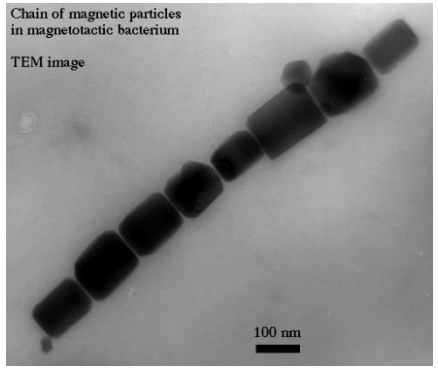
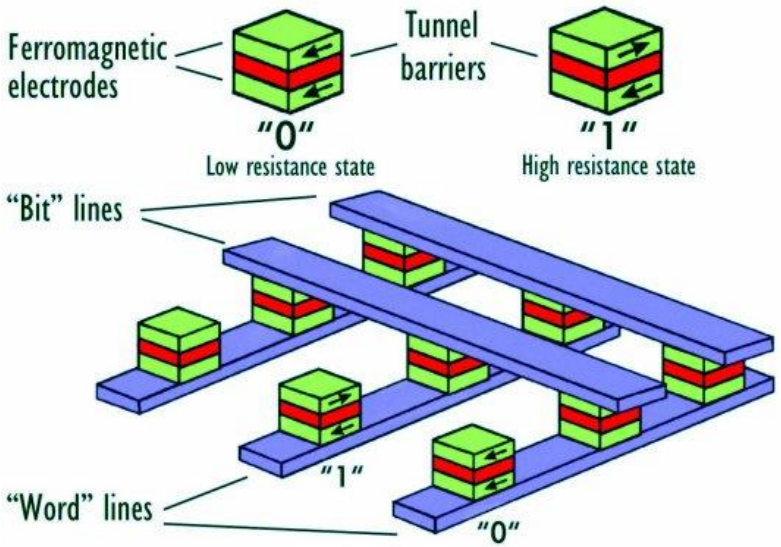
Nano-magnetism everywhere

Credit Card



Magnetotactic bacteria synthesize magnetic particles between 30 and 100 nm, big enough to have a permanent magnetic moment, but small enough to be a single domain.
[images by R. James, University of Western Australia; see also R. Blakemore. "Magnetotactic Bacteria." *Science* 190, 377 (1975)].

