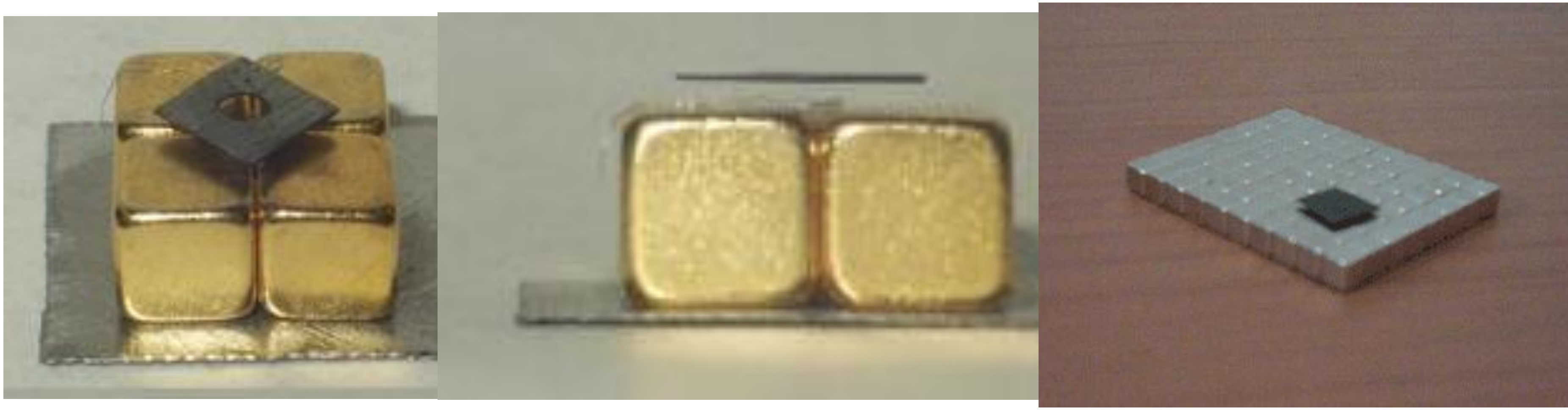
Graphite levitating on a magnet by diamagnetism



Measuring low magnetic signals with magnetic force microscopy: absence of ferromagnetism in graphite grain boundaries.

Julio Gómez-Herrero

science

IMAGINENANO

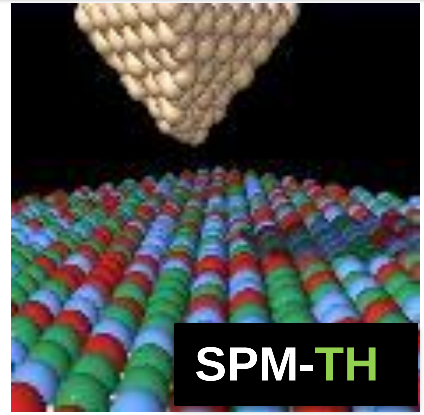
Bringing together Nanoscience & Nanotechnology

graphene 2011

In collaboration with….

David Martínez-Martín

Nanoforces Group



Theory

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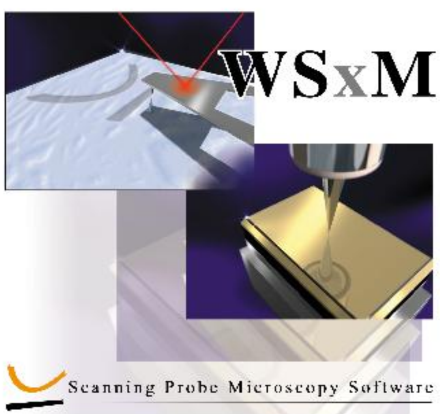
Agustina Asenjo



NANOTEC
ELECTRONICA

Technical support

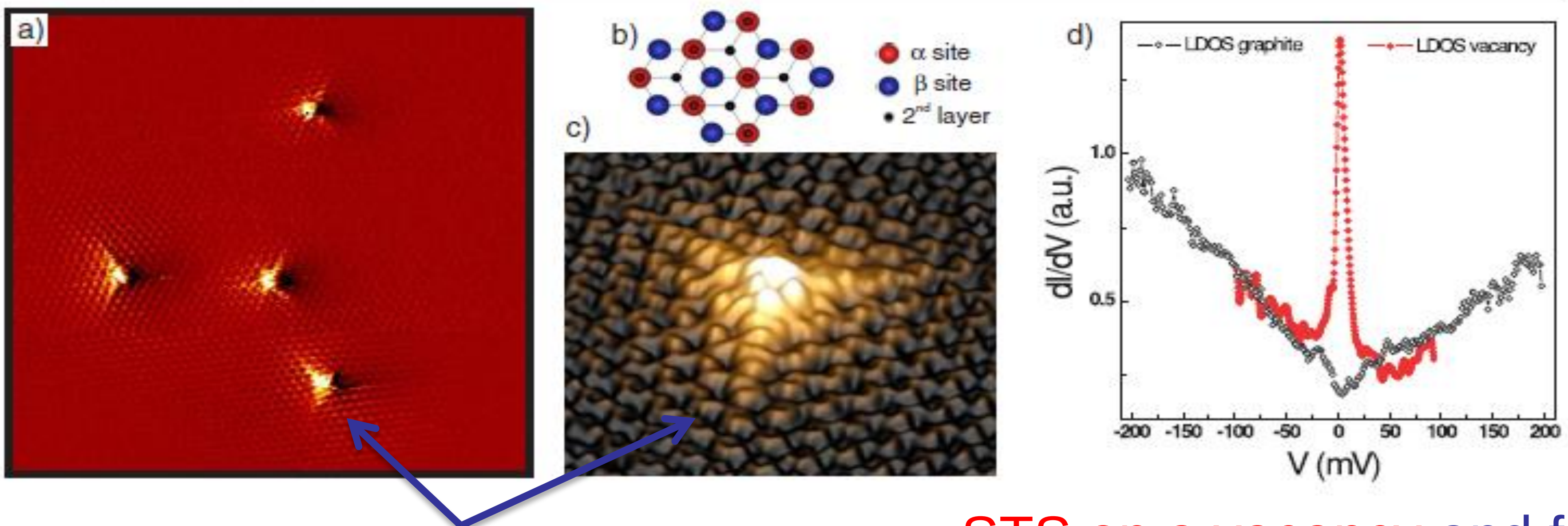
localized states in graphite defects

•graphene/graphite present localized states near defects and zig-zag edges.

