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Magnetism in graphene induced by point defects

Irina Grigorieva

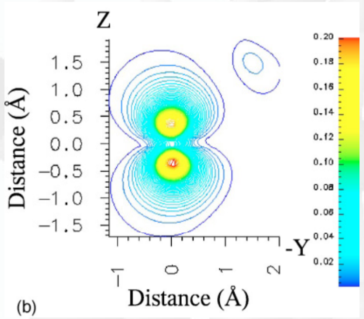
Rahul Nair, Margherita Sepioni, I-Ling Tsai, Andre Geim

in collaboration with Arkady Krasheninnikov &Ossi Lehtinen (University of Helsinki)

Theory: many possible reasons for magnetism

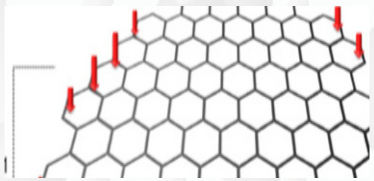
✓ magnetism in pure-carbon systems:

- atomic-scale defect (adatoms, vacancies) carry $\mu \approx \mu_B$



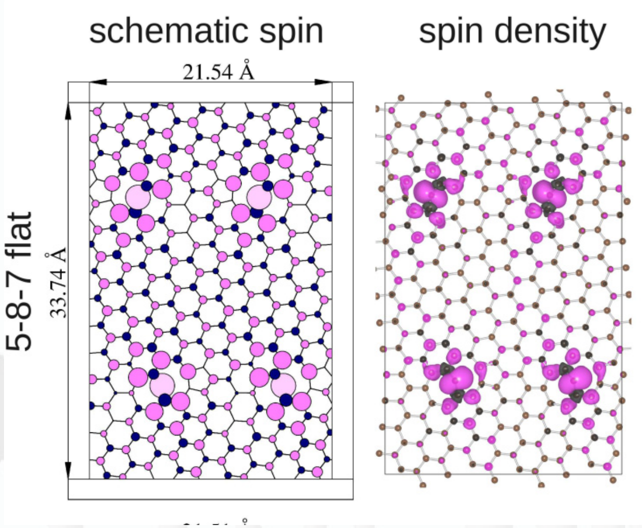
Lehtinen et al, *PRL* (2004)
Yazyev & Helm, *PR B* **75**, 125408 (2007)
Kumazaki & Hirashima, *J. Phys. Soc. Jpn.* **76**, 064713 (2007)
Uchoa et al, *PRL* **101**, 026805 (2008)
Palacios et al, *PR B* **77**, 195428 (2008)
Singh & Kroll, *J. Phys: Condens. Matter* **21**, 196002 (2009)
Krasheninnikov et al, *PRL* (2009)
W. Li et al, *J. Mater. Chem.* **19**, 9274 (2009)
Venezuela et al, *PR B* (2009)
Lopez-Sancho et al, *PR B* (2009)
Faccio et al, *PR B* (2008), ...

- spin-polarised states at zig-zag edges

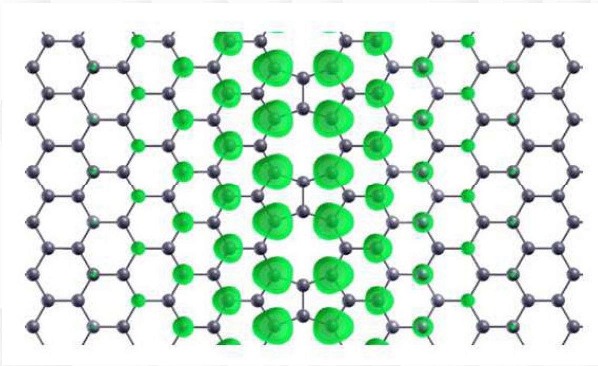


Harigaya, Enoki (2001,2002)
Fujita et al (1996); Kobayashi et al (2006);
Son et al, *Nature* (2006)

Theory: many possible reasons for magnetism



- specific types of defects within grain boundaries : Akhukov, Fasolino, Gornostayev, Katsnelson, **arXiv:1112.0160**



- 1D defects: ferromagnetic ground state at domain boundaries: S.S. Alexandre, A. D. Lucio, A. H. Castro Neto and R. W. Nunes, **arXiv:1109.6923**

- ferromagnetism due to H-vacancies in graphane: Berashevich & Chakraborty, *Nanotechnology* **21**, 355201 (2010)

spontaneous magnetism in bilayer graphene, E. V. Castro et al, *PRL* (2008)

Experiment: very few direct measurements

- need macroscopic quantities of graphene to detect magnetic moments directly (at least 1-2 mg)

- most experiments either indirect (STM, transport) or using graphite rather than graphene

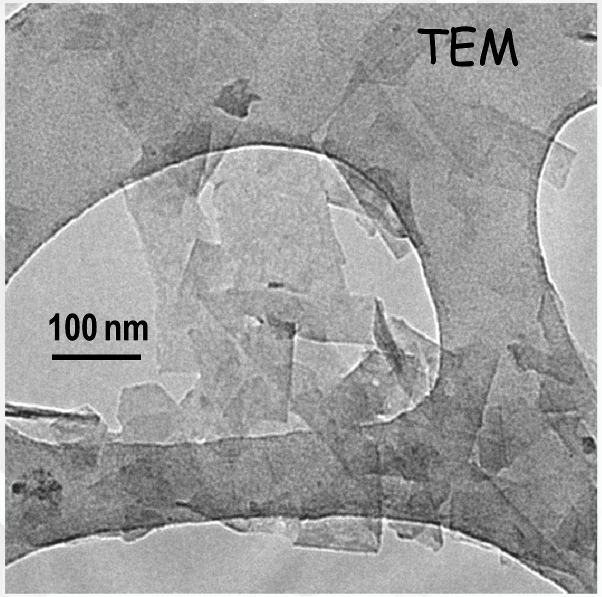
macroscopic samples of graphene

15 min centrifugation

40-50 hours sonification in organic solvent (NMP)

stable suspension of non-coagulated graphene crystallites

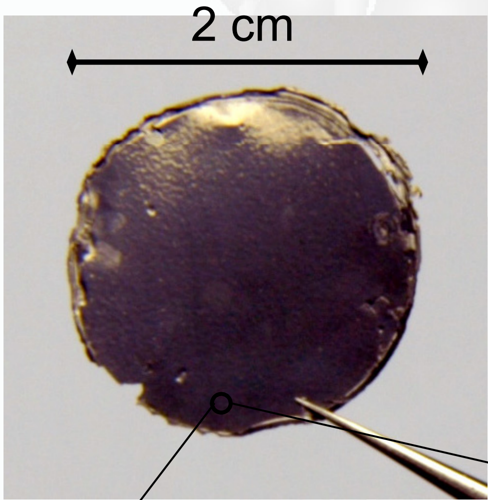
Manchester, Nanolett '08
Dublin group, Nature Nano '08



