Magnetism of low-dimensional structures

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Low-D magnetic structures
- applications
- single-domain particles
- superparamagnetism
- intrinsic magnetic properties
  - -moments
  - -anisotropy
  - -order

Introduction to x-ray magnetic circular dichroism (XMCD)

Case studies
- -Co clusters on Pt(111)
- -Co atomic chains on vicinal Pt(111)

Atoms

- Ionic moments
- Isotropic response to a magnetic field

Solids

- Crystalline structure:
  - bands, non-integer moments
  - FM/AFM coupling
  - anisotropy

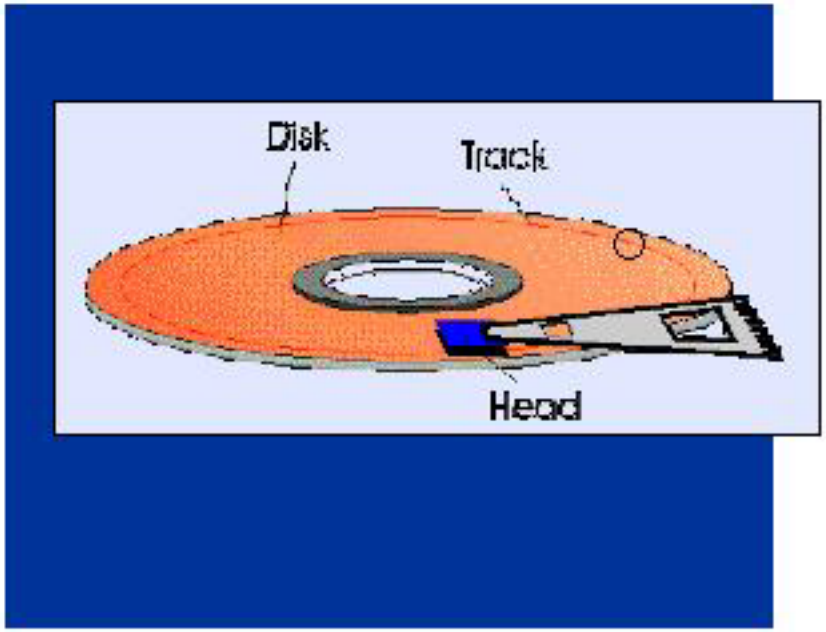
Low-D magnetic structures

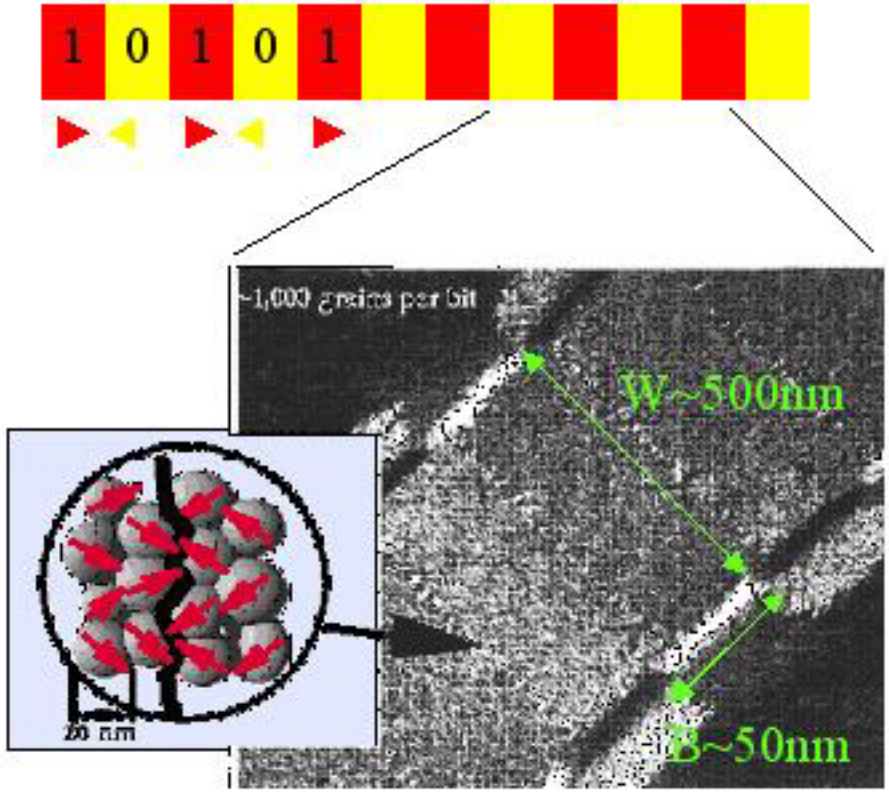
- Formation/survival of magnetic moments in solids
- Magnetic ordering
- Magnetic anisotropy
- Tailoring the magnetic properties

Applications:

- magnetic data storage
- spintronics

Magnetic recording technology

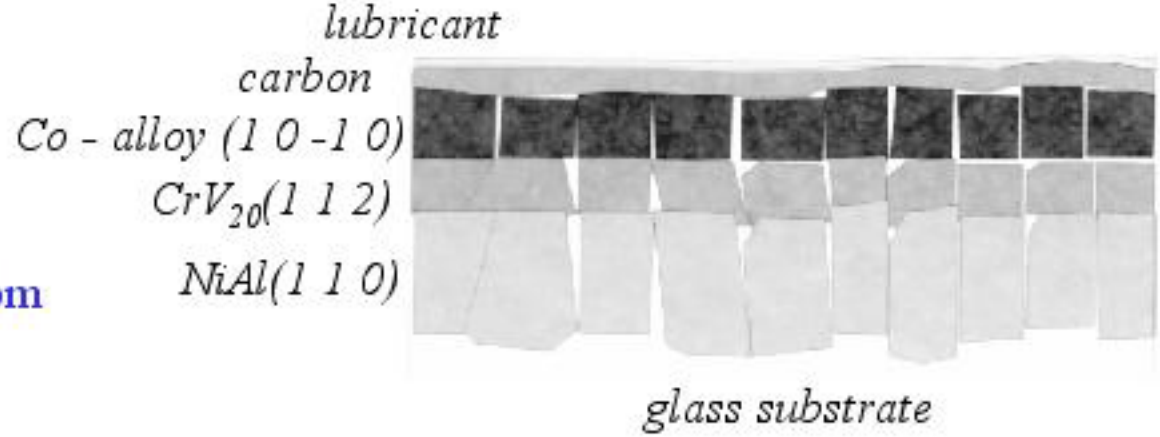




Modern recording materials:

CoXYZ alloys (X=Pt, Ni; Y=Cr,Ta,B,P; Z=Nb,Mo).

Co *c*-axis magnetic anisotropy:
K_1=4.5 10^6 erg/cm^3 = 45 μeV/atom



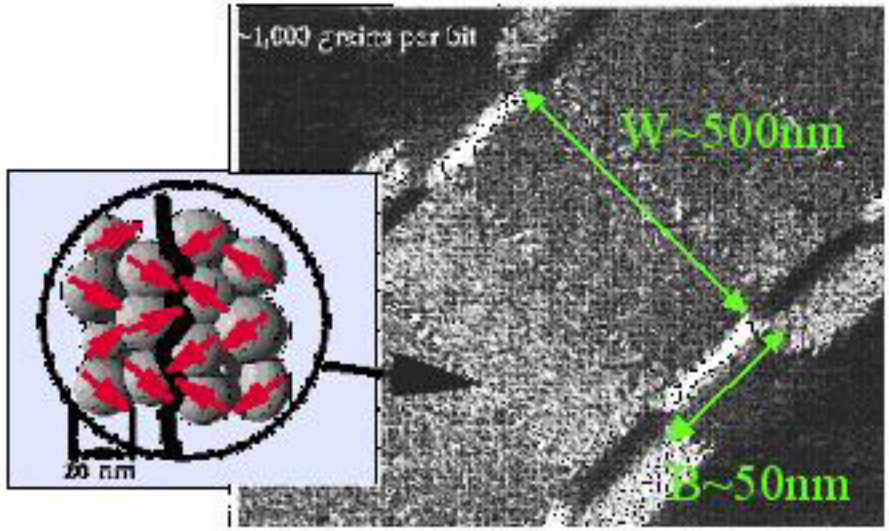
Capacity limiting factors

Signal-to-Noise Ratio: SNR **a** number of grains in each bit (~1000).

To keep the SNR constant the number of grains is kept fixed. Therefore smaller bits imply smaller grain size. Grain size reduction results in the reduced stability of the magnetization *vs* thermal fluctuations.

Transition Width:

Demagnetizing fields associated with regions of opposite magnetization increase the transition (bit) width.. Moreover, grains have non-uniform boundaries that increase the magnetic noise in the read out process.