M. Ugeda *et al.*

PRL **104**, 096804 (2010)

week ending
5 MARCH 2010



STM topography images of 4 vacancies in graphite (UHV, 4 K)

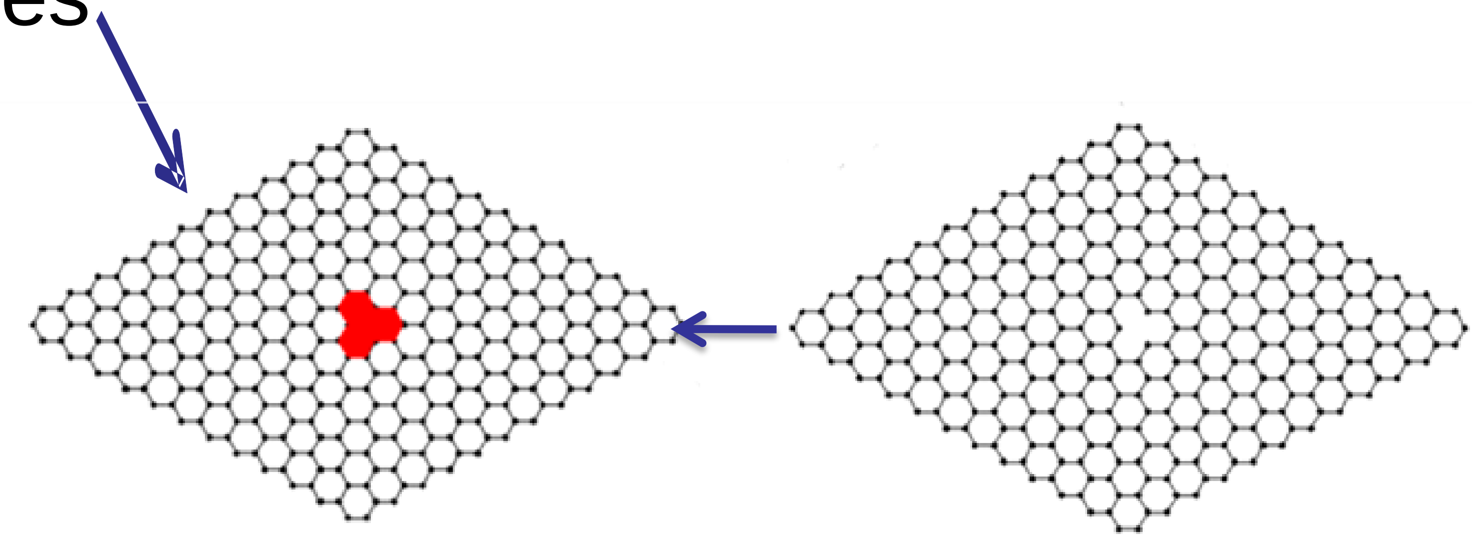
STS on a vacancy and far away from the vacancy

•Y. Shibayama *et al.* Phys. Rev. Lett. **84**, 1744 (2000).
•K. Harigaya *et al.* , Chem. Phys. Lett. **351**, 128, (2002).
•J. Fernandez-Rossier and J. Palacios, Phys. Rev. Lett. 99,177204 (2007).

Magnetism and defects in graphite/graphene

•These states may give rise to magnetic moments of about $1\mu_B$.

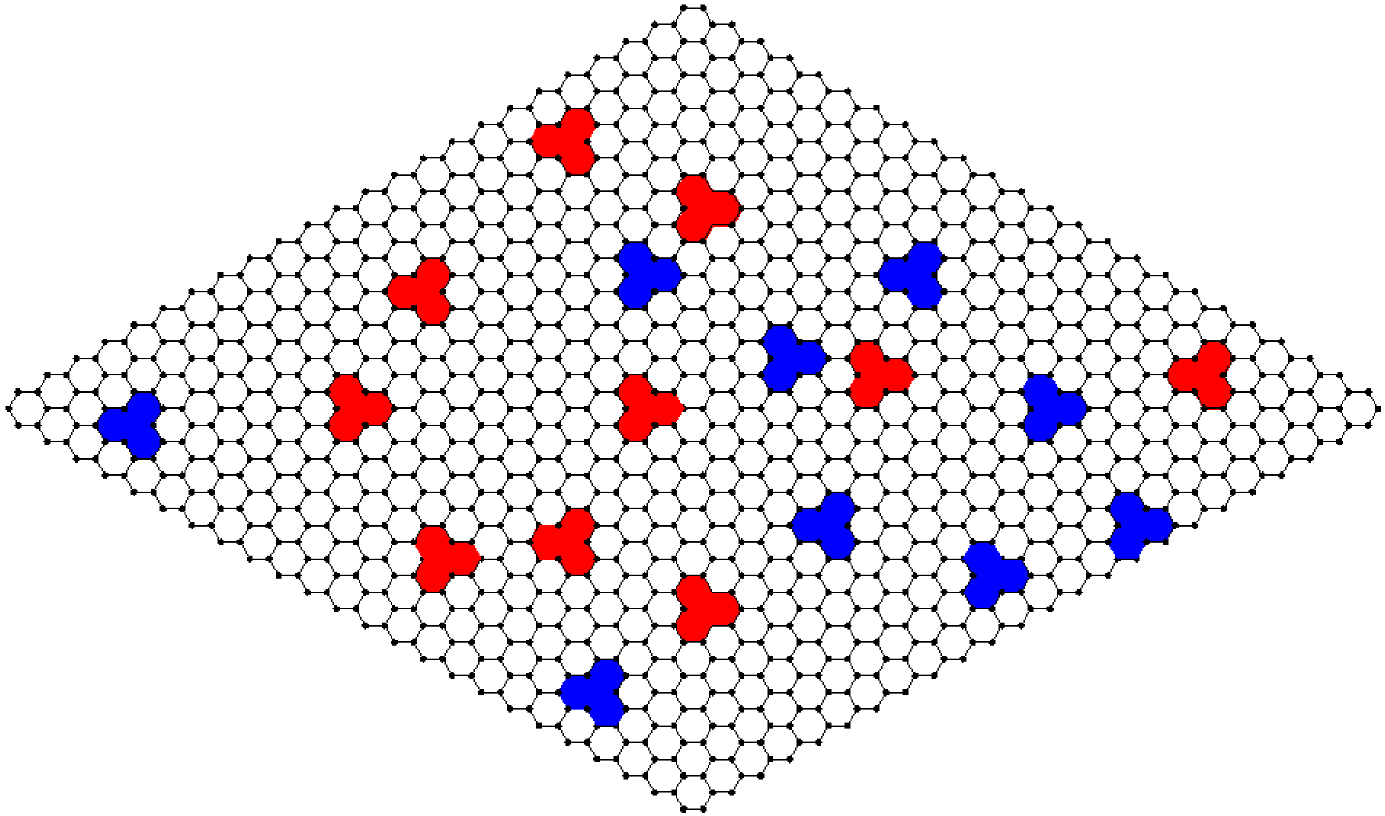
Zig-zag edges



Magnetic moment

•Y. Shibayama *et al.* Phys. Rev. Lett. **84**, 1744 (2000).
•K. Harigaya *et al.* , Chem. Phys. Lett. **351**, 128, (2002).
•J. Fernandez-Rossier and J. Palacios, Phys. Rev. Lett. 99,177204 (2007).

