

Nano-objects: (some) fabrication methods, (some) magnetic properties.



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<http://lab-neel.grenoble.cnrs.fr/themes/couches/ext/slides/>



I. Fabrication methods

- ➡ 1. Epitaxial self-assembly & self-organization
- ➡ 2. Other routes: electrochemistry, chemistry,
physical paths to clusters, exotic means
- ➡ 3. Future prospects for self-organization.

II. Selected topics for Magnetism

- ➡ 1. Magnetic order
- ➡ 2. Magnetic anisotropy
- ➡ 3. Magnetization reversal and superparamagnetism.
- ➡ 4. Micromagnetism



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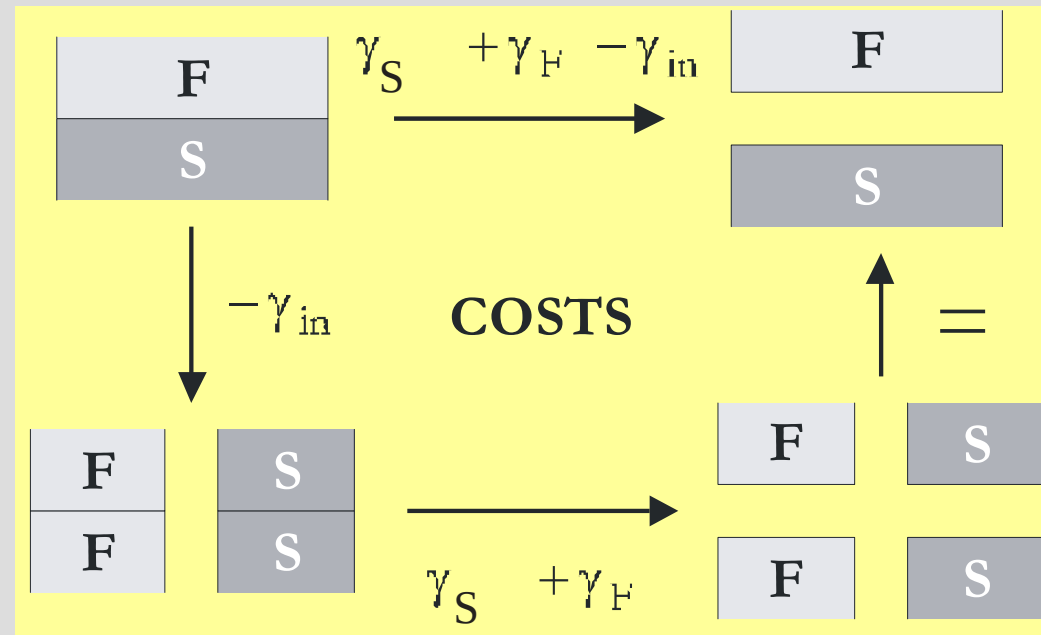
II. Selected topics for Magnetism

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- ➡ **4. Micromagnetism**



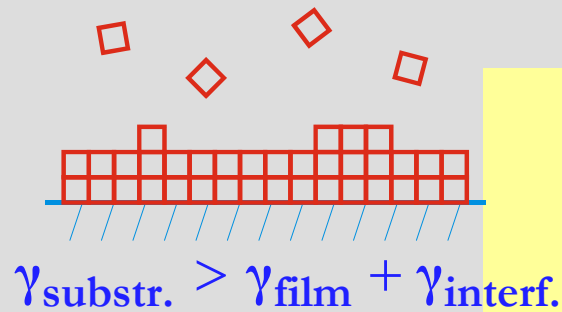
Macroscopic concept:
surface/interface
energies.

2D

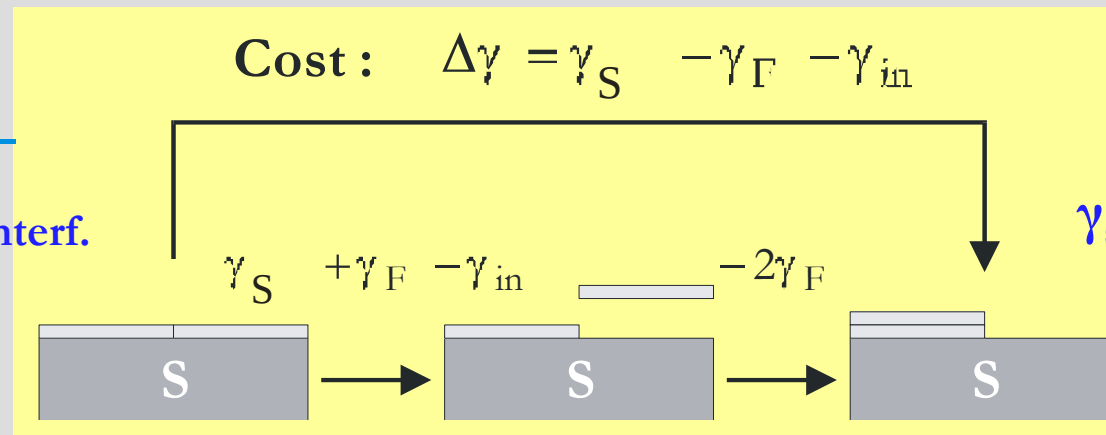
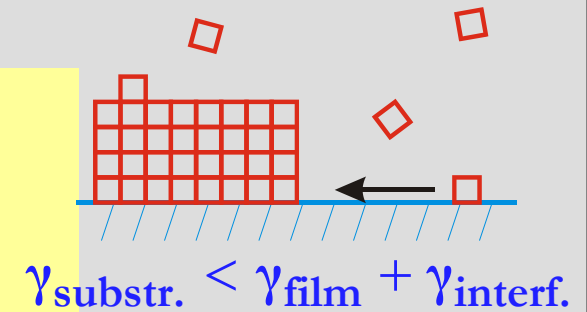


3D

Franck van der Merwe



Volmer-Weber



E.Bauer, Z.Kristallogr.110, 372 (1958)

E.Bauer, Phys.Rev.B 33, 3657 (1986)

What is the shape of the droplet of a crystal?



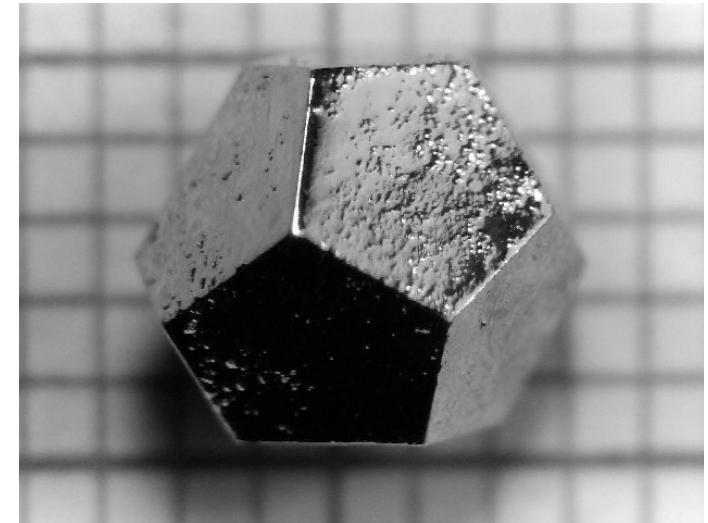
Magnetite (« Loadstone »)

<http://geology.about.com>



Quartz

<http://www.theimage.com>



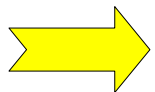
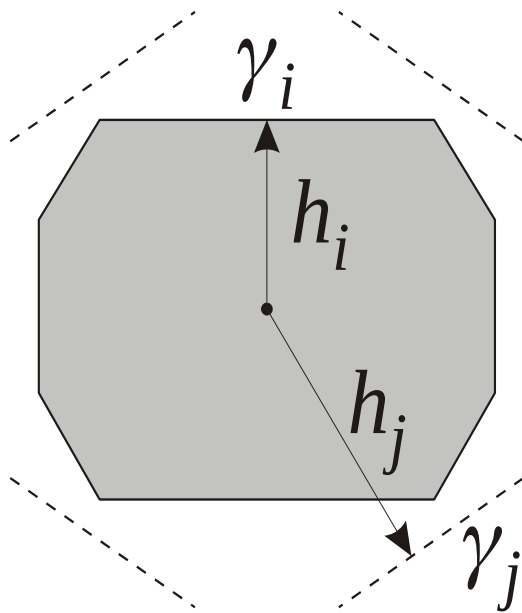
Ho-Mg-Zn

<http://cmp.ameslab.gov/personnel/canfield/>

Wulff's theorem

Free crystal (growth from melt)

$$\frac{\gamma_i}{h_i} = \text{Constant}$$

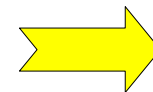
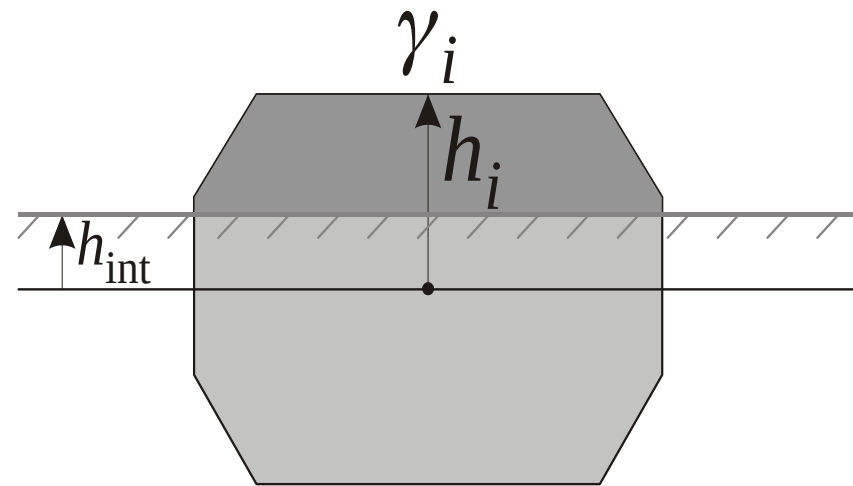


No facets with high surface energy

Wulff Kaishev's theorem

Supported crystal (growth on surfaces)

$$\frac{\gamma_i}{h_i} = \frac{\gamma_S - \gamma_{\text{int}}}{h_{\text{int}}} = \text{Constant}$$

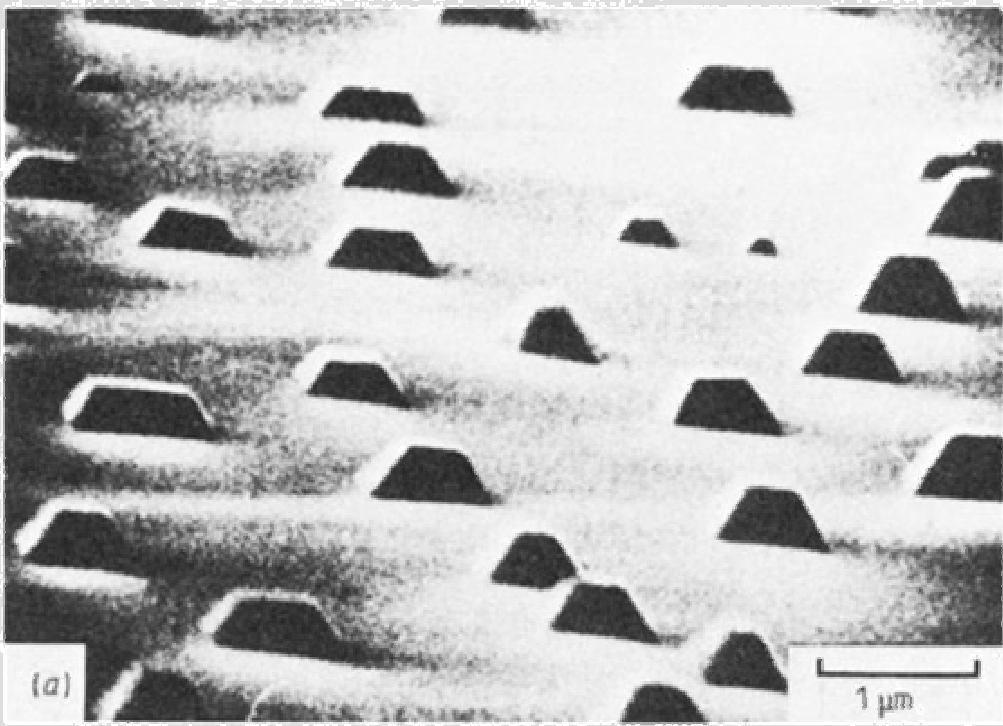


Truncated crystal

See references in: P. Müller and R. Kern, Surf. Sci. 457, 229 (2000)

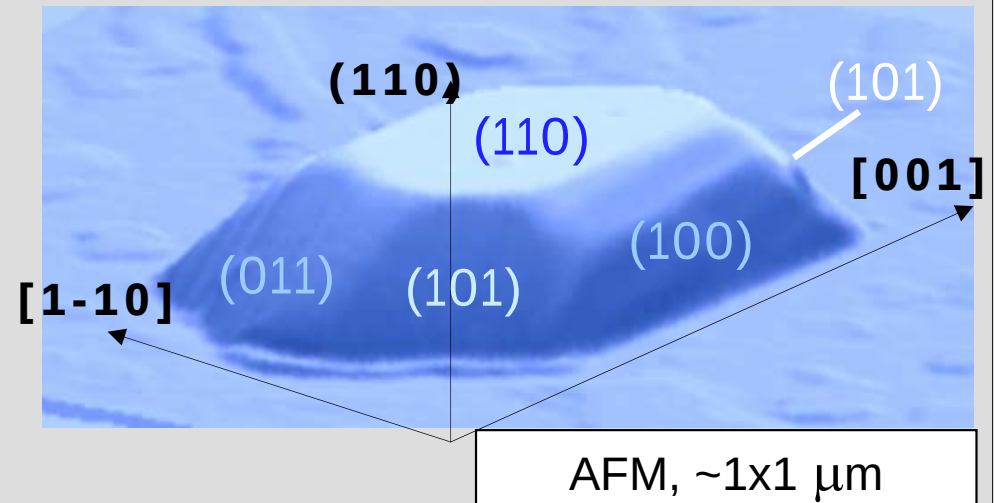
Examples of 3D dots

Ag(20Å)/Mo(001) @ 550°C



K. Hartrig, *Surf. Sci.* 74, 69 (1978).

Fe/Mo(110) @ 450°C



P.-O. Jubert *et al.*, *PRB* 64, 115419 (2002)

O. Fruchart *et al.*, to be submitted

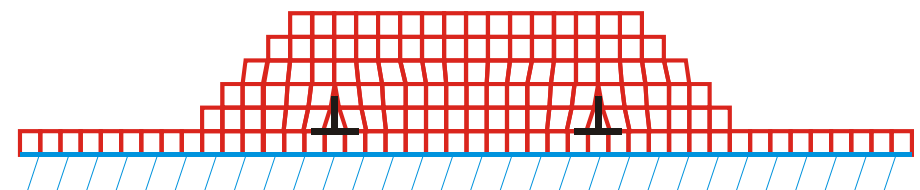
Parameters to play with:

Substrate orientation (dot symmetry)

Temperature (density and size) and
Amount deposited (size)

Epitaxial misfit

Surfactants, overlayer, etc.



Model, application to semiconductors:

H. Mariette *et al.*, *C. R. Physique* 6, 23 (2005).

Theory

Equilibrium nano-shape changes induced by epitaxial stress (generalised Wulff-Kaishew theorem)

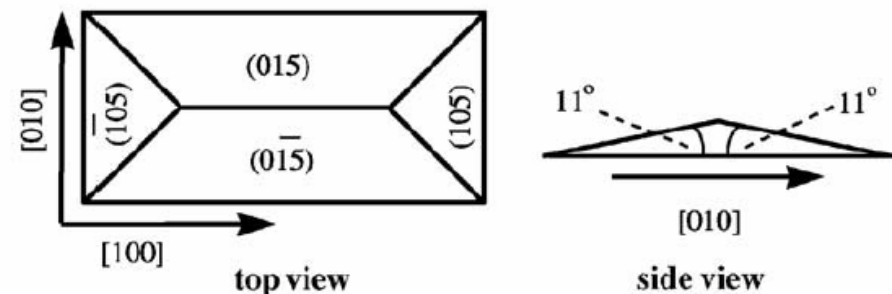
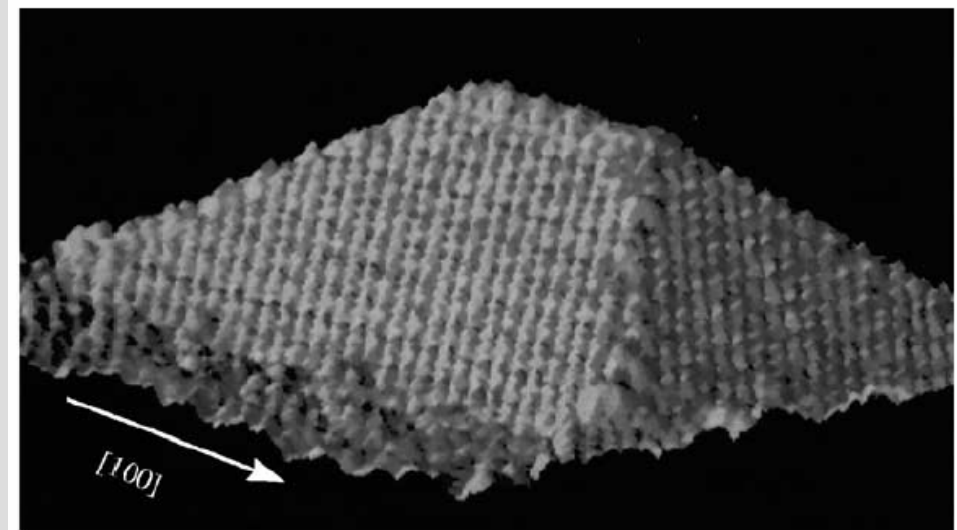
P. Müller and R. Kern,
Surf. Sci. 457, 229 (2000)

Takes into account both elastic relaxation and plastic relaxation (misfit dislocations)

« One of the most striking results is that the equilibrium shape is no more self-similar with size as it is when no epitaxial strain exists »

Also available: continuum and discrete numerical simulations

Example: Ge/Si(001), hut shape



I.W. Mo et al., Phys. Rev. Lett. 65, 1020 (1990)

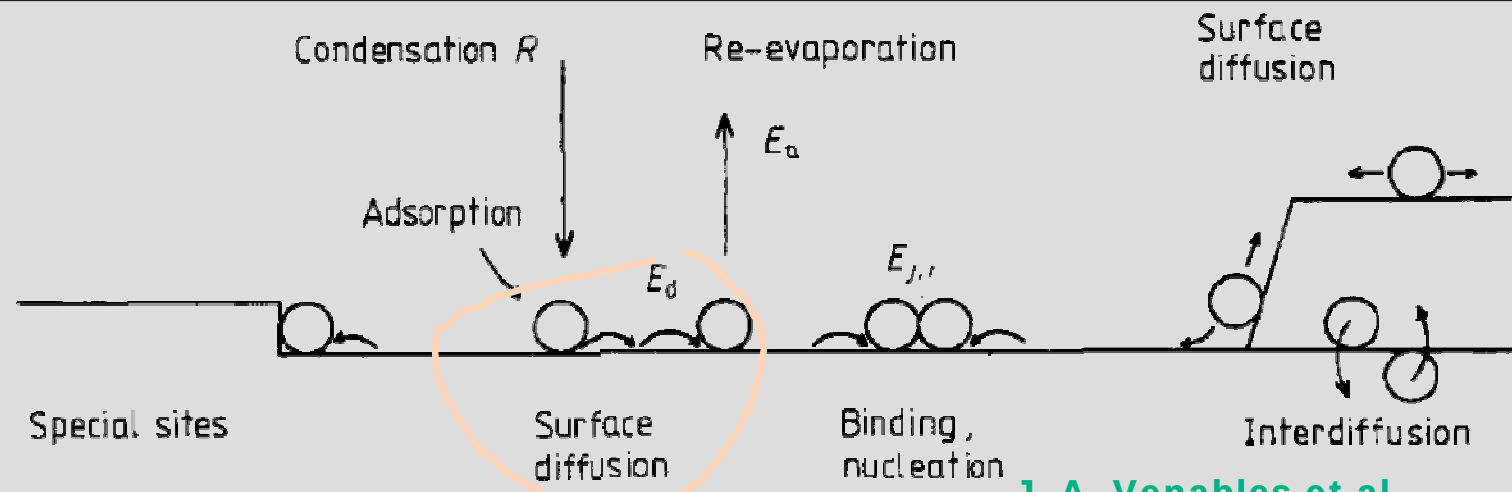
Applicable to:

Very small 3D dots: semiconductors (mostly IV-IV and III-V, including magnetic)

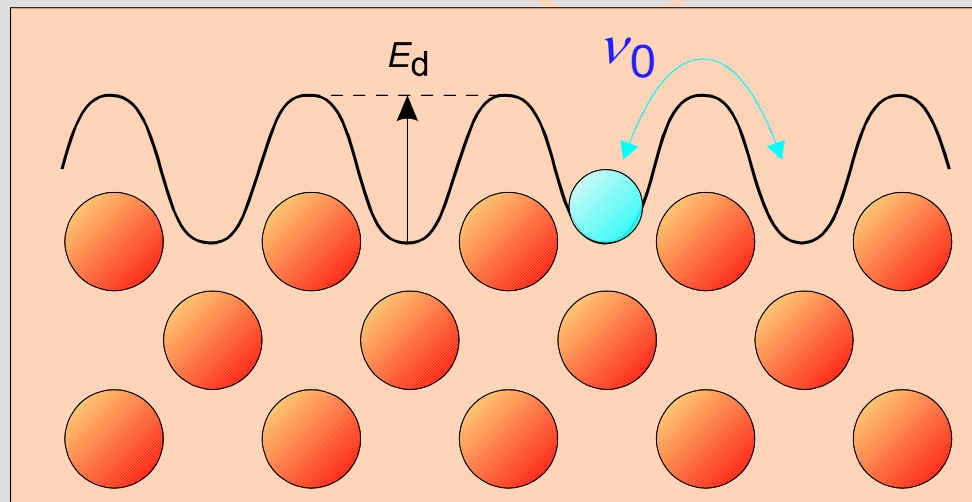
Also available:

Continuum and discrete numerical calculations

Atomic Surface Processes



J. A. Venables et al.,
Rep. Prog. Phys. 47, 399 (1984).



Mean distance
after elapse of time t

$$\langle R \rangle = \sqrt{4Dt}$$

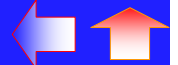
Diffusion coefficient

$$D = \frac{\nu_0}{4} \exp(-E_d / k_B T)$$

$\nu_0 \approx 10^{12}$ Hz Attempt frequency

E_d

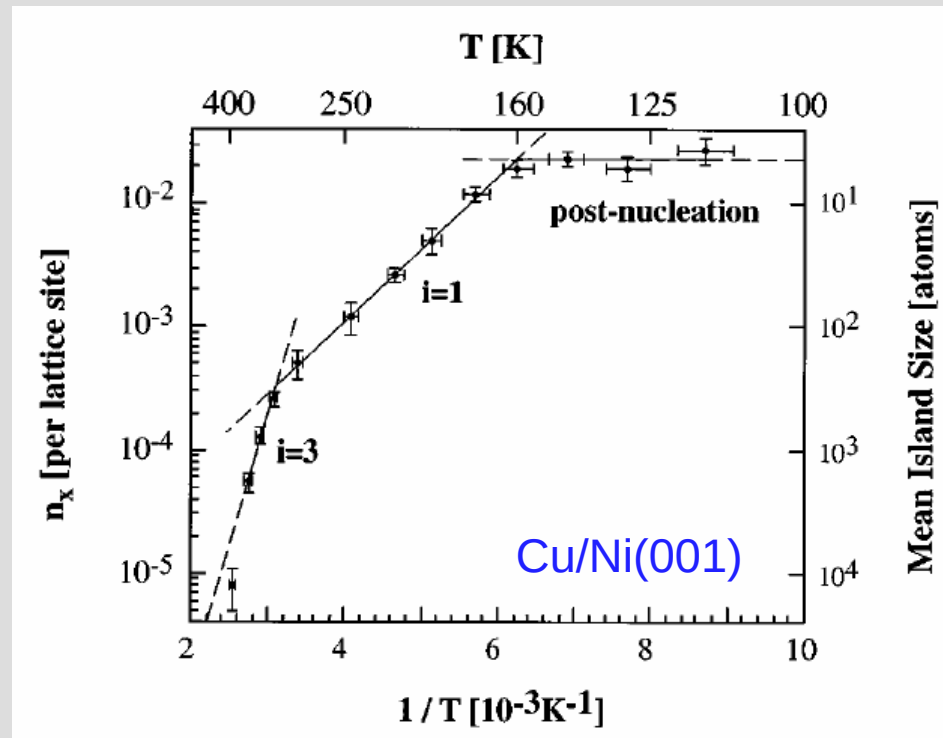
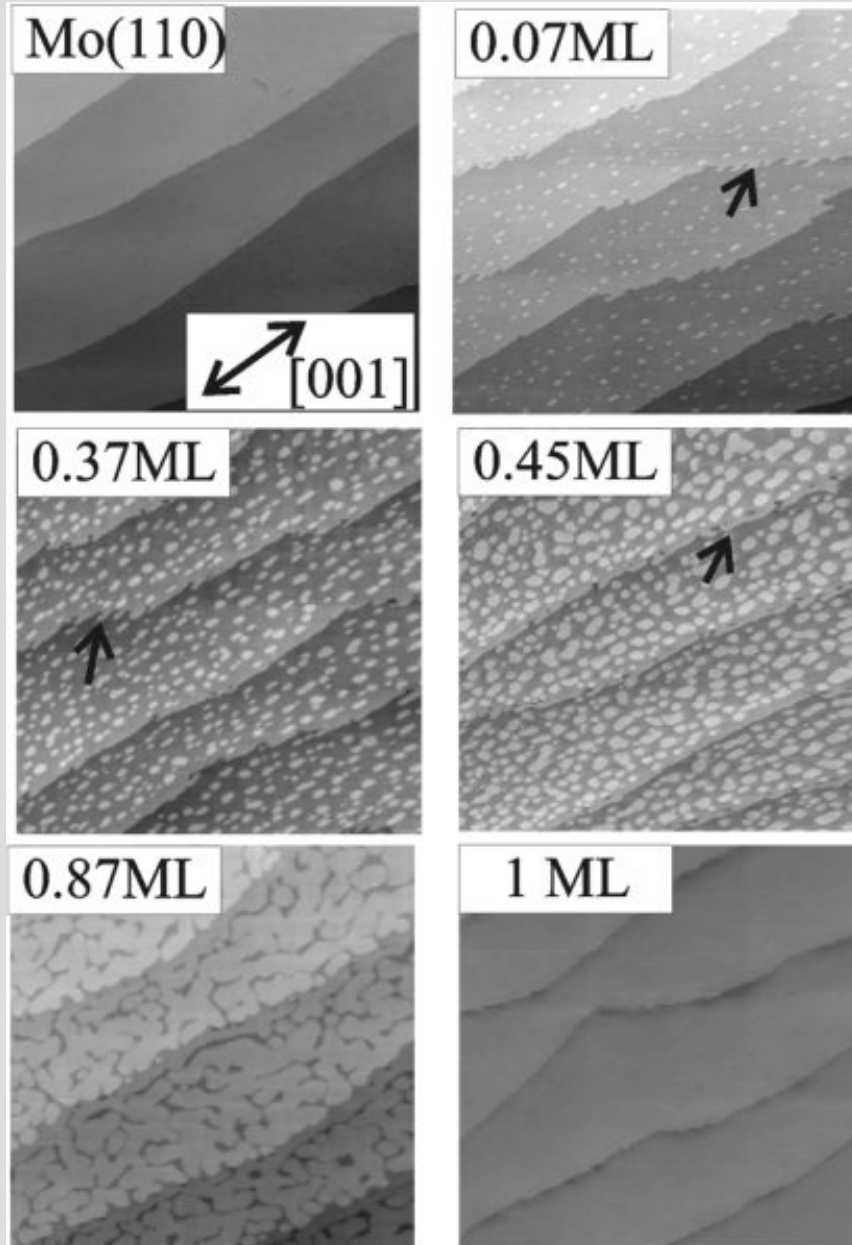
Diffusion barrier



Rate equations: maximum island density

J. A. Venables et al.,
Rep. Prog. Phys. 47, 399 (1984).

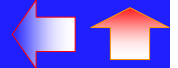
$$n_{\max} \sim \left(\frac{D_0}{F} \right)^{-\frac{i^*}{i^*+2}} \exp \left[\frac{i^* E_d + (E_{i^*} - E_1)}{(i^* + 2) k_B T} \right]$$



B. Müller et al., PRB54, 17858 (1996)

Ex: Fe/Mo(110) by PLD

P. O. Jubert et al., Surf. Sci. 522, 8 (2002).



Rate equations: island size distribution

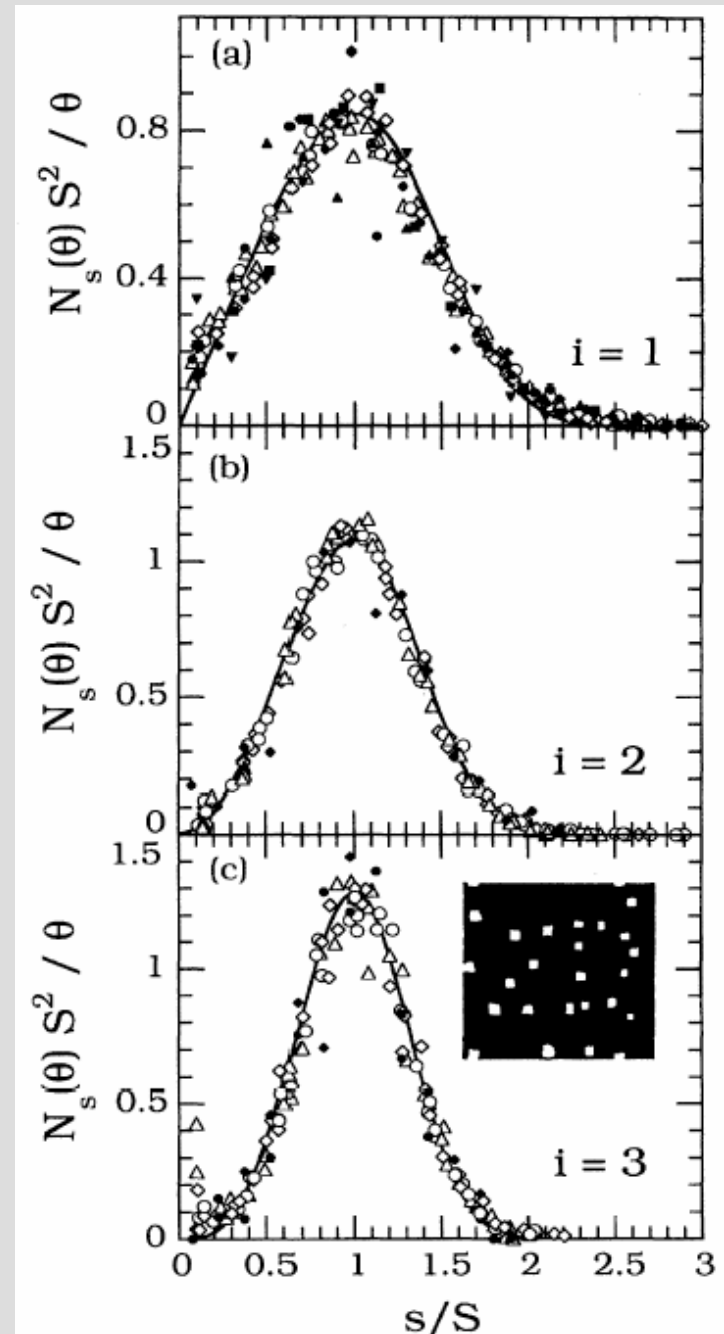
No analytical solution.

Empirical solution proposed:

$$f(u = S / \langle S \rangle) = C_i u^{i*} \exp(-i * a_i u^{1/a_i*})$$

Fe/Fe(001)
Simulations,
experiments,
analytical

J. G. Amar et al., PRL74, 2066 (1995)

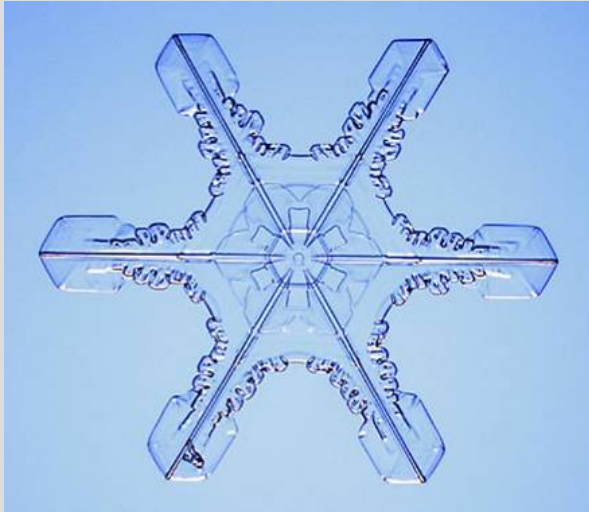




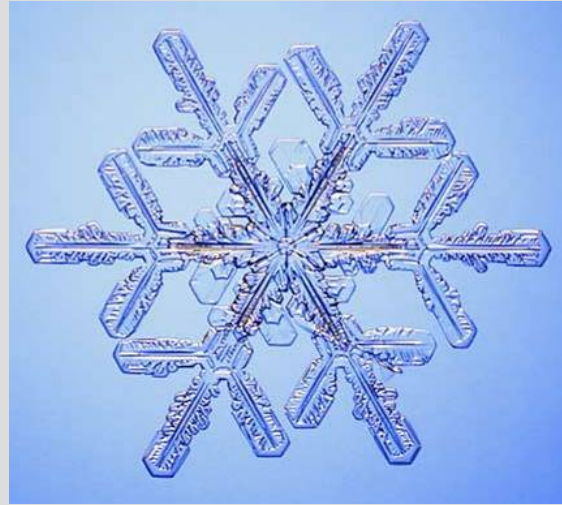
Snowflakes

Shape of islands: kinetics, symmetry etc.