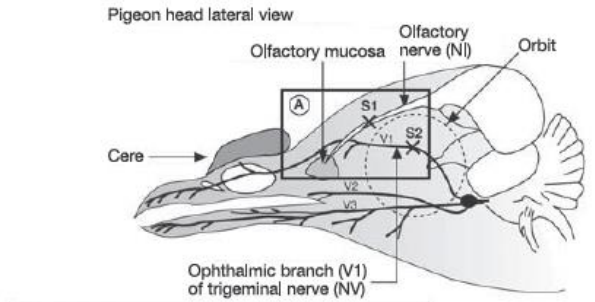
MRAM: Magnetic Random Access Memory



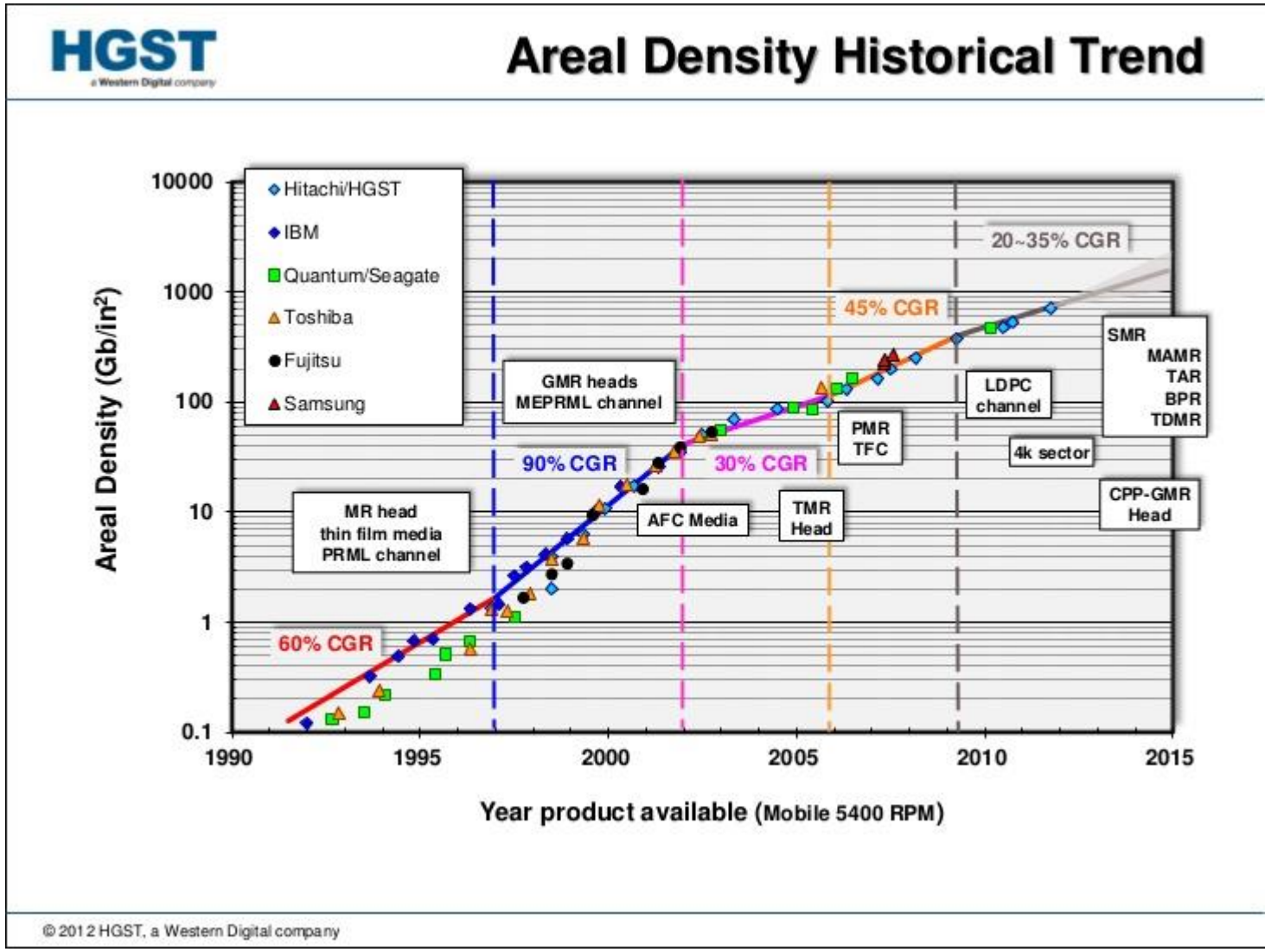
Magnetoreception and its trigeminal mediation in the homing pigeon

Cordula V. Mora[1]*, Michael Davison[2], J. Martin Wild[3] & Michael M. Walker[1]

Nature **432**, 508 (2004)