Interaction between individual magnetic moments



The question: is graphite/graphine ferromagnetic?

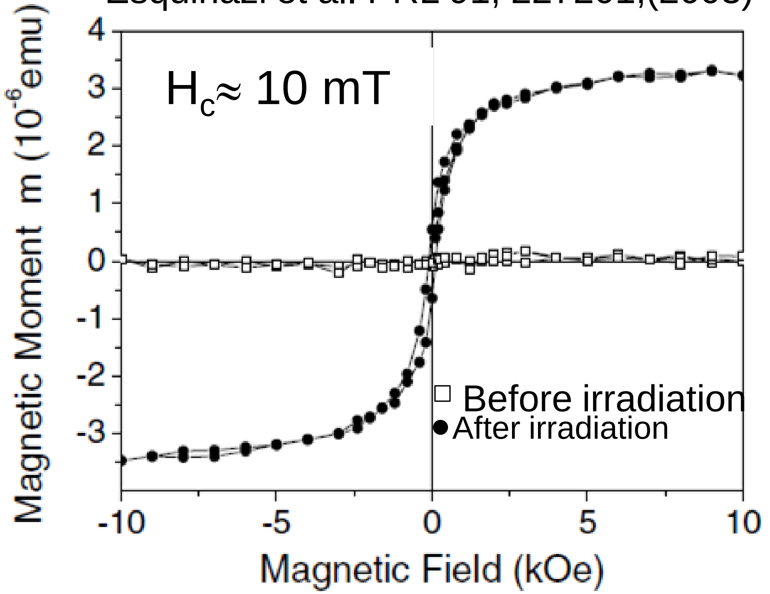
First material without f or d orbitals exhibiting ferromagnetism

ferromagnetism in irradiated graphite

•During the last 10 year there has been Intense experimental research led by Prof. Esquinazi searching for ferromagnetism in graphite irradiated samples (irradiation produces defects).

•The main technique is magnetometry. In particular, *superconducting quantum interference devices* (**SQUID**),

Esquinazi et al. PRL 91, 227201,(2003)



See also:

R. Hohne *et al.* Adv. Mat. **14**, 753, (2002)

M. Ramos *et al.* PRB, **81**, 214404, (2010)

However the extreme sensitivity of SQUID may introduce artifacts and there is not a complete agreement in the the scientific community.

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

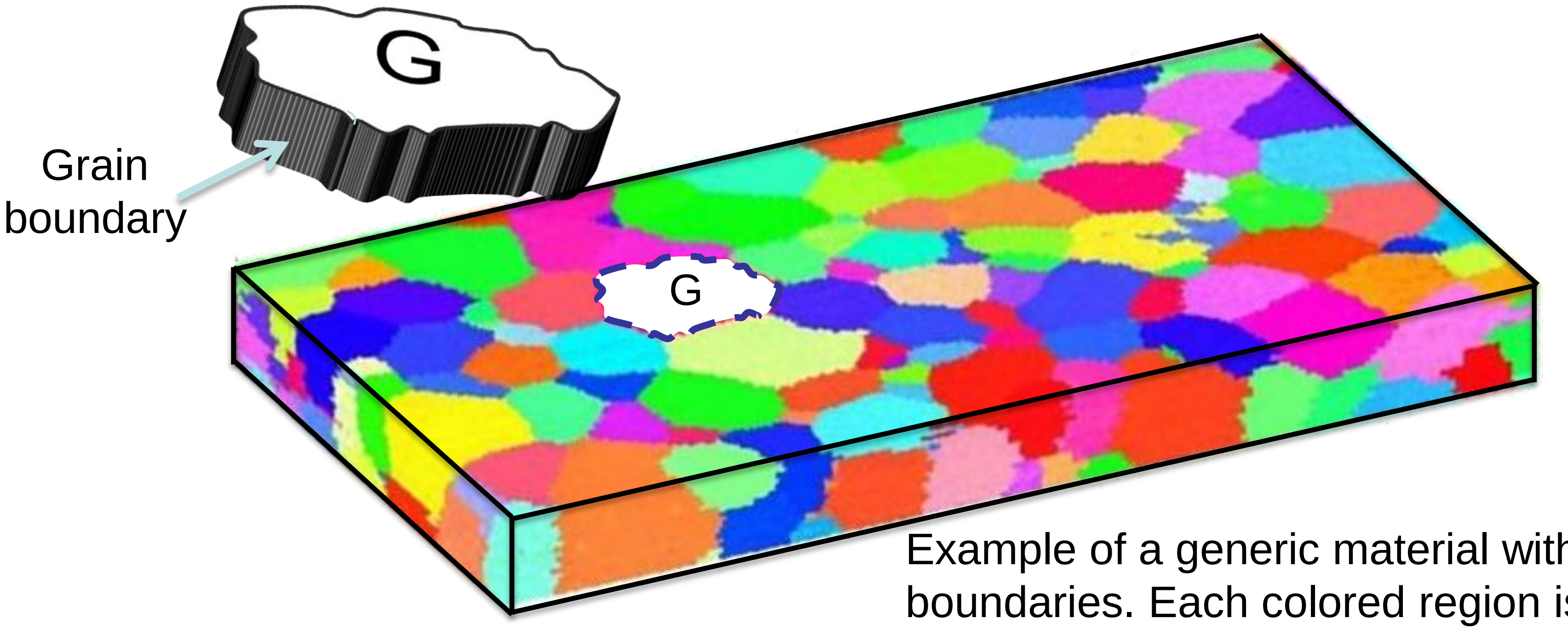
Defects and grain boundaries

- Most of the experiments are carried out not in graphite single crystals but in Highly Oriented Pyrolytic Graphite (HOPG).

- HOPG presents large domains with a single orientation (the size of the domains depends on the sample quality).

- The domains are separated by grain boundaries (a 2D surface).

