

1. Title of the project

Exploring magnetism in graphene.

2. Applicant

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3. Institute

Physics of Nanodevices

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4. Abstract

We propose to investigate the possibilities of turning graphene from a paramagnetic into a ferromagnetic state. This goal can be approached from two sides: making graphene magnetic on itself (intrinsic) by introducing impurities, like hydrogen chemisorbed sites and vacancies, or using the proximity effect, where magnetism is imposed by ferromagnetic interactions with a neighbouring material. We aim to measure the size of magnetisation and strength of exchange field with the use of the non-local spin-valve technique. Focus of our research will be the influence of defects concentration, type of defects and device geometry on the spin signal in graphene. Transport measurements include spin-precession and spin-relaxation studies with different contact materials (ferromagnetic/nonmagnetic) and its relative arrangement within non-local spin-valve device geometry. Additionally, we want to study the influence of temperature and external magnetic field on the observed signal. At the final stage the usefulness of the system for spin-filtering as well as for other spintronic applications will be considered. In our project, we will strongly profit from collaborations with physics groups within and outside our institute.

5. Duration of the project

4 years, starting from October 2009

6. Personnel**6.1 Senior scientists**

Name	Task in project	Time
Prof. Dr. Ir. B.J. van Wees	Supervision and management	5%
Dr. T. Banerjee	Supervision	5%
Prof Dr. L.H. Tjeng	Supervision	5%
Dr. C. Józsa	Supervision and analysis	2%

6.2 Junior-scientists and technicians

Name	Task in project	Time
PhD student	Experiments and analysis	90%
Tjeng based researcher	Deposition of EuO on graphene	20%
B. Wolffs	Technical support	5%
Ing. S. Bakker	Technical support	5%

7. Cost-estimates

7.1. Personnel positions

One 'onderzoeker in opleiding' position for four years.

7.2. Running Budget

20 k€/year

7.3. Equipment

Extending and facilitating the available equipment for plasma etching (RIE) with the hydrogen line.

Equipment	Costs
Hydrogen storage containers	5 k€
Safety pipes and engines for hydrogen	20 k€
TOTAL	25 k€

7.4 Other support

The project is part of the larger research program of Spintronics and valleytronics of FOM. Involved personnel described above is employed via Zernike Institute for Advanced Materials or associated research programs.

7.5 Budget summary (in k€)

	2009	2010	2011	2012	2013	TOTAL
<u>Personel (positions)</u>						
PhD students	18	43	43	43	33	180
Postdocs	-	-	-	-	-	-
Technicians	-	-	-	-	-	-
Guests	-	-	-	-	-	-
Personnel (costs)	18	43	43	43	33	180
Running budget	16	35	20	20	16	107
Equipment FOM-part	-	-	-	-	-	-

8. Research proposal

8.1 Introduction

Recently, magnetism of carbon-based materials is of particular technological interest. First of all, it could reduce the demand for magnetic materials with d and f – orbital shell (iron, mangan, rare earth metals). Secondly, carbon-based magnetic materials would greatly extend the limits of technologies relying on

magnetism in metals or diluted magnetic semiconductors (DMS), like flexibility, processibility or production costs. Relatively cheap, chemically and physically stable, room temperature metal-free magnets could find applications in medicine, nanotechnology and telecommunications, and give the prospect for carbon-based electronics. Even more promising is the application of such materials at the nanoscale level in magnetic and spin electronics devices (spin-filters, spin-inverters, spin-transistor, spin qubit).

Pure carbon systems, particularly graphite in its ideal pristine form, are nonmagnetic or paramagnetic. However, several experimental groups reported the occurrence of ferromagnetic signal of a different strength in graphite samples after proton irradiation [1, 2], or other treatments – chemical modification, electron bombardment, hydrogen plasma treatment, even at room temperatures (see Fig.1). The presence of magnetic metals as dopants was experimentally excluded (or it was at negligible level), indicating that magnetism comes from the graphite itself.

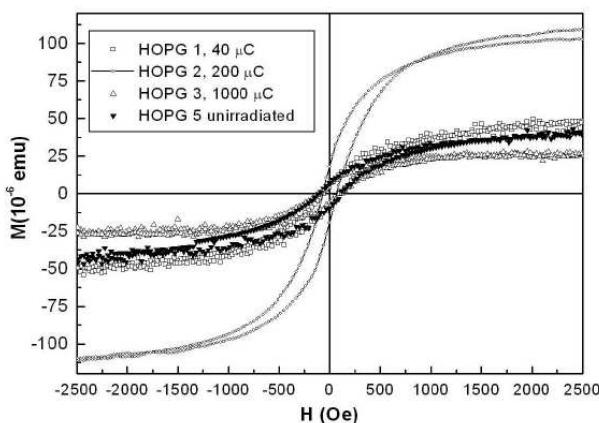


Fig. 1. Measurements of the total magnetic moment of proton irradiated highly oriented pyrolytic graphite (HOPG) with different irradiation doses. After [2]. The sample had showed some ferromagnetism already before proton treatment, which was strengthened by the irradiation. This effect is attributed to the creation of various defects, as described in Section 8.2.

