Core-Shell 3d-MgO Nanospheres

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Outline

- Why have we chosen the Fe(Co)/MgO epitaxial system?
- NPs structural characterization: X-ray and TEM
- Magnetic characterization: SQUID, Mössbauer and XMCD
- Catalysis Expectations
- Spintronics: Nanoparticles tunneling devices
- Biomedicine:
  - Toxicology
  - Hyperthermia
  - MRI

Why the Fe/MgO epitaxial system?

- History
- Economy
- Ecology
- Ferromagnetism & Biocompatibility
- Facility and beauty

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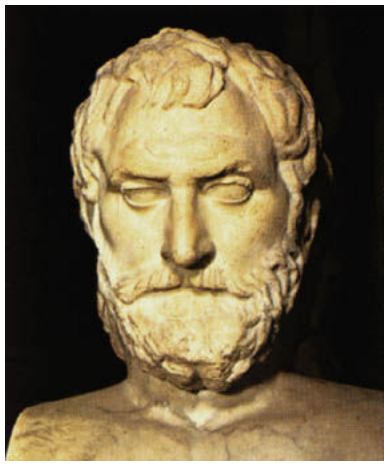
http://en.wikipedia.org/wiki

The MgO and the magnetism were related from the beginning

Fe-Mg-oxides



Thales, S. VI B.C.

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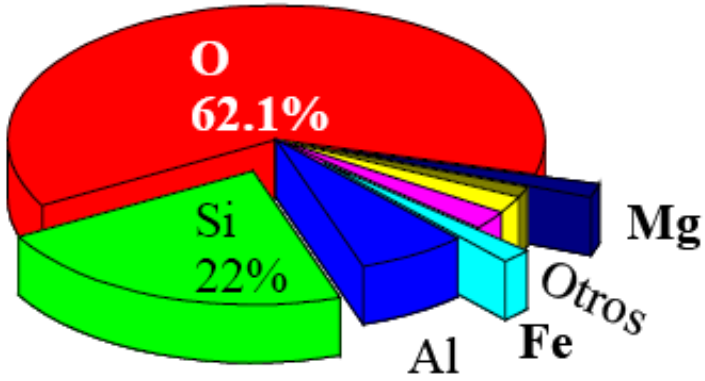
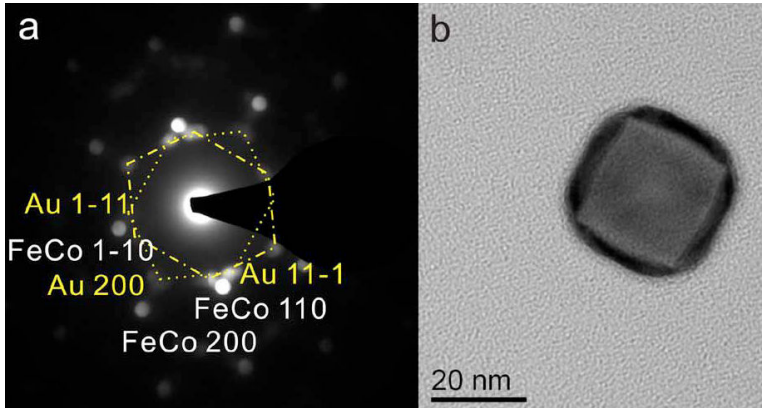


Magnesium is the 9th most abundant element in the universe by mass. It constitutes about 2 wt.% of the ***Earth's crust***, and it is the 3rd most abundant element dissolved in ***seawater***.

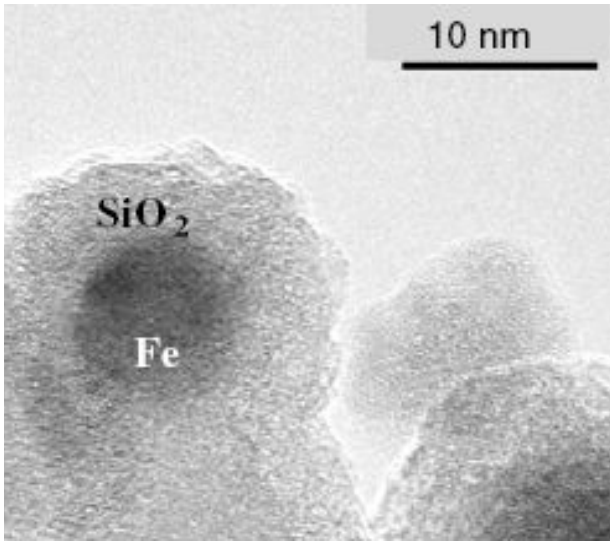
MgO has anti-microbial/fungicide properties due to its basicity (similar to Ag^{2+}) and is the 11th most abundant element by mass in the human body. Gram-/Gram+ **Stoimenov et al. J. Am. Chem. Soc. (2007)**

Fe is the best-known magnetic material. circa 4 g Fe as ***proteins*** within the human body. Co –as well-

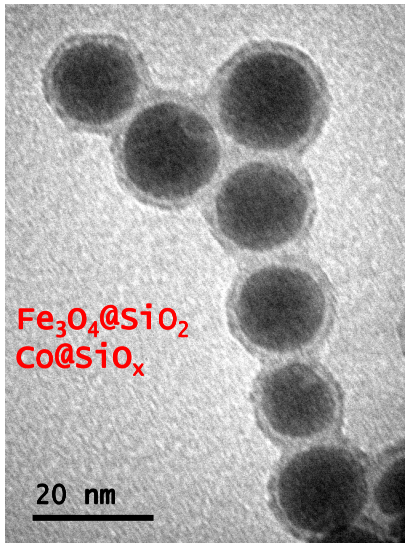
References… complex, expensive and little flexible



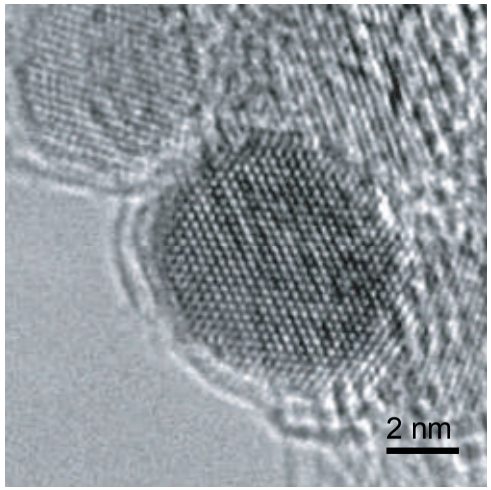
Xu et al. Appl. Phys. Lett. (2007)
superparamagnetic



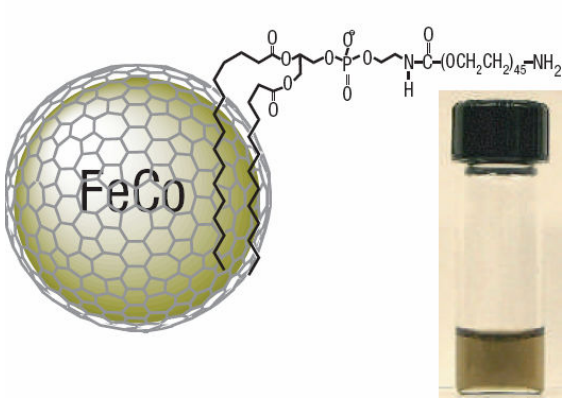
Fernández-Pacheco et al.
Nanotech. (2006)



Salgueiriño-Maceira et al.
Adv. Func. Mater (2005)



Seo et al. Nature Mater. (2006)
superparamagnetic



phospholipid-poly(ethylene glycol)

Au is expensive. In addition to SiOx, etc. unlike Fe, Mg, Co …they are not already present in the body in significant quantities

Soppimath et al. Adv. Mater. 17 (2005) 318 'Thermally Responsive Core-shell NPs for Targeted Drug Delivery'
Jiang et al. Nature Nanotech. 3 (2008) 145 'Nanoparticle-mediated cellular response is size-dependent'

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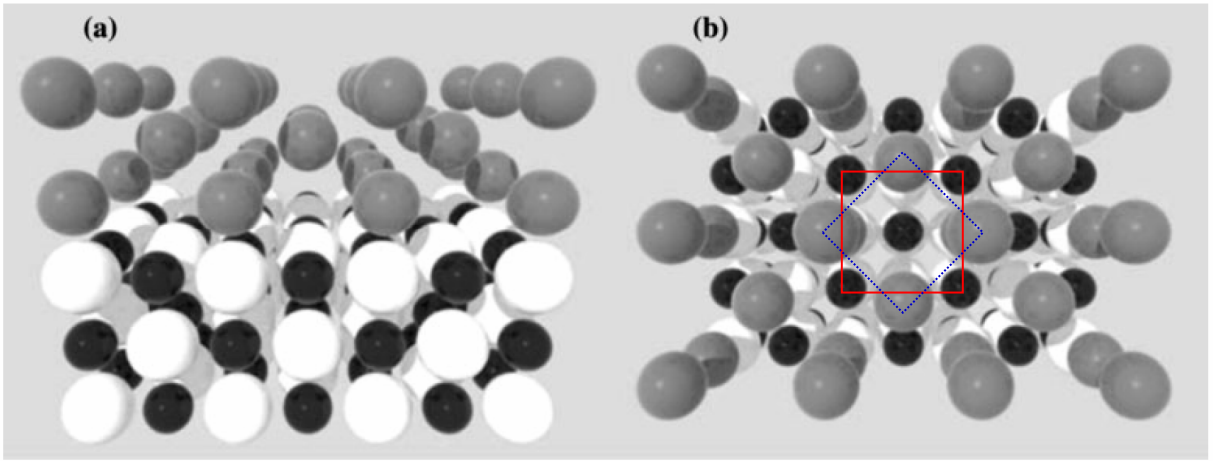
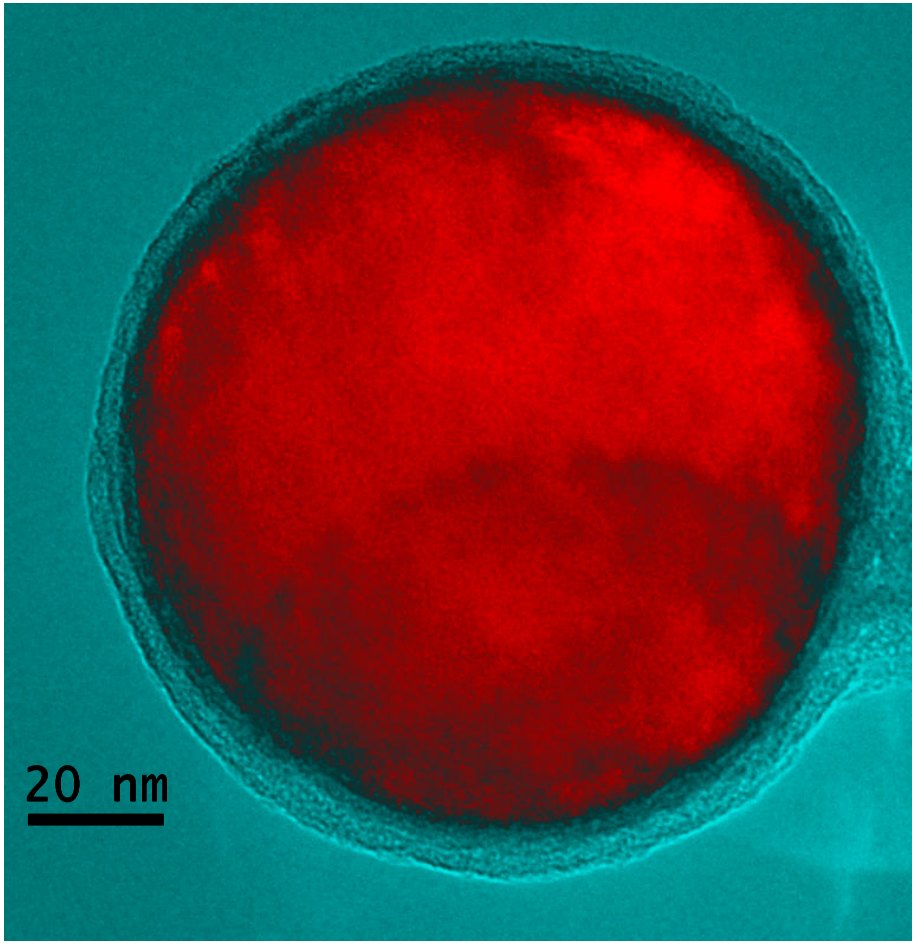
Attending to thermodynamic considerations, and values reported in the literature for the **Fe (2.9)** and **MgO (1.2 J.m^{-2})** surface energies, it is more preferable for the MgO to be present at the surface, thus promoting ***self-assembling***

dark spheres- Mg
white ones- oxygen
grey medium- Fe
(a) Side view
(b) planar view



