Magnetic Order in Carbon Structures

Past, Present and Future Research

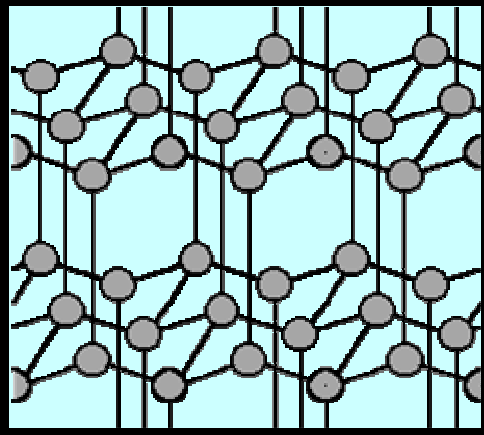
P. Esquinazi

University of Leipzig

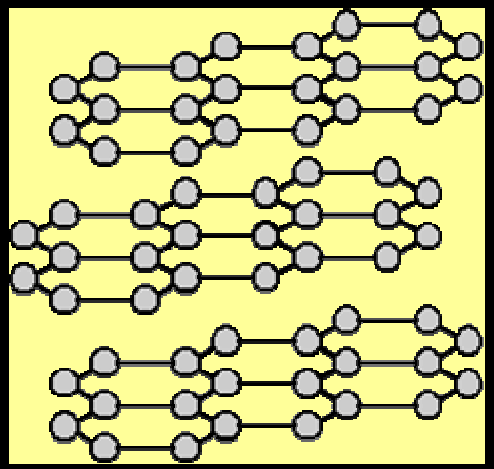
Carbon C

(K) $2e^-$ in 1s, (L) $2e^-$ in 2s und $2e^-$ in 2p: $6e^-$

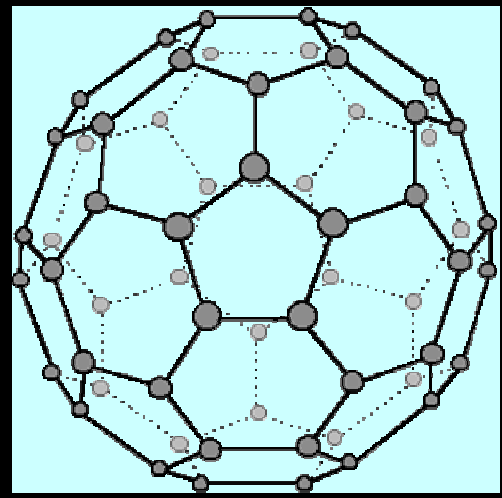
Diamond



Graphite



Fullerene



Introduction – crash course in magnetism

Magnetism		
Momentum of electrons (spin + orbit) => magnetic moments		
Bohr magneton: $m_B = \mu_0 e \hbar / (2m) = 1{,}165 \times 10^{-29}$ Vsm (T m^3) ~ 10^{-20}emu		
Diamagnetism	**Paramagnetism**	**Ferromagnetism**
orbit	isolated spins	interacting spins
Interaction with external magnetic field: $B = \mu_0 (1 + \chi) H$		
$\chi = - (10^{-8} .. 10^{-4})$	$\chi = + (10^{-6} .. 10^{-3})$	$\chi = + (10^{-2} .. 10^{6})$
		$T < T_C$: M # 0 for H=0

Magnetic Prejudice based on experience and theory, since 1928

W. Heisenberg, Z. Phys. 49, 615-636

619

**

Zur Theorie des Ferromagnetismus.

Von **W. Heisenberg** in Leipzig.

Mit 1 Abbildung. (Eingegangen am 20. Mai 1928.)

Die Weissschen Molekularkräfte werden zurückgeführt auf ein quantenmechanisches Austauschphänomen; und zwar handelt es sich um diejenigen Austauschvorgänge, die in letzter Zeit von Heitler und London mit Erfolg zur Deutung der homöopolaren Valenzkräfte herangezogen worden sind.

Einleitung. Die ferromagnetischen Erscheinungen sind in formal befriedigender Weise durch die bekannte Weisssche Theorie* gedeutet worden. Diese Theorie basiert auf der Annahme, daß jedes Atom im Kristall eine richtende Kraft durch die übrigen Atome des Gitters erfährt, die proportional der Anzahl der bereits gerichteten Atome sein soll. Der Ursprung dieses atomaren Feldes war dagegen völlig unbekannt, und einer Deutung der Weissschen Kräfte auf Grund der klassischen Theorie standen folgende Schwierigkeiten im Wege: Magnetische Wechselwirkungskräfte zwischen den Atomen sind stets um einige Größenordnungen kleiner als die aus den ferromagnetischen Experimenten folgenden atomaren Felder. Elektrische Wechselwirkungen führen zwar zur richtigen Größenordnung; dagegen würde man eher erwarten, daß die elektrischen Wechselwirkungen zweier Atome dem Quadrat des Cosinus ihres gegenseitigen Neigungswinkels als dem Cosinus proportional wären, entgegen den Voraussetzungen der Weissschen Theorie. Andere Schwierigkeiten wurden noch ausführlich von Lenz** diskutiert, und es gelang Ising***, zu zeigen, daß auch die Annahme richtender, hinreichend großer Kräfte zwischen je zwei Nachbaratomen einer Kette nicht genügt, um Ferromagnetismus zu erzeugen.

In ein neues Stadium ist der ferromagnetische Fragenkomplex getreten durch die Uhlenbeck-Goudsmitsche Theorie des Spinelektrons. Insbesondere folgt aus dem bekannten Faktor $g = 2$ beim Einstein-de Haas-Effekt (der ja eben bei ferromagnetischen Substanzen gemessen wurde), daß sich in einem ferromagnetischen Kristall nur die magnetischen Eigenmomente der Elektronen, gar nicht die Atome orientieren. Damit fällt wieder die Möglichkeit fort, die Weissschen Kräfte als elektrische Wechselwirkungen, abhängig von der relativen Spinrichtung der Elektronen,

* P. Weiss, Journ. de phys. (4) **6**, 661, 1907 und Phys. ZS. **9**, 358, 1908.
** W. Lenz, Phys. ZS. **21**, 613, 1920.
*** E. Ising, ZS. f. Phys. **31**, 253, 1925.

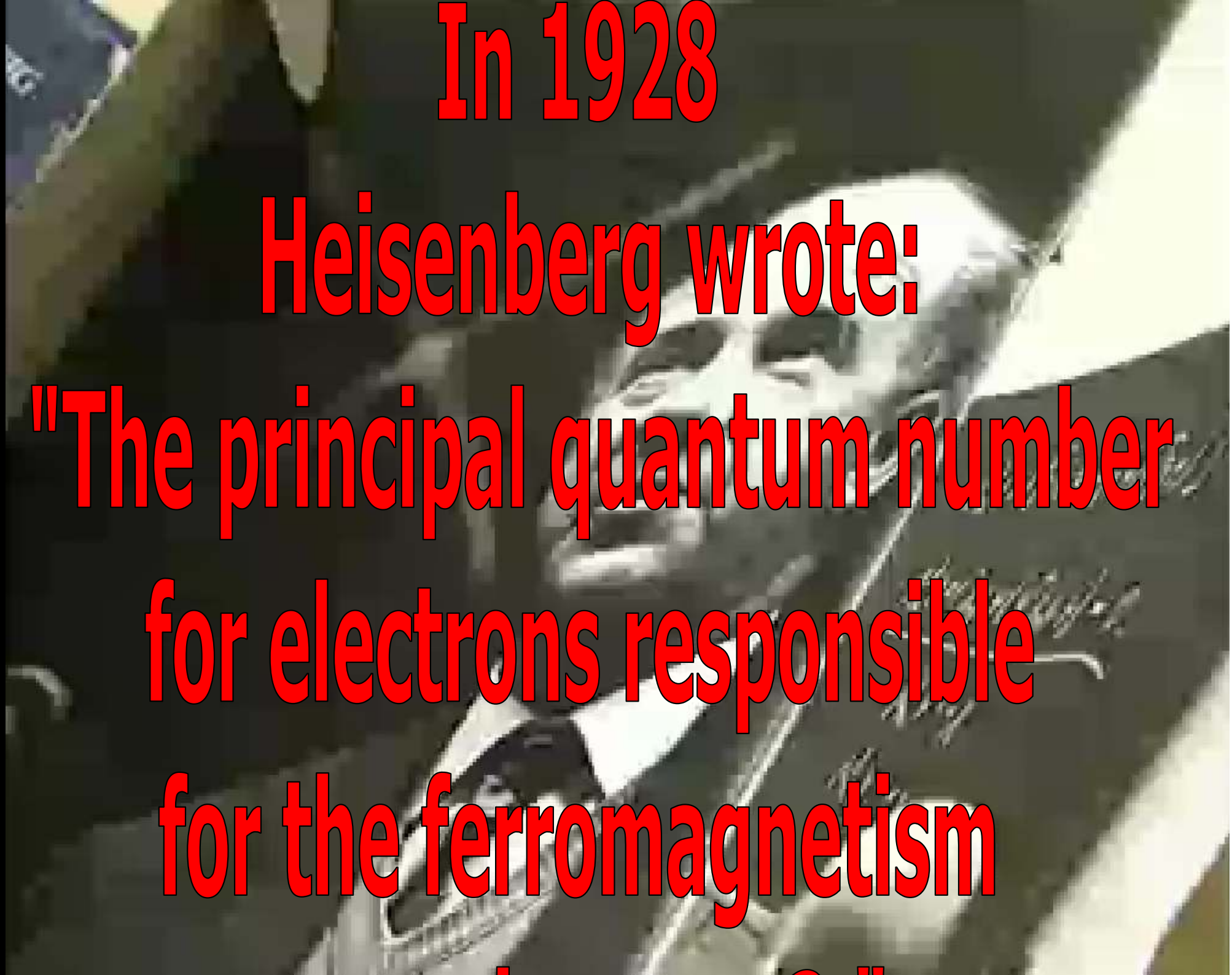
Schlußbemerkungen. Die hier beschriebenen Rechnungen führten zu zwei Bedingungen für das Auftreten von Ferromagnetismus:

1. Das Kristallgitter muß von solcher Art sein, daß jedes Atom mindestens 8 Nachbarn hat.

2. Die Hauptquantenzahl der für den Magnetismus verantwortlichen Elektronen muß $n \gtrsim 3$ sein.

Beide Bedingungen zusammen reichen noch lange nicht aus, um Fe, Co, Ni vor allen anderen Stoffen auszuzeichnen; aber Fe, Co, Ni genügen den Bedingungen. Es war ja auch zu erwarten, daß die hier entworfene Theorie einstweilen nur ein qualitatives Schema bieten kann, in das die ferromagnetischen Phänomene später vielleicht eingeordnet werden. Die Theorie bedarf einer Erweiterung für den Fall mehrerer Austauschelektronen pro Atom; ein eingehenderes Studium der $J_{(kl)}$-Werte sowie der Verteilungskurve der Termwerte wird erforderlich sein. Auf diese Fragen wie auf einen eingehenderen Vergleich der Theorie mit den experimentellen Resultaten hoffe ich später eingehen zu können.

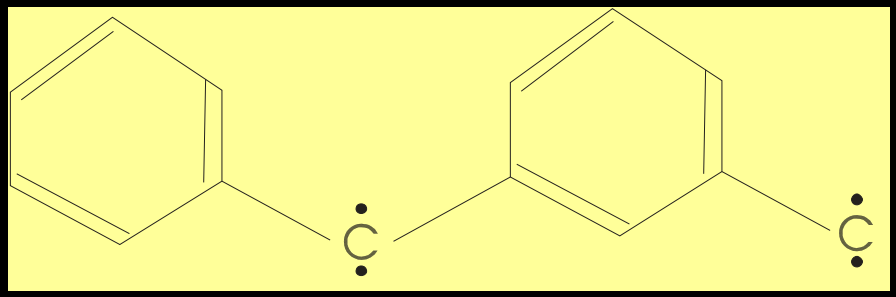
Leipzig, Institut für theoretische Physik der Universität.



Pictures from the film by Lotta Skoglund, Utbildningsradion

1968

- Possible „Ferromagnetic States“ of some Hypothetical Hydrocarbons“, Theoret. Chim. Acta (Berlin) 10, 372-376



Noboru Mataga
Department of Chemistry
Osaka University

„Hydrocarbons with conjugate π-electron systems may show Ferromagnetic spin alignment due to the topology of the Molecular orbitals.”