Nowadays, a new carbon system – graphene - offers its several useful properties for electronic and magnetic studies, bringing back the hopes for carbon-based ferromagnet. Graphene consists of one atomic thick carbon sheet, obtained for the first time in 2004 [3] by mechanical exfoliation out of the bulk graphite. It forms hexagonal carbon rings, arranged in honeycomb lattice. Each carbon bonds covalently to 3 neighbouring carbons via sp^2 orbitals (orbitals formed from hybridization of one s-orbital and two p-orbitals). The remaining p-orbital, perpendicular to the plane of the ring, doesn't participate in the bond-formation, and its electron is shared within the ring. This collective character of p_z -orbital leads to the formation of a huge π -conjugated electron system and high conductivity. The high symmetry of the graphene lattice results in conical, linear shape of the band structure, with the zero-gap between conduction and valence band. The linear energy dispersion relation, similar to the case of photons, results in high group velocities of carriers and high mobilities (even 10 times larger than in the fastest silicon heterostructures). What is more, electrons in graphene have a long scattering length, experience small spin-orbit interactions (which scales with atomic number $\sim Z^4$, where for carbon $Z=6$), small hyperfine

interactions (non zero interactions with spins of nuclei occur only for carbon isotope C¹³, which is only 1% in graphite), and because of that have a large spin lifetime. This means that a spin polarized current can be sustained over large distances (spin relaxation length $\geq 2\mu\text{m}$ at room temperature). From above it is clear that graphene has a huge potential in spintronics as a transport medium, which already is being explored. Combining it with magnetic properties can give a device for manipulation of spins, and may bring the tool to overcome the limitations of present spintronics, where graphene has already proved its functionality.

8.2 Origin of magnetism in graphene

The intrinsic magnetism in carbon-based systems is often explained theoretically by the presence of undercoordinated carbon orbitals due to impurities, boundaries or defects [4, 5]. These defects produce quasilocalized states close to the Fermi level and can give rise to a net magnetic moment. There is an exchange interaction between the spin of graphene carriers and the adatom localised spins, which induce carrier polarization. The graphene lattice is the bipartite lattice consisting of two interpenetrating hexagonal sublattices of carbon atoms (labeled A and B on Fig 2).

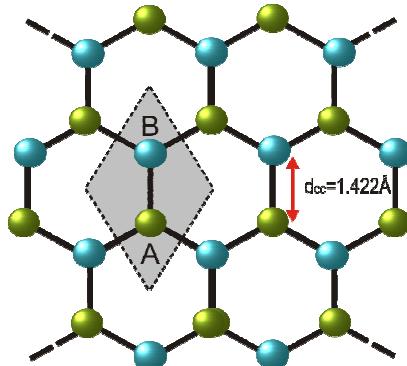


Fig. 2. Two sublattices of graphene: A and B. A gray rhomb indicates the unit cell.

When a defect is created in the A lattice, only the p_z orbitals of carbon atoms in the B sublattice contribute to the quasilocalized, spin-polarized states, and vice versa.

There are three possible defects that might be responsible for magnetic ordering:

- **hydrogen adatom** (Fig. 3) A chemisorbed hydrogen forms with the carbon σ-bond and causes its rehybridization from the sp² orbital configuration into sp³ taking out one of the p-orbitals from the π-π* band system. If adsorption occurs on a A lattice site the spin-density localizes on B lattice sites (see Fig. 3b). From the point of view of Valence Band theory (VB) when a H atom has been adsorbed on the surface, an unpaired electron is left on one of the neighbouring C atoms, which due to resonant is shared with the nearest neighbours (at B lattice sites). The latter contains most of the 1μ_B magnetisation previously carried by the H

atom species. There is one mid-gap state for each spin species, and the degeneracy is lifted when the exchange-correlation effects are taken into account leading to separation of the graphene bands for spin-up and spin-down states with a magnetic moment of $1 \mu_B$ per defect and exchange splitting 0.23eV at 0.5% defect concentration [4]. The difference in the spin-up and spin-down electron density of states at the Fermi level creates two different tunnel barrier heights, which can be studied using spin-polarized current.