High density magnetic recording: the rush to the nano

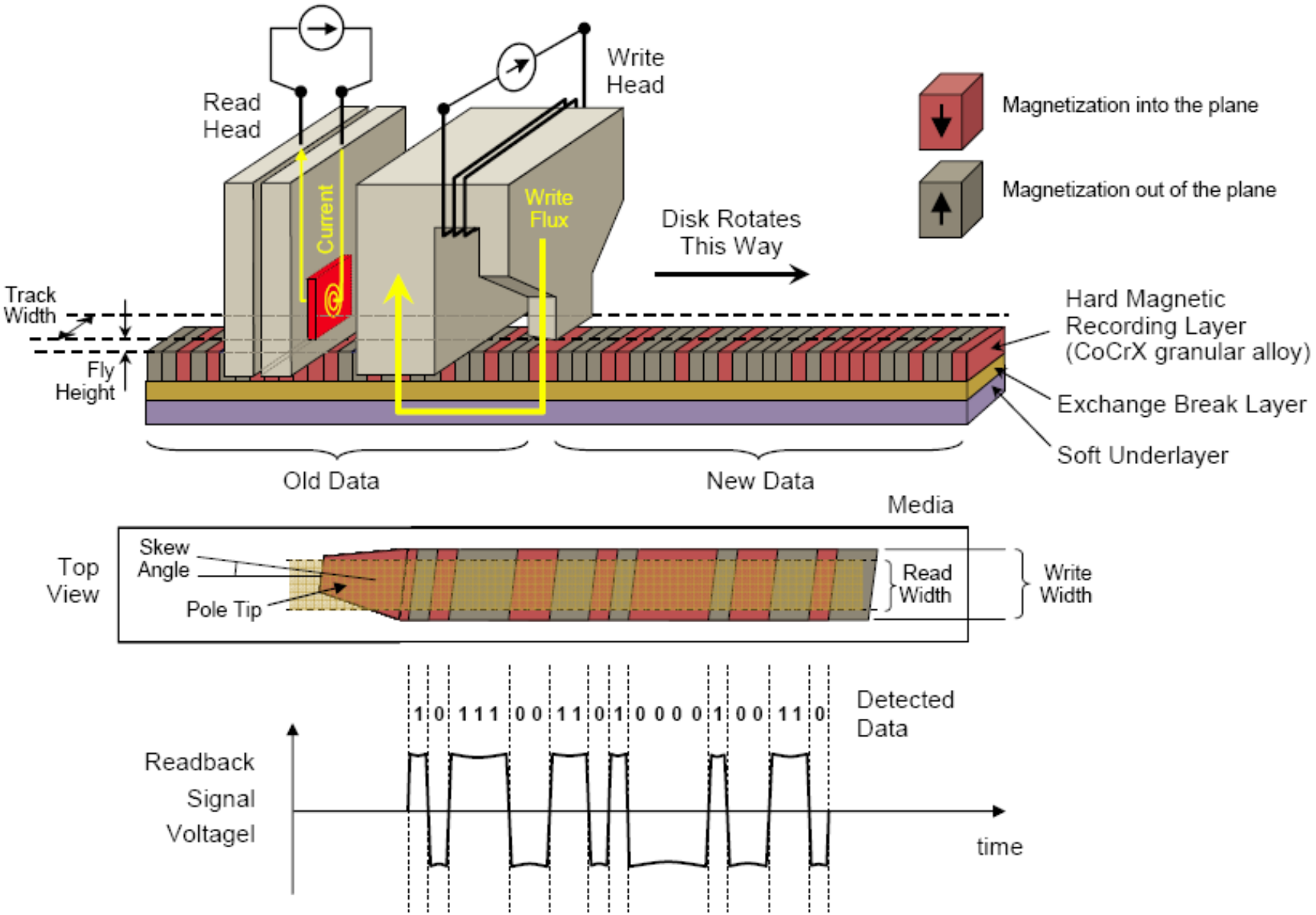


32Tb on 10 platters ->
About 1.0-1.5 Tb/in^2

20-25 nm pitch

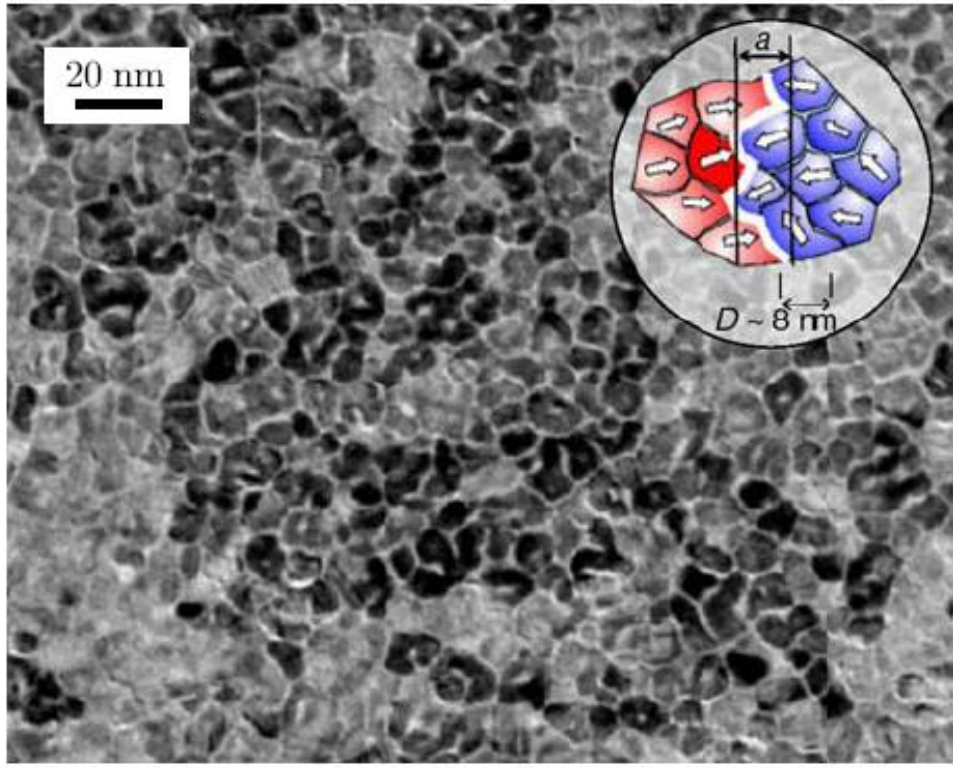
See also https://www.seagate.com/innovation/hamr/