FM in organic substances with only s- and p-electrons

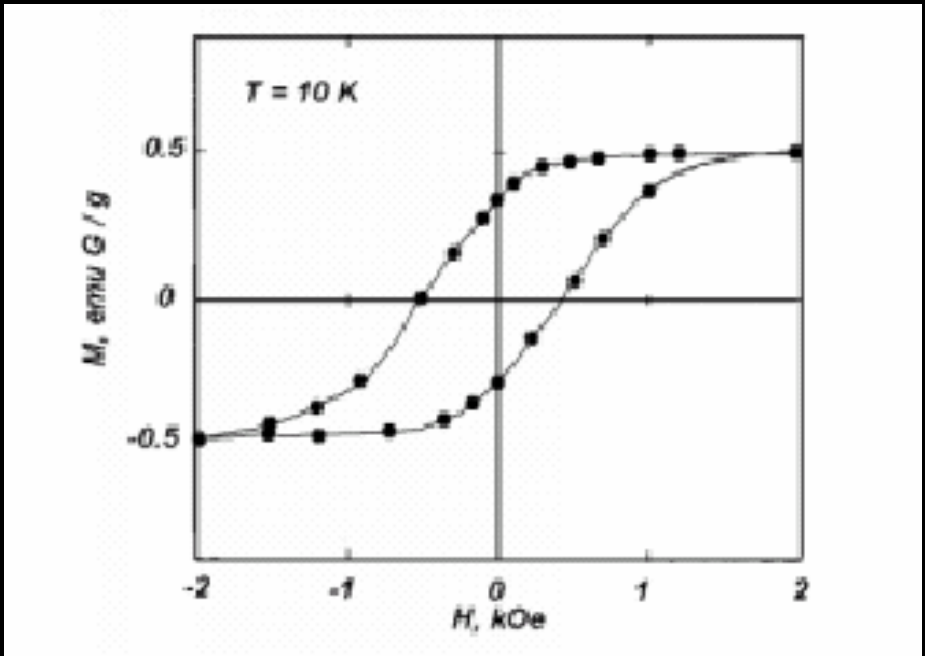
1974-1978

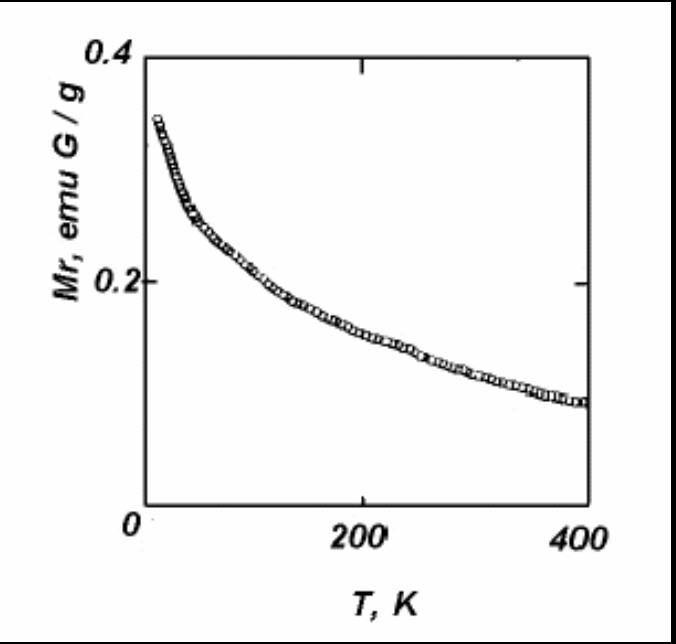
- N. Tyutyulkov and I. Bangov, „Electronic Structure of Some Hypothetical Polymeric Nonclassical Hydrocarbons“, Compt. Rend. Acad. Bulg. Sci. 27 (1974) 1517.

- A. A. Ovchinnikov, „Multiplicity of the Grond State of large Alternant Organic Molecules with Conjugated Bonds“, Theoret. Chim. Acta (Berlin) 47 (1978) 297.

1989. Ferromagnetic pyrolytic Carbon made by CVD using adamantane as starting material:

K. Kawataba et al., Synth. Met. 33, 399





Saturation magnetization M_s = 0.5 emu/g

Remanent magnetization M_r = 0.35 emu/g

Coercive Field H_c = 600 Oe

Curie Temperature T_c > 400 K !

Magnetic impurity concentration < 25 ppm,

if FM then their contribution < 0.003 emu/g

Macroscopic Magnetic Ordering Phenomena in organic materials

(„recognized“ by the community)

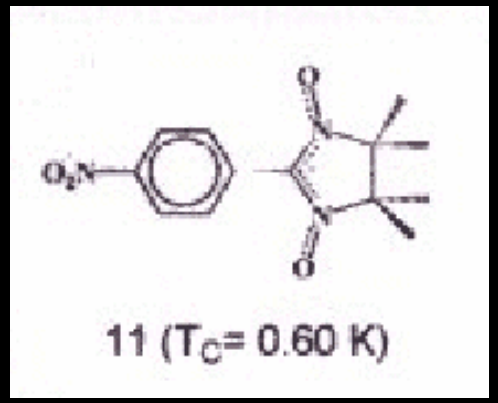
1991: Ferromagnetism at

$T_c = 0.6$ K

in p-NPNN ($C_{13}H_{16}N_3O_4$)

P. Turek et al., Chem. Phys. Lett. 180, 327 (1991)

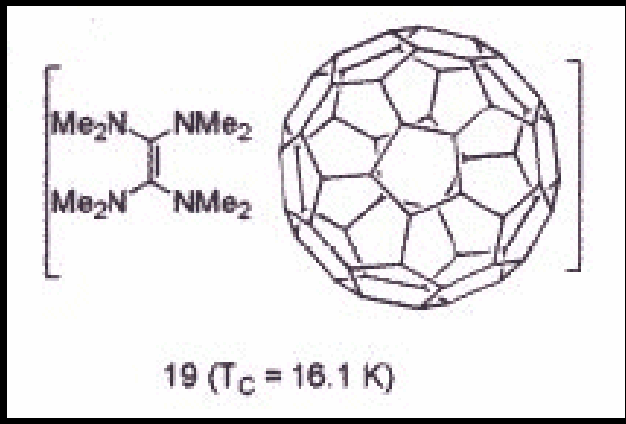
M. Tamura et al., Chem. Phys. Lett. 186, 401 (1991)



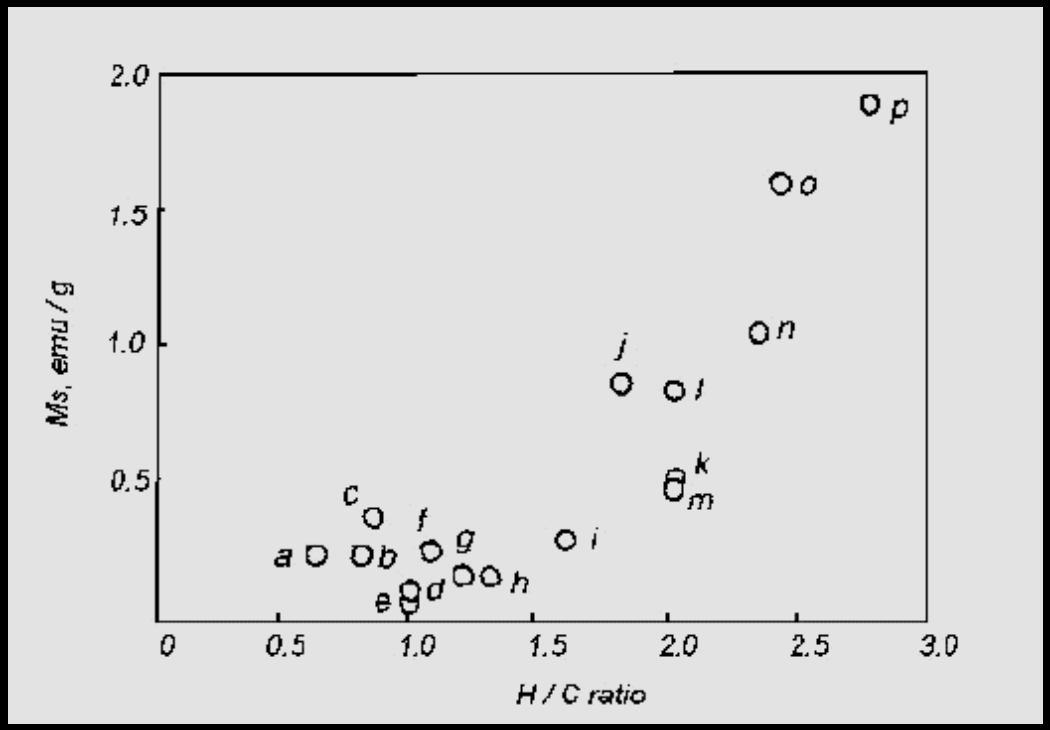
$T_c = 16$ K in $[TDAE]^+C_{60}^-$

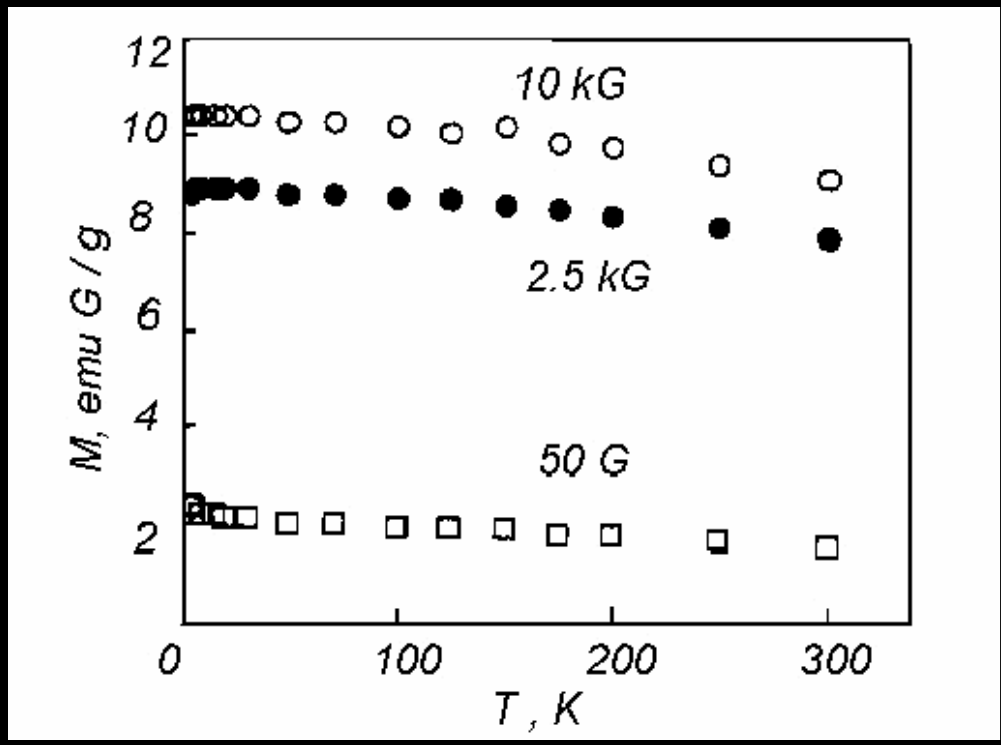
$(C\ N_2(CH_3)_2)_2^+\ C_{60}^-$

P. M. Allemand et al., Science 253, 301 (1991)



1992. Amorphous-like Carbon prepared by hydrogen-rich starting materials





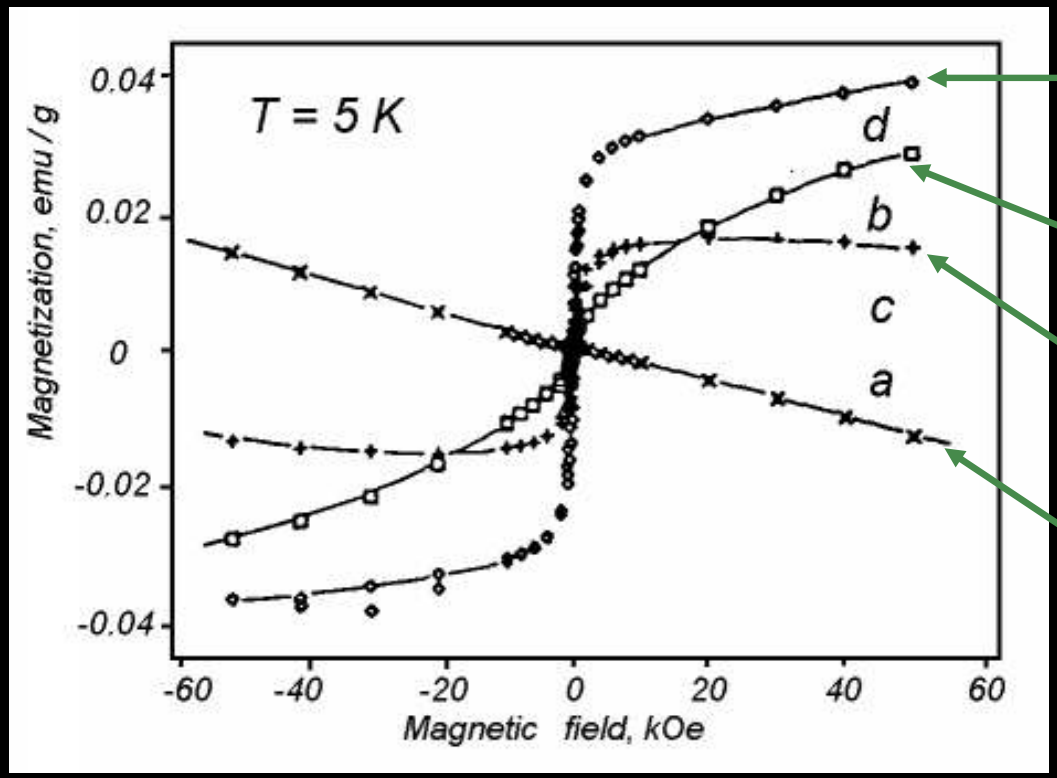
K. Murata et al., J.Chem.Soc.,Chem.Commun.18, 1265 (1991); 7, 567 (1992)

Evidence for a mixture of sp^2 and sp^3 carbon atoms favored by atomic hydrogen.