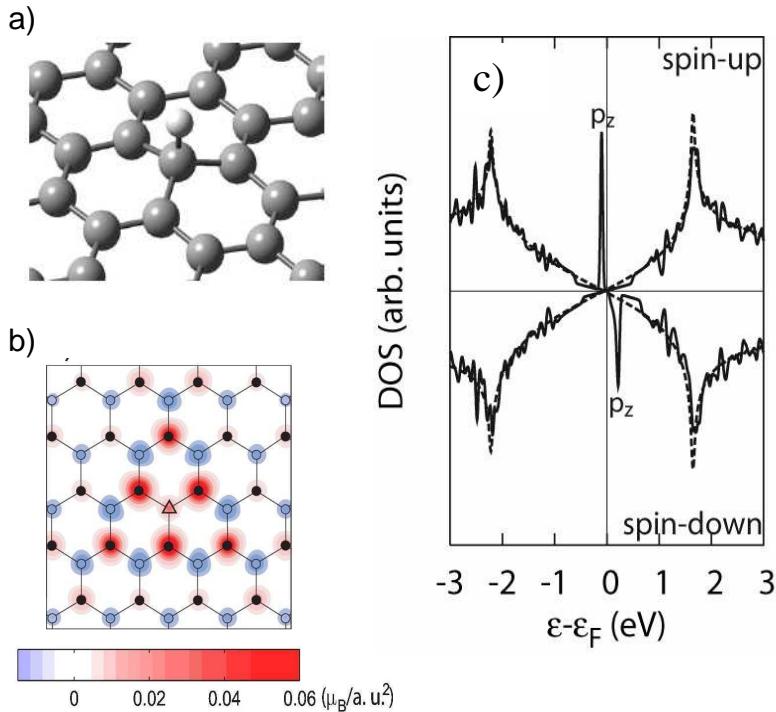


Fig. 3. A hydrogen chemisorbed defect. Topography of the graphene with adsorbed H (a), the spin-density projection around the defect site (b), the graphene band structure with localised defect states for different spin orientations (c). For defects present in the distance $6 \cdot a_{C-C}$ ($a_{C-C} = 1.42\text{\AA}$) the separation between the band maxima for majority and minority spins is 0.23eV and increases with the decrease of the defects distance. The dashed line shows the density of states for the ideal graphene. After [4].

A necessary condition for ferromagnetic ordering to occur is the presence of defects **in the same sublattice** (A or B). When two defects, closely situated, occupy different sublattices, antiferromagnetic arrangement is more favourable. From this argument it is clear why, when we increase the number of impurities in graphite, the magnetic moment firstly increases, but after reaching its maximum value it goes down as with the increase of hydrogen coverage above some threshold value also antiferromagnetic correlations start to dominate. Moreover, a full hydrogenation (placing hydrogen on each carbon-site of the graphene ring) will not only decrease the total ferromagnetic signal, but also results in an insulating form: graphane. Therefore it is necessary to identify optimal conditions for maximal ferromagnetic ordering. The Stoner criterion for ferromagnetism originating from impurity bands requires satisfaction of the condition: $n_{imp} \cdot I_{eff} / W_{imp} > 1$, where I_{eff} is an on-site interaction parameter, W_{imp} is the width of the impurity band and n_{imp} is the fraction of impurity atoms, with $1\mu_B$ per defect [17]. The flat hydrogen defect band has a very narrow peak ($W_{imp} < 0.2\text{eV}$), which is necessary to stabilize magnetic ordering at higher temperatures. Preliminary

calculations for typical values $I_{\text{eff}}=1\text{eV}$, $W_{\text{imp}}=0.1\text{eV}$, require $n_{\text{imp}}>0.1$ to get Curie temperature $T_C>0\text{K}$. Although the Stoner criterion is known to overestimate Curie temperature in 3d band ferromagnetic metals, the authors in [17] argue that it may not be the case for impurity-band ferromagnetism and the obtained T_C values are close to predicted.

- **carbon vacancy** (Fig. 4). This defect is obtained by removing carbon atom from the graphene sheet. Two out of the three carbon atoms deflect their bonds forming a pentagonal ring. The bond of the third carbon is left unsaturated [2], which generates a magnetic moment of $1.45\mu_B$ and an exchange splitting of 0.14 eV for 0.5% defect concentration [4]. This magnetic moment ranges from $1.12-1.53\mu_B$ per vacancy depending on the defect concentration.

There is disagreement among theoreticians, whether vacancies couple ferromagnetically only when placed within the same sublattice, or irrespectively to the type of sublattice, A or B. Lehtinen *et al.* found that additional hydrogen adsorption on the vacancy can destroy the magnetism [12]. On the other hand, Zhang *et.al.* concluded that the presence of nitrogen around a vacancy can produce larger macroscopic magnetic signals as compared to a standalone carbon vacancy [13].