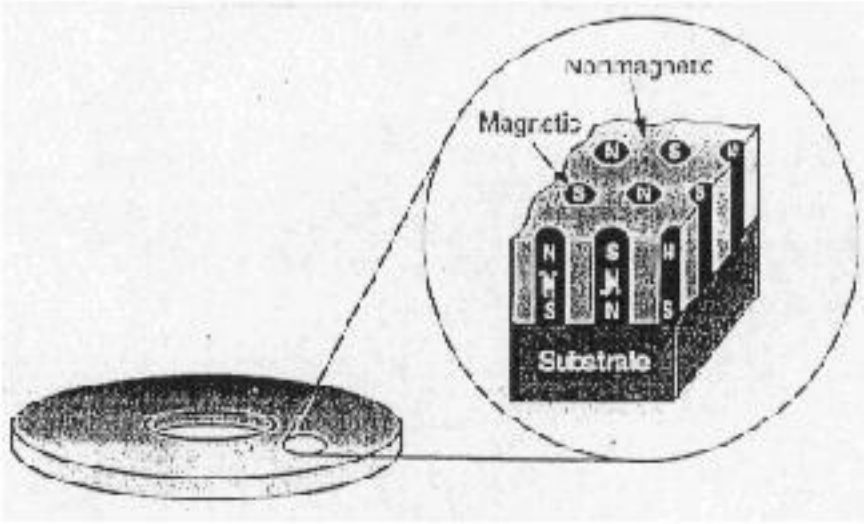
Perspectives for nanostructured materials

Reduce grain size ⇔ increase the coercivity, i.e., the magnetocrystalline anisotropy

Reduce the transition width ⇒ Perpendicular recording
Uniform grains

Patterned media:

the bit cell is not defined during writing (formatting), but is predefined by some nanostructuring method. Most capacity contraints can be lifted if continuos thin film media are replaced by single-domain magnetic elements uniformly embedded in a nonmagnetic disk. Each bit is a single domain particle having a uniform, well-defined shape, a prespecified location and only two possible states of magnetization. Size contraints and crystalline + shape anisotropy are the key parameters involved in the magnetic 'bit' structure.



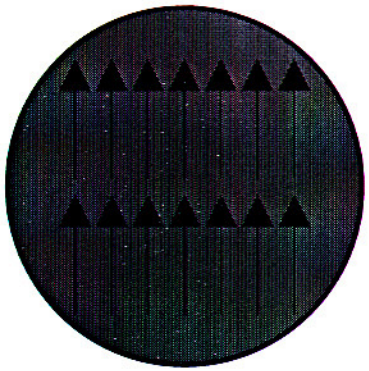
[More on magnetic storage: D. Weller and A. Moser, IEEE Trans. Mag., 35, 4423 (1999);
See also http://www.research.ibm.com/resources/news/20010518_whitepaper.shtml]

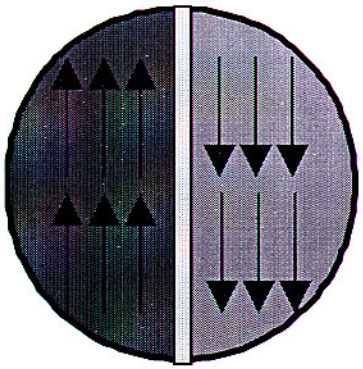
Magnetism in low-dimensional systems: basic questions

Ferromagnetic phenomena are a property of crystalline matter, i.e. of large number of atoms arranged in an ordered lattice. What happens as the number of atoms or the dimensions of a ferromagnetic systems are reduced?

- Domains
- Stability of the magnetization *vs* thermal fluctuations
- Orbital and spin magnetization
- Magnetic anisotropy *vs* atomic structure (particle size, shape, etc.)

Single-domain particles





	γ mJ m^{-2}	R_{sd} nm
Fe	2.6	6
Co	9.3	34
$SmCo_5$	78	764

The creation of domain walls costs energy, there are no walls if the gain in magnetostatic energy is smaller than the wall energy cost.

wall energy of the two domains configuration: $E_w = \gamma \pi R^2$

γ - wall energy/unit area

Gain in magnetostatic energy of the two domains configuration (1/2 the single-domain energy)

$$E_m = \mu_0 M_s^2 \frac{V}{12} = \mu_0 M_s^2 \pi \frac{R^3}{9}$$

Domain formation is unfavorable when $E_w > E_m \Leftrightarrow R < \frac{9\gamma}{\mu_0 M_s^2}$

Single-domain particles: the Stoner-Wohlfart model

Magnetization of a single-domain particle in an external field.

$$E = E_{Zeeman} + E_{mc} + E_{dm}$$

Suppose $\mu = MV$ = const. for any H value (coherent rotation) and, for simplicity, $E_{dm} = 0$. Φ = const.

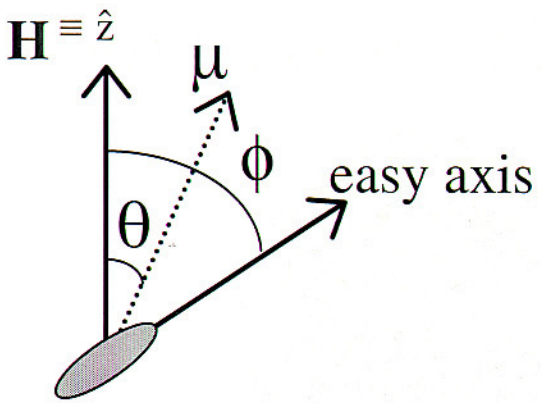
$$E = -\mu H\cos\theta - K_1 V \cos^2(\theta-\phi) \qquad (1)$$

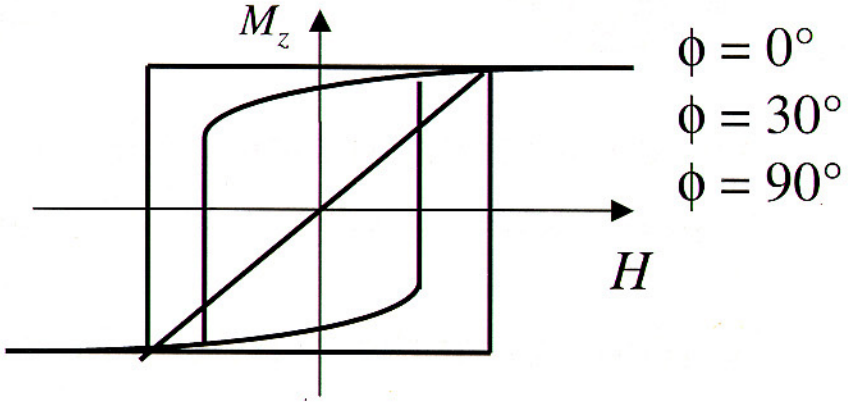
The magnetiic moment $\mu = \boldsymbol{M}V$ will point along a direction that makes E a minimum:

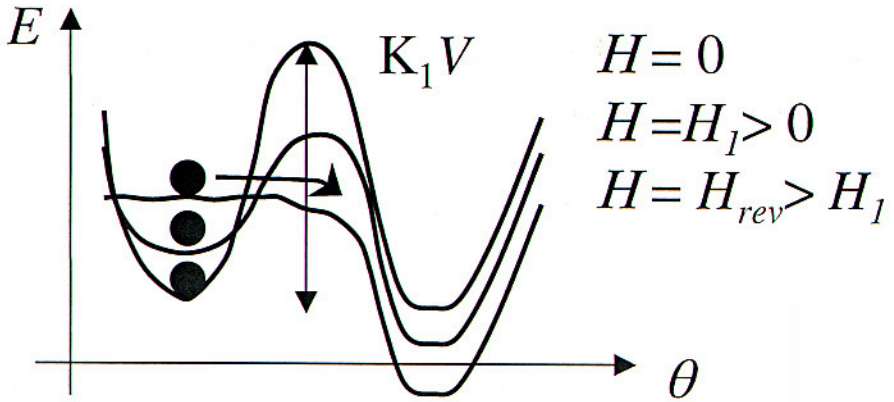
$$\frac{\partial E}{\partial \vartheta} = \mu H \sin\vartheta + K_1 V \sin(2(\vartheta - \varphi)) = 0 \qquad (2)$$

Eq. 2 can be solved for θ and we can plot $M_z = M\cos\theta$ (this is what one usually measures) as a function of H.

The reversal field is the field at which the energy minimum in eq. (1) vanishes ($\partial^2 E/\partial\vartheta^2 = 0$)



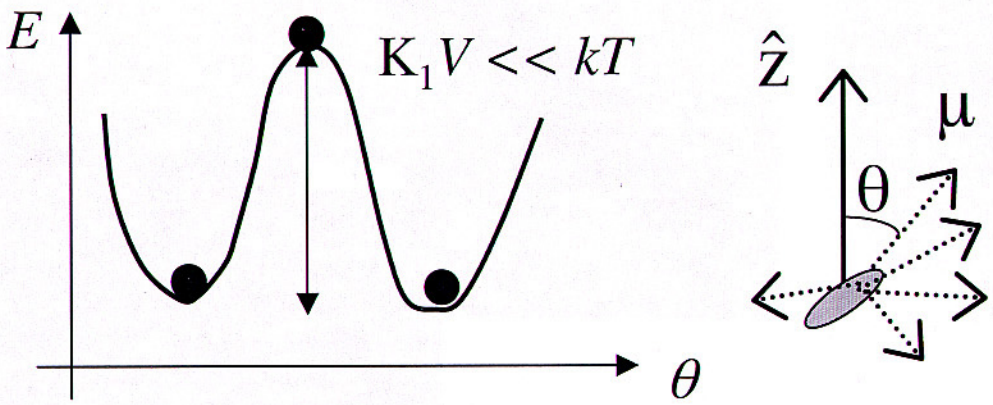




[More on magnetization reversal: W. Wernsdorfer, cond-mat/0101104 v1]

The superparamagnetic limit

The magnetic anisotropy energy of a particle is proportional to its volume. As the volume reduces the magnetic energy of the particle approaches its thermal energy kT and the magnetization vector fluctuates in the same way as in a classical paramagnetic system.