- A grain boundary is seen as a line (surface step) on the sample surface

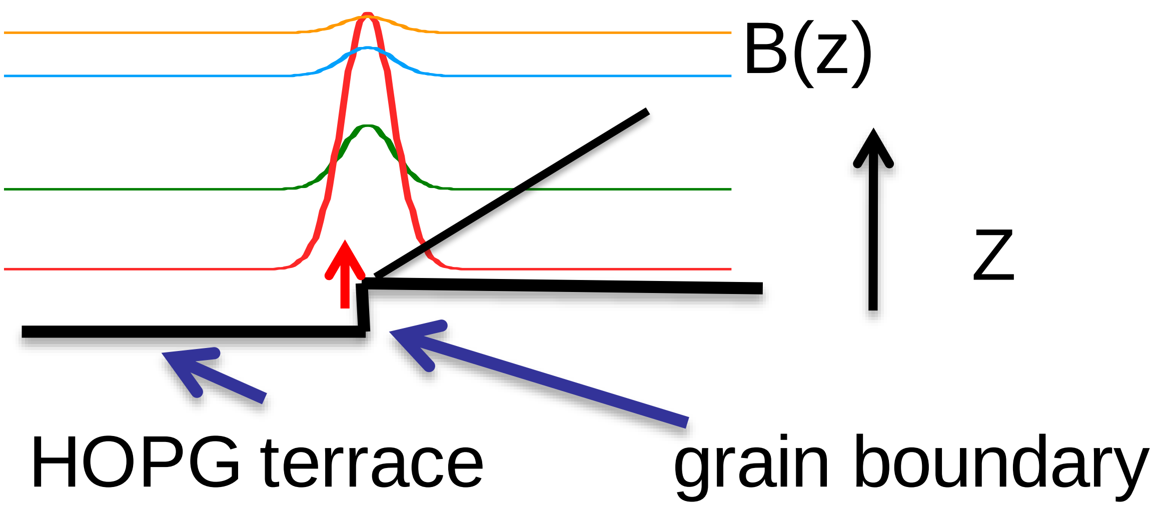


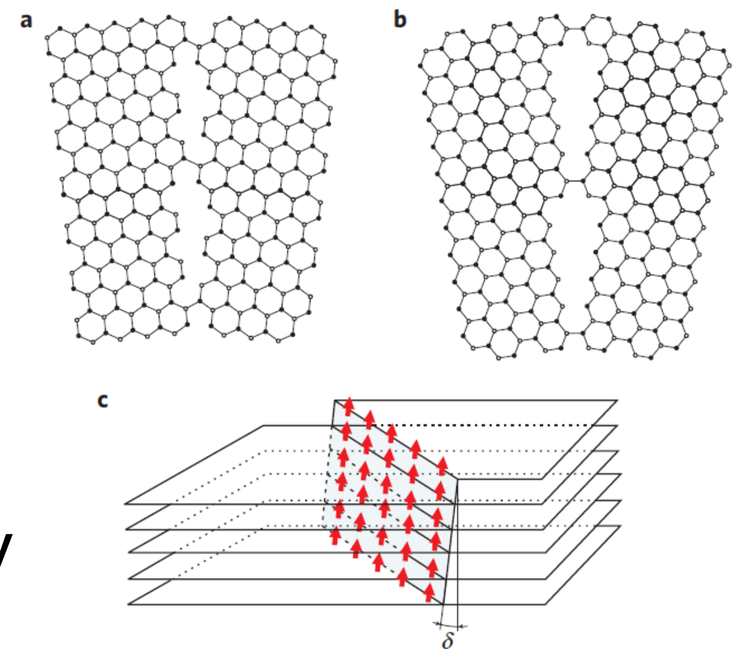
Example of a generic material with grain boundaries. Each colored region is a grain.

Defects and grain boundaries

•**According to** Cervenka et *al. [Nat. Phys.* **5**, 840,(2009)] grain boundaries in graphite can be visualized as a 2D plane defects propagating to the volume.

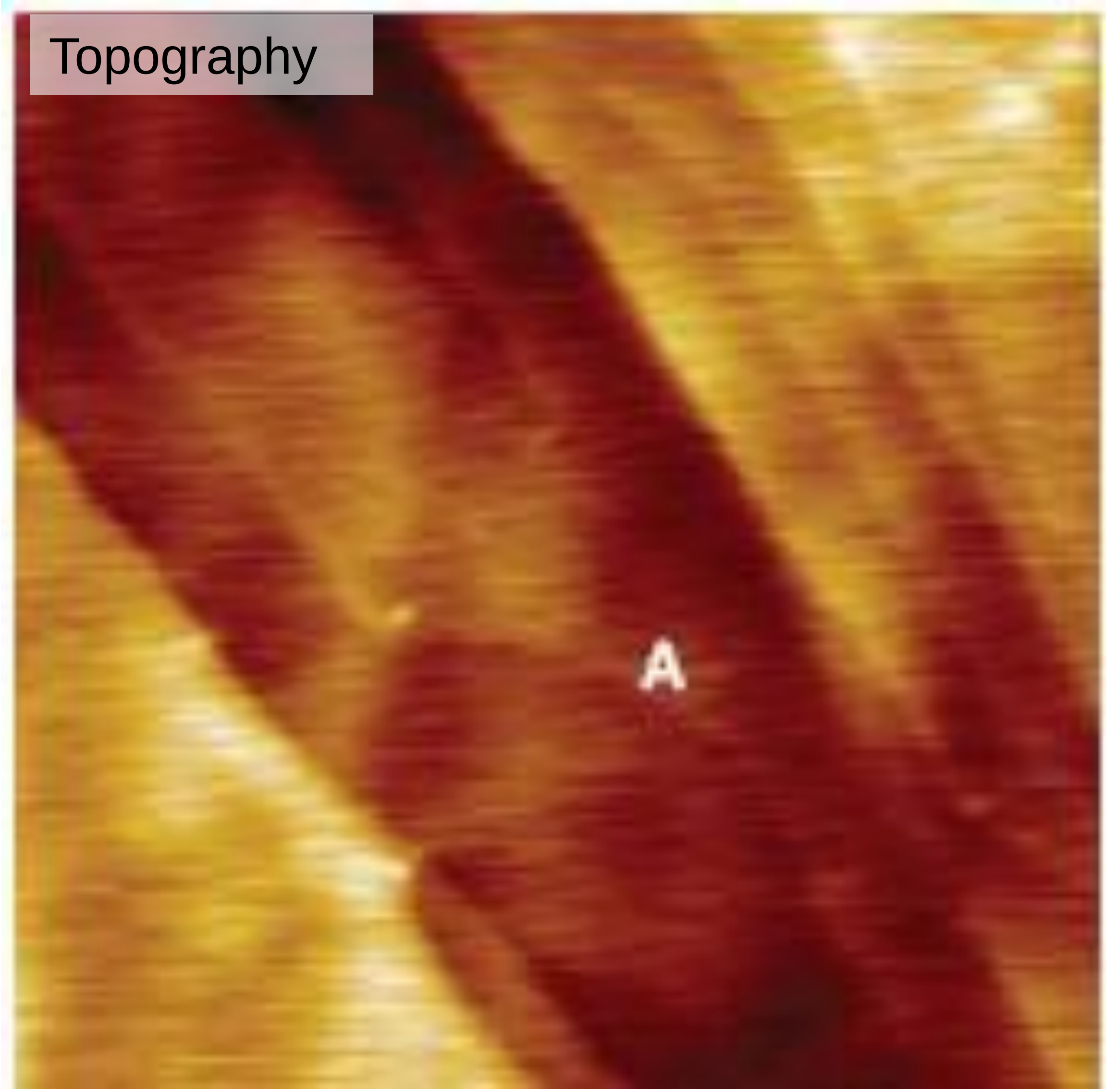
•The implication is that grain boundaries should present a magnetic field gradient of **~0.1-1 mN/m at 50 nm** from de surface that **should be possible to detect with magnetic force microscopy (MFM).**