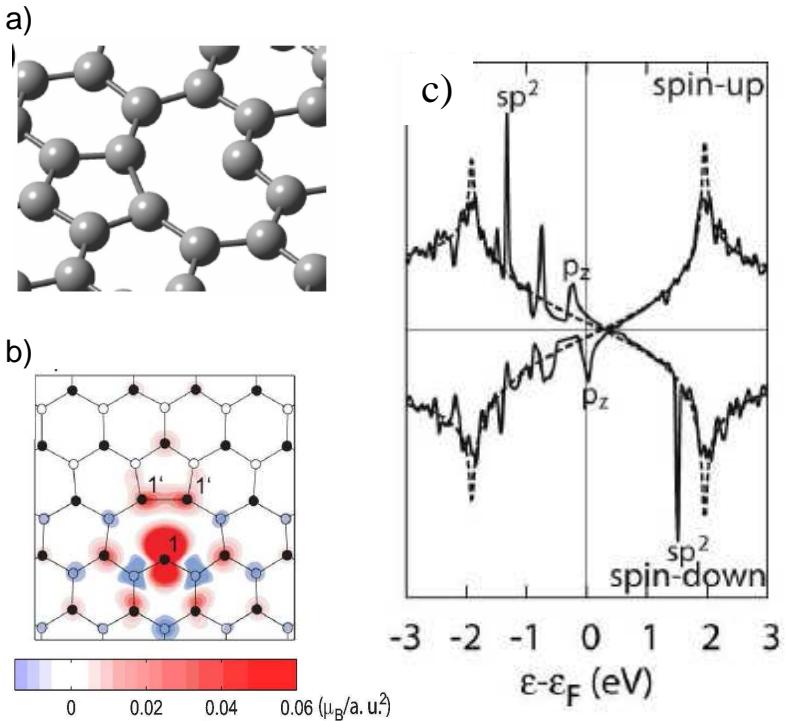


Fig. 4. Carbon vacancy. Topography of graphene with a defect (a), the spin-density projection around the defect site (b), graphene band structure with the localised defect state (c). For defects present in the distance $6 \cdot a_{\text{C-C}}$ ($a_{\text{C-C}}=1.42\text{\AA}$) the separation between the band maxima for majority and minority spins is around 0.6eV . The dashed line shows the density of states for the ideal graphene. After [4].

- **zigzag edge**, in graphene nanoribbons (Fig. 5). Near the zigzag edge, strongly localized edge states occur, leading to the sharp peak in the density of states around the Fermi level and formation of the bandgap. The difference in total energy per atom on the edge between non-spin-

polarized and spin-polarized edge states is found to be a few tens of meV (20meV for zigzag nanoribbon with the number of zigzag chains $N_z=8$, 24meV for nanoribbon with $N_z=16$, in both cases nanoribbon has the width of 12 dimer lines) [15]. Magnetization per edge atom (terminated by H), for each spin on each sublattice is $0.43\mu_B$. The spin polarization has ferromagnetic coupling on the same edges, while anti-ferromagnetic coupling between the two opposite edges [5] (Fig. 6a). Interaction between spins on opposite edges increases with decrease of the width of the ribbon.

When a transverse electric field is applied, it reacts oppositely on oppositely oriented spin states at the opposite edges. The electrostatic potential on the left edge is lowered ($e\Delta V < 0$), whereas the one on the right edge is raised ($e\Delta V > 0$). Correspondingly, the energies for localized edge states on the right side are shifted upwards and those on the left side downwards, eventually leaving states of only one spin orientation at E_F (Fig. 6b) creating a ferromagnetic phase.

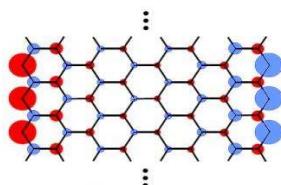


Fig. 5. Topography of the graphene nanoribbon with schematic spin-density distribution at edges. Different colours indicate different spin-orientation and an antiferromagnetic arrangement with respect to the opposite edge. After [5].

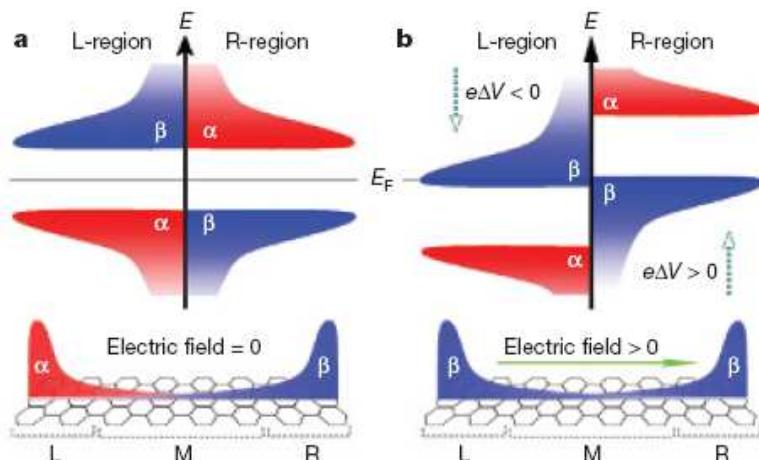


Fig. 6. Density of states for different spins in graphene nanoribbon. A case without transverse electric field (a) and with (b). The shift of the states lead to gap-opening for spin α -states (red) and the gap-narrowing for β -spin (blue). After [5].