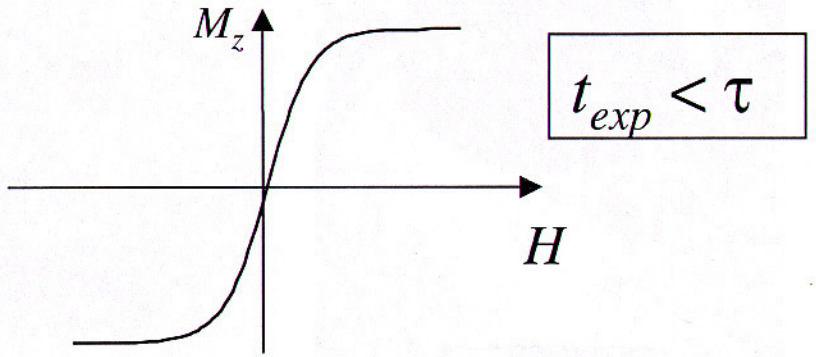
The magnetization density M of an assembly of N identical particles in thermal equilibrium at the temperature T is given by classical Boltzmann statistics:

$$M_z = \frac{N\mu}{V}\langle\cos\theta\rangle = \frac{N\mu}{V}\frac{\int \cos\theta \exp(-E/\mathrm{k}T)\,\mathrm{d}\Omega}{\int \exp(-E/\mathrm{k}T)\,\mathrm{d}\Omega}$$

For $\mathrm{K}_1 V << kT$ one obtains the Langevin function

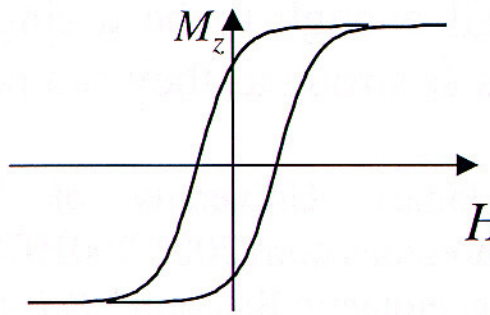
$$M = \frac{N\mu}{V}\mathrm{L}\left(\frac{\mu H}{\mathrm{k}T}\right)$$

where $\mu = \Sigma_i \mu_i$ is the particle total magnetic moment.



Avg. time (relaxation time) it takes to jump from one minimum to the other (at H=0)

$$\tau = \tau_0 \exp\left(\frac{\mathrm{K}_1 V}{\mathrm{k}T}\right), \quad \tau_0 \approx 10^{-10}\mathrm{s}$$



$t_{exp} < \tau$

$T < T_B$
Blocking temperature

Shape Anisotropy

When a specimen of finite size is magnetized by an external magnetic film, the free poles which appear on its ends will produce a field directed opposite to the magnetization, proportional to the free pole density and therefore to the magnetization M.

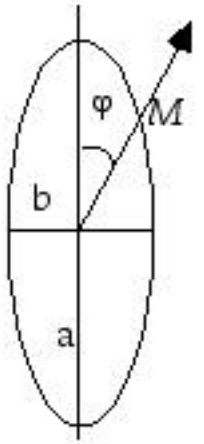
$$\boldsymbol{H}_d = -\mathrm{D}\boldsymbol{M} \qquad \textit{demagnetizing field}$$

where D is the *demagnetizing factor (tensor)* which depends only from the shape of the specimen. The magnetostatic energy due to $\boldsymbol{H}_d$ for a magnetic material of volume V is

$$E_{\mathrm{dm}} = -\frac{\mu_0}{2}\int_V M \cdot H_{dm}\, dV$$

This contribution to the total energy of the system is usually neglected for bulk ferromagnetic materials, but it has very important effects in the case of thin films and small particles.

For a **rotational ellipsoid** with semiaxes b = c, a, the magnetostatic energy density as a function of the magnetization M is



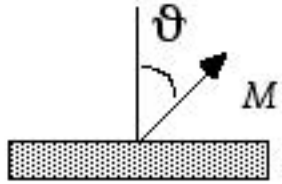
$$E_{\mathrm{dm}} / \mathrm{V} = -\frac{\mu_0}{2} M^2 (\mathrm{D_a} \cos^2\varphi + \mathrm{D_b} \sin^2\varphi)$$

for a>>b, $D_a \ll D_b$, we have $D_a = (b^2/a^2)(\ln(2a/b)-1)$.

The energy is minimized if the magnetization lies parallel to the long axis($\varphi = 0$).

In the case of **thin films** all the elements of the tensor D are zero except for the direction perpendicular to the layer: $D_\perp = 1$. Therefore the magnetostatic energy contribution per unit volume of a film is

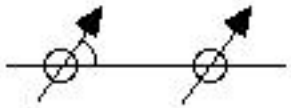
$$E_{\mathrm{dm}} / \mathrm{V} = -\frac{\mu_0}{2} M^2 \cos^2\vartheta$$



hence an **in-plane orientation is preferred**. The magnetostatic energy strongly influences the domain structure of a thin film.

Magnetocrystalline Anisotropy

The magnetocristalline energy term depends on the simmetry of the crystal which defines the interaction directions between neighbouring atoms.



In the case of particles with uniaxial anisotropy or in the case of fcc (111) and (100) films with volume V the anisotropy energy can be described by the simple formula

$$E_{mc} = -KV\cos^2\vartheta$$

where **q** is the angle between the magnetization and the easy axis.

	$\mu_0 M_s$ (T)	K_1 (10^6 J m^{-3})
Fe	2.15	0.05
Co	1.81	0.53
Ni	0.62	-0.005
$SmCo_5$	1.07	17.2
CoPt	1.01	4.9

Anisotropy and saturation magnetization at room temperature for some common magnetic materials. K_1 for Fe and Ni is a uniaxial estimate. (10^6 J m^{-3} ~ 10^{-4} eV/atom).

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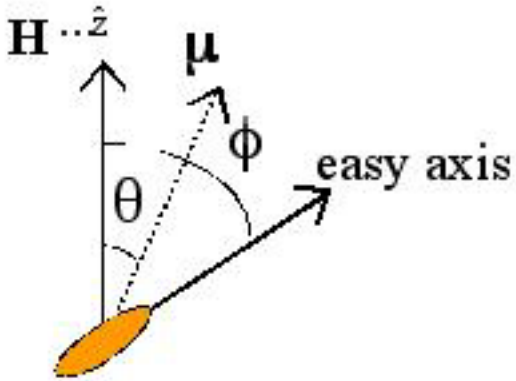

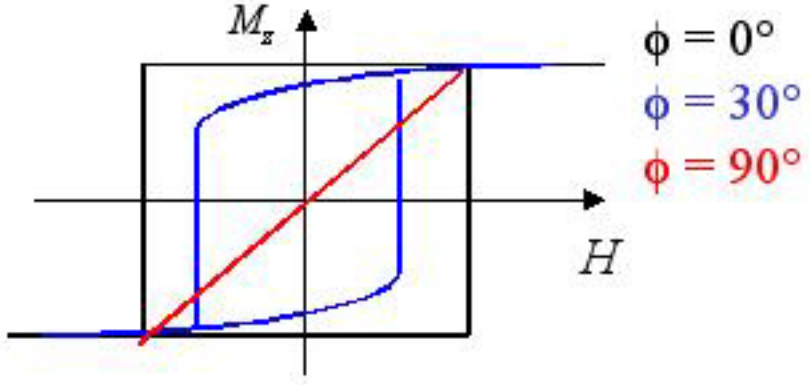

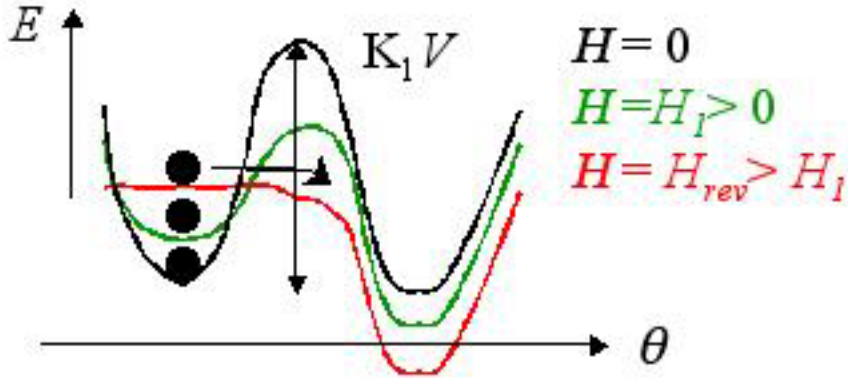

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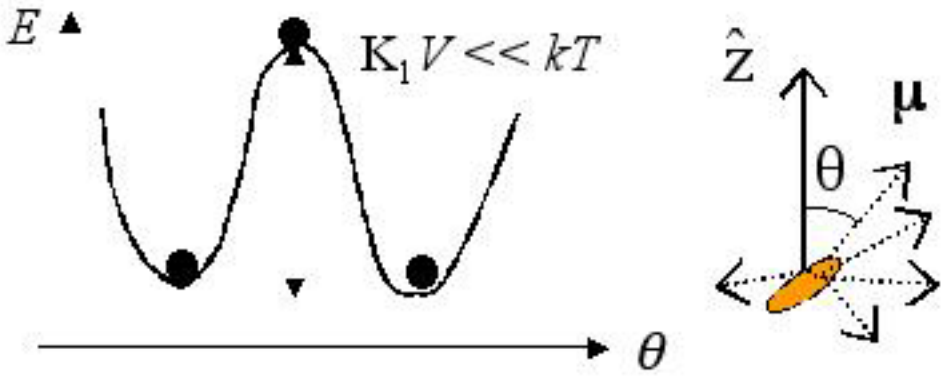