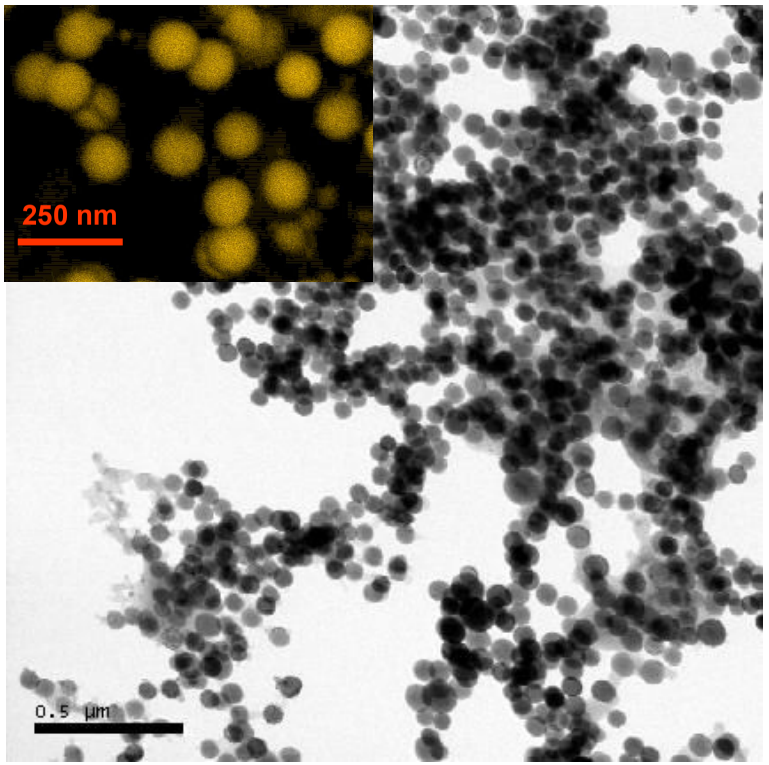
Fe_{bcc} 2.866 Å - MgO_{fcc} 2.21 Å

Expectations… simple, cheap, general technique

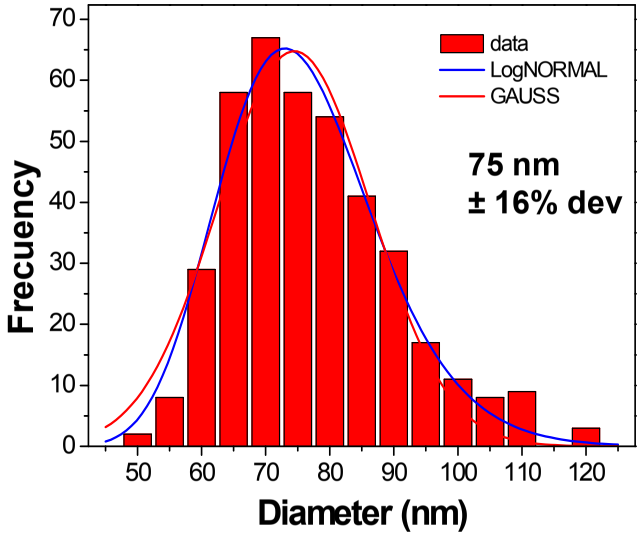


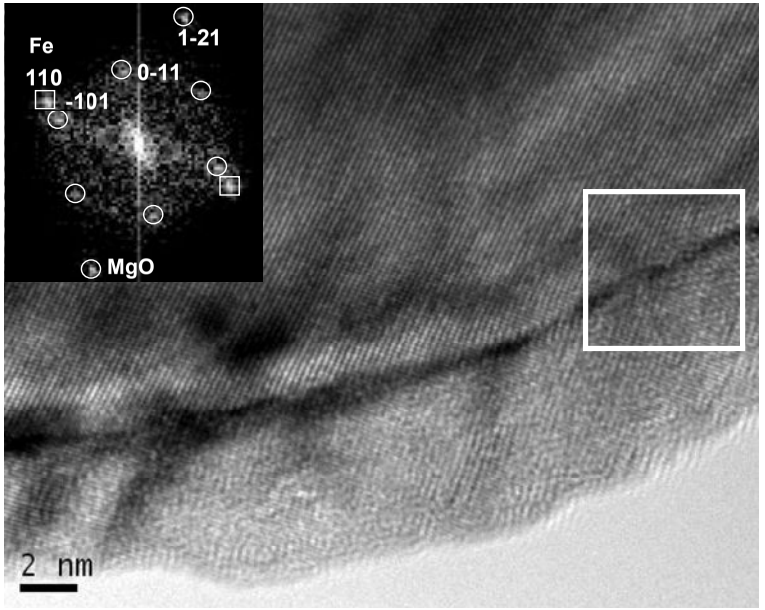
I’m not good at chemistry, hence physical routines are preferred. We use heat to vaporize bulk-sized starting materials. As the vapour cools, its atoms condense into NPs. An easy-to-use general technique for making dozens of different types of NPs. Researchers should have little trouble in scaling up the technique.

Results: Structure by TEM-SEM



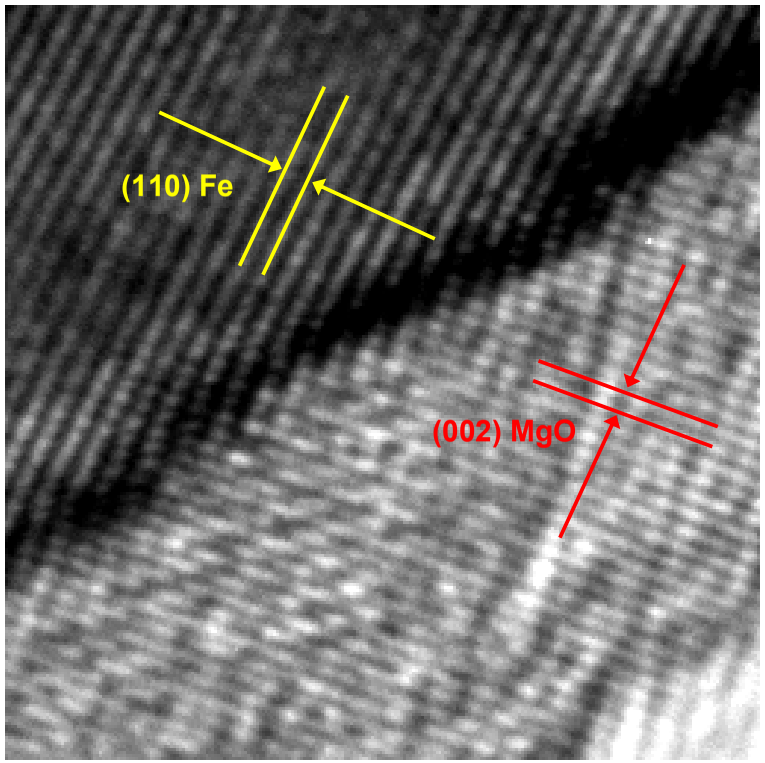
electron microscopy images after drop-casting a solution onto a TEM grid (inset: on Si substrate)



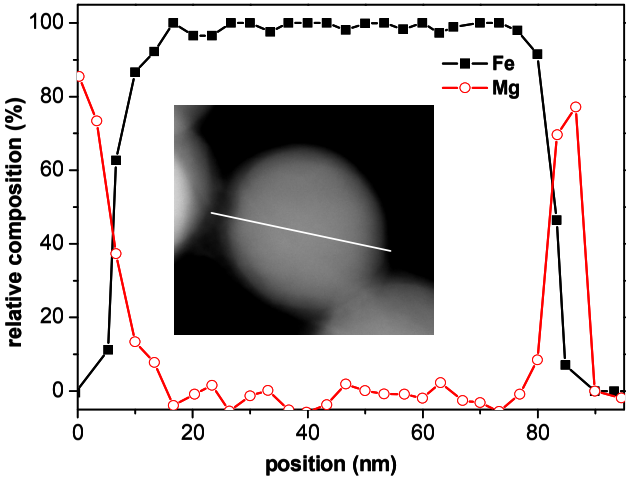


Interfacial HRTEM and FFT pattern

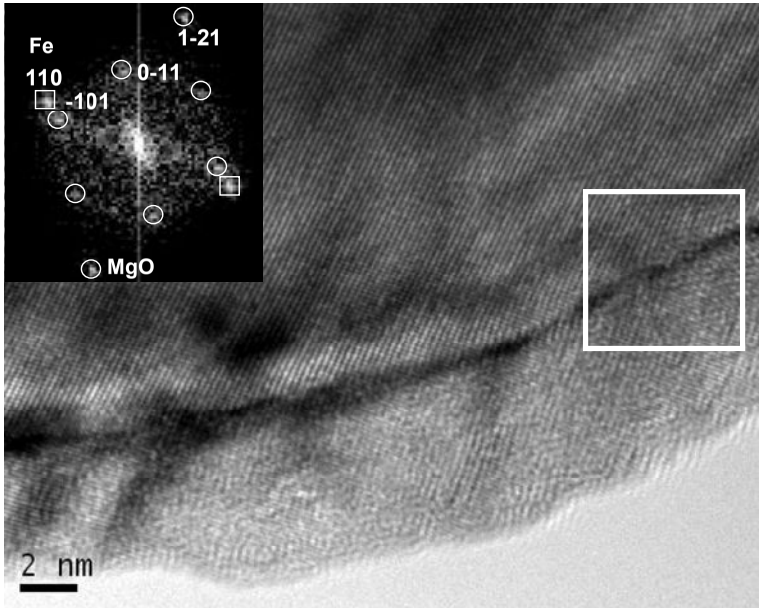
Results: Structure by TEM-SEM



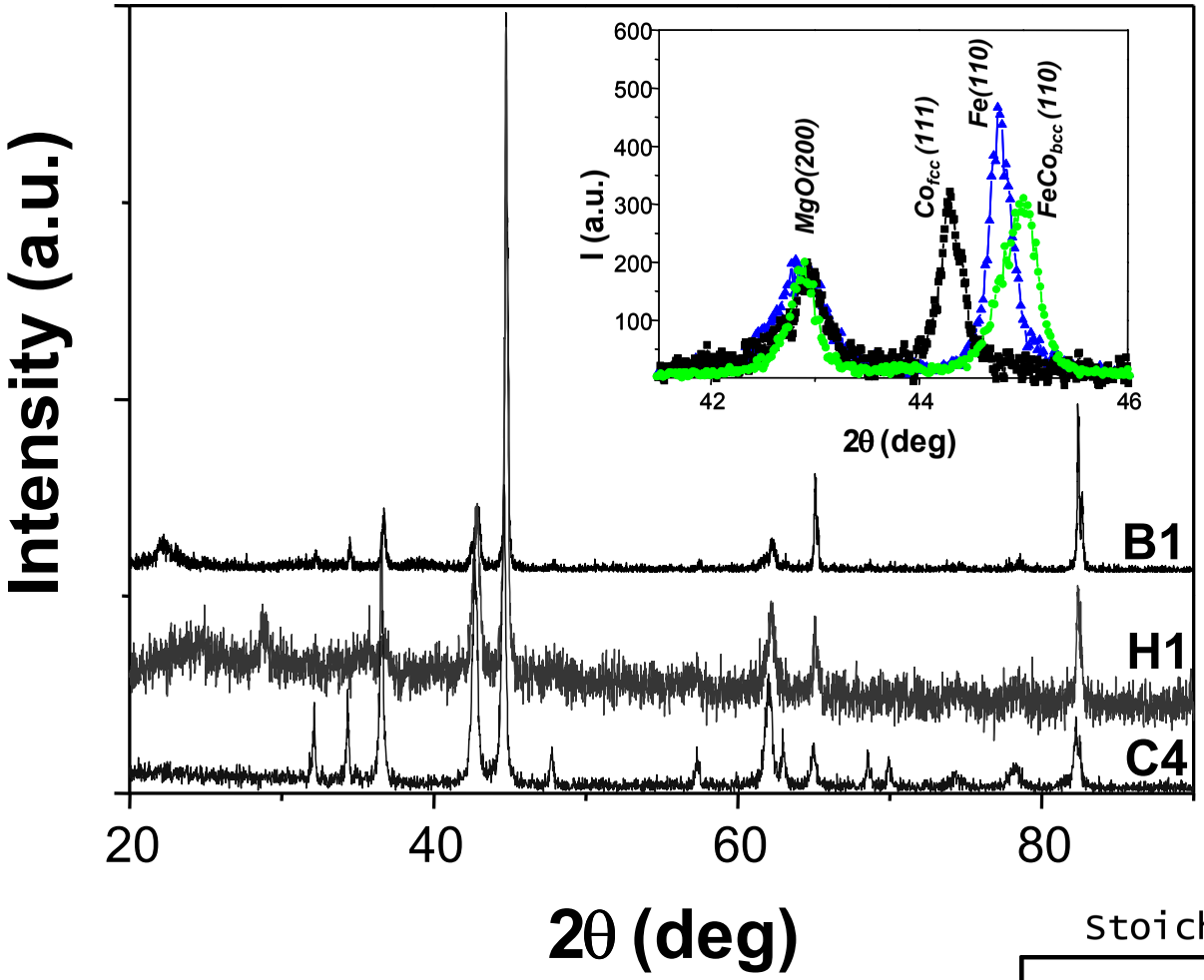
partially coherent interfaces with cube-on-cube orientation. Dislocations, plane bending and 7º tilting are also observed