Moreover, when an external transverse electric fields is applied the valence and conduction edge-state bands associated with one spin orientation close their gap, whereas those associated with the other orientation widen theirs (Fig. 6b). Hence, depending on the field strength the zigzag nanoribbon can be tuned into a half-metallic state, with insulating behaviour for one spin type and metallic behaviour for the other.

In prospect for room temperature spintronic devices based on graphene edges the crucial parameter is the spin-correlation length, which is closely related to the formation of ferromagnetic domains. Analysis of different types of fluctuations of magnetic moment in graphene showed that transverse fluctuations are the main limiting factor for the spin correlation length, which is found to be $\sim 1\text{nm}$ at room temperature but starts increasing exponentially for $T < 10\text{K}$ (above $1\mu\text{m}$) [16]. The spin correlation length can be improved not only by lowering the temperature but also by increasing the magnetic anisotropy (by applying external field or by chemical functionalizations). This whole direction awaits experimentation.

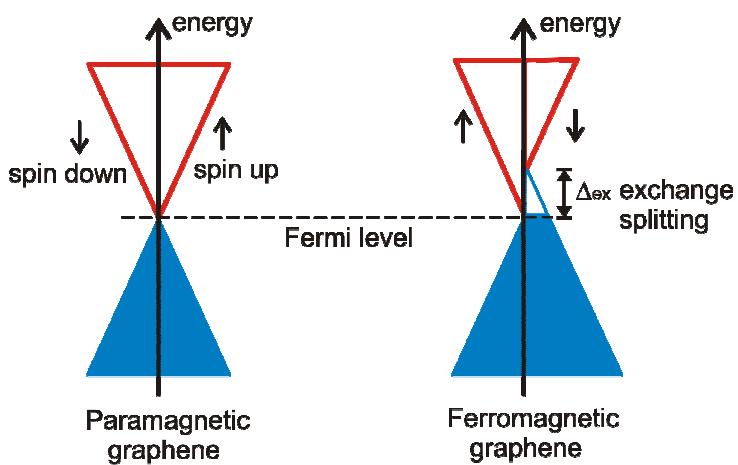


Fig. 7. Change of the band structure due to the splitting of the spin-up and spin-down states (Stoner magnetism model for graphene).

As the alternative, it is possible to induce ferromagnetism in graphene exploring a proximity effect, where we deposit a layer of ferromagnet on top of graphene. The exchange field present in the ferromagnet induces an exchange field in a neighbouring material – in this case graphene. The proximity effect can be effectively realised for graphene because it is a 2 dimensional material, on the contrary to bulk materials, where spin imbalance would be induced just at the interface. Europium Oxide (EuO) among different ferromagnetic materials, seems to be the most proper for spin transport studies. It is an insulator, with $E_g = 1.12\text{eV}$ and $T_C = 69\text{K}$, hence it can be also used as a top-gate. Induced exchange splitting is estimated to be in the order of 5 meV [6], which results in shift of the bands for different spin orientation, as schematically indicated on Fig. 7. The advantage of this approach is that we could induce ferromagnetism locally, just at one part of the graphene flake, leaving the other part intact.

Similar proximity effect can be also realised with the use of ferromagnetic metals, however the high resistance of graphene (few $\text{k}\Omega$) comparing to metals will prevent the spin-polarised current to propagate through magnetic graphene.

8.3. Preparation of magnetic graphene

There are many techniques which allow introduction of defects and impurities into graphene, the mentioned earlier proton irradiation, hydrogen plasma

treatment, chemical processing. Most of them require a sophisticated equipment and experience. However, a relatively simple and controllable method of graphene hydrogenation, easily adaptable to our laboratory possibilities, is electron beam exposure of HSQ film (Hydrogen Silsesquioxane, EBL resist) on graphene. Its two different structures are presented on Fig. 8.

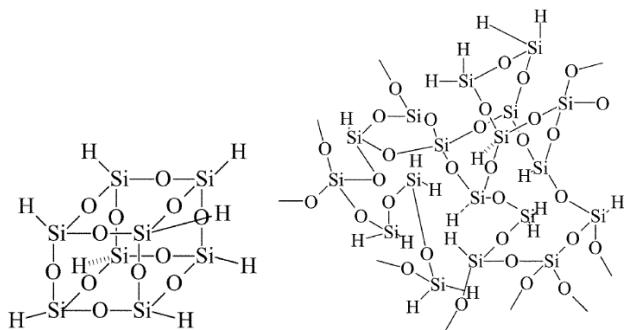


Fig. 8. Structure of the hydrogen silsesquioxane HSQ
(a) cage form, (b) network form.
After [7].

Electron irradiation stimulates breaking of the Si-H bonds of HSQ, and provides hydrogen atoms to graphene. Binding energies per atom obtained from theoretical calculations range from $\sim 0.8\text{eV}$ to $\sim 1.9\text{eV}$, with barriers to sticking in the range $0.0\text{-}0.2\text{eV}$ [9]. The hydrogenation effect was justified by the occurrence of Raman D band in graphene on SiO_2 substrate [8] (band around 1350 cm^{-1} , see Fig. 9), which is a marker of defect density. The intensity of the D band increases with increase of the beam exposure dose, and respectively the intensity of the H-Si band of HSQ on SiO_2 decreases, which is a fingerprint that indeed the adsorption of atomic hydrogen occurs.