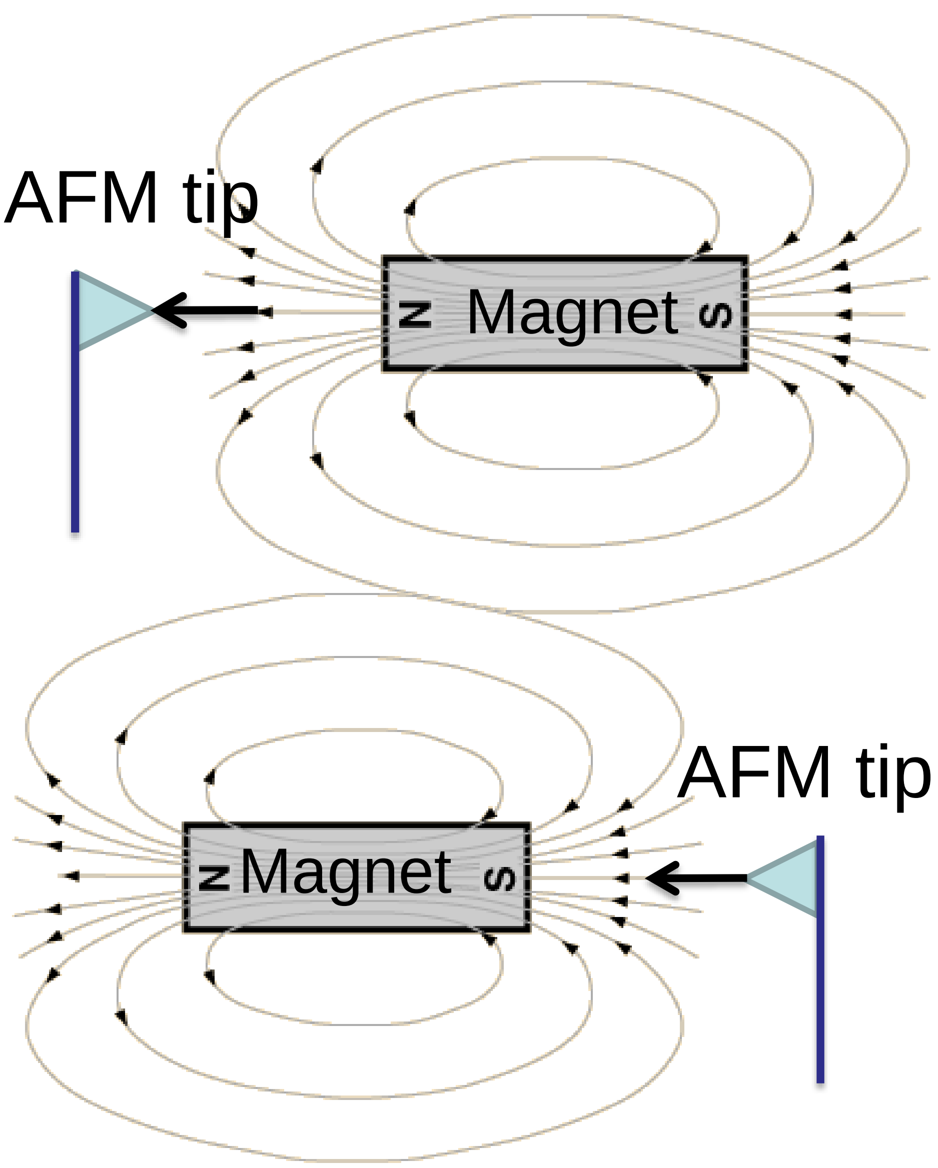
Two examples of grain boundaries in HOPG

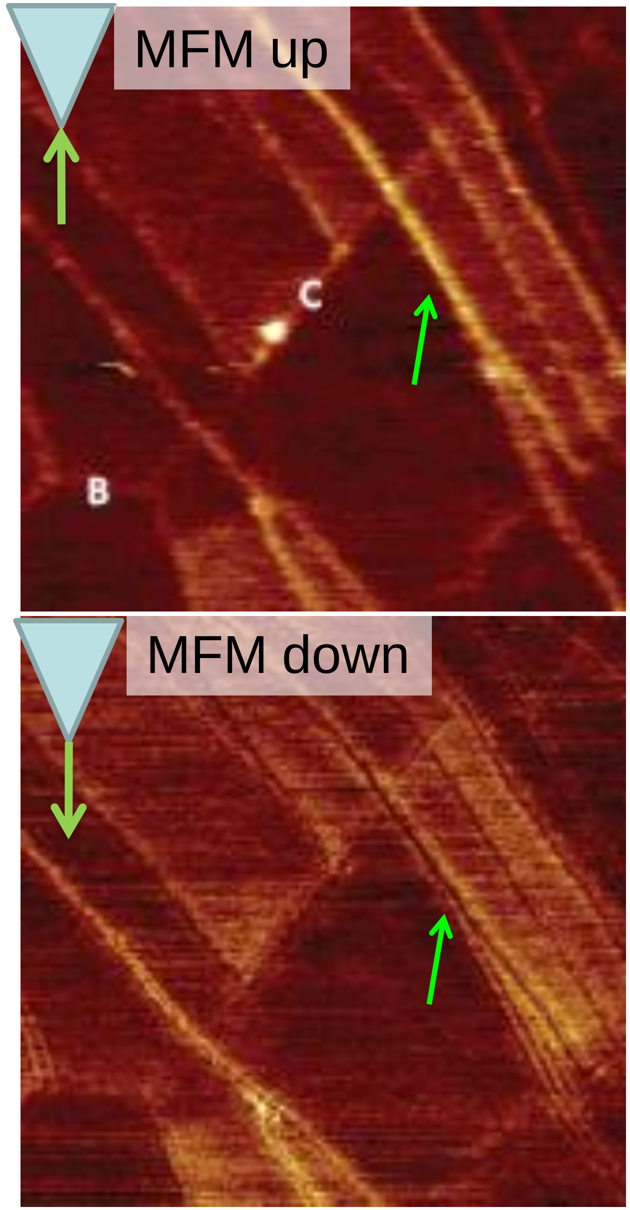
Ferromagnetism in graphite grain boundaries



Data from Cervenka, Katsnelson and Flipse *Nat. Phys.* **5**, 840,(2009)

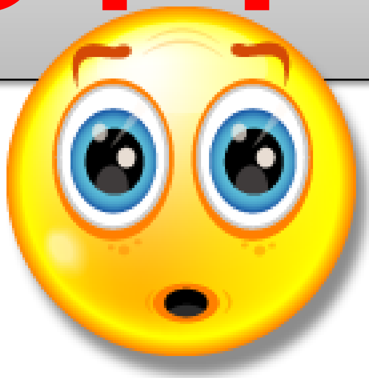
Ferromagnetism in graphite grain boundaries