Epitaxial relationship as the one normally found in thin films



Results: Structure by X-ray



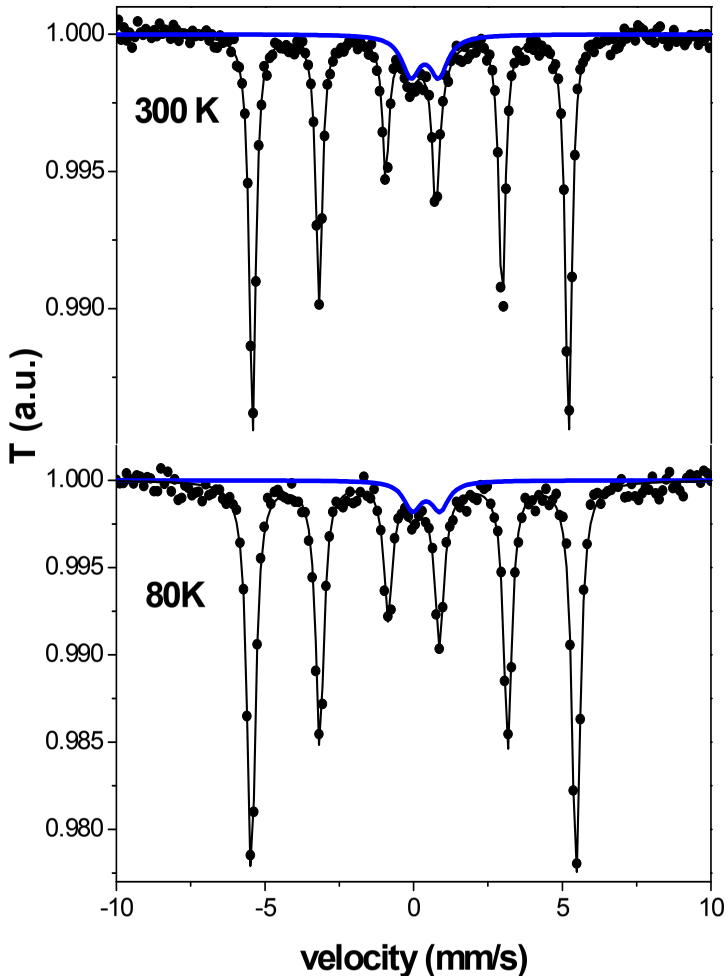
X-ray powder diffraction patterns of as-prepared product, from a mixture of MgO-Mg-Fe (sample B1), solely MgO-Fe (H1, middle) and MgO-Mg-Fe_2O_3 (C4). The inset depicts the selected MgO-fcc (200) and Fe-bcc (blue), FeCo-alloy or Co-fcc (black) peaks

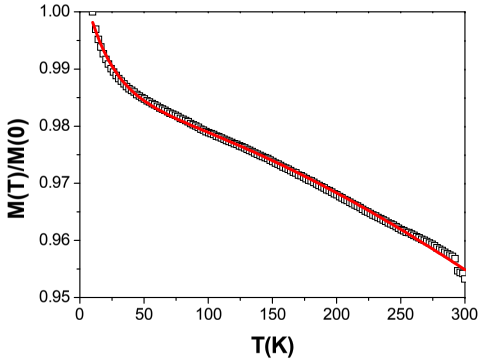
Stoichiometry depending on target

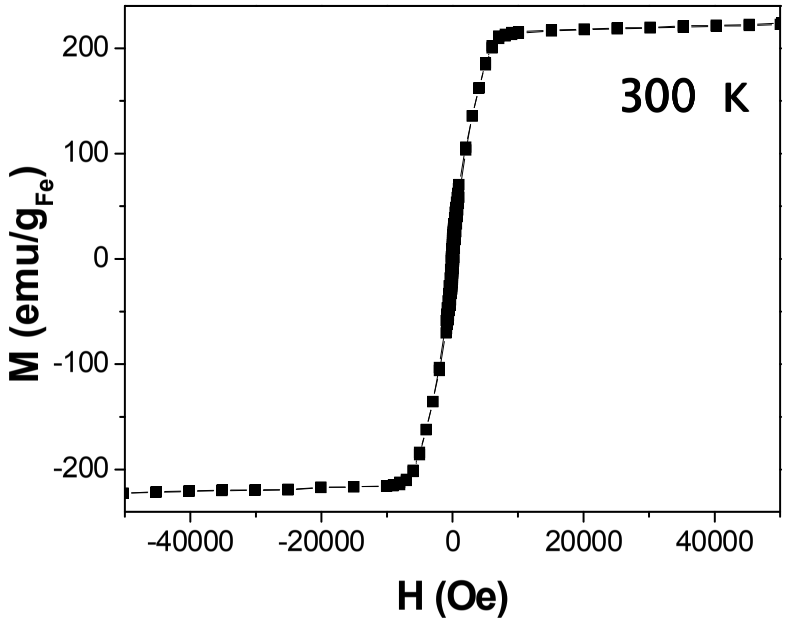
material	lattice <a> parameter ± 0.005 Å	bulk a (Å)
MgO_{fcc}	4.218	4.211
Fe_{bcc}	2.866	2.866
$Fe_{40}Co_{60\ bcc}$	2.847	2.82-2.87

Results: Magnetic Properties by Mössbauer and SQUID

No diminish of the properties was detected over several months storage under high humidity-temperature Barcelona's ambience conditions



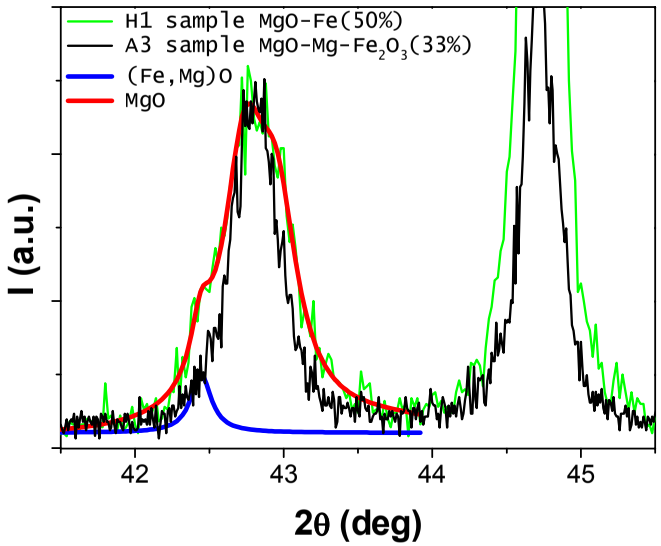


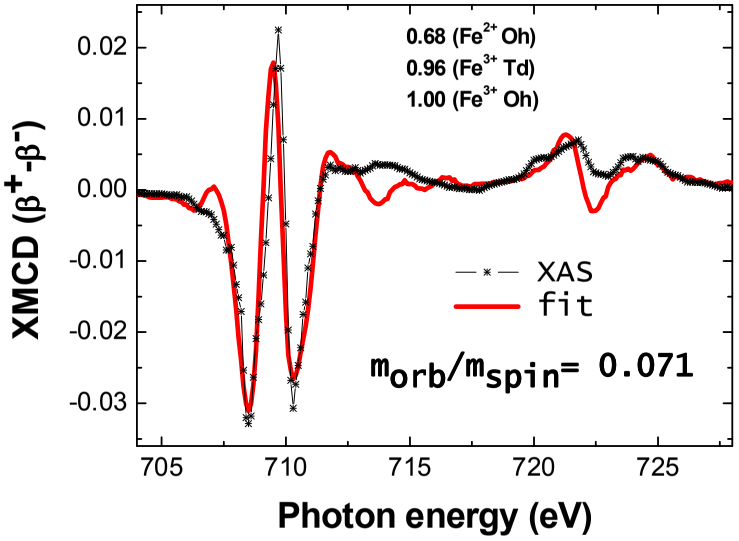


(Fe,Mg)O spin disordered surface

Results: Structure by X-ray and XMCD

Since MgO decomposes into Mg and O_2 in the gas phase, this technique provides a method for Fe^0 processing via magnesiothermic reduction. Mixing magnesium and iron oxides, for example, produced Fe-MgO core-shell NPs

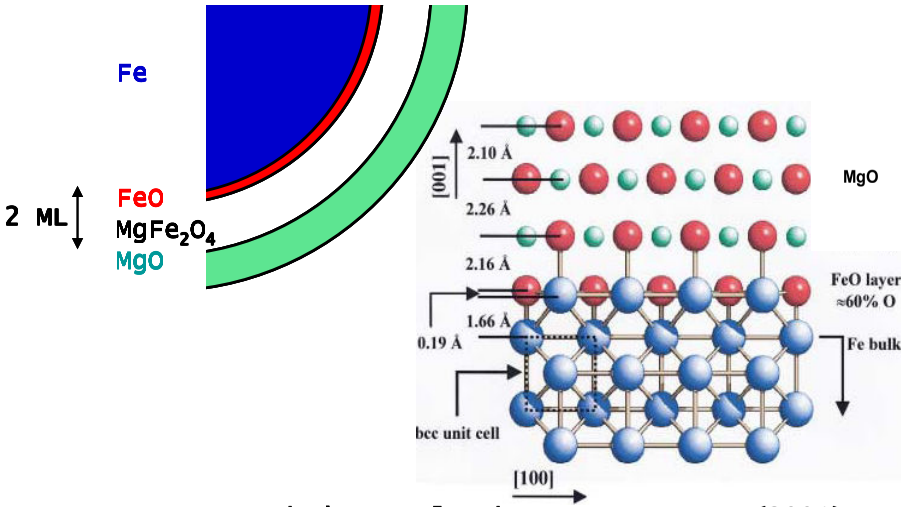




Asymmetric peak can roughly be resolved into symmetric peaks at 42.8°(MgO) and 42.6°(Fe-MgO solution)

- Fe^{3+} to compensate charge from Mg^{2+}
- adding Mg to prevent interface oxides