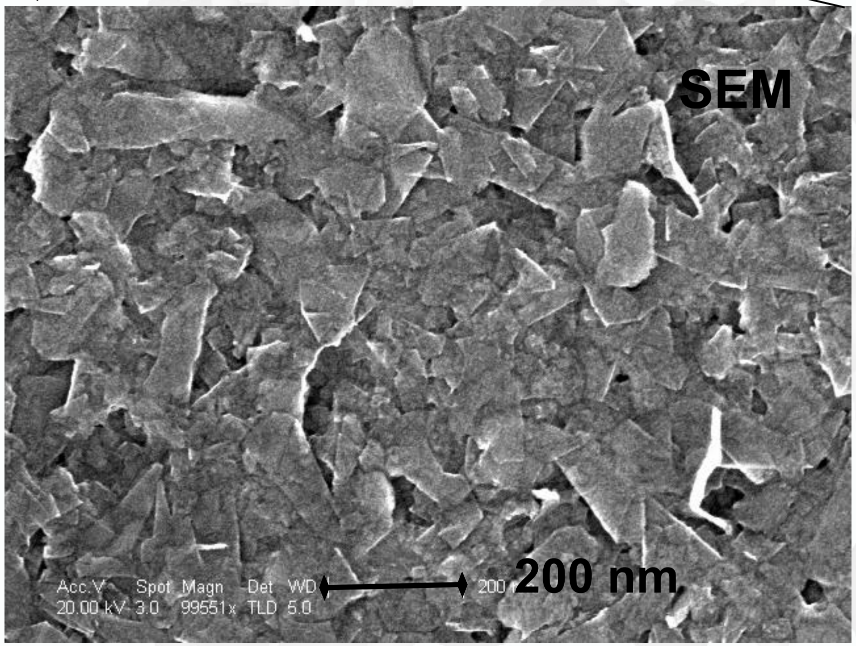
graphene laminate

graphene suspension
directly from HOPG

Manchester, *NanoLett '08*
Coleman et al, *Nature Nano '08*



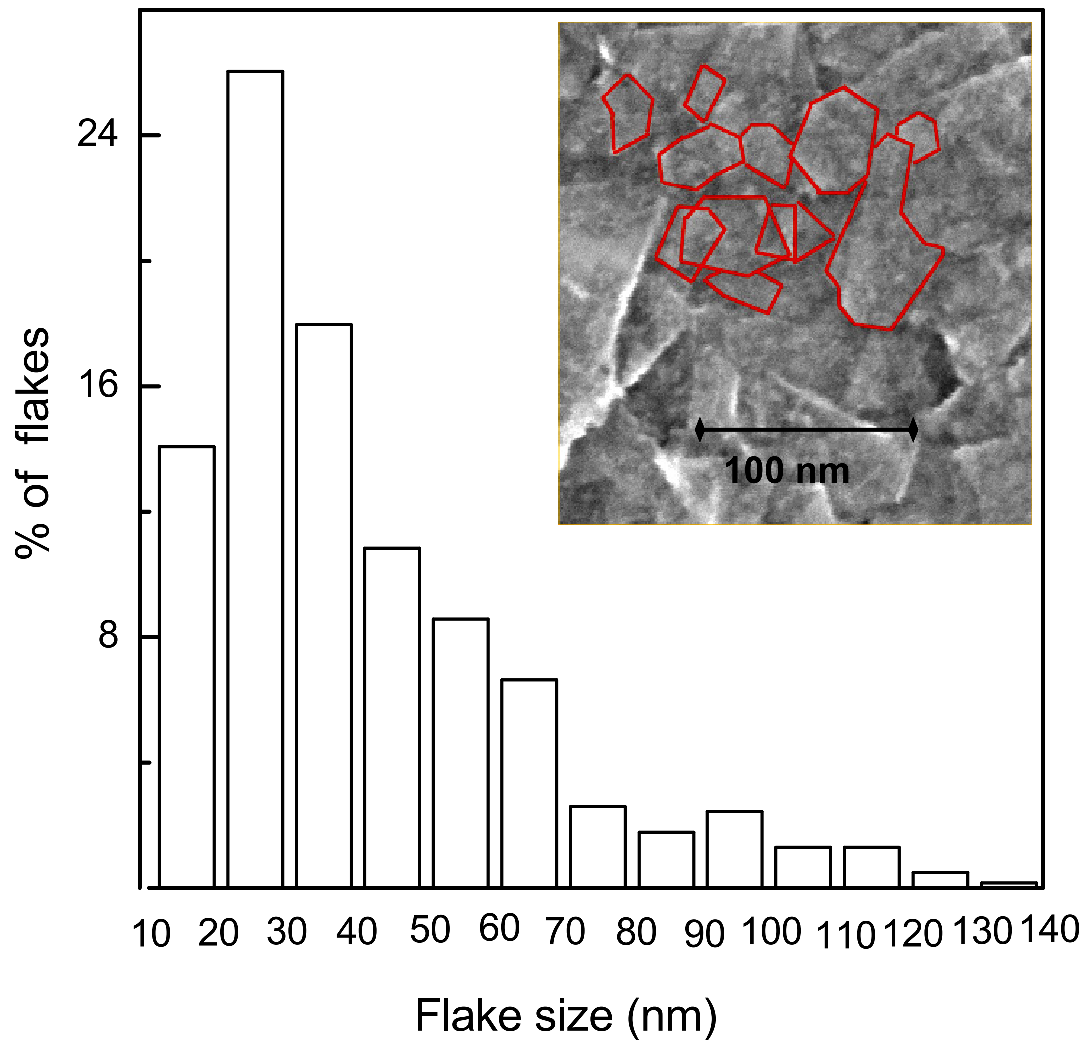
- layers of non-interacting crystallites
  - ~50% monolayers
  - metallic
  - porous and fragile
  - few μm thick;
  - weight ~several mg



GREAT CARE taken not to contaminate
NO magnetic impurities >10 ppm

collection of graphene nanocrystals

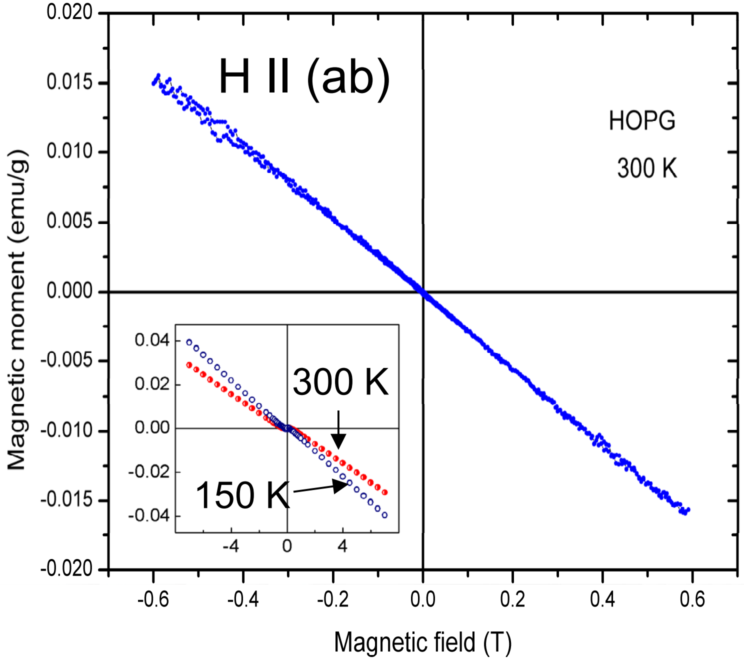
- most crystallites smaller than 40nm in size
- irregular shapes but crystallographic edges
- no re-stacking into graphite: spacing between layers 3.36 to 3.86 Å
- smallest crystallites are distorted hexagons



