

Epitaxy and magnetic materials

O. Fruchart



Institut NEEL

CNRS & Univ. Grenoble - Alpes

Grenoble - France



Institut Néel, Grenoble

<http://perso.neel.cnrs.fr/olivier.fruchart/>



Modern applications of magnetism

Where does 'nano' contribute ?

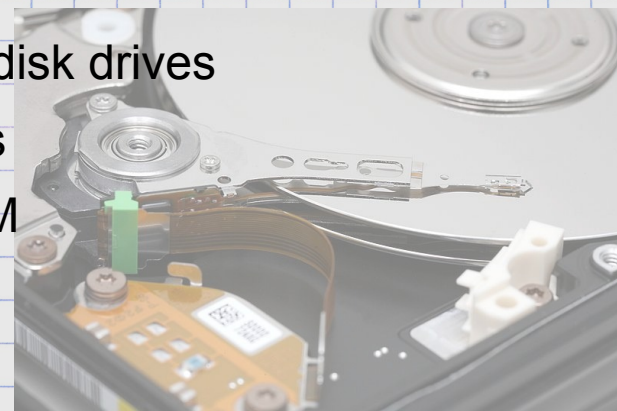
Sensors

- ⇒ Compass
- ⇒ Encoders
- ⇒ Field mapping
- ⇒ HDD read heads



Data storage

- ⇒ Hard disk drives
- ⇒ Tapes
- ⇒ MRAM



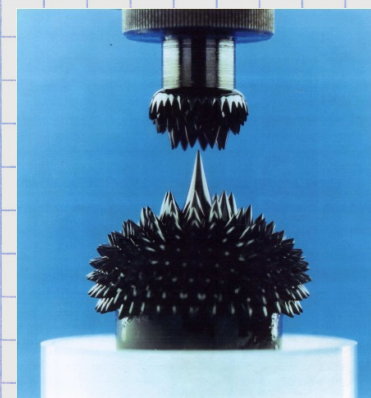
Materials

- ⇒ Magnets
(→ motors and generators)
- ⇒ Transformers
- ⇒ Magnetocaloric



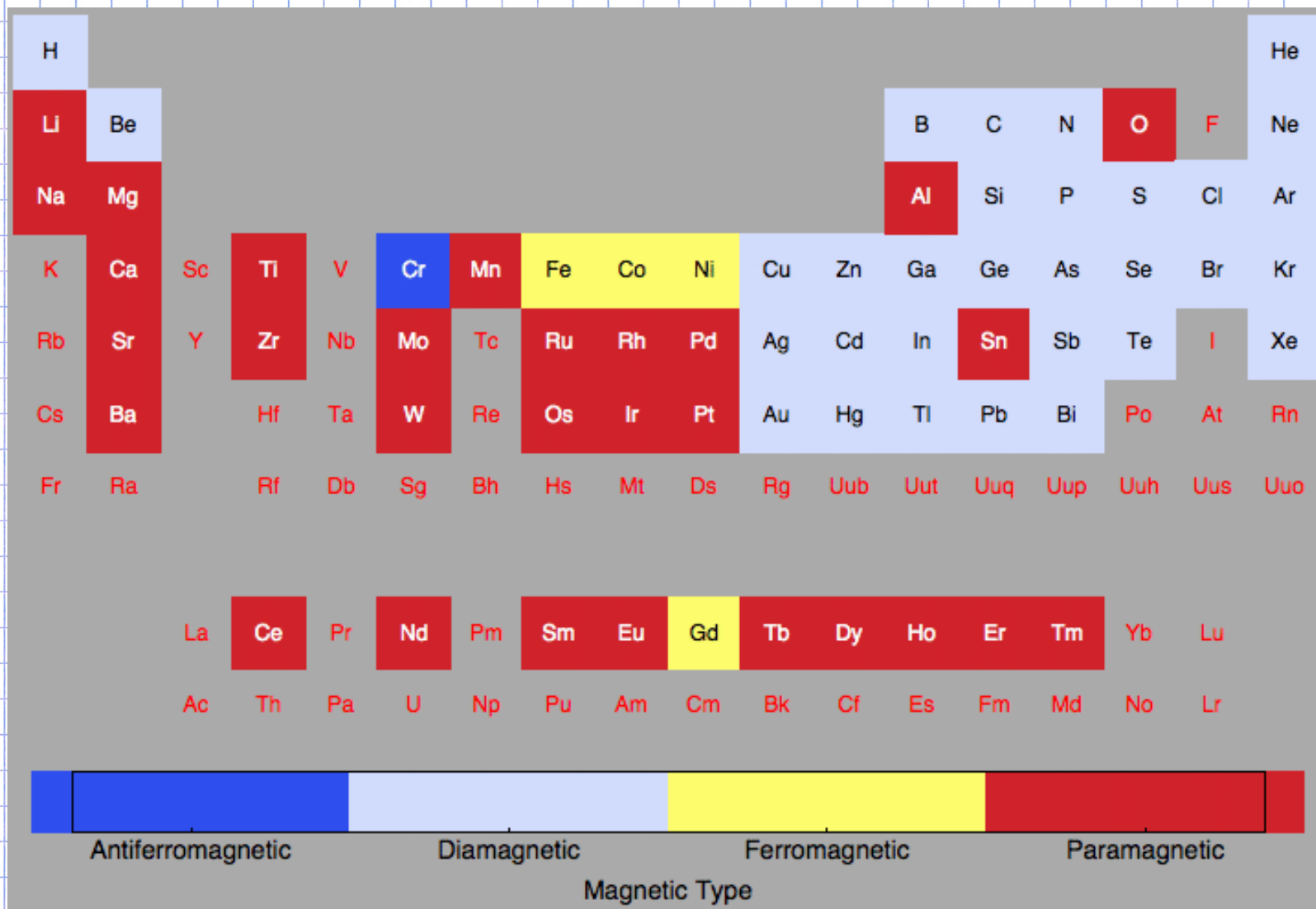
Nanoparticles

- ⇒ Ferrofluids
- ⇒ MRI contrast
- ⇒ Hyperthermia
- ⇒ Sorting & tagging





Magnetic properties of single elements at room temperature

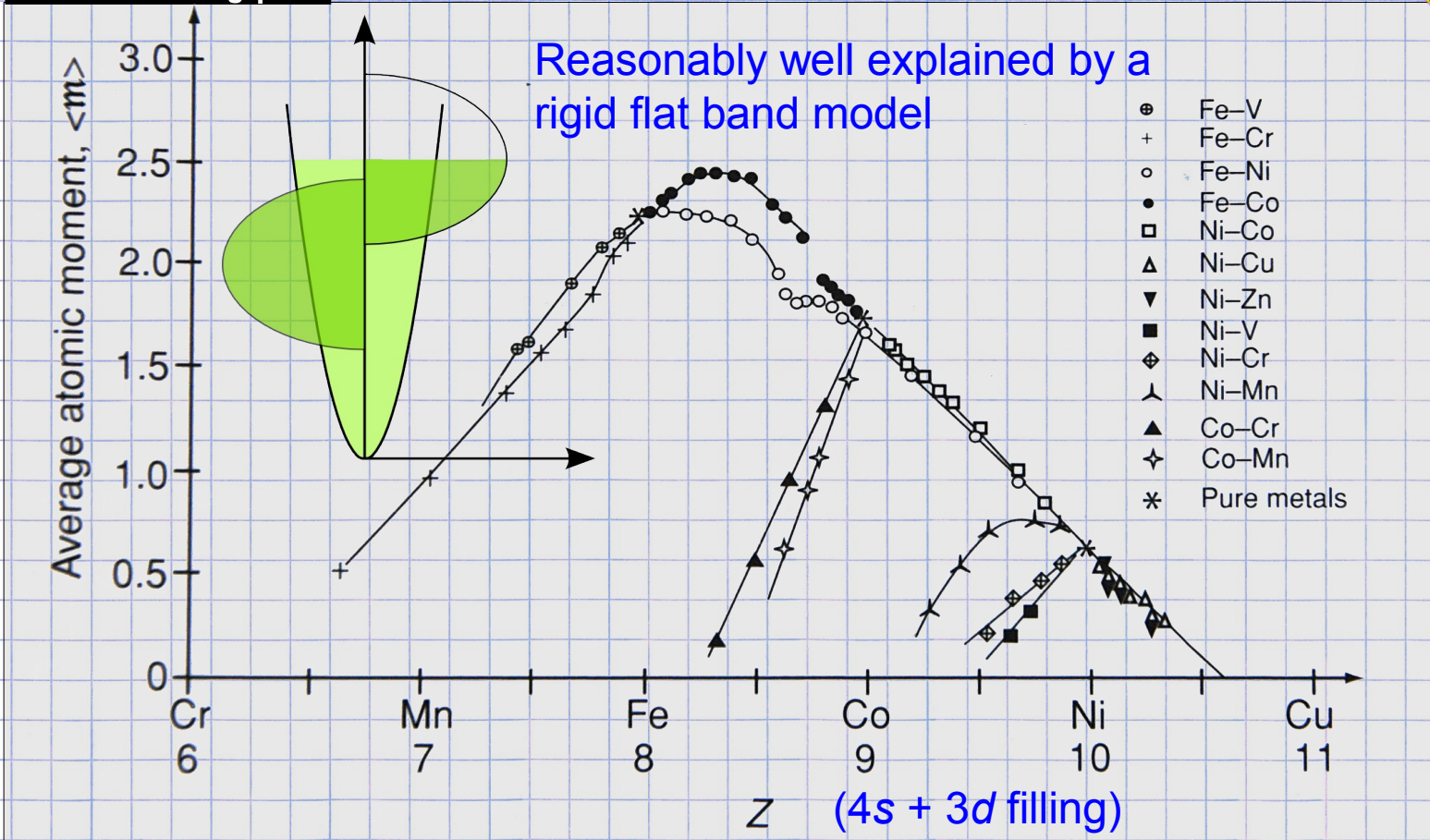


Periodictable.com



Do not use Hund's rules to estimate atomic moments

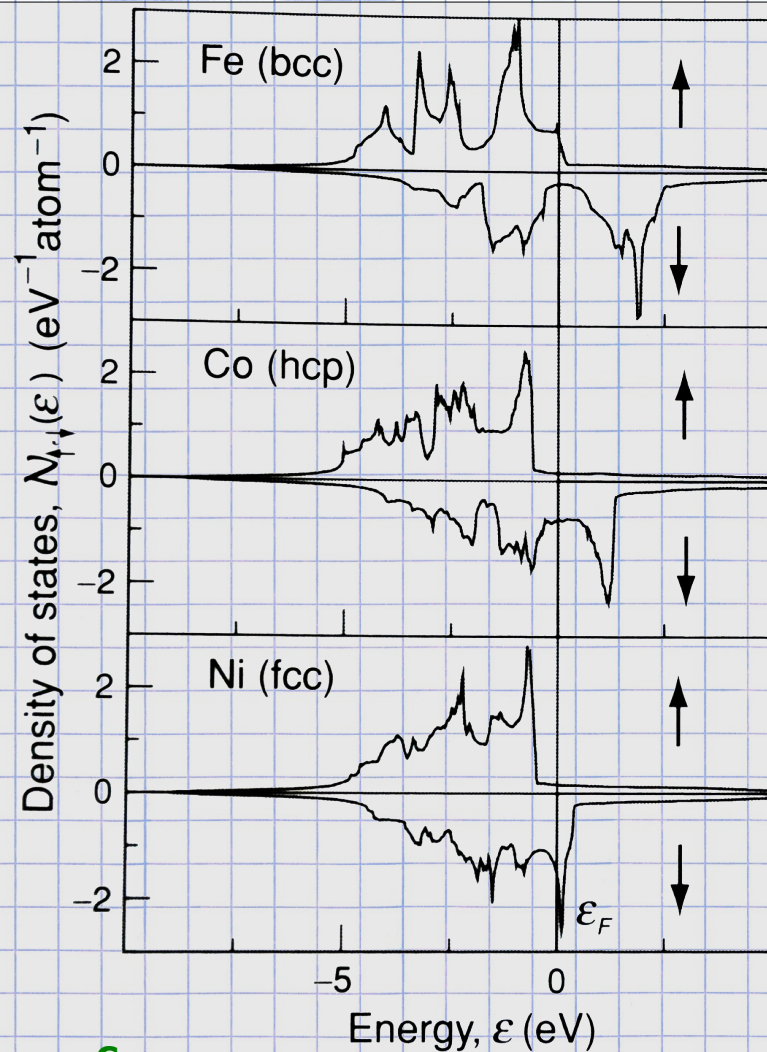
Slater-Pauling plot



From: Coey



Band structure and density of state of 3d ferromagnets



- ⇒ Not parabolic bands
- ⇒ Even simple quantities are sometimes difficult to understand
- ⇒ Anisotropy of DOS
→ importance of epitaxy