The recording mechanism in a HDD: a condensate of concepts

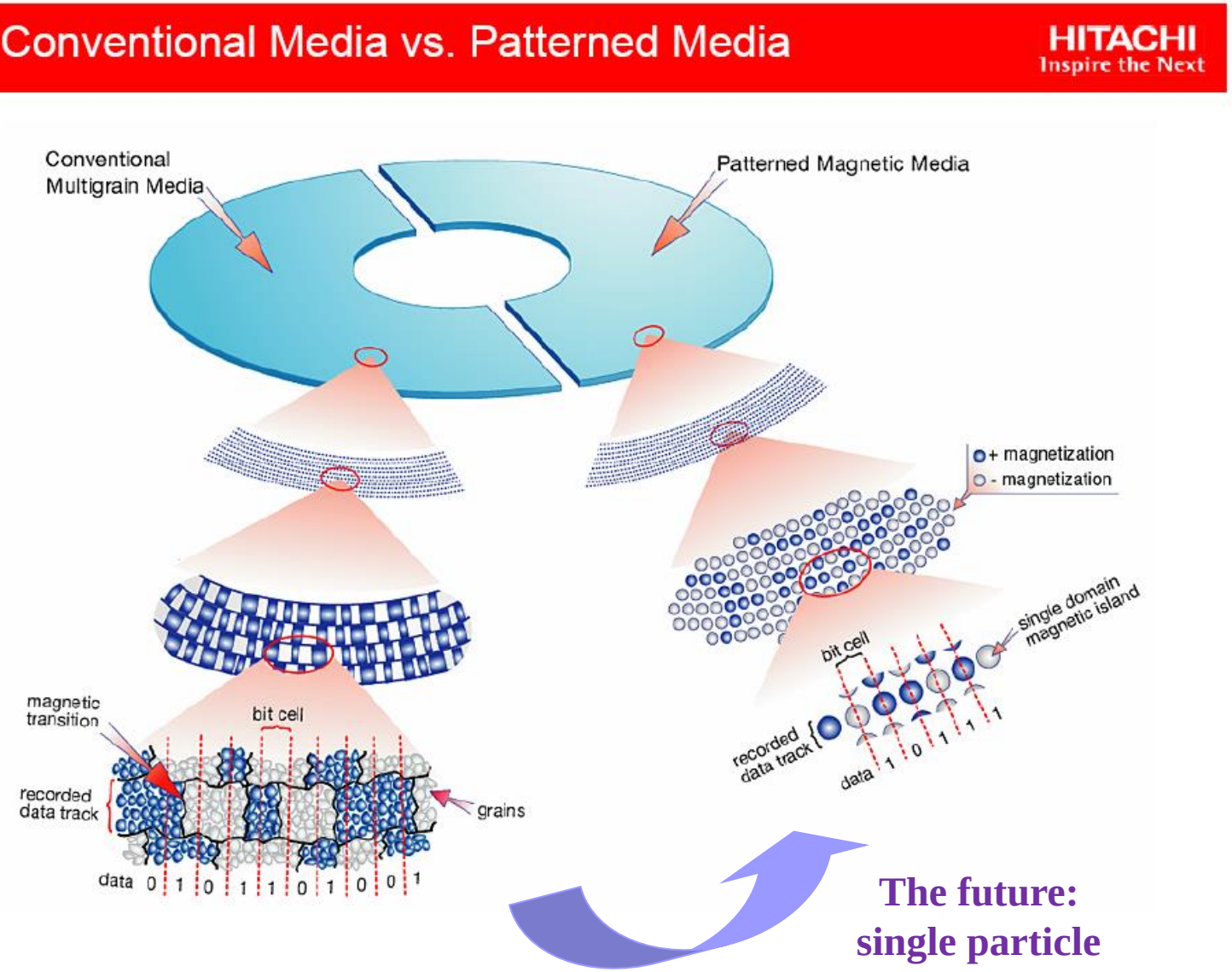


The storage media

TEM (Transmission electron microscopy) image of CoCrPt recording layer with in-plane magnetization.



The inset sketch the border between two bits.