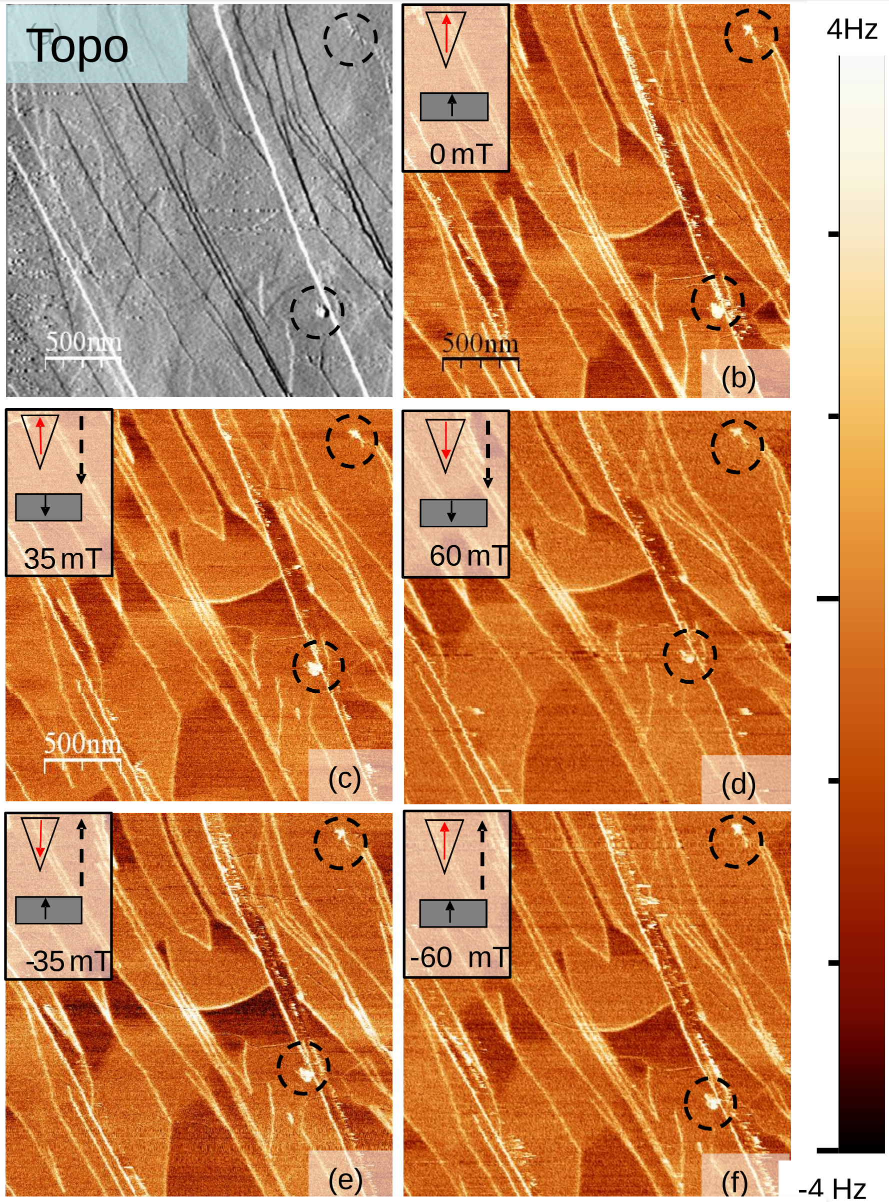
Data from Cervenka, Katsnelson and Flipse *Nat. Phys.* **5**, 840,(2009)

How can it be??



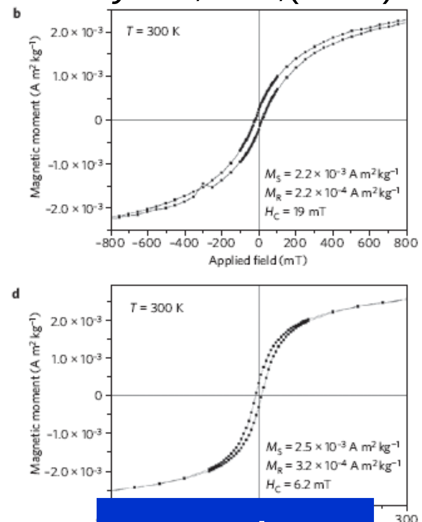
We have imaged many times graphite looking for magnetic signal and **we have never ever seen anything like this**

MFM on HOPG with external magnetic field



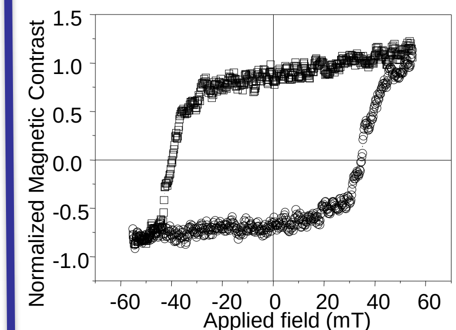
Amplitude, 7nm, Retrace , 50nm

Data from Cervenka, Katsnelson and Flipse *Nat. Phys.* **5**, 840,(2009)



Sample
Hc~20mT

Variation of the tip magnetization as a function of the external magnetic field



TIP
Hc~45mT

The contrast along the steps does not vary with the external magnetic field.
The implication is:
We do not observe ferromagnetism

D. Martínez – Martín, M. Jaafar, J. Gómez – Herrero, R. Pérez and A. Asenjo, *Phys. Rev. Lett*. 105, 257203 (2010)

Where is the origin of the discrepancy?

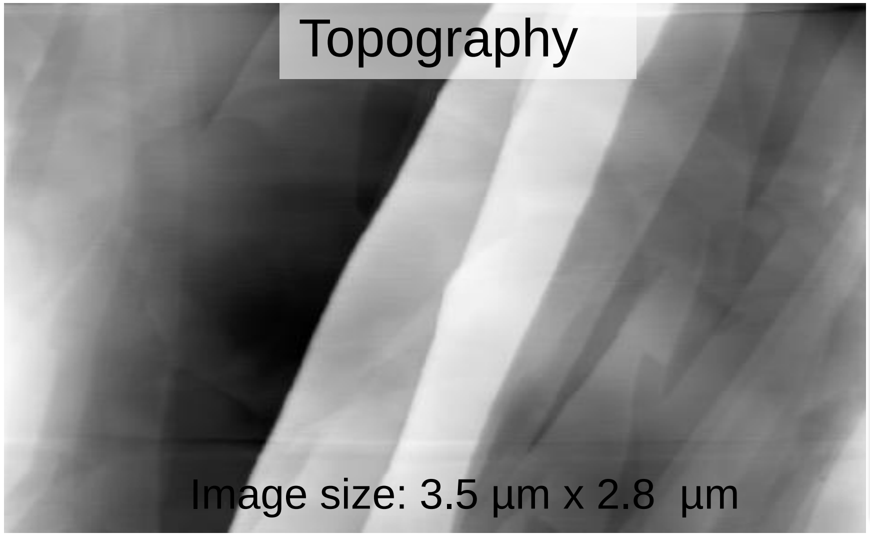
We attribute the discrepancy with the work by Cervenka, Katsnelson and Flipse [*Nat. Phys.* **5**, 840,(2009)] to the inadequate operating mode used to obtain the MFM data:

Their images were taken with at **very large amplitude : 100 nm at 50 nm lift distance** [1], that implies **hard tip-sample contact** and, therefore, the linear approximation that they use to relate phase and force gradient is obviously not valid any longer.