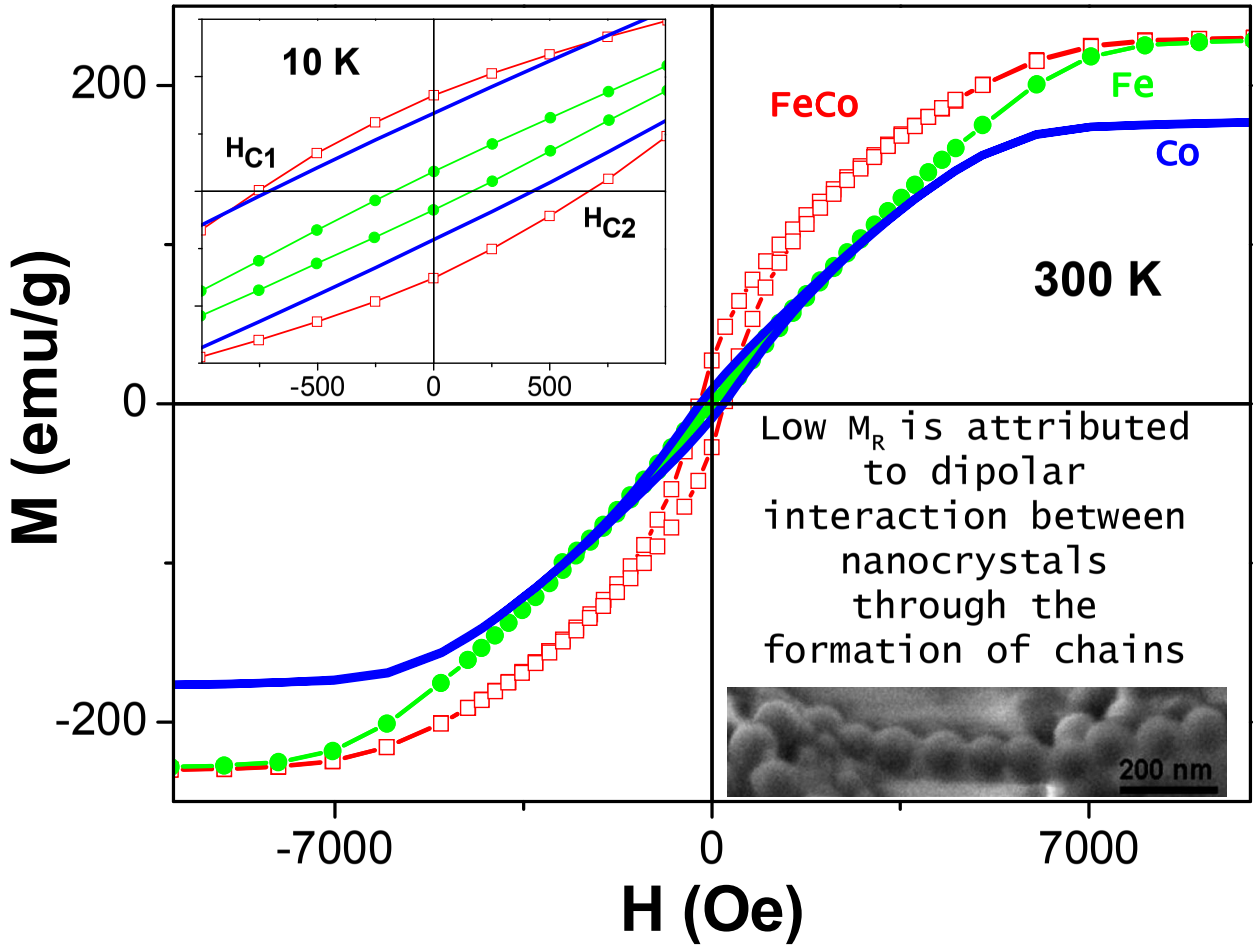
K. Tsunekawa, et al. Appl. Phys. Lett.(2005)



Meyerheim et al. Phys. Rev. Lett. (2001)

Results: Magnetic Properties by SQUID

$H_C(FeCo) > H_C(Co) > H_C(Fe)$ but nonetheless
$H_{ex}(Co) > H_{ex}(FeCo)$



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High magnetization particles coated with inorganic magnesia for biomedicine, catalysis and spintronics applications

• An easy-to-use general technique for making dozens of different types of <u>metal oxide nanoparticles that could have a major impact on everything from catalysts to electronics</u>.

Fischer-Tropsch process $(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$ invented in petroleum-poor but coal-rich Germany in the 1920s, to produce liquid fuels. There are investigations underway to reduce CO_2 emissions by using solar power to convert waste CO_2 into CO (if heated to 2400°C) from where the FT process can then convert it to hydrocarbons *http://www.sandia.gov*

Hydrogen economy is a proposed method of deriving energy by reacting H_2 with oxygen: Metal hydrides transport

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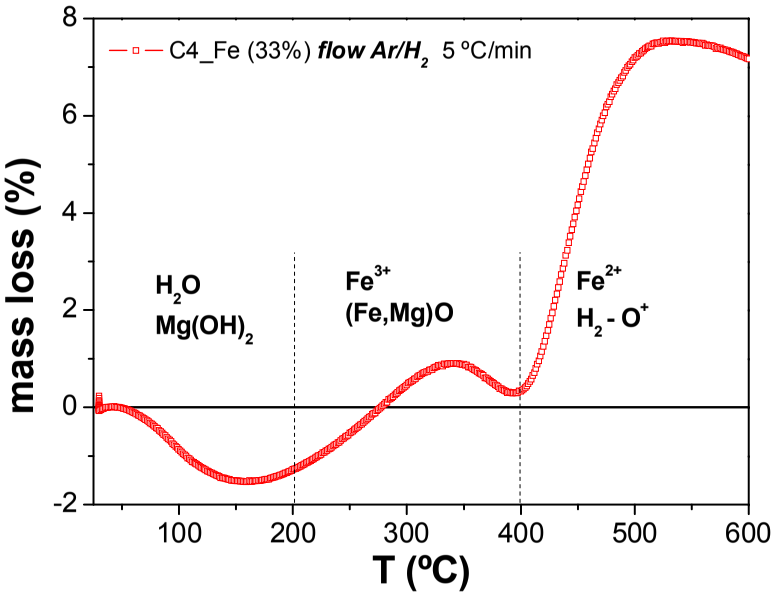

MgH_2 is a relatively cheap material. It contains as much as 7.6 wt % hydrogen

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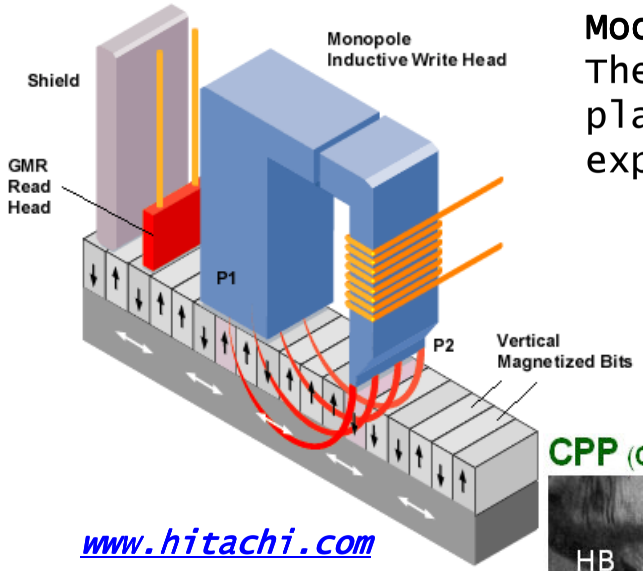


www.hitachi.com

Moore's law

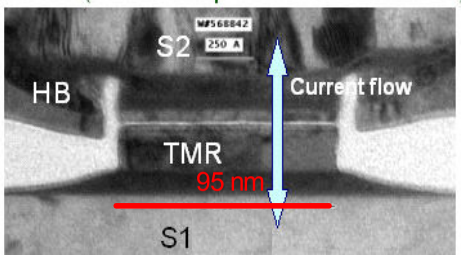
The number of transistors that can be inexpensively placed on an integrated circuit is increasing exponentially, doubling approximately every two years

do not really apply for magnetic-based technology

Inductive Ferro-cores$_{50's}$ → AMR → GMR$_{90's}$ → TMR$_{2006}$

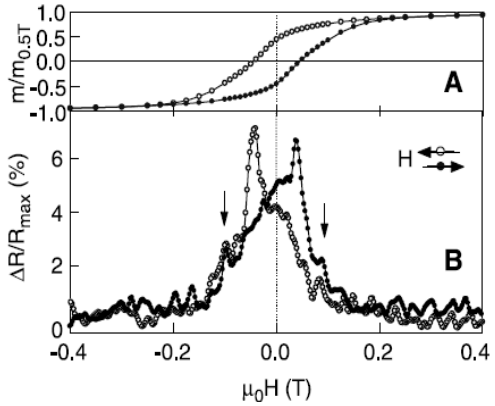
Areal density Tbit/in^2 ↔ Nanofrabrication

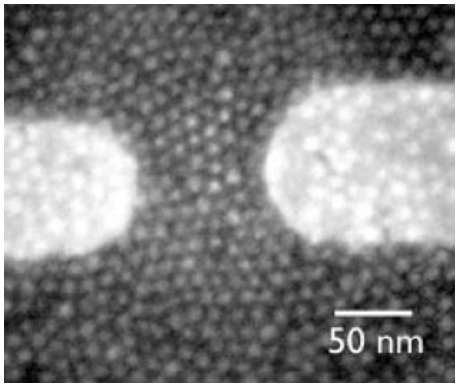
CPP (Current Perpendicular to the Plane)



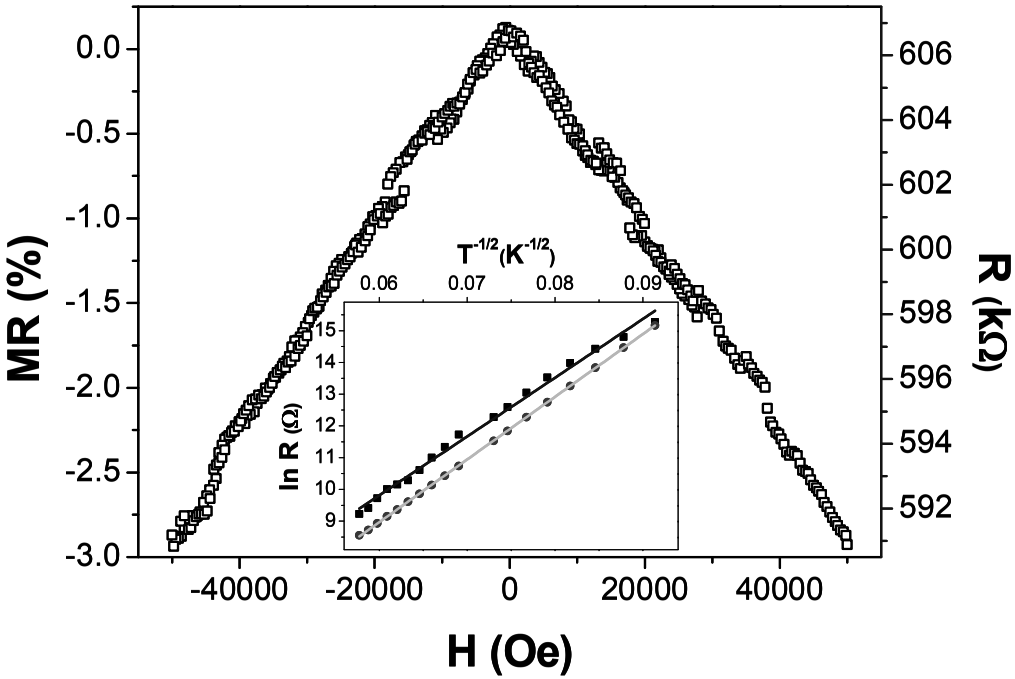
MgO-based TMR

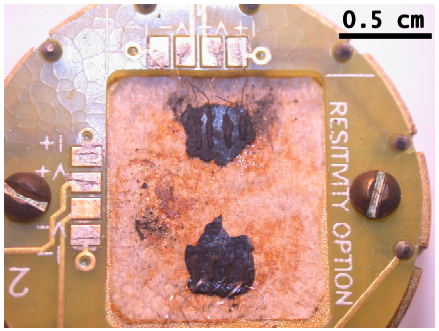
Results: Magnetoresistance in pellets





Black & Sun, Science (2000)