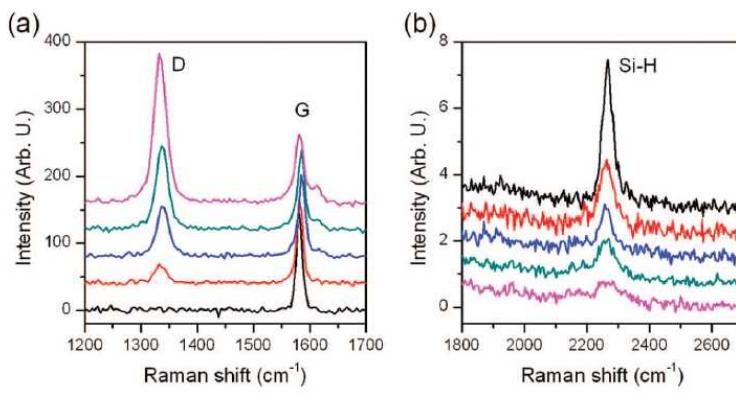


Fig 9. Raman spectra of the single layer graphene sheets at various stages of hydrogenation by HSQ (a), and Raman spectra of HSQ films on SiO_2 (b). After electron irradiation at 30keV , irradiated doses were: $0, 1, 2, 4$ and 8 mC/cm^2 (from black to pink, respectively), after [5].

An alternative approach is the fabrication of the nanoribbon, with the use of plasma etching. In our group we were able to design graphene flakes of the width below 100nm . The resolution of the electron beam lithography used in our group

(RAITH e-LINE) is 4nm, at beam acceleration voltage 10kV. Although this level of resolution is practically not achievable, due to limitations related to used resist, some experimental groups were able to pattern lithographically nanoribbons down to 10nm width, with the use of HSQ and oxygen plasma etching [14].

Placing the parallel side gates (see Fig.10) enables the control of the spin-density and ferromagnetism at the edges, according to the mechanism described in Section 8.2, and in [3]. Ferromagnetism increases with decrease of the ribbon width.

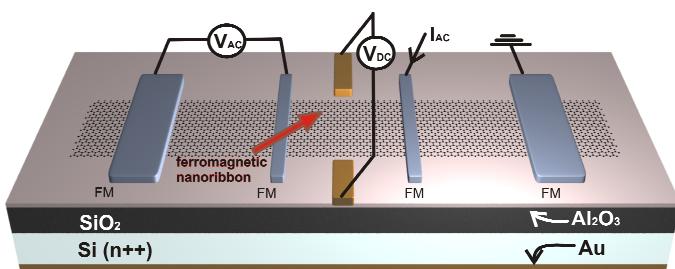


Fig. 10. Imposing ferromagnetism in a nanoribbon by applying a transverse electric field with the side gates. The configuration of contacts corresponds to the non-local spin-valve technique, described in details in the Section below.

For the purpose of magnetic studies, argon plasma etching for shaping the graphene structure seems more proper than oxygen, as theoretical calculations predict that adsorbed at edges oxygen may lead to antiferromagnetic ordering. These predictions however need also to be verified, as others report non-zero total magnetic moment also in oxygenated graphene [10]. Our collaborators, from Surface and Thin Film Group run by Prof. Rudolf at Zernike Institute, can provide us the graphene flakes at different stages of oxygenation. This enables detailed investigations of oxygen content on magnetism in graphene.

Inducing magnetism via the proximity effect requires deposition of ferromagnetic material in the contact with graphene. Deposition of material by thermal evaporation on graphene is possible thanks to its high robustness. Graphene can stand temperatures up to 900C. When dealing with EuO, however, we must be aware of many experimental challenges during preparation. This compound is very unstable, and easily oxidize into Eu₂O₃, resulting in dramatic insulator to metal transition (undesirable for electrical measurements). Successful deposition of thin films on silicon dioxide was reported, with the use of reactive MBE, indicating that the integration with graphene is possible. To prevent the oxidation of EuO, a few-nanometer-thick layer of Al₂O₃ is commonly deposited on top. The Zernike Institute already collaborates with the group of Prof. Tjeng from

University of Cologne (Germany) who has the necessary expertise in the growth of EuO thin layers.

Introducing the impurities in different fabrication processes (like ion or electron irradiation) enables us to modify this effect up to the certain limit, however several studies on graphite indicate that the challenge lays in performing it in controllable and reproducible way. However, too many defects lead to the decrease of ferromagnetic signal, as it is indicated in Fig. 1, indicating subtle interplay between amount of quasilocalised states with respect to the strength and type of the magnetic interactions.