Ferromagnetism in Fullerene

1996. Ferromagnetism in C60 induced by Photoassisted Oxidation

(Y. Murakami and H. Suematsu, Pure & Appl.Chem. 68, 1463 (1996)



Exposed in air for 3 months

Exposed to light in O for 2.5 hs.

Annealed in vacuum at 400 °C

Pristine C60 crystal

Curie temperature T_c ~ 800 K !

Renaissance of magnetic carbon since 2000 – new magnetic carbon phases

Kopelevich, Esquinazi,et al., JLTP 119 (2000) 691	Ferromagn. in HOPG , $T_C > 500$ K
Makarova,..Esqu.,et al. Nature 413 (2001) 716:	Ferromagn. 2d C_{60}-polymer, $T_C = 500$ K
Esquinazi et al. PRB 66 (2002) 24429:	Ferromagn. in HOPG , $T_C > 500$ K
Coey et al,. Nature 420 (2002) 156:	Ferromagn. in Graphite, $T_C > 400$ K
Esquinazi et al. PRL 22 (2003) 227201:	H^+-impl. into HOPG , M increases
Kopelevich et al. PRB 22 (2003) 92408:	Microporous carbon, local ferromagnet.
Kusakabe et al. PRB 67 (2003) 92406:	Hydrogenated nanographite (LSDA)
Park et al. PRL 91 (2003) 237204:	Curved carbon nanostruct. (LSDA)
Andriotis et al. PRL 90 (2003) 26801:	C_{60}-polymer, vac.+sp^2/sp^3 (TB-MD)
Rode et al. PRB 70 (2004)	C-nanofoam , paramagnetism M =0.4 emu/g @ 1.8 K

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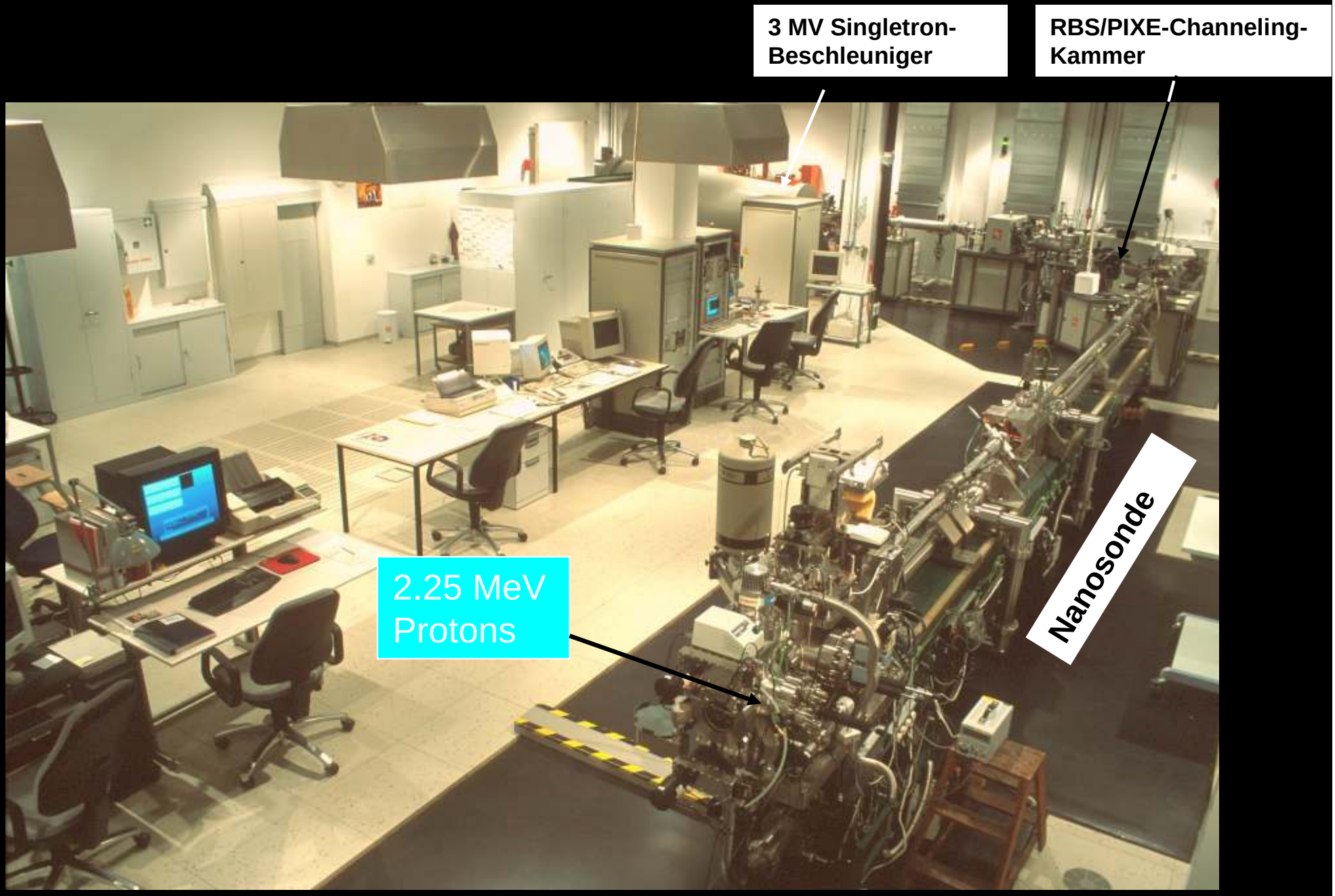
2003-2005

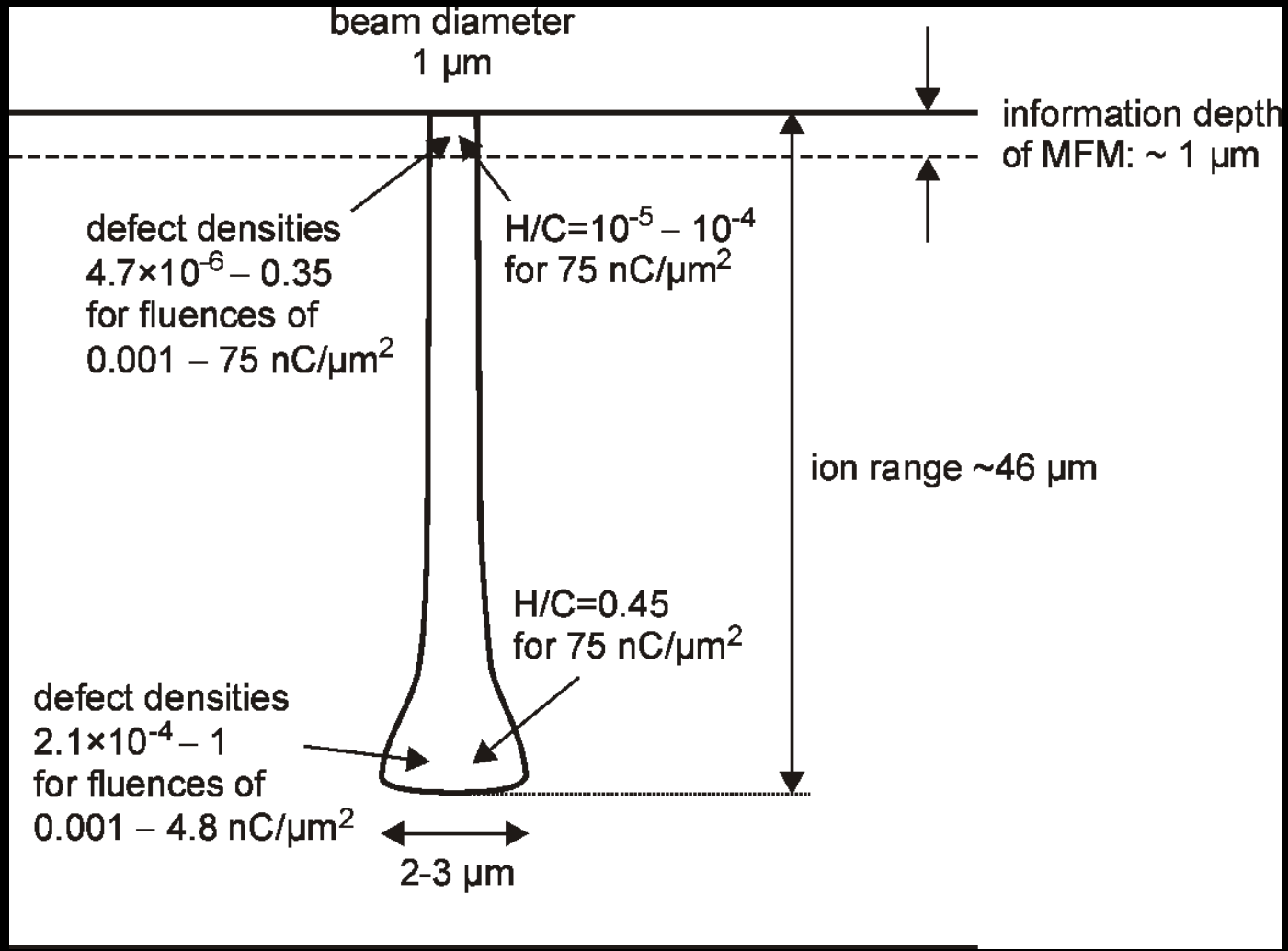
An example of the
Present Research

„Proton Irradiation on
carbon structures:
inducing magnetism and measuring
the magnetic impurities“