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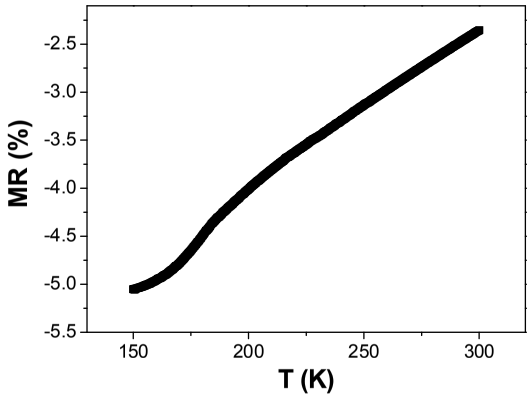
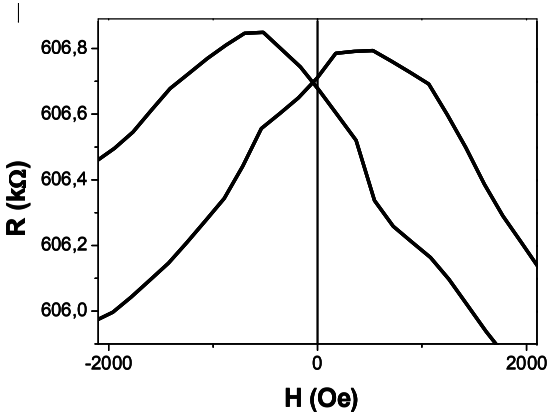
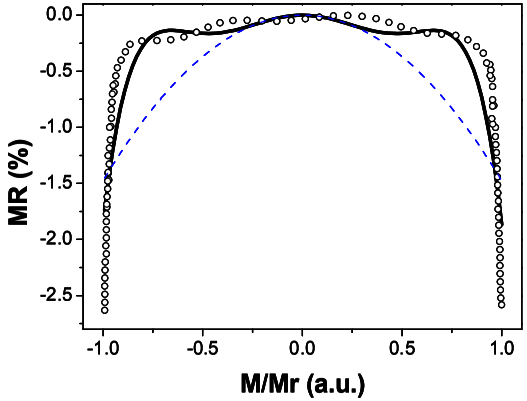
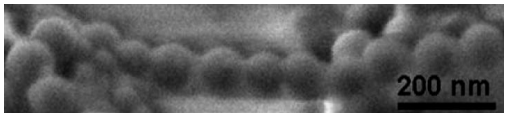
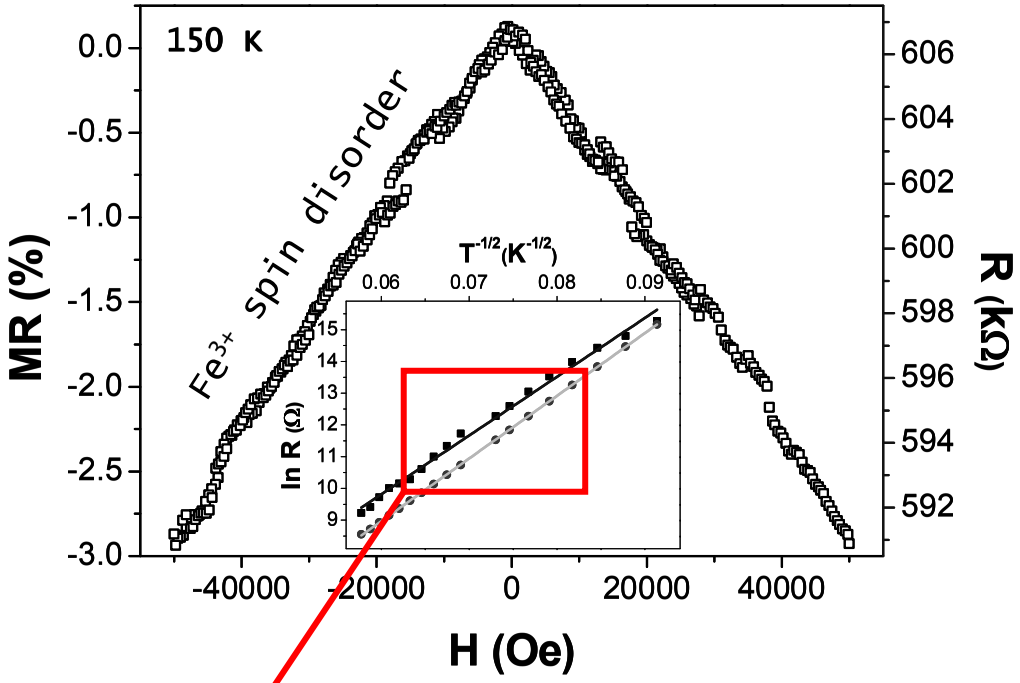






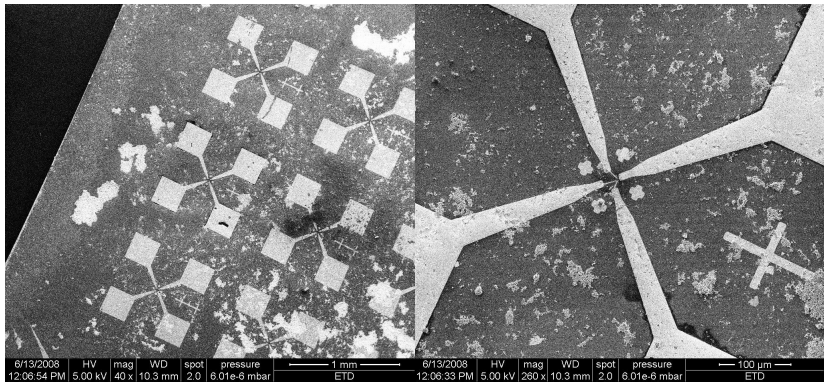
NPs interaction

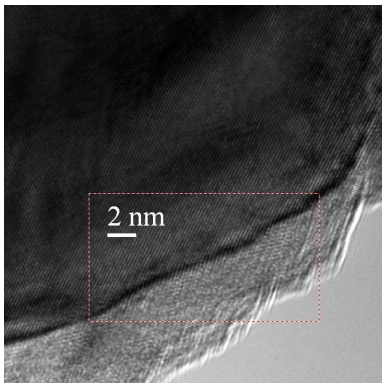


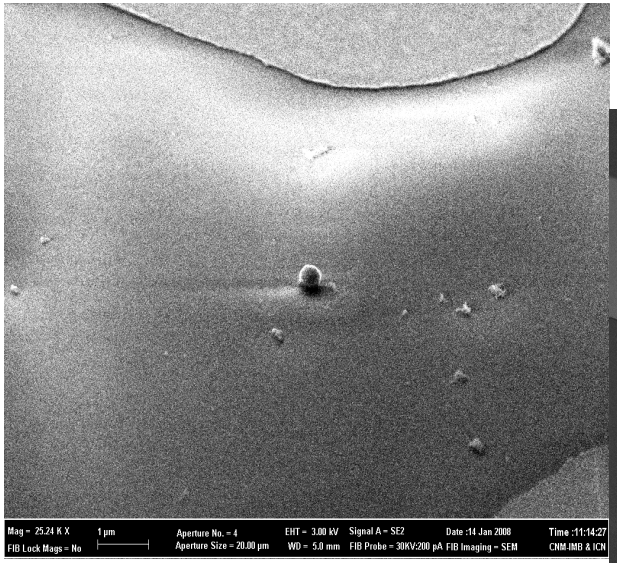


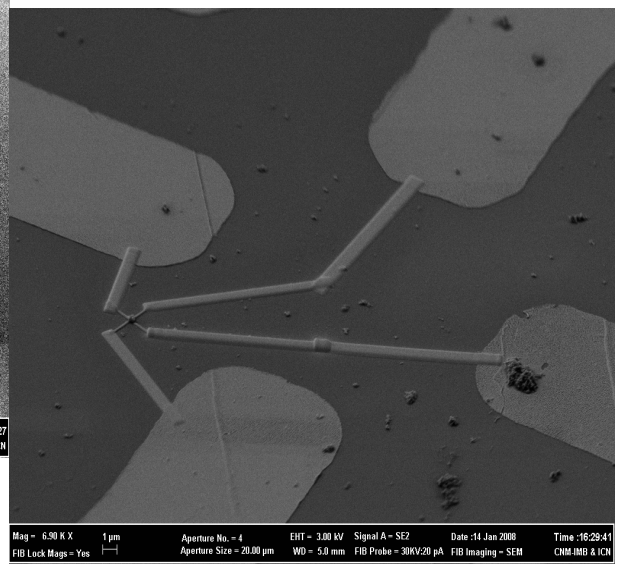
Hopping-conductivity through MgO
Activation energy **790 ± 30 meV**

Results: Tunnelling spectroscopy
‘catching’ a particle

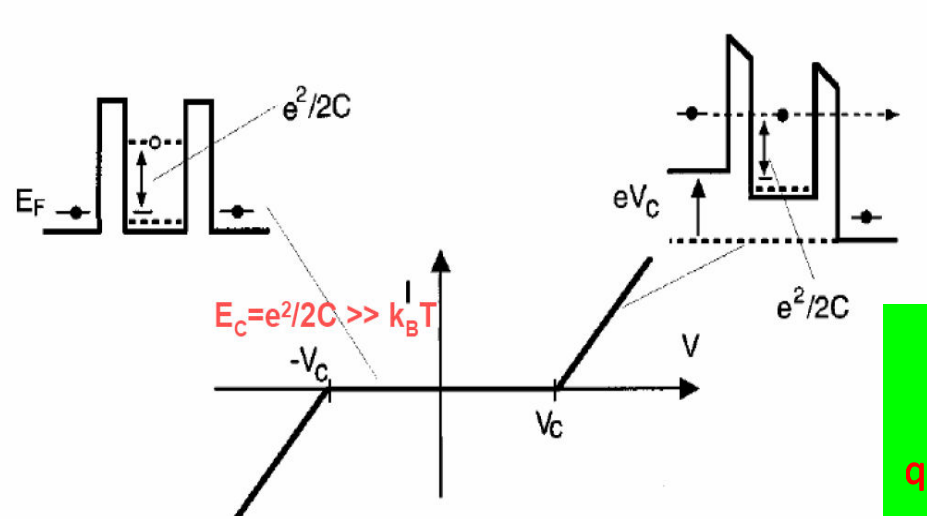




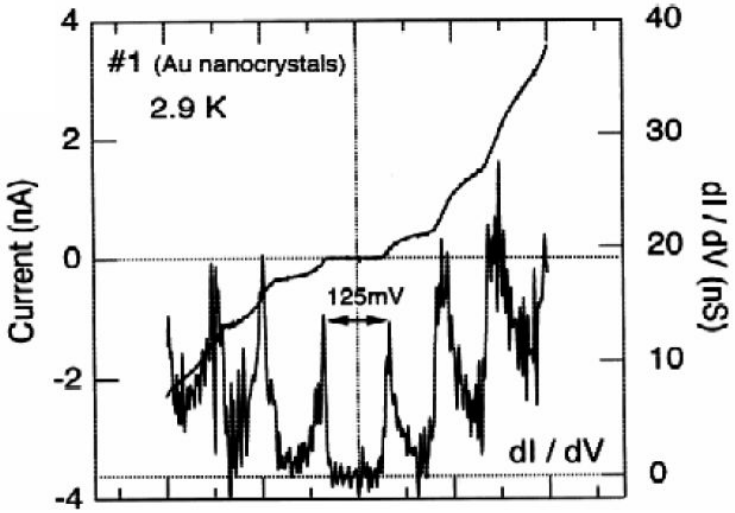




References: Coulomb staircase



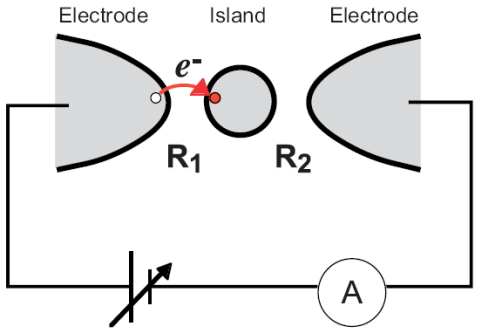
Current–voltage characteristics showing a Coulomb gap for $-V_c < V < V_c$
Above $\pm V_c$ the electrons can cross between source and drain.