Each bit consist of several tens of grains. The bit size and shape is defined during the head writing process

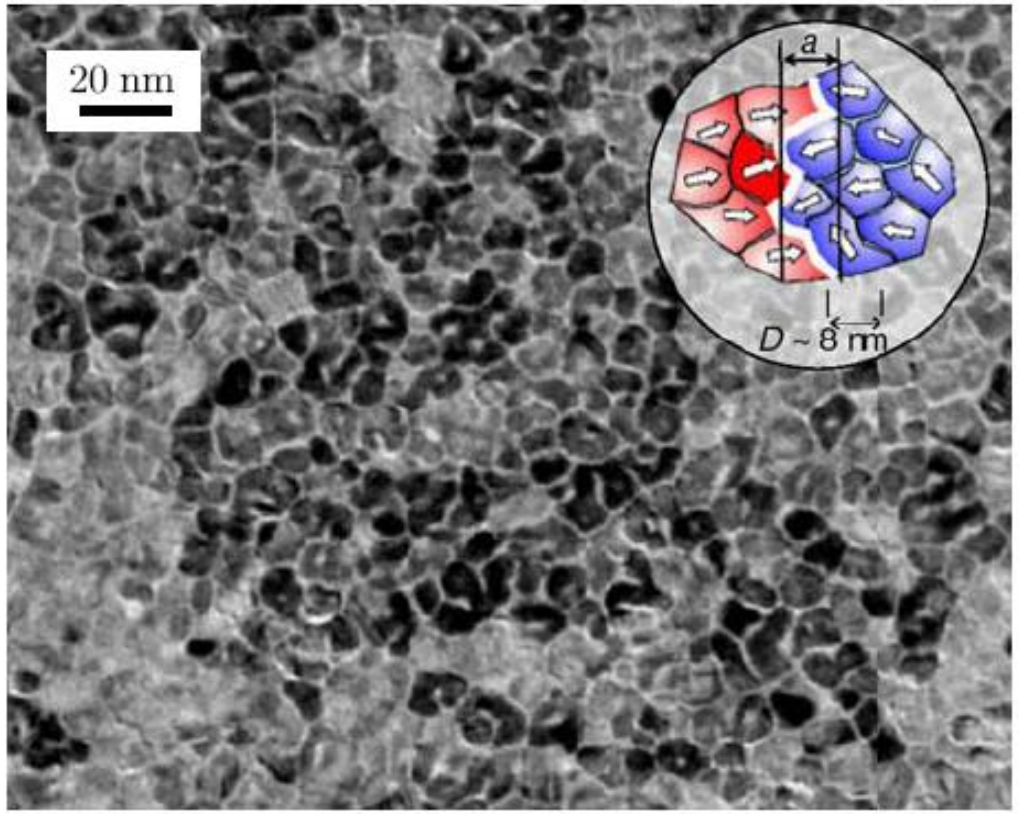


The future: single particle per bit

1 bit ≈ 50 grains

Moser, *et al.* J. Phys. D: Appl. Phys. **35**, R157 (2002). T. R. Albrecht, *et al.* IEEE Trans. Magn. **51**, 0800342 (2015).