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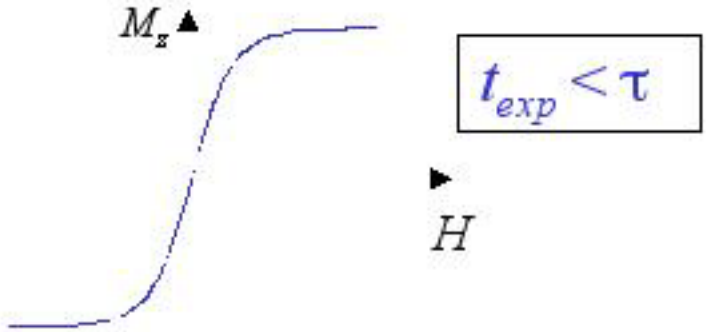

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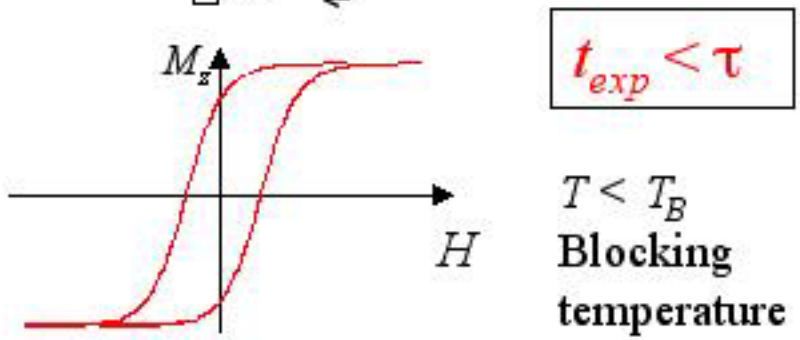
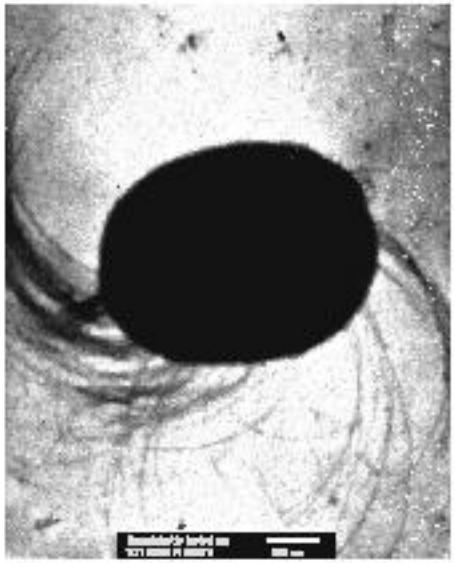
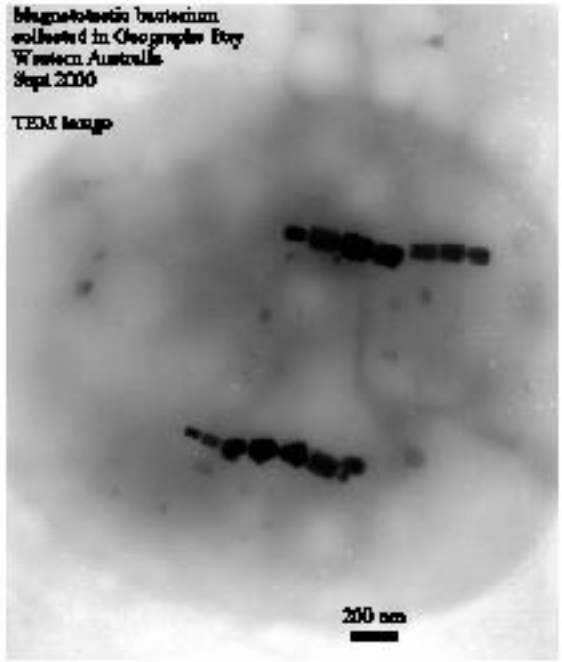
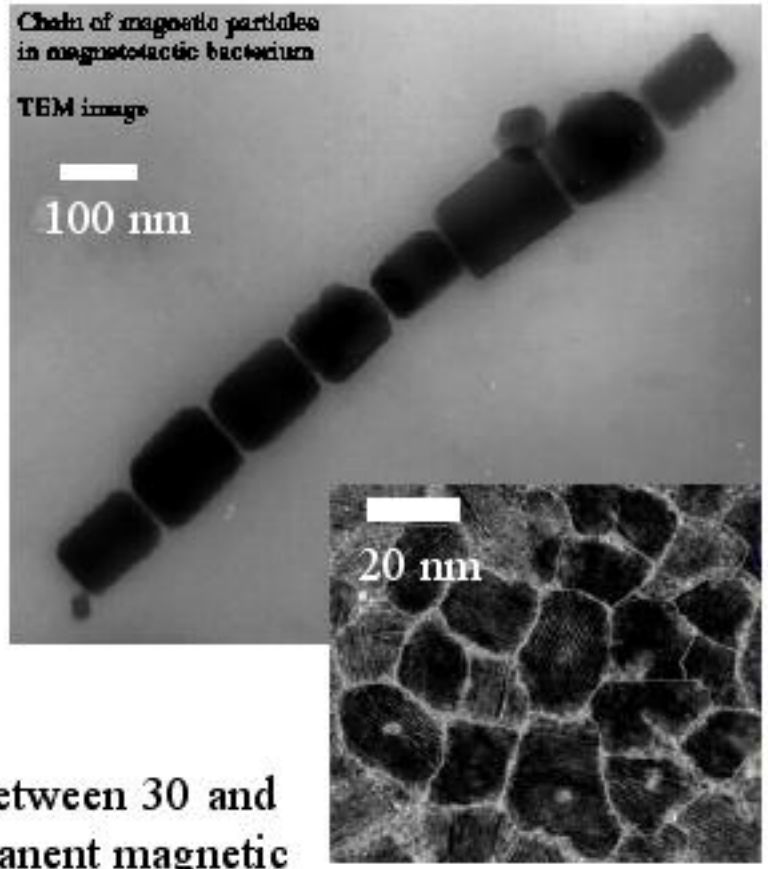


$T < T_B$ Blocking temperature

Nature does it better: magnetotactic bacteria





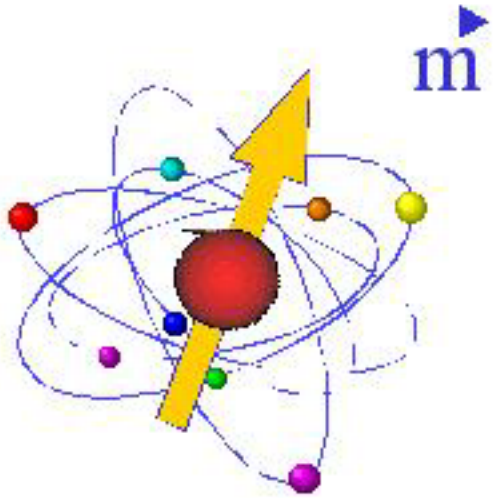


Magnetotactic bacteria synthesize magnetic particles between 30 and 100 nm in every dimension, big enough to have a permanent magnetic moment, but small enough to be a single domain. This makes the magnetic particles as strong as they can possibly be for their size.

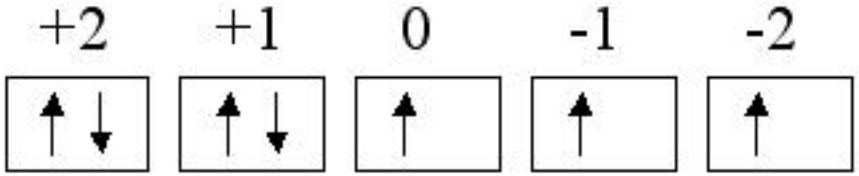
IBM 25 Gbits/in ^{2} recording medium

[images by R. James, University of Western Australia; see also http://www.strangehorizons.com/2001/20010702/living_lodestones.shtml
R. Blakemore . "Magnetotactic Bacteria." *Science* 190, 377 (1975)].

Orbital and spin magnetic moments: the atomic limit



Ground state of a $3d^7$ ion (e.g., Co^{2+})



$$L = 3, S = 3/2, J = 9/2$$

$$m_L = -L\ \mu_B = -3\ \mu_B\ ,$$

$$m_S = -2S\ \mu_B = -3\ \mu_B\ ,$$

$$m_{at} = -\,g\,J\,\mu_B = 6\ \mu_B$$

Hund's rules:

1) Total spin $S = \Sigma_i s_i$ is maximized

2) Total orbital momentum $L = \Sigma_i l_i$ is maximized

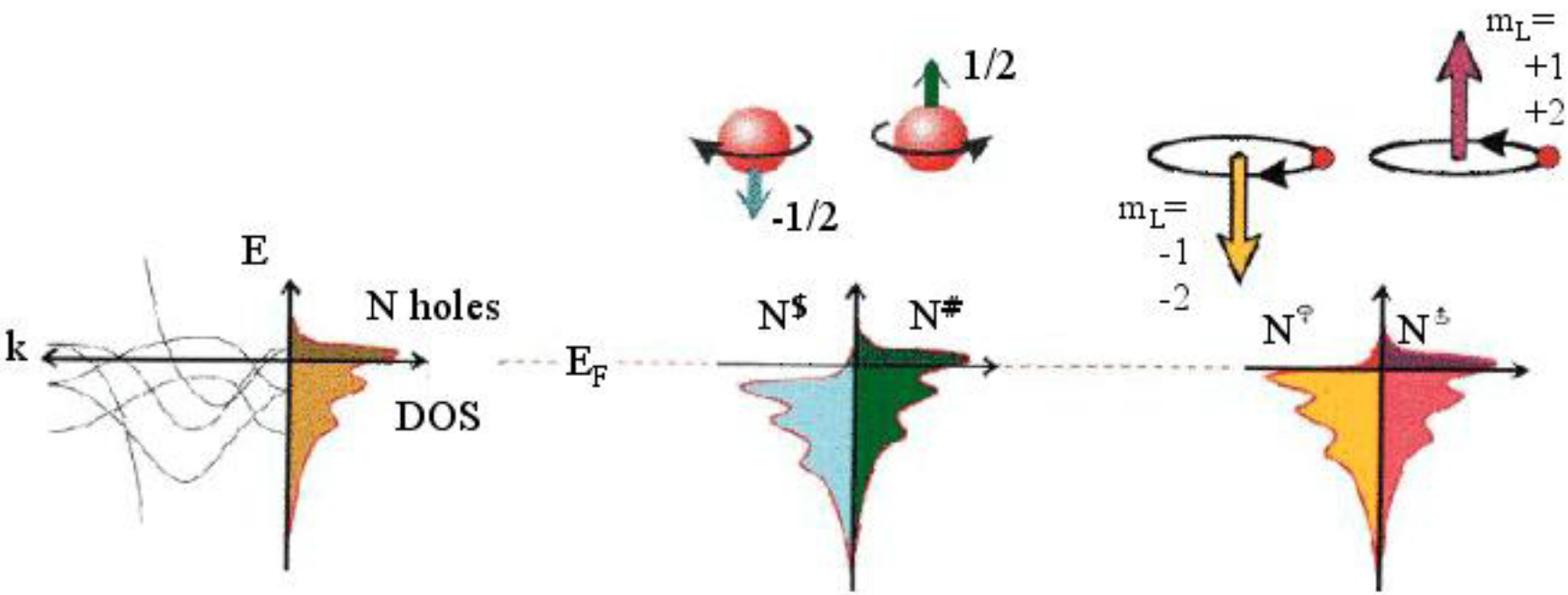
3) L and S couple parallel ($J=|L+S|$) if $n>5$,
L and S couple antiparallel ($J=|L-S|$) if $n<5$.

Orbital and spin magnetic moments in 3*d* metals

d-band occupation

Spin moment

Orbital moment



Material	N holes
Fe	3.4
Co	2.5
Ni	1.5

m_s^{tot}	m_s^{d}	m_s^{sp}
2.19	2.26	-0.07
1.57	1.64	-0.07
0.62	0.64	-0.02

m_{orb}
0.09
0.14
0.07

Quenching of the orbital magnetic moment in 3*d* metals:

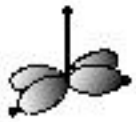
Experiments show that 3*d* ions in solids have $L \neq 0$, $J \neq S$ and $g \neq 2$.

The crystal electric field produced by surrounding ions in a solid defines a particular set of (real) wavefunctions for which the mean value of the orbital moment is zero (balance of $+/-m_L$).

The crystal field gives a reduction of the orbital moment depending on its symmetry and strength.

d wavefunctions in cubic symmetry

t_{2g}

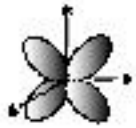


$d_{x^2-y^2} = 1/\sqrt{2}\,(|+2\rangle + |-2\rangle)$

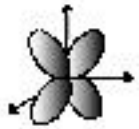
$d_{3z^2-r^2} = |0\rangle$

e_g

$d_{xy} = i/\sqrt{2}\,(|+2\rangle - |-2\rangle)$



$d_{yz} = i/\sqrt{2}\,(|+1\rangle + |-1\rangle)$



$d_{xz} = 1/\sqrt{2}\,(|-1\rangle - |+1\rangle)$

Orbital moment and magnetocrystalline anisotropy in 3*d* metals

crystal field → electron orbits → fixes L relative to the crystal lattice

Different L values along different crystal directions

Direction with the largest component of L → Lowest spin-orbit energy → easy direction of magnetization

$$H_{so} = \xi \mathbf{S} \cdot \mathbf{L}$$

$$E_a = \langle H_{so}(S_z) \rangle - \langle H_{so}(S_x) \rangle$$

- ξ spin-orbit constant
- S spin
- L orbital moment

2nd order perturbation theory [P. Bruno, PRB 39, 865 (19

$$E_a = \xi(/ + \mu_B)(m_L{}^x - m_L{}^z)$$

$$m_L{}^z \propto \xi / W^y$$

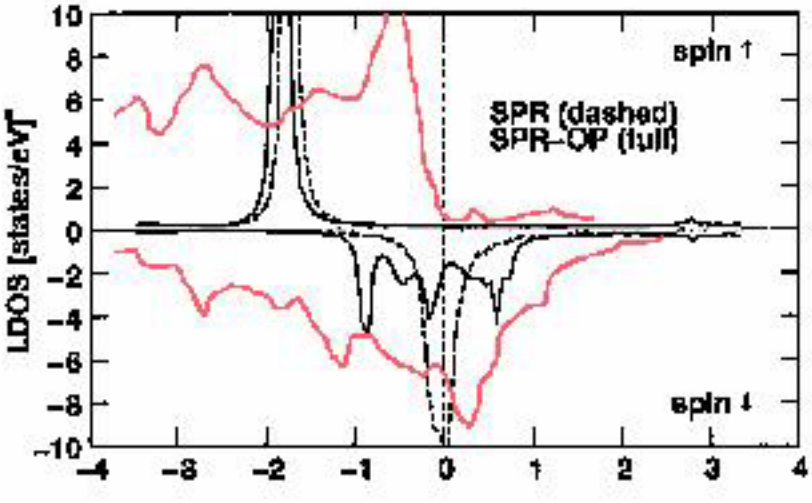
- m_L orbital magnetic mc
- W minority electrons bandwidth

[see also H. A. Dürr et al., *Science* 277, 213 (1997)]

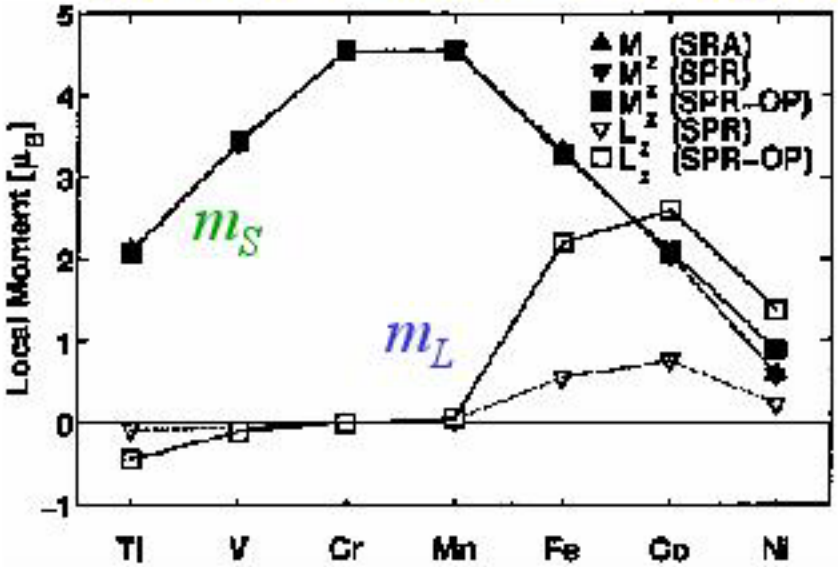
Orbital moment in low-dimensional structures

Co adatom DOS on Ag(100)

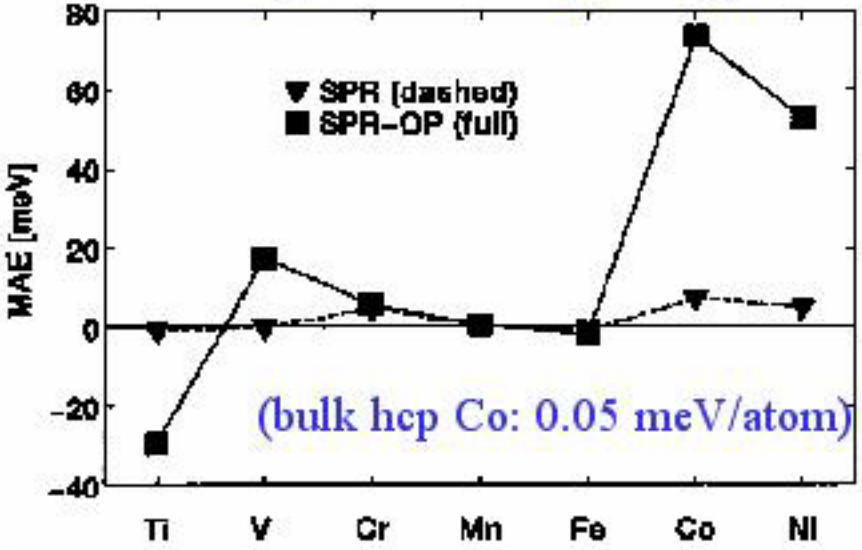
Co bulk DOS



Spin and orbital moments 3*d* ad Ag(100)