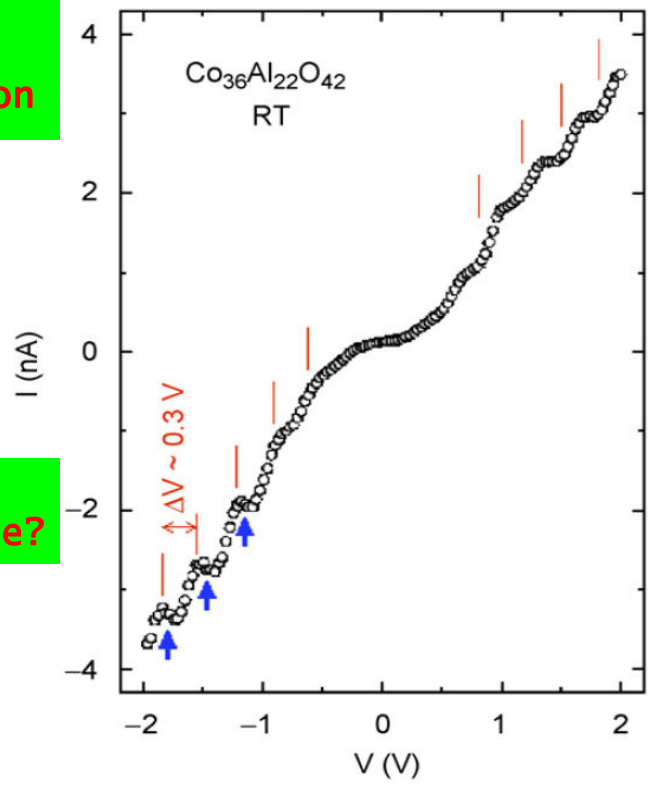
Inoue et al. Thin Solid Films (1999)

Charge + Energy quantization

Material independence?

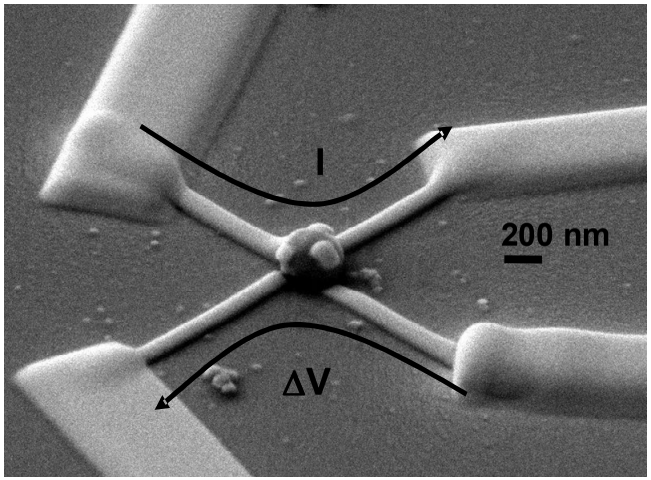


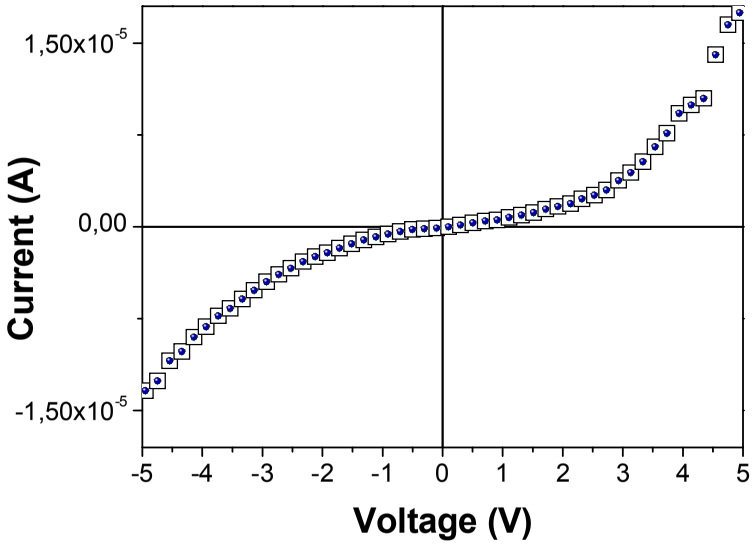
single-electron tunnelling device

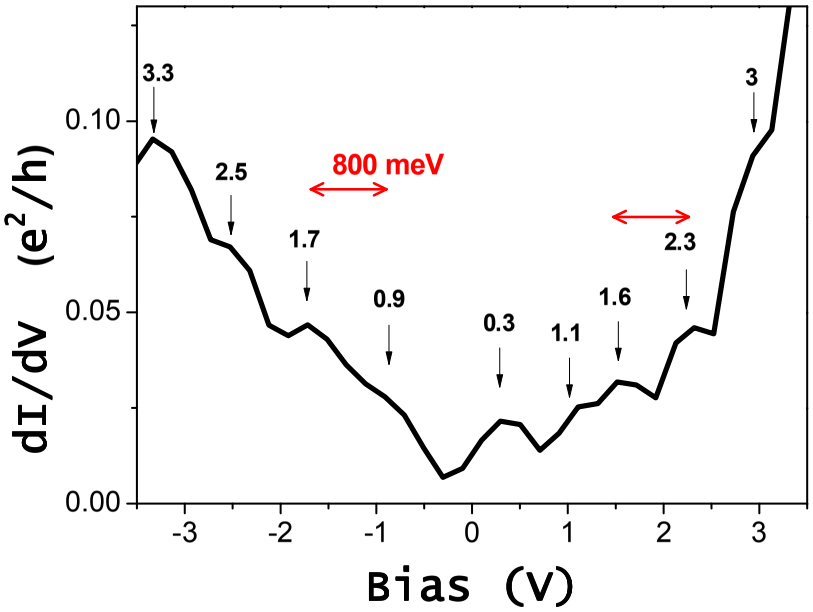


Mitani et al. Phys. Reports (2007)

Results: Tunnelling spectroscopy



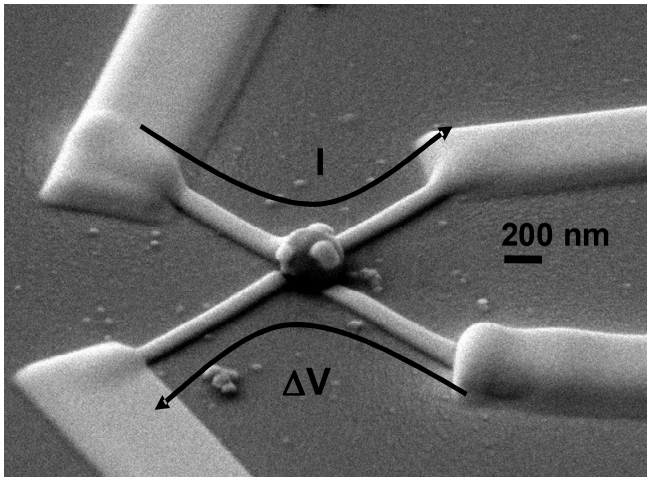


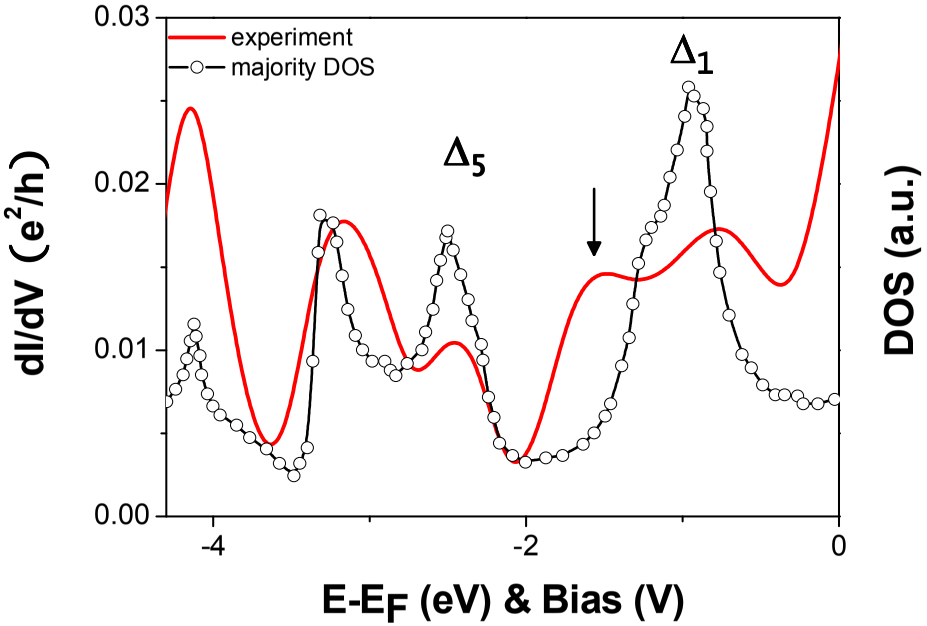


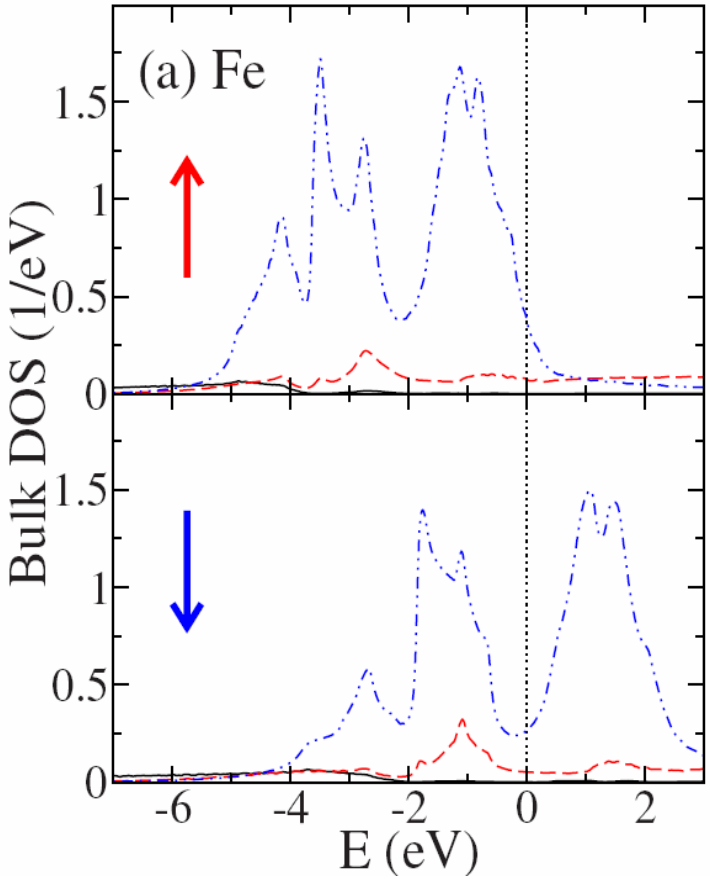
K_BT ~ 26 meV at 300K
G << e^2/h

I-V results relate with the characteristic charging energy (Coulomb) derived from the temperature dependence of pressed pellets **790 ± 30 meV**

Results: Tunnelling spectroscopy
Coherent transport through crystalline MgO barriers





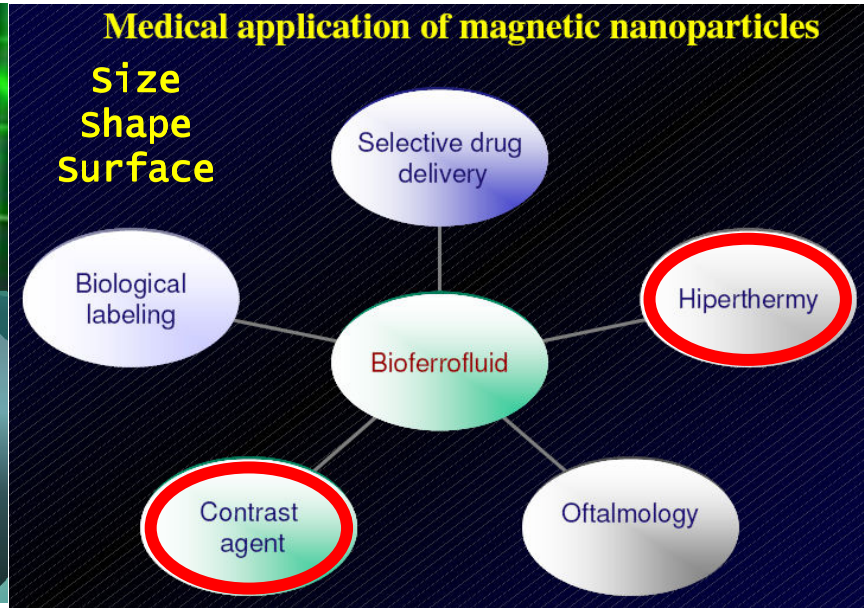


http://mits.nims.go.jp

Butler et al. & Mathon et al. Phys. Rev. B (2001)

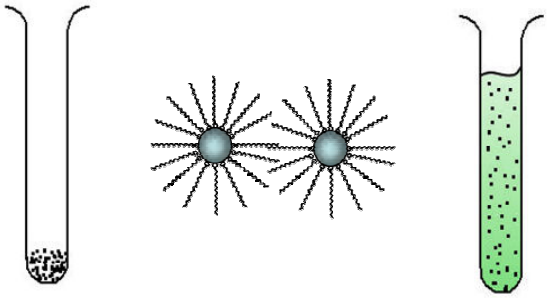
High magnetization particles coated with inorganic magnesia for biomedicine, catalysis and spintronics applications

• An easy-to-use general technique for making dozens of different types of metal oxide nanoparticles that could have a major impact on everything from catalysts to electronics.