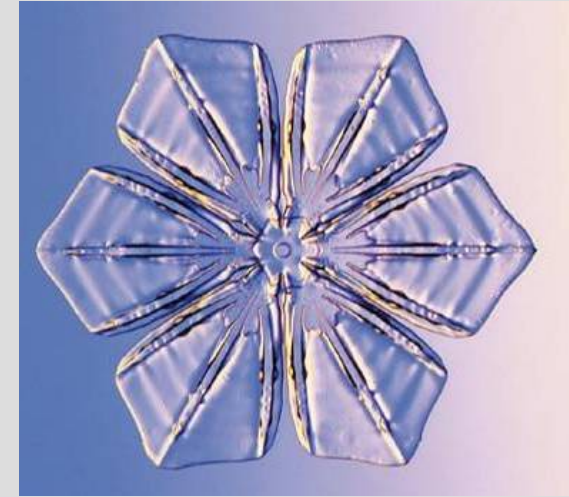
(National geographics)



Pt/Pt(111) 200K

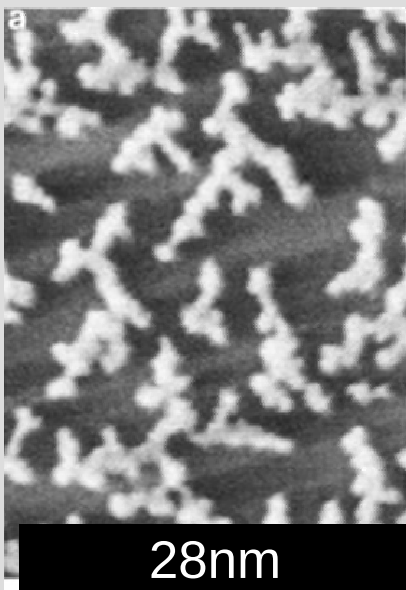


400K

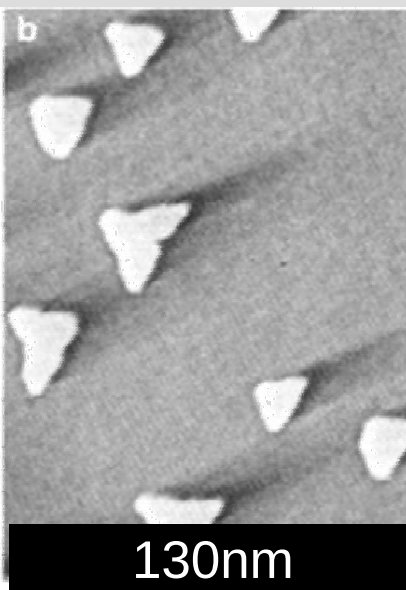


Cu/Pd(110)

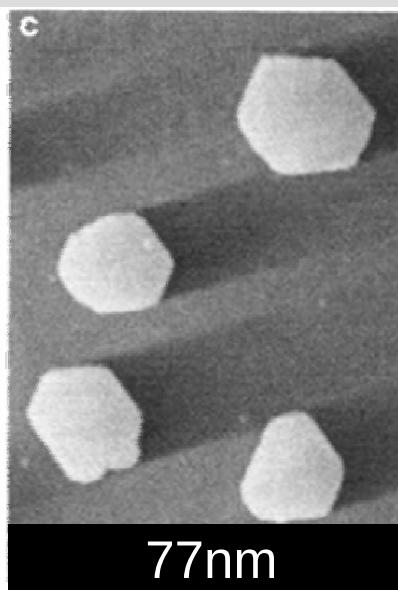
265K



28nm

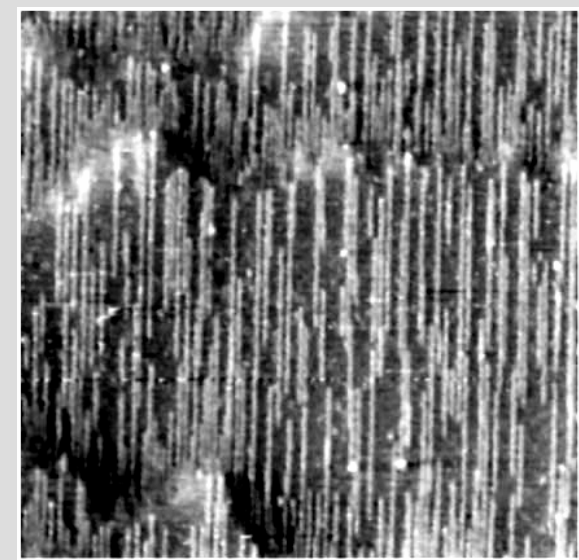


130nm



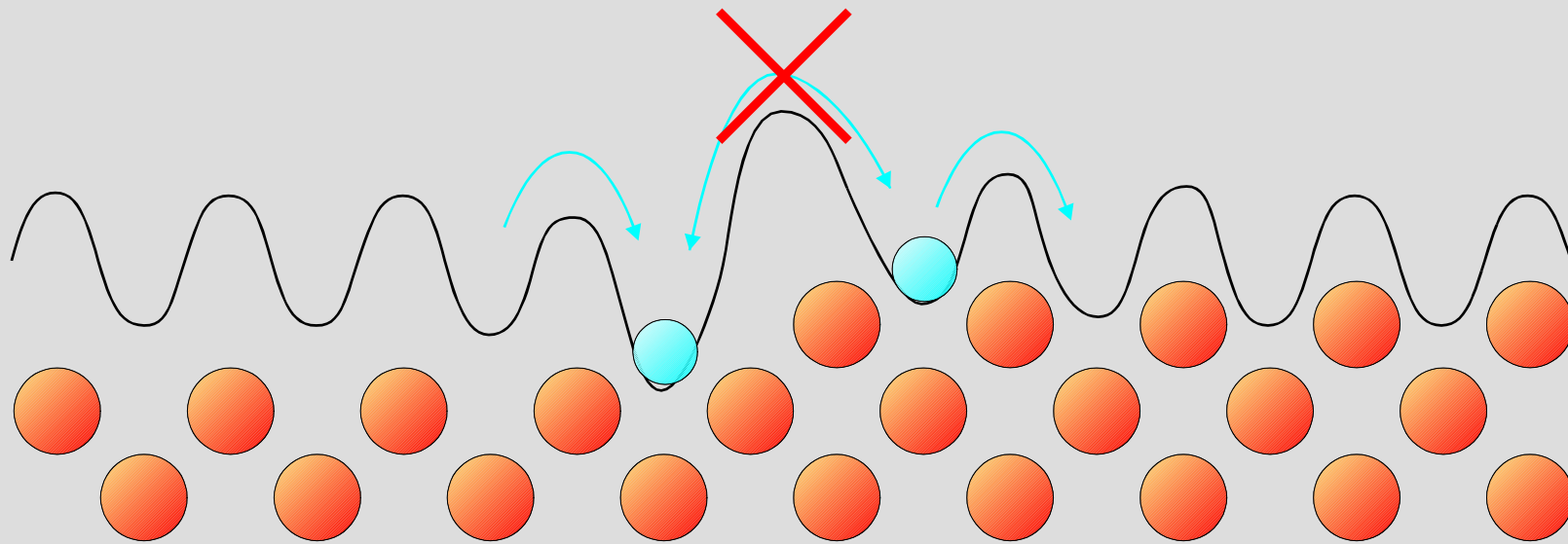
77nm

T. Michely, PRL70, 3943 (1993)

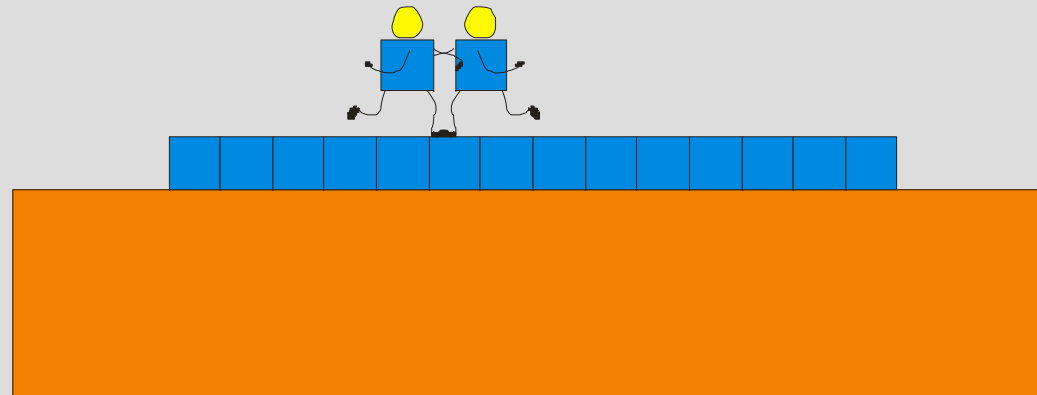


J. P. Bucher, Europhys. Lett. 27, 473 (1993)

Schwoebel barrier: origin

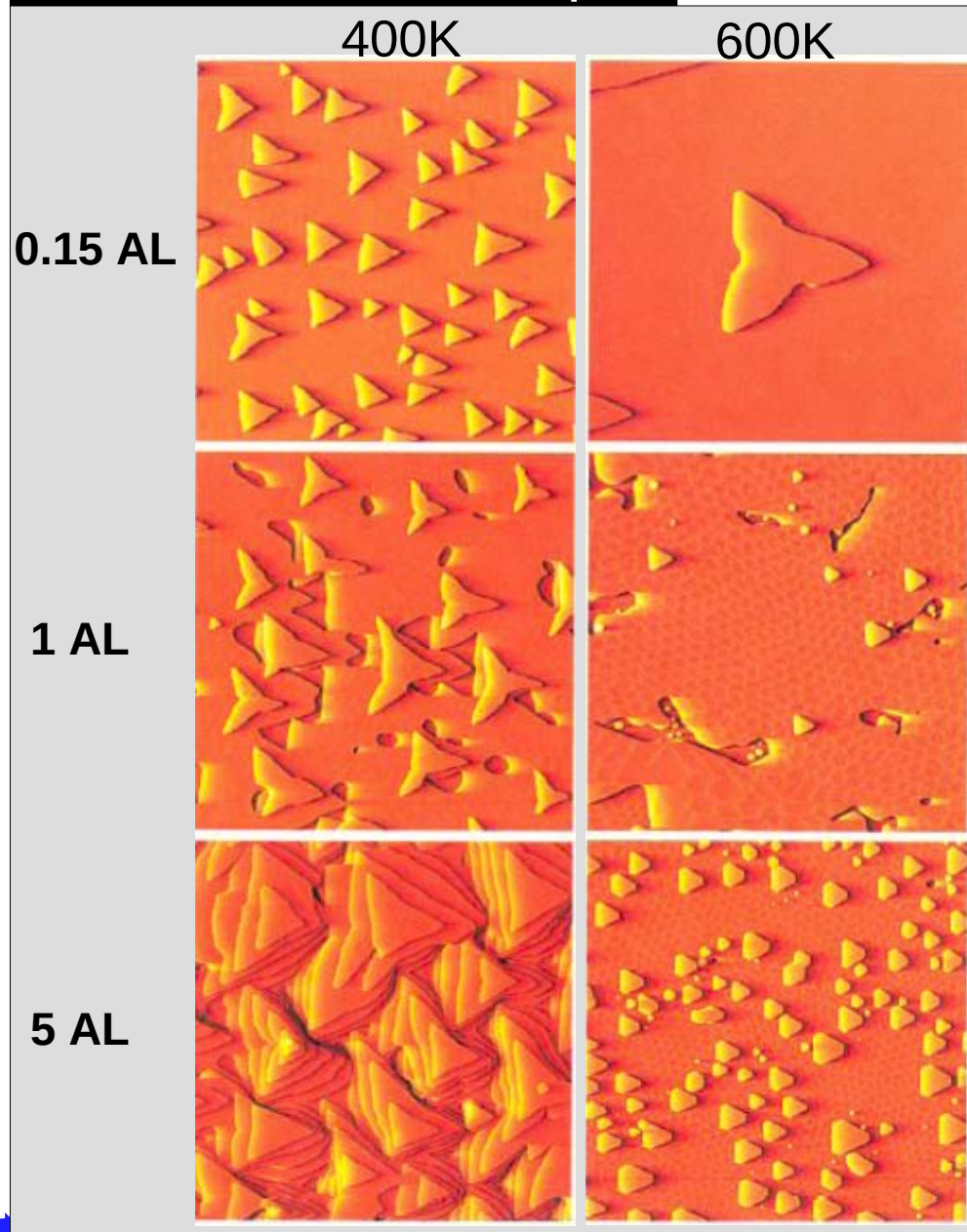


Step edges cannot be crossed below a threshold temperature



Schwoebel barrier: example

Pt/Pt(111)

**Depending on symmetry:**

Huts and holes: (111), (001), hcp(0001).

Trenches: (110), etc.

Other parameters to play with the Schwoebel barrier:

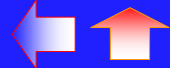
Surfactants (Pb, Sb, O etc.)

Ex: J. Camarero et al., PRL76, 4428 (1996)

Deposition method (Ex: PLD versus MBE)

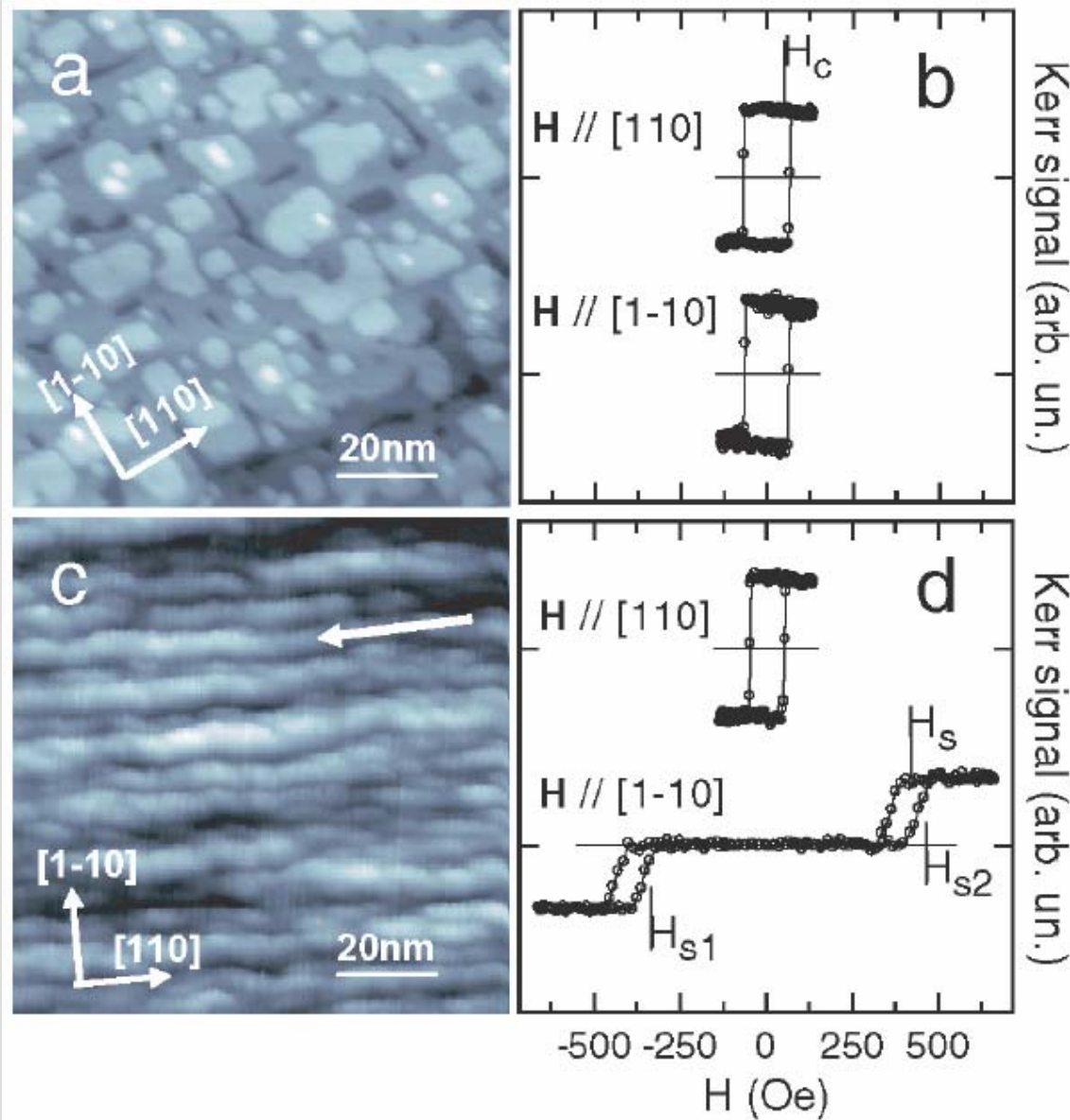
Review: J. Shen et al., Surf. Sci. Rep. 52, 163 (2003)

T. Michely and Krug, *Islands, mounds and atoms*, Springer (2004)



Ion etching: 'Inverse growth'

Co/Cu(001)



As-grown

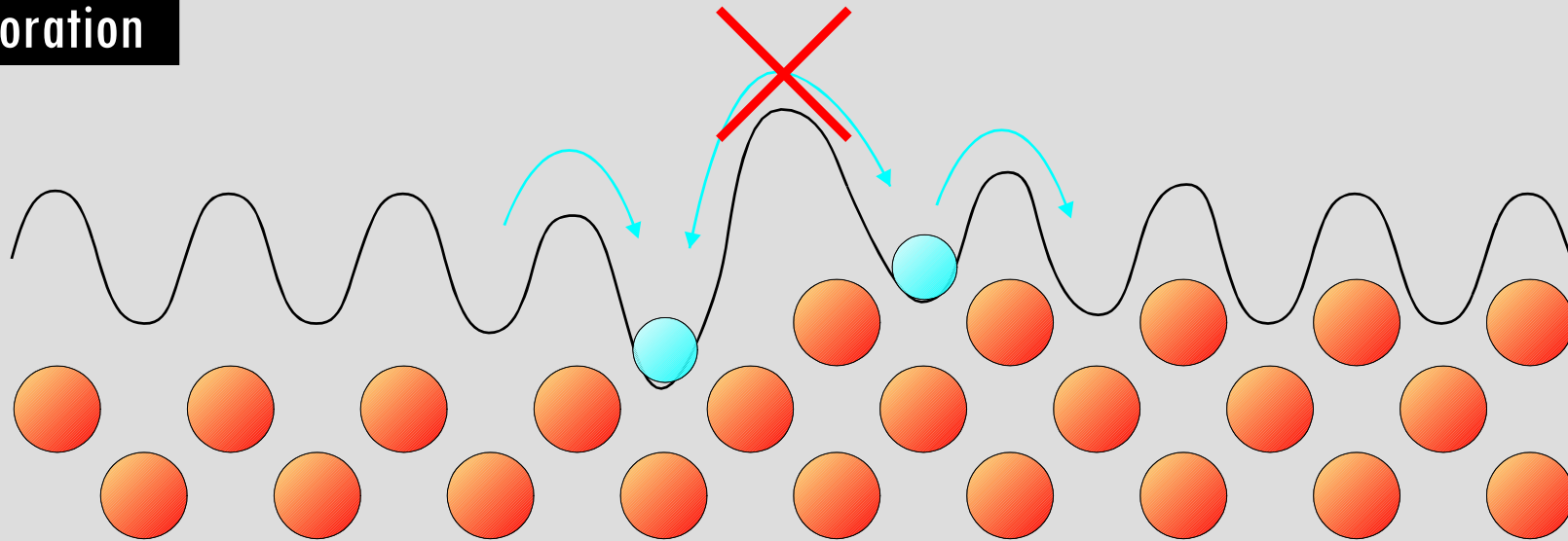
Tilted
Incidence
Ion etching**Other process:**Create pattern by ion
etching, then deposit

REVIEW:

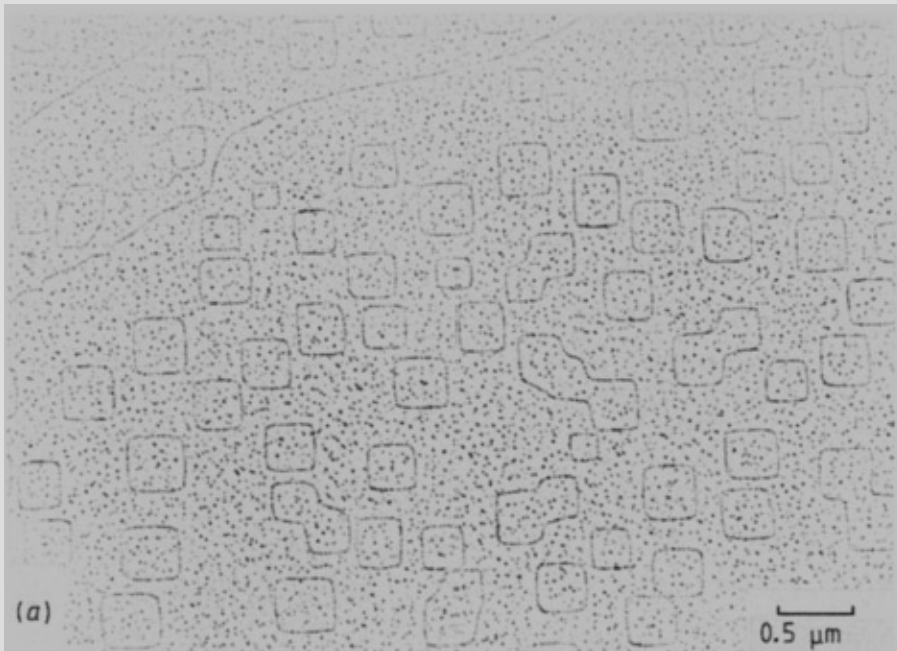
C. Teichert,
Phys. Rep. 365,
335 (2002)

R. Moroni et al., PRL91, 167207 (2003)

Step decoration



Adatoms are trapped at the lower side of the step



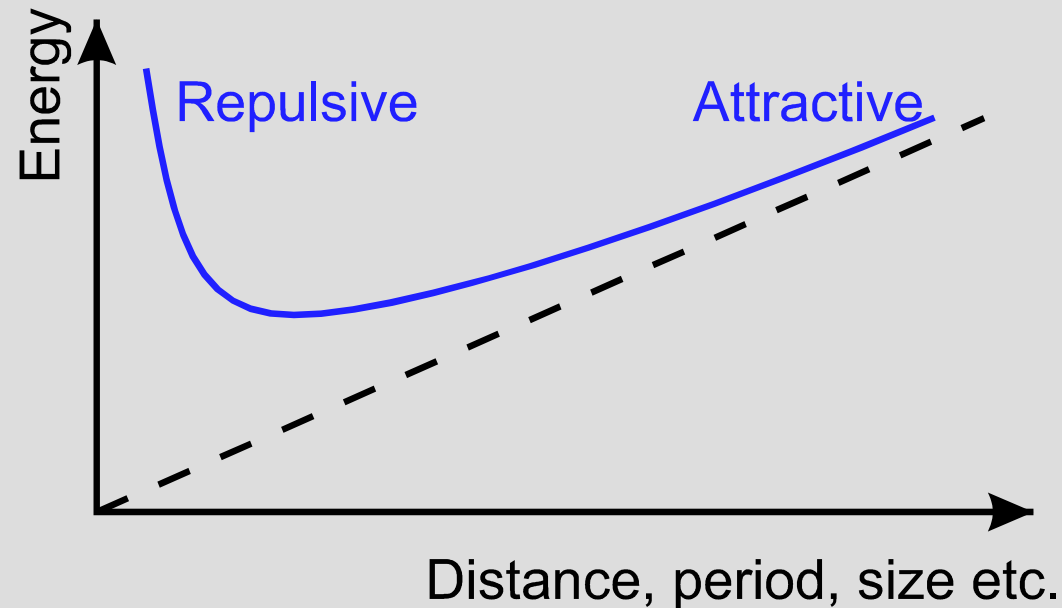
First report of step decoration

G. A. Bassett, Phil. Mag. 3, 1042 (1958)

H. J. Meyer et al., J. Cryst. Growth 49, 707 (1980).

So far, nanostructures, however not order. Could be called self-assembly.

What can determine characteristic length scales and order in physics?



Fields of interest for us:

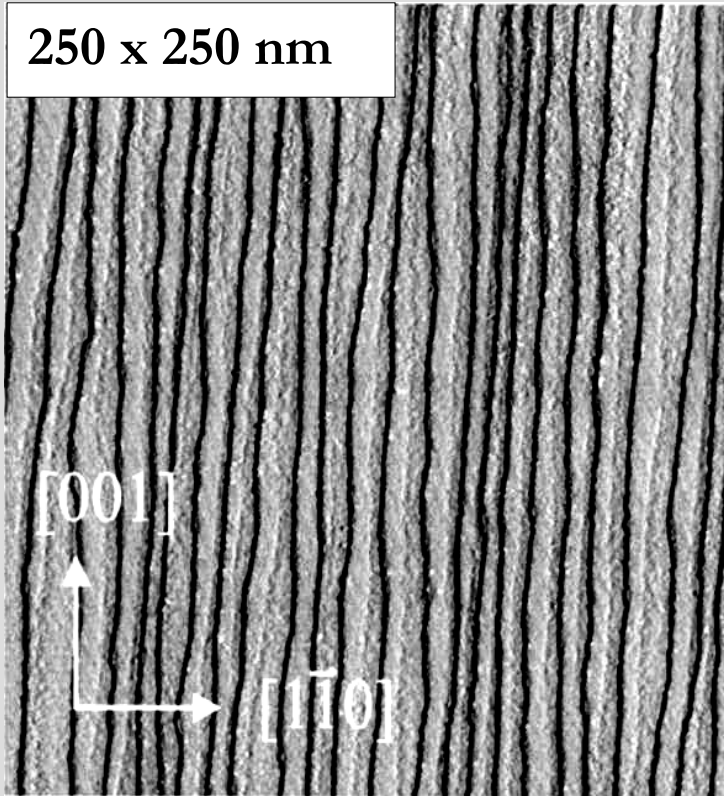
- Magnetism (wall width etc.)
- Surfaces (reconstructions etc.)



Stripes

Fe(0.5ML) / W(110)

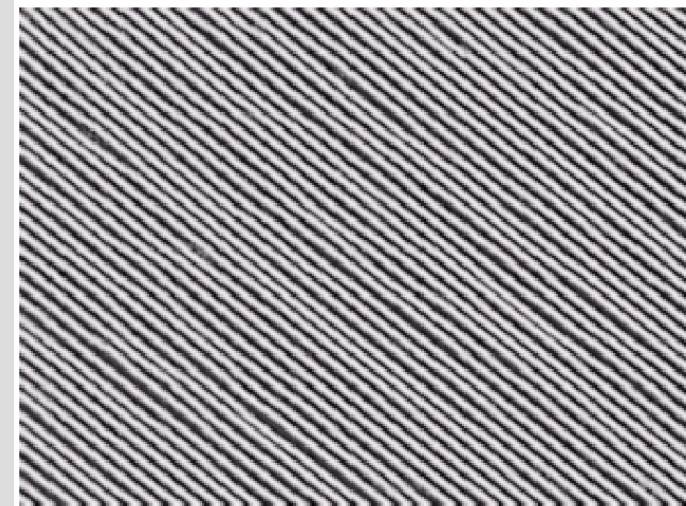
250 x 250 nm



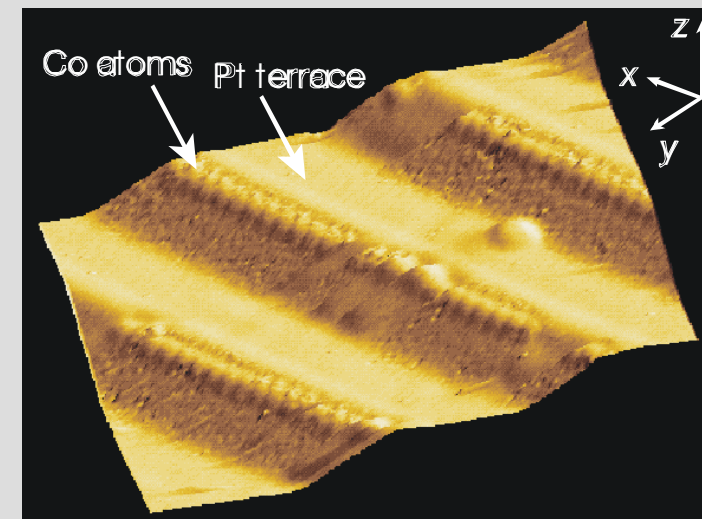
J.Hauschild *et al.*, Phys.Rev.B57, R677(1998)

Wires (monoatomic)

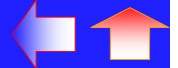
Co(0.15ML) / Pt(997)



100 Å



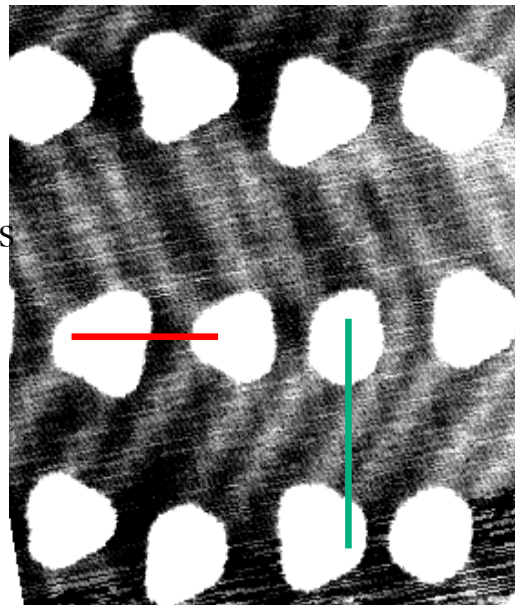
P. Gambardella *et al.*, Nature 416, 301 (2002)



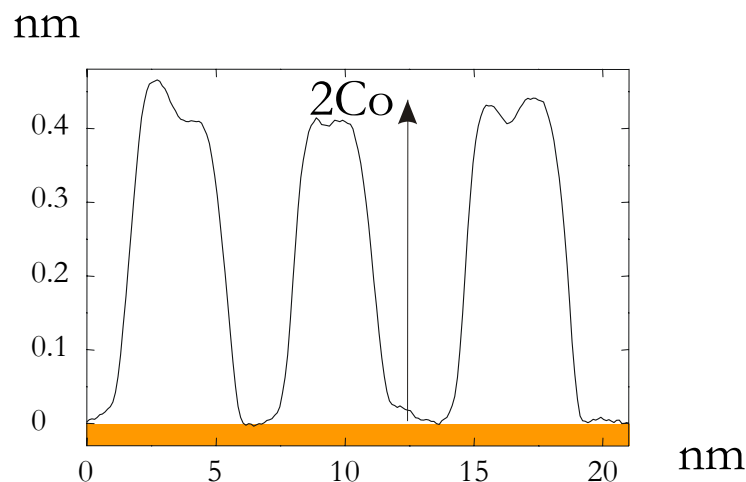
- Co, Ni, Fe :
Nucleation at the
elbows of the chevrons

7.5nm

(0.20AL Co@300K)



12-13nm



350 x 350 nm



O. Fruchart et al.

Fe, Ni : 1 AL-high dots

D.D. Chambliss et al., PRL **66**, 1721 (1991)

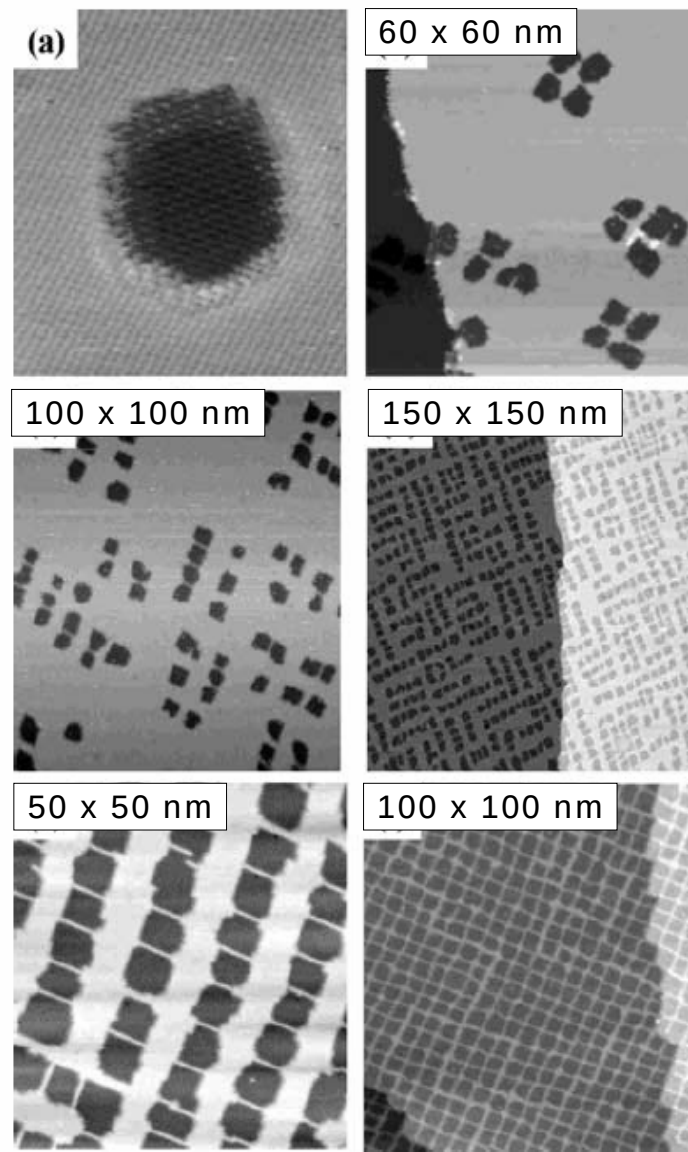
B.Voigtlander et al., PRB **44**, 10354 (1991)

- Medium-ranged organization
- Steps do not necessarily disturb the order
[see also:
V.Repain, Europhys. Lett., **47** (4), 435 (1999)]

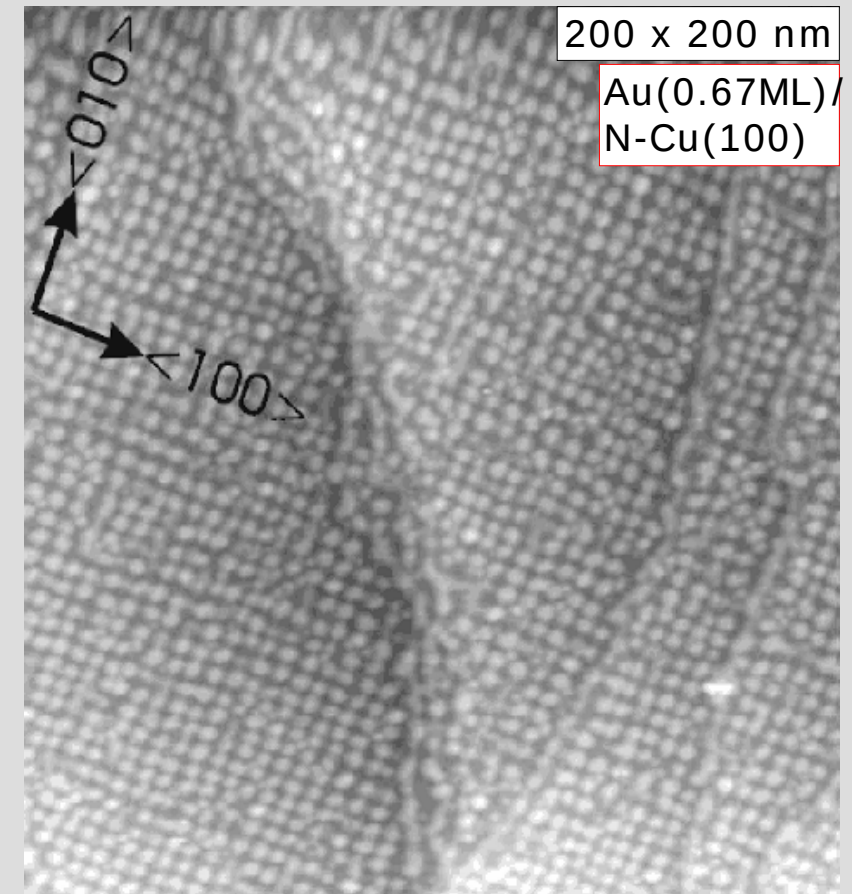


Gas adsorption**N on Cu(001)**

First study: T.M.Parker, Phys.Rev.**B56**, 6458(1997)



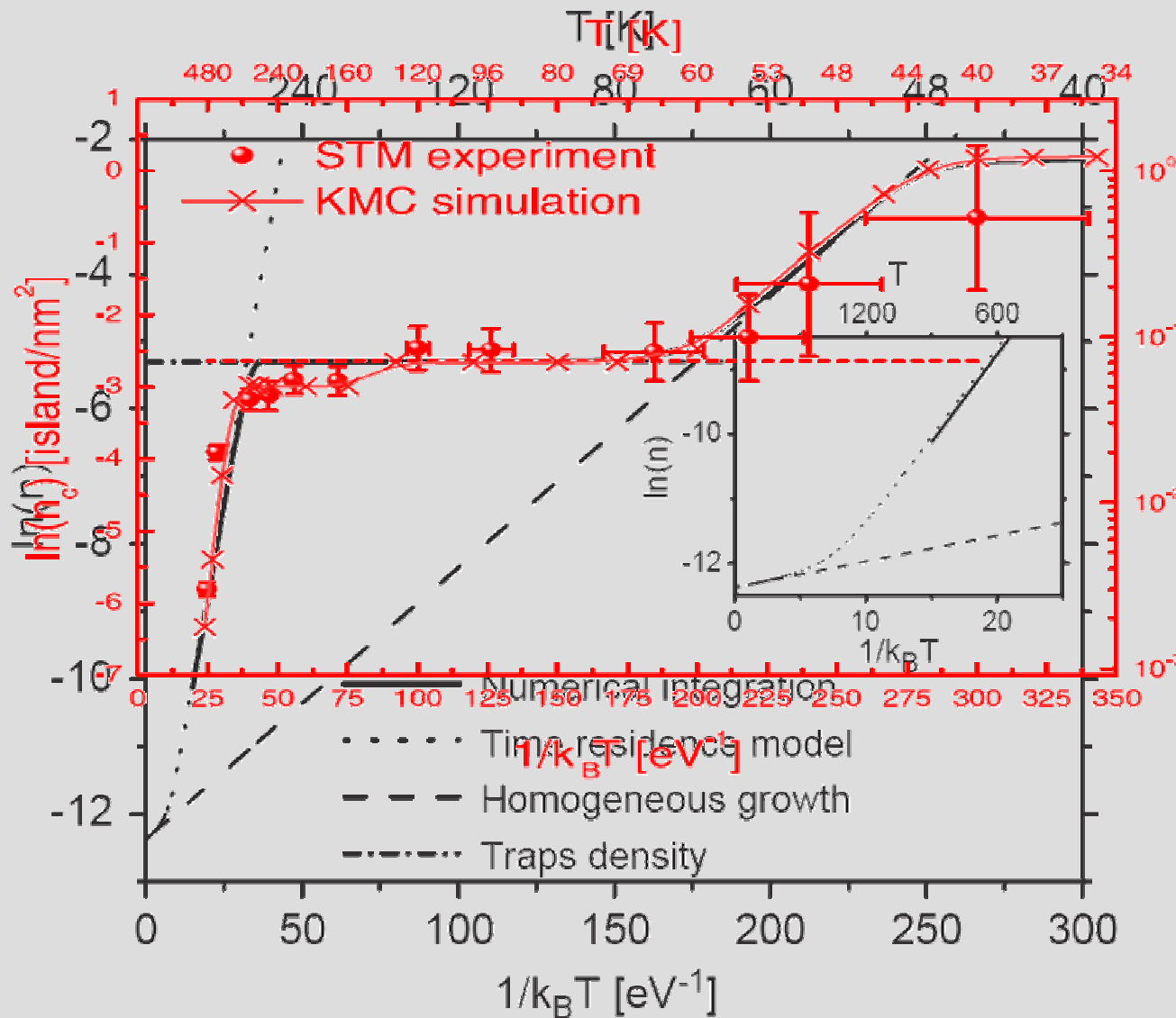
S. Rousset et al., Mater. Sci. Engineer. B 96, 169 (2002)

Overgrowth of Au

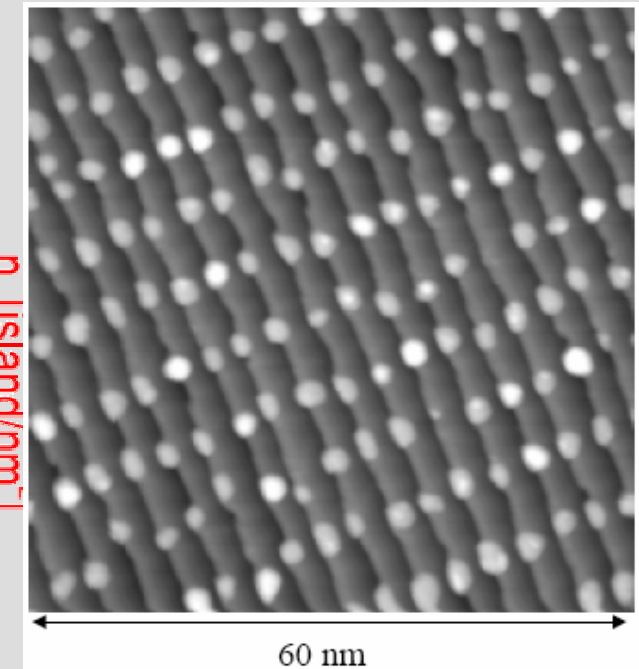
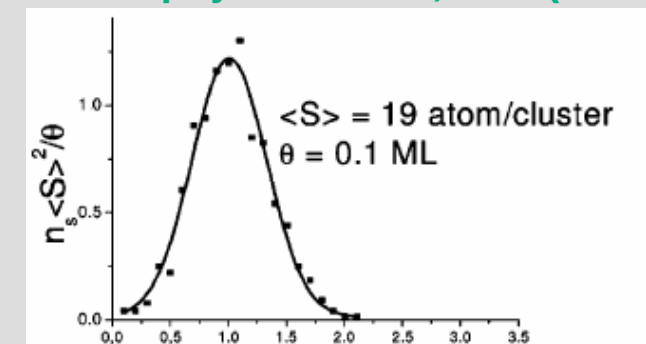
H. Ellmer et al., Surf. Sci. 511, 183 (2002)

Nucleation rate equations for self-organization

Co/Au(788)



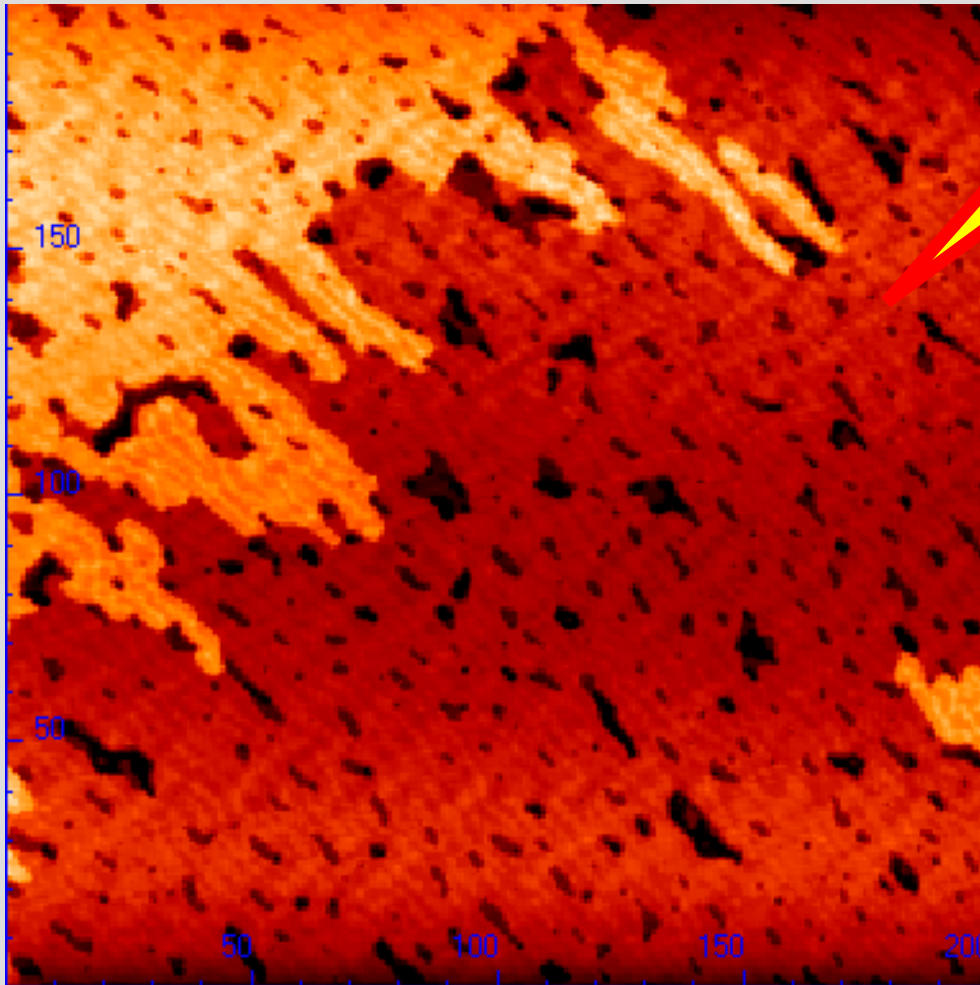
S. Rohart et al., Surf. Sci. 559, 47 (2005)

V. Repain et al.,
Europhys. Lett. 58, 730 (2002)

Reduced size distribution

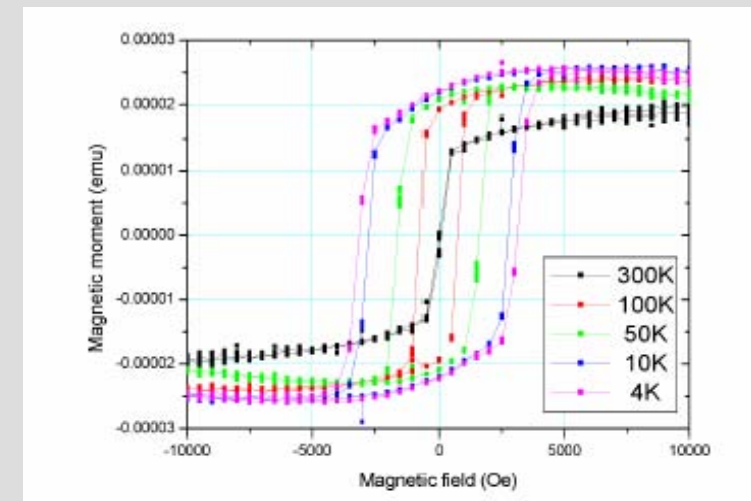
Self-organization during deposition

Fe-Ag/Mo(110)



See poster by
Bogdana BORCA

Alternating Fe and Ag stripes:
'lateral multilayer'
(period: 3.5nm)



Blocking temperature: 190K

B. Borca et al., submitted to JAP

First demonstration:

E. D. Tober et al., PRL 81, 1897 (1998)

E. D. Tober et al., APL 77, 2728 (2000)

Friedel crystals

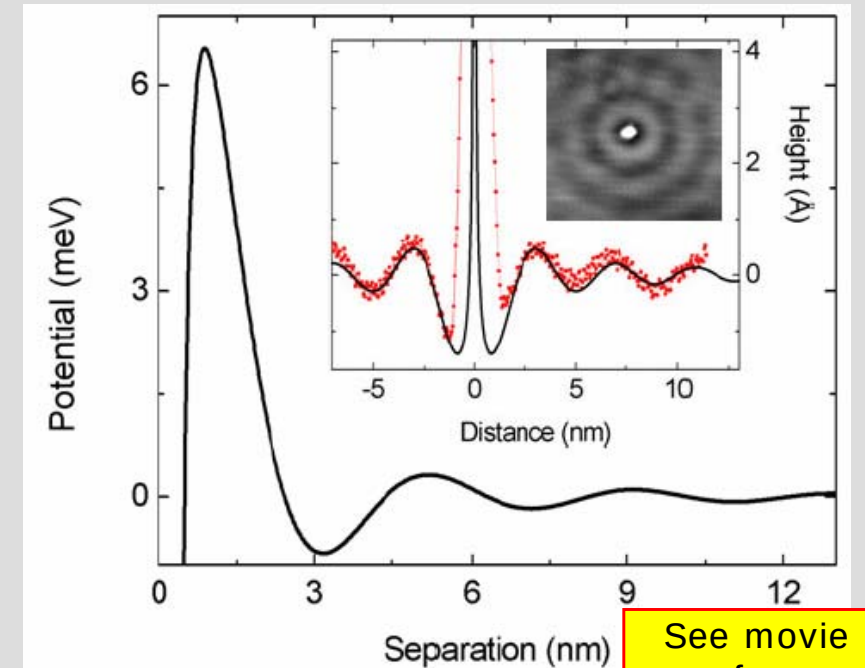
Ce(1AL)/Ag(111) @ 3.9K



STM, 69x69nm

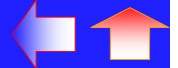
See movie
for
Co/Cu(111)

Supra-crystal stabilized by surface states oscillating around adsorbates



See movie
for
Ce/Ag(111)

Figure 9. Calculated two-body interaction potential of Ce adatoms on Ag(111) (equation (2)). Inset: $21 \times 21 \text{ nm}^2$ STM topography of a standing-wave pattern around an isolated Ce adatom on Ag(111) at 3.9 K ($U_s = -3 \text{ mV}$, $I_s = 19 \text{ pA}$). Topographic cross-section (dots) and fit using equation (1) (solid curve) as a function of distance from a single Ce adatom.