From: Coey

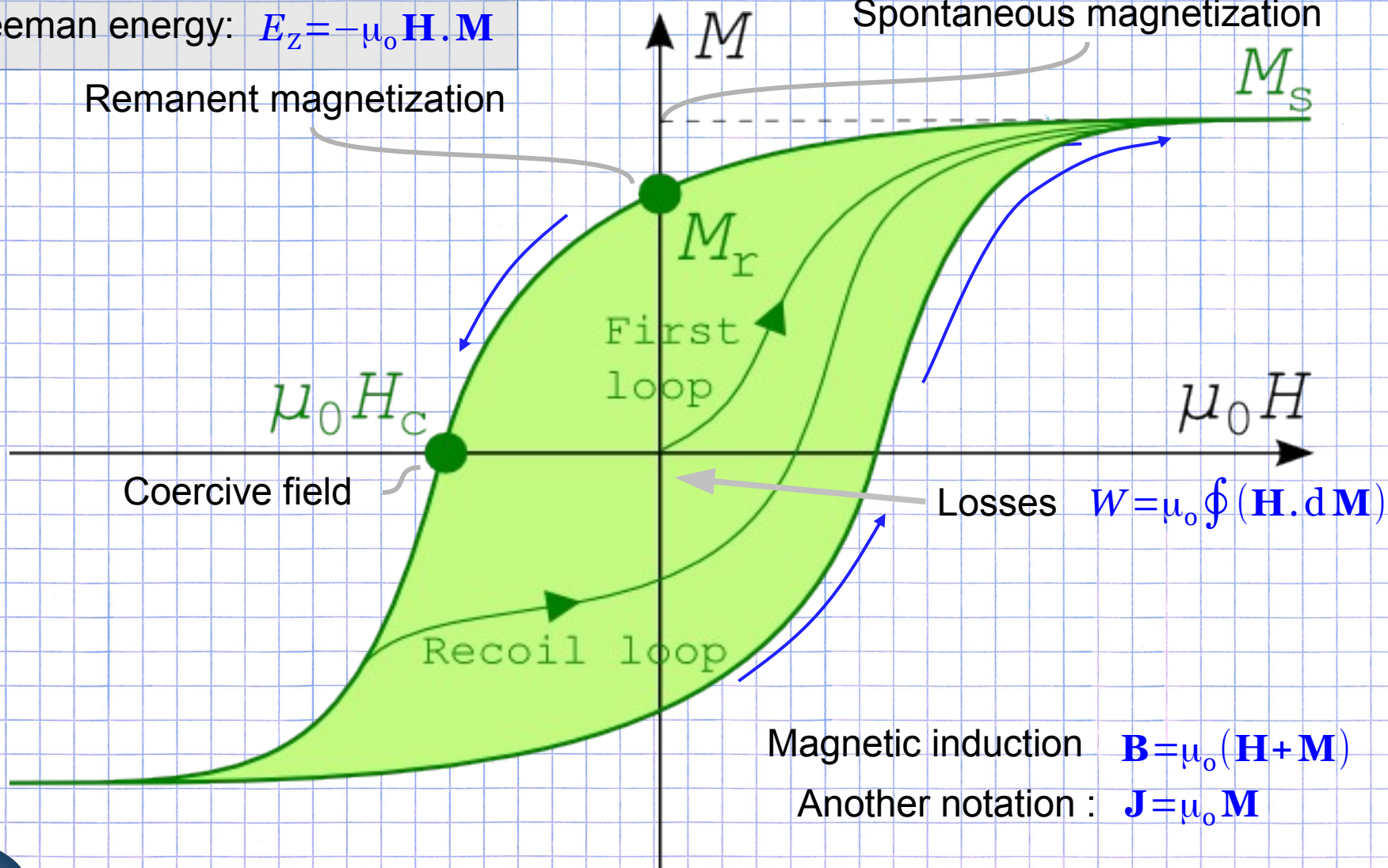


Manipulation of magnetic materials:
 → Application of a magnetic field

Zeeman energy: $E_z = -\mu_0 \mathbf{H} \cdot \mathbf{M}$

Remanent magnetization

Spontaneous magnetization

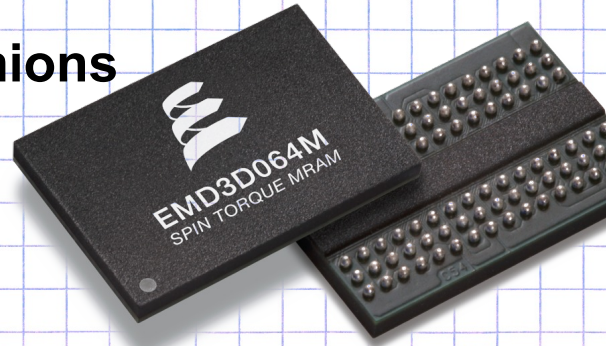
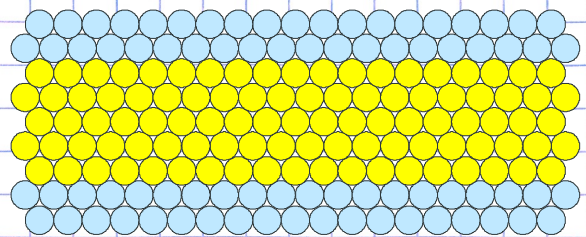
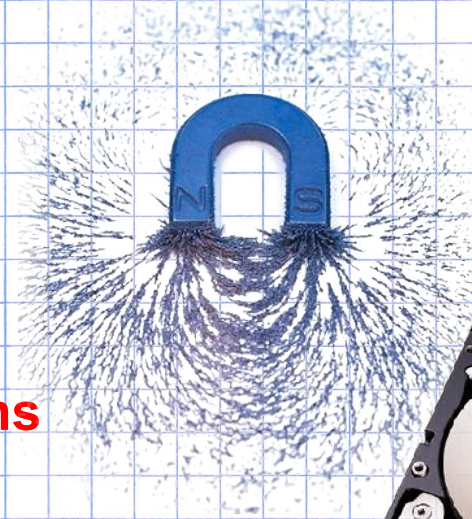


Magnetic induction $\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M})$

Another notation: $\mathbf{J} = \mu_0 \mathbf{M}$



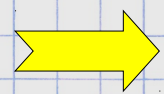
- ➔ 1. Introduction
- ➔ 2. Magnetic ordering in low dimensions
- ➔ 3. Surface / Interface magnetic anisotropy
- ➔ 4. Self-assembled / Self-organized processes
- ➔ 5. More interfacial effects: TMR, RKKY and exchange bias
- ➔ 6. Dzyaloshinskii-Moriya interactions, skyrmions





Elements of theory

- Ising (1925). No magnetic order at $T > 0K$ in 1D Ising chain.
- Bloch (1930). No magnetic order at $T > 0K$ in 2D Heisenberg (spin-waves)
- → N. D. Mermin, H. Wagner, PRL17, 1133 (1966)
- Onsager (1944) + Yang (1951).
2D Ising model: $T_c > 0K$



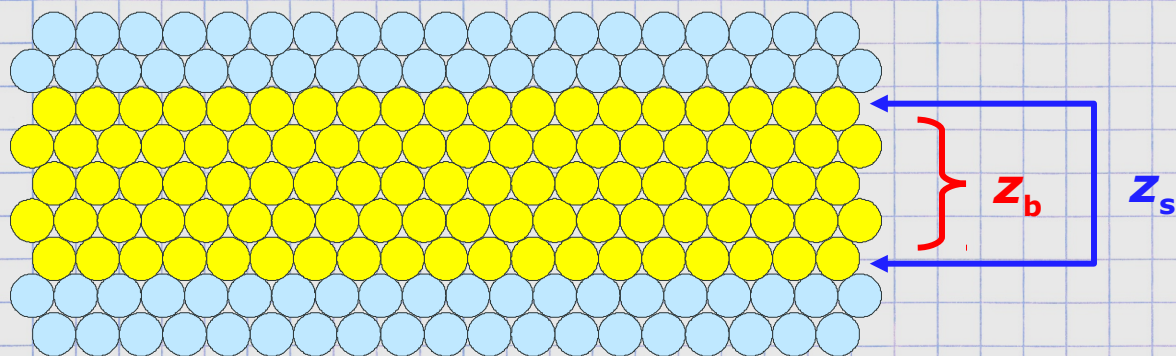
Magnetic anisotropy stabilizes ordering

Naïve views : mean molecular field

$$T_c = \frac{\mu_0 z n_{W,1} n g_J^2 \mu_B^2 J(J+1)}{3k_B}$$



z neighbors



N atomic layers : $\langle z \rangle = z_b - \frac{2(z_b - z_s)}{N}$ $\Rightarrow \Delta T_c(t) \sim t^{-1}$

Less naïve: thickness-dependent mean molecular field

$\Rightarrow \Delta T_c(t) \sim t^{-\lambda}$
 $\lambda = 1$

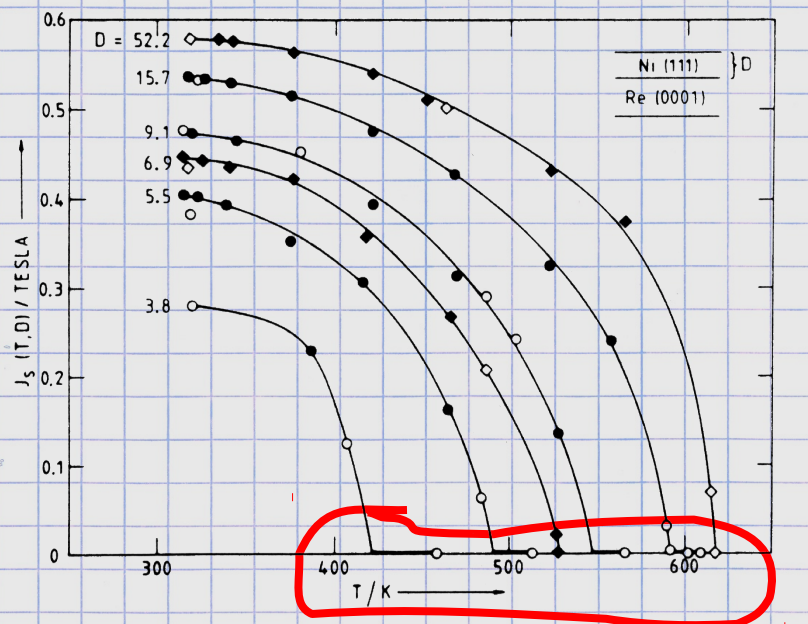
G.A.T. Allan, PRB1, 352 (1970)

Conclusion:
Naïve views are roughly correct



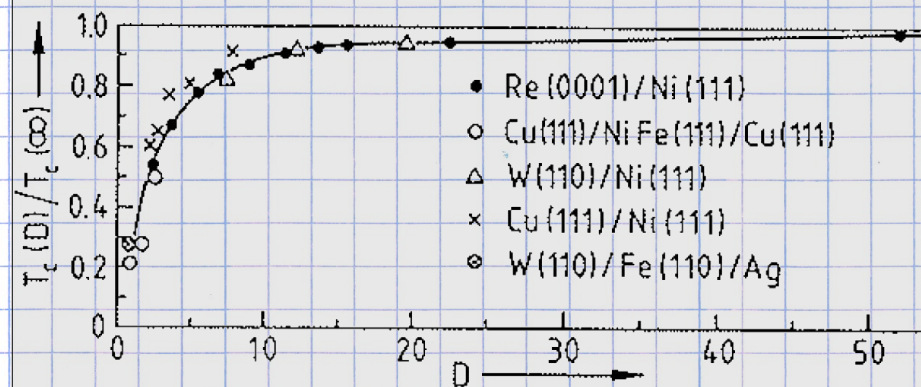
Qualitative

Ni(111)/Re(0001)



R. Bergholz and U. Gradmann, *JMMM*45, 389 (1984)

Quantitative (molecular field)