[1] Internal communication

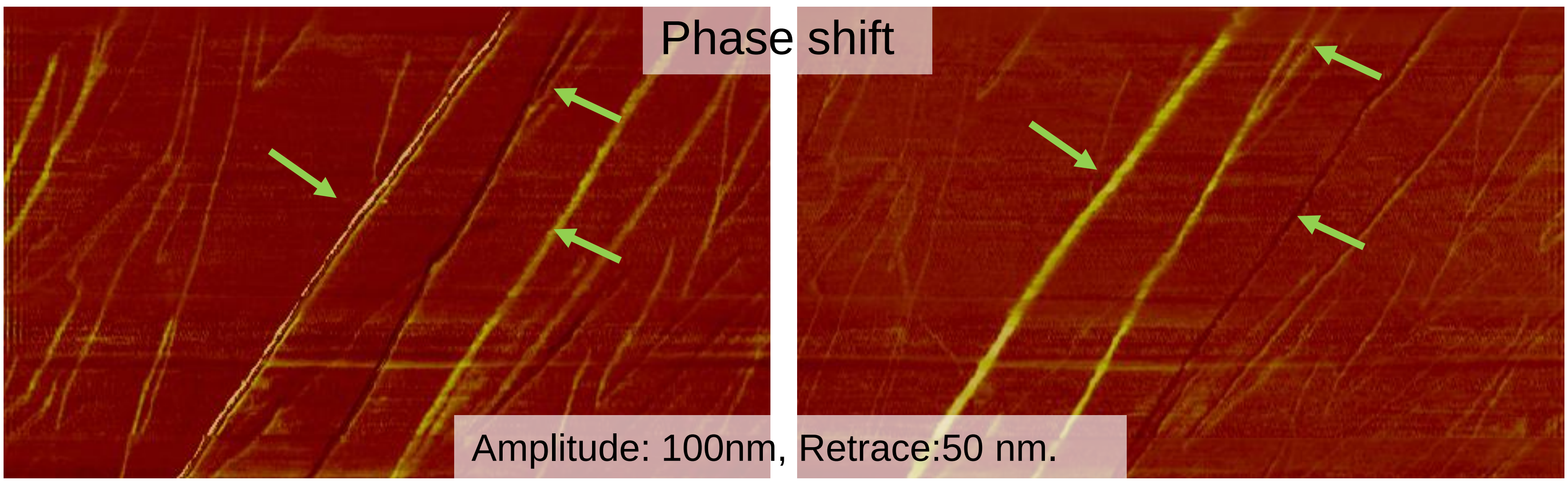
AFM Tip in hard intermittent contact.

For high oscillation amplitude everything is possible



Large amplitude MFM images show that:

Small variations in the imaging conditions (without any magnetic change) produce Contrast inversion along several steps



D. – Martín, M. Jaafar, R. Pérez J. Gómez – Herrero, and A. Asenjo, *Phys. Rev. Lett*. , 105, 257203 (2010)

Going a bit further

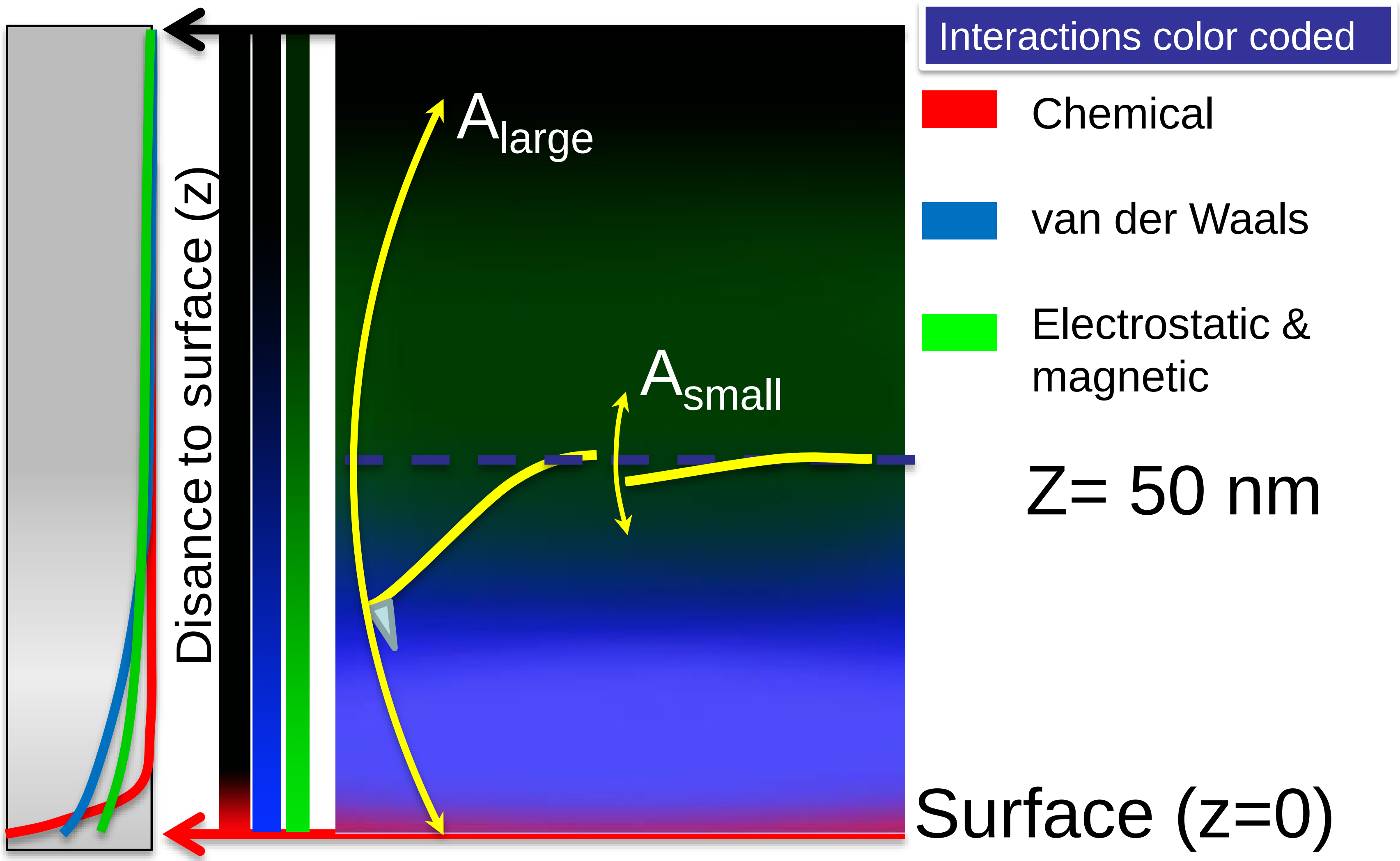
The ingredients of *tip-sample force*

There are several interactions that contribute to the tip-sample force

Interaction type	range	Characteristic length (*)
Chemical	Short	$0<\lambda_{chem}<0.5$ nm
van der Waals	medium	$0<\lambda_{vdw}<30$ nm
Electrostatic	Long	$0<\lambda_{E}<100$ nm
Magnetic	Long	$0<\lambda_{B}<100$ nm