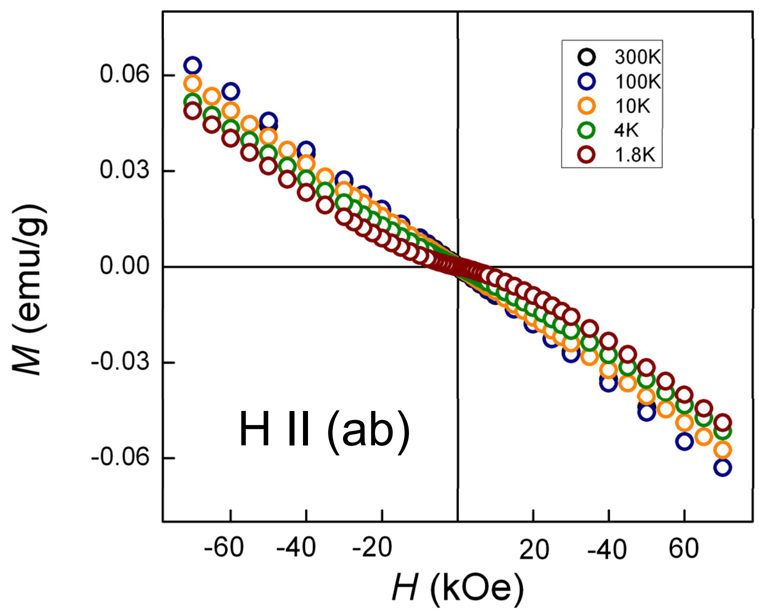
relatively narrow distribution of sizes ~30-40nm
cannot control the size

magnetisation of graphene nanocrystals

starting material: HOPG



graphene laminate



✓ diamagnetic at all temperatures

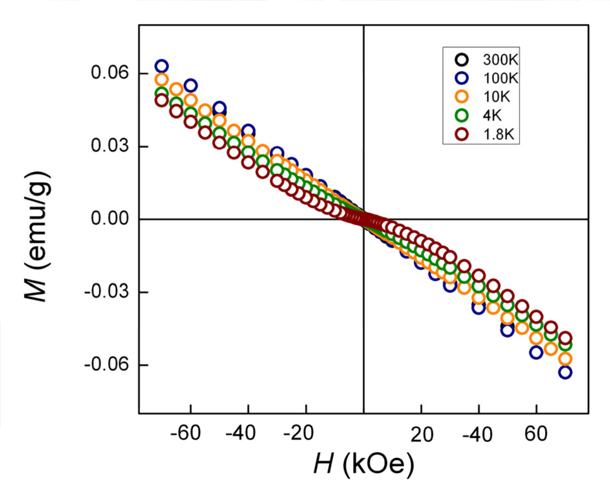
M. Sepioni et al, *PRL* **105**, 207205 (2010)

✓ mostly diamagnetic

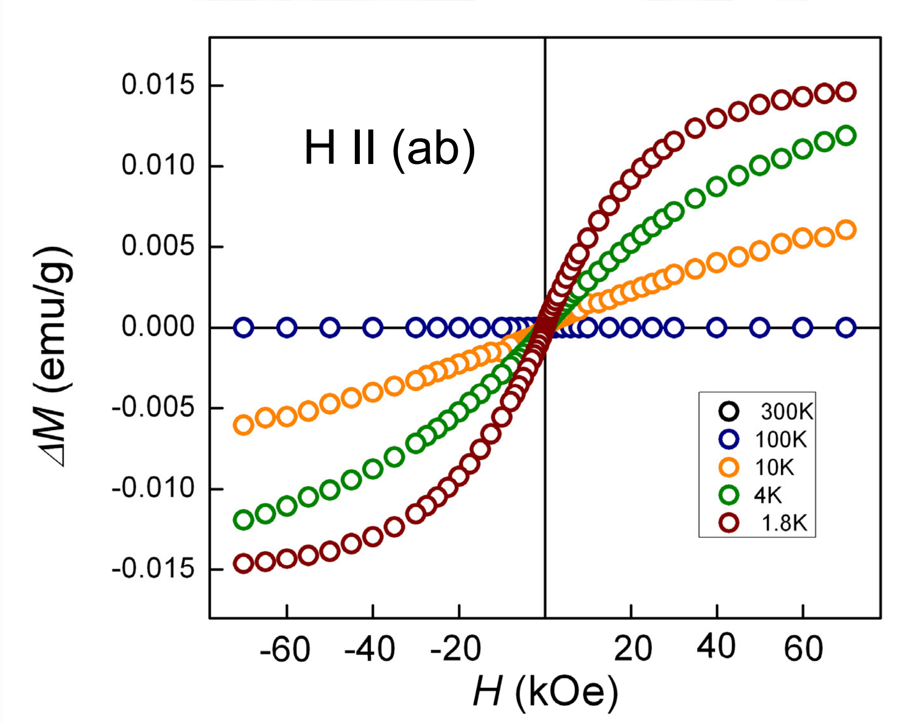
✓ weak paramagnetic signal emerges below 20K

✓ no ferromagnetism

paramagnetism of graphene nanocrystals



subtract linear
diagmagnetic background

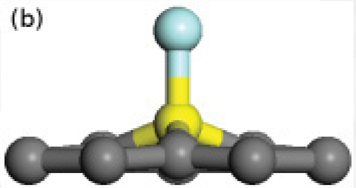


- ✓ weak but reproducible paramagnetism
- ✓ corresponds to 30-40ppm (~10^{18} g^{-1}) of non-interacting spins

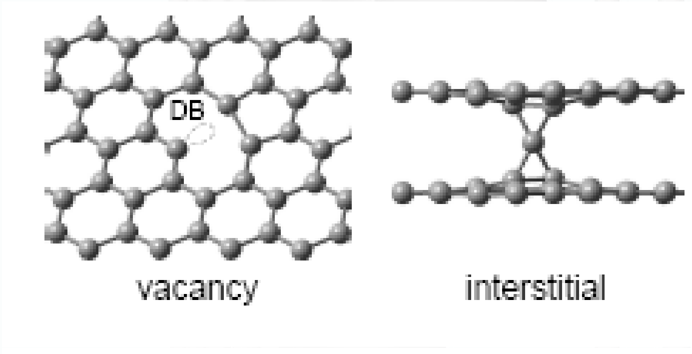
M. Sepioni et al, *PRL* **105**, 207205 (2010)

controlled introduction of defects

- two types of atomic-scale defects studied:
  - fluorine adatoms



  - vacancies produced by irradiation with energetic ions

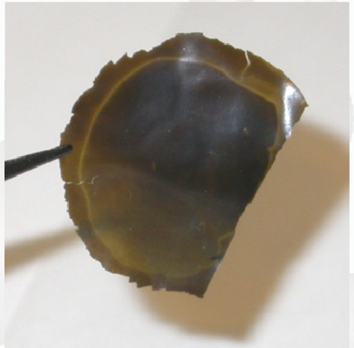


THEORY: both adatoms and vacancies are expected to carry $\mu \approx \mu_B$

P. O. Lehtinen et al, *PRL* (2004)
A. V. Krasheninnikov et al, *PRL* (2009)
O. V. Yazyev, *PRL* (2008)
P. Venezuela et al, *PR B* (2009)
M. P. Lopez-Sancho et al, *PR B* (2009)
R. Faccio et al, *PR B* (2008)
Uchoa et al, *PRL* **101**, 026805 (2008) ....