Why self-organization is interesting?

- UHV-quality of the interfaces, down to the atomic size (crucial for interface-dependant properties)
 - Reliable analysis of measurement of assemblies
 - Reproducibility, low dispersion.
- Monodispersion (fondamental and applied), more than order
- Perform 'diffraction' at the period of the organized arrays

Drawbacks

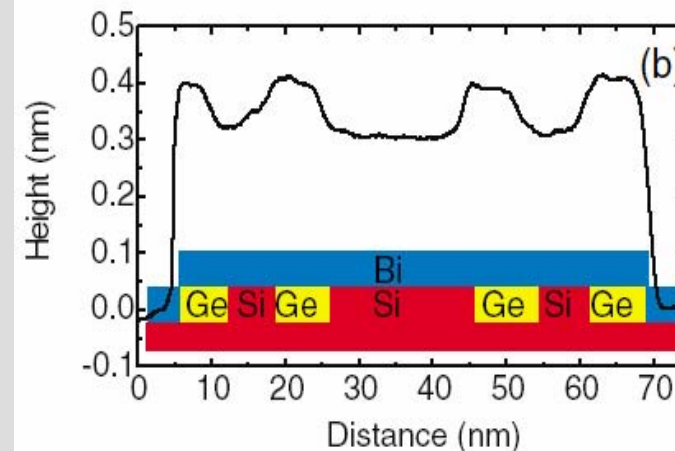
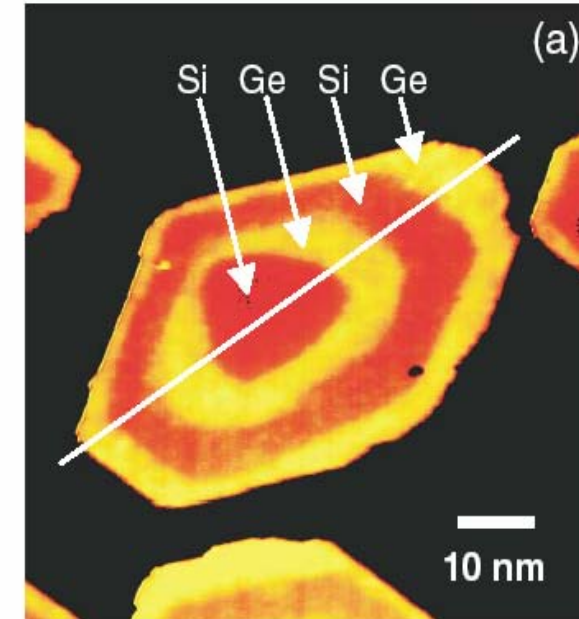
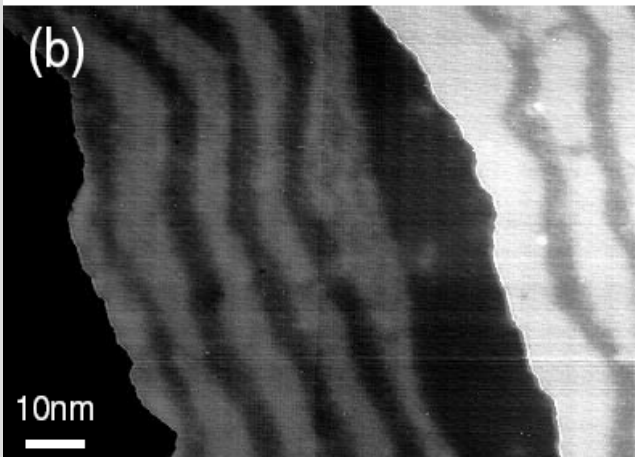
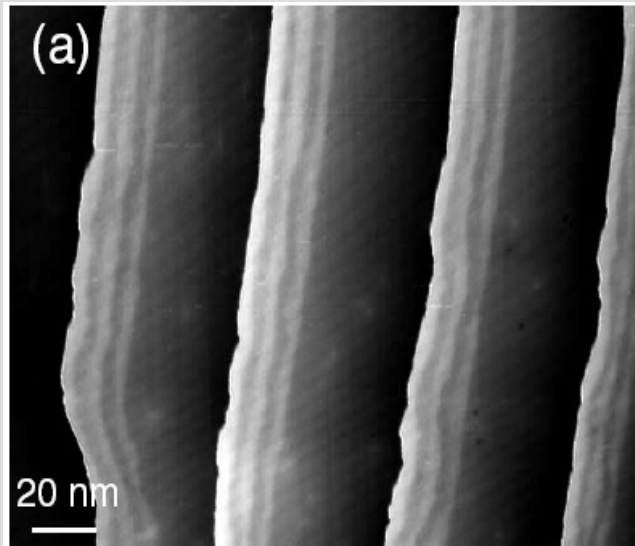
- Limited versatility
- Low amount of material available
- No magnetic functionality at 300K (see later)
- > Find new processes of self-organization

Principle: sequential deposition of two materials with step-flow growth

Nanowires

Si/Ge (Bi-capped for revealing Si and Ge)

Nanorings



M. Kawamura *et al.*, Phys. Rev. Lett. 91, 096102 (2003)

LLN, Grenoble, France.

Olivier Fruchart – European School on Magnetism – Constanta, sept. 2005 – p.25

<http://lab-neel.grenoble.cnrs.fr/themes/couches/ext/slides/>

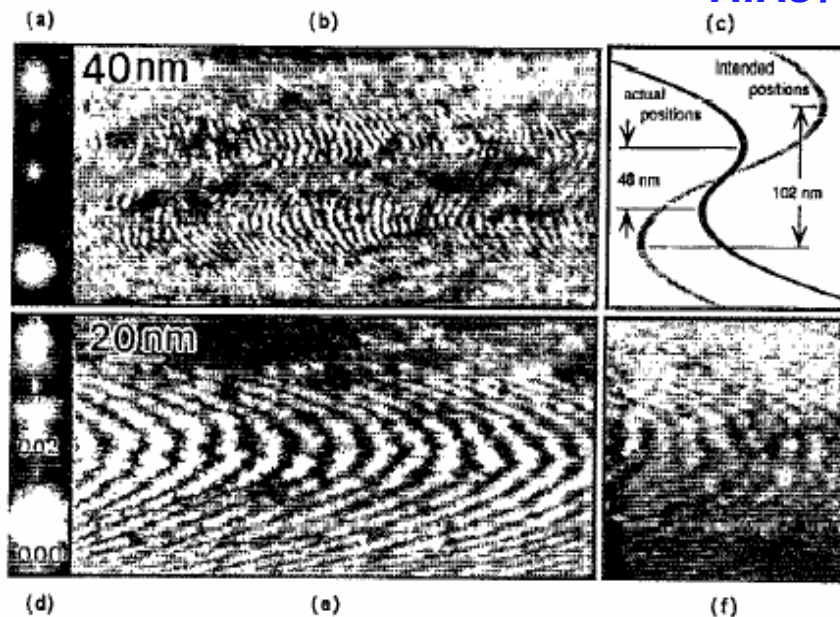
Name: Lateral Superlattices (LSLs)
or Tilted Superlattices (TSLs)
or Fractional layer superlattices (FSLs)

Principle: sequential deposition with
step-flow growth

First demonstration: P.M. Petroff, APL45, 620

(1984)

AlAs / GaAs lateral superlattice



TEM pictures

FIG. 1. TED and micrographs of SSL sample A, (a)–(c) and sample B, (d)–(f). The sample A TED pattern (a), dark-field image using the SSL streaks SL DF (b), and the intended and actual boundary geometries of the parabolic crescents (c). The sample B TED pattern (d), the SL DF image (e), and the (002)-DF image (f) are shown.

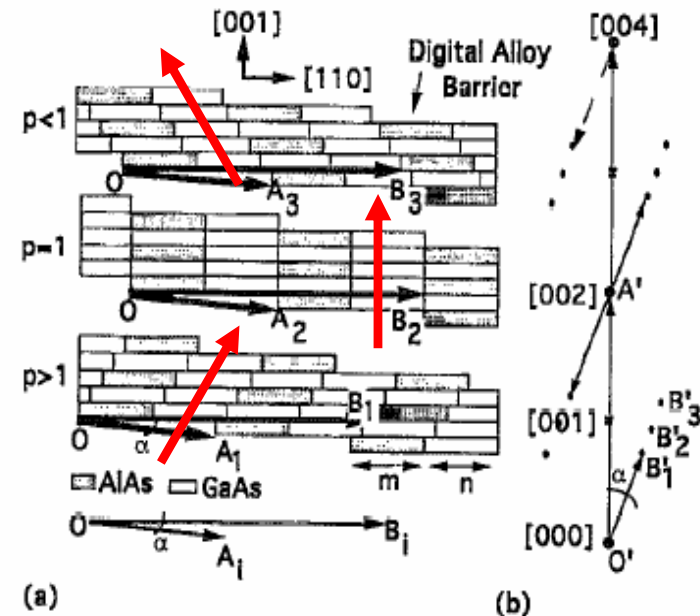


FIG. 2. A SSL on a terraced substrate depicted as three TSL slices (a), and the synthesized diffraction pattern, (b) are shown. While the real space vectors OB_i change with coverage, the superposition of reciprocal lattice vectors $O'B_i'$ predicts the formation of streaks at the observed positions.

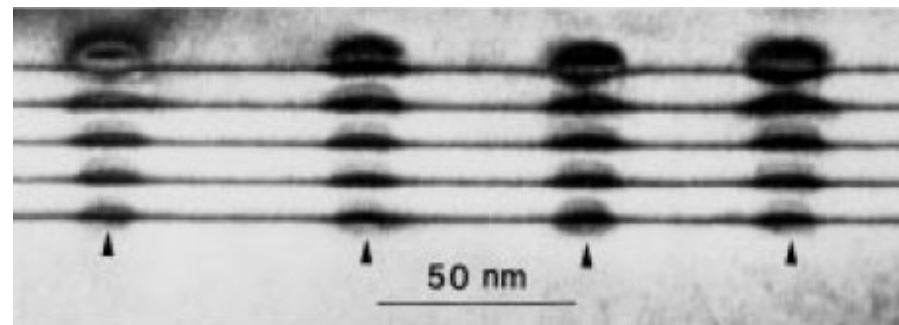
M. Kirshnamurthy, APL61, 2990 (1992)

Main obstacle: requires excellent control of both deposition rates

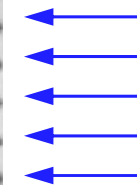
3D self-organization: dot's vertical stacking.

InAs / GaAs(100)

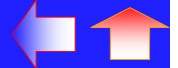
- Strain field in spacer layer :
 - ↪ vertical stacking of dots



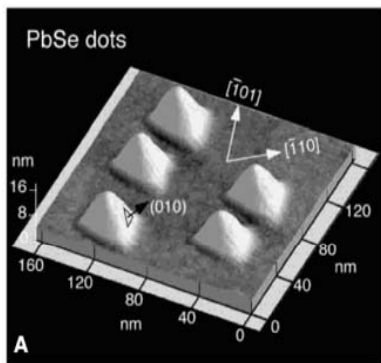
InAs



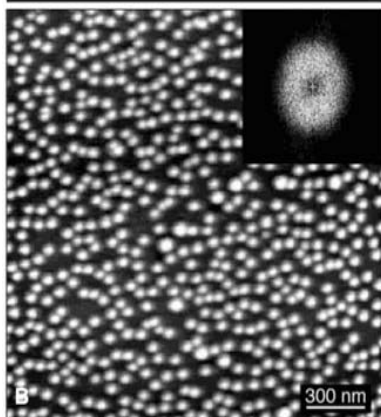
Q.Xie, Phys.Rev.Lett.75(13), 2542 (1995)



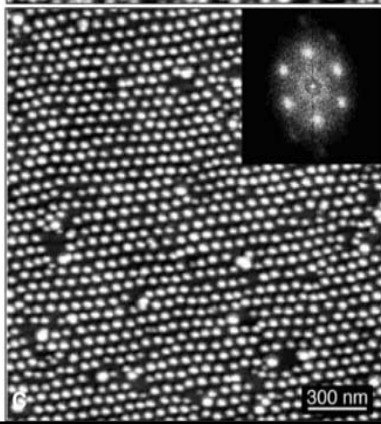
➤ From 2D assembly to 3D- organization



Zoom :
facetted dots



Single layer :
Self-assembly,
no organization.

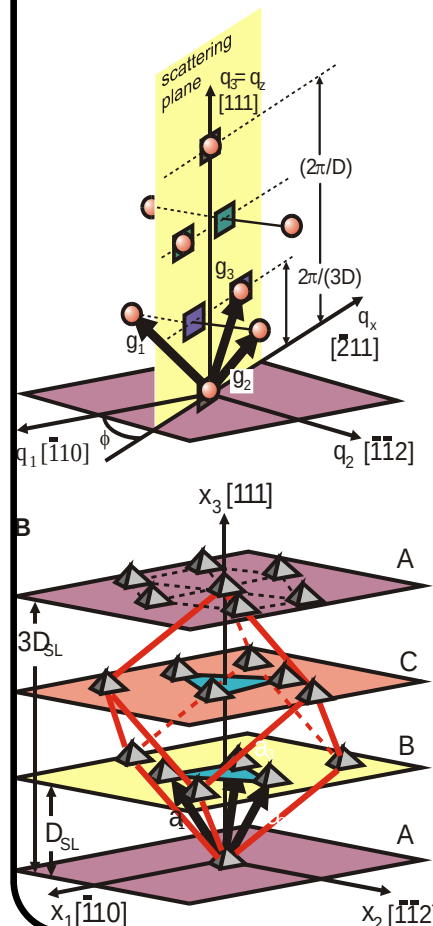


Multilayers :
improvement of
the organization.
(After 60 layers)

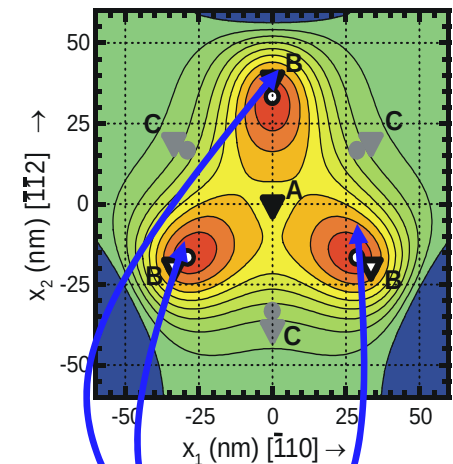
PbSe / PbTe(111)

➤ Anisotropic elastic media
↪ f.c.c. superstacking, not vertical.

X-Ray diffraction



Anisotropic in-plane
distribution of
elastic energy density



Misfit reduced by 2%

↪ preferential nucleation



G.Springholz, Science **282**, 734 (1998)

LLN, Grenoble, France.

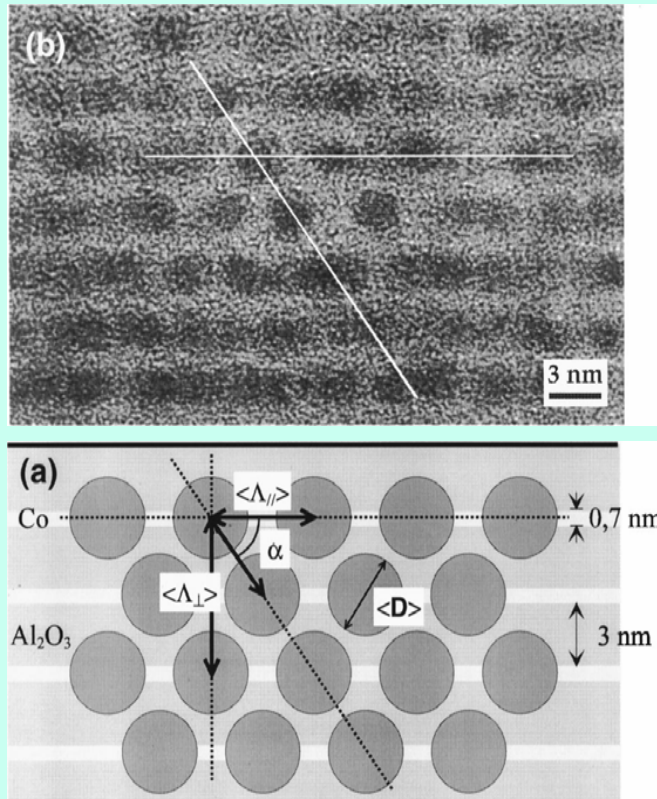
Olivier Fruchart – European School on Magnetism – Constanta, sept. 2005 – p.28

<http://lab-neel.grenoble.cnrs.fr/themes/couches/ext/slides/>

Co/Al₂O₃ granular system (sputtering)(Co: 0.7 nm/Al₂O₃: 3 nm)₁₄

REAL SPACE

TEM cross-section (Sequential sputtering)



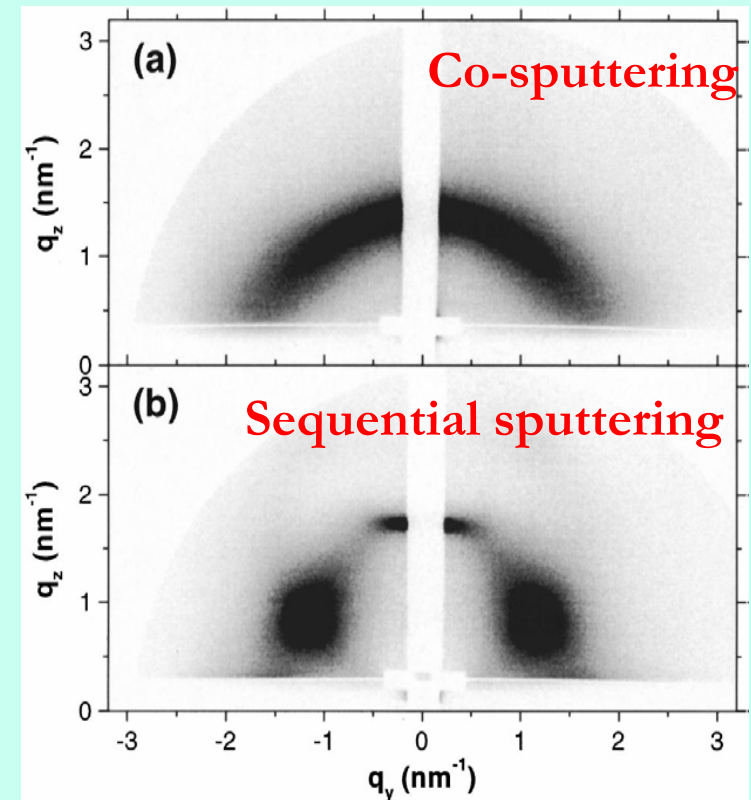
➤ FCC vertical stacking (not epitaxial)

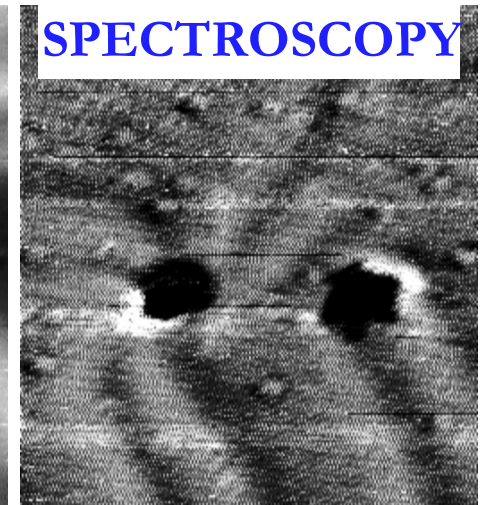
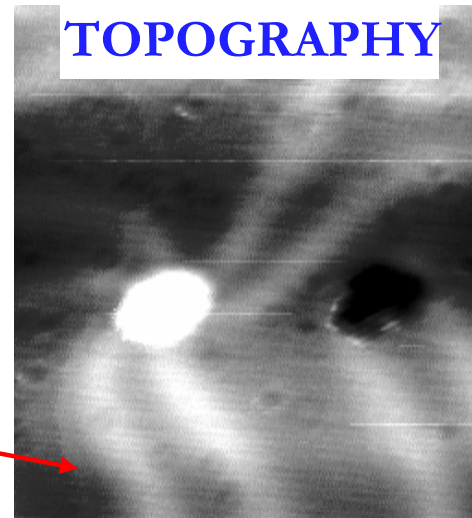
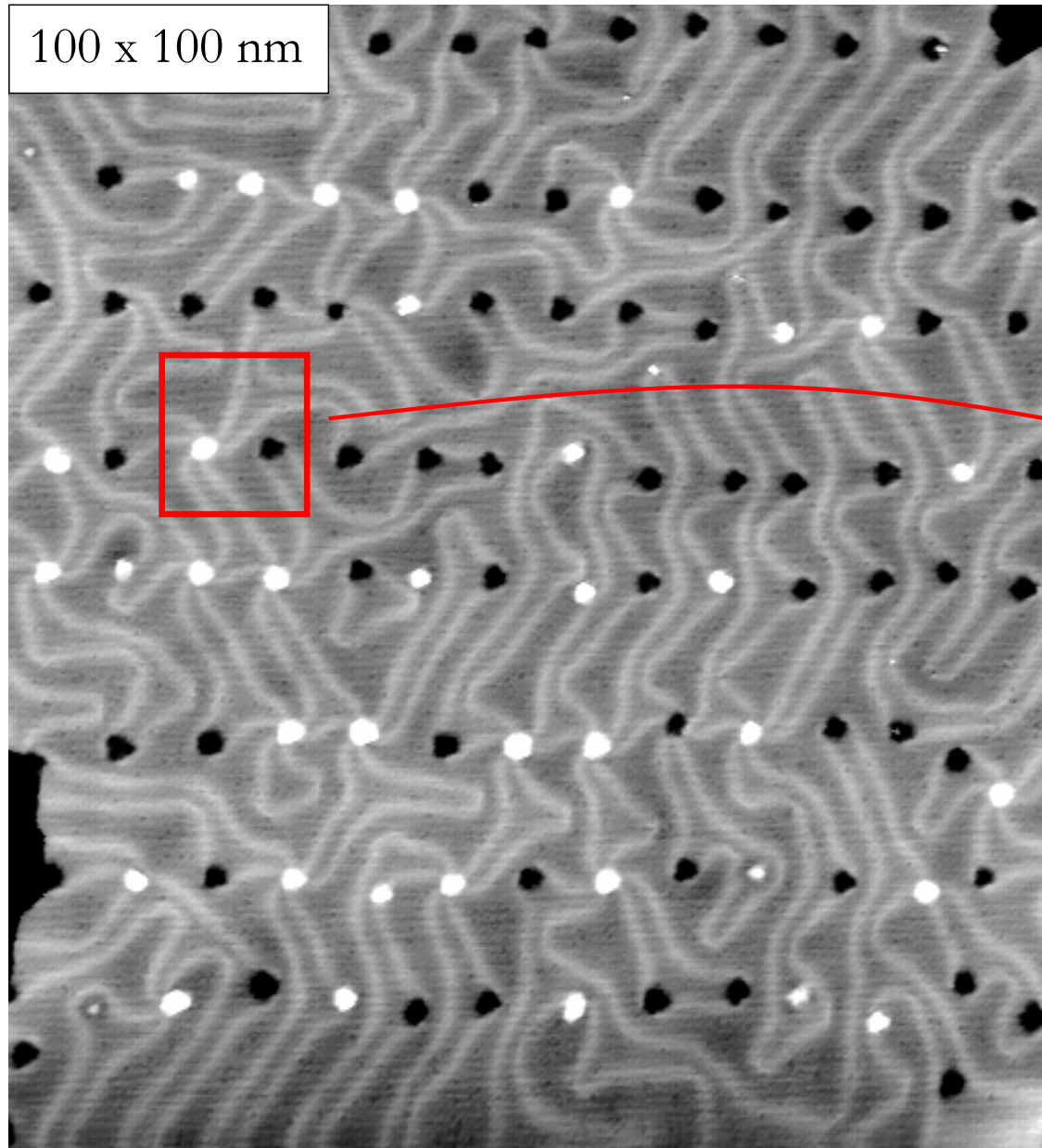
D. Babonneau, Appl. Phys. Lett. 76, 2892 (2000)

LLN, Grenoble, France.

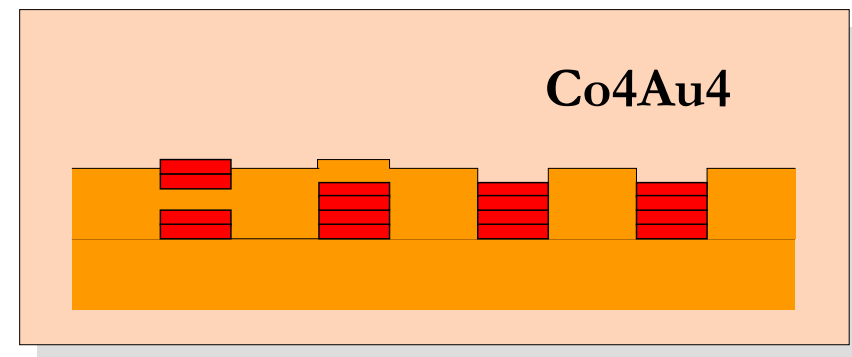
RECIPROCAL SPACE

GISAXS:

Grazing Incidence Small Angle
X-Ray Scattering



SAME AREA

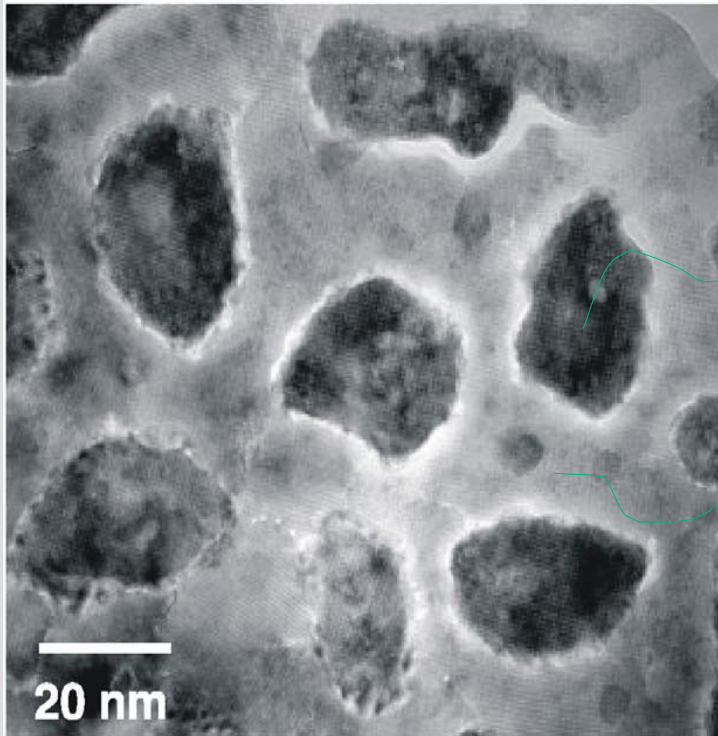


Co atoms grow only on existing dots

↪ VERTICAL COLUMNS

Structure

CoFe₂O₄ in BaTiO₃ matrix



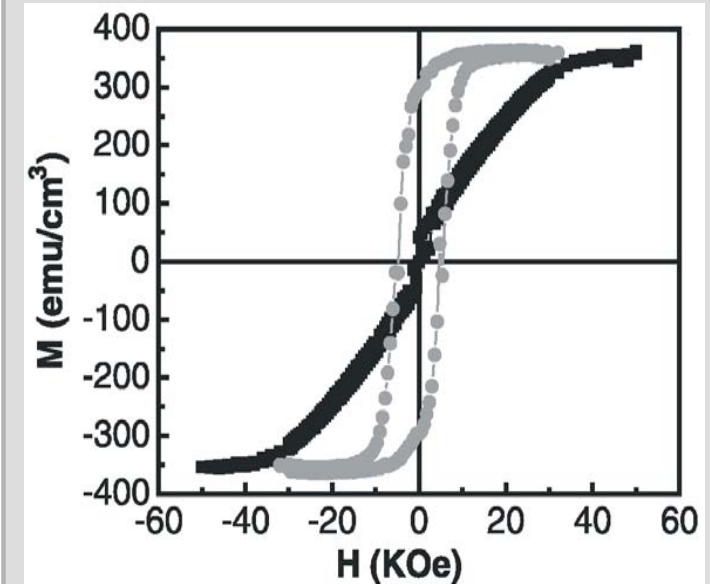
CoFe₂O₄
(ferrimagnetic)

BaTiO₃
(piezoelectric)

Deposition from a Ti-Ba-Co-Fe oxide target by pulsed laser deposition

Magnetis

m



- Room-temperature functionality
- Perpendicular anisotropy owing to matrix-induced strain in the columns

H. Zheng et al., Science 303, 661 (2004)



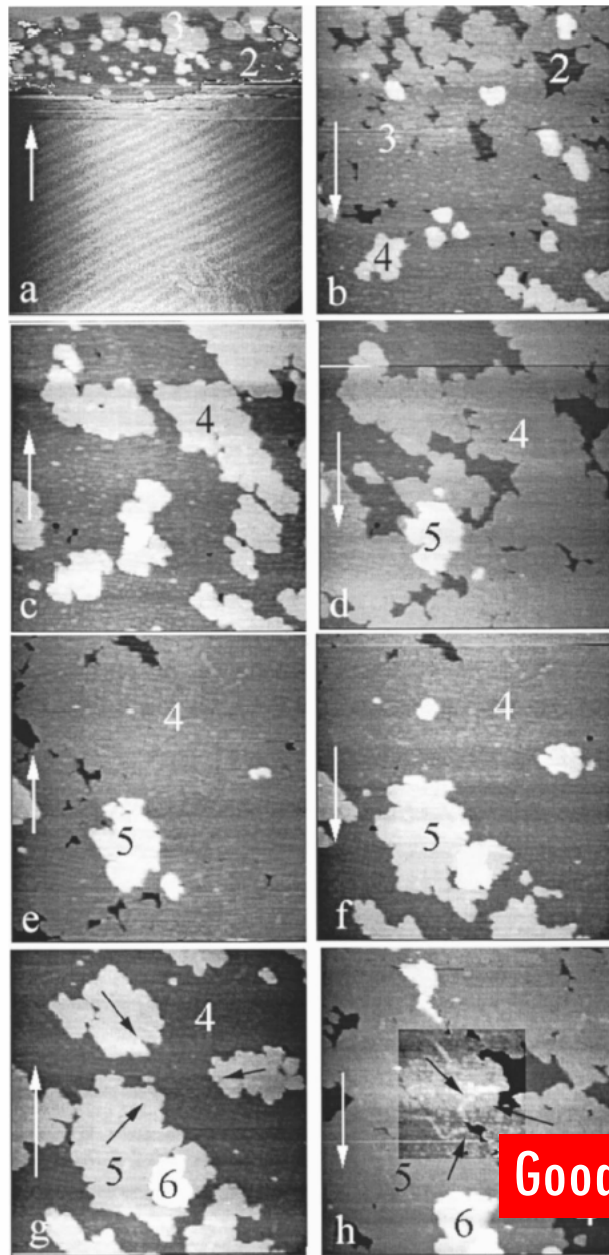
I. Fabrication methods

- ➡ 1. Epitaxial self-assembly & self-organization
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- ➡ 3. Future prospects for self-organization.

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Continuous films



Co/Au(111)/mica

Layer-by-layer growth

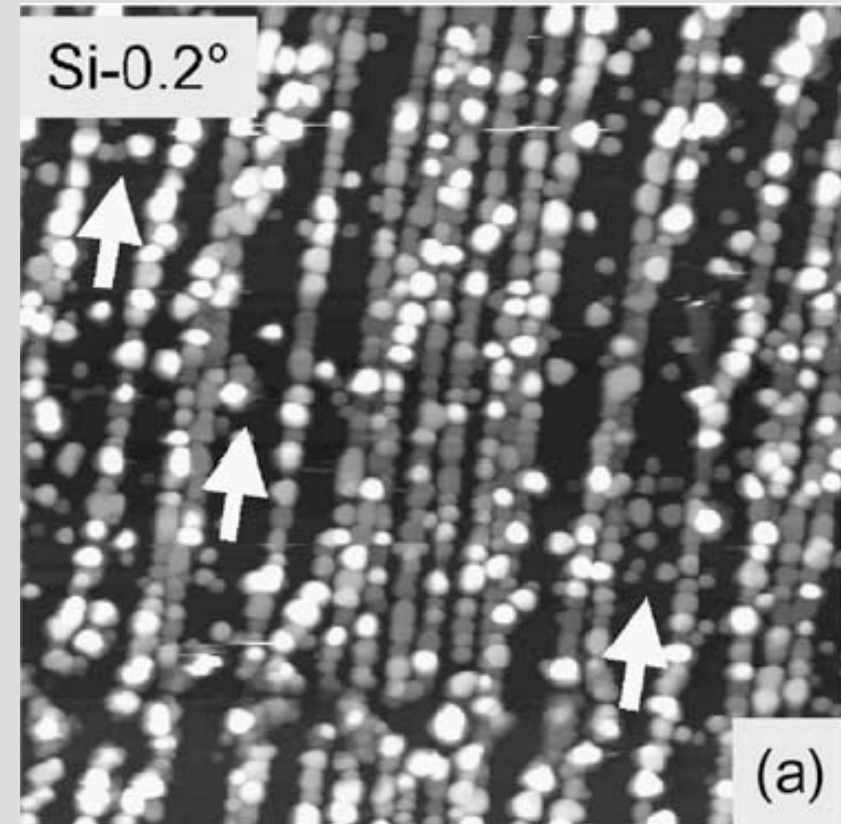
➤ Higher magnetic anisotropy Than for MBE

L. Cagnon et al.,
PRB63, 104419
(2001)

Good aspects

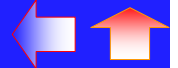
Continuous films

Au/H-Si(111)



Step decoration explained by preferential nucleation

M. L. Munford, Surf. Sci. 539, 95 (2003)



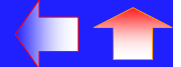
See talk by
K. NIELSCH

Advantages

- ↪ Low cost
- ↪ Versatility of ligands: fonctionalize, tune distances etc.