T_c fitted with molecular field :

$$\Delta T_c(t) \sim t^{-1}$$

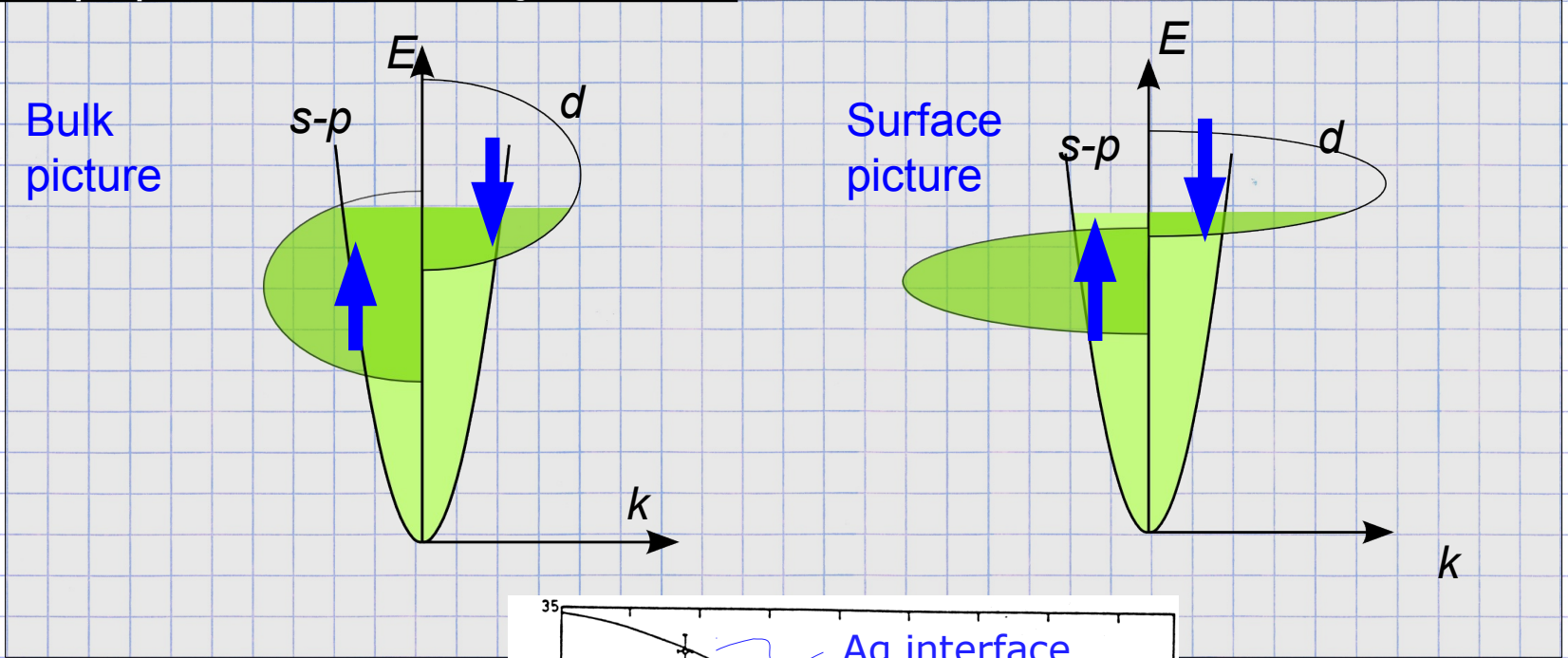
U. Gradmann, *Handbook of Magn. Mater.* Vol.7, ch.1 (1993)

Ordering temperature decreases with thickness
 Noticeable below ≈ 1 nm

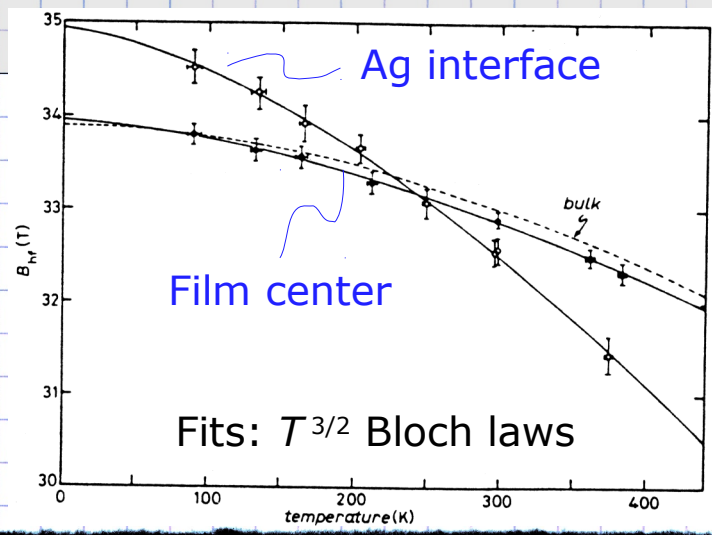


Enhanced moment at surfaces

Simple picture: band narrowing at surfaces



In practice:
20-30 %, however
decays faster with
temperature

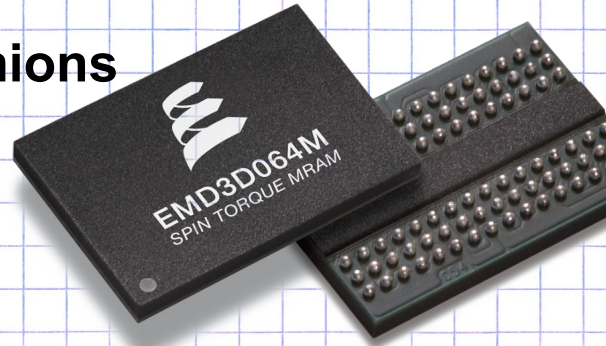
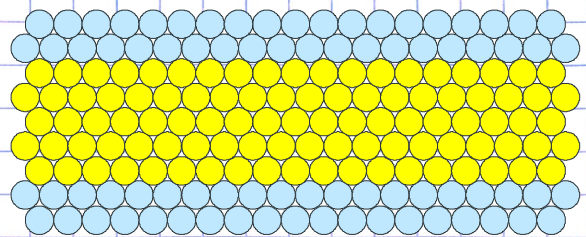
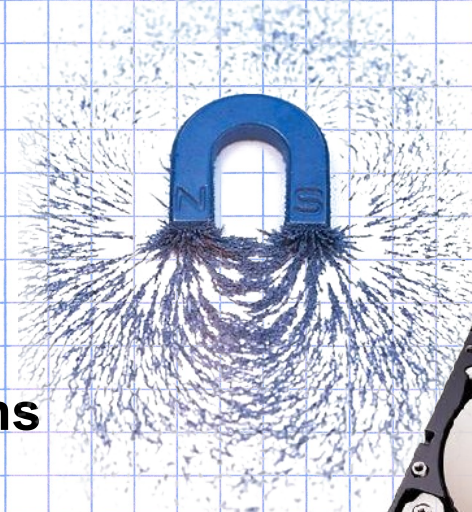


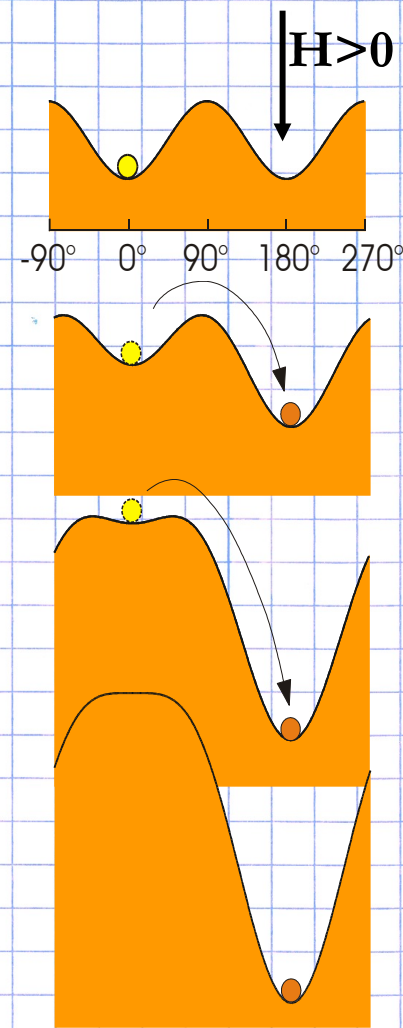
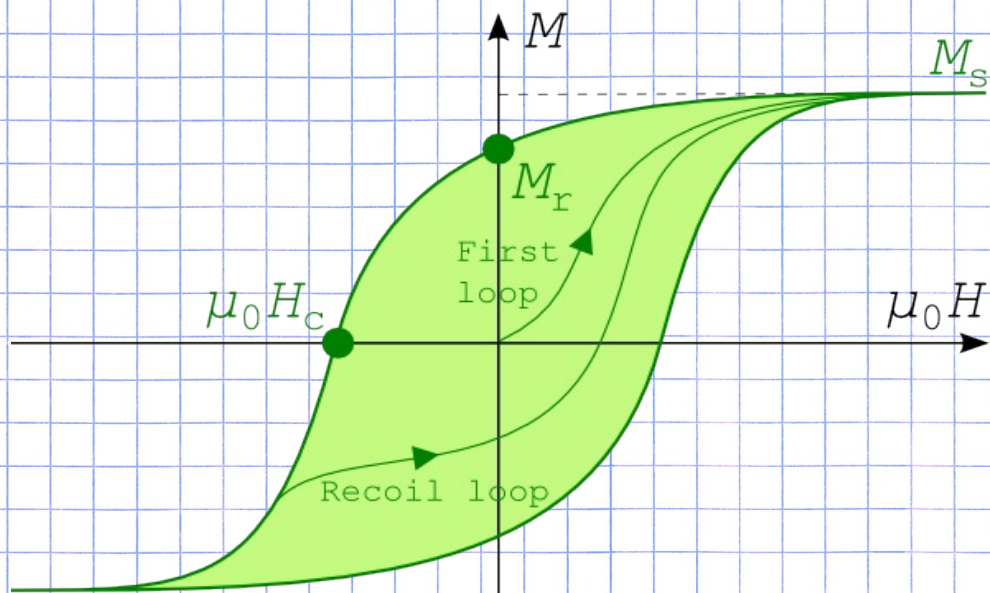
Ag/Fe(110)/W(110)
U. Gradmann et al.



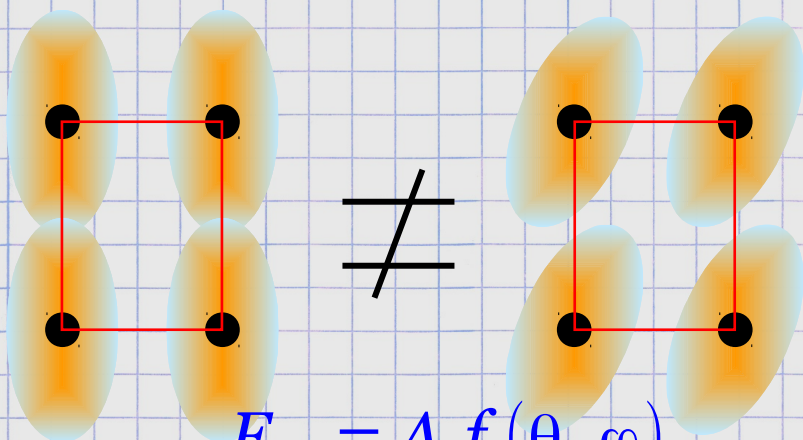


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Magnetocrystalline anisotropy energy



$$E_{mc} = A f(\theta, \varphi)$$

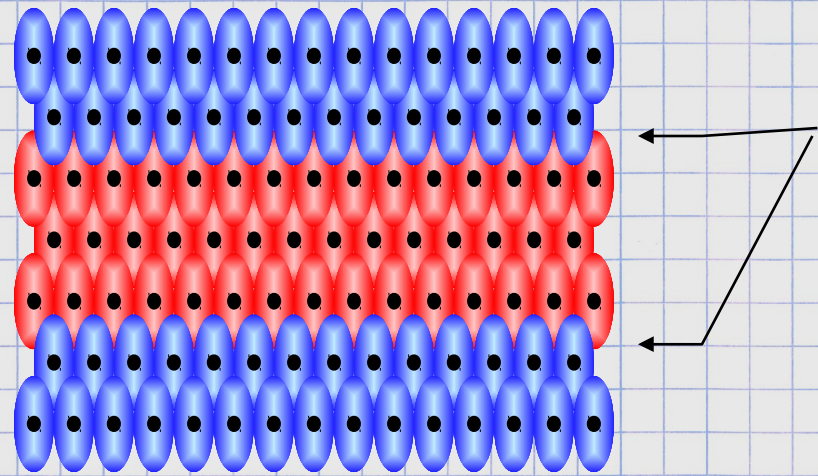
- ↻ Responsible for remanence and coercivity
- ↻ Memories, magnets



Surface anisotropy

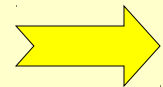
L. Néel,
J. Phys. Radium 15,
15 (1954)

« Superficial magnetic anisotropy and orientational superstructures »



Overview

Breaking of symmetry for surface/interface atoms



Correction to the magneto-crystalline energy

$$E_s = K_{s,1} \cos^2 \theta + K_{s,2} \cos^4 \theta + \dots$$

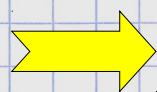
« This surface energy, of the order of 0.1 to 1 erg/cm², is liable to play a significant role in the properties of ferromagnetic materials spread in elements of dimensions smaller than 100Å »

Visionary !