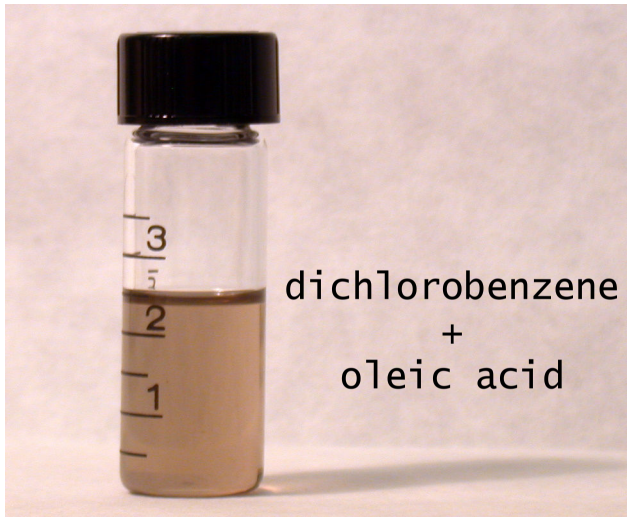


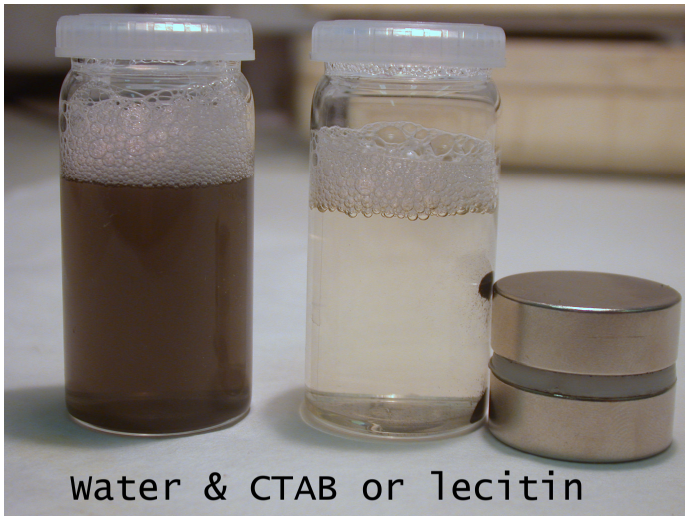
Soppimath et al. Adv. Mater. 17 (2005) 318 'Thermally Responsive Core-shell NPs for Targeted Drug Delivery'
Jiang et al. Nature Nanotech. 3 (2008) 145 'Nanoparticle-mediated cellular response is size-dependent'

Results: Fe@MgO NPs suspensions

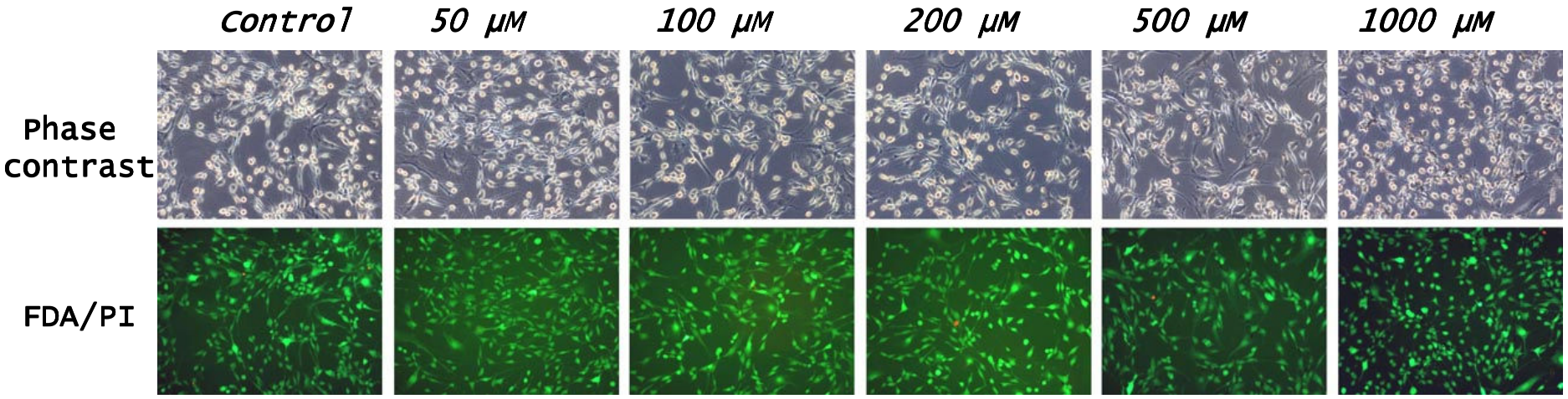


Before the NPs can act as contrast agents, they must be stabilized in water at physiological pH.
Particles are clustered near magnetic poles



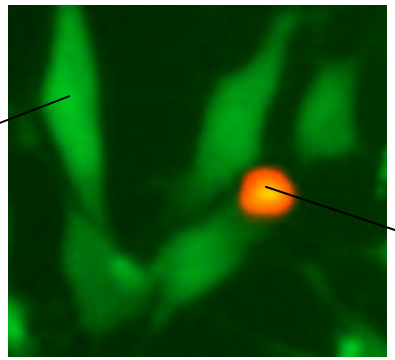


Study of Fe^0 treatment on 3T3 cell viability two different cytotoxicity methods



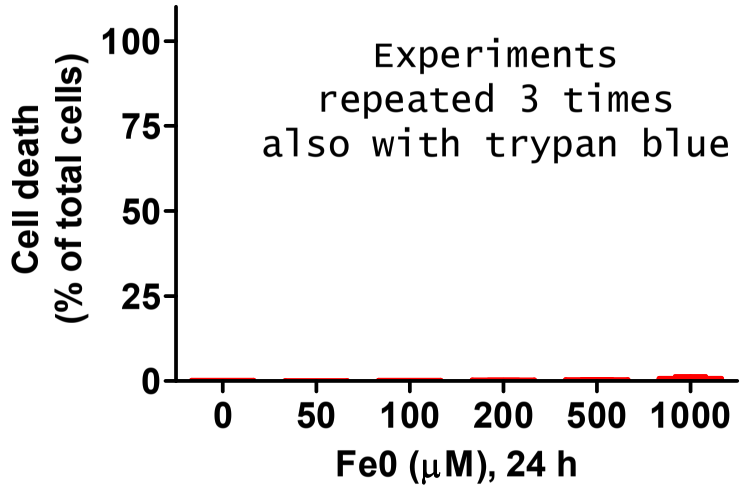
NPs do not increase cell death

Cytochemistry



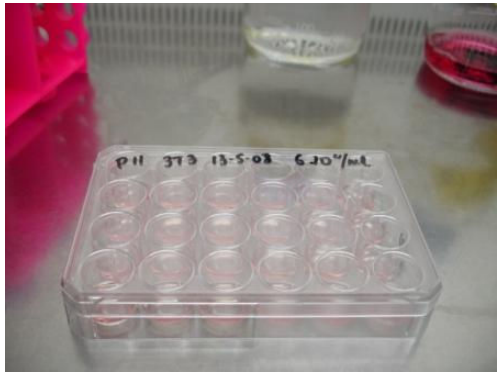
fluorescein diacetate labeled living cells

propidium iodide stain of dead cells



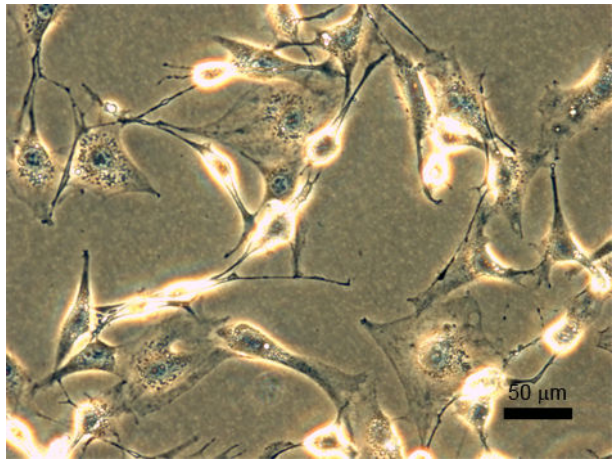
Experiments repeated 3 times also with trypan blue