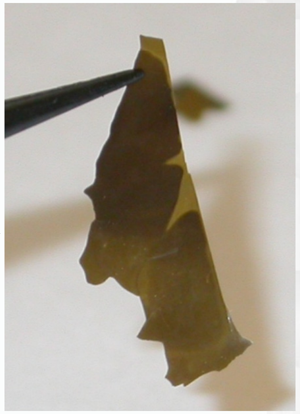
fluorinated graphene laminates

+ XeF_2, 200°C → 2h



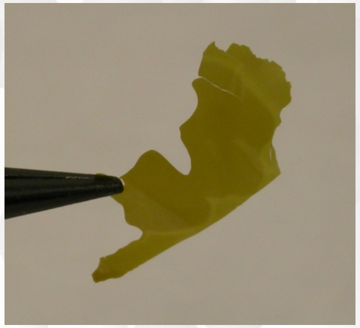
F/C = 0.26

8h



F/C = 0.68

40h



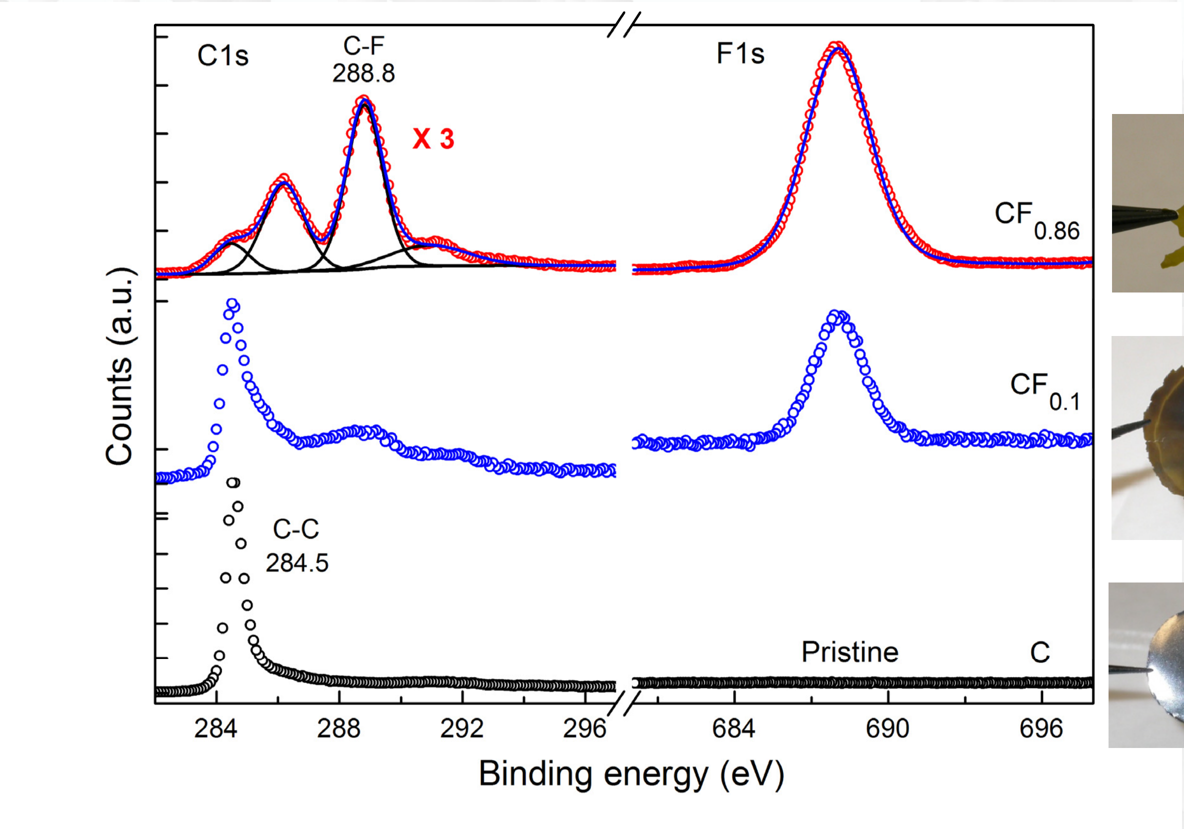
F/C = 0.9

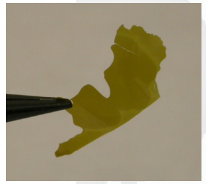
- quantitative determination of fluorine concentration (F/C ratio) by XPS

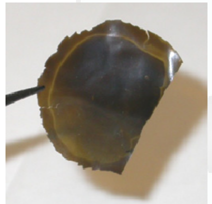
details of graphene fluorination in **R. R. Nair** ***et al*, *Small* 2010, *6, No. 24, 2877***

fluorinated graphene laminates

- quantitative determination of fluorine concentration (F/C ratio) by XPS

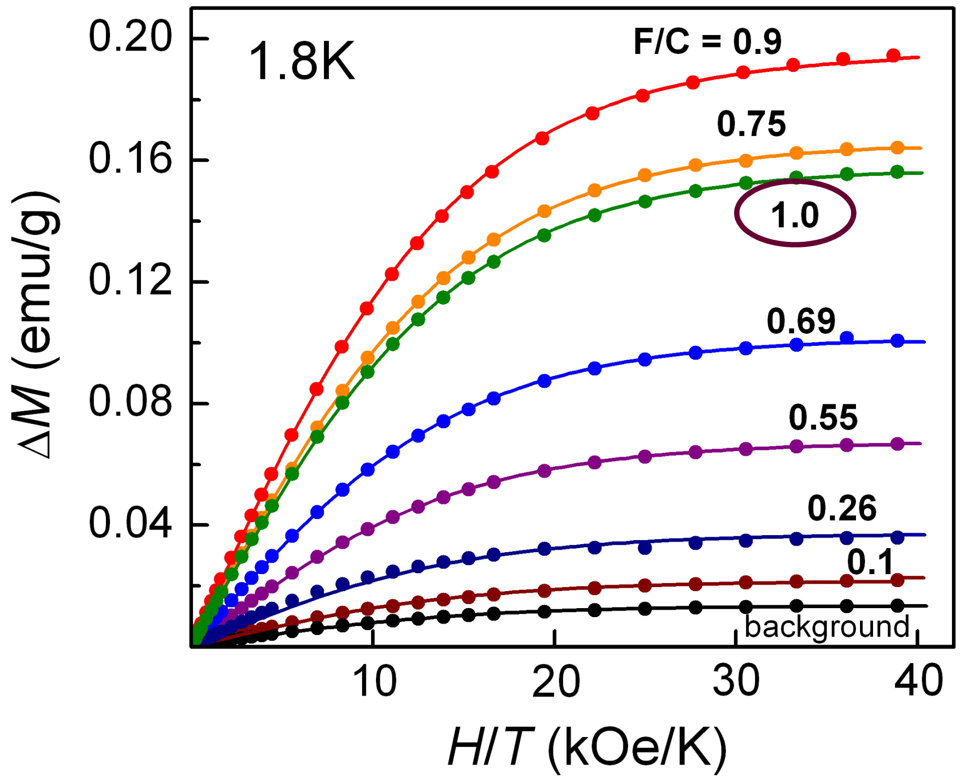






- different peaks correspond to different carbon/fluorine bonds
- dominant C-F and C-C-F bonds, i.e. fluorination occurs at the surfaces, not edges