Some basic questions …..
… simply looking at this picture

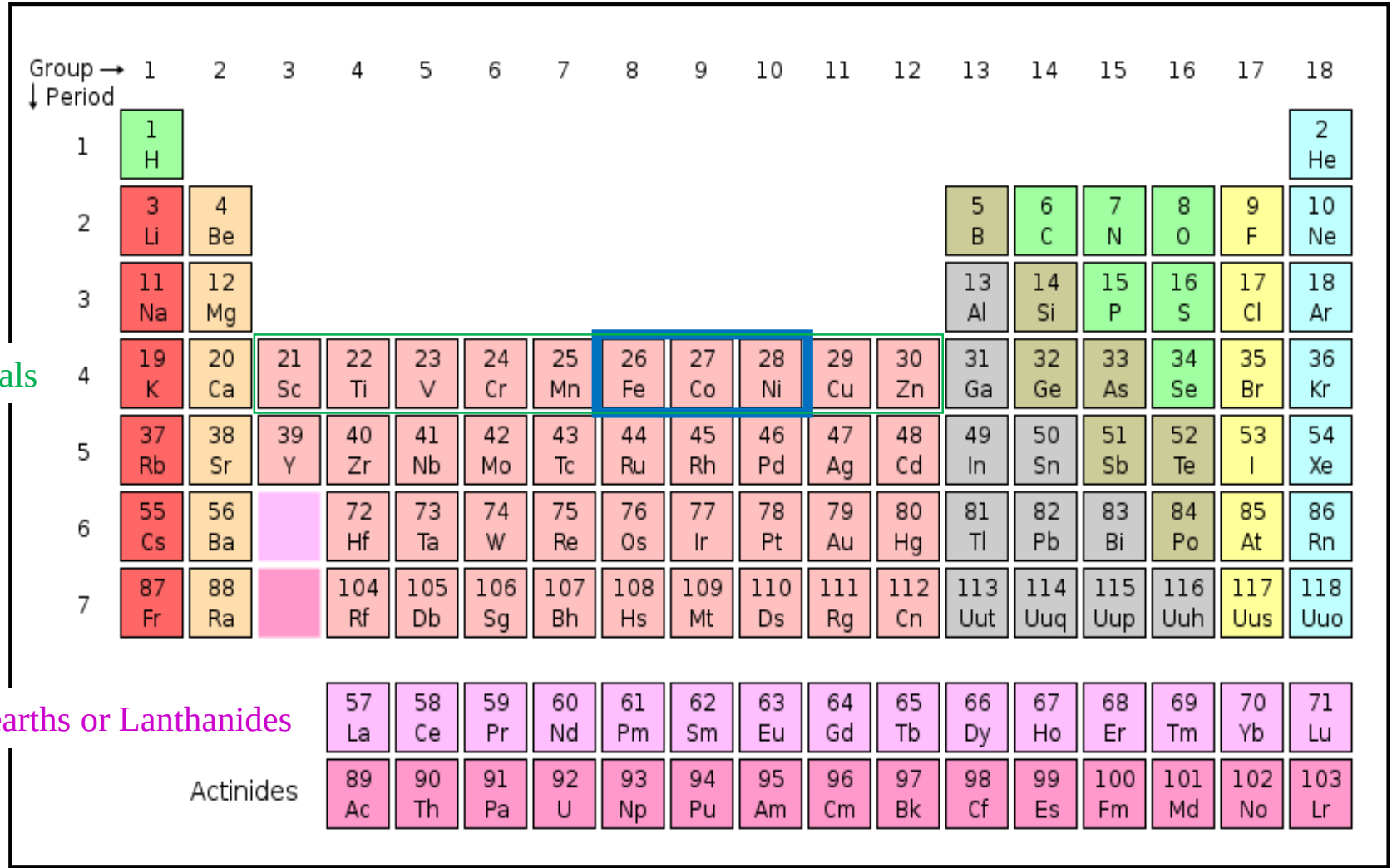


CoCrPt recording layer

1) Why every grain has a magnetic moment?
2) How the material is chosen?
3) Why every grain is magnetically decoupled from the neighbors
4) Why the grain magnetization is pointing in one specific direction?
5) Why the magnetization direction change from grain to grain?
6) Why the grain magnetization does not fluctuate with time?
7) …

Origin of the magnetic moment m_{at} (or magnetization)

- Observation: at atmospheric conditions only a few elements (Fe, Co, and Ni) have a magnetic moment
- Is this true also at the nanoscale?
- Does this means that only these 3 elements can be used in a recording media?
- SmCo is the strongest magnet at ambient conditions: why we need Sm if Sm is not a magnet?