Study of Fe^0 treatment on 3T3 cell growth

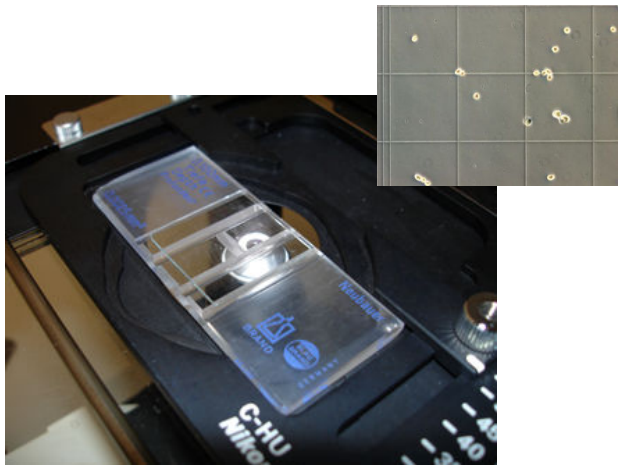


4wells x concentration

3T3 growing in exponential phase

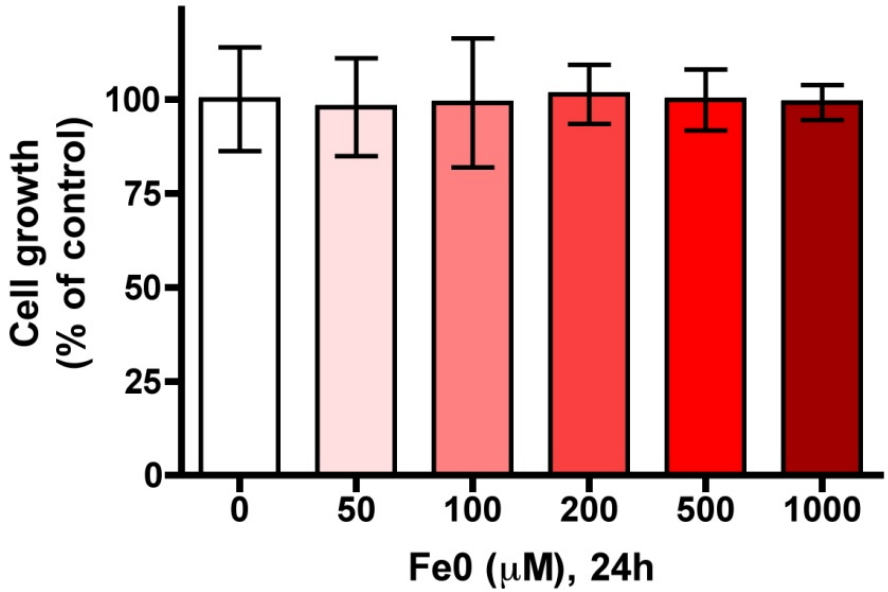


3T3 cells doubling time = 18h

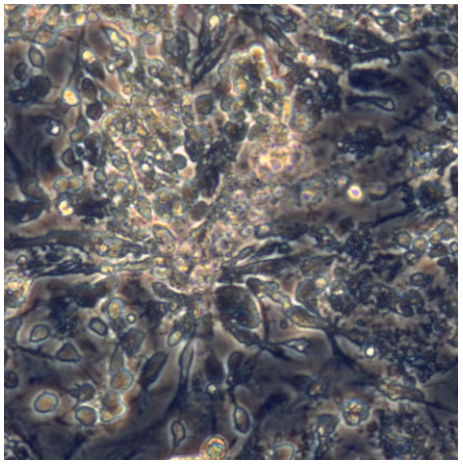


Cell counting with an hemocytometer

NPs did not decrease cell growth

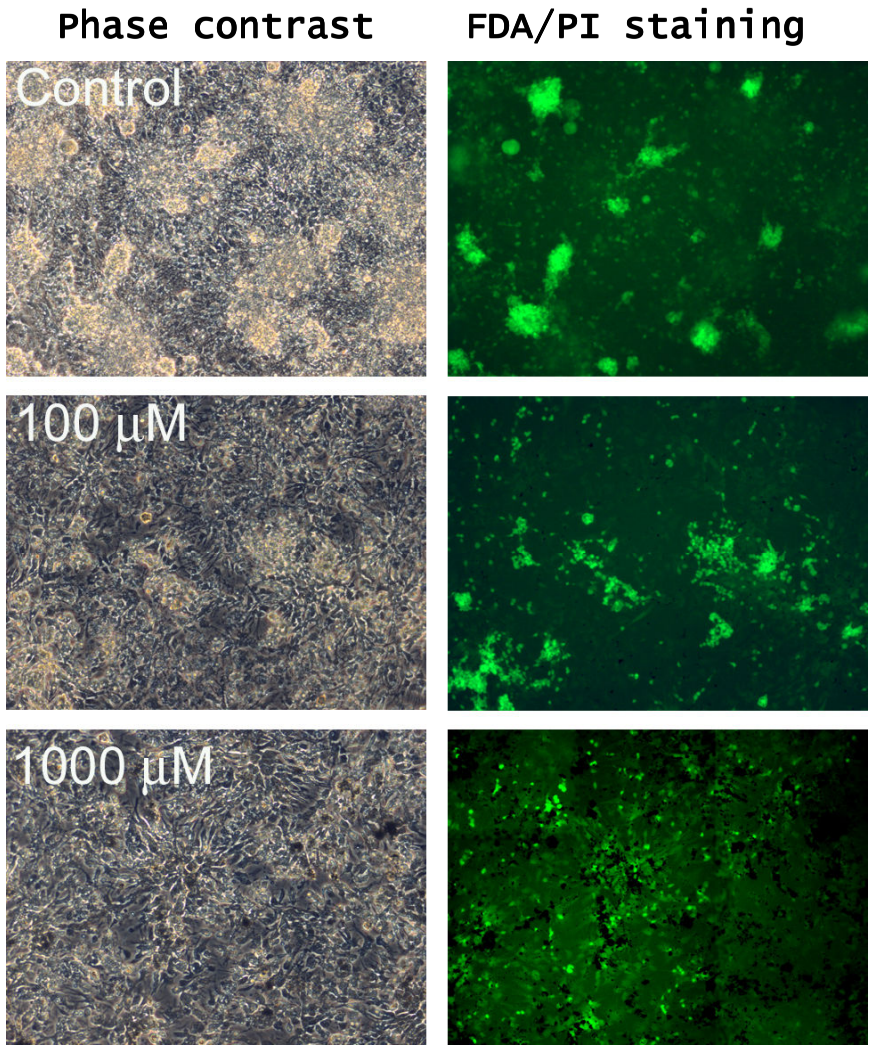


Study of Fe^0 treatment on mouse cortical neurons



Primary cultures from cerebral cortex contain neurons and glial cells

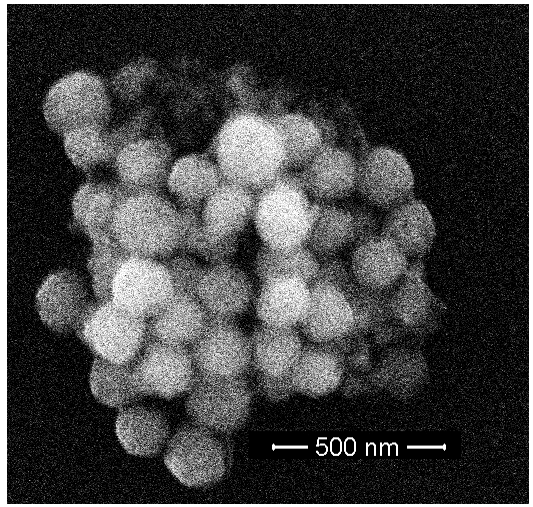
NPs did not produce cell death after 3 days of exposure

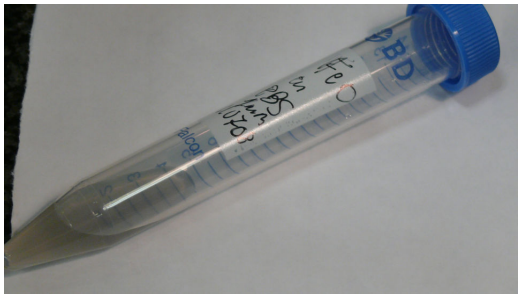


Study of Fe^0 *in-vivo*

The goal is to cross “the Death Valley“ and get these NPs as hyperthermia centres for cancer treatment and imaging technologies from preclinical development to human clinical trials

The issue is how to avoid NPs agglomeration into blood vessels (collapse) and protein adsorption on the particle surface (controls the biodistribution)





inoculation of 10 µl/g
saline solution at 1 mM Fe^0
Sacrificed after 14 days

On-going experiments: MRI

In countries outside Europe, studies on human subjects proceed long before safety and efficacy trials have begun. This is possible because in the US, for example, Food and Drug Administration (FDA) regulations allow drug quantities of less than 100 μg to be tested.

Worth of attention are the clinical test in the early 90's conducted by A. Noskov et al. in St. Peterburg's City Hospital, using ferrocarbon NPs in 100 patients with lung/liver cancer.

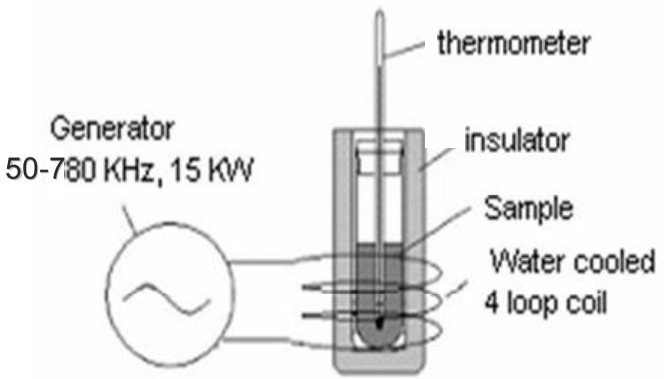
Massachusetts General Hospital
E. Rodriguez

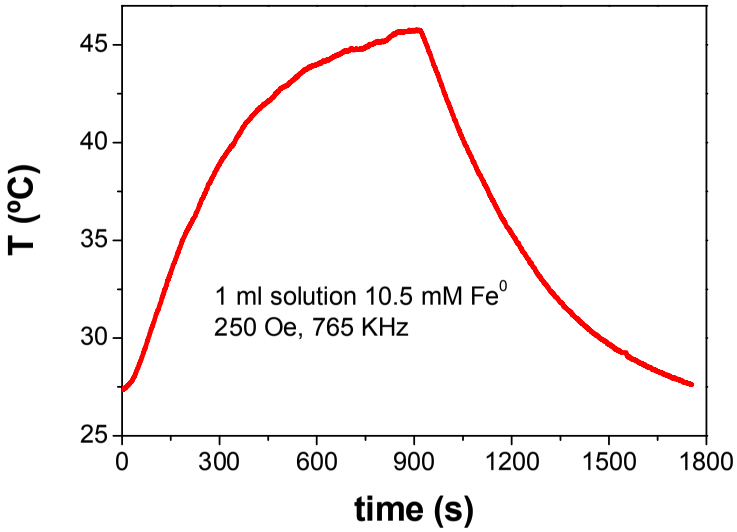
Results in solution
proton relaxativities at 0.47 T
r1 = 1.15 $mM^{-1}s^{-1}$ longitudinal
r2 = 152.4 $mM^{-1}s^{-1}$ transversal
might be useful to produce darker images
r2/r1= 132 (higher ratio, better contrast)

On-going experiments: hyperthermia

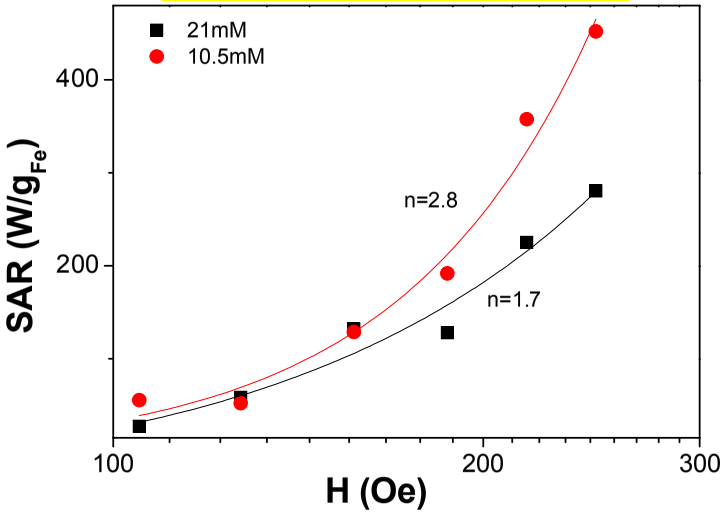
clinical oncology takes advantage of the higher sensitivity of tumor tissues to elevated temperatures (42-46˚C).

Contrary to other methods, radio-waves heat up only locally the NPs, while leaving the rest of the tissues unaffected.





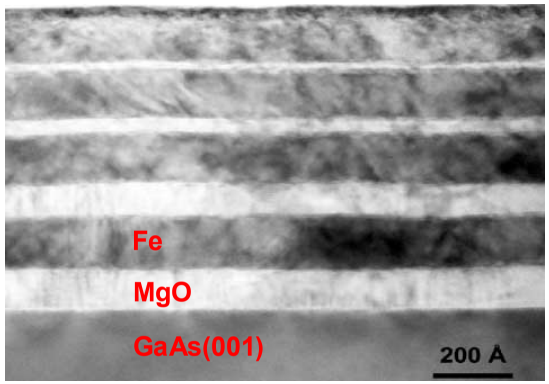
$$SAR = \frac{W}{m_{Fe}} = \frac{\Delta Q}{\Delta t . m_{Fe}} = c \frac{m_f}{m_{Fe}} \frac{\Delta T}{\Delta t} \approx H^n$$



Future work?

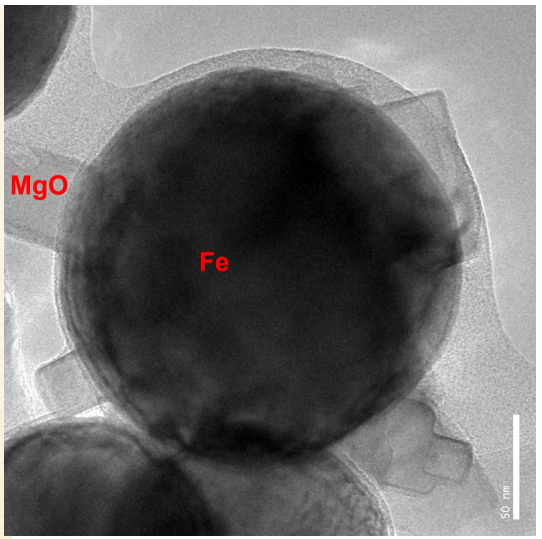
Adiabatic Hyperthermia
in vivo bioimaging MRI
Gas sensing and Hydrogen storage
Microwave-absorption for EM pollution
TMR devices

I love desserts like Tiramisu



Martínez-Boubeta et al. 2001
J. Cryst. Growth & Appl. Phys. Lett.

and gelato



Martínez-Boubeta et al. 2008