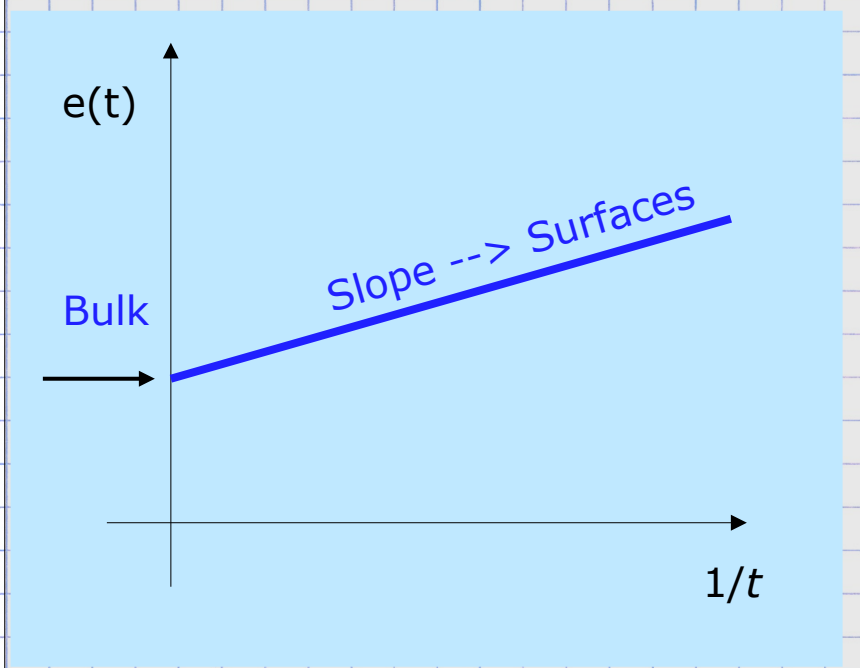


History of surface anisotropy : 1/t plot

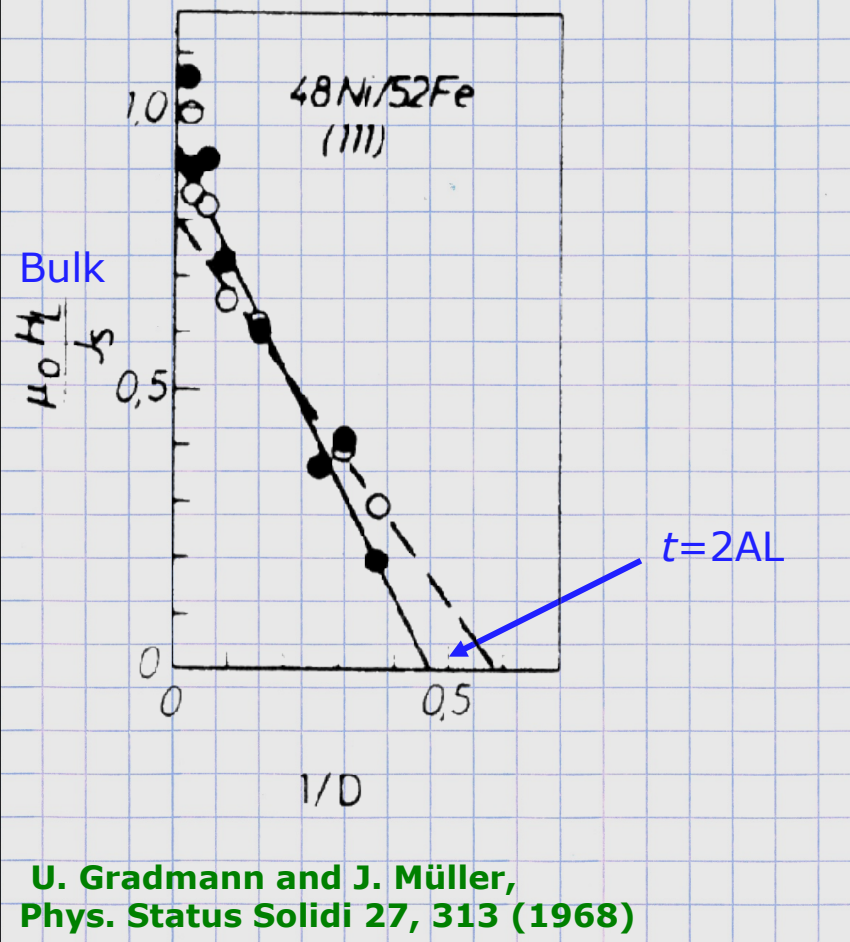
$$\varepsilon(t) = K_v t + 2K_s$$



$$E(t) = K_v + \frac{2K_s}{t}$$



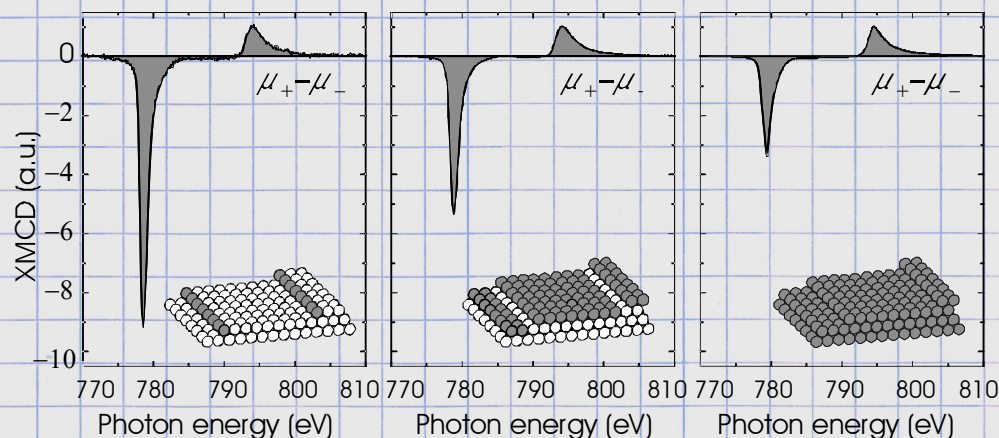
First example of perpendicular anisotropy





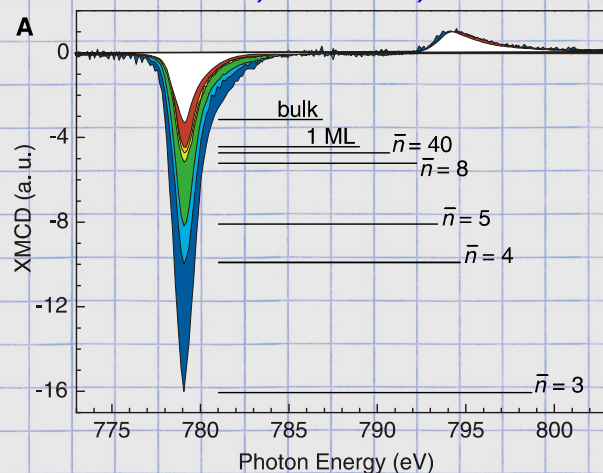
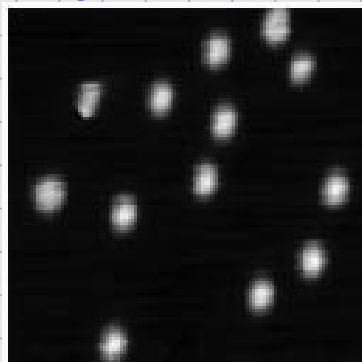
Experimental systems

Co on vicinal Pt(111) probed by Xray dichroism



P. Gambardella et al., *Nature* **416**, 301 (2002)

Single atoms at surface. STM, 8.5nm, 5.5K



P. Gambardella et al., *Science* **300**, 1130 (2003)

Results

- Bulk Co: $40\mu\text{eV}/\text{atom}$
- Co ML: $140\mu\text{eV}/\text{atom}$
- Co bi-wire: $0.34\text{meV}/\text{atom}$
- Co wire: $2\text{meV}/\text{atom}$
- Co bi-atom: $3.4\text{meV}/\text{atom}$
- Co atom: $9.2\text{meV}/\text{atom}$

↪ **Dramatic dimensional effect**

Practical use : past and trends

↪ 3d (mostly Co and Co\Ni) with heavy metal (Pt, Au, Pd...).
Critical thickness 1-2nm

M. T. Johnson, *RPP* **59**, 1409 (1996)

U. Gradmann, *Handbook* **7**, Bushow (1993)

↪ Bonding with oxide : Al_2O_3 ,
 MgO ... ($\rightarrow t_c$ up to 3.5nm)

A. Manchon, *JAP* **103**, 07A912 (2008)

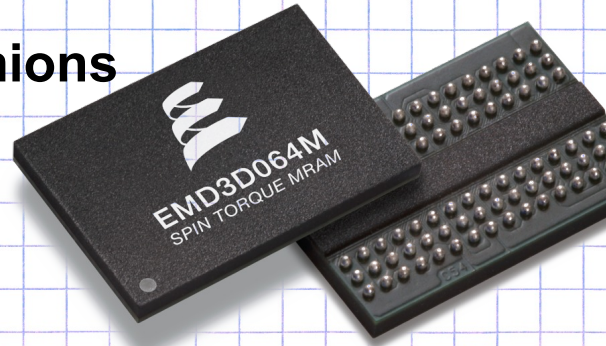
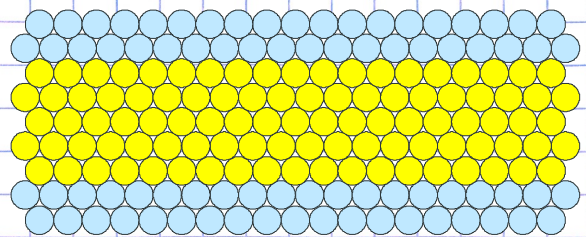
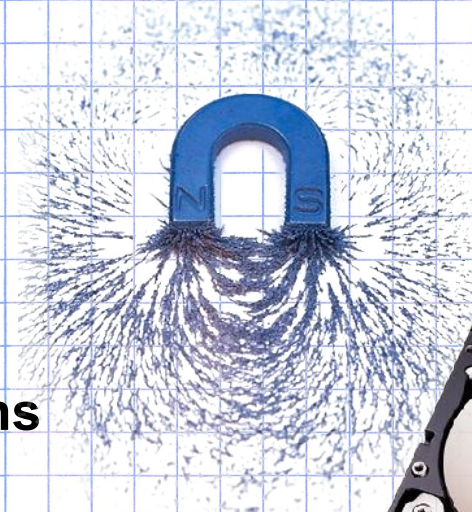
I. G. Rau, *Science* **344**, 988 (2014)

↪ Interface with graphene

J. Coraux, *J. Phys. Chem. Lett.* **3**, 2059 (2012)



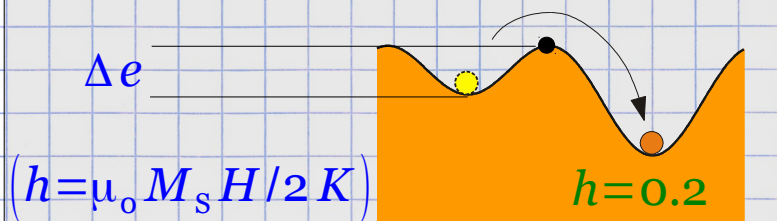
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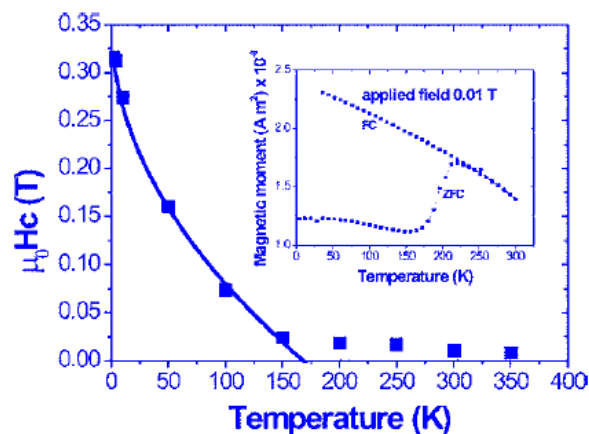


Barrier height

$$\Delta e = e(\theta_{\max}) - e(0) = (1-h)^2$$



J. Appl. Phys. 99, 08Q514 (2006)



Thermal activation

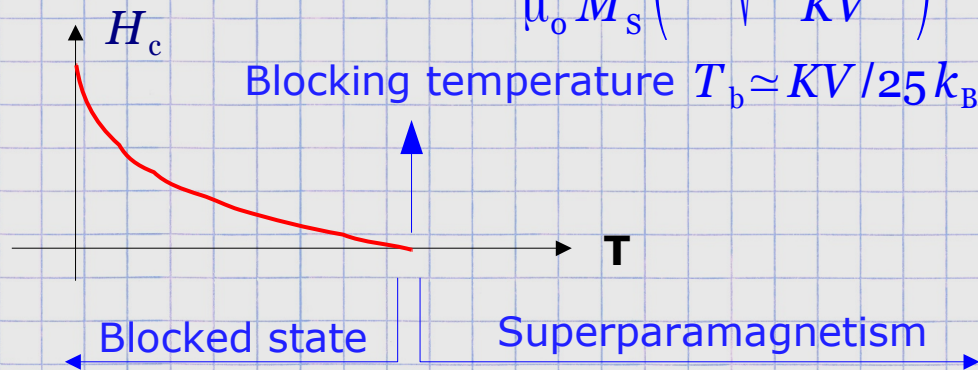
Brown, Phys.Rev.130, 1677 (1963)

$$\tau = \tau_0 \exp\left(\frac{\Delta \mathcal{E}}{k_B T}\right) \implies \Delta \mathcal{E} = k_B T \ln(\tau / \tau_0)$$

$$\tau_0 \approx 10^{-10} \text{ s}$$

Lab measurement: $\tau \approx 1 \text{ s} \implies \Delta \mathcal{E} \approx 25 k_B T$

$$\implies H_c = \frac{2K}{\mu_0 M_s} \left(1 - \sqrt{\frac{25 k_B T}{KV}}\right)$$