paramagnetism in fluorinated graphene



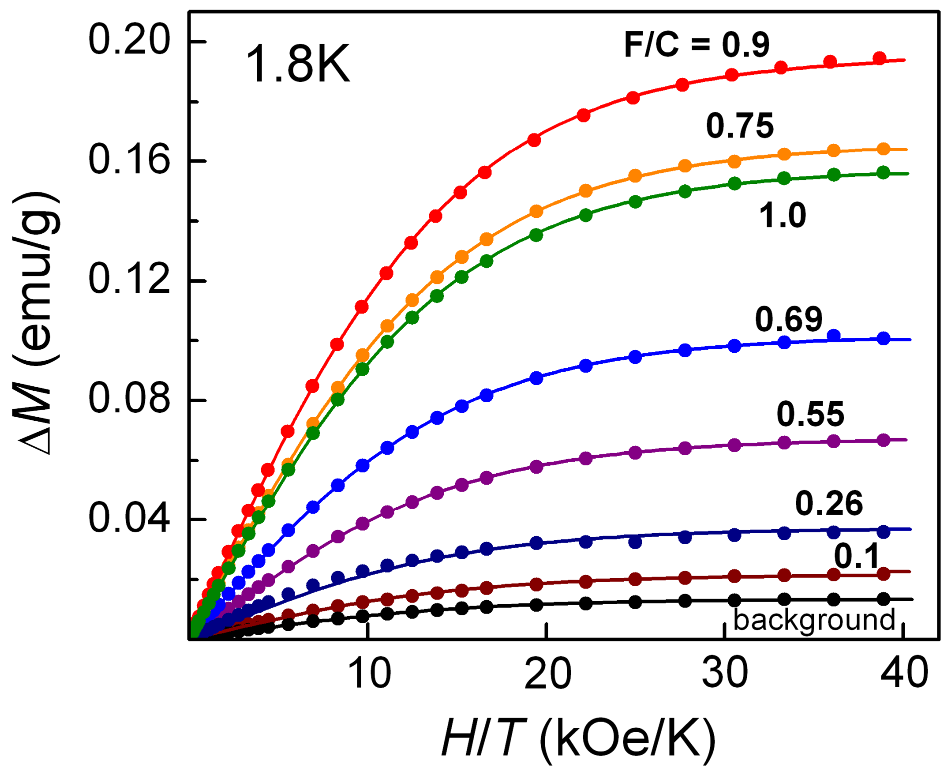
diamagnetic background subtracted

- 15-times greater saturation magnetisation compared to pristine graphene for 90% fluorination
- slight decrease in *M* for full fluorination but still strongly paramagnetic

R.R. Nair et al, ***Nature Physics***, January 2012, DOI **10.1038/NPHYS2183**

✓ much larger magnetisation values than for ferromagnetism reported in graphite

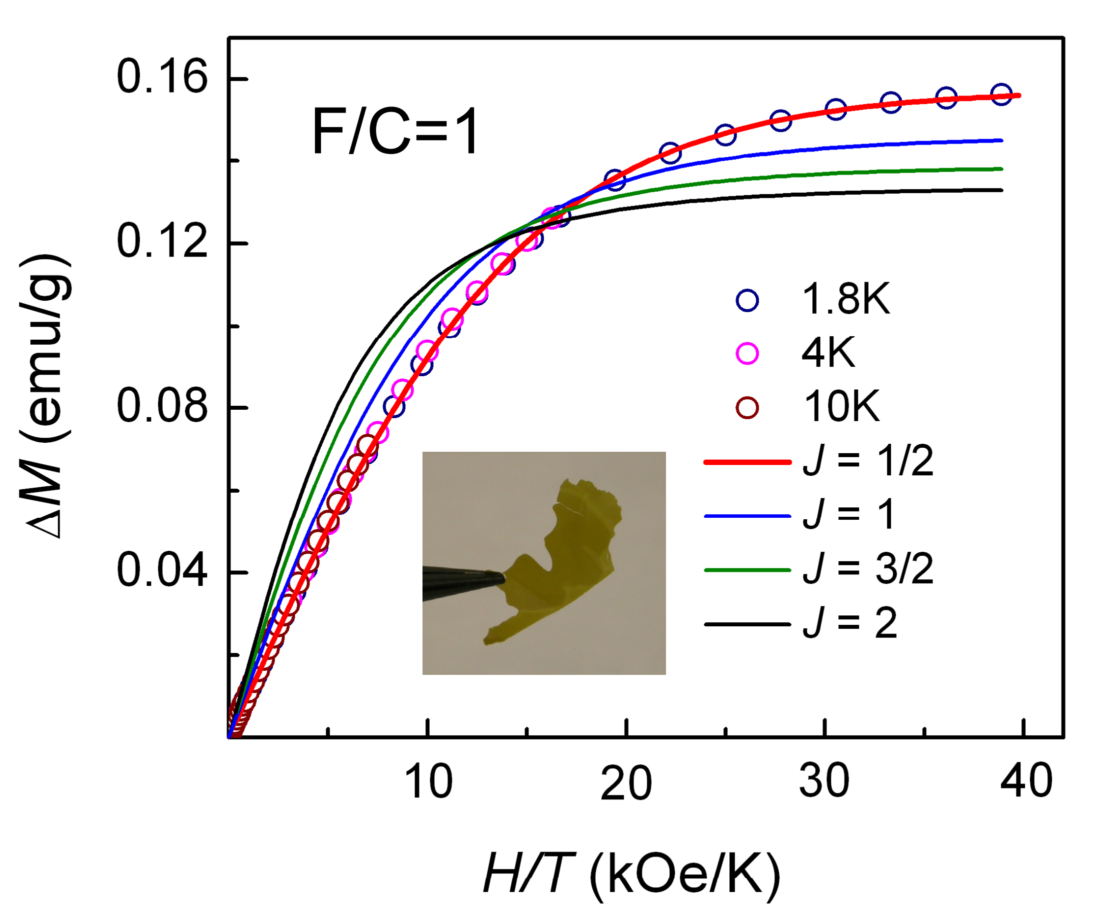
paramagnetism in fluorinated graphene



- for all fluorinations: excellent fits to the Brillouin function for J=S=1/2 ⇒ non-interacting paramagnetic centres with magnetic moments $\approx\mu_B$

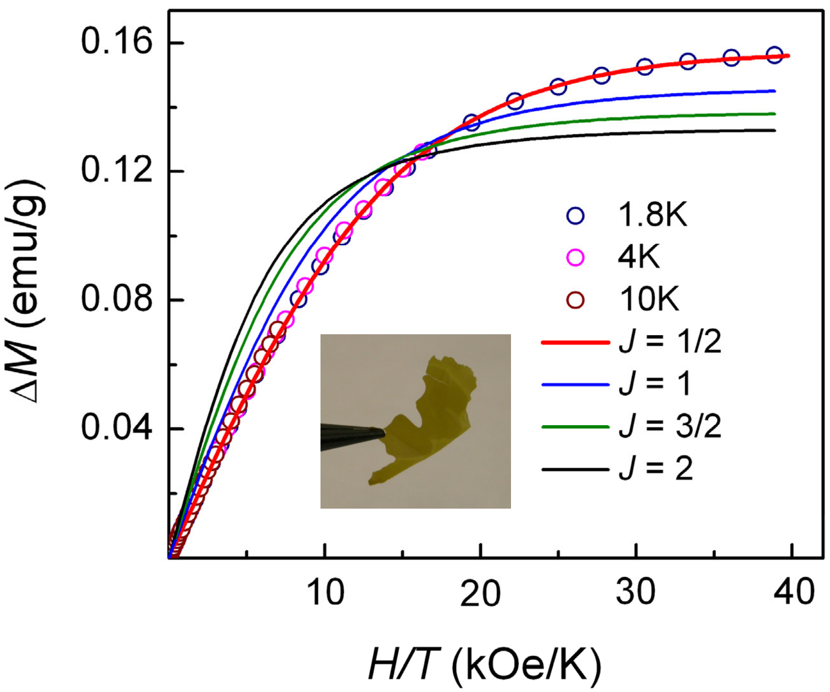
$$M = NgJ\mu_B \cdot \left[\frac{2J+1}{2J} ctnh\left(\frac{(2J+1)x}{2J} \right) - \frac{1}{2J} ctnh\left(\frac{x}{2J} \right) \right]$$ where $$x \equiv gJ\mu_B B / k_B T$$

