature of the ground state.

The bipartite nature of the lattice and the presence of the partially filled π system of electrons in the 5132 net-work 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 anti-parallel to that on its nearest neighbour. The operation of this mechanism to produce a long range spin polarisation within the sheet is evident in the spin density displayed in Fig. 3 and has been observed previously in it bonded carbon networks.

It is notable that this mechanism extends the validity of Liebs theorem beyond a nearest neighbour model. The predicted ferromagnetic nature of the overall interaction is also entirely consistent with

previous studies of interactions between extended defects in graphene ribbons8.9. It is clear from the spin alternation mechanism that the ferromagnetic coupling between the localised spin moments depends on the defects being arranged on the same sub-lattice of the graphene sheet. A regular arrangement on opposite sublattices would lead to antiferromagnetic coupling, as seen by Yazyev et al. at short separation", and a random arrangement of defects would be expected to lead to a ground state of intermediate spontaneous magnetisation.

FIG. 3: (color on line) Isovalue surfaces of the spin density of the graphene sheet with a defect separation of 20 A. The red (at 0.021 μ_B/A) and blue (at -0.021 μ_B/A)) 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 polarised lattice is clearly visible.

To analyse the semiconducting properties of the electronic structure of the system considered in the present study, we show in Fig. 4 the energy bands for the ferromagnetic state of a triangular array of defects at a separation of 20 A . This choice of array facilitates the comparison of the electronic structure of defective graphene with that one of perfect graphene, which is taken here as a benchmark. The previously analysed structures (parallel chains and hexagonal arrangement of defects) show the same qualitative features as in the triangular case.

The presence of the defects and the magnetic ordering break the symmetry of the graphene π system, opening band gaps of 0.51 and 0.55 eV in the majority and minority 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. (We note that the value of the band gap is reduced to 0.1 eV when adopting a generalised gradient approximated functional.)

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 localise and the band gap scales as L-1 with the ribbon width.

FIG. 4: (color on line) 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 20 A plotted with respect to the Fermi energy (EF). The rather flat impurity bands near the Fermi energy, which are associated with the states localised at the defect, are indicated in red.

Recently Yazyev et al. reported ferromagnetism in graphene induced by the presence of defects but the magnetic coupling mechanism proposed differs strongly from that described in the current work. In Ref. 11 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 amd 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 Ref. 11. 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 same functional as adopted in Ref. 11) but is due to the arrangement of defects. In Ref. 24, the authors study the same H-chemisorption defect as in Ref. 11, but consider a different arrangement of defects (specifically, the unit cell in Ref. 24 has zig-zag borders whereas armchair borders are used in Ref. 11). This results in a semiconducting ground state as found here. In Ref. 24 the magnetic coupling between defects was not analysed and

this is the aim of the present study. Other studies based on the tight-binding model of graphene have recently been dedicated to the assessment of exchange interaction between moments. As the validity of that model is limited to low defect concentration, only an indirect type of exchange mechanism can be assumed (namely RICKY), in contrast to the direct mechanism found here. 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 Ref. 13. The effect of the spin-orbit coupling is not included in our study since it is expected to be negligible in carbon systems. In conclusion the ground state of a two dimensional 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 25 A 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.

Acknowledgments

This work is supported by the European Union under the NEST FERROCARBON project (CEC 012881). The authors would like to thank G. Mallia for technical and scientific assistance and the Computational Science and Engineering Department of the CCLRC for providing the computing facilities.

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