E. F. Kneller, J. Wijn (ed.) Handbuch der Physik XIII/2: Ferromagnetismus, Springer, 438 (1966)

M. P. Sharrock, J. Appl. Phys. 76, 6413-6418 (1994)

↪ Coercivity and remanence features lost for small anisotropy or small size

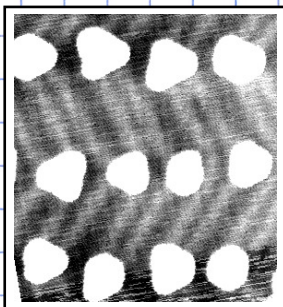
Notice, for magnetic recording :

$$\tau \approx 10^9 \text{ s} \quad KV_b \approx 40 - 60 k_B T$$

SELF-ORGANIZATION – 3D columnar growth

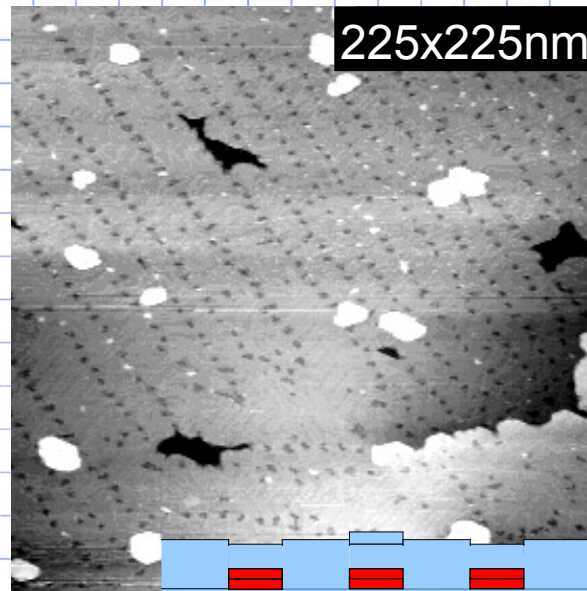


0.2ML
Co/Au(111)
@ 300K



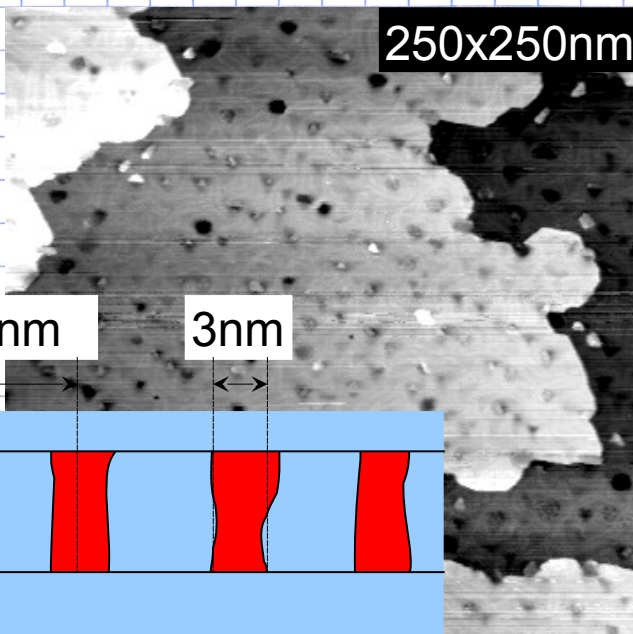
250x250nm

+3.8ML Au
@ 400K



225x225nm

+ [0.1ML Co,
0.9ML Au]_n
@ 425K

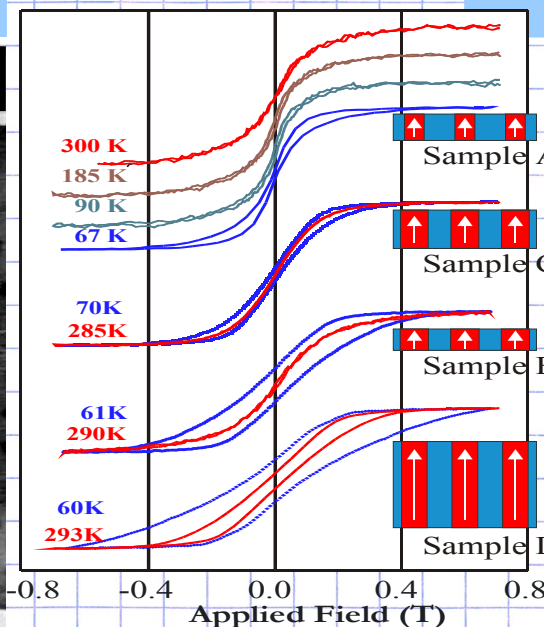


250x250nm

7.5nm

3nm

6nm



↪ 3D replication
of 2D pattern
↪ Recovery of
coercivity and
remanence
↪ Similar to columns
of CoCr for
hard disk drives

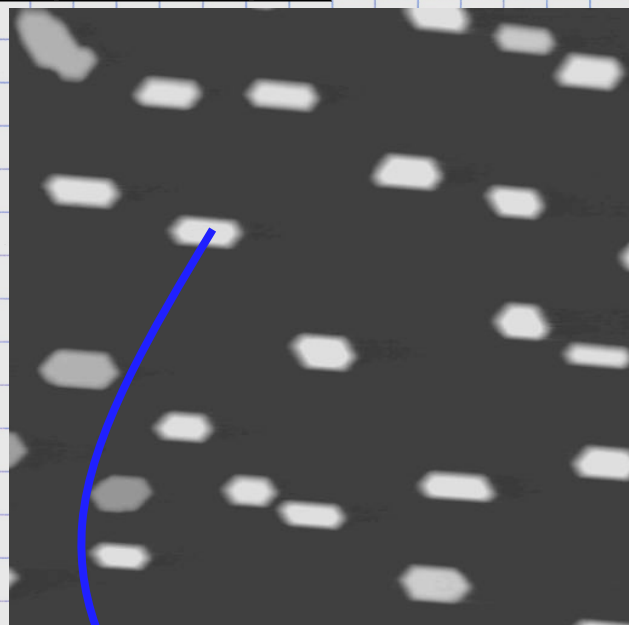
O. Fruchart et al., PRL23 (14), 2769 (1999)



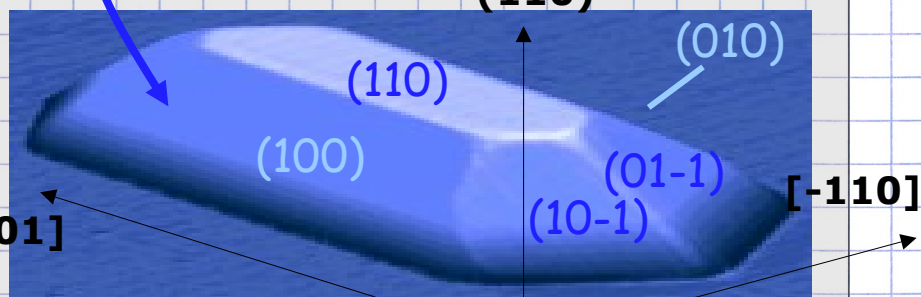


Shape in real space

Fe/W(110)/Al₂O₃(11-20)

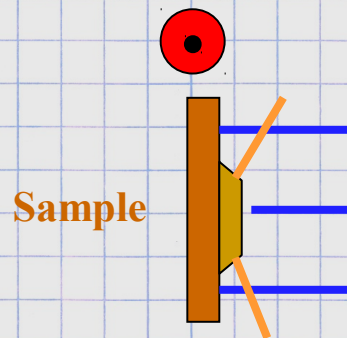


AFM
5x5 μm



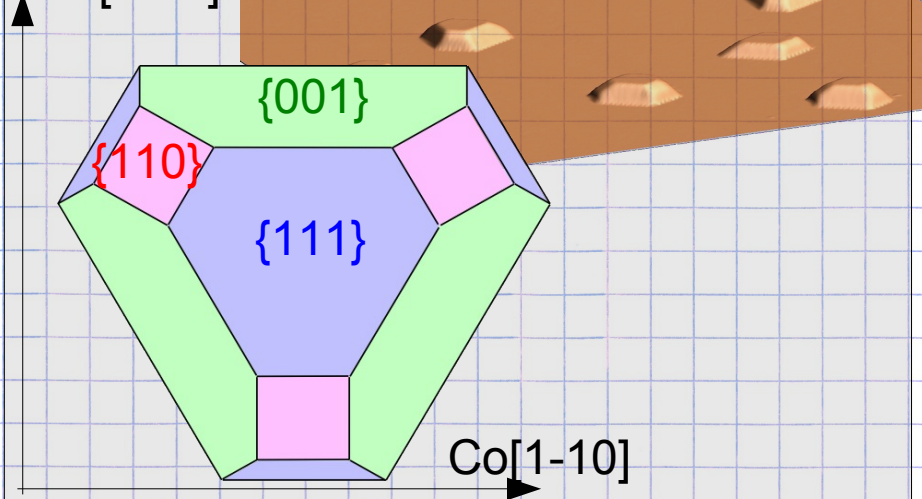
Atomically flat facets

RHEED beam



fcc Co(111) dots

Co[11-2]



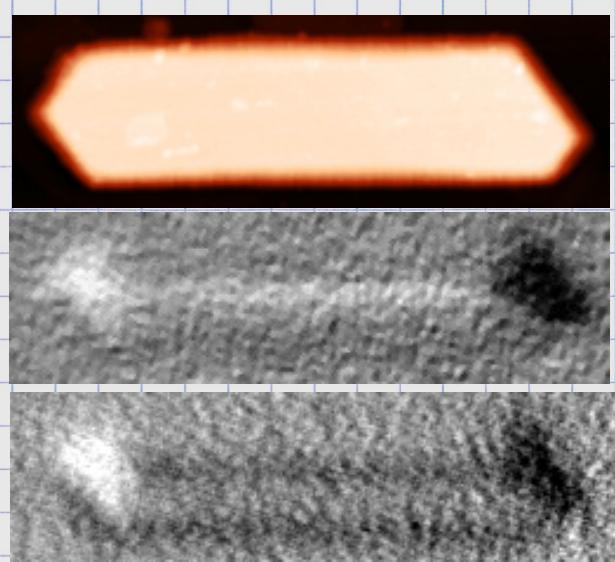
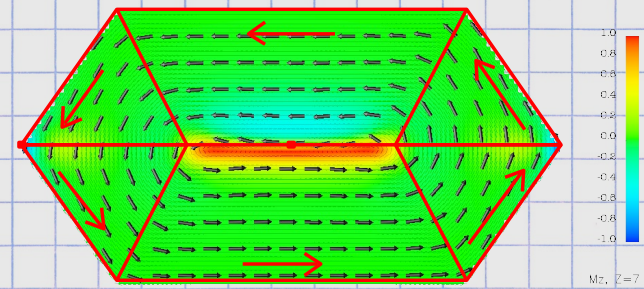
O. Fruchart et al., *J. Phys.: Condens. Matter* 19, 053001, Topical Review (2007).





Magnetization processes inside domain walls

Landau states: flux closure

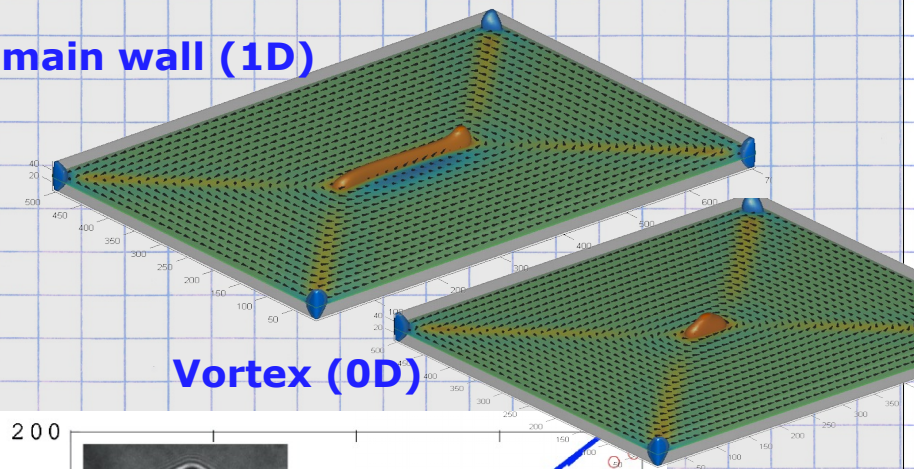


X-ray Magnetic Circular Dichroism
PhotoEmission Electron Microscopy

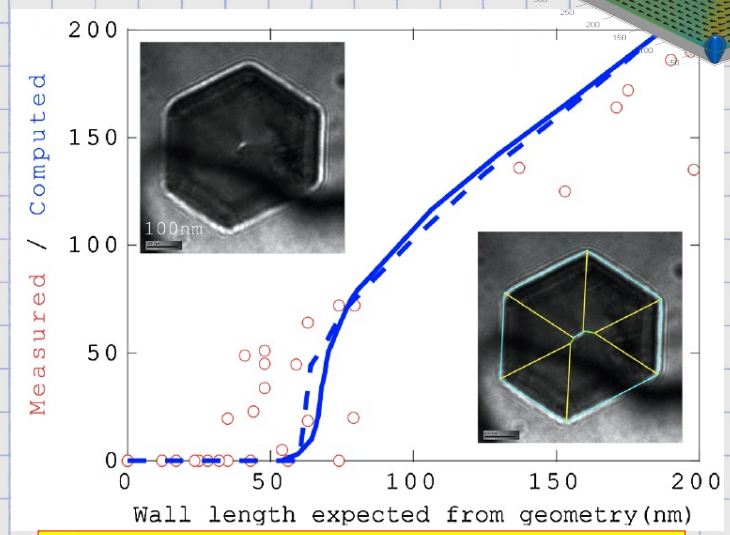
F. Cheynis et al., PRL 102, 107201 (2009)