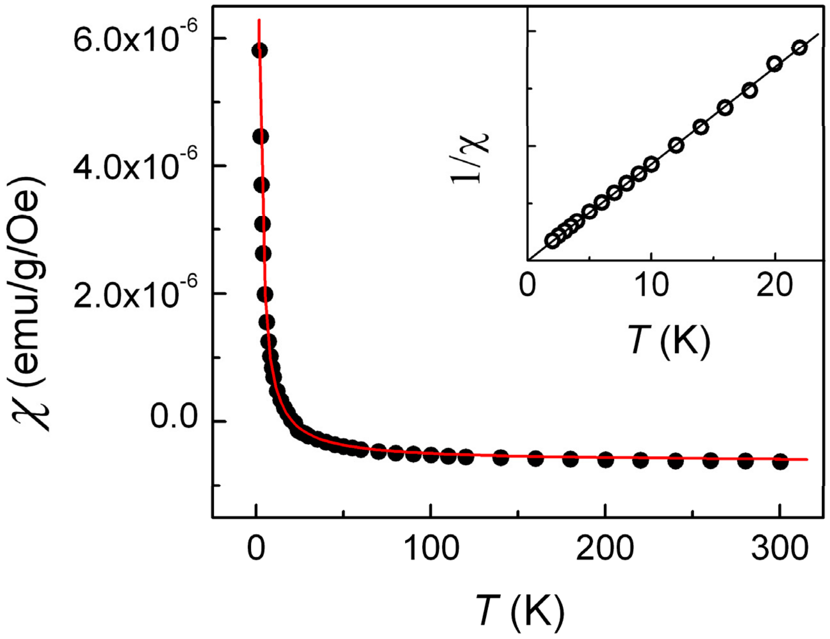
unambiguous spin-half paramagnetism



$$M = NgJ\mu_B \cdot \left[\frac{2J+1}{2J} ctnh\left(\frac{(2J+1)x)}{2J} \right) - \frac{1}{2J} ctnh\left(\frac{x}{2J} \right) \right] \quad \text{where} \quad x \equiv gJ\mu_B B / k_B T$$

unambiguous spin-half paramagnetism

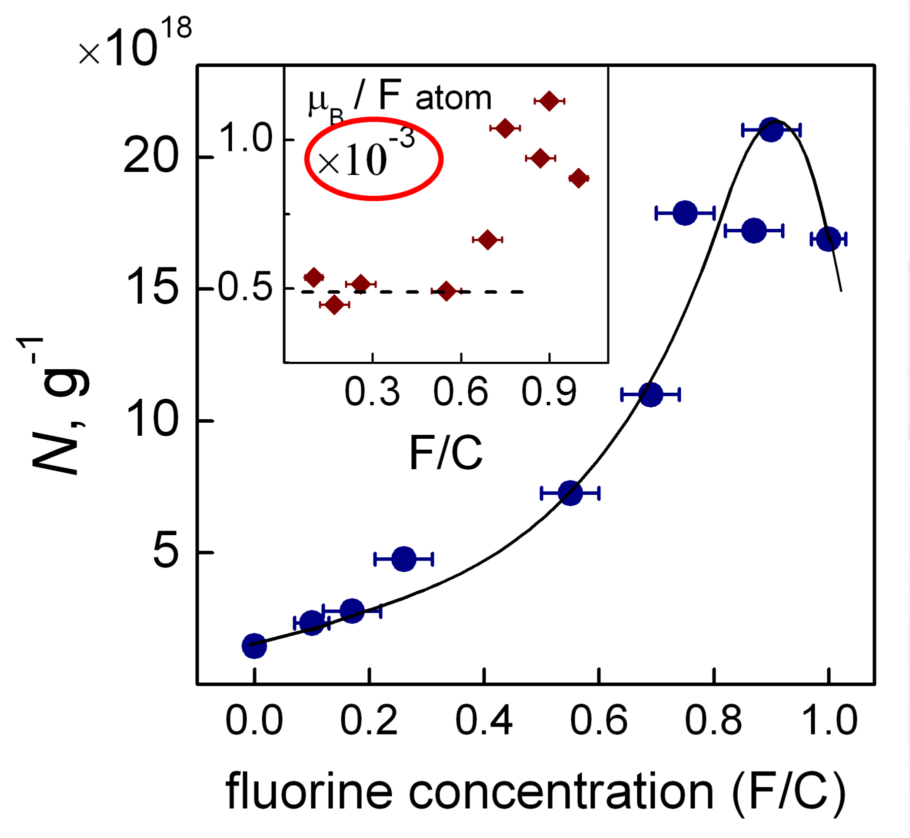




$$\chi = \frac{M}{B} \cong \frac{NJ(J+1)g^2\mu_B^2}{3k_BT} = \frac{C}{T}$$

- self-consistently, excellent fit to Curie law for paramagnetic susceptibility
- non-interacting moments

spin concentrations in fluorinated graphene

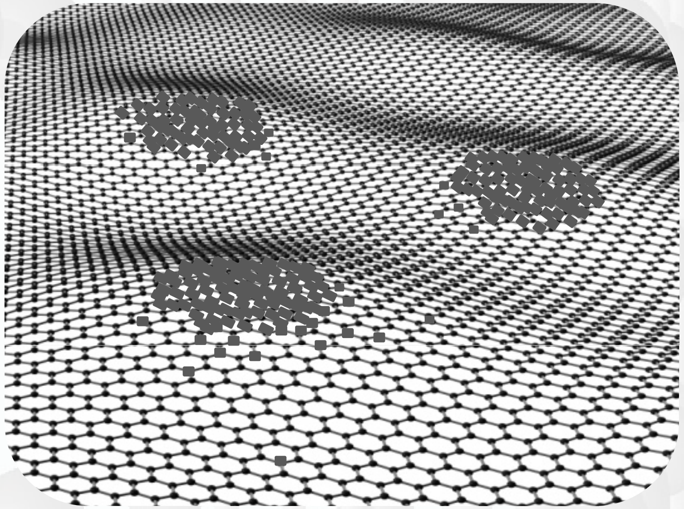


- important parameter - number of spins (magnetic moments) per defect (F adatom)

- only $10^{-3}\mu_B$ per F atom, not consistent with 'one adatom, one spin'

graphene fluorination - mechanism

- tendency towards clustering due to
  - (i) intrinsic ripples
  - (ii) low migration barriers for fluorine adatoms



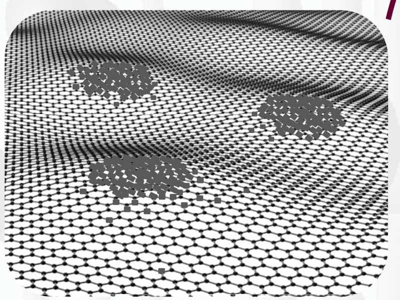
Osuna *et al, J. Phys. Chem. C* **114,** 3340–3345 (2010)

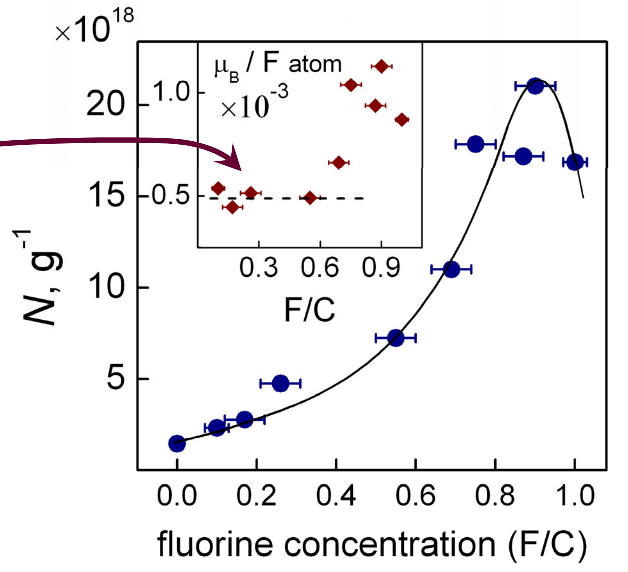
Kelly *et al*, *Chem. Phys. Lett.* **313,** 445–450 (1999).