Drawbacks

- ↪ More difficult to fabricate alloys (stoichiometry, ordering)
- ↪ Annealing can burn ligands (nearly solved)
- ↪ Moderate packing density



Clusters by physical means: 1-10nm

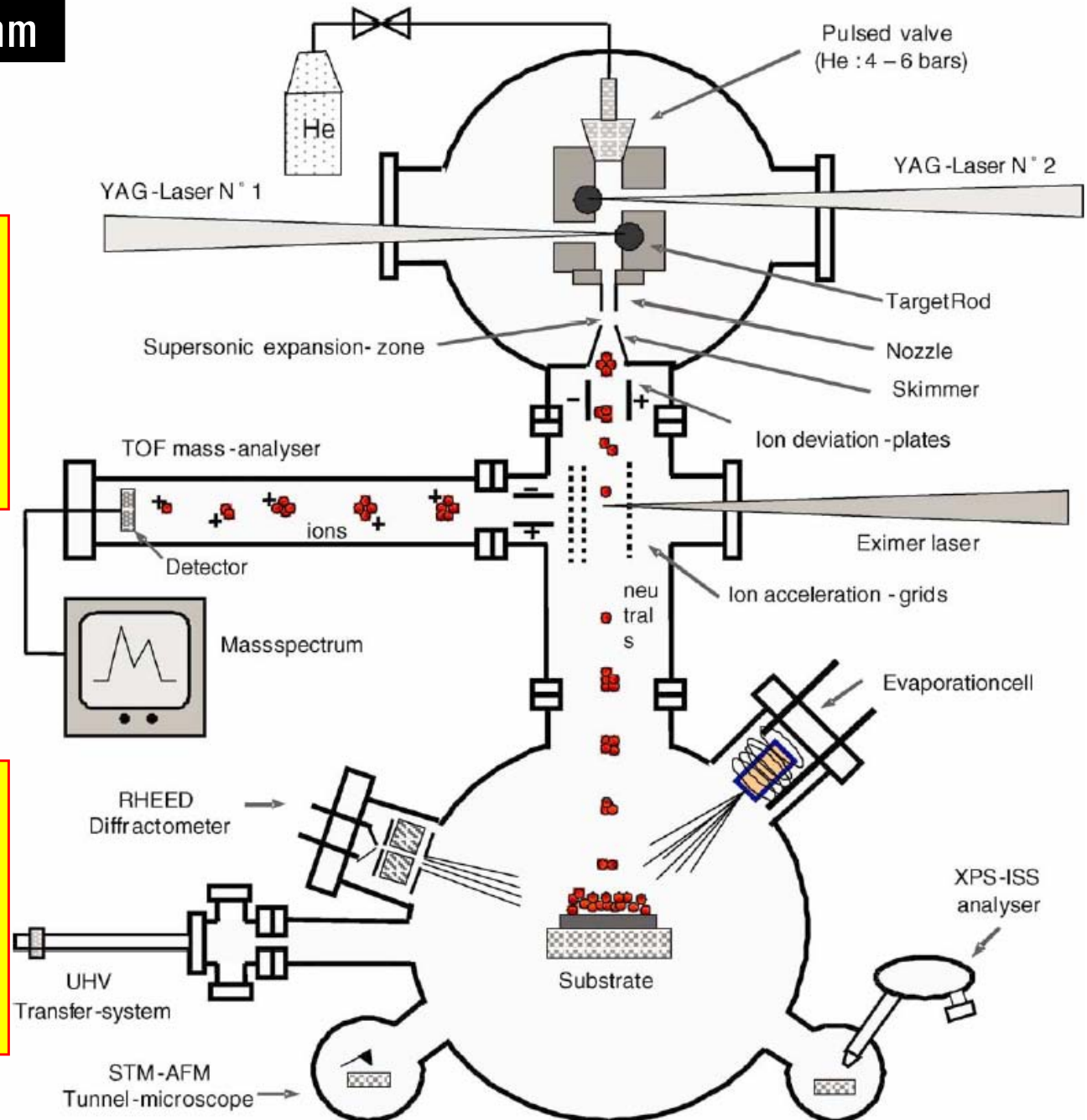
Example: Laser vaporization in inert gas

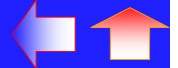
- ↪ Many elements suitable
- ↪ Mass filtering
- ↪ Bimetallic clusters available
- ↪ Landing without fragmentation

J. Bansmann et al.,
Surf. Sci. Rep. 56, 189 (2005)

Other set-ups

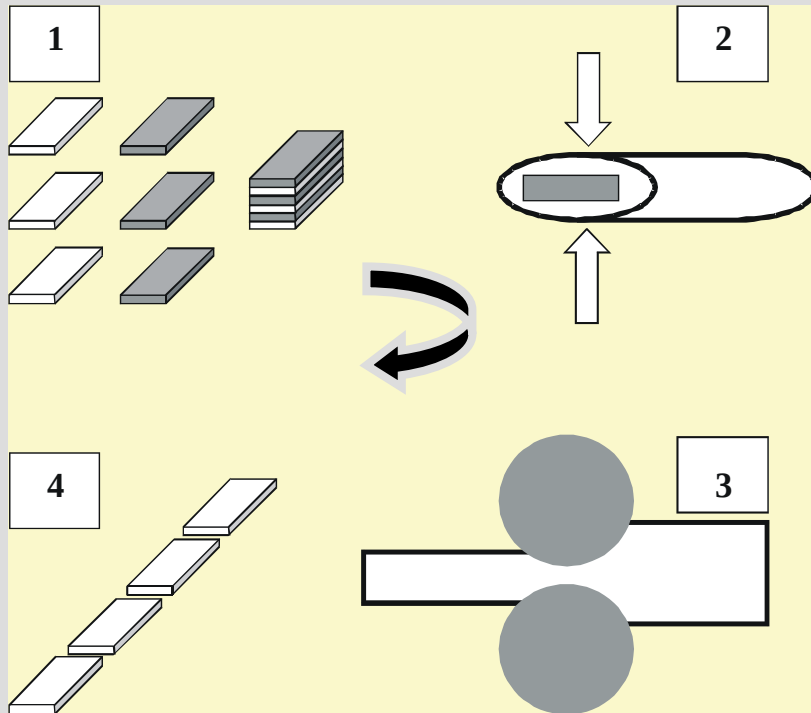
- ↪ Gas aggregation sources with thermal evaporation
- ↪ Arc Cluster Ion Source (ACIS).





Rolling and extrusion : an original route for bulk nanocomposites

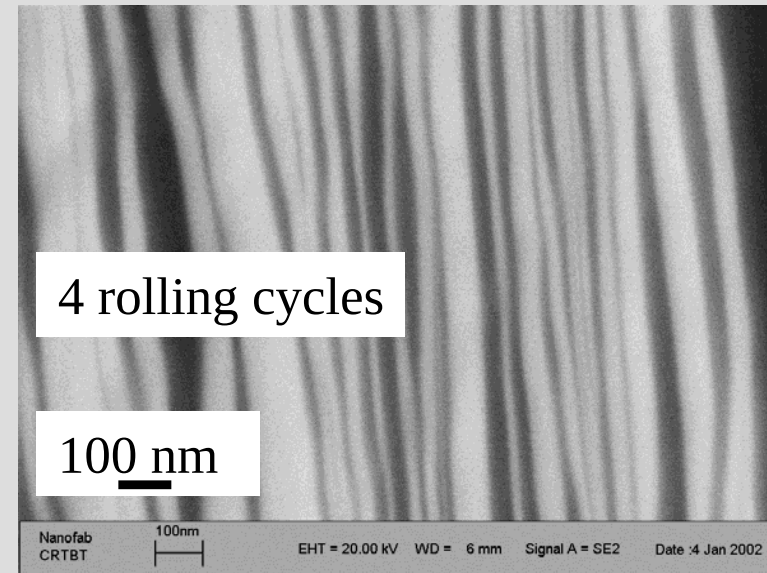
Principle



≈ 100 passes per cycle ; $t_{\text{init}}/t_{\text{final}} \approx 10$
No stress-relieving heat treatment

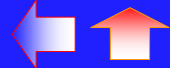
Example

FePt

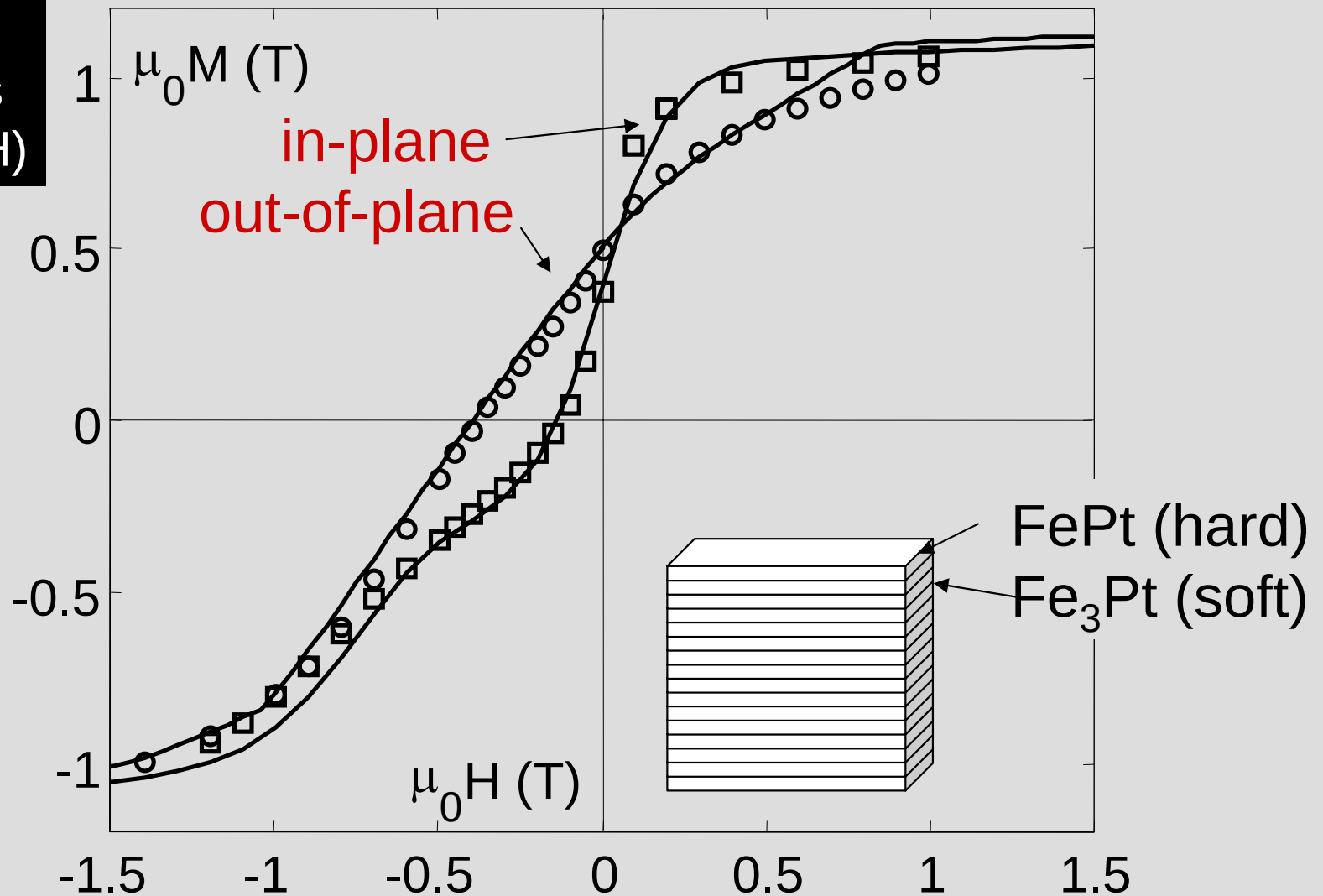


Strong texture
(close to epitaxial relationship !)

N.H. Haï, N.M. Dempsey, D. Givord, J. Magn. Mater. 262 (2003) 353



FePt/Fe₃Pt
calculated versus
experimental M(H)



↪ Dipolar spring magnet, an original concept, and bulk preparation



Personal views on self-organization

- ⇒ Thin and ultrathin films area: a few 'niche' area still exist, however leaves research to become a tool.
- ⇒ Self-organization: on step further thin films. 10-15 years old. Many advances for fundamental science, but seem to remain a niche for applications in the current state.
- ⇒ Two ways to go forward:
 - ⇒ Open new paths in self-organization: 3D, combine with other techniques.
 - ⇒ Increase versatility and improve functionality of self-organized systems, to include in devices.

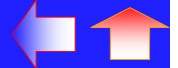


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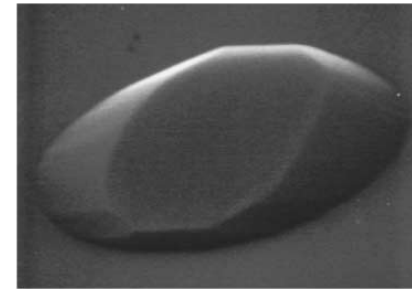


GaAs / GaAs

- **Step 1:** Deposition of SiO_2 layer
- **Step 2:** Ex-situ lithography on oxide layer, plus wet chemical etching
- **Step 3:** Growth of GaAs through windows, either in dot or antidot array, or lines.

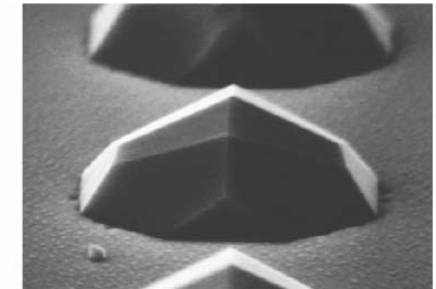
H. Hasegawa, J. Cryst. Growth 227-228, 1078 (2001)

First demonstrations on metals:
Co/Ru(0001) (groupe of S. D. Bader)



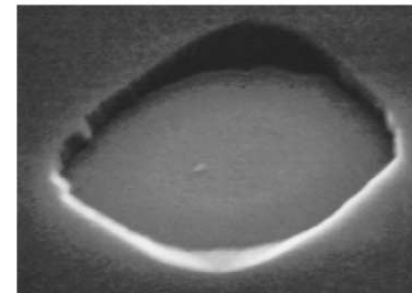
(a)

2 μm



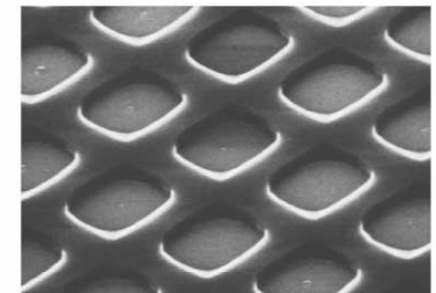
(b)

500nm



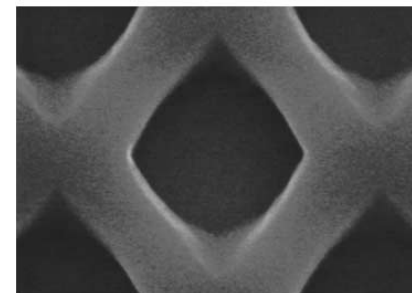
(c)

2 μm



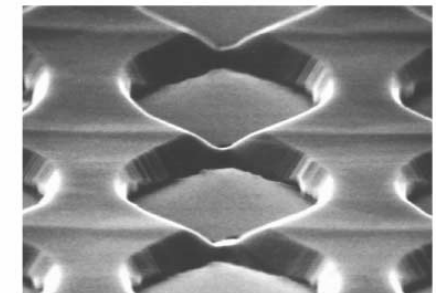
(d)

2 μm



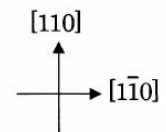
(e)

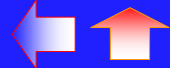
1 μm



(f)

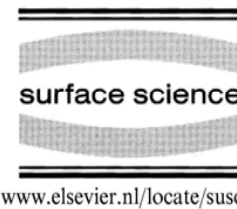
500nm





ELSEVIER

Surface Science 432 (1999) 37–53



www.elsevier.nl/locate/susc

How to control the self-organization of nanoparticles by bonded thin layers

A. Bourret *

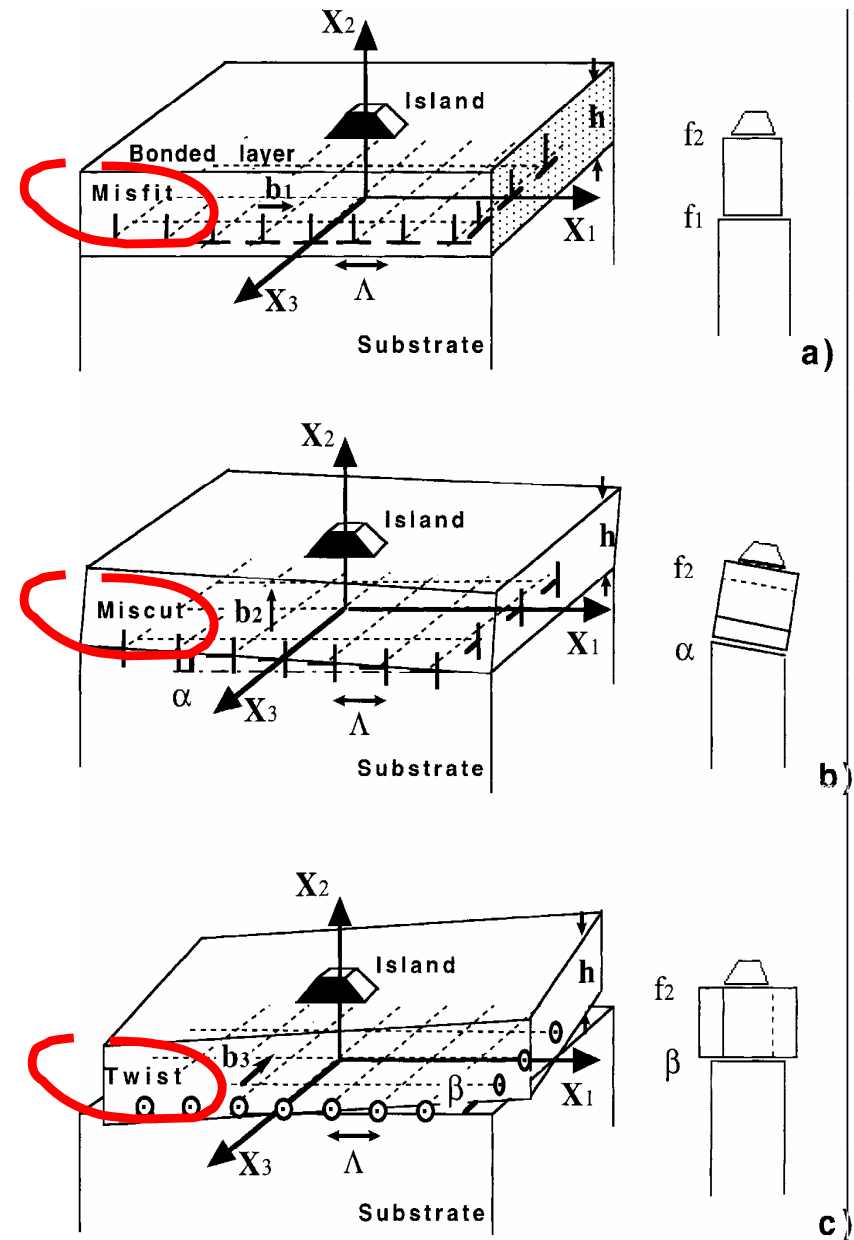
Département de Recherche Fondamentale sur la Matière Condensée, SP2M¹, CEA Grenoble, 17 rue des Martyrs 38054, Grenoble Cedex 9, France

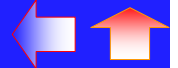
Received 21 December 1998; accepted for publication 6 April 1999

➤ Substrate bonding and smart cut process.

↪ array of dislocations arise from either:

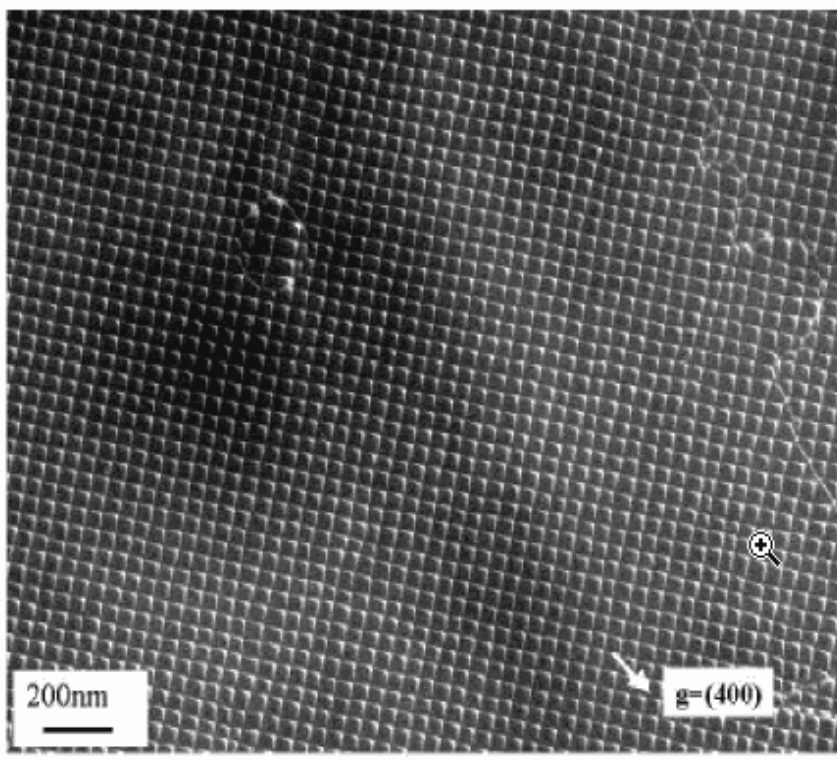
- Misfit
- Miscut
- Twist





Step 1: wafer bonding

Screw dislocations

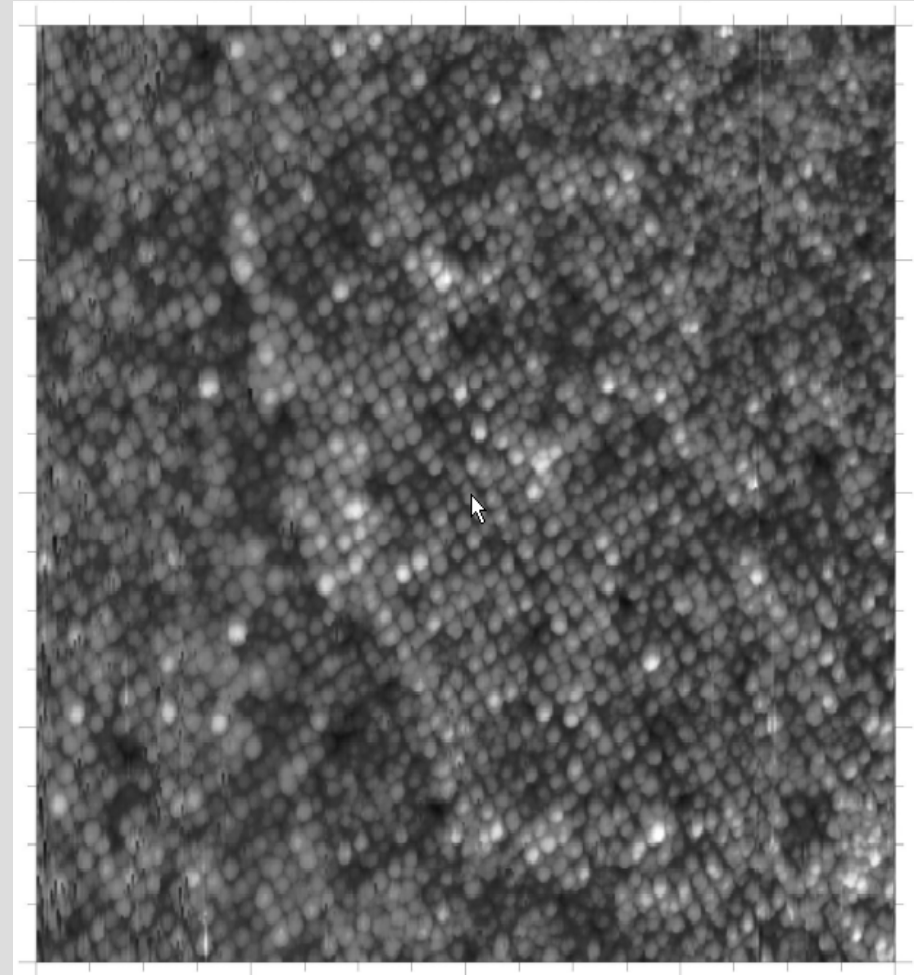


J. L. Rousseau *et al.*, APL80, 4121 (2002)

CEA-Grenoble

Step 2: template for growth

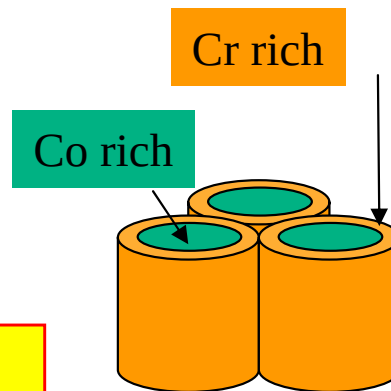
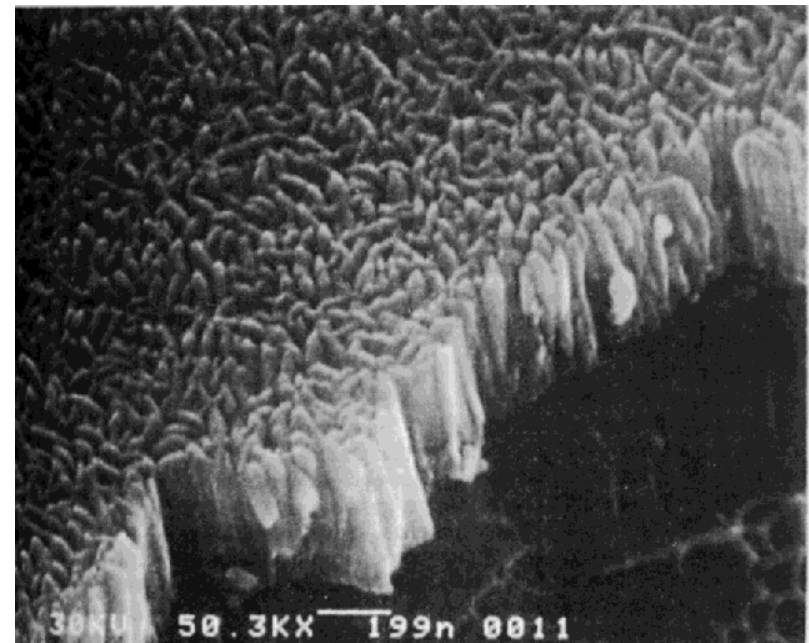
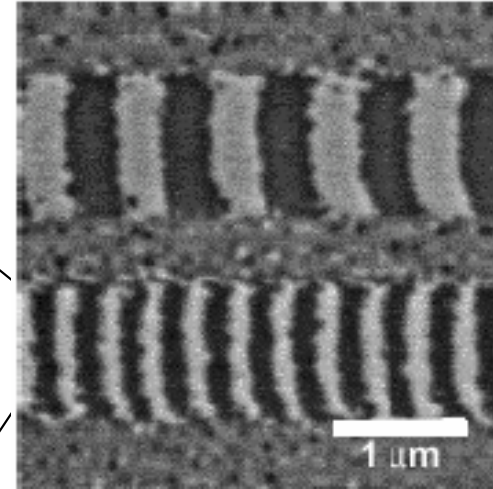
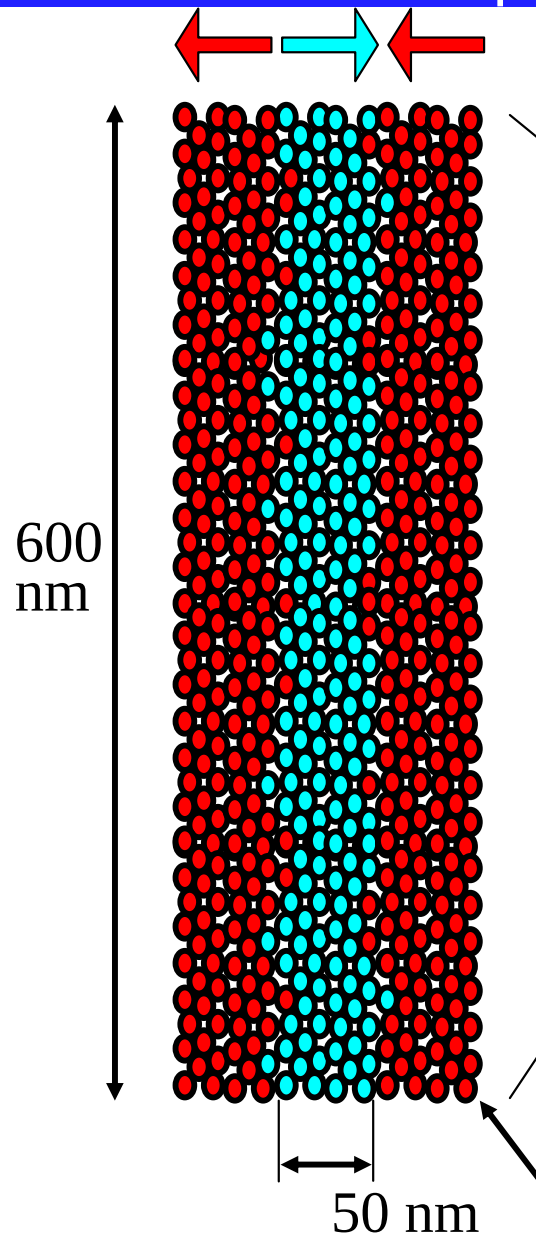
1. Chemical etching > corrugation enhanced
2. Growth (here: Ge/Si)



J. Eymery, Habilitation (2003)
F. Leroy, Surf. Sci. 545, 211 (2003)



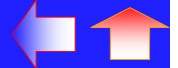
Principle of granular media



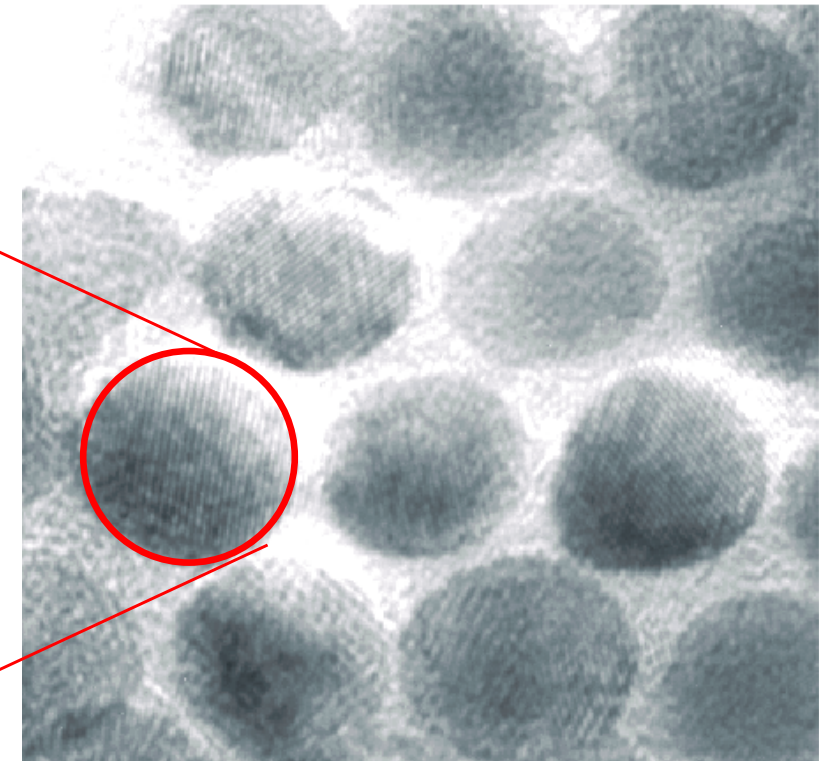
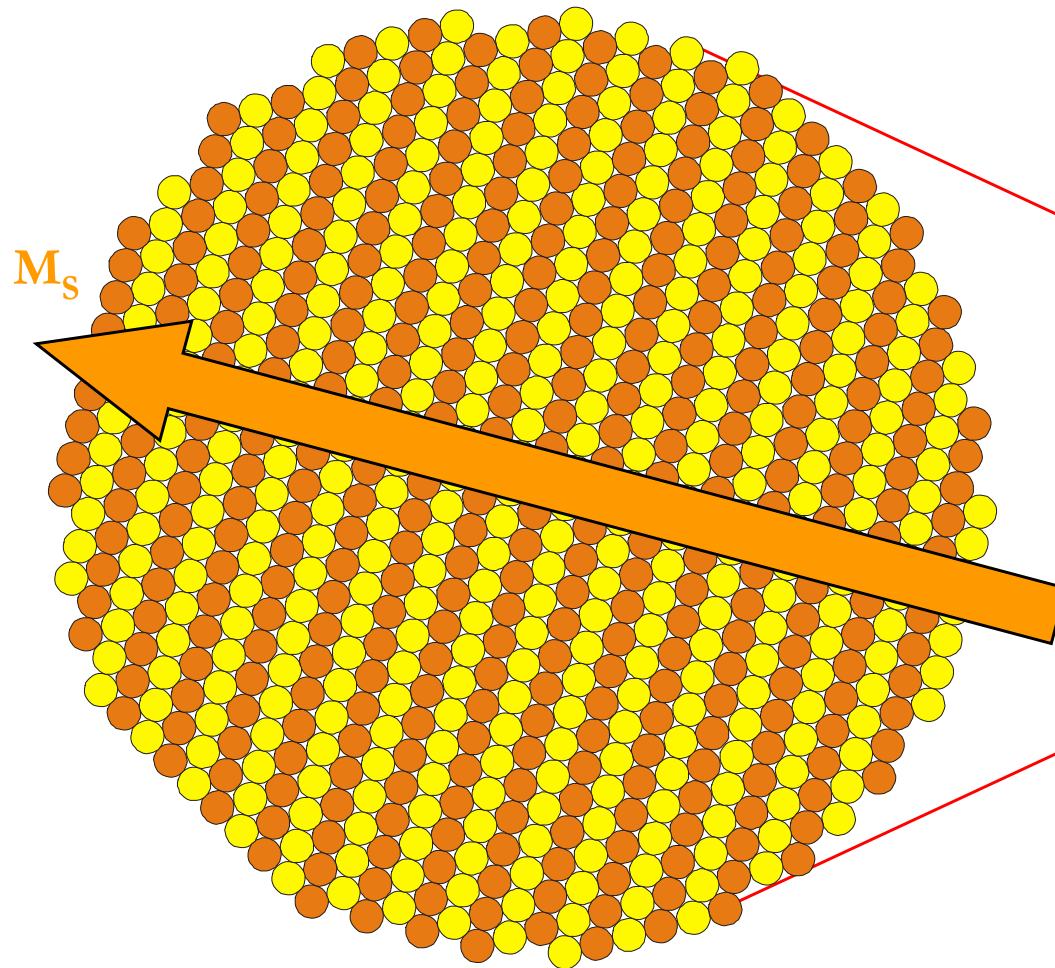
Grain : 10 nm

CoPtCrTaB hard disk

High number of grains per bit



$L1_0$ phase : alternation of Fe and Pt monoatomic planes
→ extremely high magnetocrystalline anisotropy K



Random orientation of anisotropy axes

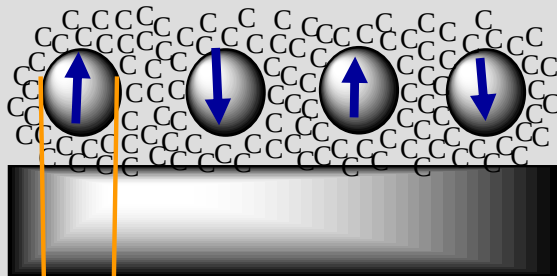
Nanoparticles self-organized on a surface (mono- or multilayers)

Future recording media?