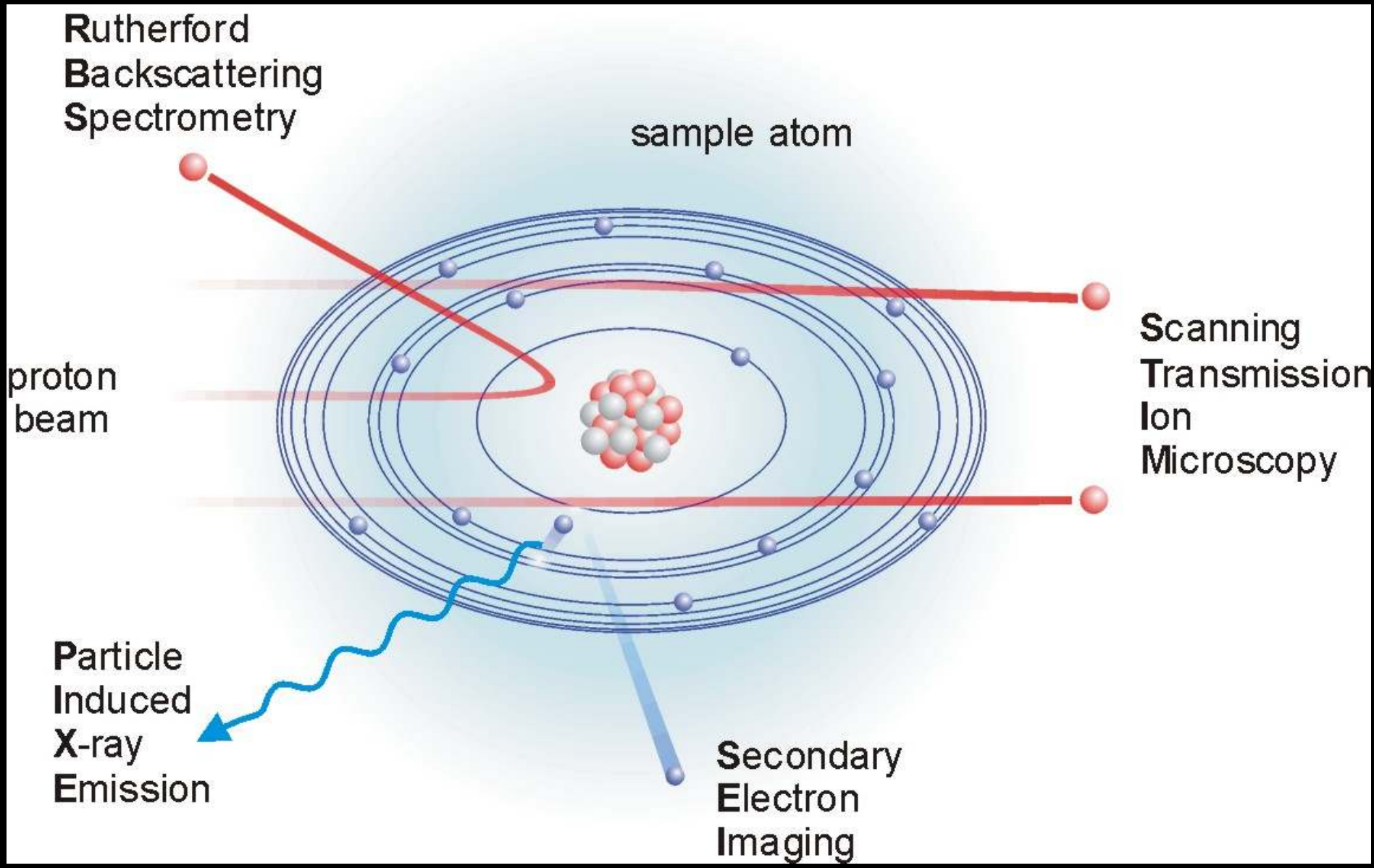
Ionenstrahllabor LIPSION



SRIM2003 Monte Carlo Simulation for 2.25 MeV protons

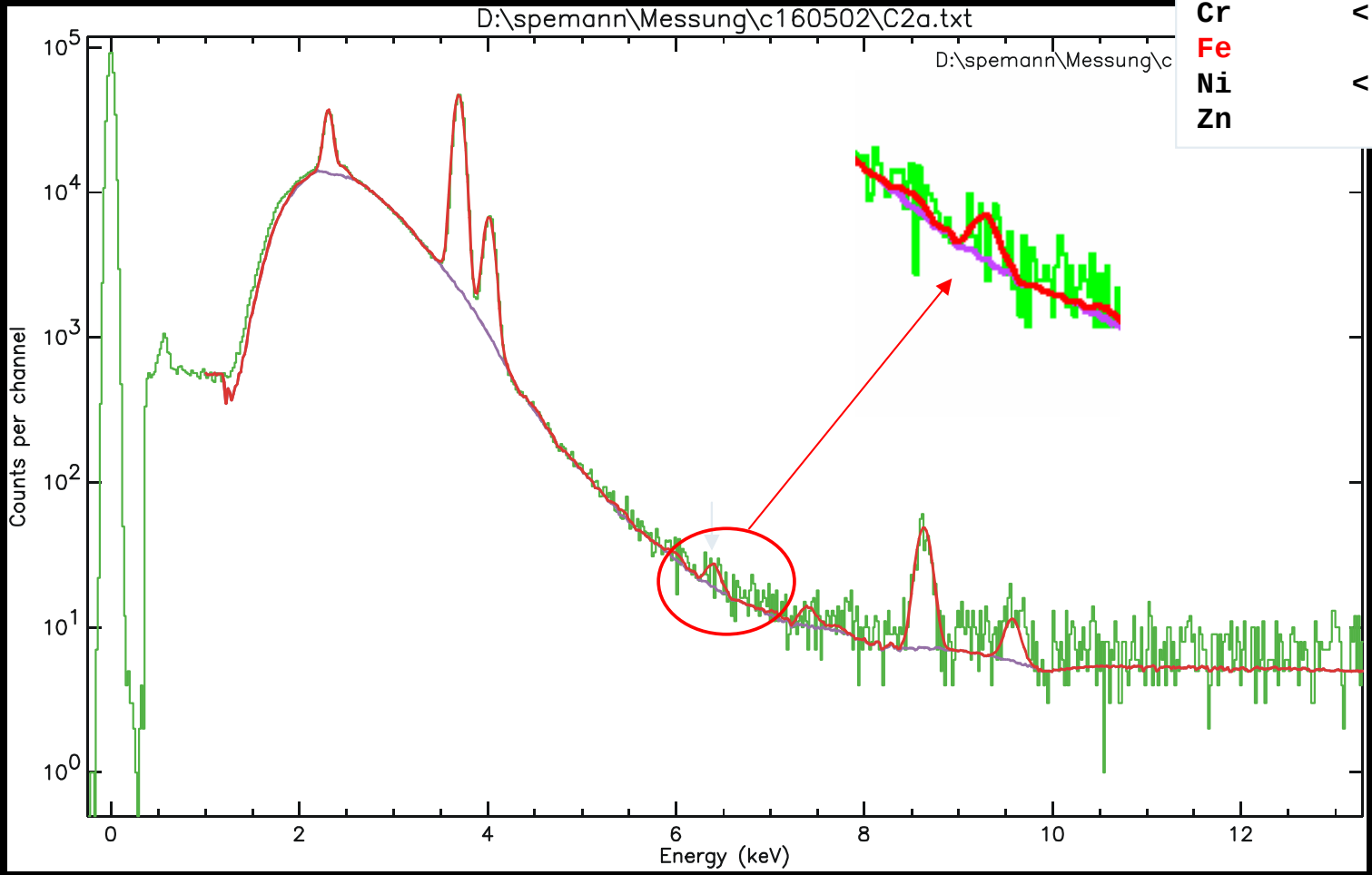


Analytical Methods



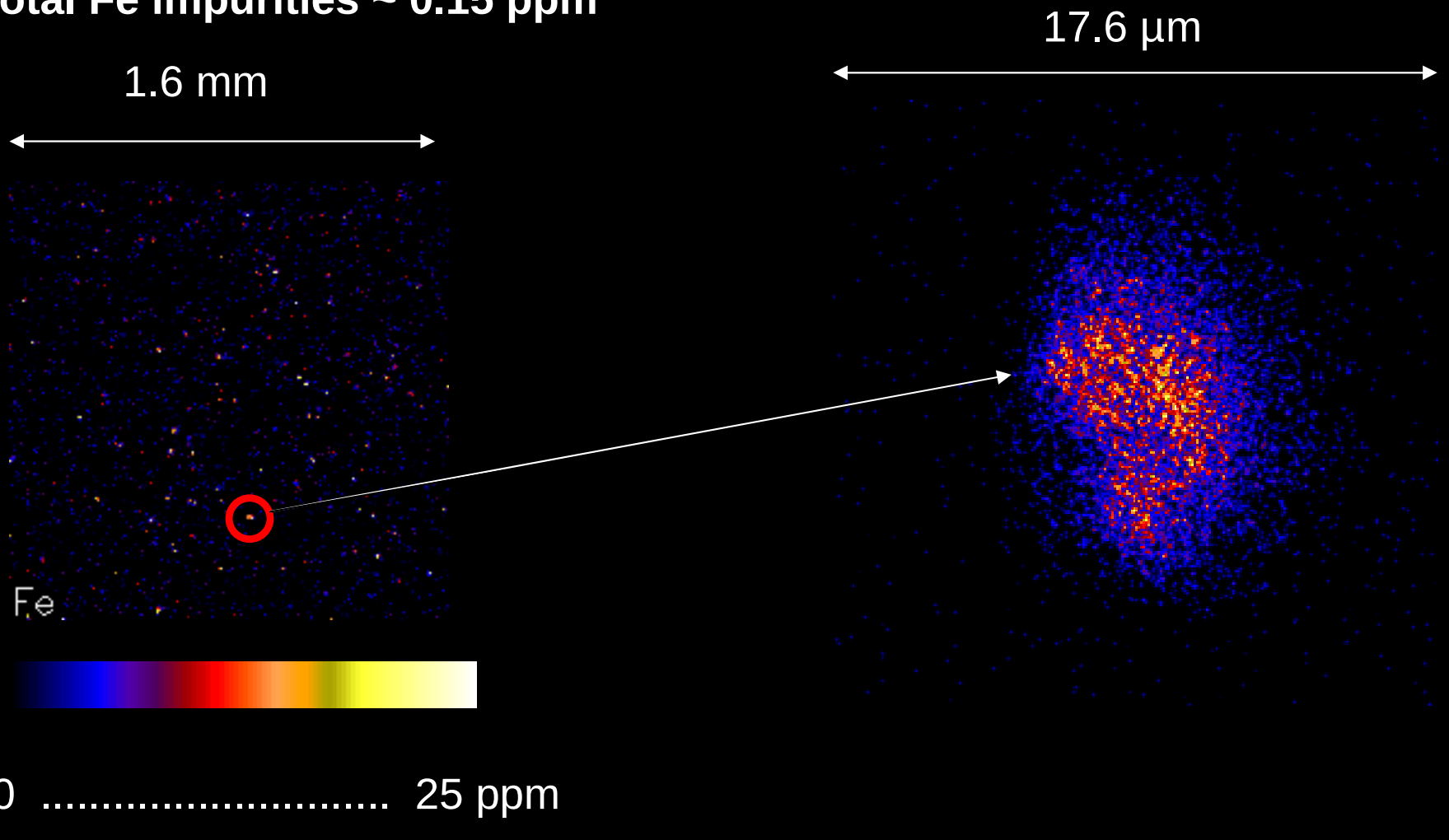
Graphite sample

Concentration. (µg/g)		MDL
S	292	1,8
Ca	434	0,56
Ti	< 0,31	0,31
Cr	< 0,21	0,21
Fe	0,4	0,19
Ni	< 0,39	0,39
Zn	6,1	0,59



PIXE measurements HOPG sample, Fe concentration

Total Fe impurities ~ 0.15 ppm



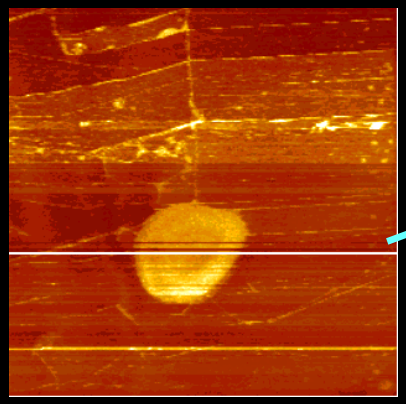
Induced Ferromagnetism by Proton Irradiation in Graphite

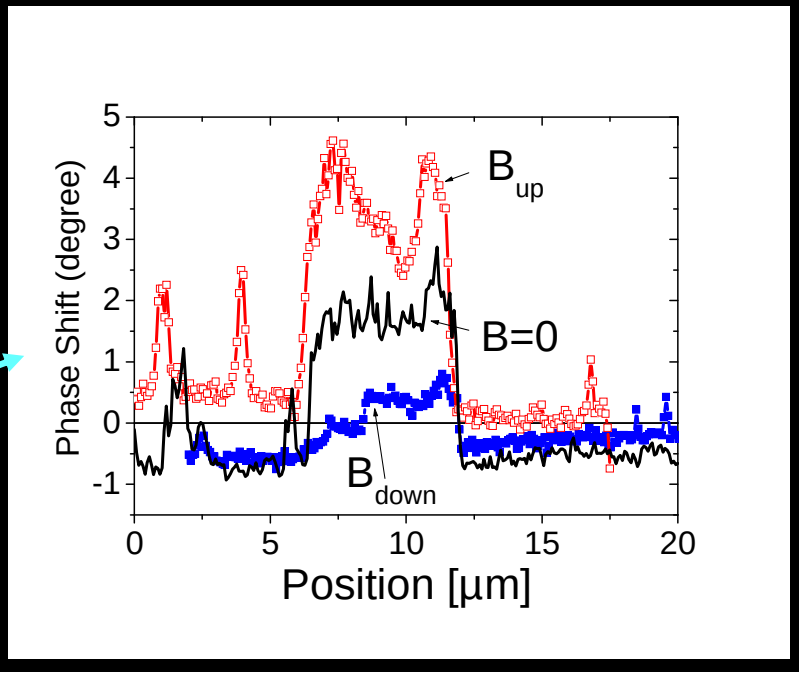
K.-H. Han et al., Adv. Mat. 15, 1719 (03)