Magnetic anisotropy energy



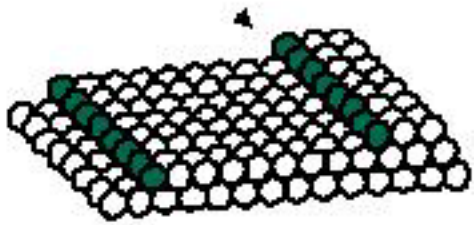
Reduced dimensions

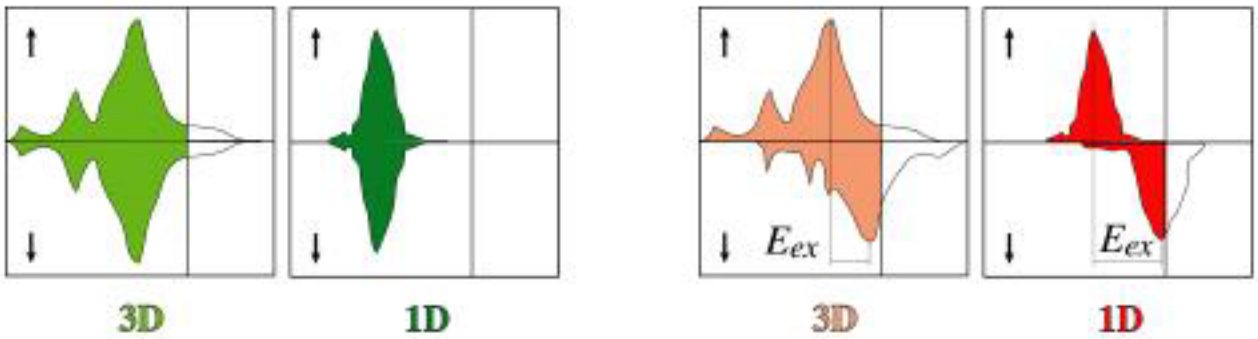
- 3d electron localization
- larger spin and orbital moments
- larger magnetic anisotropy

[LDA-SPR calculations,
B. Nonas et al.,PRL 86, 2146 (2001)]

3*d* exchange splitting: valence band photoemission

0.12 ML



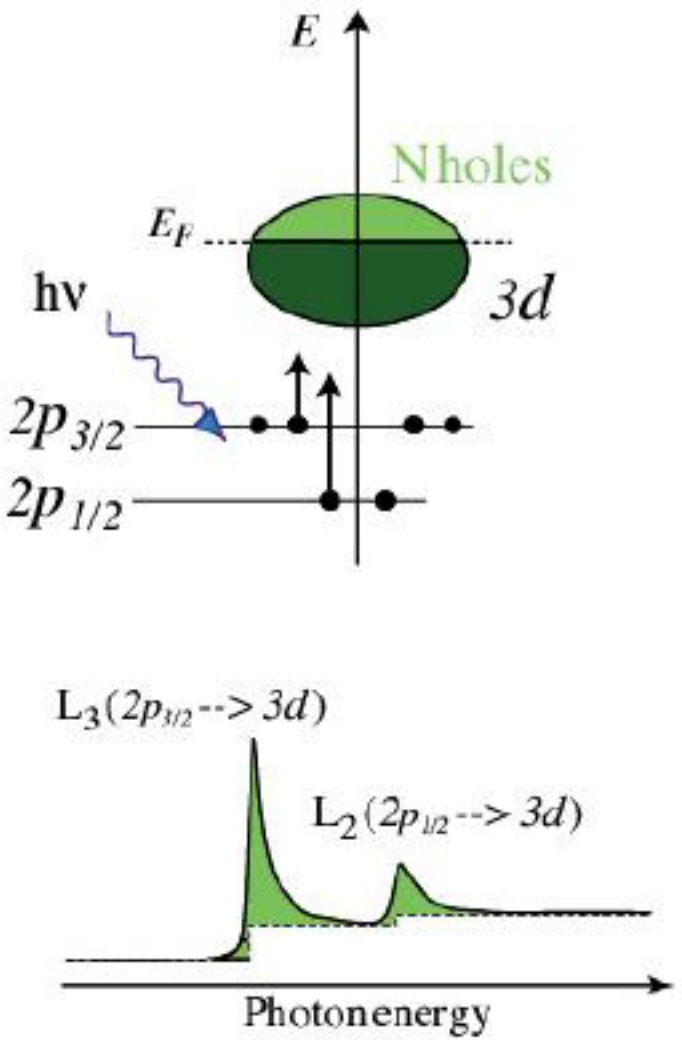


3*d* localization in 1D narrows the Co, Cu bands leading to larger E_{ex} in Co

⇑ higher magnetic moments

[PRB 61, R5133 (2000)]

X-ray absorption spectroscopy (XAS): $2p \rightarrow 3d$ transitions



Dipolar transitions

$$\acute{o} = \left|\left\langle 3d\left|\vec{a} \cdot \vec{r}\right|2p\right\rangle\right|^2 \tilde{n}(E)$$

Spin-flip transitions are forbidden

→If one could preferentially excite spin-up photoelectrons in one measurement and spin-down ones in another, the difference in the transition intensity would reflect the difference in the up and down holes of the *d* shell ($N^{\#} - N^{\$}$), i.e. the spin moment.

→ Use of circularly polarized light

X-ray magnetic circular dichroism (XMCD)

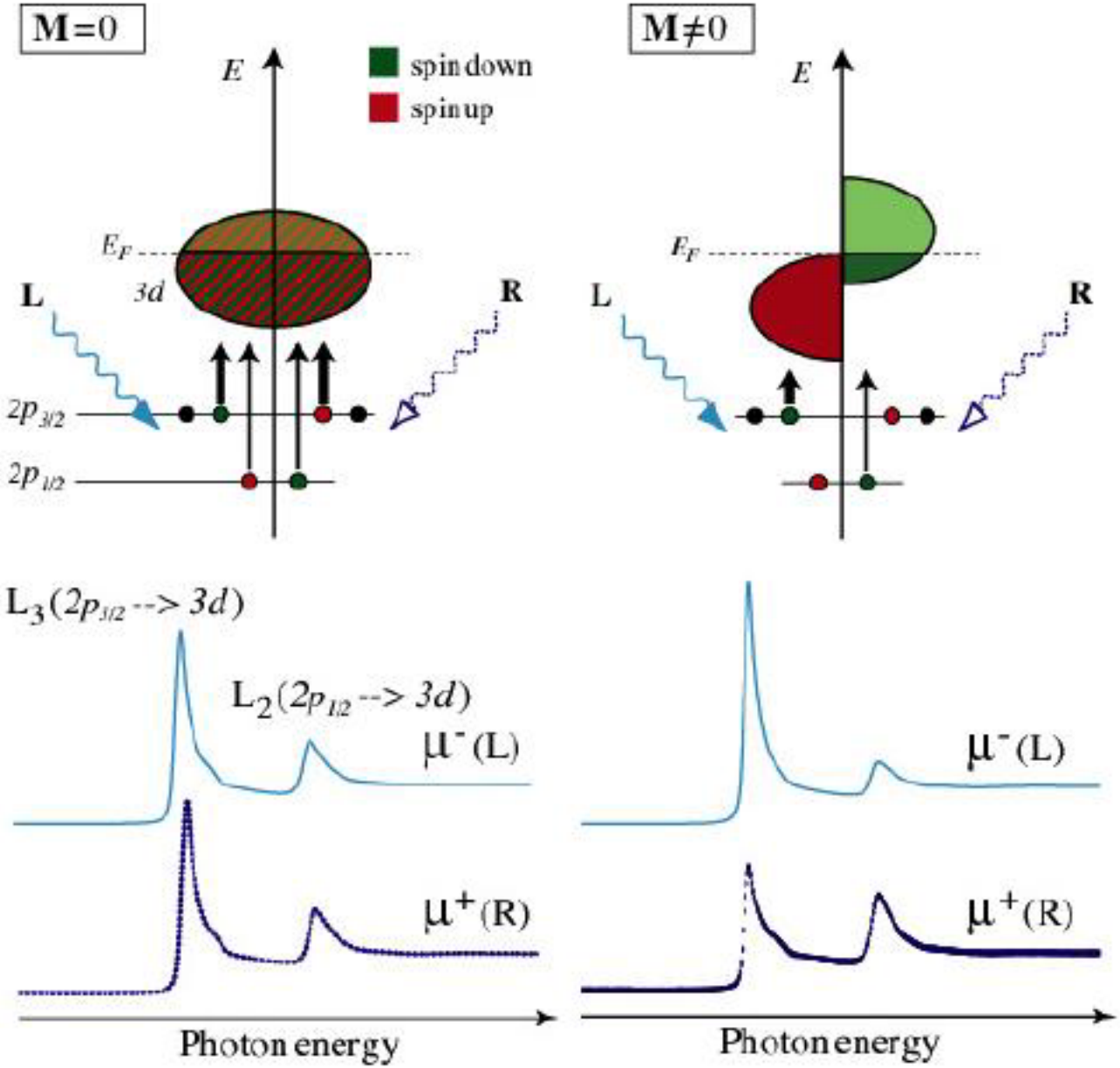
R and L circularly polarized photons create photoelectrons with opposite spins.