Ewels *et al*, *Phys. Rev. Lett.* **96,** 21610 (2006).

paramagnetism due to clusters of fluorine atoms

up to F/C ~ 0.5





- clustering of adatoms $\Rightarrow$ bipartite nature of graphene lattice becomes important

Yazyev, *Rep. Prog. Phys.* **73**, 056501 (2010)
Wehling, Katsnelson, Lichtenstein, *Chem. Phys. Lett.* **476**, 125 (2009)
Rappoport, Uchoa, Castro Neto, *Phys. Rev. B* **80**, 245408 (2009)

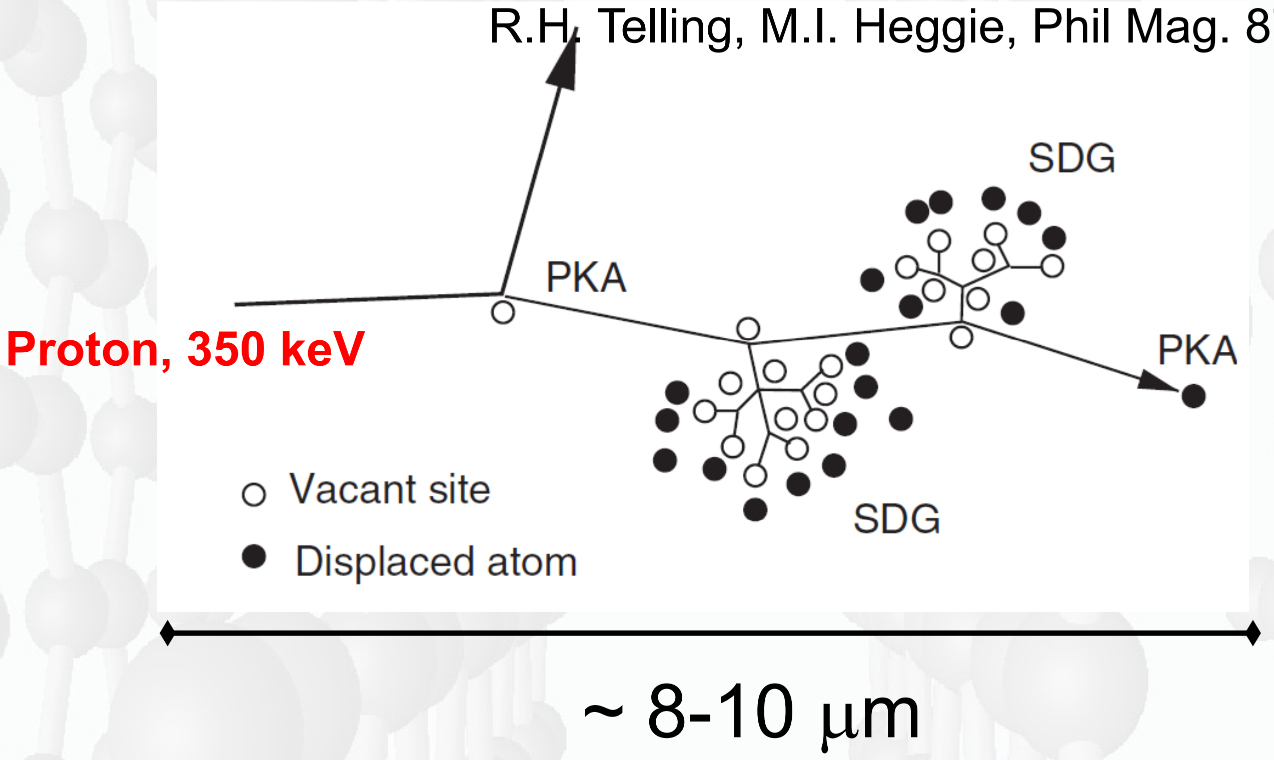
- total spin is determined by the spin imbalance between the two sublattices : $S = \frac{1}{2}|N_A - N_B|$

- observed N_s implies one spin per cluster of ~2000 atoms (~8 nm size)

- even at F/C ≈ 1 (=0.999), still ~0.1% defects (missing F atoms)

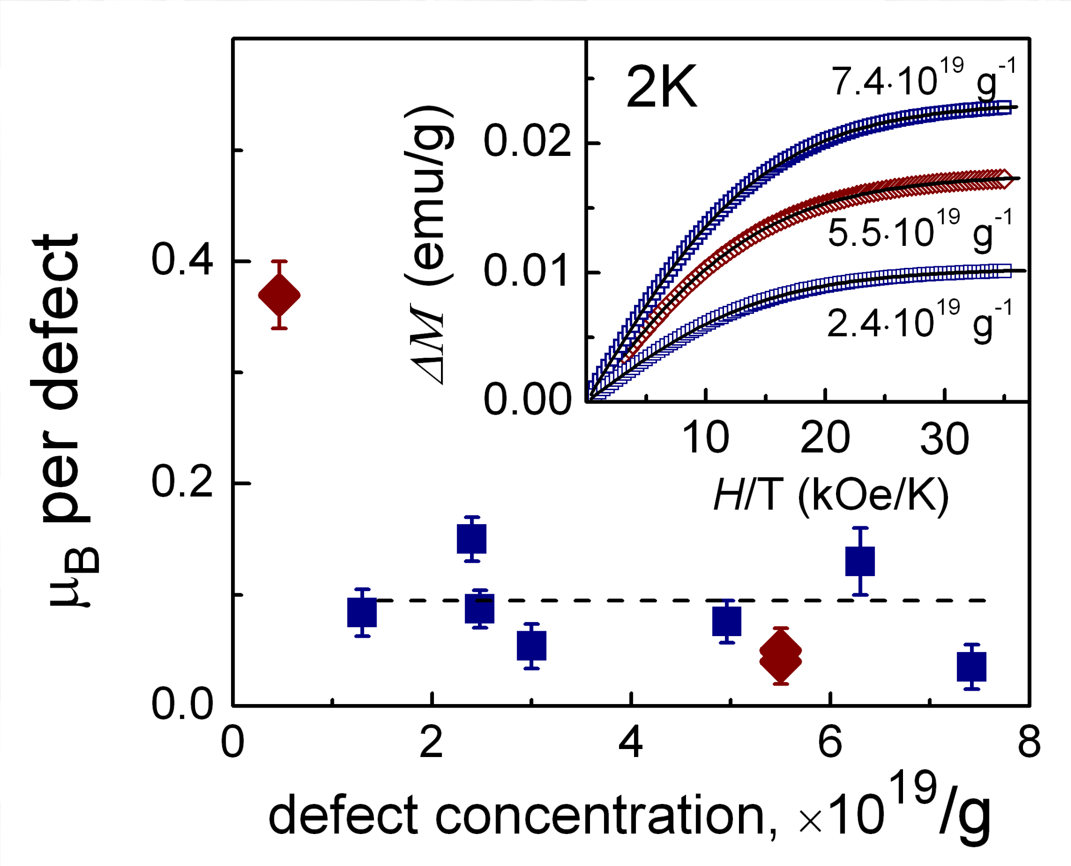
irradiated graphene laminates

R.H. Telling, M.I. Heggie, Phil Mag. 87, 4797 (2007)



- advantage compared to graphite: samples sufficiently thin (3-4μm) to ensure uniform defect distribution → well defined defect concentrations;
- used two different types of ions: protons and carbon ions (C^{4+})
- no implanted ions, only vacancies