Dose: 12.6 nC/μm²

Spot →

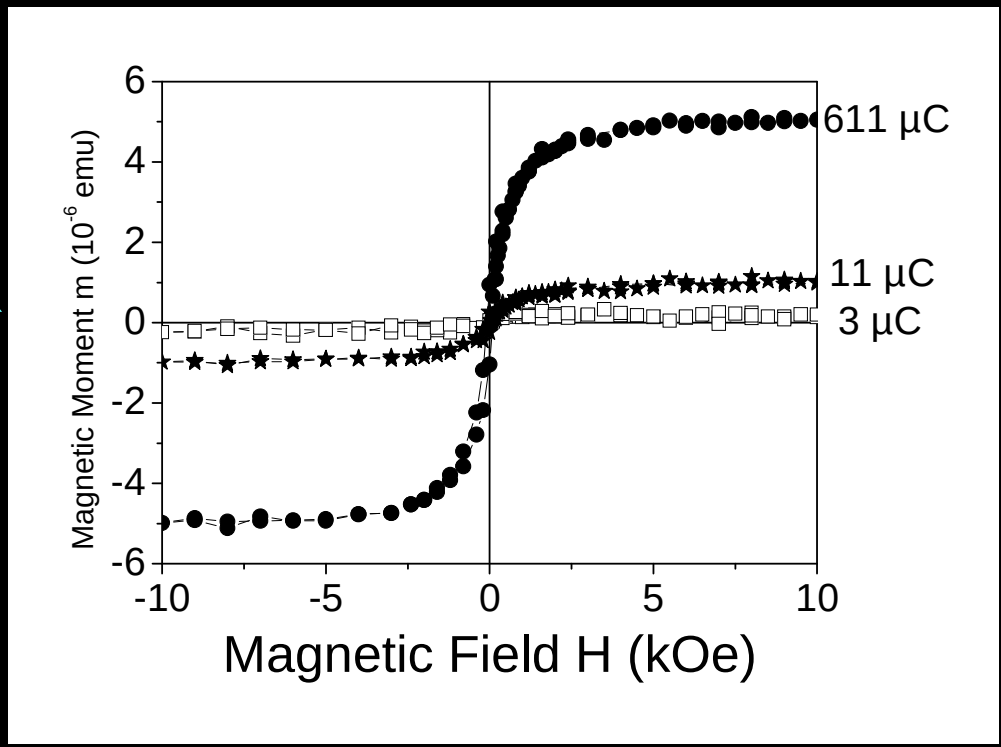
MFM →





Large area irradiation

SQUID →

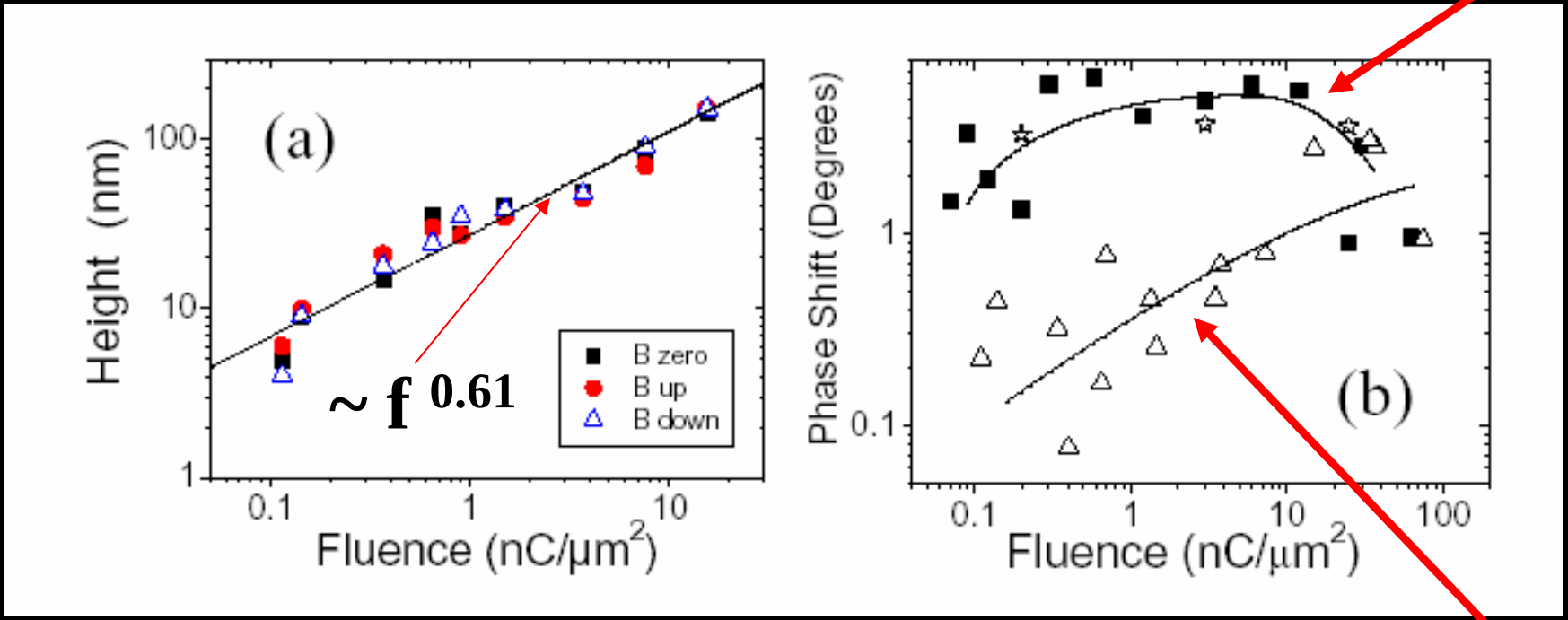


P. Esquinazi et al., Phys. Rev. Lett. 91, 227201(2003)

Maximum Phase Shift as a function of irradiation fluence in HOPG

AFM

Current I = 0.17 nA



MFM

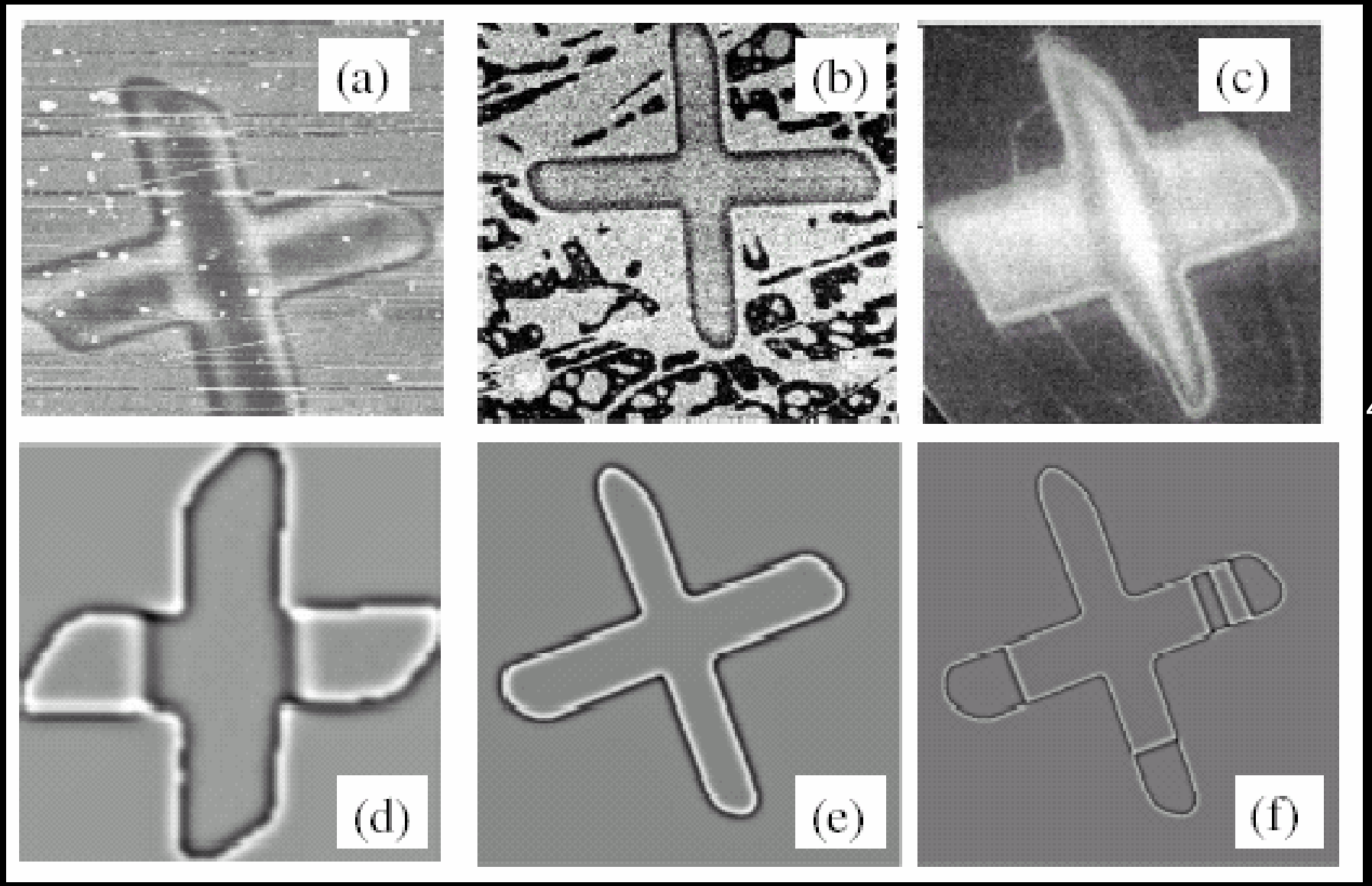
Current I = 0.86 nA

Maximum swelling height

Magnetic crosses on *graphite* surfaces and their numerical simulations of Magnetic Force Microscopy