8.4. Measurement techniques

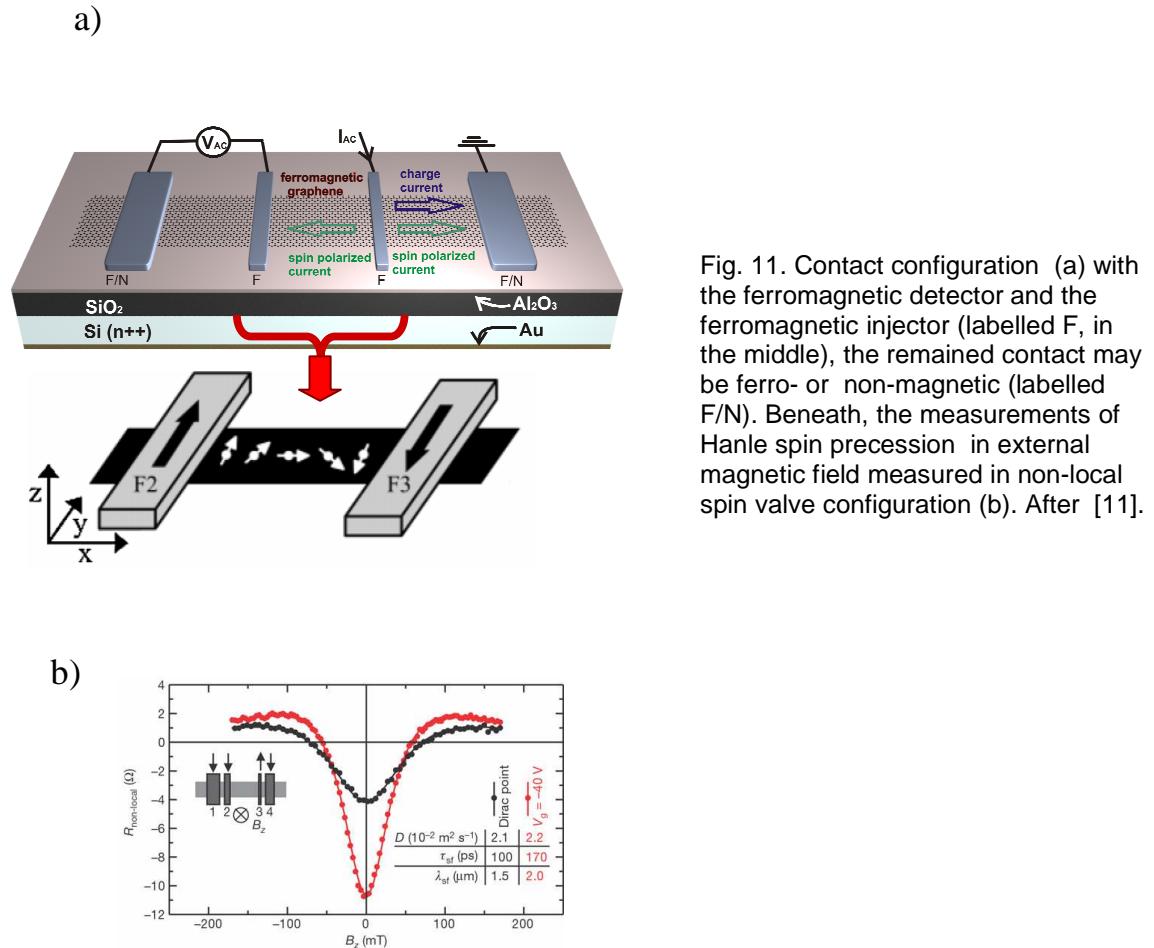
The magnetic susceptibility of graphite sheets is so high that the paramagnetic signal can completely dominate the ferromagnetic one. In case of graphene, preliminary calculations of total magnetisation for one hydrogen defect per 10 carbon rings gives values $M \approx 5 \cdot 10^{-13}$ emu, which is below the resolution of the commercially available equipment. Although ferromagnetic interaction can be quite strong, such a low value of magnetisation comes from the fact, that the system itself is very small and difficult to probe, questioning the adequacy of standard measurement techniques on the magnetic moment (commercial Superconducting Quantum Interference Device (SQUID) has a resolution up to $5 \cdot 10^{-10}$ emu, Magnetic Force Microscope MFM up to $1 \cdot 10^{-12}$ emu). The resolution of SQUID can be improved when building up the device on the sample (placing nanoloop around the flake), but this requires designing and calibrating the whole measurement setup from the very beginning.