Since:

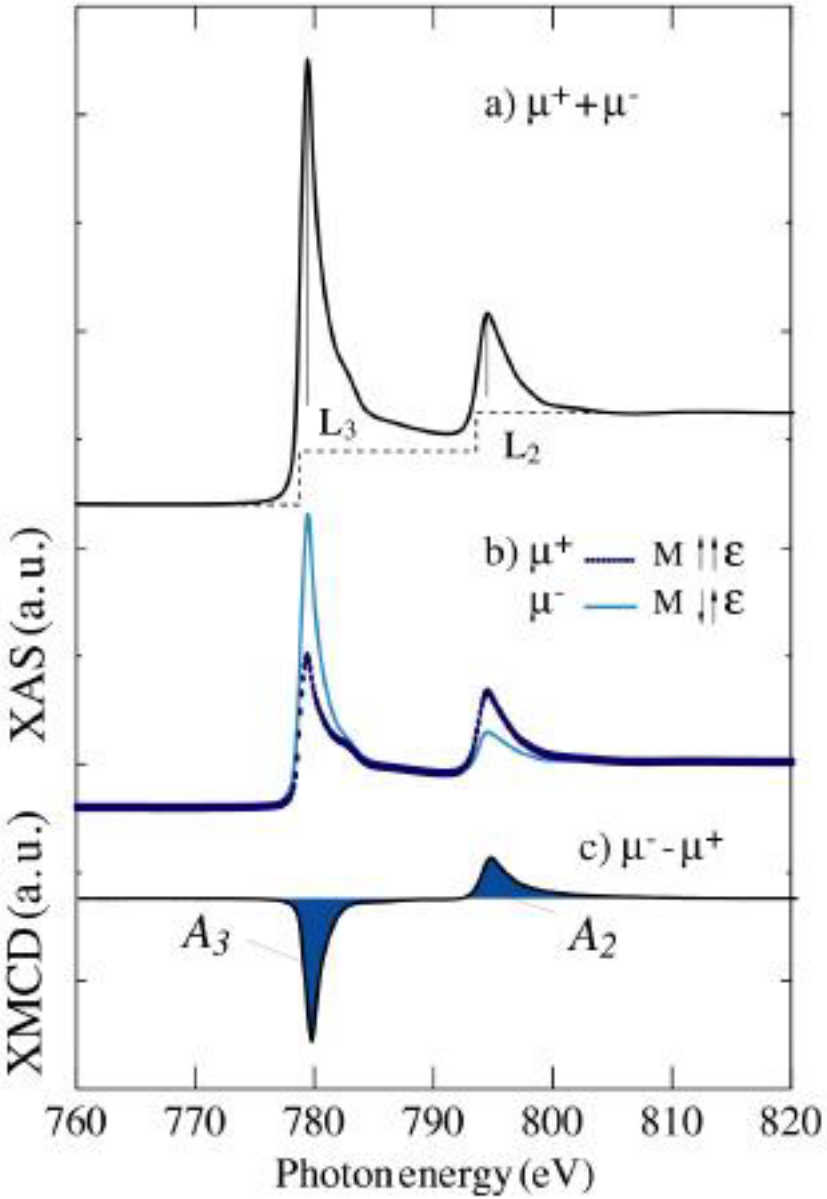
$p_{3/2}$ (L+S coupling)

$p_{1/2}$ (L-S coupling)

The spin polarization of the photoelectrons is opposite at the L_3 and L_2 edges



XMCD at the L_3, L_2 edges of Co



Sum rules

$$m_S = C\,\mu_B\,(A_3 - 2A_2)$$

$$m_L = C\,\mu_B\,(A_3 + A_2)$$

$$m_L/m_{Seff} = (A_3 + A_2)/(A_3 - 2A_2)$$

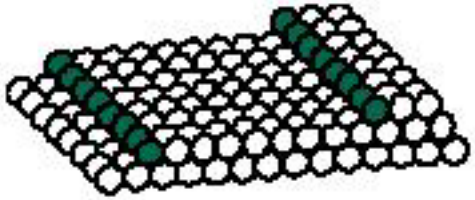
B. Thole et al., PRL 68, 1943 (1992)

P. Carra et al., PRL 70, 694 (1993)

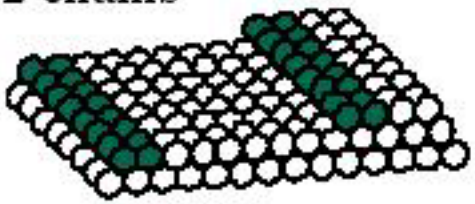
J. Stöhr and H. König, PRL 75, 3748 (1995).