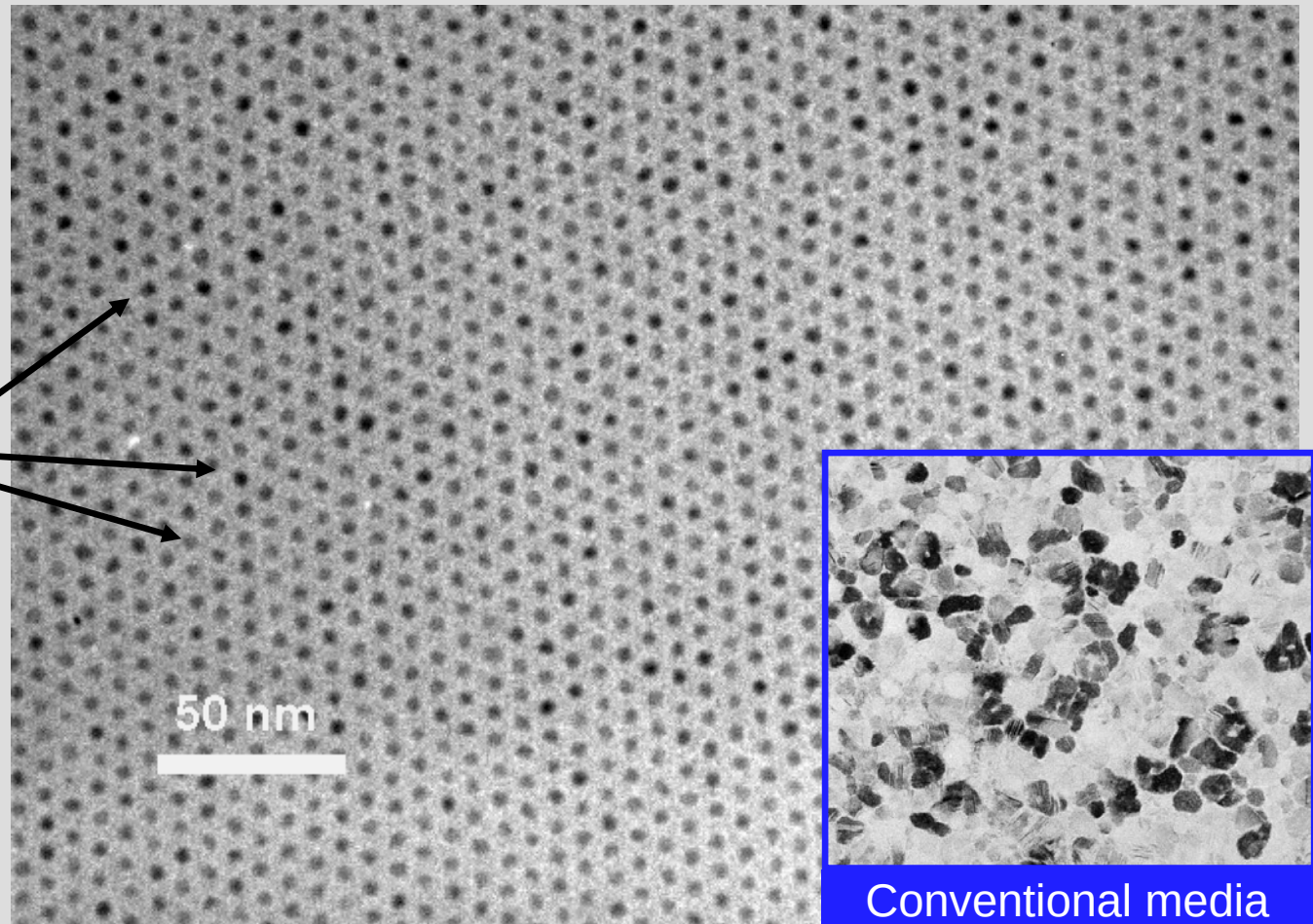
FePt nanoparticles
in an organic matrix

Cross-section

"1" "0" "1" "0"



Diameter : 6 nm



Conventional media

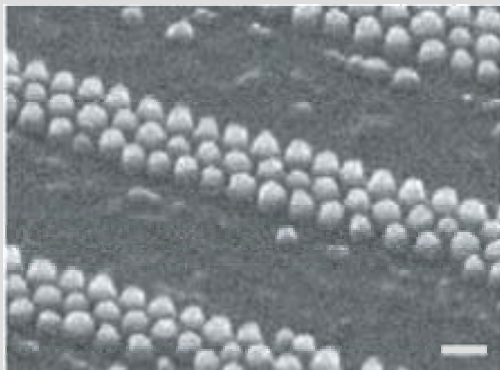
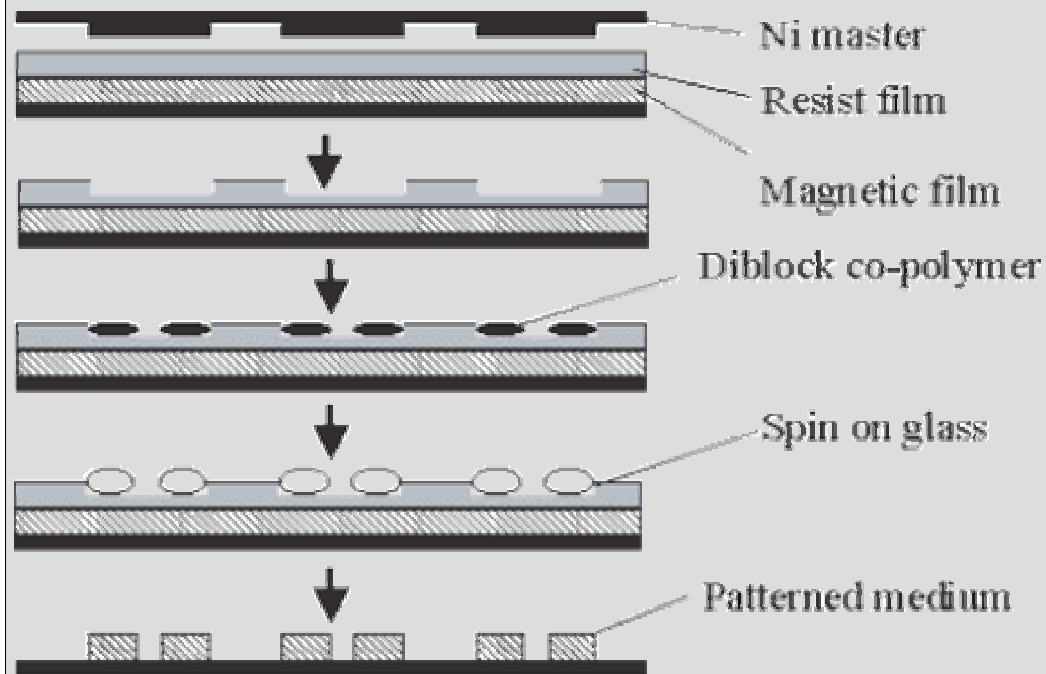
Good aspects

- ↪ Weak cost
- ↪ Compatible with existing techno
- ↪ Weak size distribution

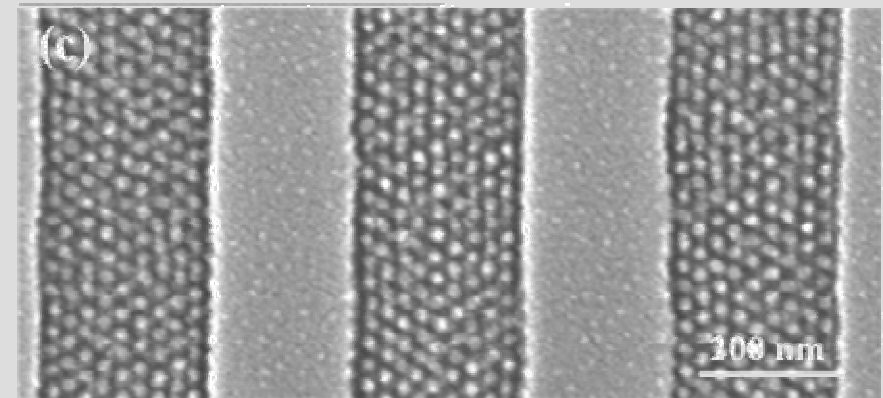
Weak aspects

- ↪ Weak effective magnetization
- ↪ Middle-range order only
- ↪ Distribution of anisotropy axes (should be solved)

$\text{Co}_{74}\text{Cr}_6\text{Pt}_{20}$, 40nm diameter



Dots of Silica

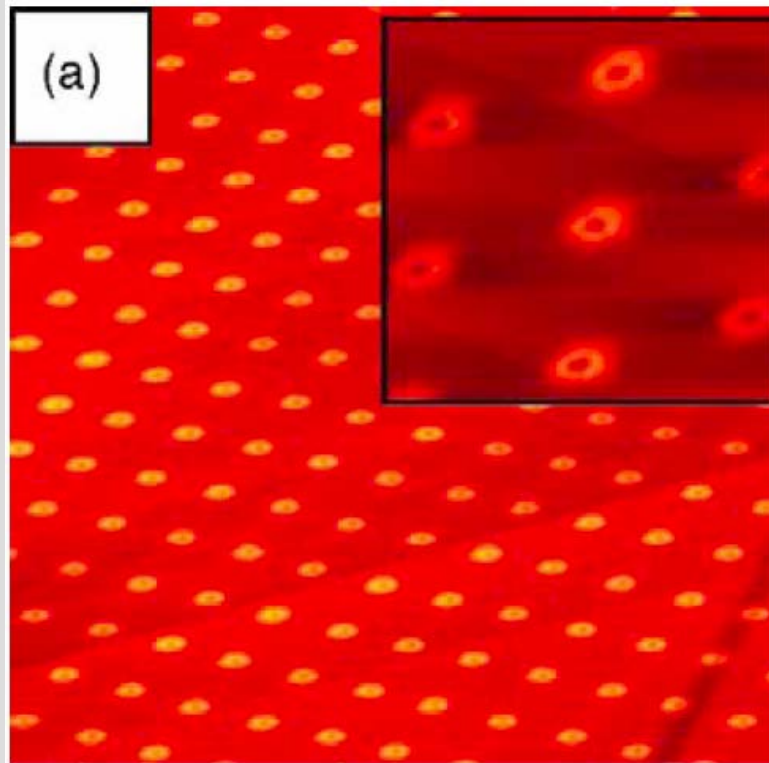


Different approaches

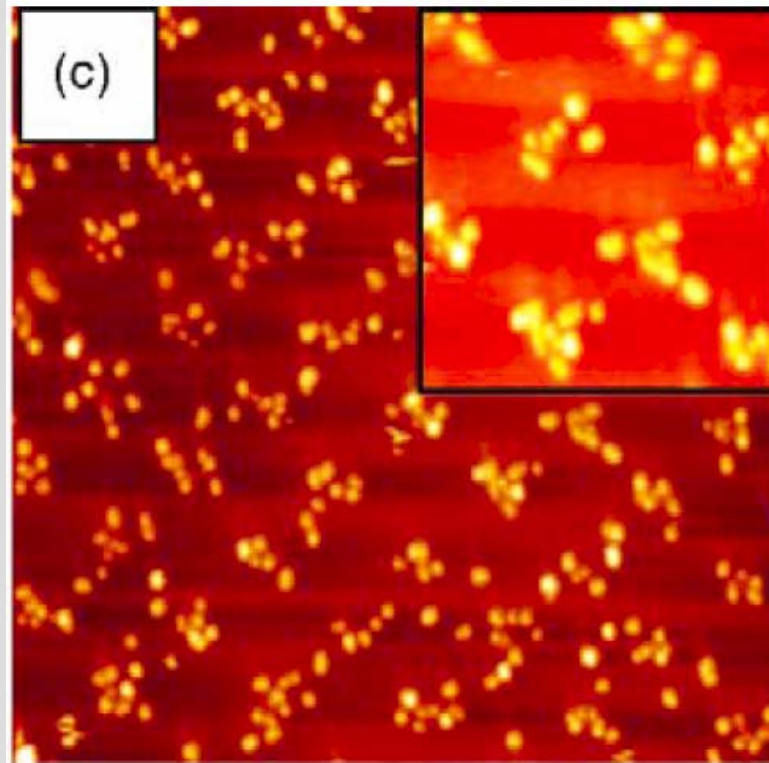
- Di-block co-polymers, then transferred by etching (rather than lift-off)
- Deposition of clusters fabricated by chemical means (less promising?)

Cluster landing guided by Focused Ion Beam (FIB)

HOPG functionalized with FIB



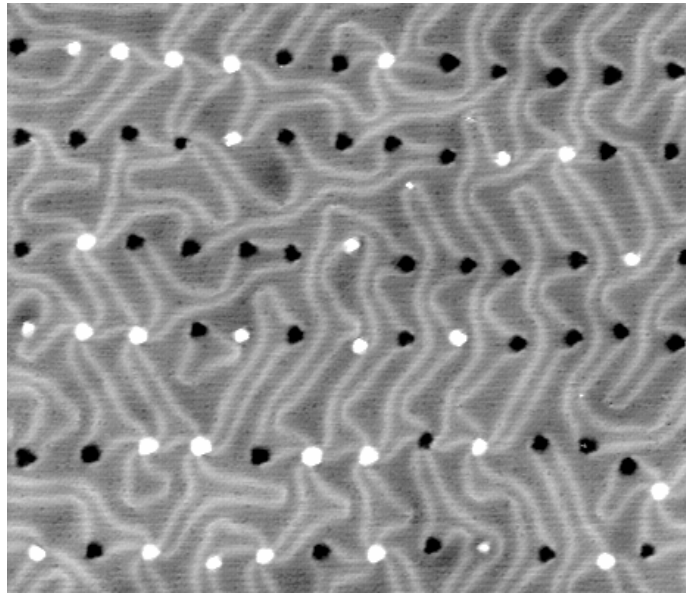
10^{-2} AL of Au₇₅₀ clusters



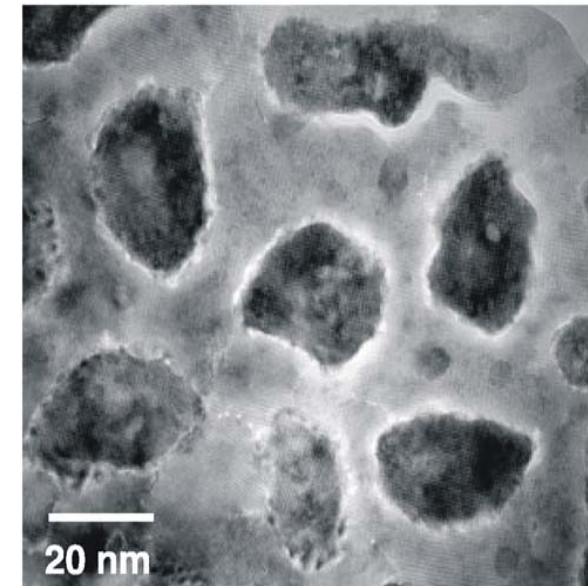
Images: 3.4 microns

REVIEW: J. Bansmann et al., Surf. Sci. Rep. 56, 189 (2005)

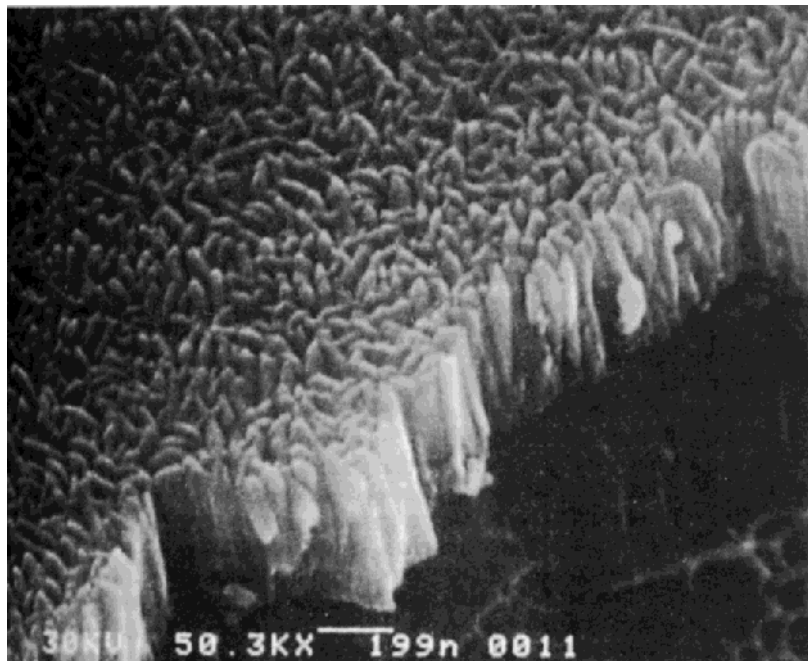
Is anything
really new?



Co pillars in Au(111)



CoFe₂O₄ in BaTiO₃ matrix



CoPtCrTaB hard disk



Volcanic organs, Scandola, Corsica.

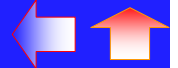


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- ➔ **3. Magnetization reversal and superparamagnetism.**
- ➔ **4. Micromagnetism**

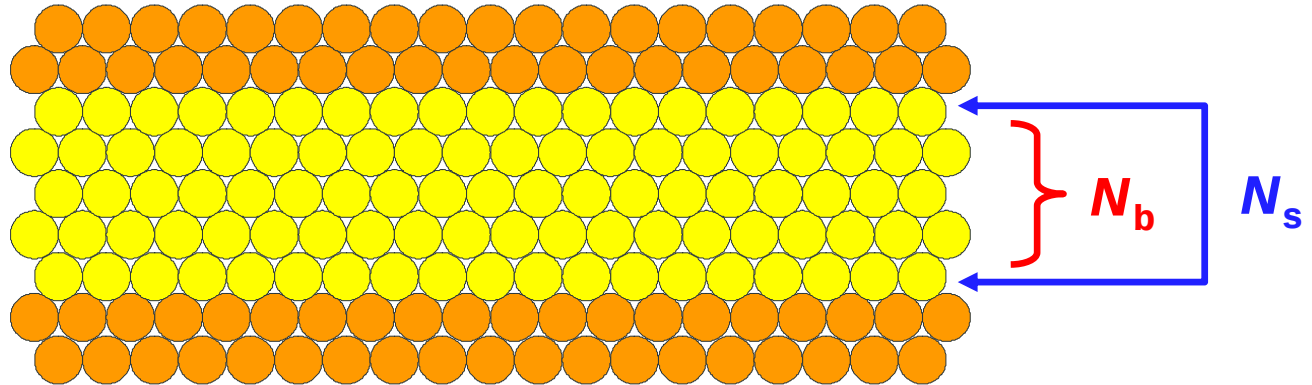


Naïve model

$$T_c = \mu_0 \cdot \frac{J+1}{3J} \cdot \frac{Nw_0 M_0 m_0}{k_B}$$

Molecular field

N neighbors



$$\bar{N} = N_b - \frac{2(N_b - N_s)}{t} \quad \longrightarrow \quad \Delta T_c(t) \sim t^{-1}$$

Less naïve...

Thickness-dependant molecular field

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

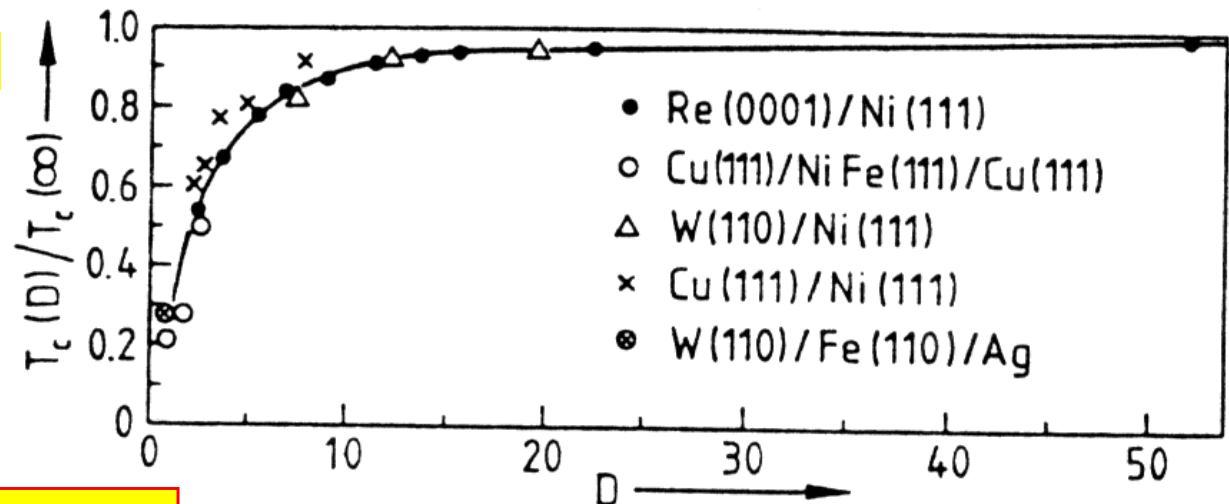
$$\lambda = 1$$

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

Conclusion:

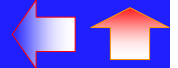
Naïve views are roughly correct

Experiments



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

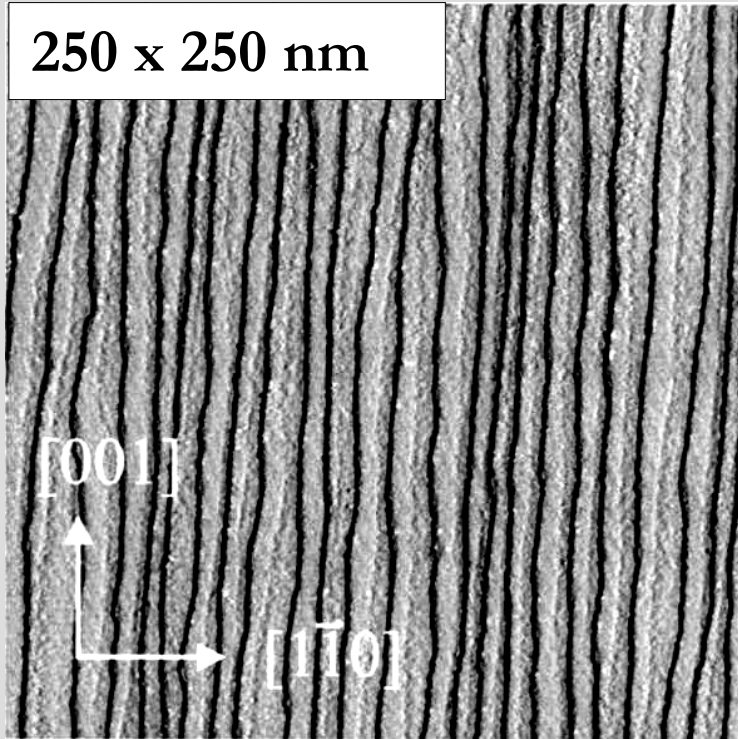




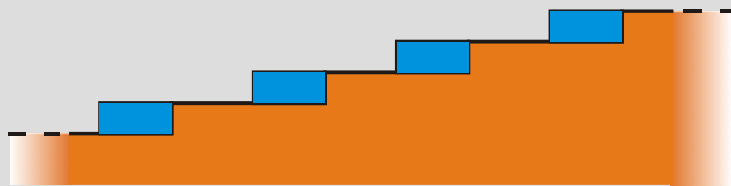
Stripes on vicinal surfaces

Fe(0.5ML) / W(110)

250 x 250 nm

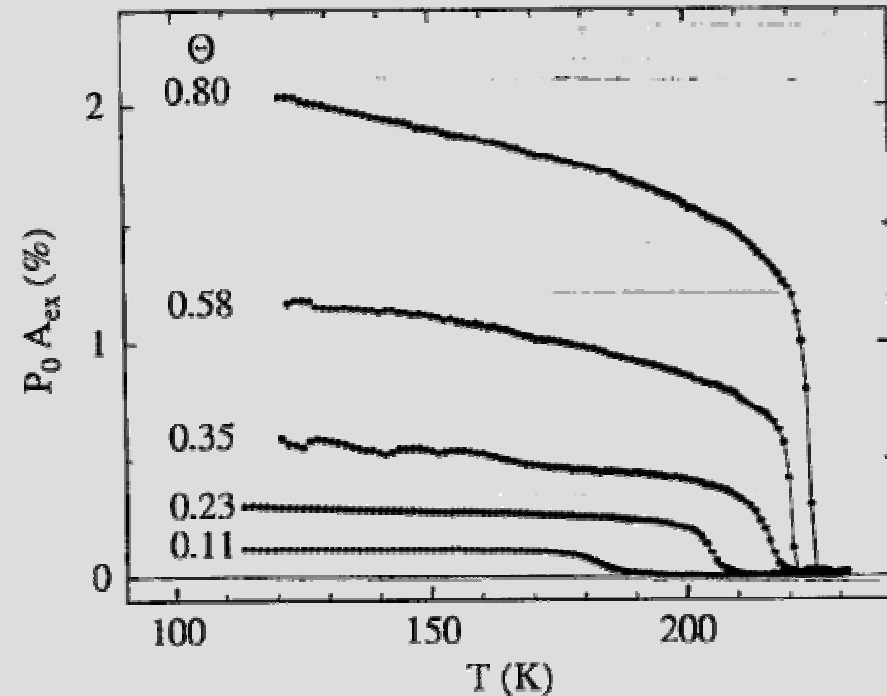


J. Hauschild *et al.*,
Phys.Rev.B57, R677(1998)



Magnetic order in 2D: finite-size scaling

Curie temperature as a function of stripe width



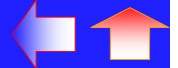
$$T_C(n)/T_C(\infty) \propto 1 - (n_0/n)^\lambda$$

$\lambda = 1.03$ in agreement with Ising model (=1)

H. J. Elmers *et al.*, PRL73, 898 (1994)

$\lambda = 1.2 \pm 0.3$ for Fe stripes / Pd(110)

D. Li *et al.*, PRB64, 144410 (2001)



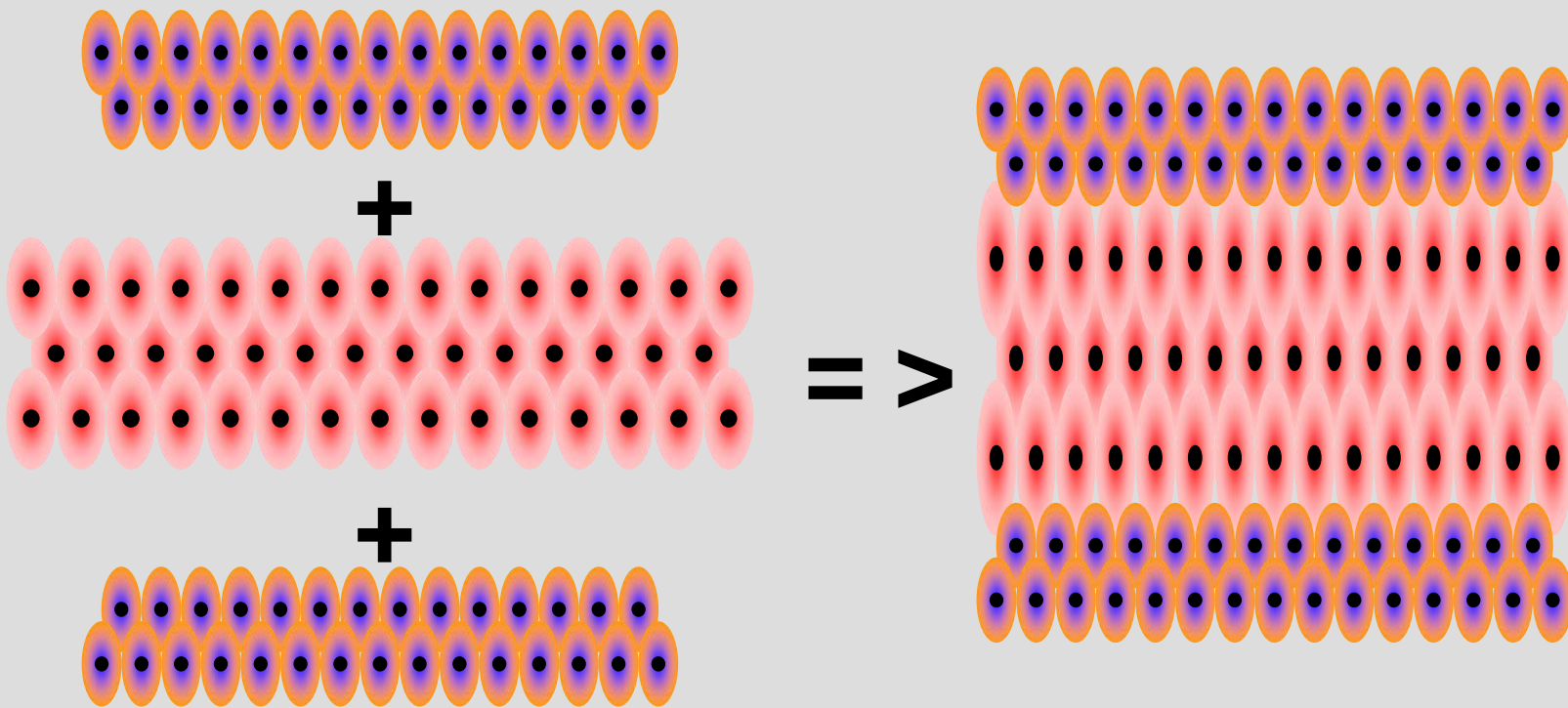
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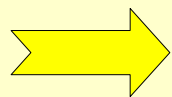
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- ➡ 2. **Magnetic anisotropy**
- ➡ 3. Magnetization reversal and superparamagnetism.
- ➡ 4. Micromagnetism

Magneto-elastic anisotropy



Effect

Deformation of crystal structure



Correction to the
magneto-crystalline energy

Result

$$E_{\text{mel}} = K_{\text{mel},1} \cos^2(\theta) + \dots$$

$$K_{\text{mel},i} \sim B_i \varepsilon$$

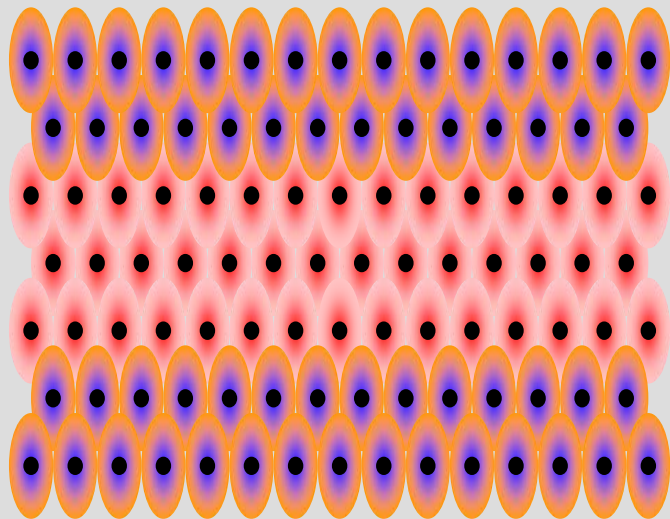
Occurs in all nanostructures ($\leq 5\text{nm}$):

Thin films and stripes, supported islands, free clusters etc.

Surface / Interface anisotropy

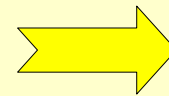
L. Néel, J. Phys. Radium 15, 15 (1954)

« Superficial magnetic anisotropy and orientational superstructures »



Effect

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 »

Pair model of Néel:

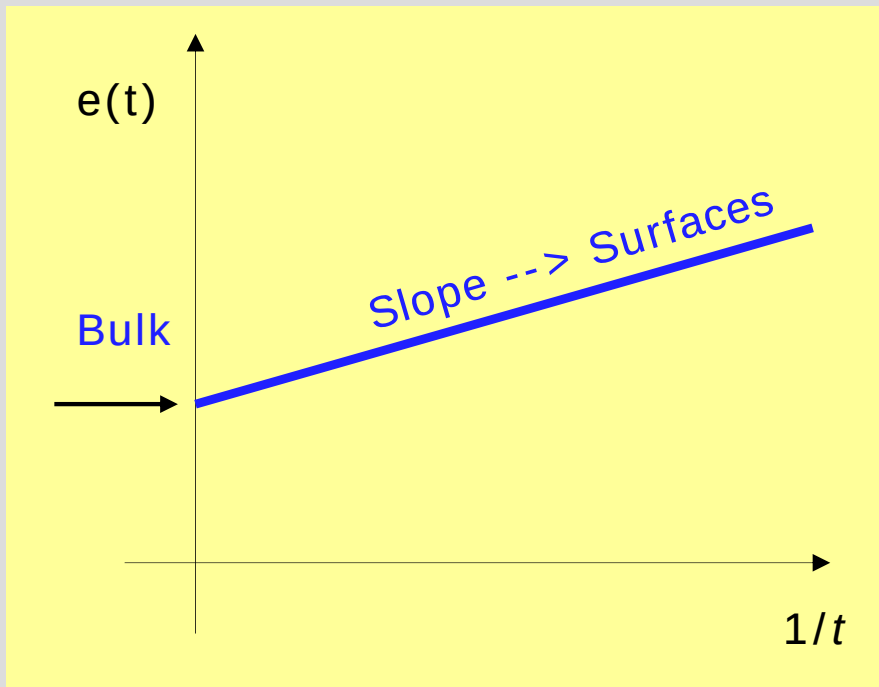
- K_s estimated from magneto-elastic constants
- Does not depend on interface material
- Yields order of magnitude only

Again, occurs in all nanostructures ($\leq 5\text{nm}$)

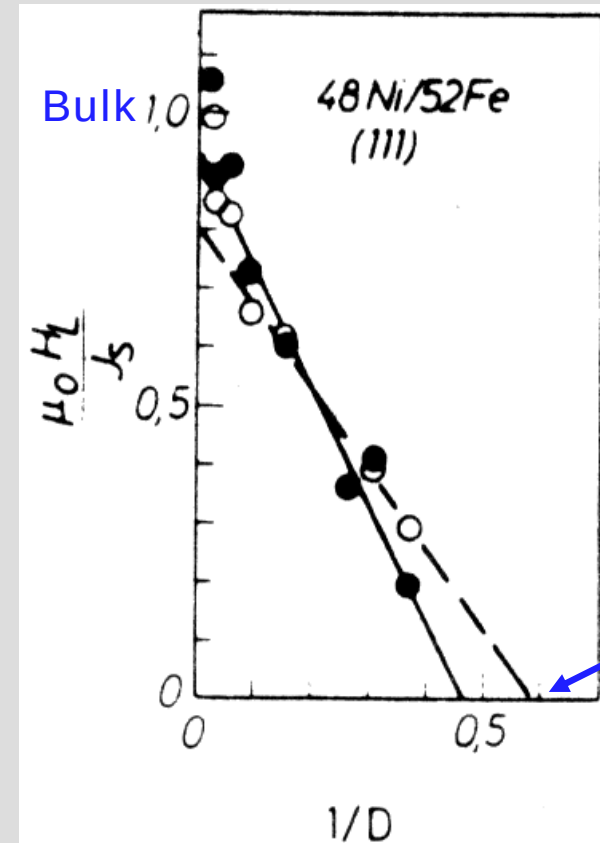
History of surface anisotropy : $1/t$ plots

$$E_{\text{tot}}(t) = k_V t + 2k_S$$

$$\Rightarrow e(t) = k_V + \frac{2k_S}{t}$$



First hint for perpendicular anisotropy

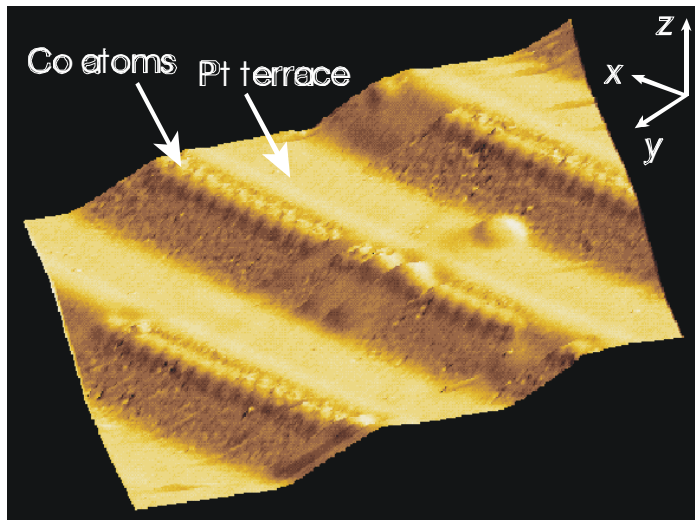


U. Gradmann and J. Müller,
Phys. Status Solidi 27, 313 (1968)

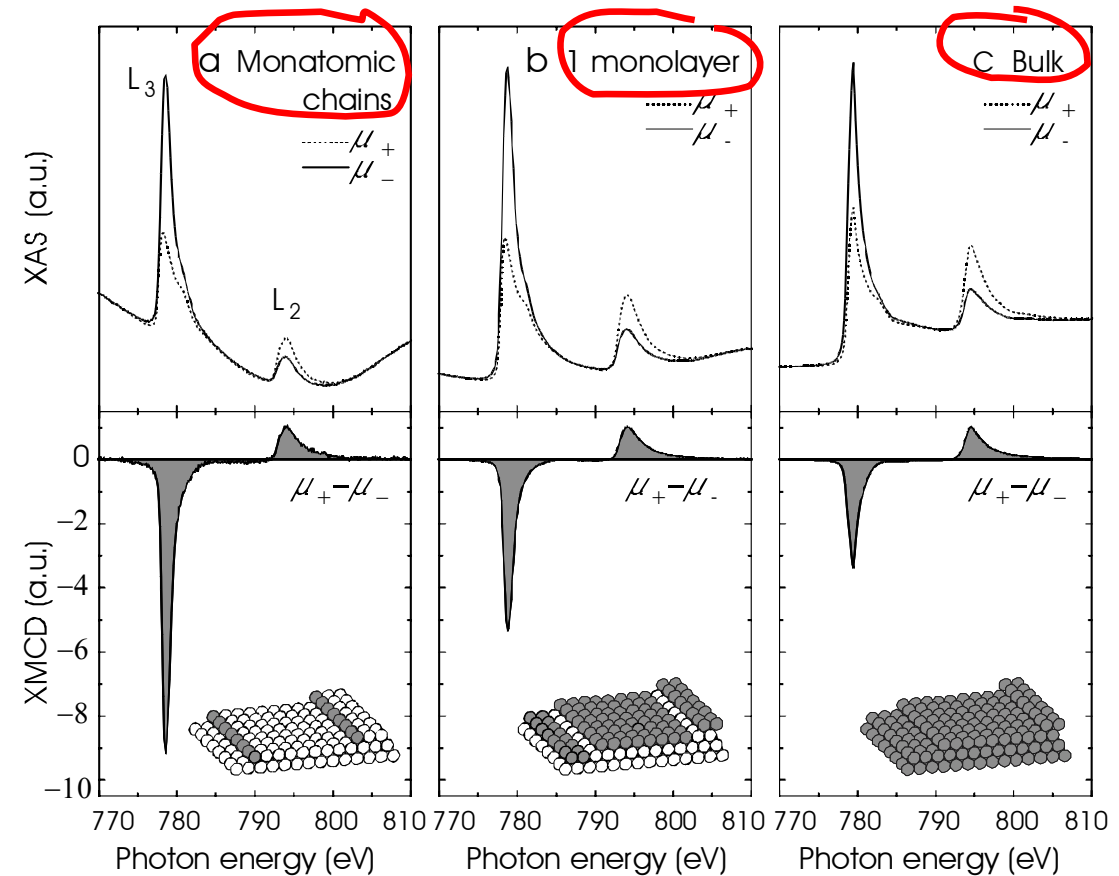
In reality, surface and magneto-elastic anisotropy are entangled. Separation is experimentally difficult, if not impossible quantitatively

From surface to wires (1D)

Self-organized Co/Pt(997)

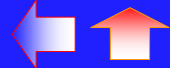


Magnetic circular dichroism



$$\mu_L \approx \int L_3 + \int L_2$$

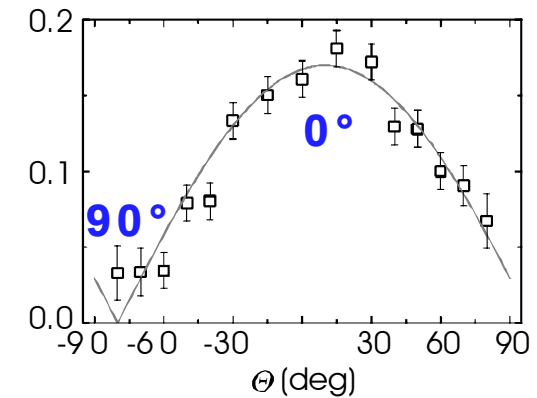
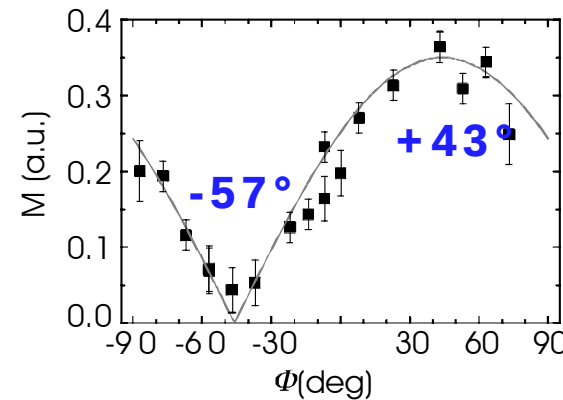
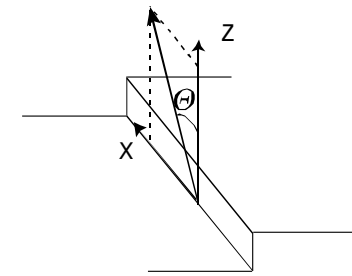
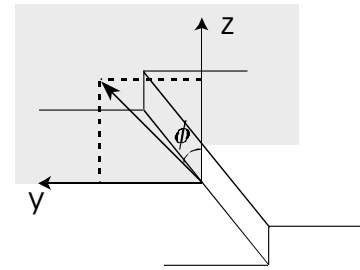
$$\mu_S^{\text{eff}} \approx -\int 2L_3 + 4\int L_2$$



From surface to wires (1D)

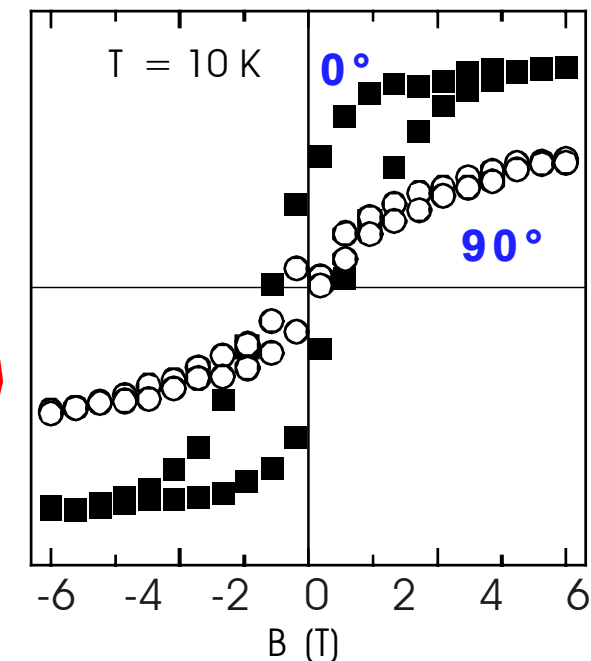
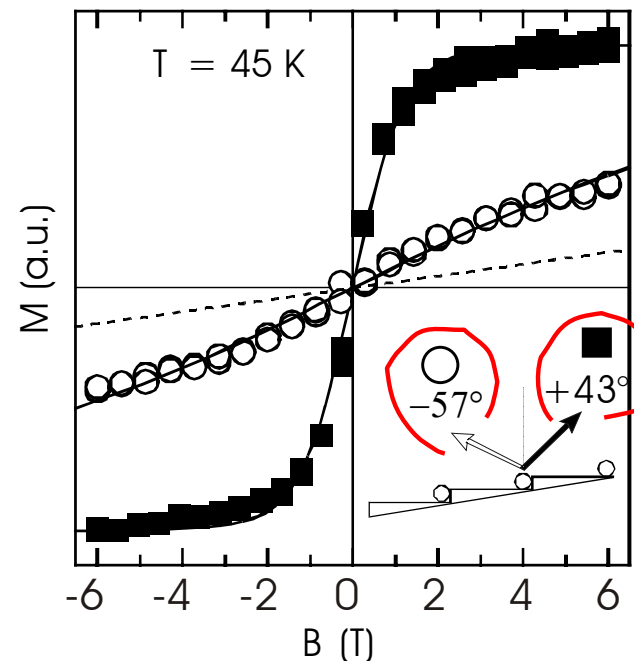
Qualitatively:

Easy axis of magnetization perpendicular to the wires, but not the the mean film surface, nor to Pt(111)



Quantitatively

- 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: $2\text{meV}/\text{atom}$

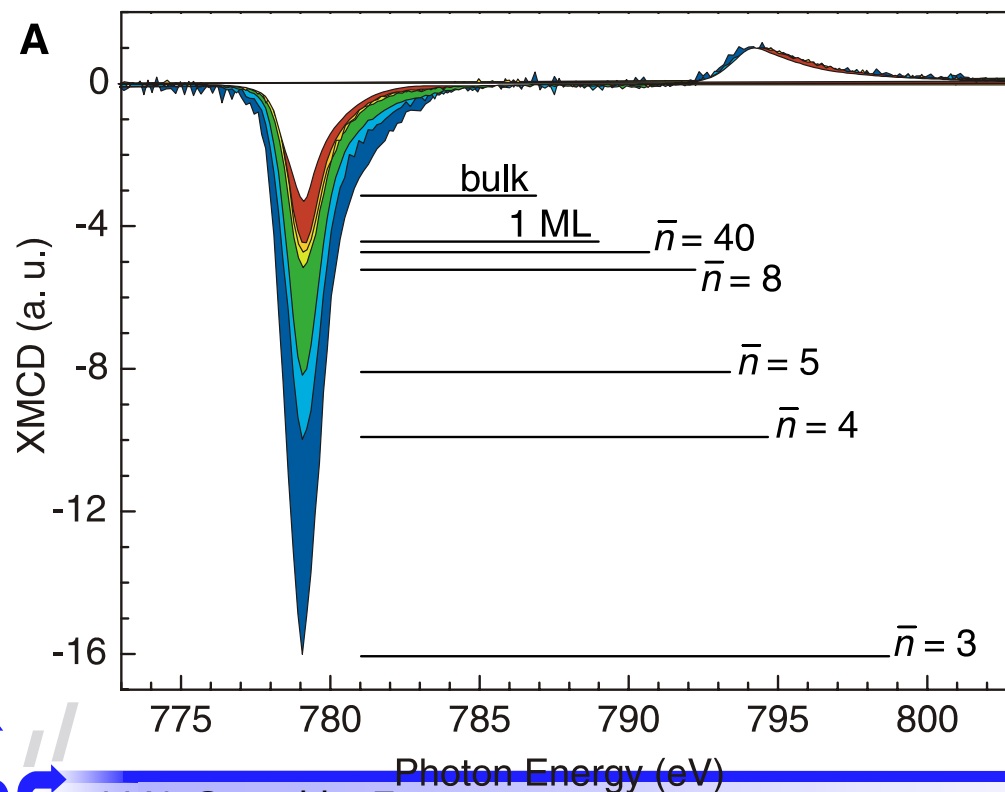


From surface to atoms (0D) **Co/Pt(111)**

Giant Magnetic Anisotropy of Single Cobalt Atoms and Nanoparticles

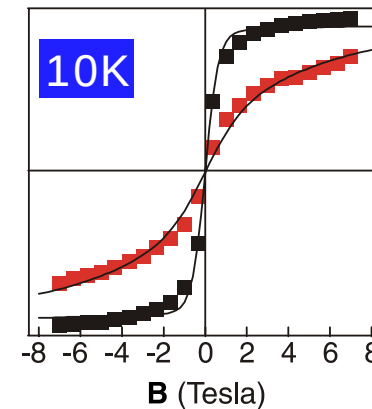
P. Gambardella,^{1,2*} S. Rusponi,^{1,2} M. Veronese,³ S. S. Dhesi,^{4,†}
C. Grazioli,³ A. Dallmeyer,⁵ I. Cabria,⁵ R. Zeller,⁵
P. H. Dederichs,⁵ K. Kern,^{1,2} C. Carbone,^{3,5} H. Brune¹

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

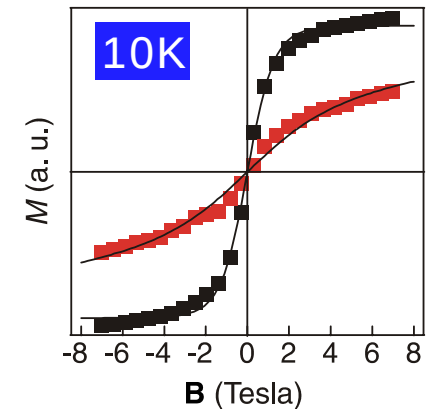


LLN, Grenoble, France.