20 μm

Flying „Paloma“

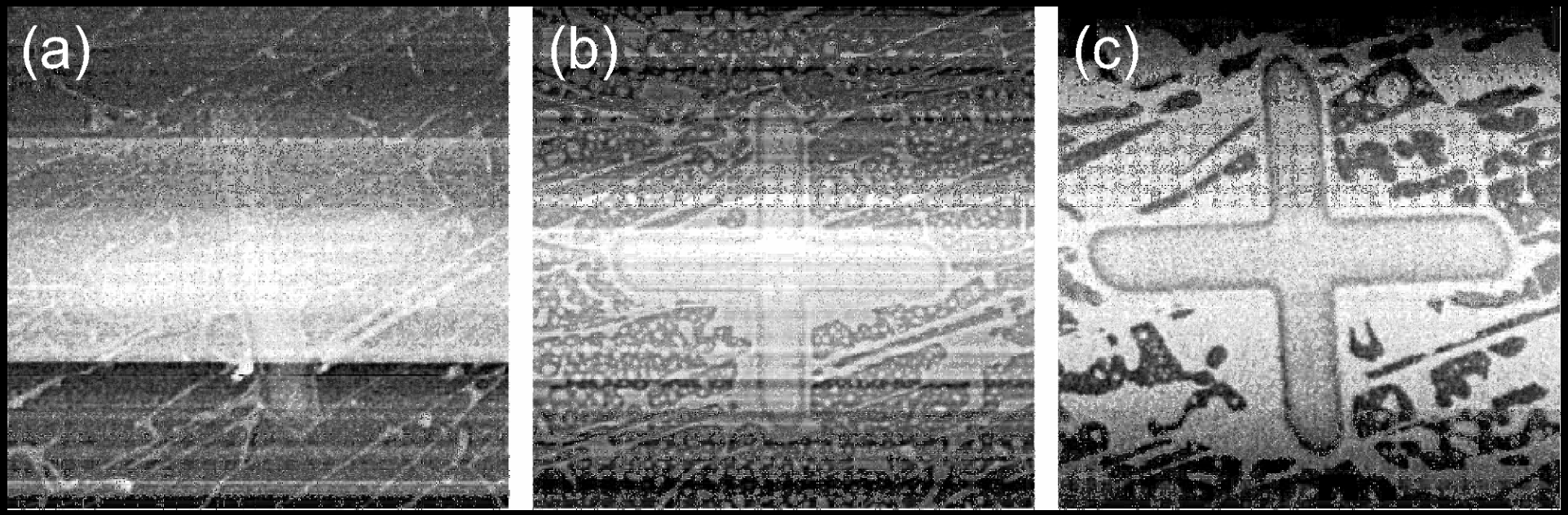


40 μm

Time dependent signals suggest the importance of hydrogen diffusion

1 day after

34 days after

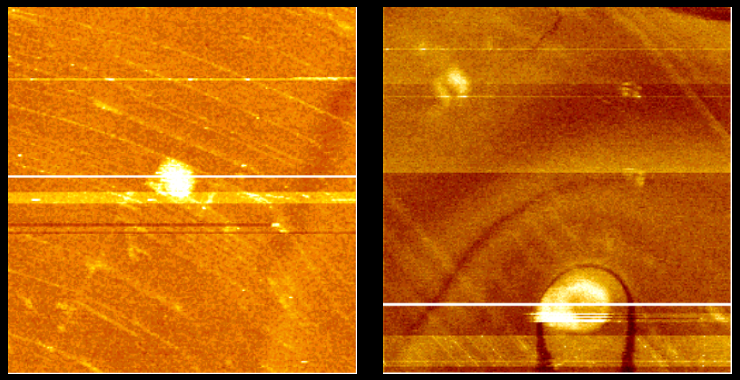


8 days after

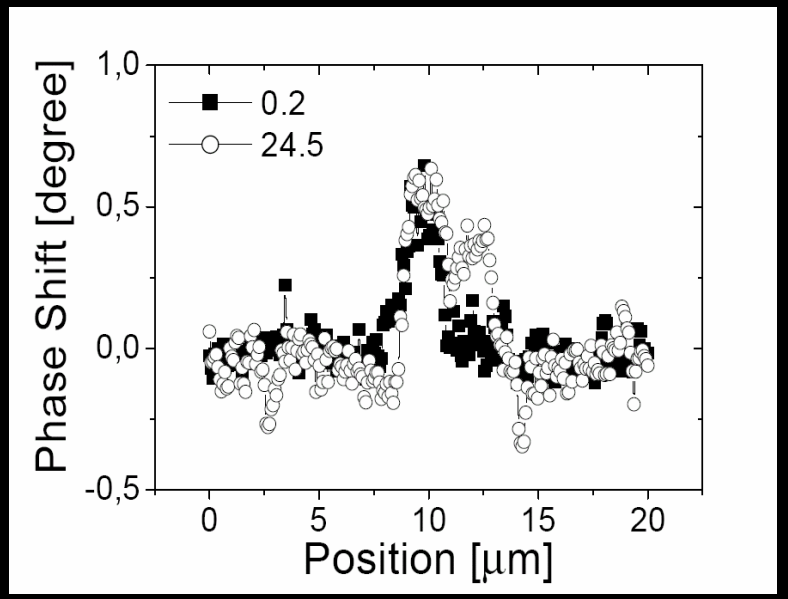
Thermal Aging Effects at the irradiated surface of HOPG

One day after irradiation

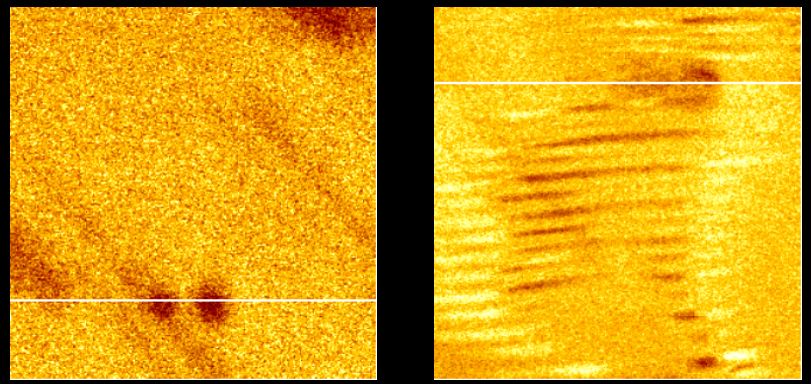
MFM

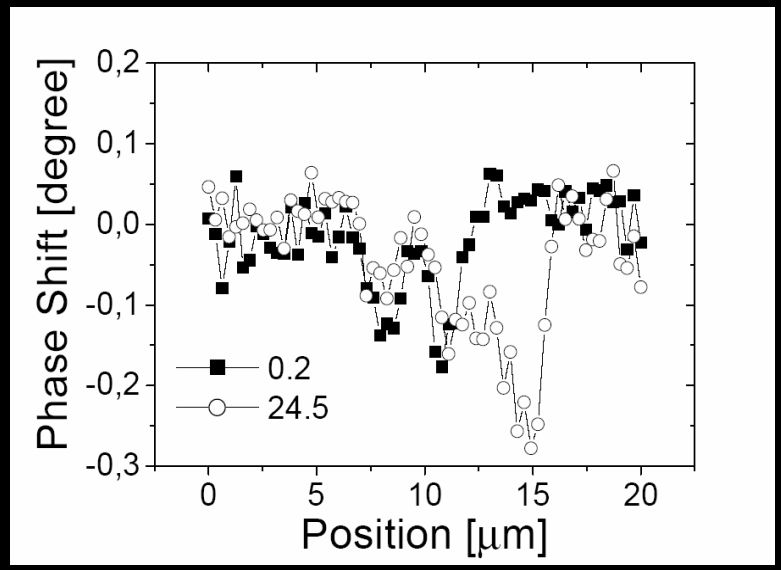


0.2 nC/µm² **24.5 nC/µm²**

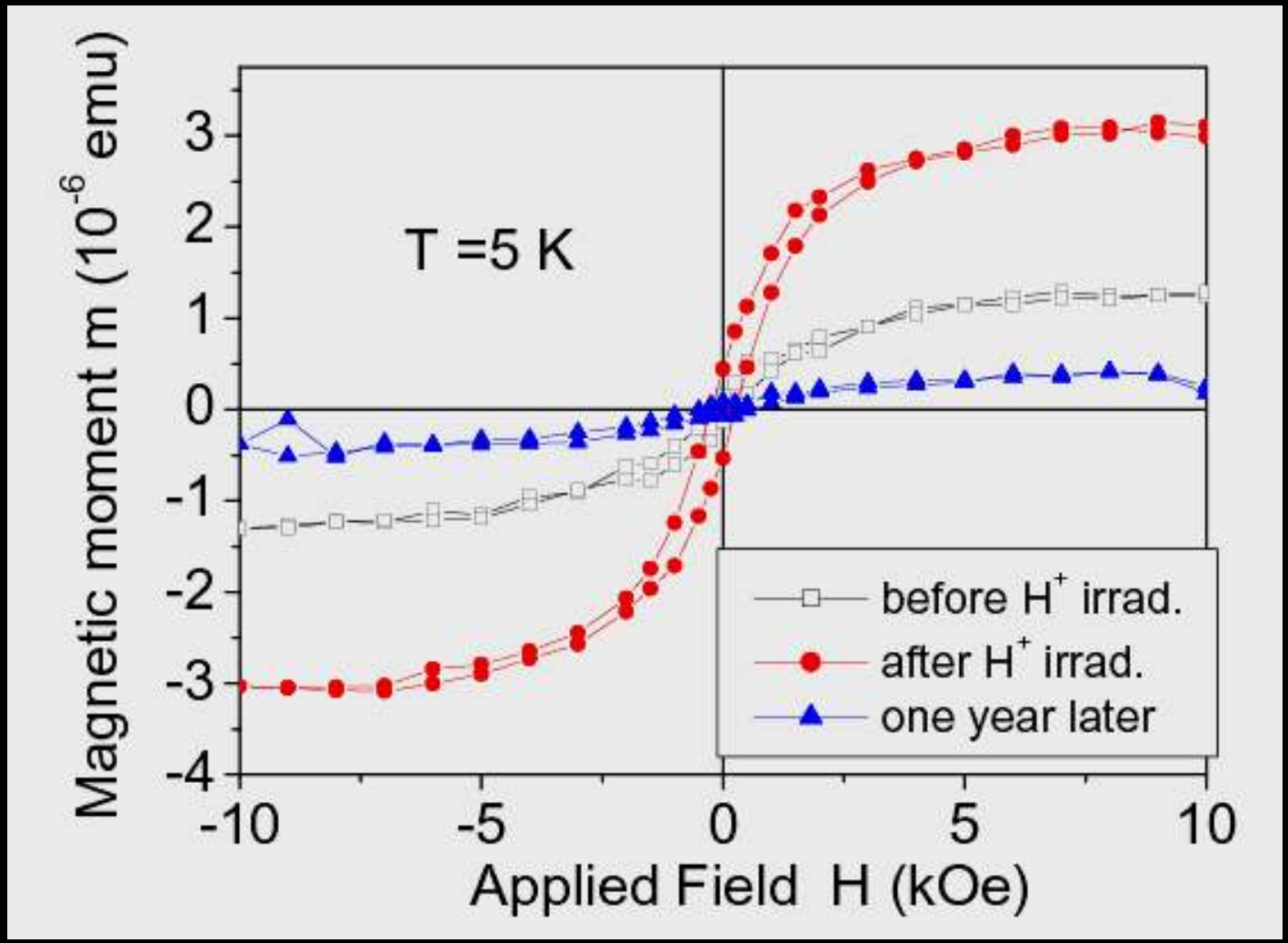


8 months after irradiation





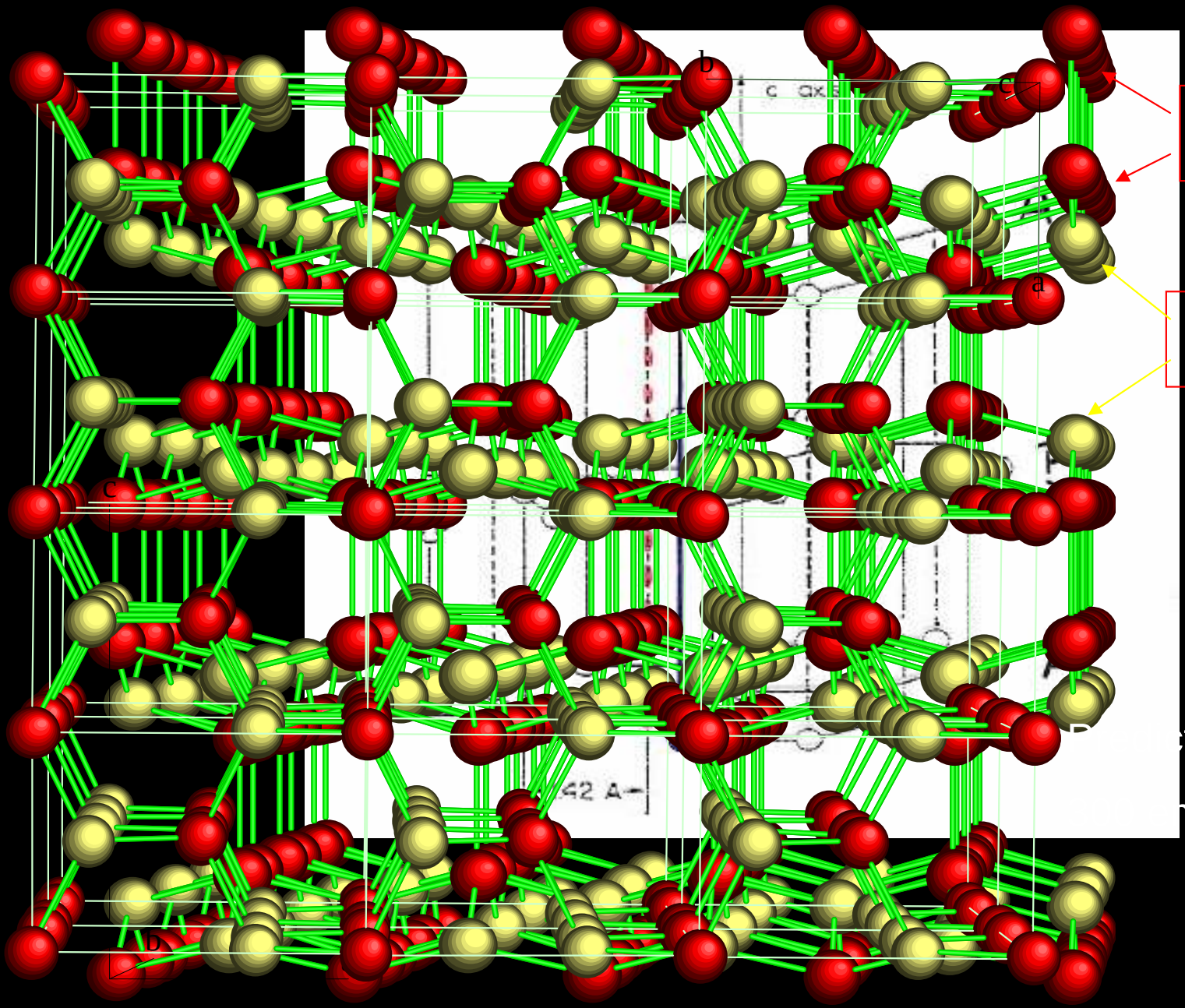
Thermal aging effects in irradiated carbon films



Models

- One of the first studies on the influence of topological defects on the electronic structure of graphene of this century: **González, Guinea, Vozmediano**, 2001. Electron-electron interactions in graphene sheets. Phys. Rev. B 63, 134421.
- Several more ...