Instead, I propose electrical studies of the influence of magnetic ordering in graphene on spin-precession and spin scattering with the use of the **non-local spin-valve technique**. The advantage of this technique is the fact that the charge current can be separated from the spin current, as they are governed by different mechanisms. When current is injected into a nonmagnetic material, charges, driven by the potential difference between the contacts, travel from the injecting electrode to the charge sink (ground). However, when the ferromagnetic contact injects the spin-polarised current into the non-magnetic material, a spin imbalance is created. Excessive spins tend to equalize their concentration and hence diffuse in all directions, not only in the direction of charge current. Pure diffusive spin-current can be detected at the other side of the device by ferromagnetic detector. The electrical resistance varies depending on the orientation of the spins in the detector with respect to spin-polarisation of incoming current (Giant Magnetoresistive effect, resistance is low for the same spin-alignment, while high for the opposite one).

Measurements of magnetic properties of graphene can be done in two possible configurations:

- **ferromagnetic injector and ferromagnetic detector**

Injected spins into magnetic graphene will experience the local exchange field from the defects, which results in its magnetisation precession and different non-local resistance. Equivalent effect in an external magnetic field is called Hanle precession, see Fig. 11. From the precession length we can estimate exchange field of the magnetic graphene and size of its magnetisation.



- **non-magnetic injector and ferromagnetic detector**

The injected current is not spin-polarised, but because of ferromagnetism in graphene the detected current is (see Fig 12). Magnetic graphene has a different coercive field than the detecting ferromagnetic contact, hence spin-valve measurements of the resistance will give the information of the size of this field.

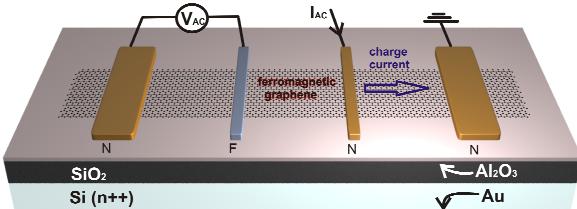


Fig. 12. Contact configuration for the case of non-magnetic injector and ferromagnetic detector.

In both configurations an interlayer of Al_2O_3 between metal and graphene is introduced to create a tunnel barrier and prevent an impedance mismatch (graphene resistance is much higher than the resistance of metal contacts). This tunnel barrier improves spin injection/detection and prevents spins from backscattering into the ferromagnetic contact.

All the measurements are to be performed in very low temperatures (below 10K), to extend the spin correlation length and reduce thermal fluctuations, which may destroy expected magnetism.

8.5 Goal of the project

Our aim is to develop a reliable investigation method for detection of magnetism based on electrical studies of non-local spin-valve technique for graphene [11]. We want to verify theoretical predictions, indicating possibilities of turning graphene from the paramagnetic into the ferromagnetic state. With the contribution from collaborators, we want to create magnetism in graphene exploring two approaches: intrinsic magnetism due to presence of impurities and proximity effect, induced by deposition of insulating ferromagnetic material. Focus of our research will be the influence of defects concentration, type of defects and device geometry on spin signal in graphene. Transport measurements include spin-precession and spin-relaxation studies in different contact arrangement (ferromagnetic/nonmagnetic) within non-local spin-valve geometry and influence of temperature as well as external magnetic field on the observed signal. Apart from the importance of these studies for fundamental understanding where the magnetism in carbon-systems comes from, at the final stage the usefulness of the system for spin-filtering as well as for other spintronic applications will be considered.

8.6. Collaborations

In our project the different methods for graphene to become magnetic will be applied in collaboration. Hydrogenation of graphene and designing nanoribbon can be done by our group, deposition of EuO on graphene can be done in the group of Prof. Tjeng, while oxygenated graphene can be supplied by group of Prof. Rudolf. Most of experimental verification can be done in our group with the

use of already existing measurement setup. We have, and are planning to set up, several collaborations outside our institute. With the contribution from collaborators, it might be possible to perform detailed surface studies of defects and its magnetic moment, which at this preliminary level are unclear.

9. Infrastructure

The Physics of Nanodevices group has a variety of processing and measuring facilities. For this project the most important are:

- a digital instruments Nanoscope IV room temperature atomic force microscope.
- a clean room equipped with general processing facilities such as a spin-coater (for mask), heater, resist developer and a reactive ion plasma etcher;
- a Raith e-line electron beam lithography system;
- a JEOL inspection scanning electron microscope;
- an electronic measurement setup for spin-valve measurements at different temperatures and at different magnetic fields

We are planning to extend the functionality of our measurement facility (reactive ion plasma etcher RIE) by realizing additional gas line for hydrogen.

10. Application perspective in industry, other disciplines or society

The study of the origins of magnetism in carbon system, as well as controllable methods of its implementation represent not only fundamental importance.

Carbon-based magnetic materials would greatly extend the limits of technologies relying on magnetism in metals or diluted magnetic semiconductors (DMS), like flexibility, processibility or production costs. Relatively cheap, chemically and physically stable, room temperature metal-free magnets could find applications in medicine, nanotechnology and telecommunications, and give the prospect of carbon-based electronics. The most promising are, however, nanoscale application in magnetic and spin electronics devices (spin-filters, spin-inverters, spin-transistor, spin qubit), and possibly push the concept of spintronics out of the laboratory.

11. References

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