Dimensionality cross-over : from 0D to 1D textures

Domain wall (1D)



Vortex (0D)

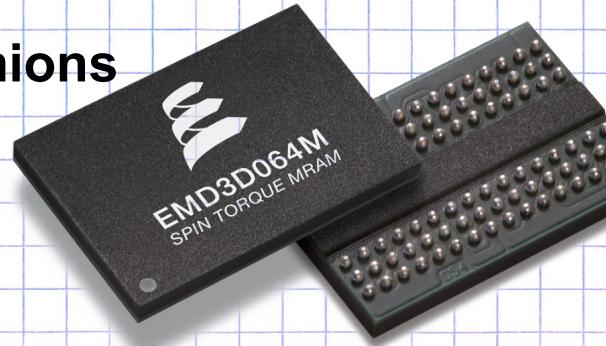
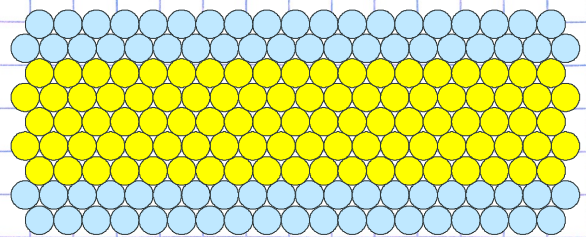
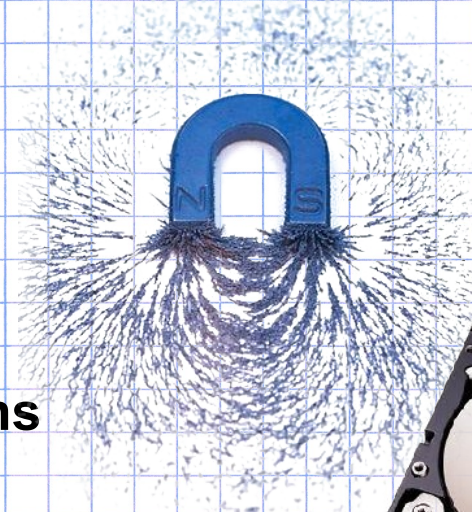


Transition is of second order

A. Masseboeuf et al., PRL 104, 127204 (2010)

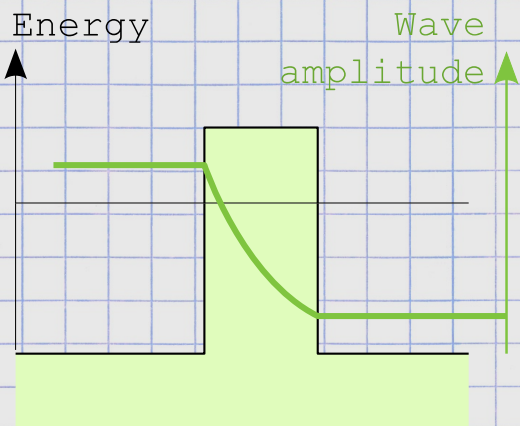


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Tunneling resistance



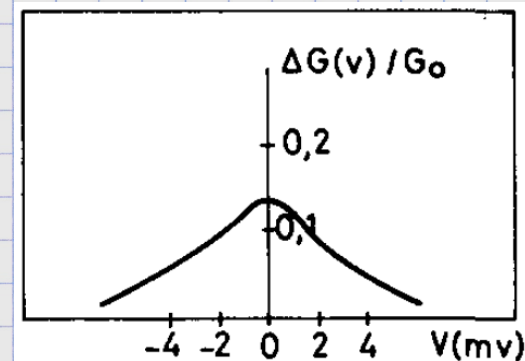
⇒ Exponential decay of wave functions in the barrier

⇒ Used in high sensitivity sensors, memory reading, HDD head...
 ⇒ TMR should be bound to circa 50 % (3d ferromagnets)

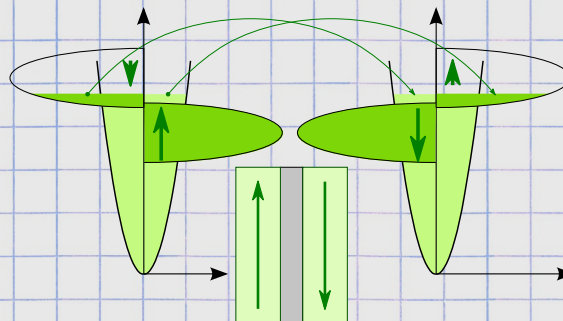
Tunneling magneto-resistance

⇒ Discovery at 4.2K for Fe/Ge/Fe stacks

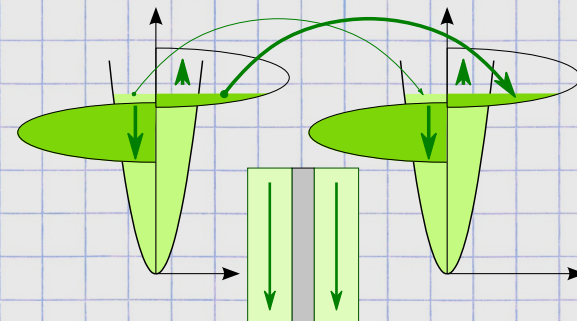
M. Julliere, *Phys. Lett.* 54A, 3, 225 (1975)



Antiparallel (AP)



Parallel (P)

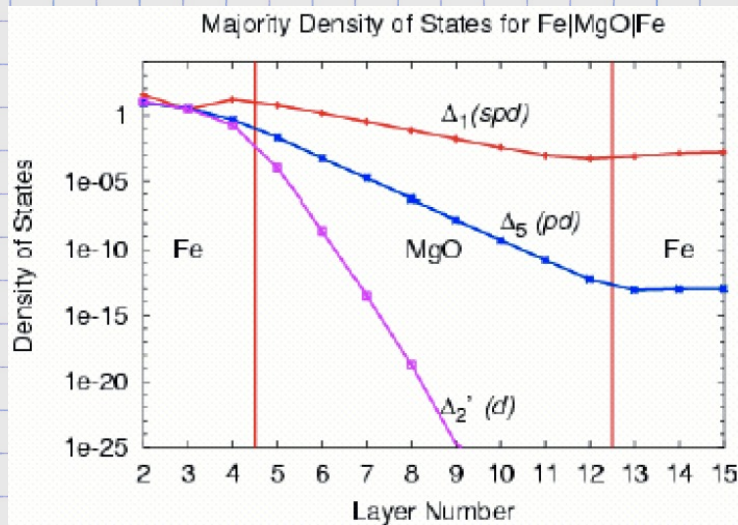
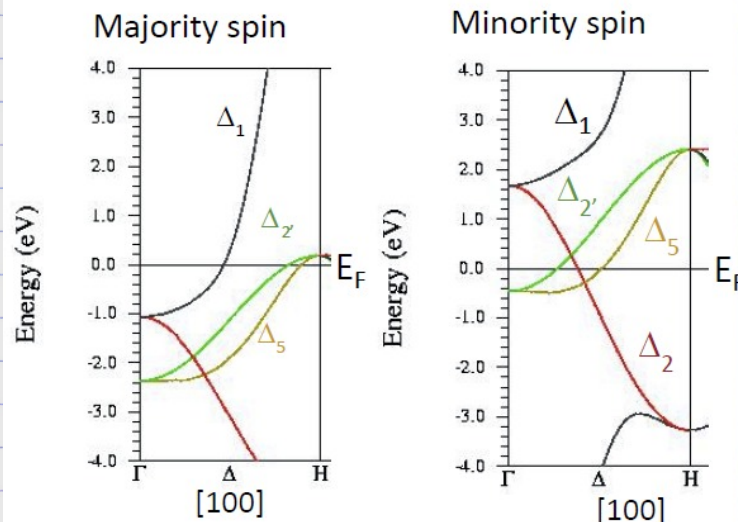


⇒ Define polarization :
$$P = \frac{D_{Maj} - D_{Min}}{D_{Maj} + D_{Min}}$$

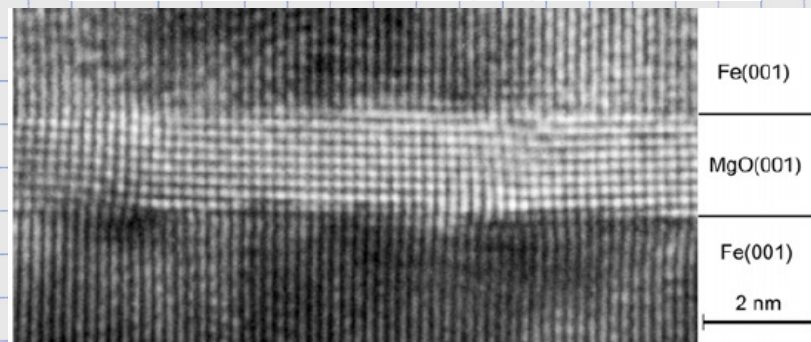
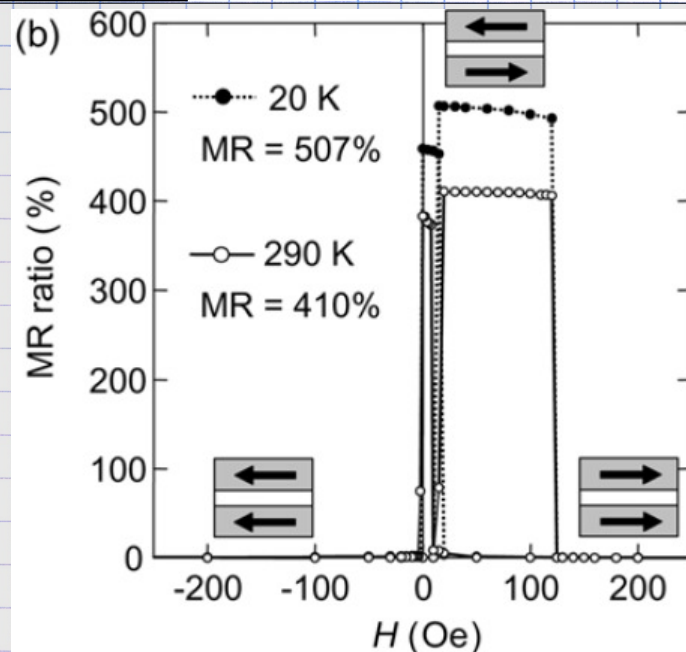
⇒ Define and evaluate TMR ratio :
$$TMR = \frac{\Delta R}{R_p} = \frac{2P^2}{1 - P^2}$$



Prediction



Implementation



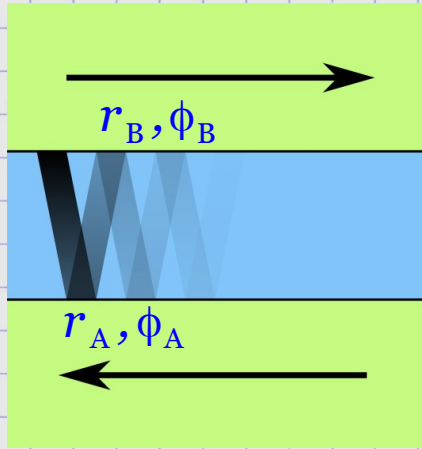
S. Yuasa, J. Phys. D 40, R337 (2007)

⇒ NB : >500 % with CoFeB electrodes

Butler et al., Phys. Rev. B 63, 220403 (R) (2001)