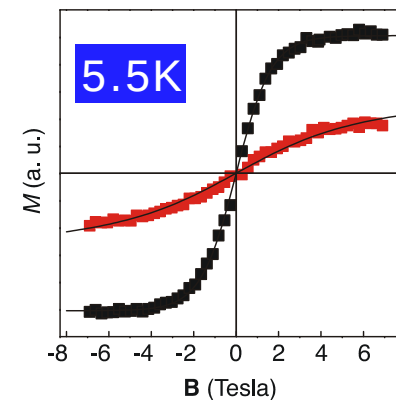
8 atoms



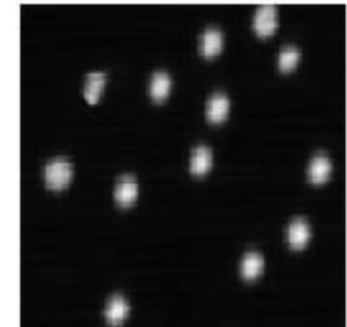
4 atoms



1 atom



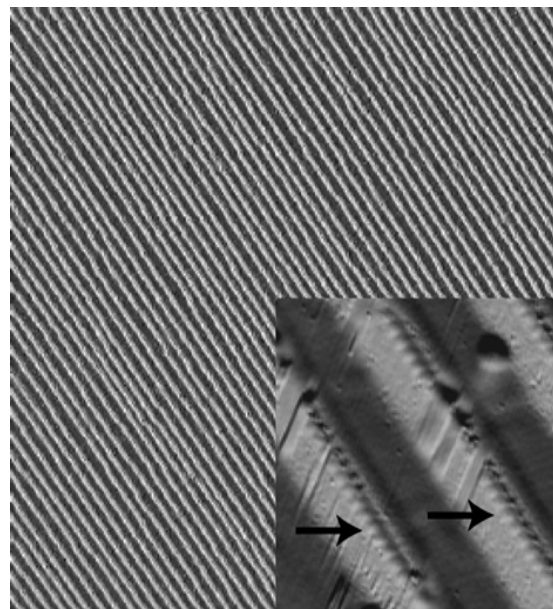
STM, 8.5nm, 5.5K



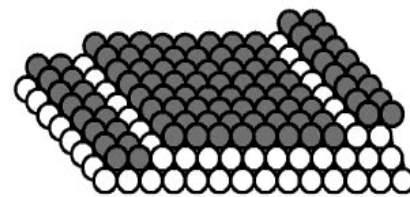
Results:

- Easy axis of magnetization perpendicular to Pt(111)
- Measure of orbital momentum and its anisotropy, not directly magnetic anisotropy

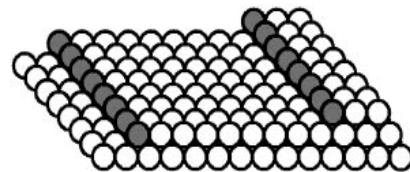
Co / Pt(997)



Terraces ~ 1 ML



Chains ~ 0.12 ML

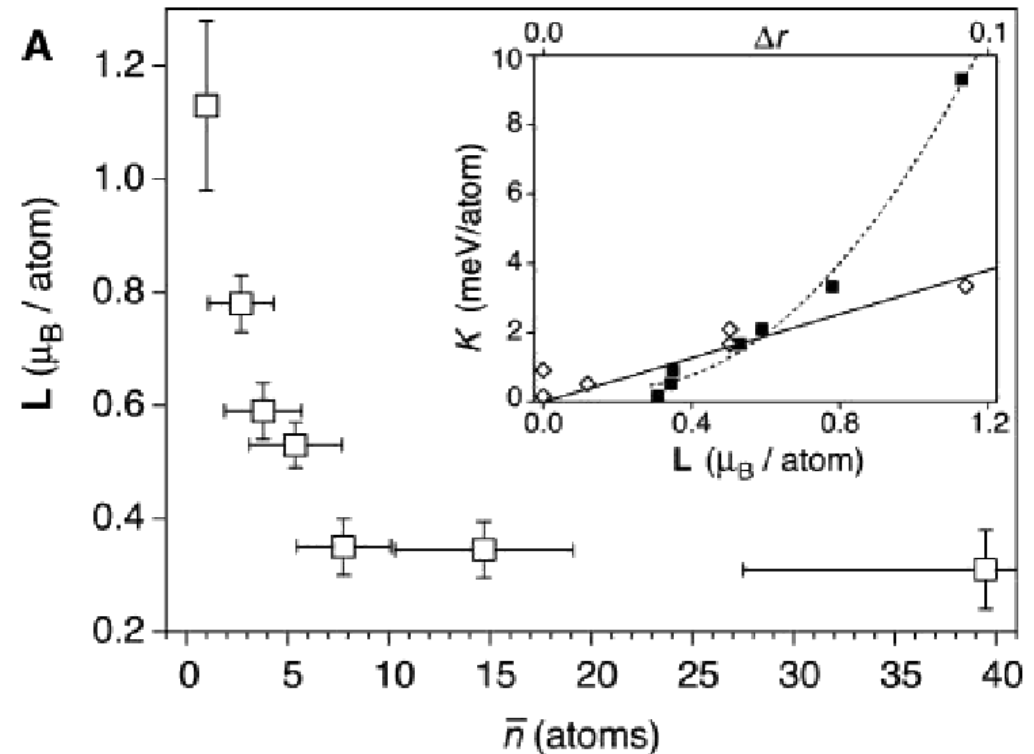


A. Dallmeyer et al., Phys.Rev.B 61(8), R5153 (2000)

Overview

- Bulk: $m_L = 0.14 \mu_B/\text{at.}$
- Surface: $m_L = 0.31 \mu_B/\text{at.}$
- Bi-atomic wire: $m_L = 0.37 \mu_B/\text{at.}$
- Mono-atomic wire: $m_L = 0.68 \mu_B/\text{at.}$
- bi-atom: $m_L = 0.78 \mu_B/\text{at.}$
- atom: $m_L = 1.13 \mu_B/\text{at.}$

Co / Pt(111)



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

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

Conclusions

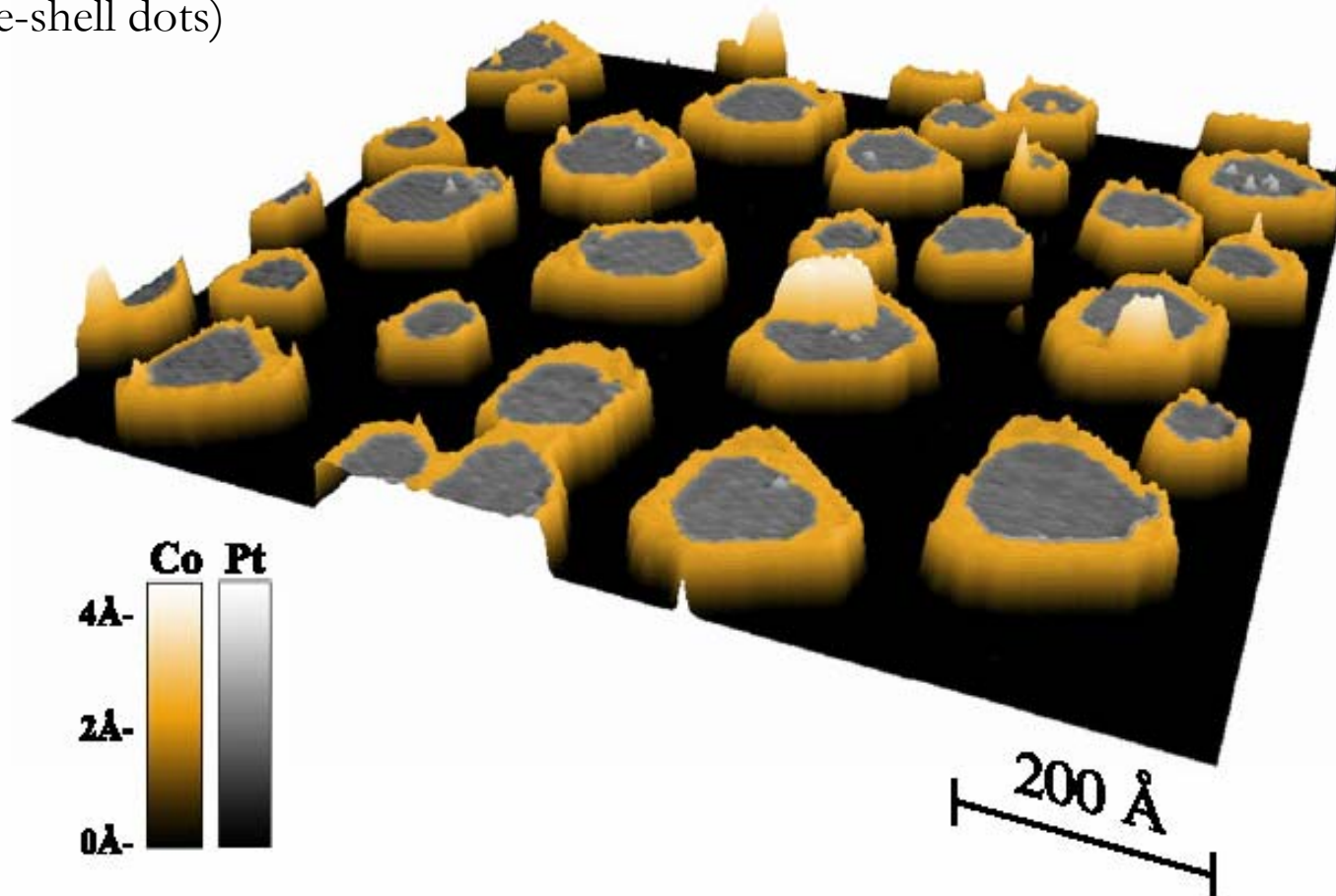
- From bulk to atoms: considerable **increase of orbital moment**
- **2 atoms closer to wire than 1 atom**
- **bi-atomic wire closer to surface than wire**

Also studied in clusters, see

J. Bansmann et al., Surf. Sci. Rep. 56, 189 (2005)

Manipulation of edge anisotropy Pt brims around Co/Pt(111)

(core-shell dots)



S. Rusponi et al., Nature Mater. (2003)

Blocking temperature = 150-300K

- Self-organization : study concepts
- Growth engineering > towards materials?



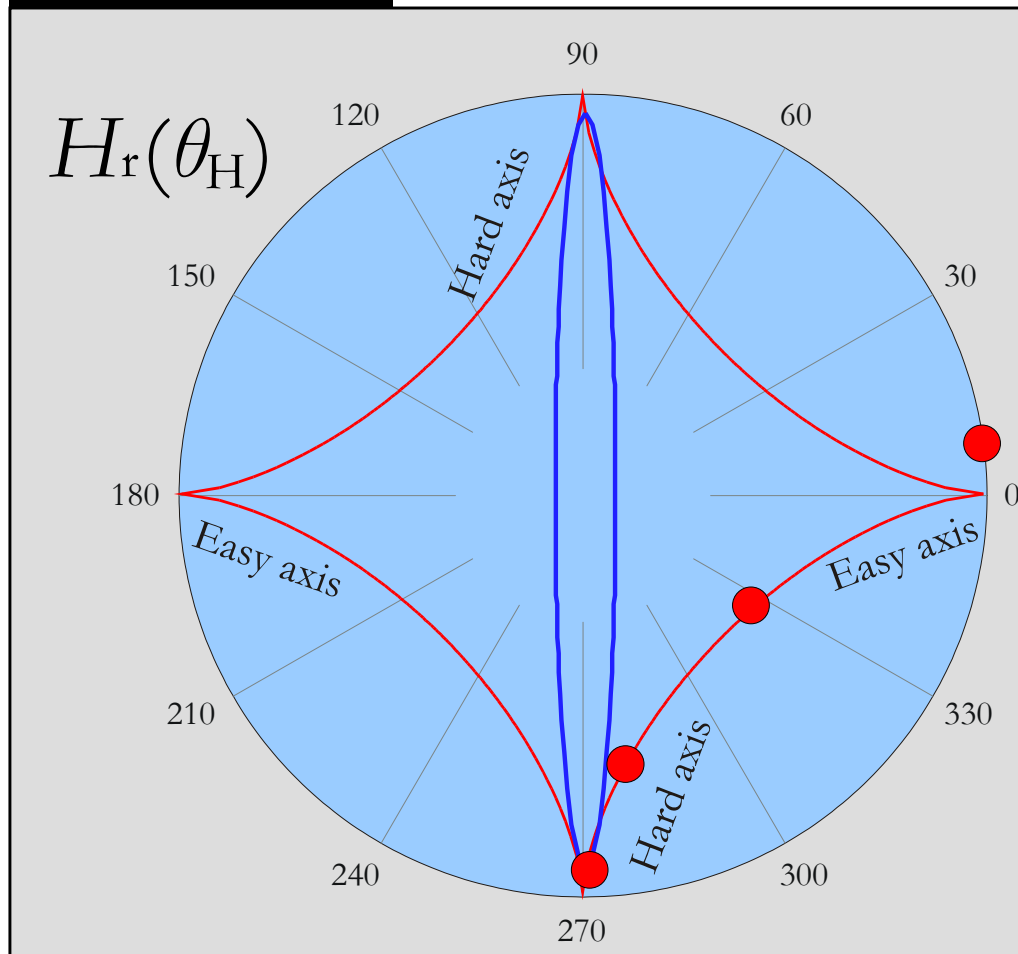
I. Fabrication methods

- ➔ 1. Epitaxial self-assembly & self-organization
- ➔ 2. Other routes: electrochemistry, chemistry, physical paths to clusters, exotic means
- ➔ 3. Future prospects for self-organization.

II. Selected topics for Magnetism

- ➔ 1. Magnetic order
- ➔ 2. Magnetic anisotropy
- ➔ 3. Magnetization reversal and superparamagnetism.
- ➔ 4. Micromagnetism

'Astroid' curve

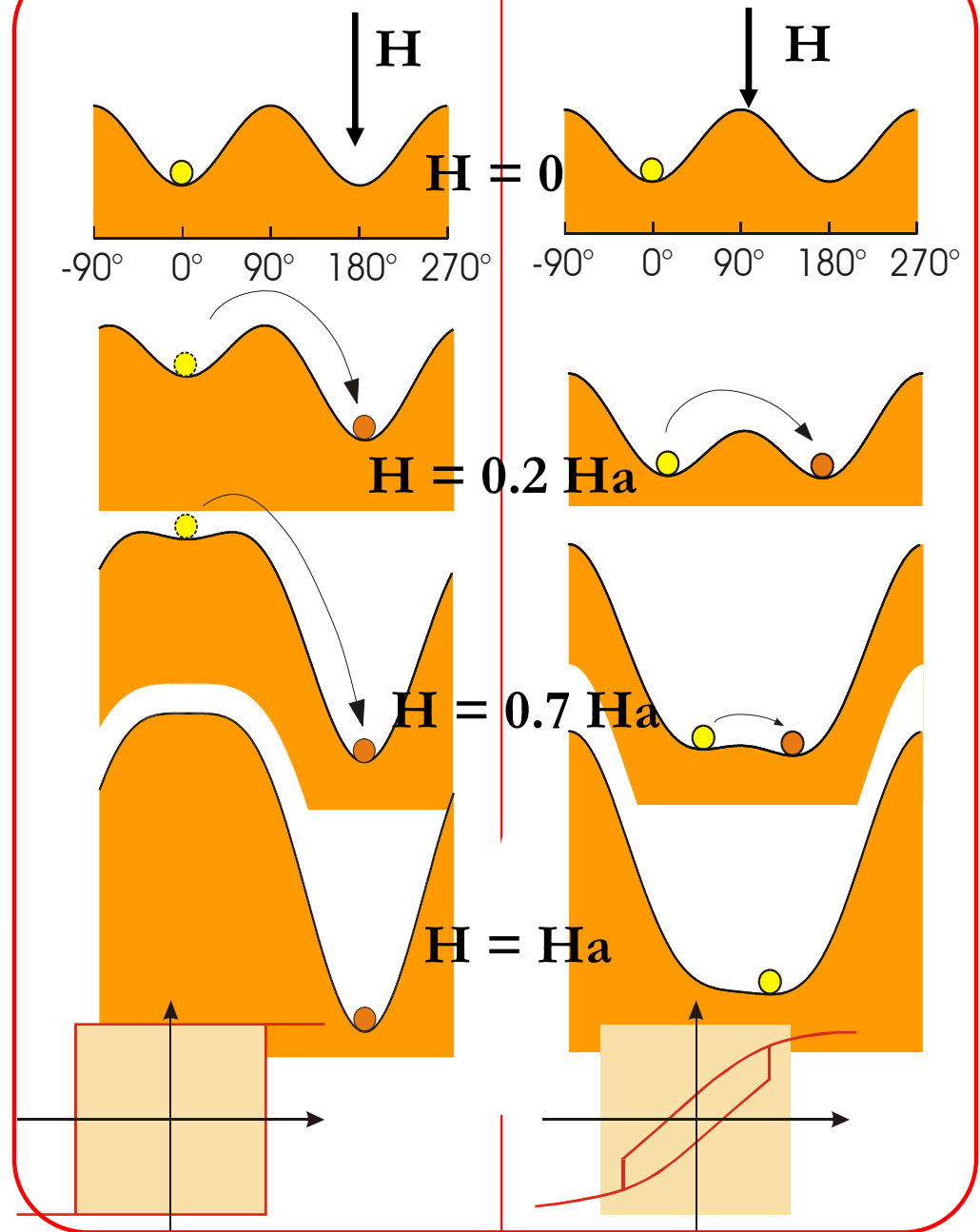


Notes:

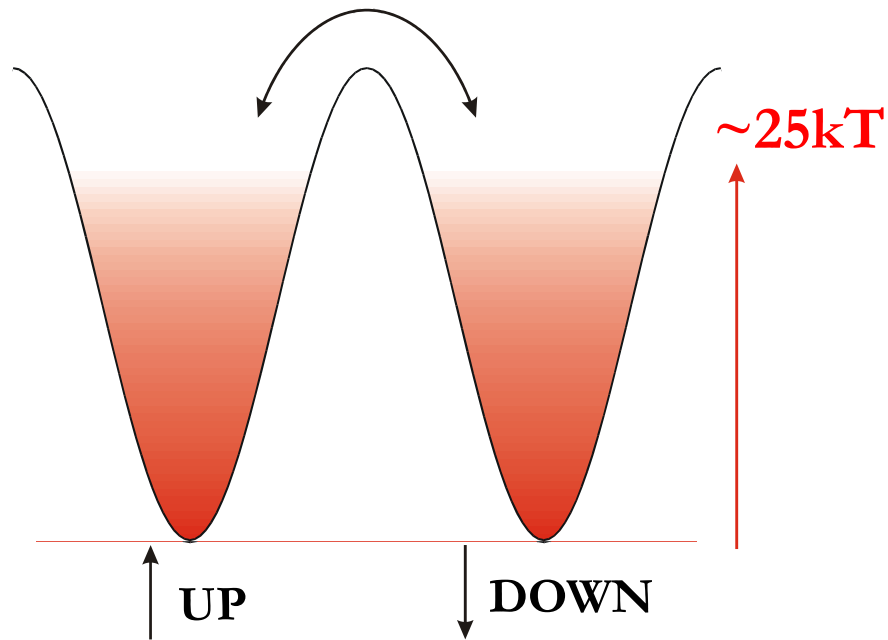
- * $H_r(\theta)$ is a signature of reversal modes
- *Coercive field $\neq$ Reversal field

EASY

~ HARD



Anisotropy barrier



Anisotropy barrier $E_B \sim KV$

Formalism for thermal excitations

Phenomenological model

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

- Probability for non-reversal

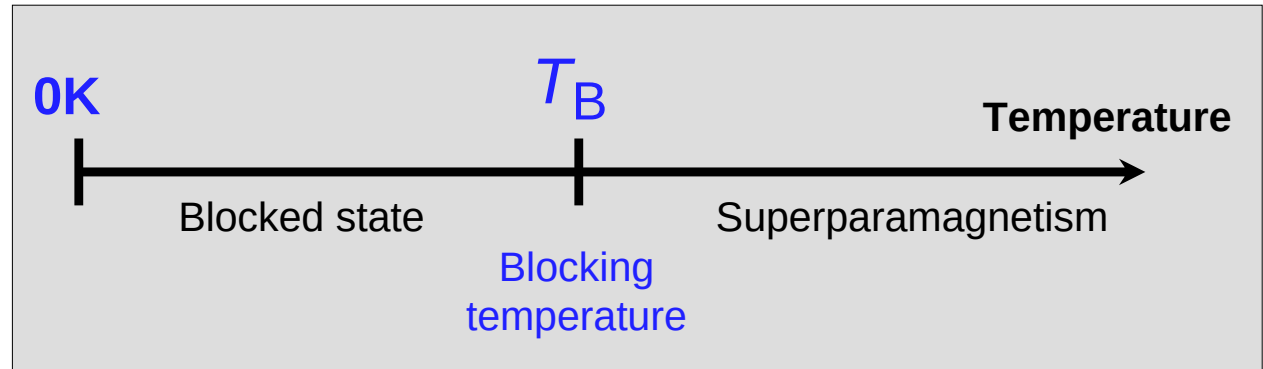
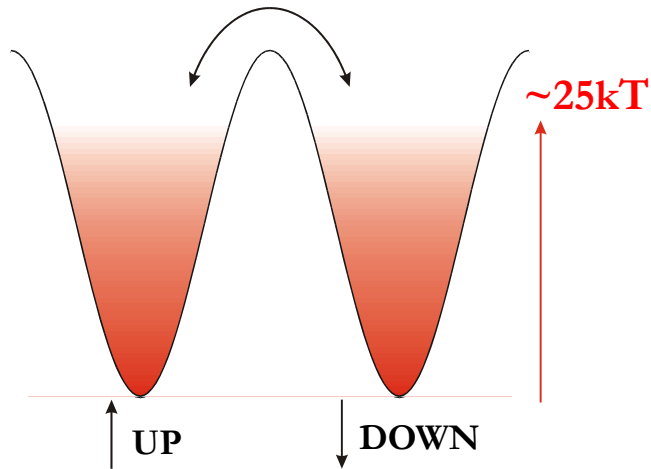
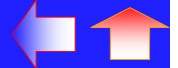
$$P(t) = e^{-t/\tau}$$

- Mean waiting time for reversal

$$\tau = \tau_0 e^{E_B / k_B T} \quad \tau_0 \approx 10^{-10} \text{ s}$$

- ↪ Energy barrier required to prevent magnetization reversal during duration t

$$E_B = k_B T \ln(t / \tau_0)$$



Formalism for thermal excitations

(...)

$$E_B = KV_B = k_B T \ln(t / \tau_0)$$

Superparamagnetism: orders of magnitude

Laboratory : $t = 1s$

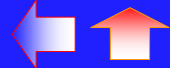
$$V_B \approx 25 k_B T / K$$

Recording : $t \gg 10^9 s$

$$V_B \approx 40 - 60 k_B T / K$$

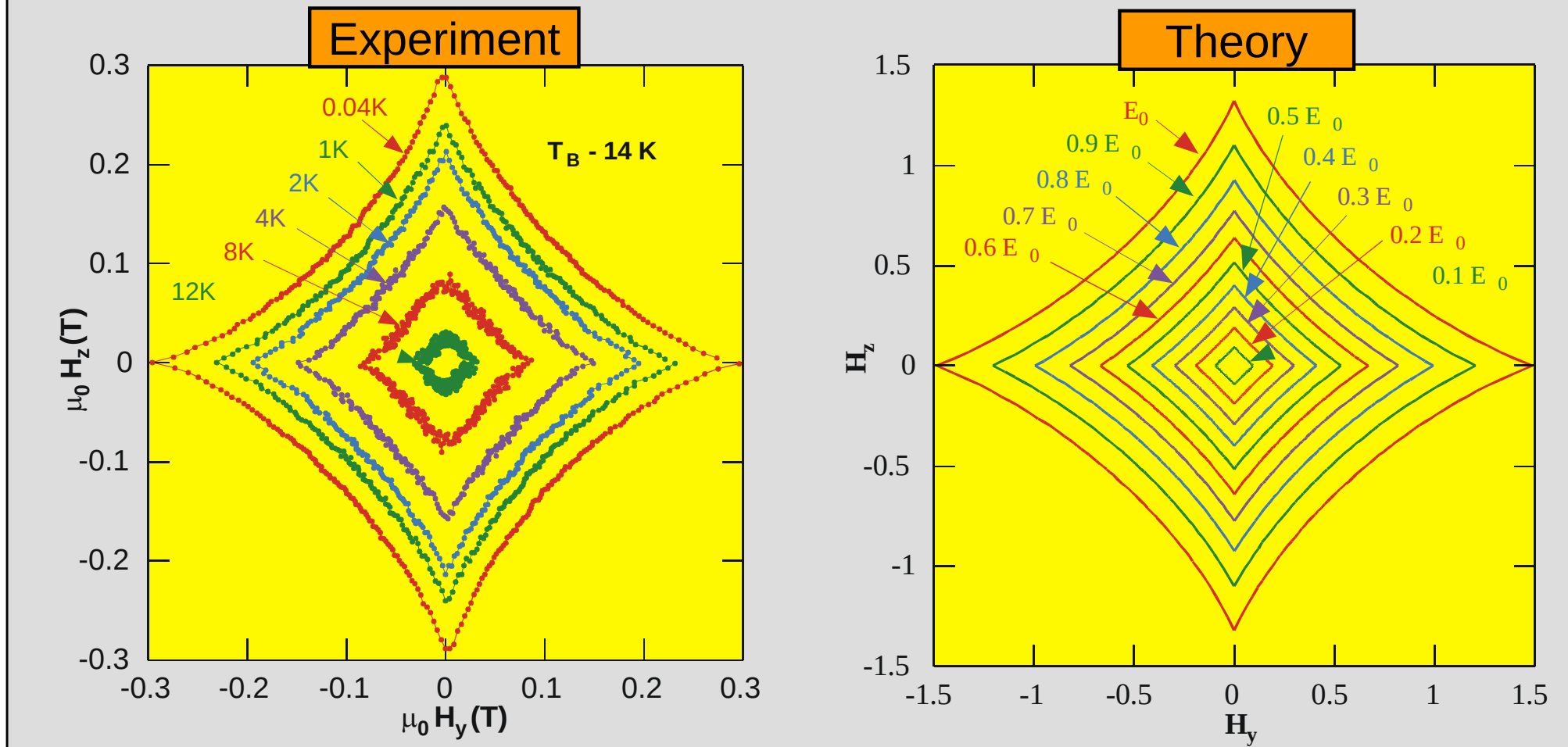
Magnetic recording with one grain per bit ($V = V_B$, discrete media) more favorable than $V = N V_B$





Temperature dependence of the switching fields of a 3nm Co cluster

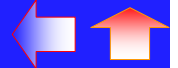
Measurement technique: micro-SQUID



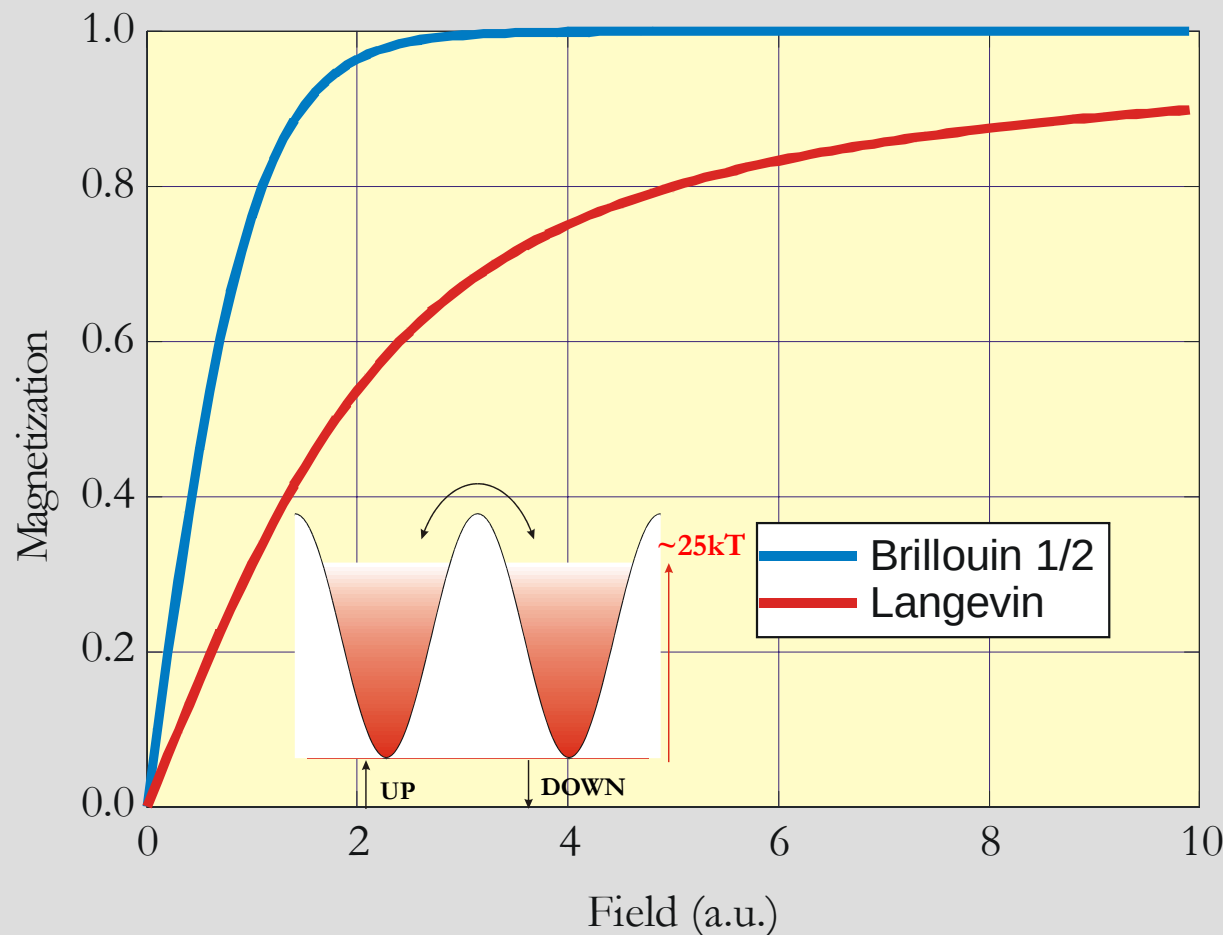
W. Wernsdorfer, M. Jamet et al.

Good agreement with the Stoner-Wohlfarth model and Néel-Brown theory





Which fitting function ?



Extremely weak anisotropy

Langevin function

$$m = \tanh(h), \quad h = \beta\mu_0\mu H$$

Strong uniaxial anisotropy

Brillouin 1/2 function

$$m = 1 / \tanh(h) - 1 / h$$

Other cases:

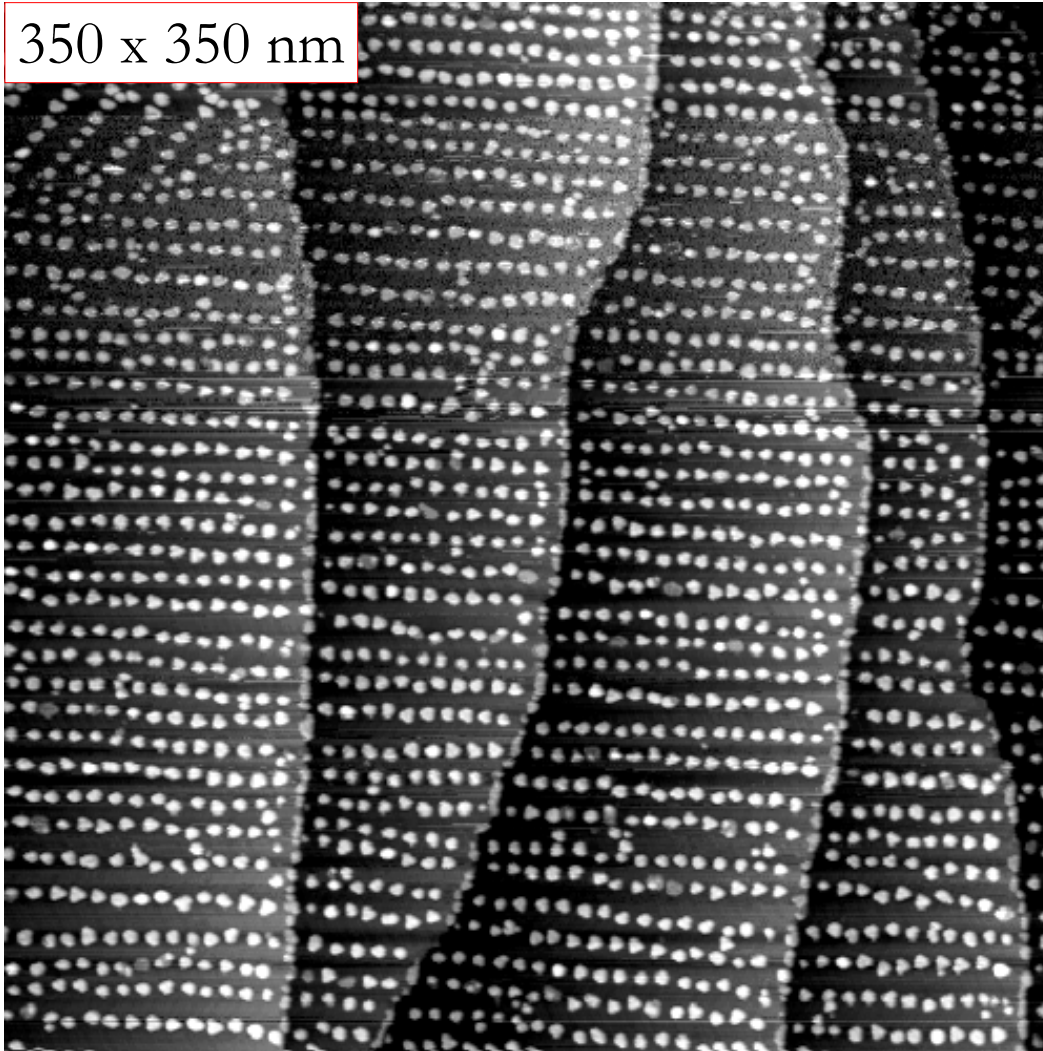
moderate or tilted anisotropy, distributions etc.