From diamagnetic graphite to a ferromagnetic diamond-graphite ferromagnet



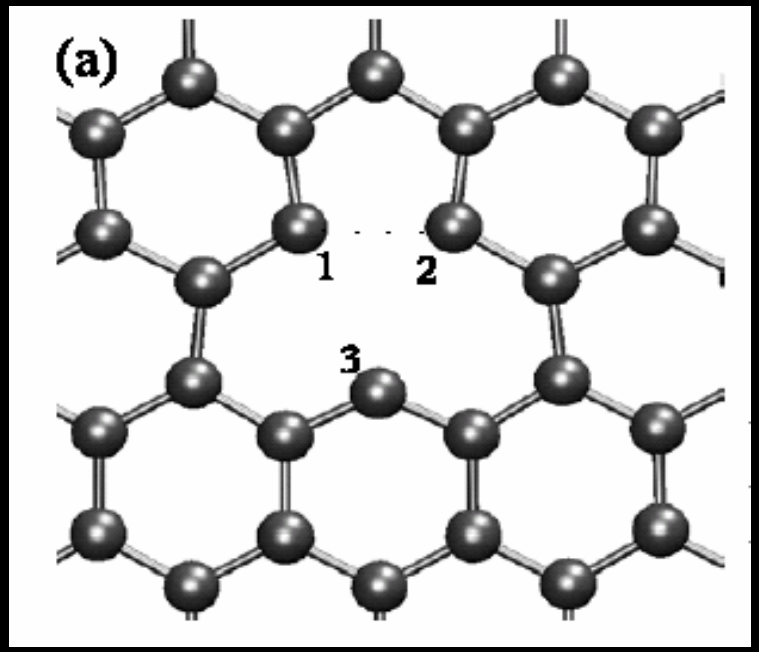
sp^3 C-atom

sp^2 C-atom

ted Magnetization:

mu/g !!!

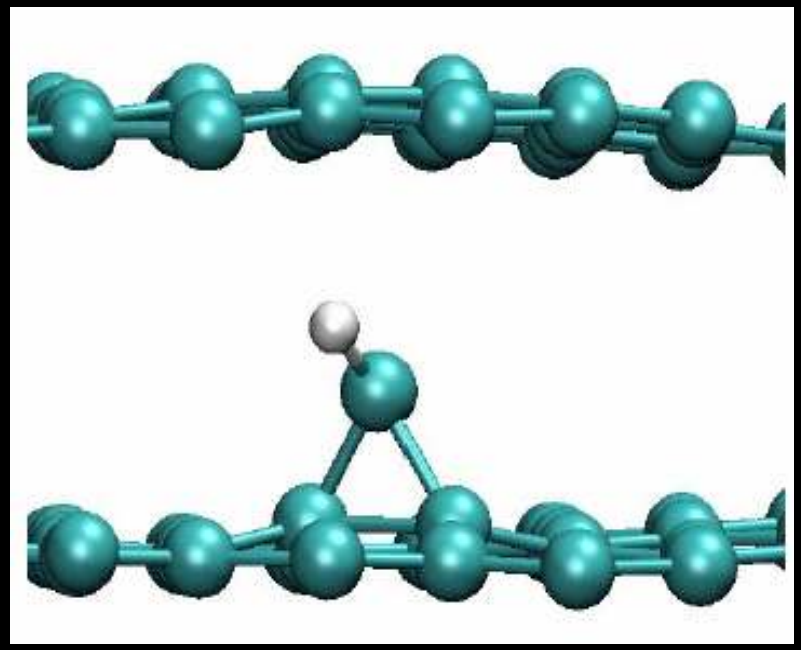
A.A. Ovchinnikov and I.L. Shamovsky, J. Molecular Structure 251, 133 (1991)



Ma et al., NJP 6, 68 (2004)

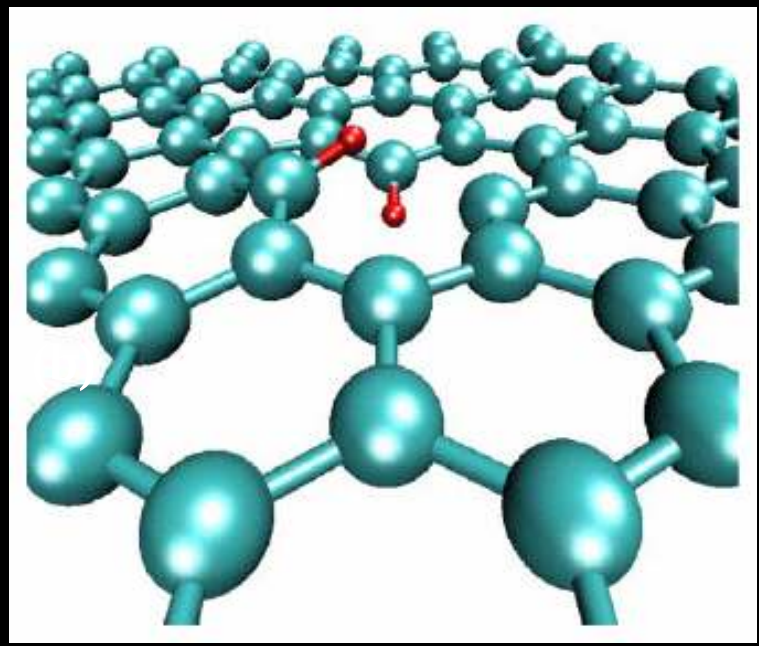
= 1.04 μ_B

Lehtinen et al., PRL 93, 187202 (2004)



1.2 μ_B

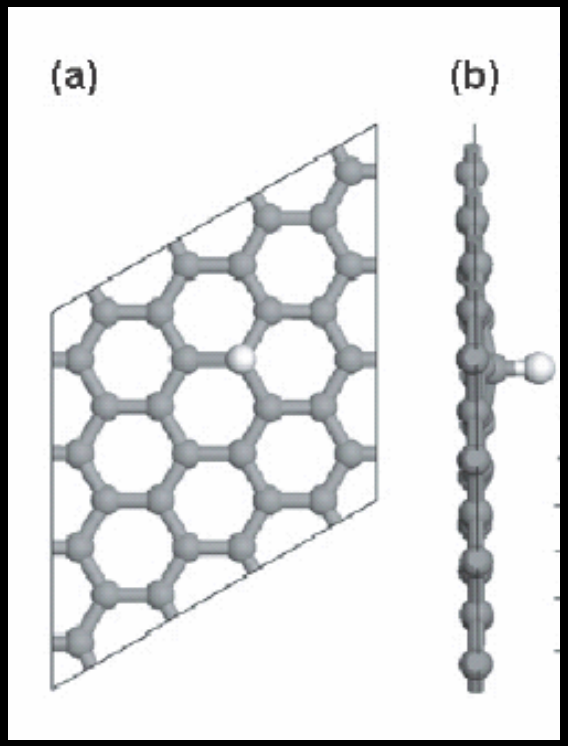
0.9 μ_B



Hallmark of Perfect Graphene

E. J. Duplock, M. Scheffler, and P. J. D. Lindan

PHYS. REV. LETT. **92**, 225502 (2004)



Adsorption of atomic hydrogen on graphene opens a substantial gap in the electronic density of states in which lies a spin-polarized gap state.

Hydrogen atom causes long-range effects in graphite

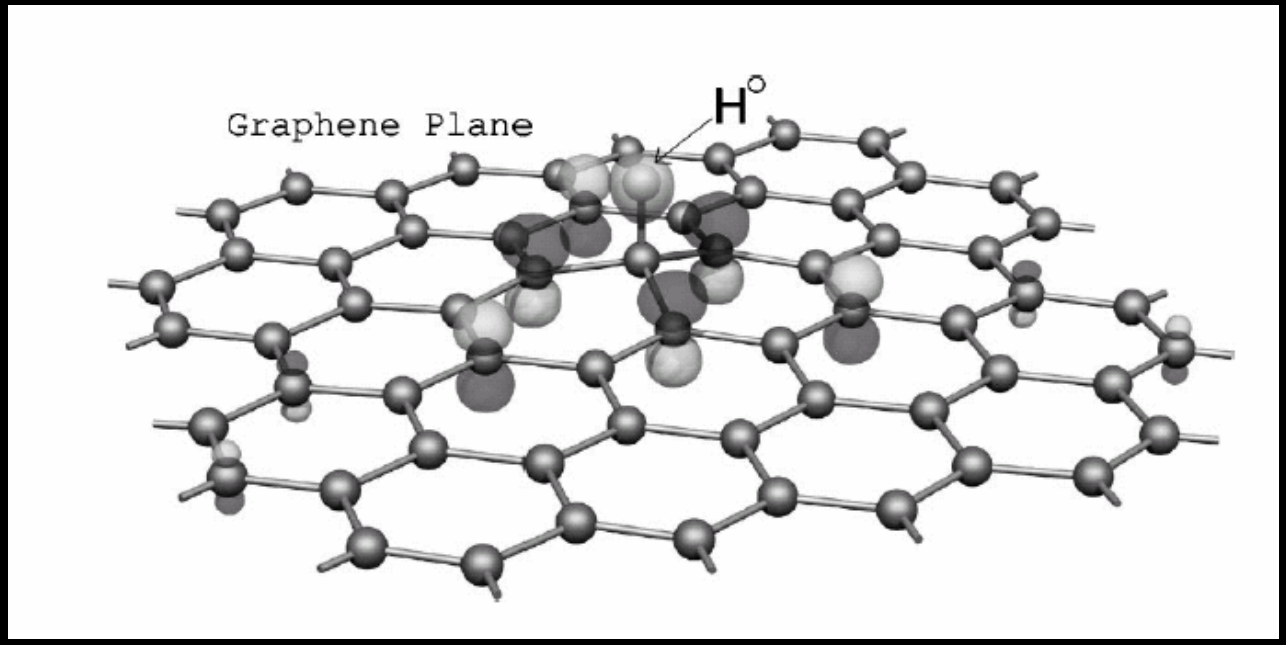
PHYSICAL REVIEW B **66**, 155107 (2002)

Evidence for local moment formation around a positive muon in graphite

J. A. Chakhalian, R. F. Kiefl, S. R. Dunsiger, W. A. MacFarlane, and R. Miller
Department of Physics and Astronomy, UBC, Vancouver, British Columbia, Canada V6T 1Z1

These results indicate that a local moment forms around the muon due to the low carrier density.

3). These observations establish that the local electronic structure around the muon has a much different magnetic response than the conduction electrons of graphite. In par-



S.F.J. Cox *et al.*, J. Phys.: Condens. Matter **13**, 2169 (2001).

PHYSICAL REVIEW B **67**, 092406 (2003)

Magnetic nanographite

Koichi Kusakabe* and Masanori Maruyama†
Graduate School of Science and Technology, Niigata University, Ikarashi, Niigata 950-2181, Japan
Received 2 October 2002; revised manuscript received 11 December 2002; published 28 March 2003