The physics

Spin-dependent quantum confinement in the spacer layer



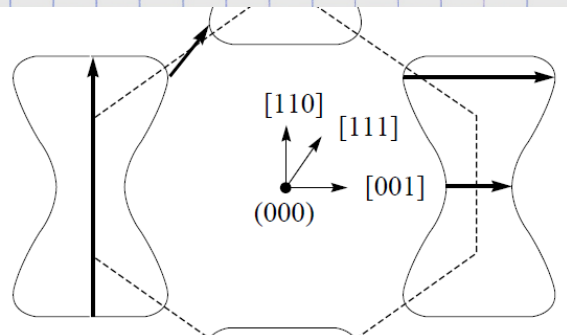
Forth & back phase shift

$$\Delta\phi = qt + \phi_A + \phi_B$$

Spin-dependent

$$r_A, \phi_A, r_B, \phi_B$$

⇒ Constructive or destructive interferences with spacer thickness



Cu Fermi surface

⇒ Depends on crystal direction

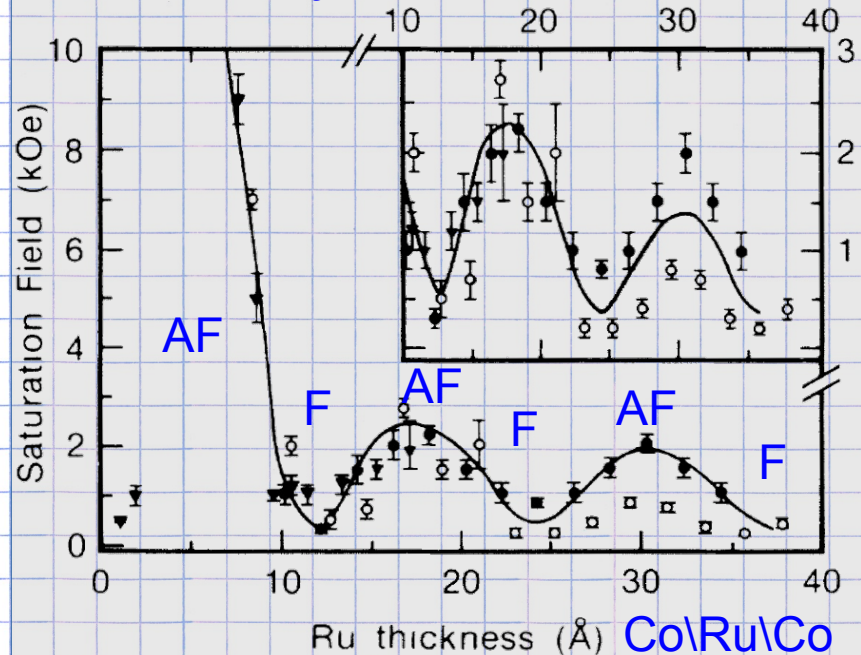
Illustration

Coupling strength:

$$E_S = J(t) \cos\theta \quad \text{in } J/m^2$$

$$\theta = \langle m_1, m_2 \rangle$$

$$\text{with: } J(t) = \frac{A}{t^2} \sin(q_\alpha t + \Psi)$$



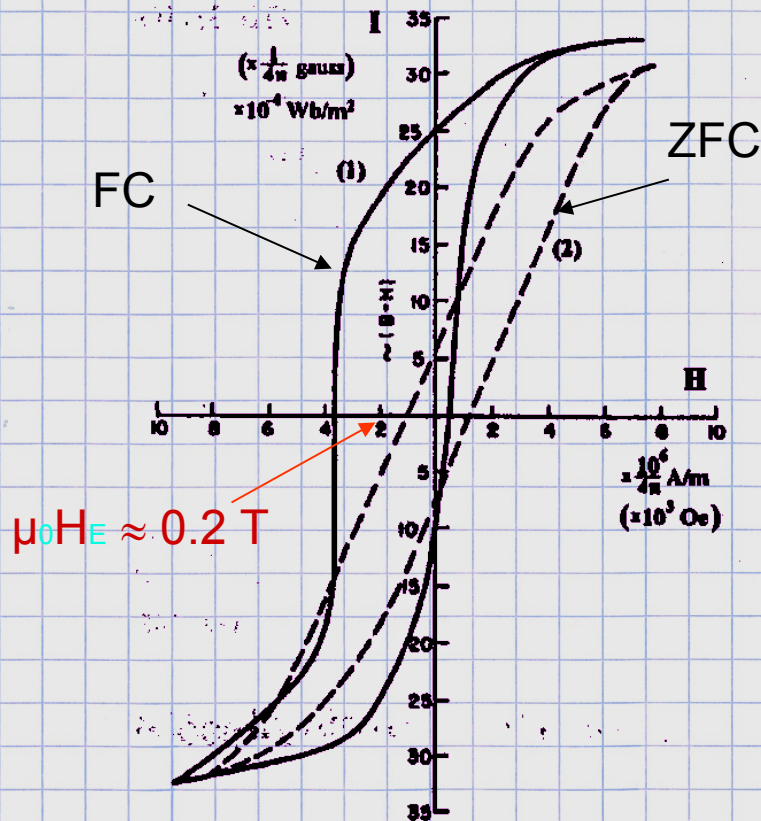
S. S. P. Parkin et al., PRL64, 2304 (1990)

P. Bruno, J. Phys. Condens. Matter 11, 9403 (1999)

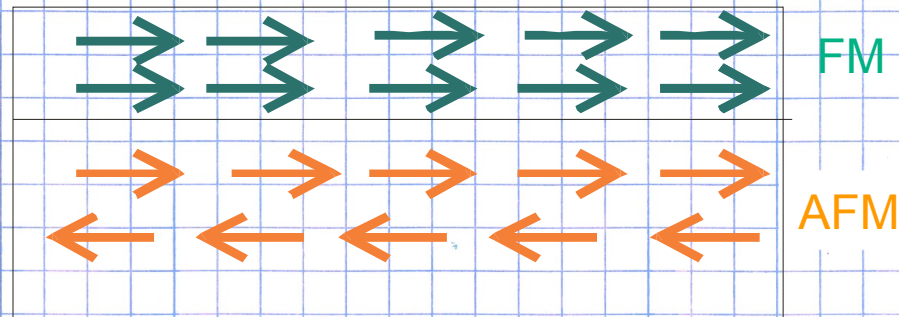


Seminal studies

Oxidized Co nanoparticles



Meiklejohn and Bean,
Phys. Rev. 102, 1413 (1956),
Phys. Rev. 105, 904, (1957)



Field-cooled hysteresis loops

↪ Shift in field

↪ Increase coercivity

Exchange bias

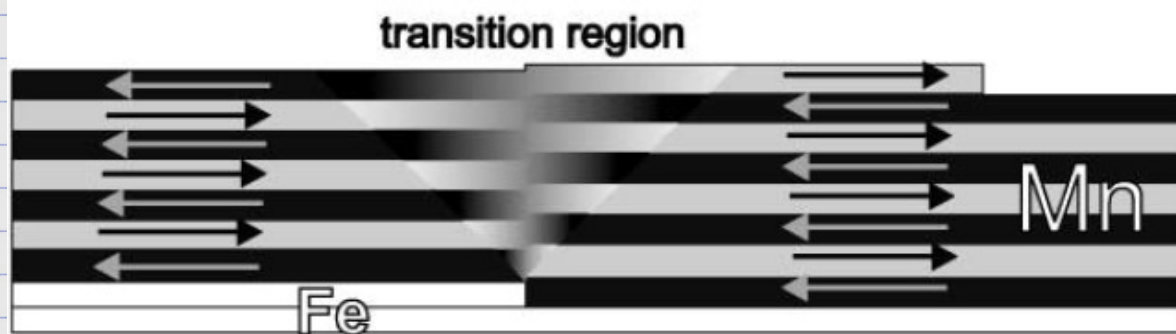
J. Nogués and Ivan K. Schuller
J. Magn. Magn. Mater. 192 (1999) 203

Exchange anisotropy—a review

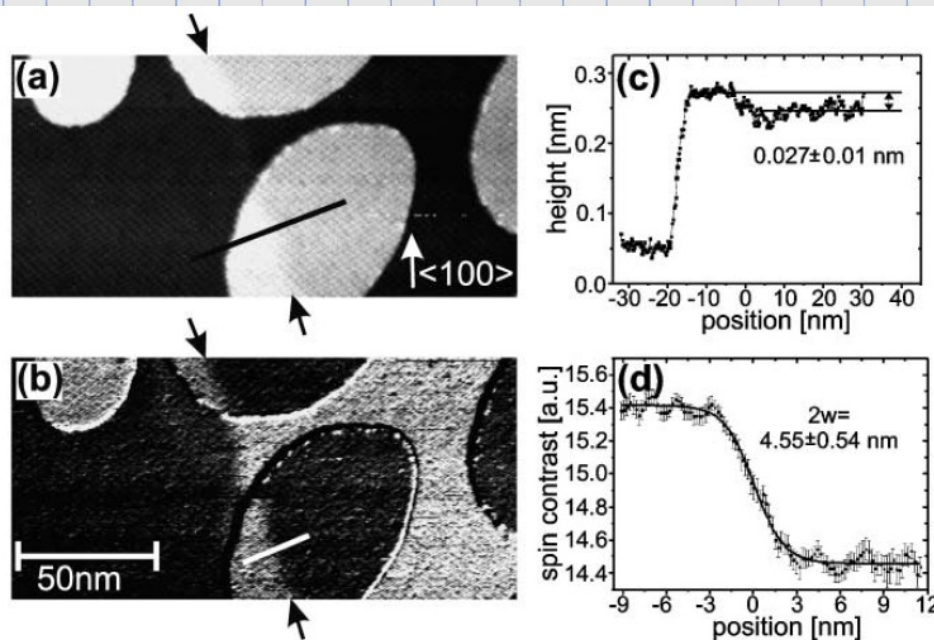
A E Berkowitz and K Takano
J. Magn. Magn. Mater. 200 (1999)



Frustration starting at step edges



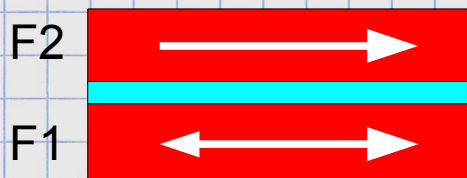
Analysis with spin-polarized STM



U. Schlickum, *Phys. Rev. Lett.* **92**, 107203 (2004)



RKKY Synthetic Ferrimagnets (SyF) — Basics



Crude phenomenology:



$$M = \frac{|e_1 M_1 - e_2 M_2|}{e_1 + e_2} \quad K = \frac{e_1 K_1 + e_2 K_2}{e_1 + e_2}$$

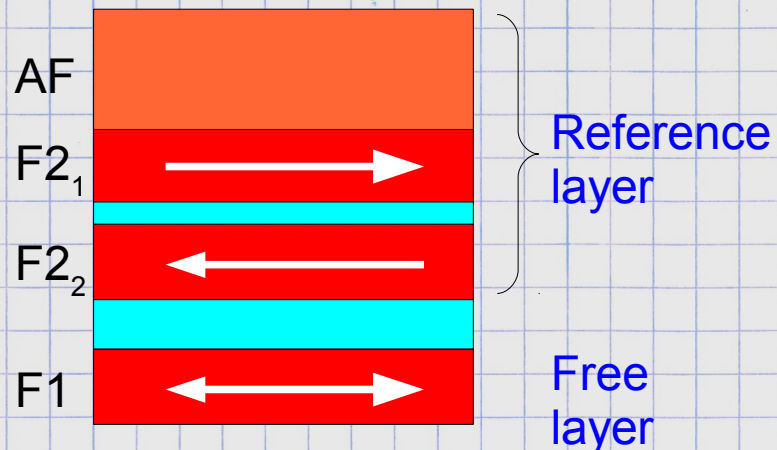
$$H_c \approx \frac{e_1 M_1 H_{c,1} + e_2 M_2 H_{c,2}}{|e_1 M_1 - e_2 M_2|}$$

⇒ Enhances coercive field

⇒ Reduces cross-talk

Spin valves

⇒ 'Free' and reference layers



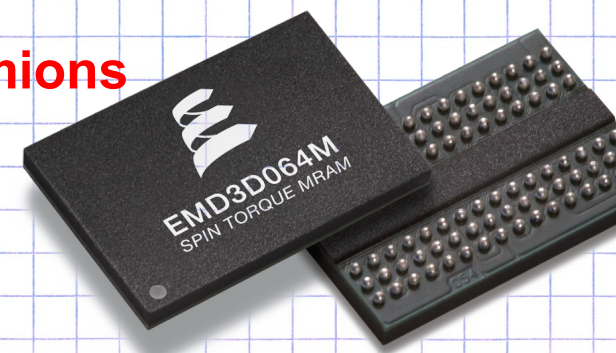
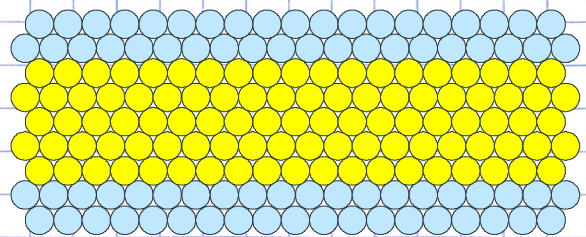
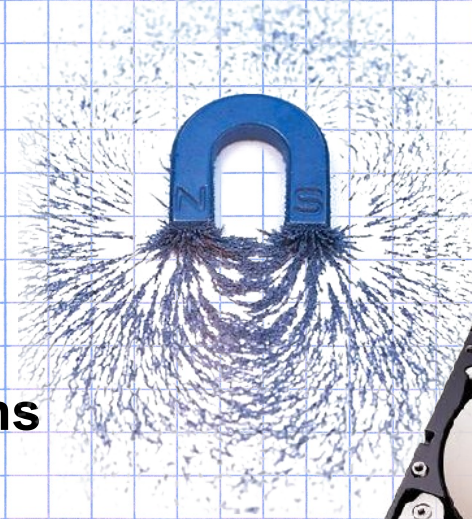
Practical aspects

⇒ Ru spacer layer (largest effect)

⇒ Control thickness within a few Angströms !