Numerical fitting

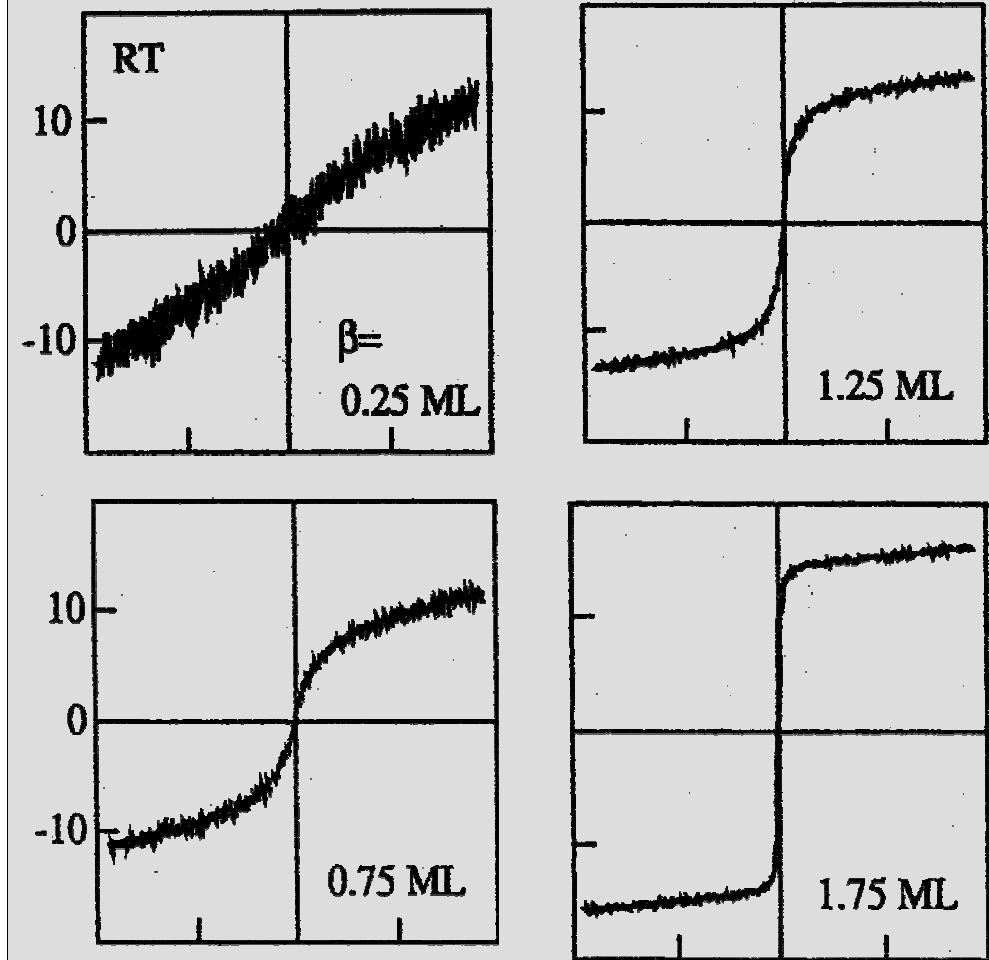
- Yields an estimation of the magnetic moment per particle μ
- Fitting with inadequate functions yields errors on μ
- Thermal variation of anisotropy constants neglected...

Example: Co/Au dots

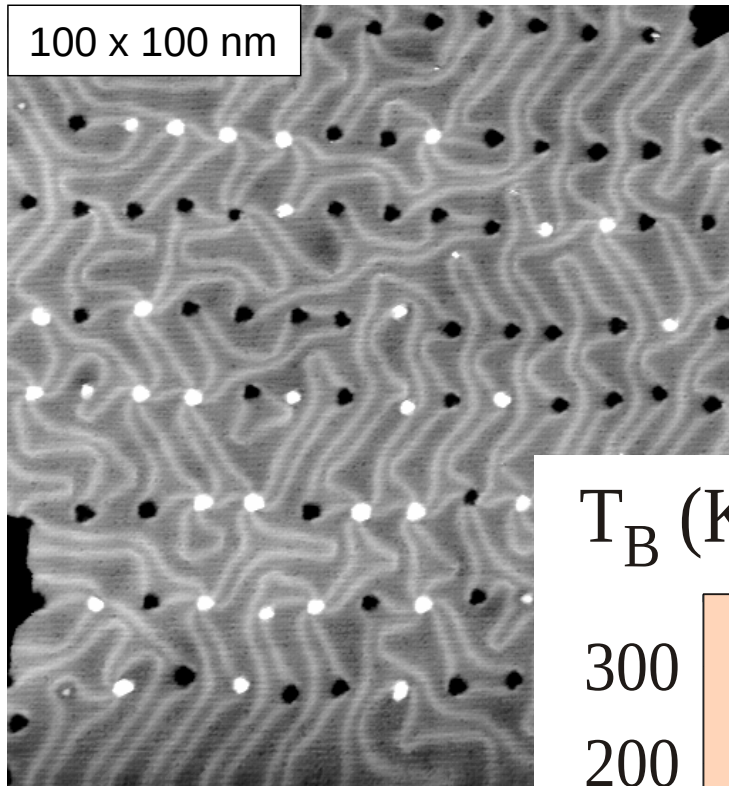
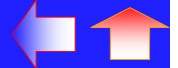
350 x 350 nm



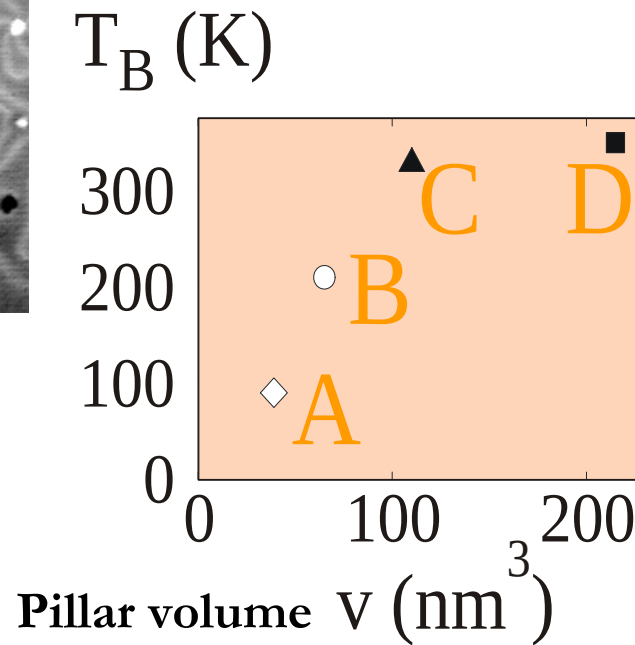
O. Fruchart et al.



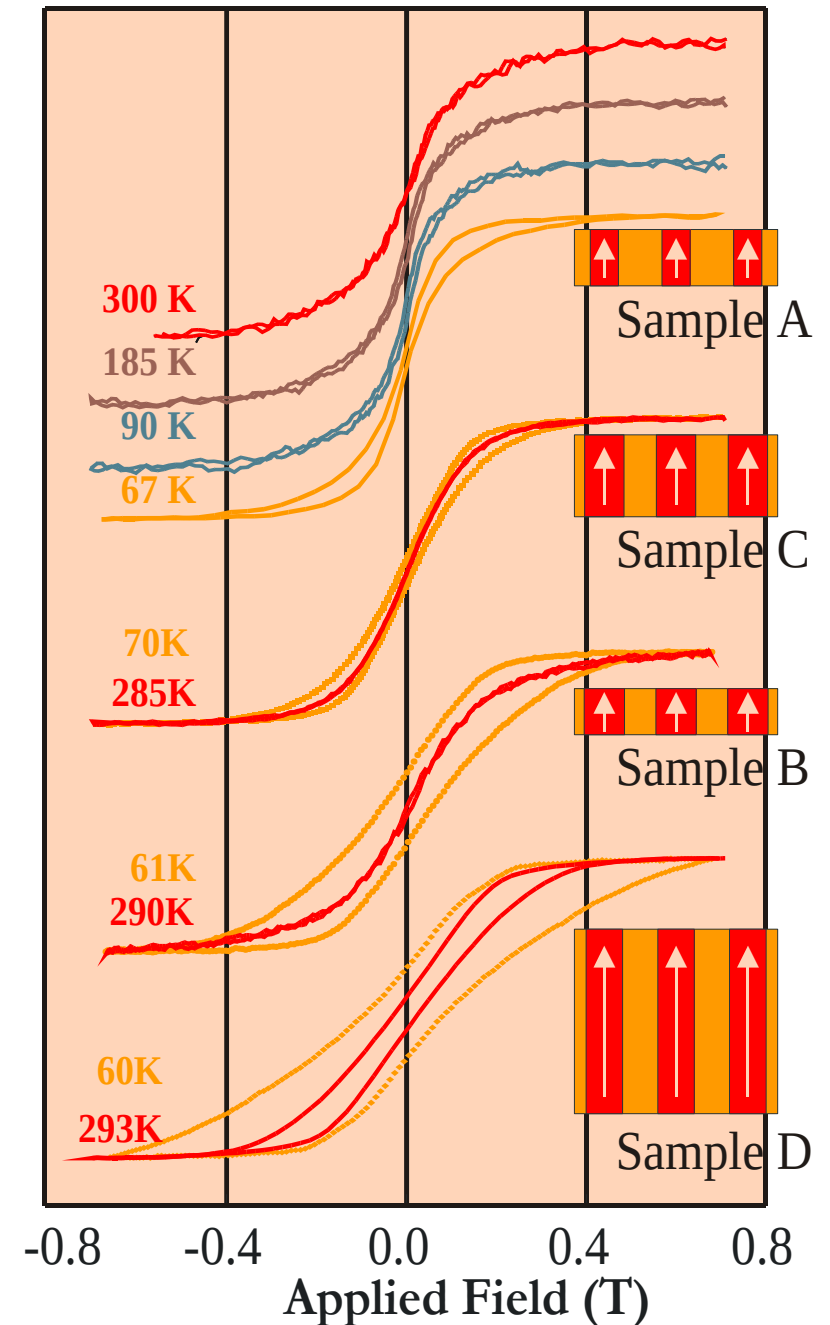
H. Takeshita et al., JMMM165, 38 (1997)

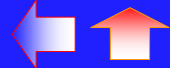


Co/Au(111)



Vertical structures delay the occurrence of superparamagnetism

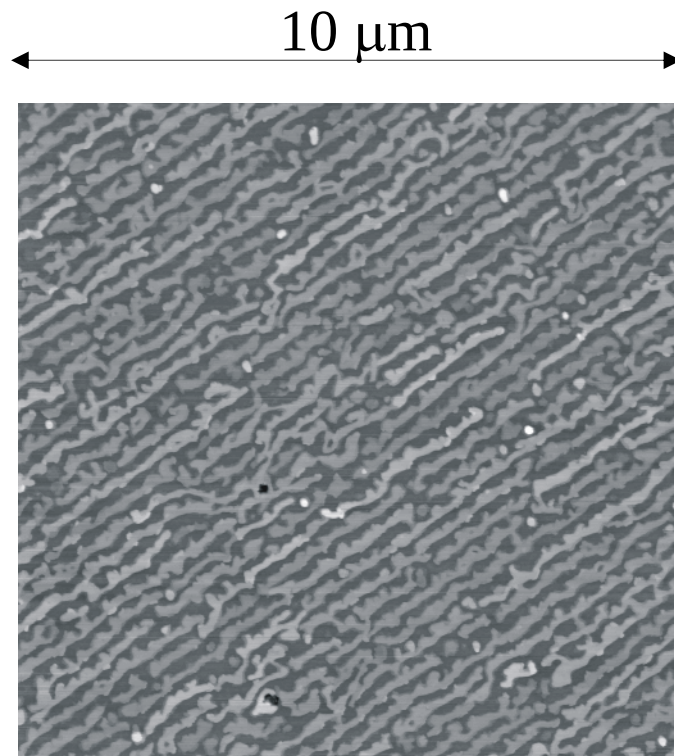




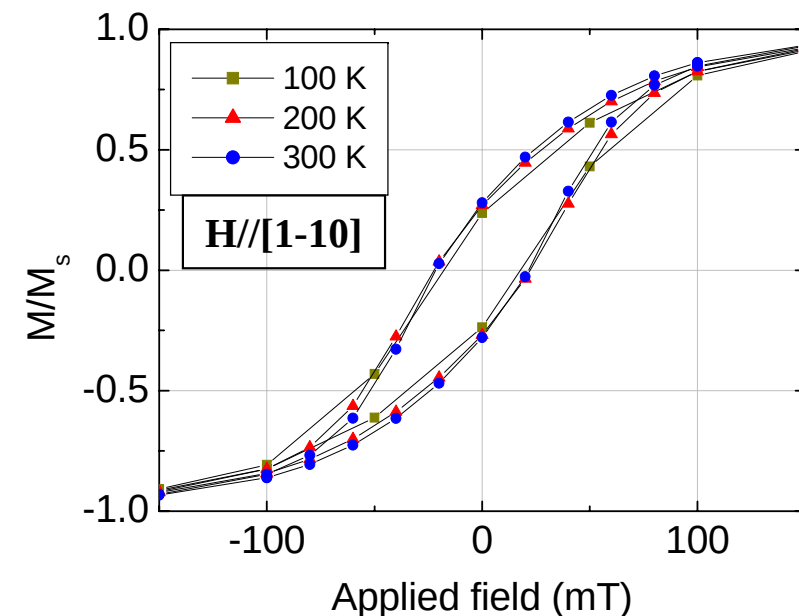
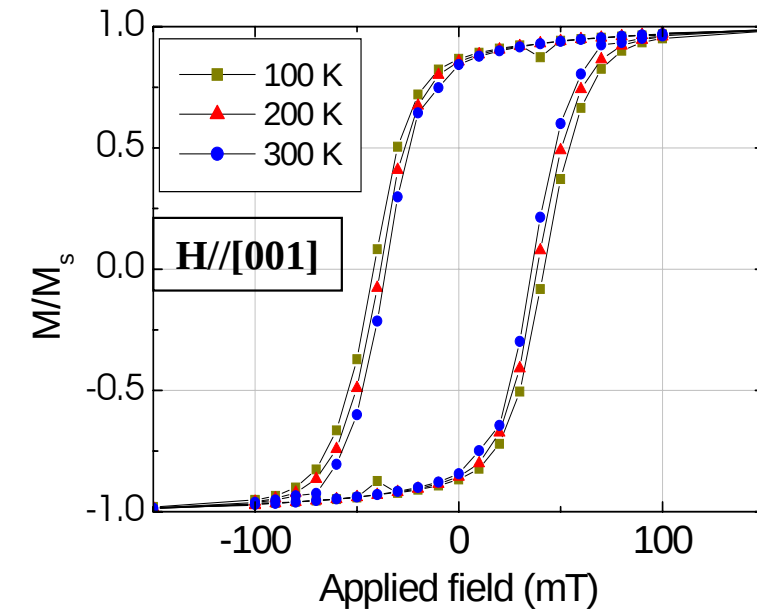
Coercivity and remanence at 300K

Sapphire \ W \ Mo\Fe(3nm) \ Mo

Stripe height = 4.5nm



↻ **Coercivity and high remanence at 300K**
 ↻ **Weak temperature dependence**
 > **behaves like a conventional material**



Curie temperature versus blocking temperature?

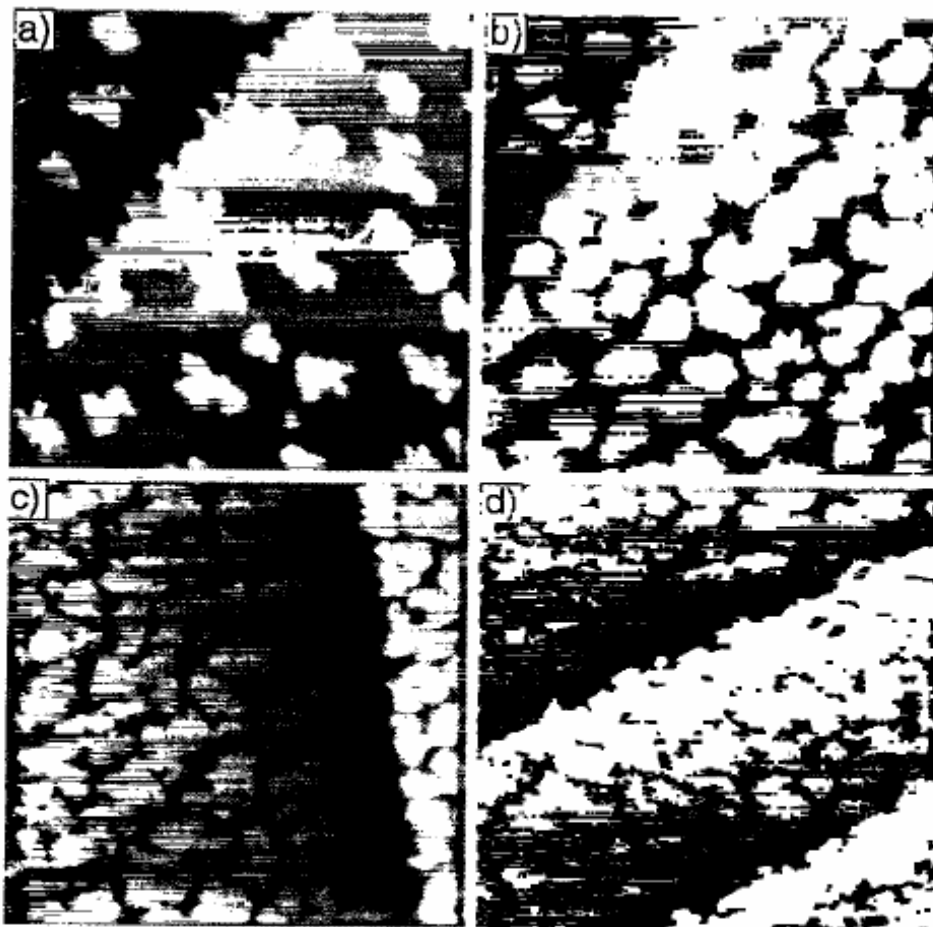
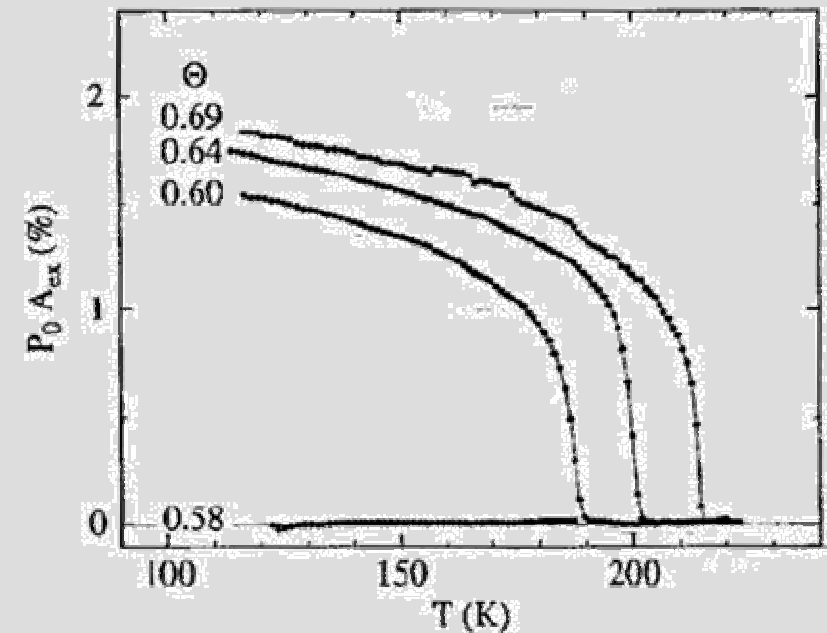
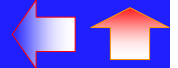


FIG. 1. STM images of Fe(110) films, prepared at RT on W(110), all $70 \text{ nm} \times 70 \text{ nm}$ in size, with [001] horizontal. (a) $\theta = 0.23$; (b) $\theta = 0.53$; (c) $\theta = 0.66$; (d) $\theta = 0.85$. Upper levels (Fe) bright; lower levels (W) dark.

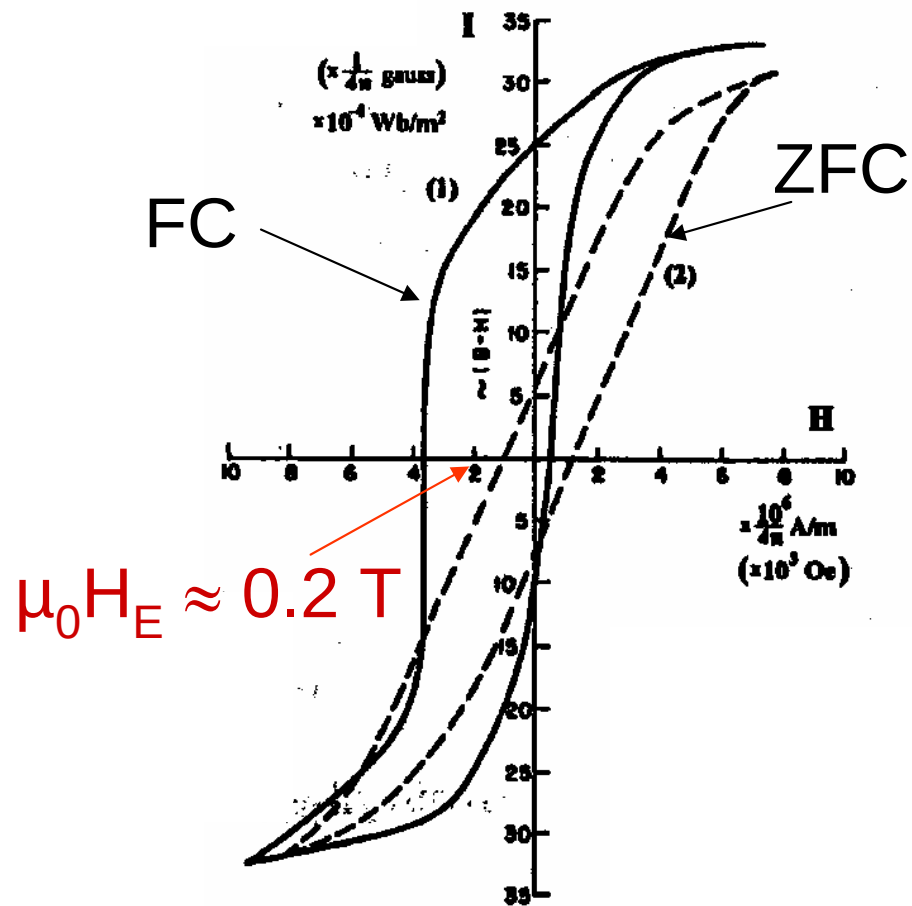
Remanence plotted as a function of temperature



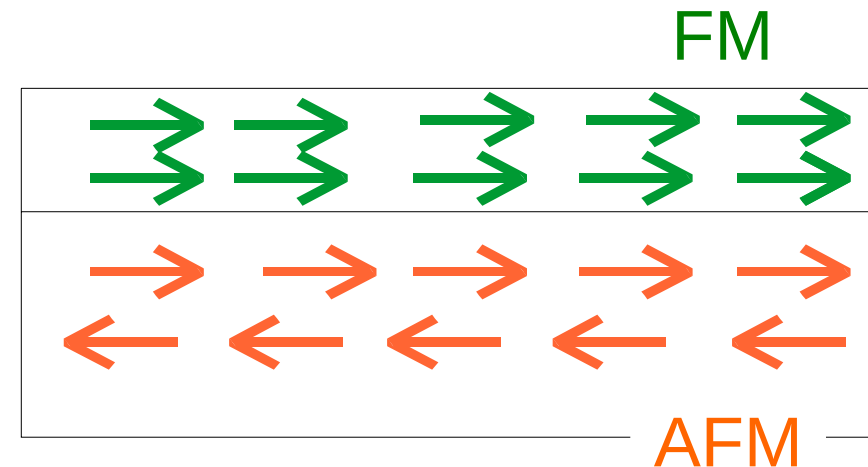
Transition from superparamagnetism to a blocked state



Oxidised Co nanoparticles



Field Cooled hysteresis loop :
-shifted with respect to M axis
- increased 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)

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

(Derived from slide: D. Givord)

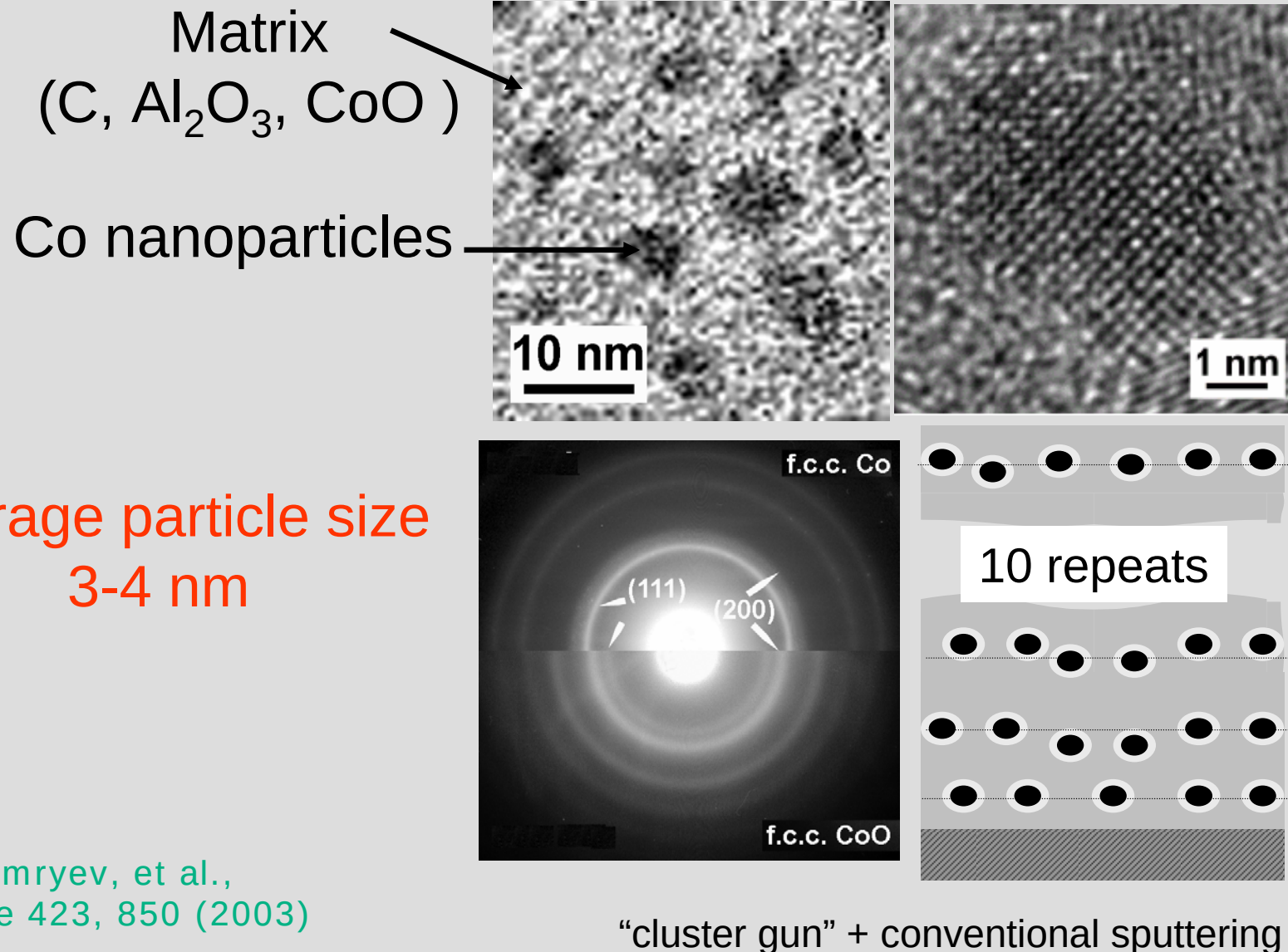


LLN, Grenoble, France.

Olivier Fruchart – European School on Magnetism – Constanta, sept. 2005 – p.71

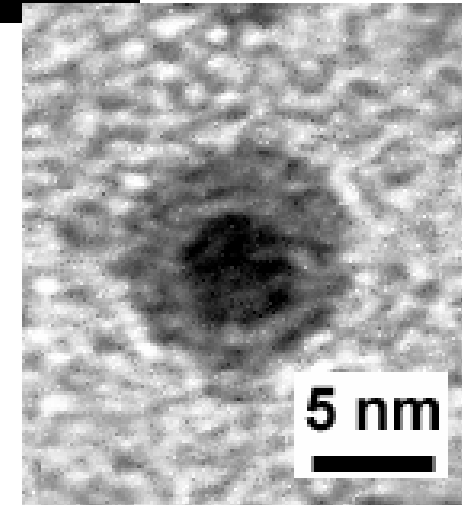
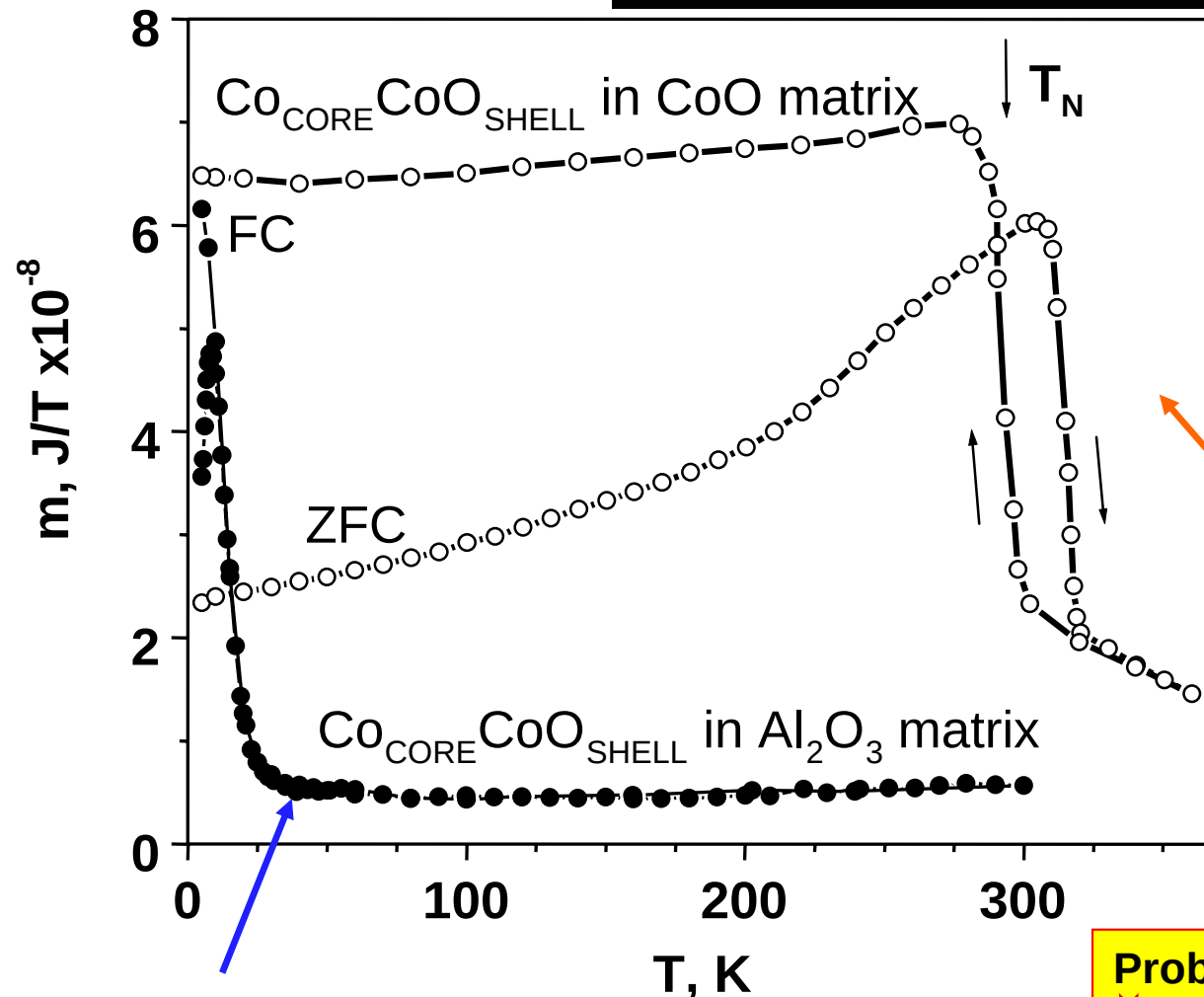
<http://lab-neel.grenoble.cnrs.fr/themes/couches/ext/slides/>

Ferromagnetic nanoparticles in a non-magnetic or antiferromagnetic matrix



V.Skumryev, et al.,
Nature 423, 850 (2003)

Dependence of the blocking temperature on the nature of the matrix



AFM matrix

$T_B \approx T_N \text{ CoO}$

V. Skumryev, et al.,
Nature 423, 850 (2003)

Non-magnetic matrix : $T_B \approx 30\text{K}$

Problems remain:

- ↪ Not all features understood
- ↪ Very sensitive on fabrication



I. Fabrication methods

- ➡ 1. Epitaxial self-assembly & self-organization
- ➡ 2. Other routes: electrochemistry, chemistry, physical paths to clusters, exotic means
- ➡ 3. Future prospects for self-organization.

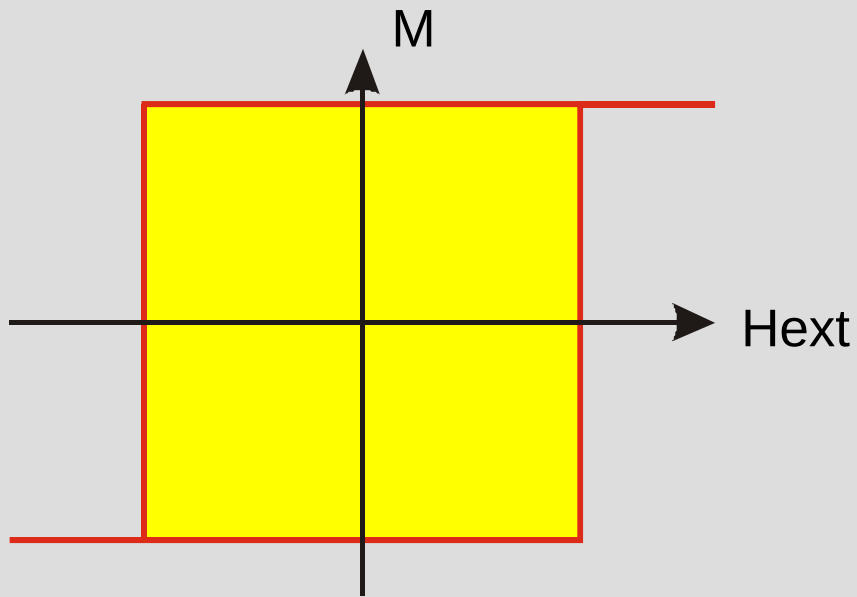
II. Selected topics for Magnetism

- ➡ 1. Magnetic order
- ➡ 2. Magnetic anisotropy
- ➡ 3. Magnetization reversal and superparamagnetism.
- ➡ 4. Micromagnetism

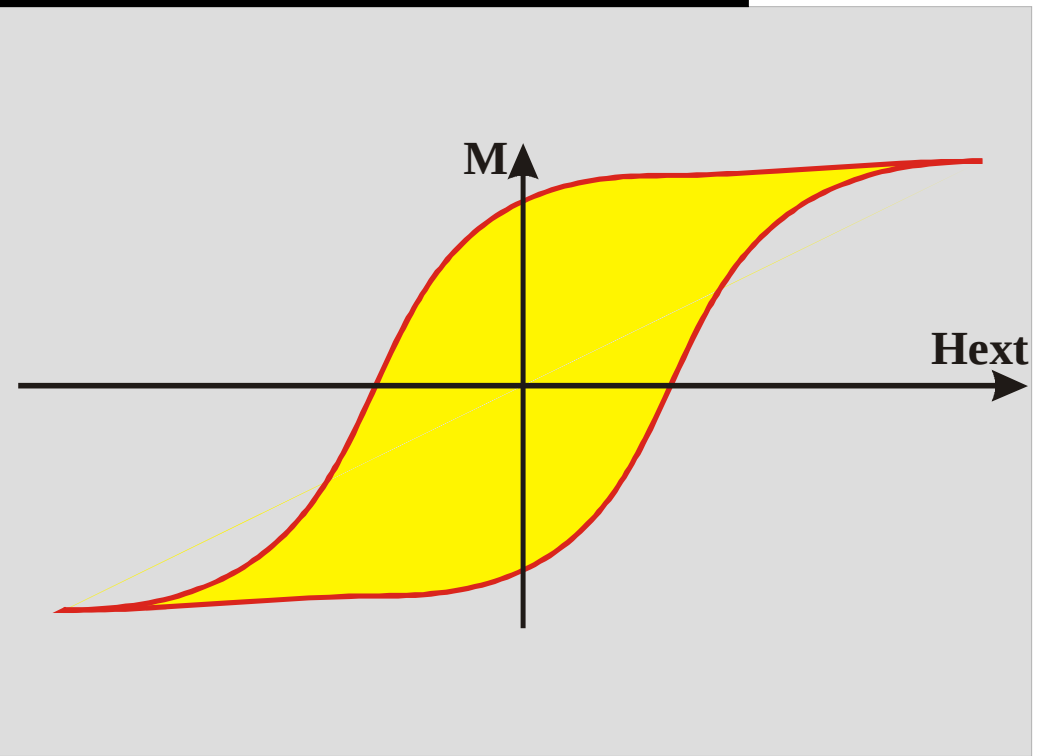
3.5. Collective dipolar properties



Expected hysteresis loop for macrospins



Hysteresis for assemblies of dots



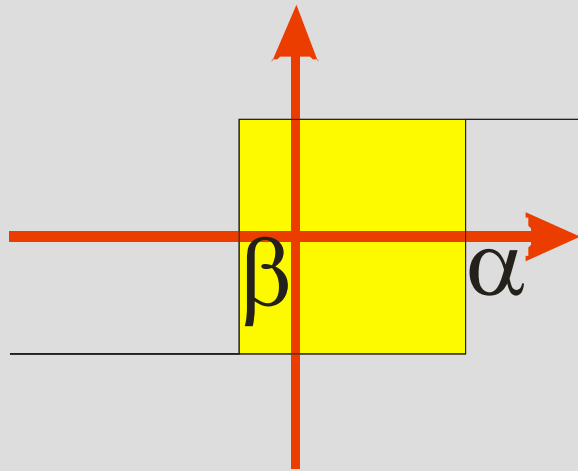
Possible effects

- Distribution of coercive fields
- (Dipolar) interactions

Preisach model

G. Biorci et al., Il Nuov. Cim. VII, 829 (1958)

I. D. Mayergoyz, Mathematical models of hysteresis, Springer (1991)

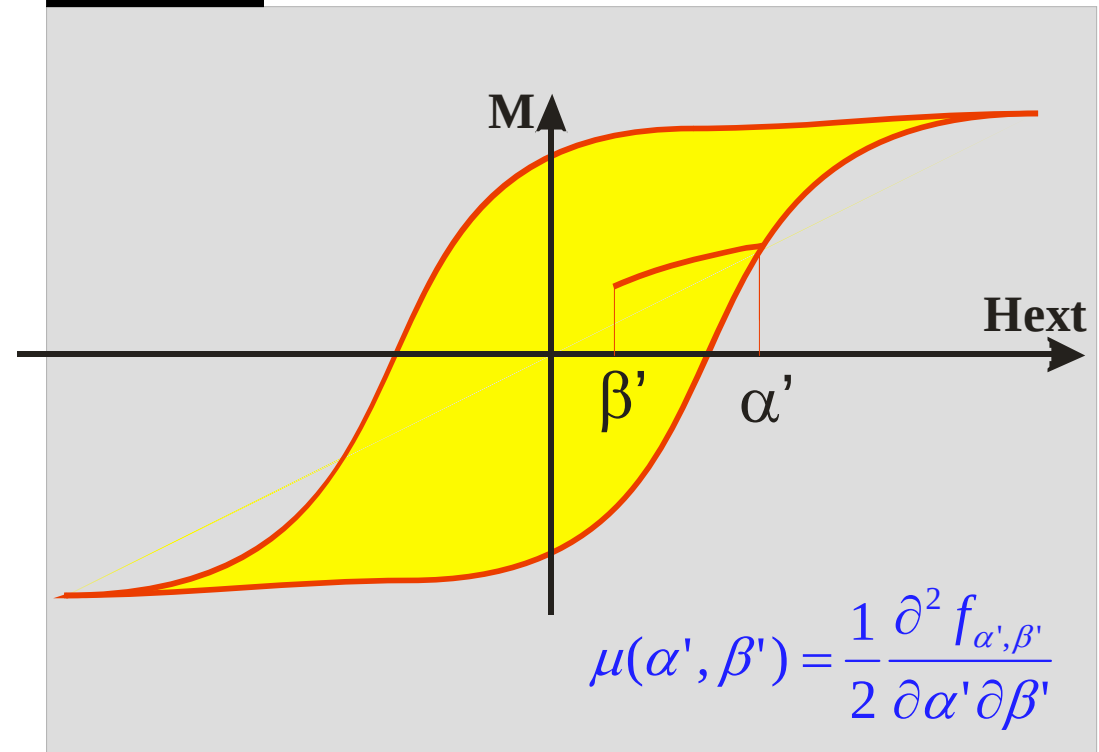


↪ Distribution function

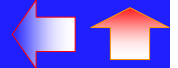
$\mu(\alpha, \beta)$ with $\alpha > \beta$

↪ No true link between real particles and μ

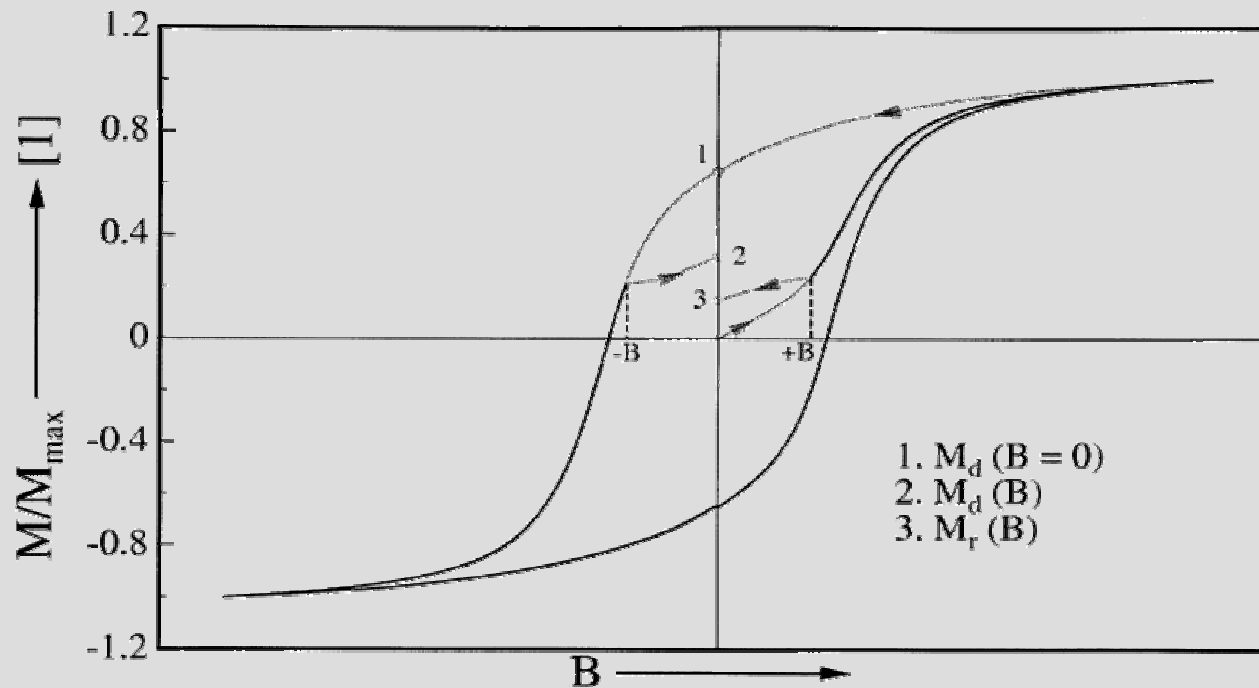
Solving



- Long experiments (1D set of hysteresis curves)
- Better suited to bulk materials with strong interactions



Henkel plots



O. Henkel,
Phys. Stat. Sol. 7, 919 (1964)

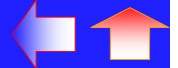
S. Thamm et al.,
JMMM184, 245 (1998)

Fig. 1. Explanation of how to measure the two different remanent magnetisations M_r and M_d .