3d transition metals

Ar $4s^2 3d^N$

Rare earths or Lanthanides

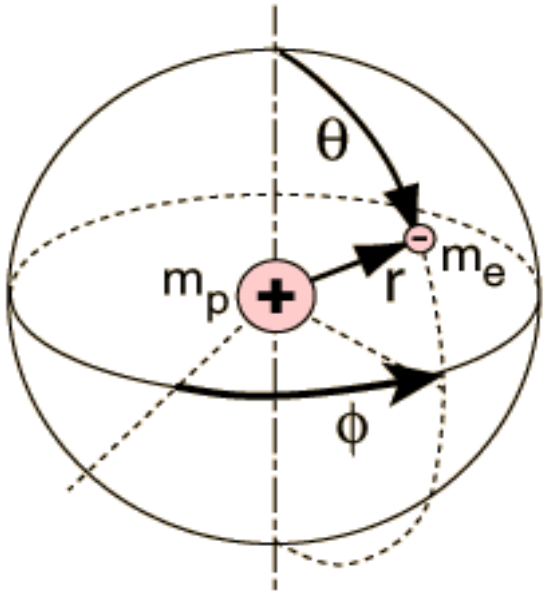
Xe $4f^N 6s^2$

Hydrogenic atom

$$H_{atom} = \sum_{i=1}^{Z} \frac{p_i^2}{2m} - \sum_{i=1}^{Z} \frac{Ze^2}{r_i^2} + \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|^2} + \sum_{i=1}^{Z} (\mathbf{l}_i \cdot \mathbf{s}_i)\xi(r_i) = H_C + V_{ee} + V_{so}$$

Example: the H atom -> Z=1

In terms of the spherical coordinates r, θ, and ϕ the wave function takes the form Ψ(r, θ, ϕ) = R(r) Θ(θ) Φ(ϕ) which gives three equations. The equation for each of the three variables gives rise to a quantum number and the quantized energy states of the atom can be specified in terms of these quantum numbers. A fourth quantum number arises from electron spin. Two electrons can not have an identical set of quantum numbers according to the Pauli exclusion principle.



R(r) -> principal quantum number n = 1, 2, 3,.. (K, L, M,..)
Θ(θ) -> orbital quantum number l = 0, 1, 2, …, n-1
Φ(ϕ) -> magnetic quantum number m = -l, -(l-1), …. l-1, l
σ -> spin quantum number $m_S = \pm 1/2$

$$\Psi_{nlm} = R_{nl}(r) Y_l^m \sigma$$

Y_l^m are the spherical harmonics

Isolated atom in a magnetic field B

$$H_{atom} = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m} + V(r_i)\right) + \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|^2} + \sum_{i=1}^{Z} (\mathbf{l}_i \cdot \mathbf{s}_i)\xi(r_i) + \mu_B(L + 2S) \cdot B = H_C + V_{ee} + V_{so} + V_{Zeeman}$$

$$\xi(r) = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r}$$

Spin-orbit interaction:
Interaction of the electron spin with the magnetic field generated by its own orbital motion

$$L = \sum_{i=1}^{Z} \mathbf{l}_i$$

$$S = \sum_{i=1}^{Z} s_i$$

	3d transition metals	4f rare earths
V_{ee}	1 eV	1eV
V_{so}	50-100 meV	300-500 meV
V_{Zeeman} (B=1T)	0.1 -0.2 meV	0.1 -0.6 meV

Magnetism of an isolated atom

$$H_{atom} = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m} + V(r_i)\right) + \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|^2} + \sum_{i=1}^{Z} (\mathbf{l}_i \cdot \mathbf{s}_i)\xi(r_i) + \mu_B(L + 2S) \cdot B = H_C + V_{ee} + V_{so} + V_{Zeeman}$$

The spin orbit interaction couples **L** and **S** (quantum operators) to form the total angular momentum **J**.