* Numbers can change depending on different factors such as the tip geometry

Selecting the interaction



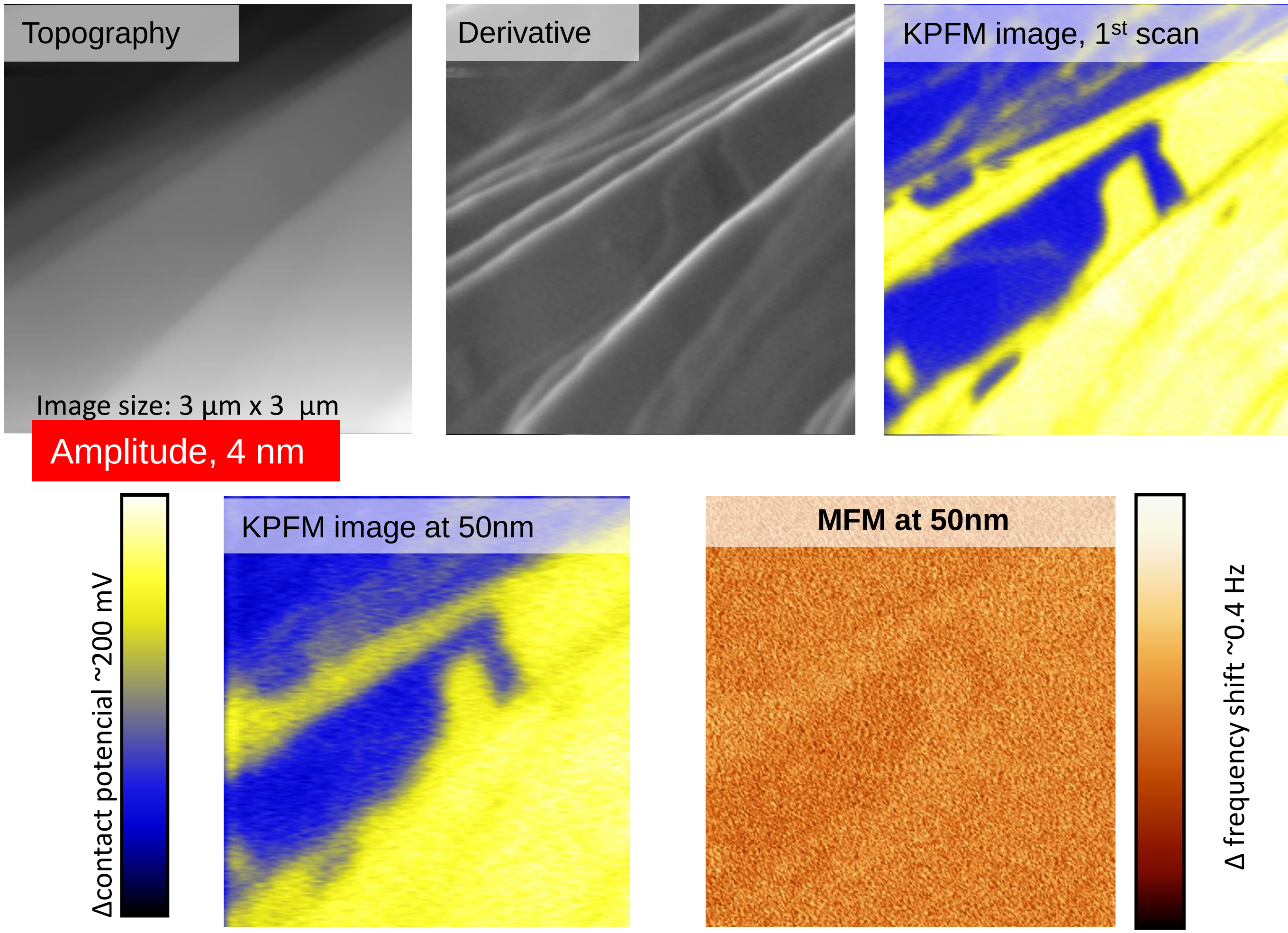
•Problem: it is very difficult to separate the electrostatic and the magnetic force.

The key elements for the experiment

- ✓ Use small oscillation amplitudes
- ✓ Remove the electrostatic component by using kelving probe force microscopy (KPFM)
- ✓ Perform the experiments in high vacuum to increase the sensitivity of the MFM signal

High sensitivity meaurements in high-vacuum

KPFM/MFM combination measured in HV-AFM with a **magnetic** probe [1]



Magnetism in graphite grain boundaries?

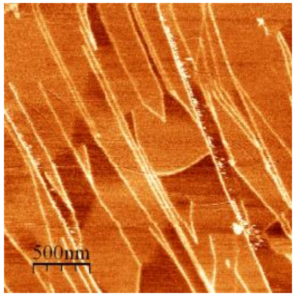
NOT OBSERVED

upper bound for the magnetic force gradient

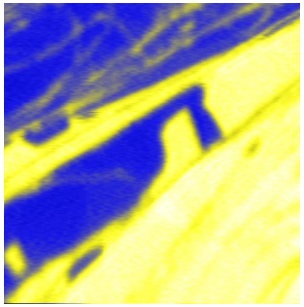
The magnetic signal, if present, is lower than **16 µN/m**
6-60 times lower than predictions

[1] D. Martínez–Martín, et al., *Phys. Rev. Lett*. 105, 257203 (2010)

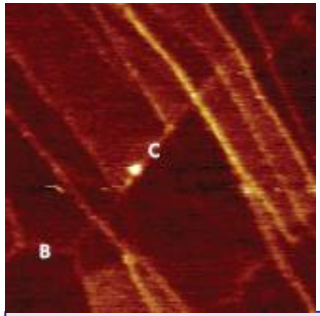
To sum up



•We have shown that the contrast observed along the **steps** on a graphite surface remains **unmodified** under an external magnetic field.



•Technical issue: first demonstration of KPFM/MFM combination.



- **Upper bound** for the magnetic signal in graphite **16 μN/m (6-60 times** lower than the theoretical prediction and **more than one order magnitude** smaller than the experimental value found by Cervenka et al.).

The bottom line of this talk: let experiments spoil a good theory