Measure of dipolar interactions

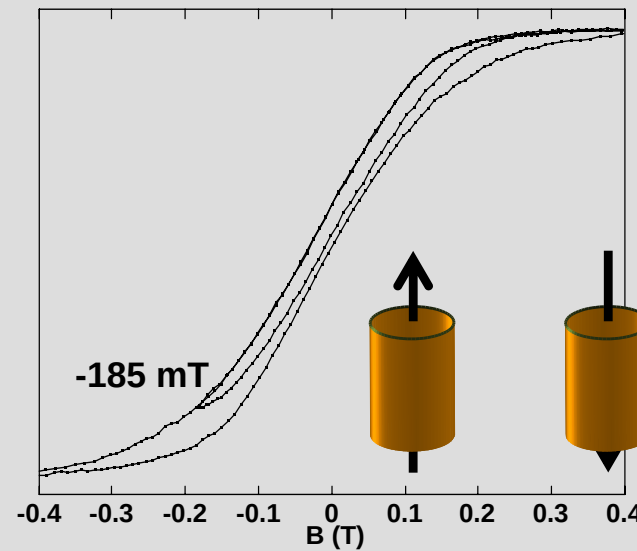
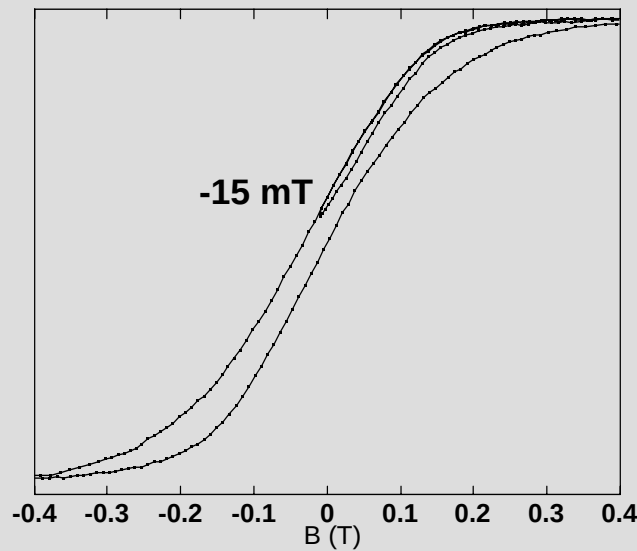
$$\Delta M_H(x) = M_d(x) - [1 - 2M_r(x)]$$

- Long experiments (ac demagnetization)
- Better physical meaning than Preisach

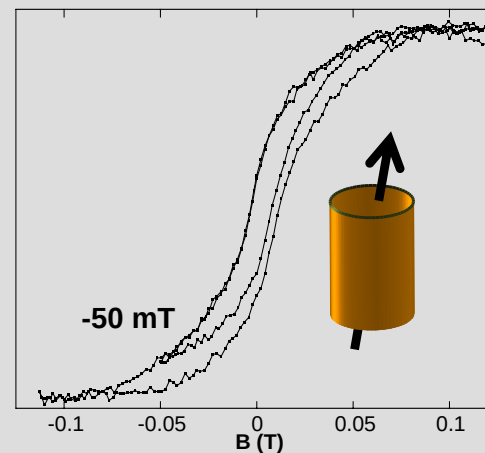
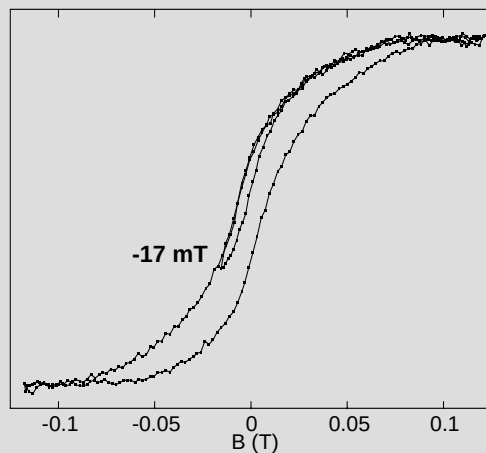


Minor loops: negative interactions

Example: dipolar interactions in arrays of Co/Au(111) pillars

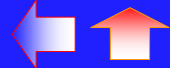


Minor loops: negligible interactions



- Faster than Henkel
- Other applications: characterization of exchange bias

O. Fruchart et al., unpublished



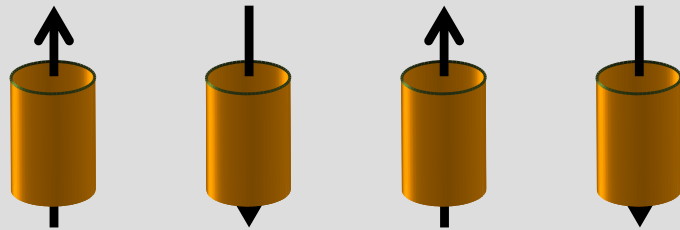
Superparamagnetic regime: plot of inverse susceptibility

- Brillouin 1/2 function

$$m = B_{1/2}(\mu_0 \mu_{Co} N H_{eff.} / kT)$$

- Effective field

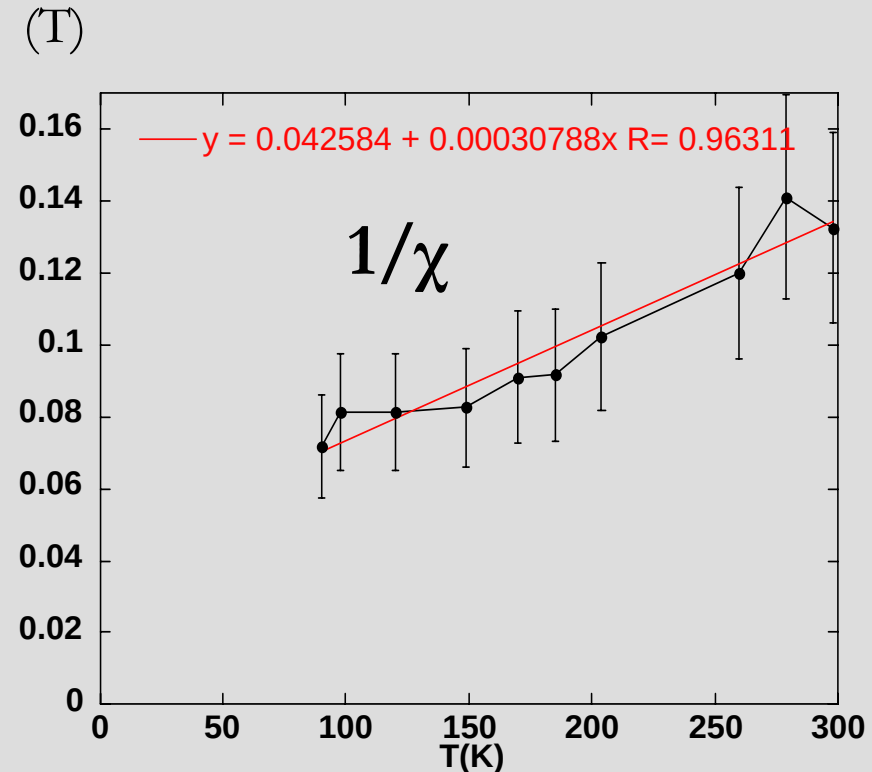
$$H_{eff.} = H + r M_s m$$



(Demagnetizing dipolar interactions)

- First order expansion:
susceptibility

$$\frac{d(\mu_0 H)}{dm} = \frac{1}{\chi} = \underbrace{-\mu_0 M_s r}_a + \underbrace{\frac{k}{\mu_{Co} N} T}_b$$



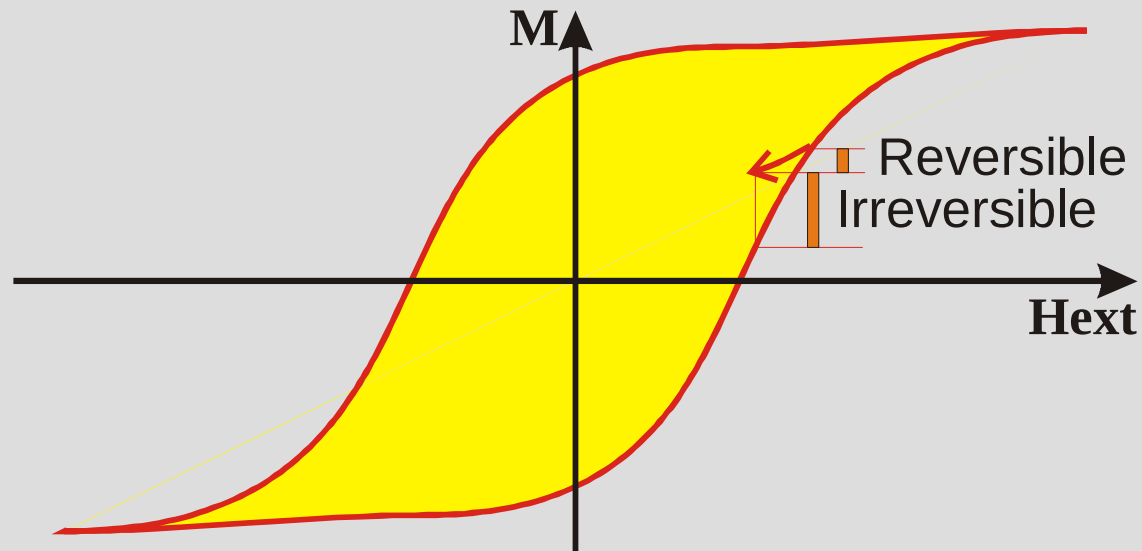
O. Fruchart *et al.*, PRL 23, 2769 (1999)

➤ No need of hysteresis

➤ Analogy with Curie-Weiss law



Distribution of properties

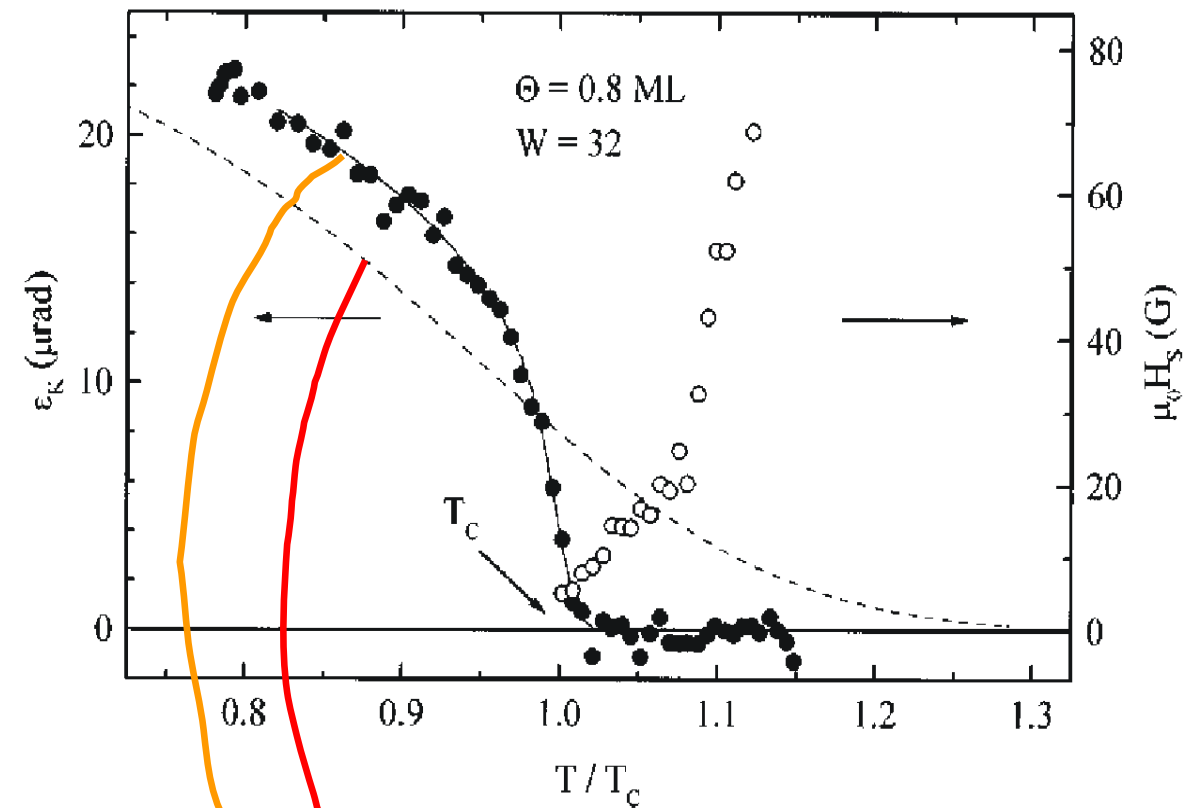
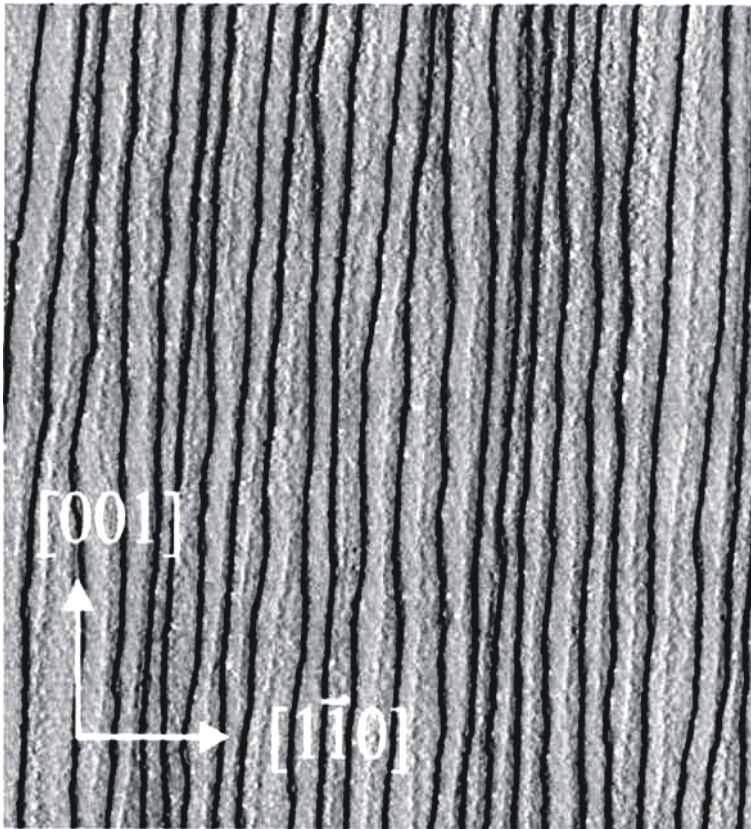


$$\rho(H_r) = \left. \frac{dm}{dH} \right|_{\text{irreversible}}$$

$H_c(T)$ for a given population of the distribution can be studied at a given stage of the reversal (10 %, 20 % etc.)

Effect of distributions and dipolar interactions are sometimes difficult to disentangle

Ferromagnetic order stabilized by dipolar interactions



J. Hauschild et al., Phys. Rev. B 57, R677 (1998)

$T_c = 179\text{K}$

Simulation without dipolar interactions

Simulation with dipolar interactions

Although weak, dipolar interactions stabilize ferromagnetic order and sharpen the transition at T_c , owing to their long range



I. Fabrication methods

- ➔ 1. Epitaxial self-assembly & self-organization
- ➔ 2. Other routes: electrochemistry, chemistry, physical paths to clusters, exotic means
- ➔ 3. Future prospects for self-organization.

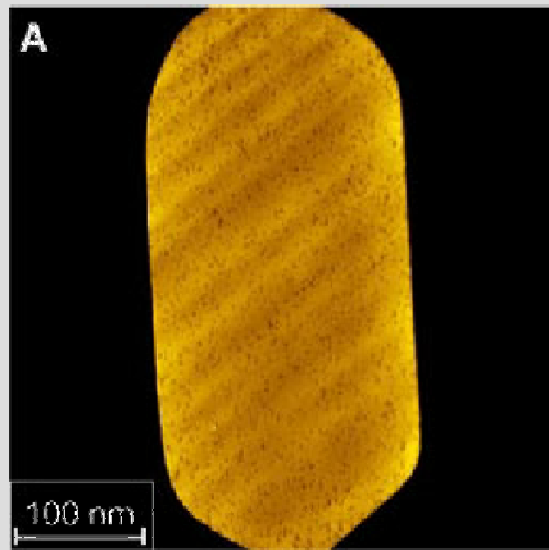
II. Selected topics for Magnetism

- ➔ 1. Magnetic order
- ➔ 2. Magnetic anisotropy
- ➔ 3. Magnetization reversal and superparamagnetism.
- ➔ 4. Micromagnetism

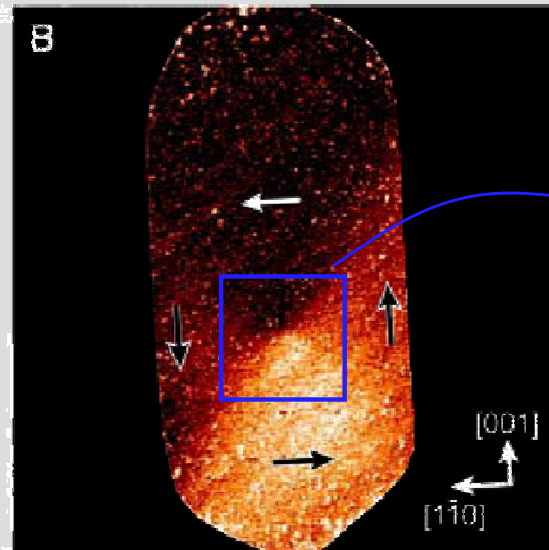
Magnetic vortex core

Spin-polarized Scanning Tunneling Microscopy on Fe/W(110) self-assembled dots

Structural image

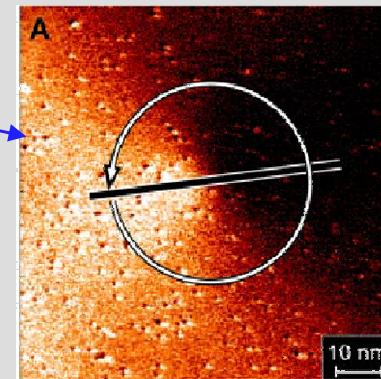


Magnetic image

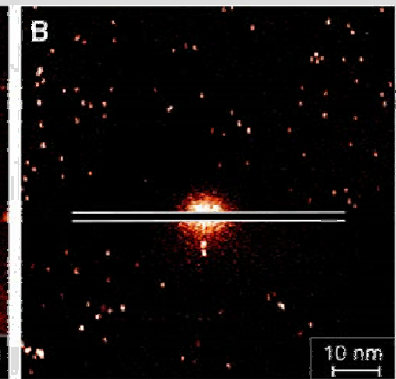


A. Wachowiak, Science 298, 577 (2002)

In-plane component of magnetization



Out-of-plane component of magnetization



...also in-field study

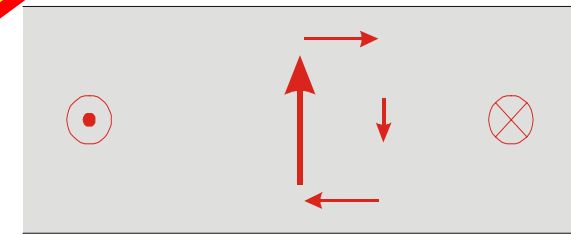
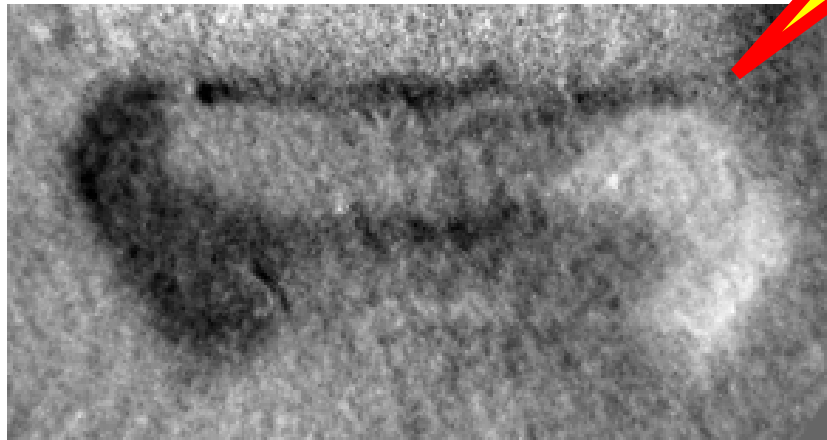
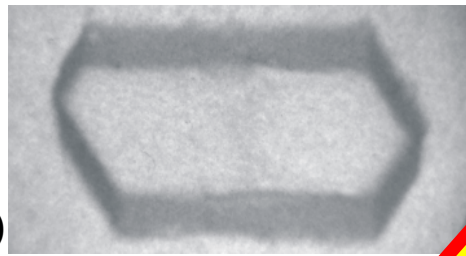
3D magnetization configurations

Technique

See poster by
Fabien CHEYNIS

(Synchrotron, Trieste)

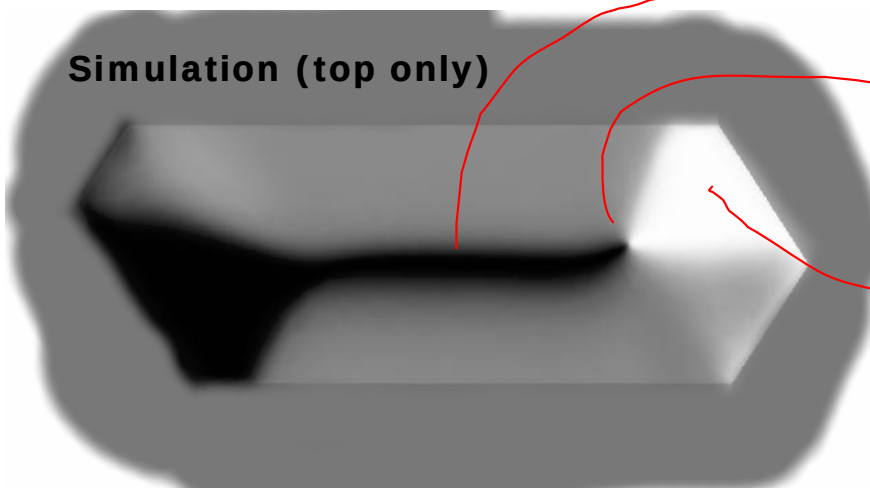
Experiment (top)



y



Simulation (top only)



Néel cap displaced
from median line

Asymmetry around vortex

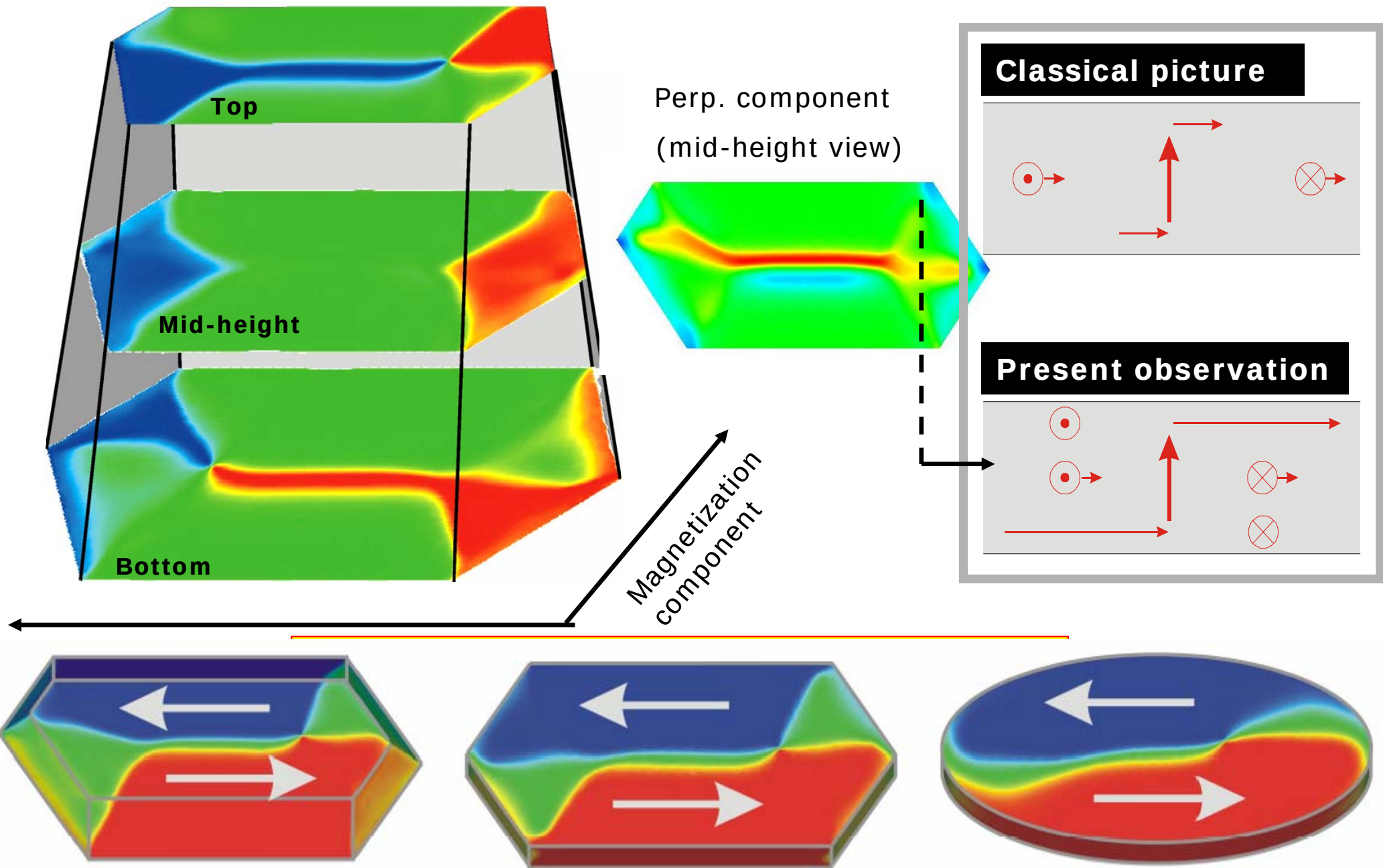
Strong asymmetry of end domains

Pseudo-2D

3D



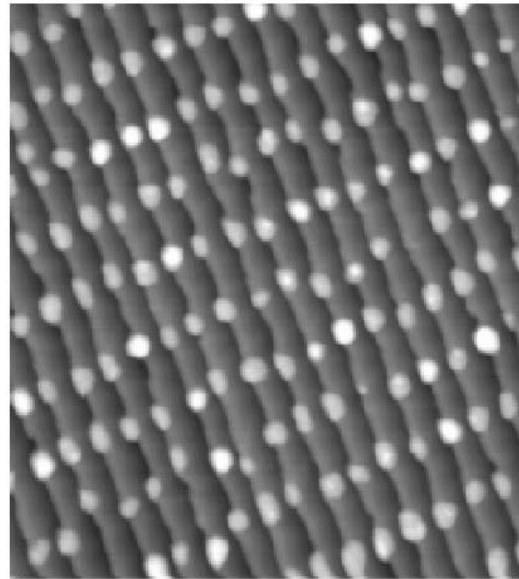
The main features are
reproduced



Fe/Mo(110) dots

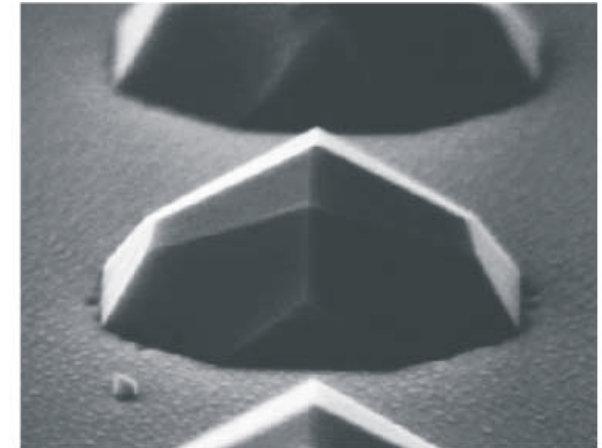


Co/Au(788) dots



60 nm

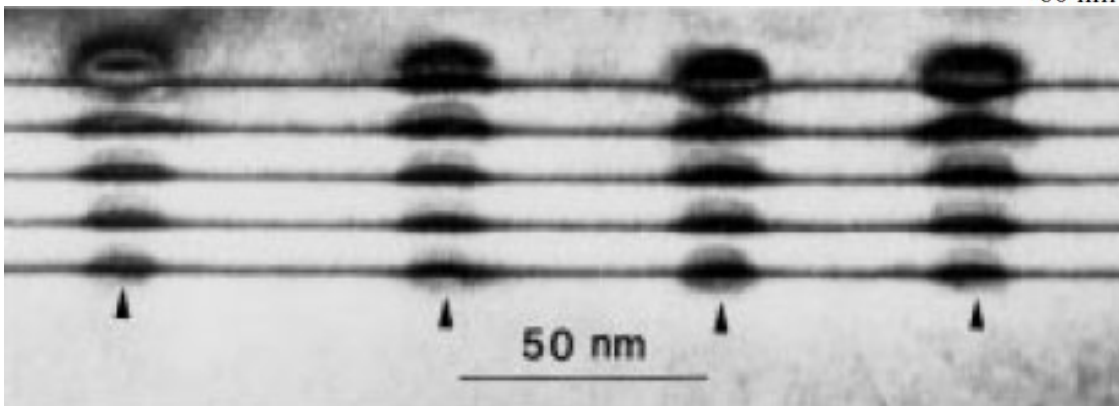
GaAs/GaAs(001) dots



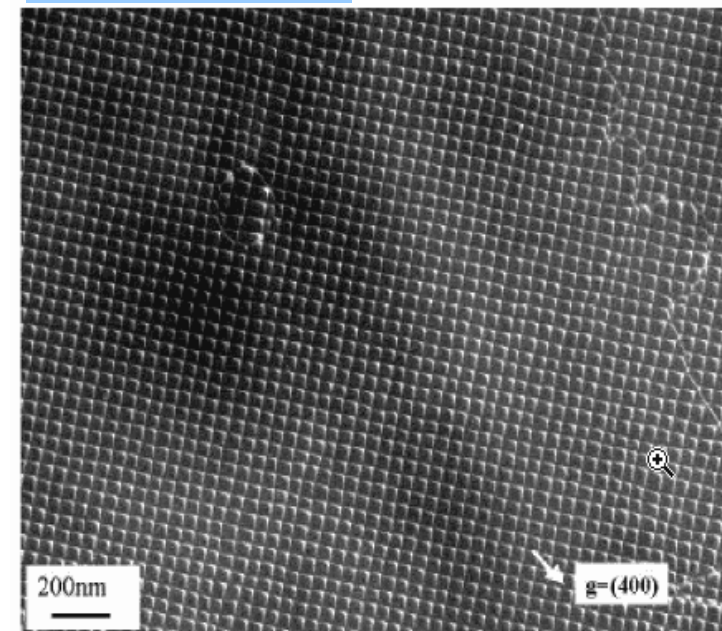
(b)

500nm

InAs/GaAs(001) dots



Si(001) bonding

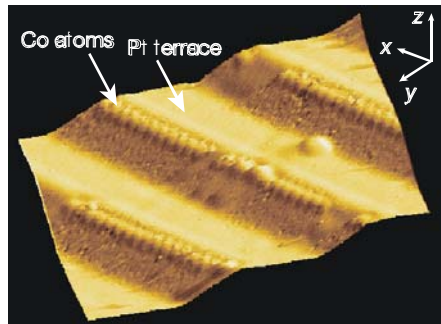


Many tricks to be used

↪ Just let your imagination help nature !

↪ Current trend: increase versatility,
combine complementary approaches

Self-assembly for magnetism



➤ Micromagnetism

Desirable: High quality (magnetic properties, observation)

➤ Ferromagnetic order in low dimension

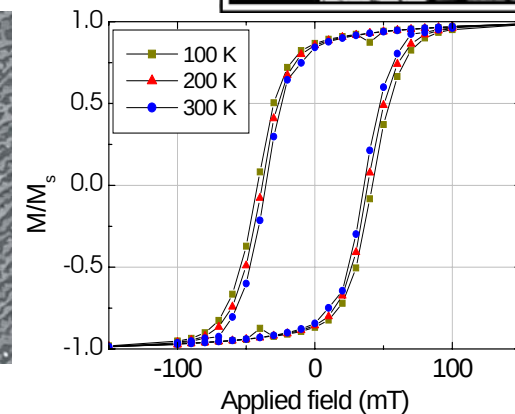
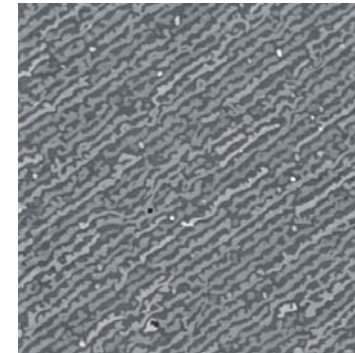
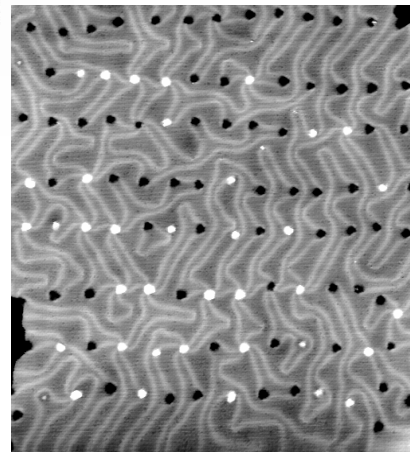
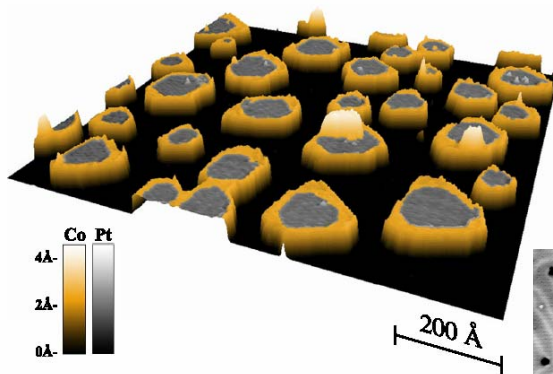
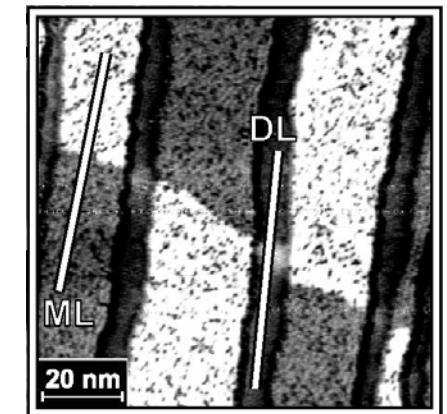
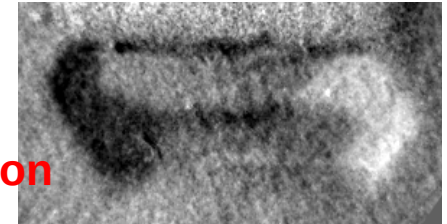
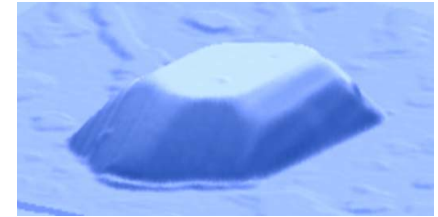
Desirable: small, high quality

➤ Spin, orbital momentum and anisotropy in low dimension

Desirable: small, high quality

➤ Fight against superparamagnetism

Fundamental obstacle for technological use



C. R. Physique 6(1) (2005): Special Issue on Self-organization at surfaces