Orbital moment in 1D atomic chains: dimensionality effects

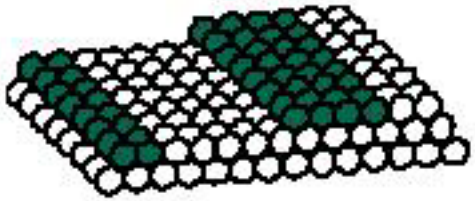
1 chain

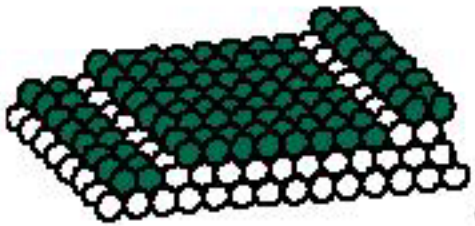


2 chains

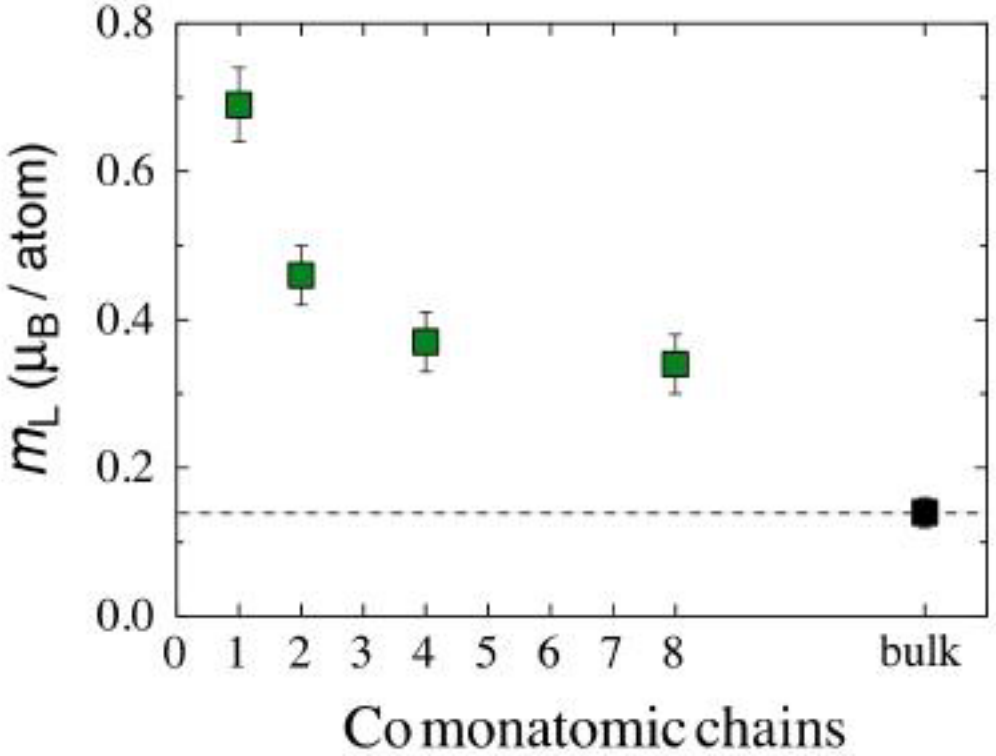


4 chains

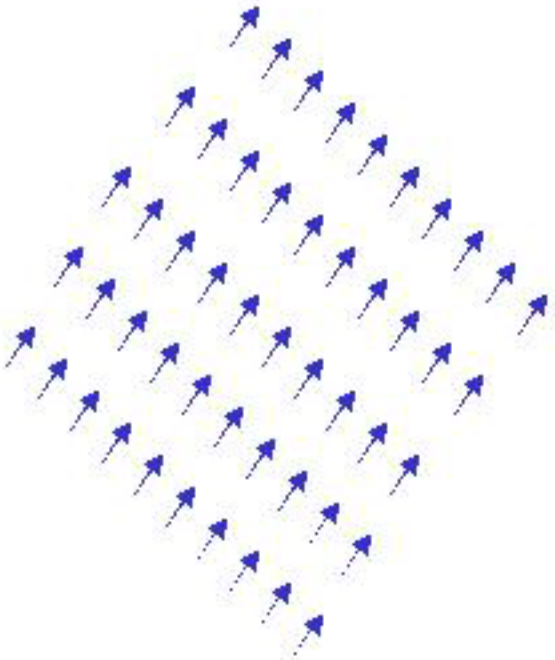


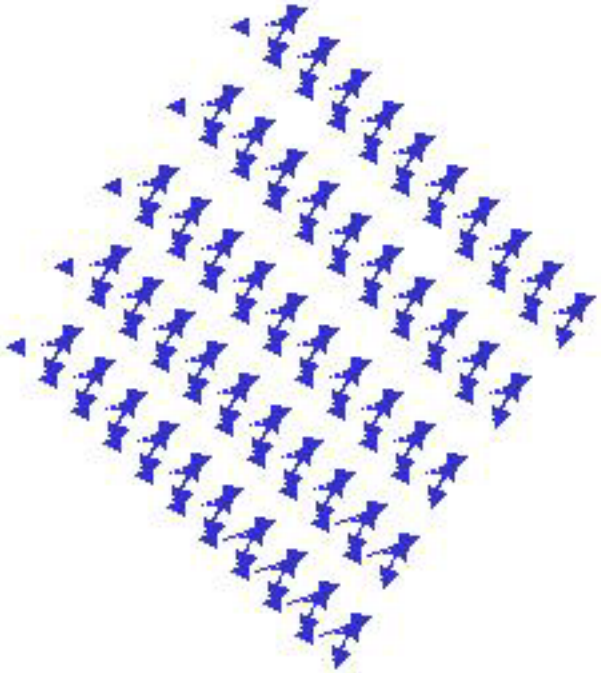


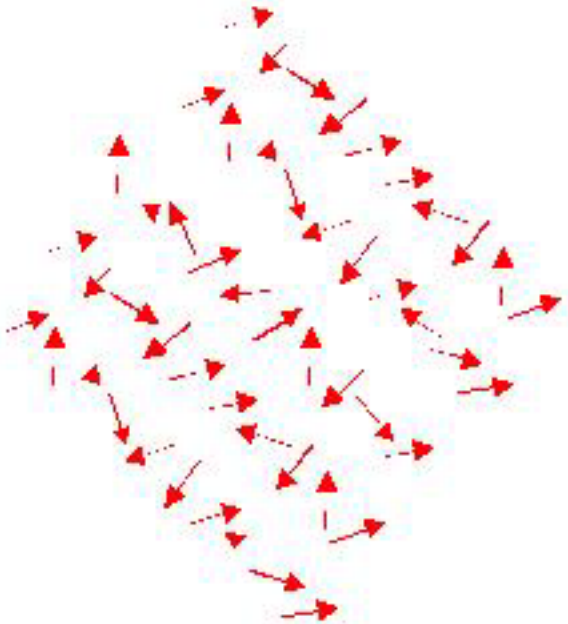
8 chains = 1 ML



Ferromagnetic order







Ferromagnetism
$T < T_C$
Superparamagnetism
$T < T_B$

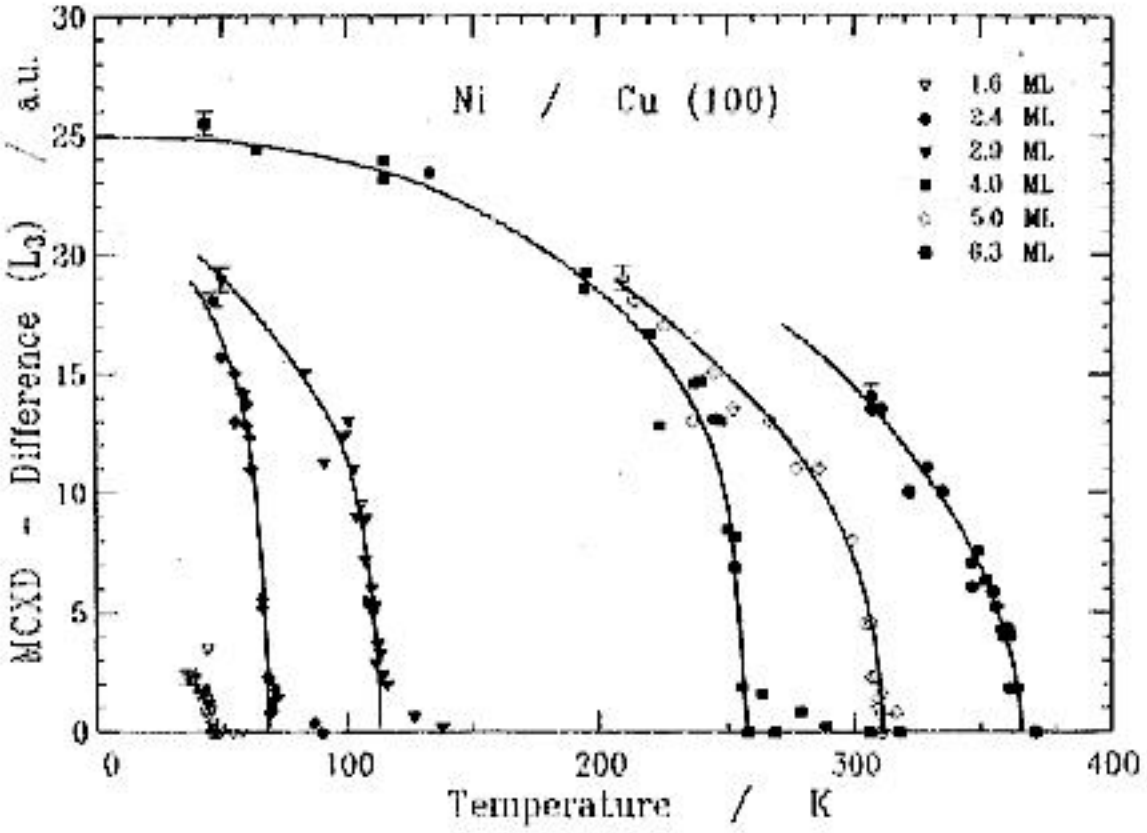
Superparamagnetism
$T < T_C$
$T > T_B$

disorder
$T > T_C$

Ferromagnetic order in 1D at $T > 0$ K ?

M_s vs T

T_C decreases with film thickness in 2D systems



[M. Tischer et al., Surf. Sci. 307-309, 1096 (1993)]

Ferromagnetic order in 1D at $T > 0$ K ?

- Heisenberg model $\Longrightarrow$ no FM state in 1D and 2D

$$H_{heisen} = -\frac{1}{2}\sum_{i,j} \mathbf{J}_{ij}\mathbf{s}_i \cdot \mathbf{s}_j - \mu \sum_i \mathbf{s}_i \cdot \mathbf{H}$$

- Heisenberg model + anisotropy $\Longrightarrow$ FM state in 2D, not in 1D

$$H = H_{heisen} - \frac{1}{2} K \sum_i \left(s_i^{\text{easy}}\right)^2$$

- Ising model $\Longrightarrow$ no FM state in 1D

$$H_{ising} = -\frac{1}{2} J \sum_{i,j} s_i^z s_j^z - \mu \mathrm{H} \sum_i s_i^z$$

Ferromagnetic order in 1D at $T > 0$ K ?

• Finite system (N localized moments):

ground state: $E=E_0$

lowest excited state: $E=E_0 + 2\,J$
(N-1 such states)

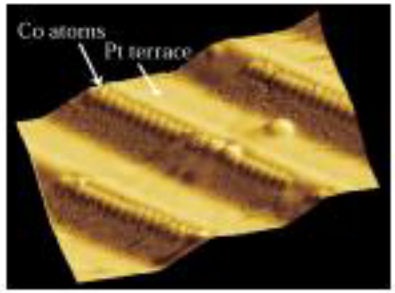
change in free energy: $\Delta F = 2\,J$ - kT ln(N-1)

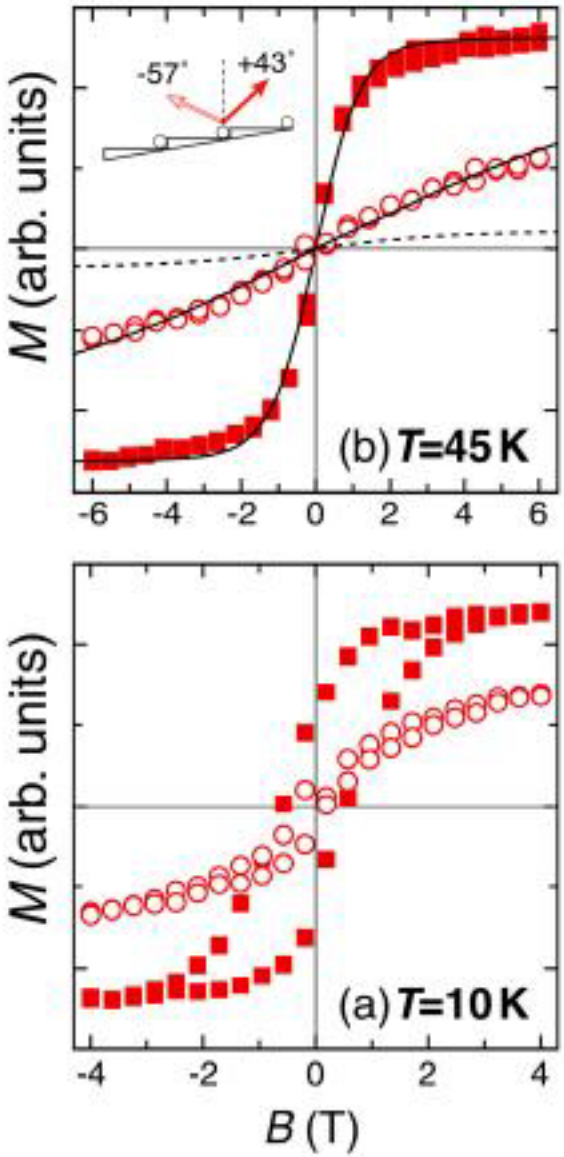
$\Delta F<0 \Longrightarrow$ no FM stable state for $N > exp(2J/\mathrm{k}T)$

$2J \approx 15$ meV for quasi-1D Fe stripes [M. Pratzer et al., PRL 87, 127201 (2001)]

At $T = 50$ K $\Longrightarrow$ no FM stable state for $N > 30$ atoms !

Ferromagnetic order in 1D Co chains





N coupled atoms

E_a anisotropy energy per atom

$< N > = 15$ atoms $\Rightarrow$ short-range FM coupling

$E_a = 2.1$ meV/atom

$\tau = \tau_0 \exp(< N > E_a / kT)$

$\tau_0 \sim 10^{-9}$ s

$\Rightarrow T_B = 15$ K $\Rightarrow$ long-range FM coupling

Summary

Low-D magnetic structures
- small particles
  - single-domain
  - superparamagnetism
  - perspectives for applications
- from the atom to the bulk:
  - -moments
  - -anisotropy
  - -order

Co clusters on Pt(111)
- 50-fold enhancement of E_a (mag. anisotropy energy)
- dramatic decrease of m_L and E_a with cluster size

Co atomic chains on Pt(997)
- m_L in 1D to 2D structures
- FM short- and long-range order in the 1D atomic limit

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P. Ohresser, S. Dhesi (ESRF ID08 Grenoble)

Intrinsic magnetic properties

depend on the atomic structure (quantum-mechanical phenomena):

- Orbital and spin moments
- Magnetic order (T_C, T_N)
- Magnetocrystalline anisotropy

Extrinsic magnetic properties

depend on the microstructure (macroscopic phenomena, e.g., magnetostatic interactions):

- Magnetic domains
- Hysteresis
- Remanence
- Coercivity