Hydrogenated nanographite can display spontaneous magnetism

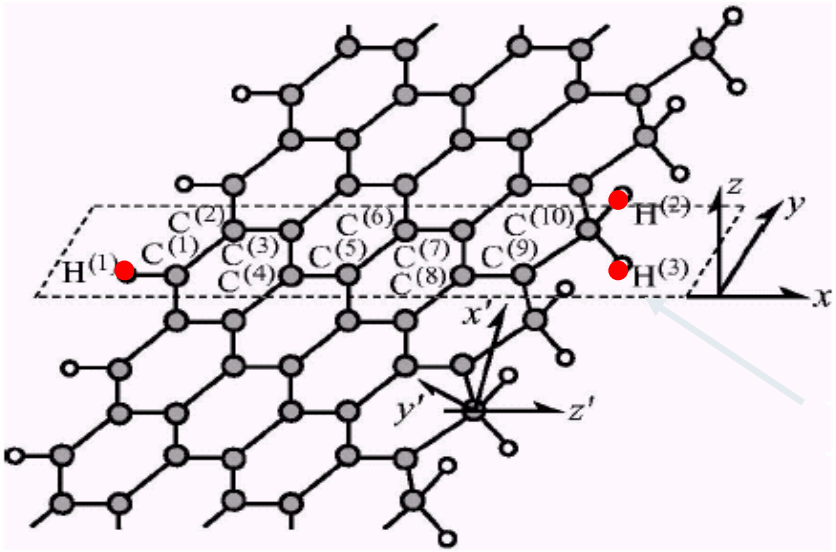
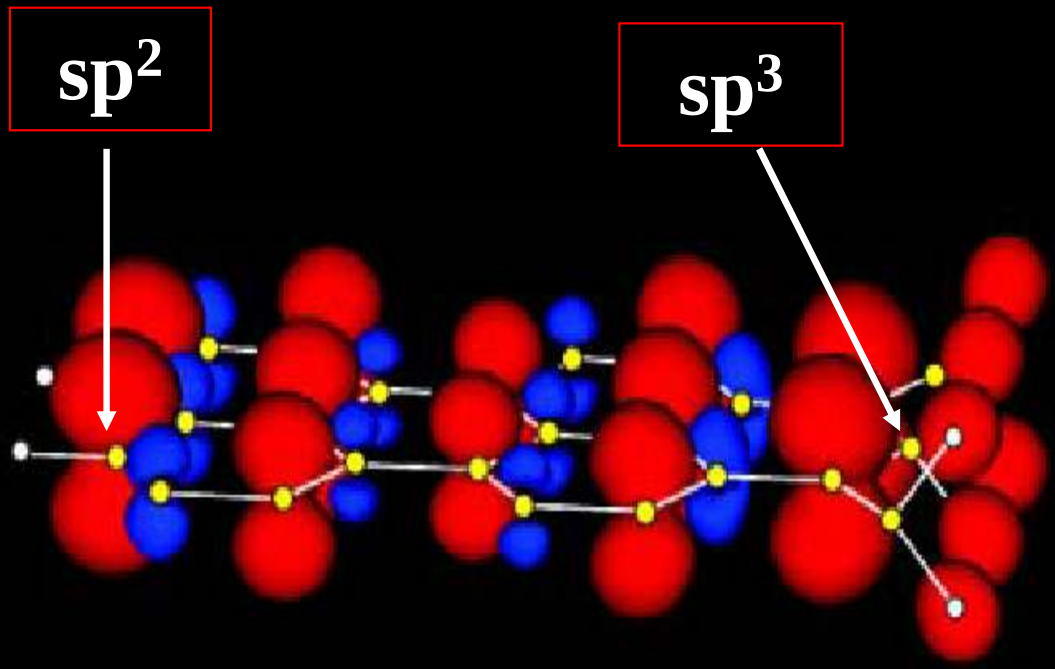


FIG. 1. A structural model of a magnetic graphene ribbon. Dark circles represent carbon atoms and open circles denote hydrogen atoms. Dashed lines represent a section of a unit cell in the x-y plane. The unit cell contains $2n$ carbon atoms and three hydrogen



Summary

Room temperature Ferromagnetism in metal-free Carbon-based structures appears to be a reality

- carbon films made from hydrocarbon targets
- highly oriented pyrolytic graphite (HOPG)
- light- and electron-polymerised C60 bulk and films under oxygen (/ H ?)
- through proton irradiation on HOPG,
Fullerene,
amorphous films,
carbon nanowalls, ...

- pressure-polymerised C60 (no clear evidence for bulk FM)

- **Ferromagnetic contribution due to impurities may still be a problem, but one should remain realistic**

Possible origins of this “new” magnetic order in solids

- Nucleation of local moments at lattice defects
- “Ordered disorder” (e.g., sp2-sp3 mixtures)
- Role of light atoms (like Hydrogen)
- Enhancement of the e-e interaction due to low density of electrons
- etc.

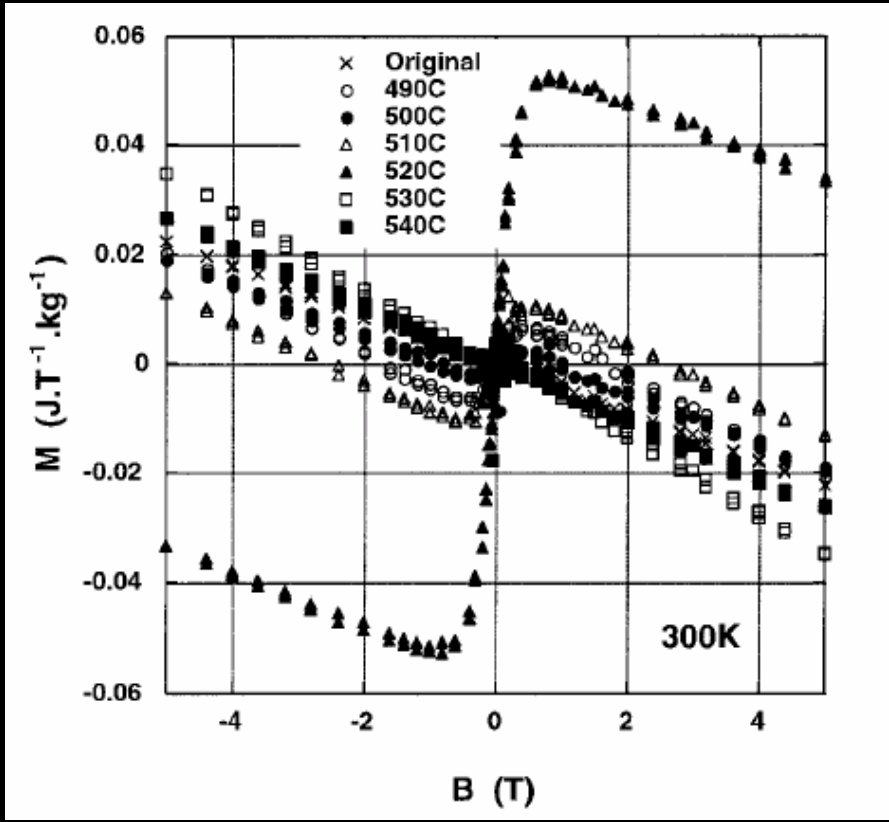
Future

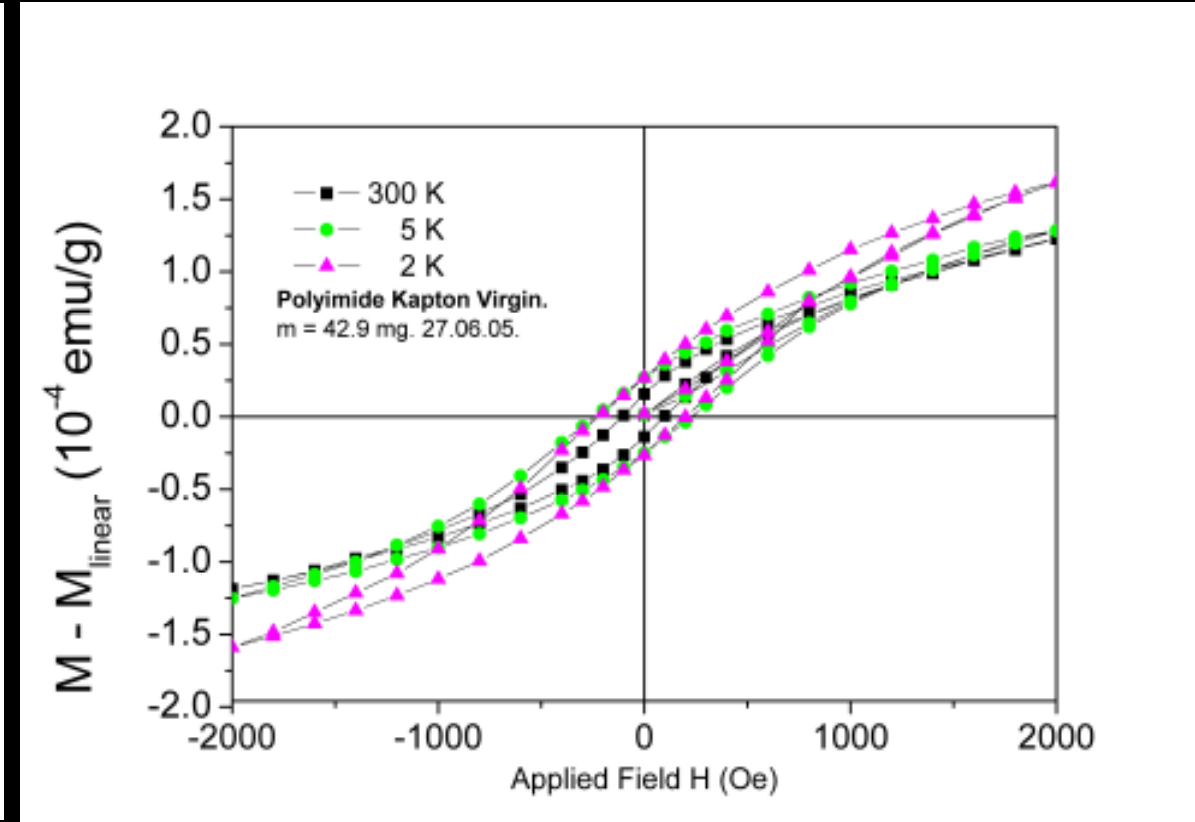
- XRD on carbon structures
- Magnetism in Polymers
- Defects in C-H molecular systems
- Magnetism in metal-free Carbon Nanotubes
- Influence of defects in dielectric oxides (e.g. Ti_xO_y, Al_2O_3, CaO, ZnO, ...)

Magnetic order in a Polyimide (C-H-O-N)

Virgin Polyimide Sample

Magnetic impurities < 1 ppm





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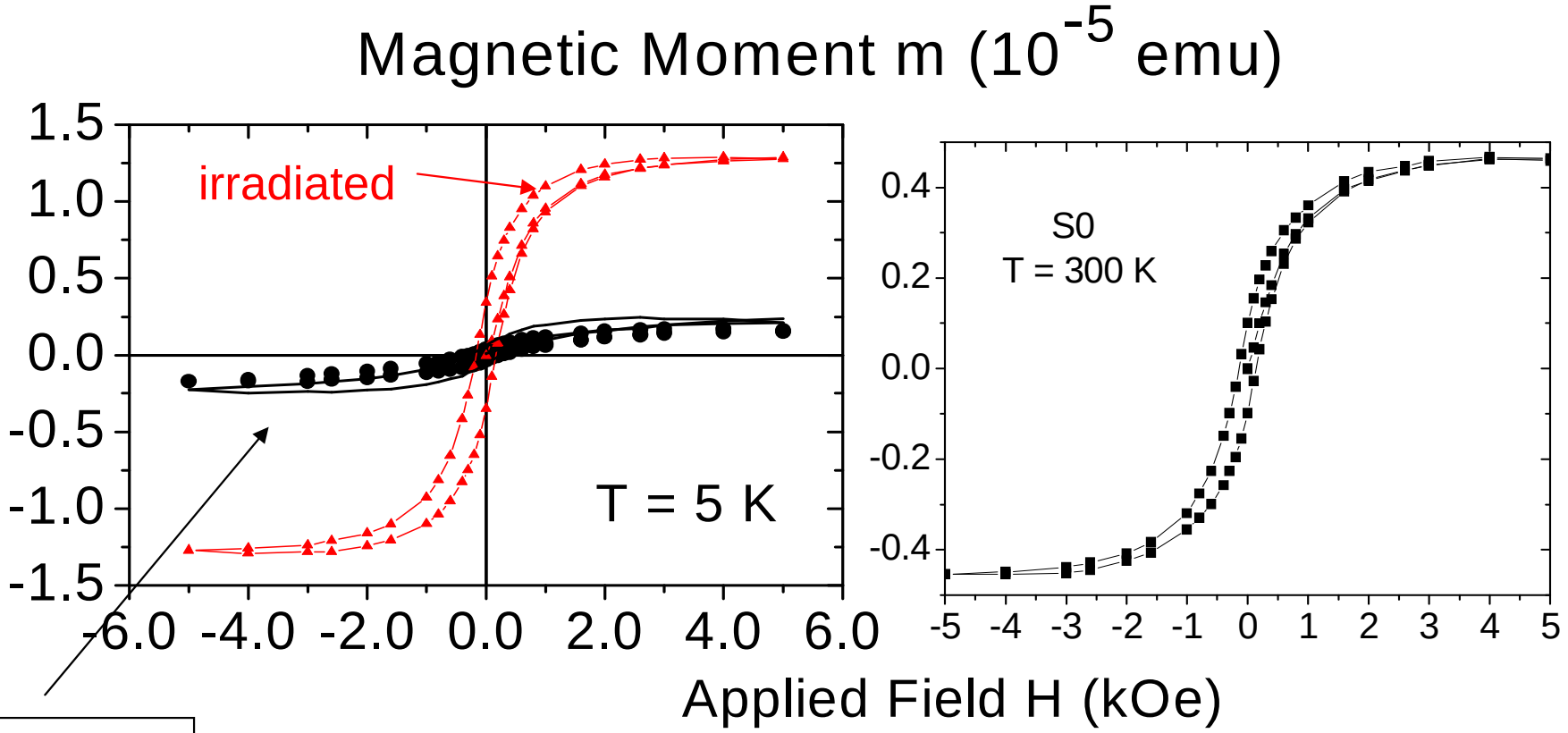
Magnetic ordering in "c"-saphire
Irradiation effects



as received