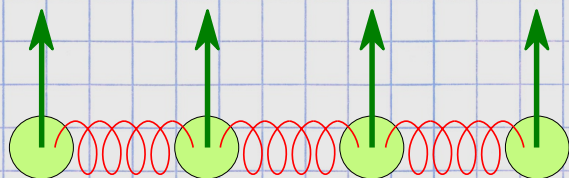
- ➔ 1. Introduction
- ➔ 2. Magnetic ordering in low dimensions
- ➔ 3. Surface / Interface magnetic anisotropy
- ➔ 4. Self-assembled / Self-organized processes
- ➔ 5. More interfacial effects: TMR, RKKY and exchange bias
- ➔ 6. Dzyaloshinskii-Moriya interactions, skyrmions





The usual ferromagnetic exchange interaction

$$E_{1,2} = -J \mathbf{S}_1 \cdot \mathbf{S}_2$$



Magnetic layer

⇒ Favors parallel alignment

⇒ Ferromagnetic ordering

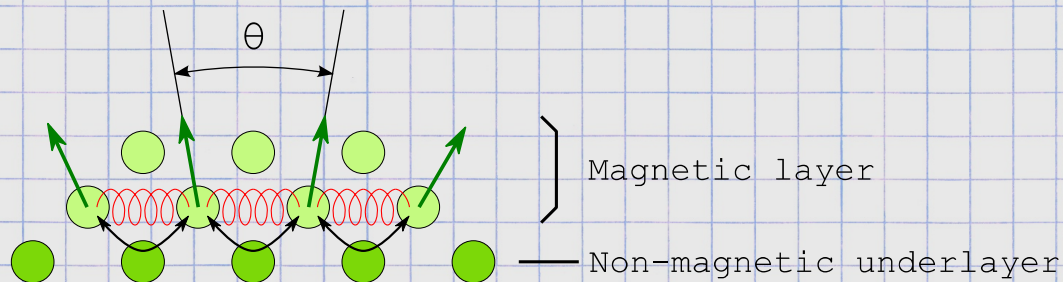
The Dzyaloshinskii-Moriya interaction

$$E_{1,2} = -\mathbf{D}_{1,2} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$$

Symmetry considerations

→ Requires absence of inversion symmetry

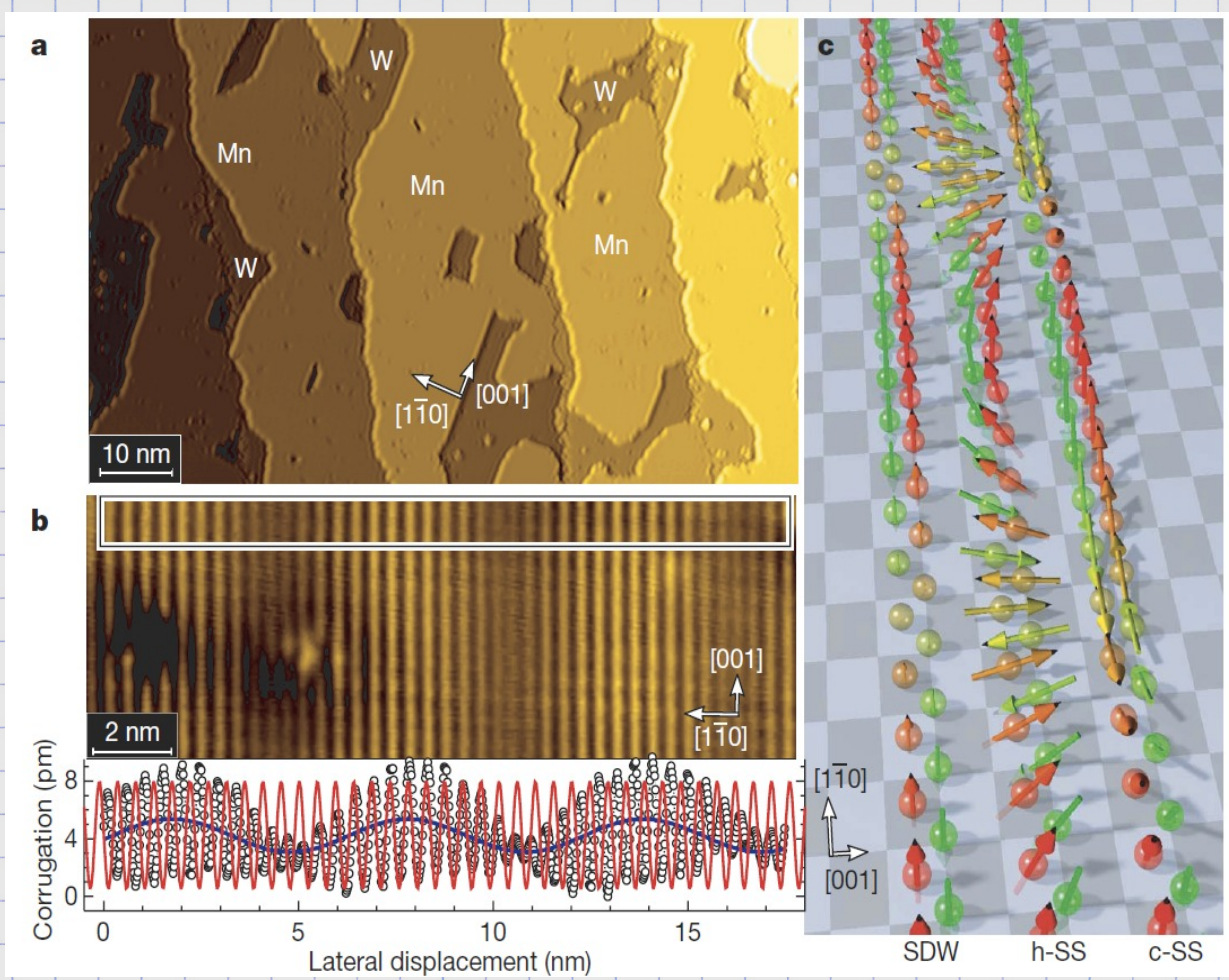
→ May be bulk or interfacial



⇒ Favors spin spirals or cycloids



Chiral spin structures at interfaces Mn/W(110)



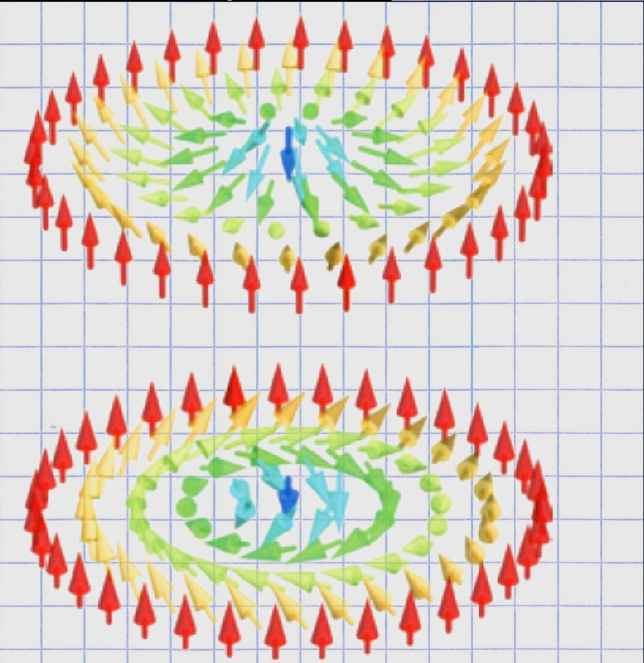
Spin-polarized STM

M. Bode et al., Nature 477, 190 (2007)





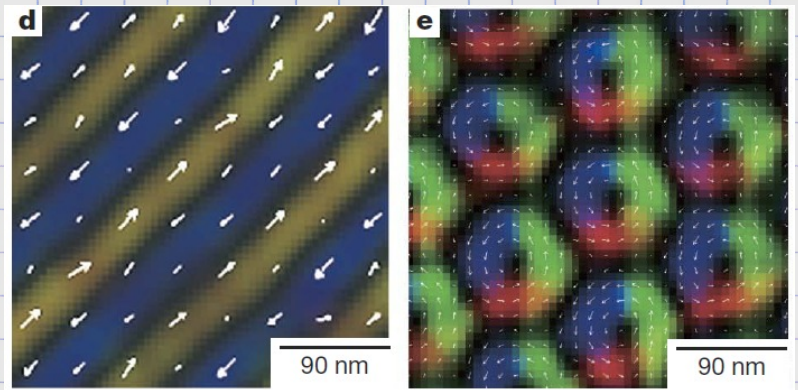
What is a skyrmion ?



- ⇒ Spiral or chiral OD texture
- ⇒ Topological protection
- ⇒ NB : is NOT a magnetic vortex

First proof (bulk) $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Si}$

Spiral phase under perpendicular field



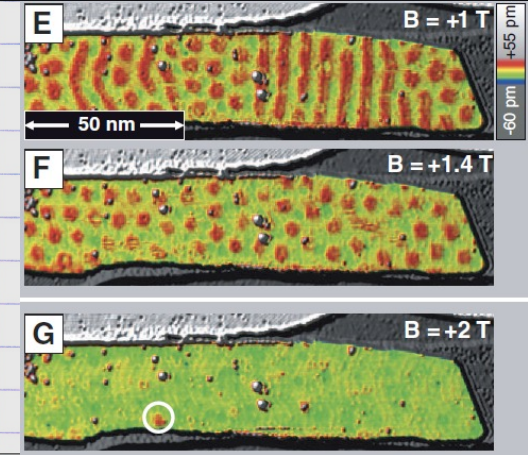
$H=0$

$H \neq 0$

⇒ Array of skyrmions

X. Z. Yu et al., Nature 465, 901 (2010)

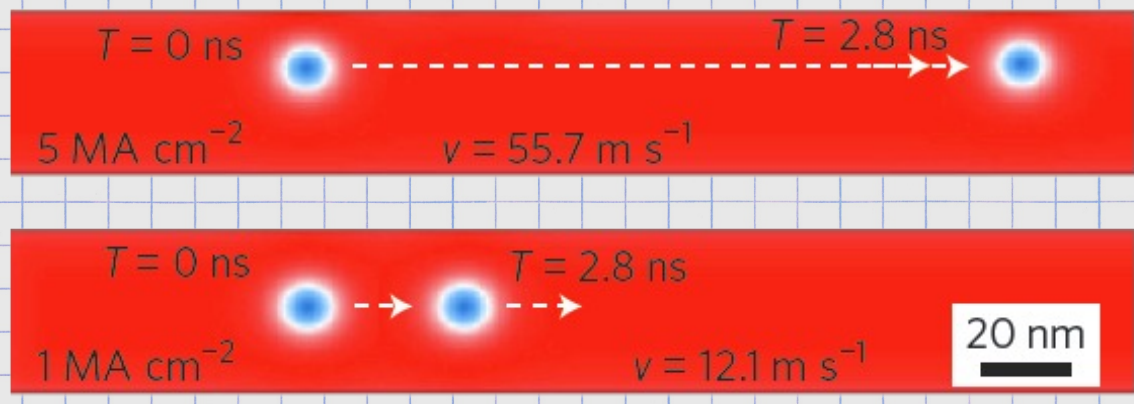
First proof (interface) Pd/Fe/Ir(111)



N. Romming, Science 341 (2013)



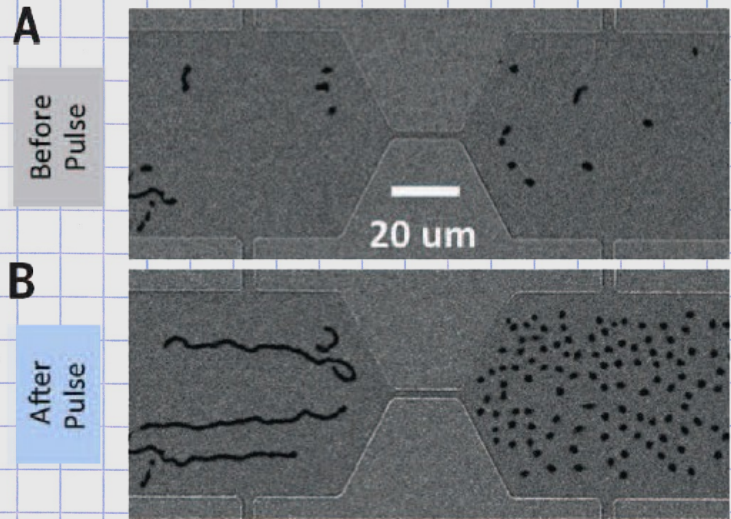
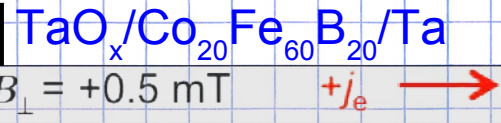
Simulations



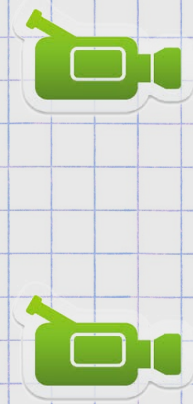
- ⇒ Single skyrmions may exist as metastable entities
- ⇒ Skyrmions may be moved with spin-polarized current (spin transfer effect)

A. Fert et al., Nature Nanotech. 8, 152 (2013)

Experiments



- ⇒ Skyrmions may be nucleated
- ⇒ Skyrmions may be moved with electric current



W. Jiang et al., Science 349, 283 (2015)

Epitaxy and magnetic materials

O. Fruchart



Institut NEEL

CNRS & Univ. Grenoble - Alpes

Grenoble - France



Institut Néel, Grenoble

<http://perso.neel.cnrs.fr/olivier.fruchart/>