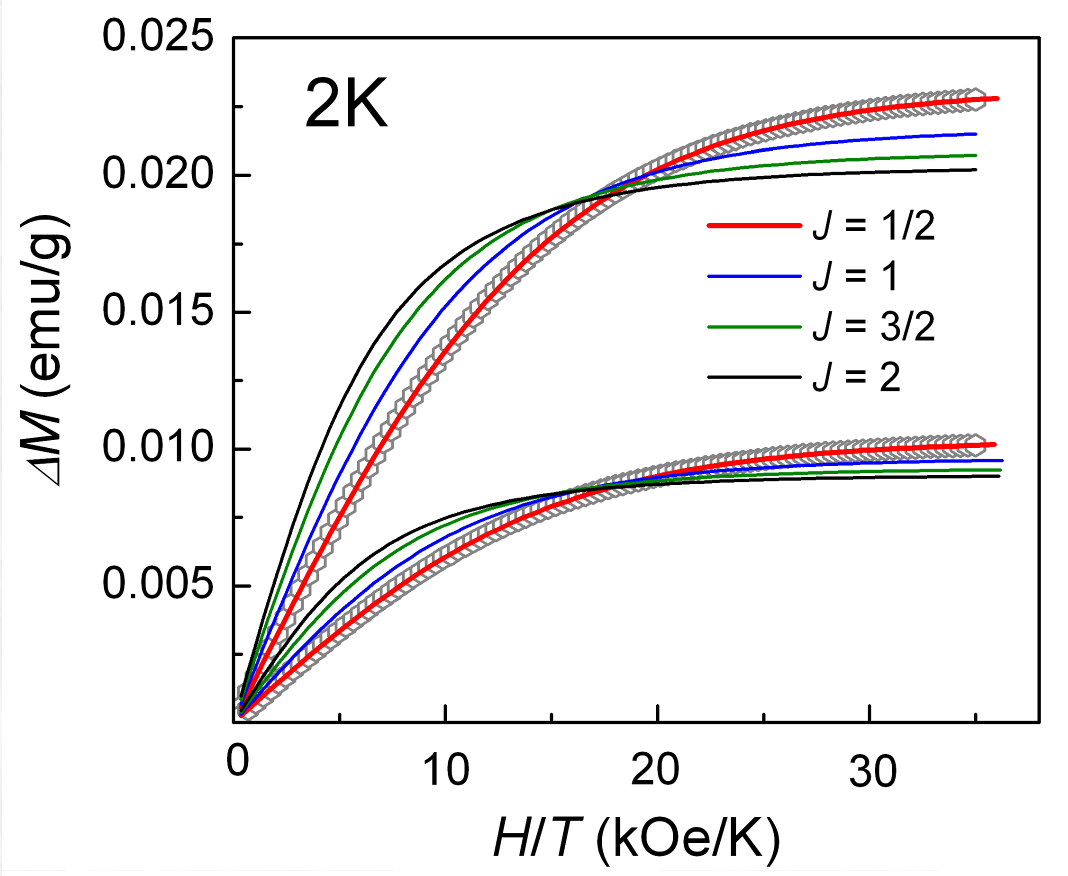
paramagnetism in irradiated graphene



R.R. Nair et al, ***Nature Physics***, online 10 January 2012, DOI**10.1038/NPHYS2183**

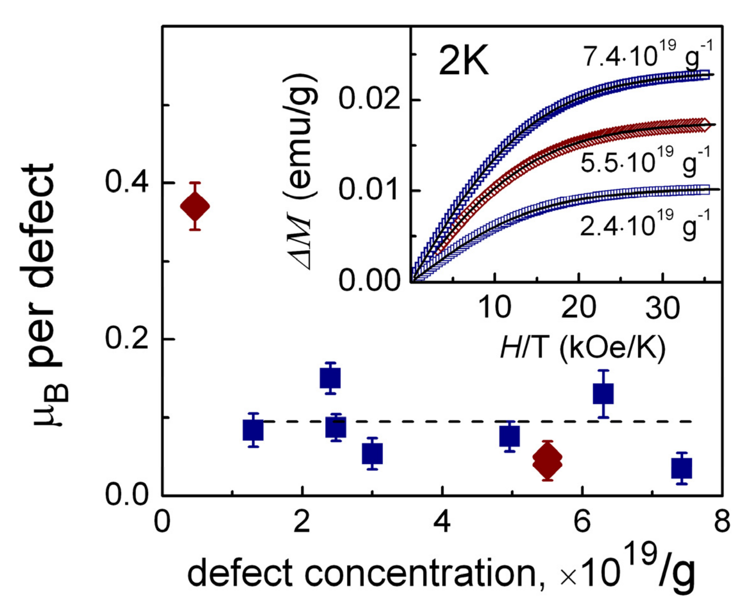
- qualitatively similar to adatoms (at first sight) :
    - paramagnetism with spin ½
    - linear increase in total magnetisation with increasing defect density;

paramagnetism in irradiated graphene



- unambiguously spin ½
- non-interacting magnetic moments

paramagnetism in irradiated graphene



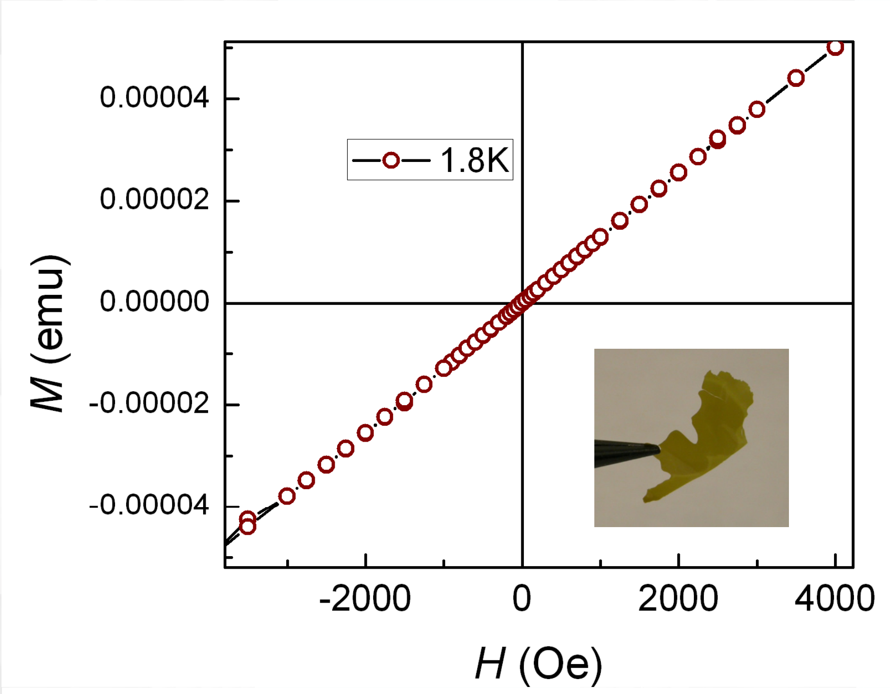
- effect of individual vacancies much greater than of individual F atoms (0.1 μ_B per vacancy)

  vacancies are not mobile and cannot cluster !

- no difference between H+ and C4+ irradiations – only the total defect concentration matters

✓ broadly agreement with theory

what of ferromagnetism ?



- no ferromagnetic signatures with high degree of accuracy (at the level of <10^{-7}emu)

- cannot rule out possibility of ferromagnetic coupling, as magnetic defects are still ~10nm apart

CONCLUSIONS

defects in graphene nanocrystals – both adatoms and vacancies - are MAGNETIC, with spin ½ (carrying $\mu \approx \mu_B$) in agreement with theory

clustering of defects reduces the overall magnetic moment due to bipartite nature of graphene lattice

no ferromagnetism – in commercially available HOPG it is most likely to be an artefact (talk for another day)