Since L and S are not independent, we can not use $|LSL_zS_z\rangle$ as basis but we need to use $|LSJJ_z\rangle$

The expectation value of the (observable) **magnetic moment $\mathbf{m_{at}}$** projected onto the field direction is given by:

$$\mathbf{m_{at}} = (1/B) \langle LSJJ_z| (\mathbf{m_L} + \mathbf{m_S}) \cdot \mathbf{B} |LSJJ_z\rangle = \mu_B \langle LSJJ_z| \mathbf{L_z} + 2\mathbf{S_z} |LSJJ_z\rangle = -\mu_B g \mathbf{J_z}$$

Orbital magnetic moment: $m_L = -L_z\ \mu_B$
Spin Magnetic moment: $m_S = -2\ S_z\ \mu_B$
Atomic magnetic moment: $m_{at} = -\ \mu_B g J_z$

$\mu_B = \frac{e\hbar}{2m_e}$-> Bohr magneton; μ_B=0.058 meV/T;

g = 3/2 + [S(S+1) –L(L+1)]/(2J(J+1)) is the Landé g-factor

N.B.: by convention **m** and **B** are parallel

Isolated atom (at finite T)

Atom described by quantum numbers |LSJJz>, with J_z assuming 2J+1 values between –J and +J

At B = 0 T these 2J+1 values are degenerate in energy
At B ≠ 0 T the 2J+1 states are split -> Zeeman split

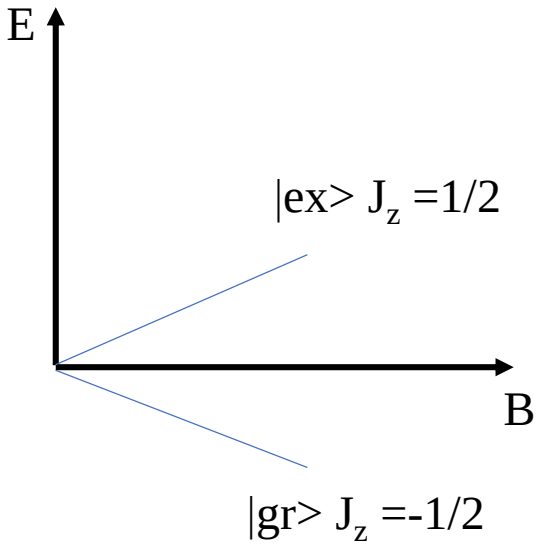
State occupation depends on B and T (Boltzmann statistic)

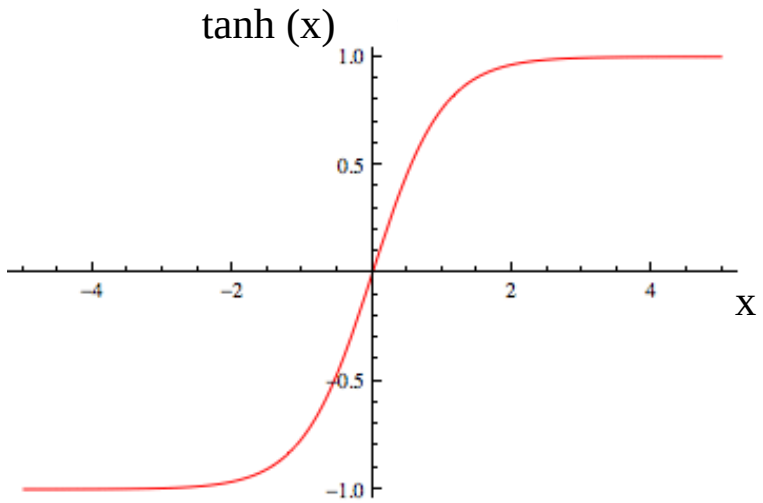
Example: atom with J = 1/2

two energy levels: $\pm J_z\, g\, \mu_B B$
occupation probability: $\exp(\pm J_z\, g\, \mu_B B/k_B T)$

$$m(B,T) = m^{\uparrow} - m_{\downarrow} = J_z g\mu_B\left(\frac{e^x}{e^x + e^{-x}} - \frac{e^{-x}}{e^x + e^{-x}}\right) = J_z g\mu_B \tanh(x) \qquad x = \frac{J_z g\mu_B B}{k_B T}$$

$$m(B,T) = \mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \qquad with\ J_z = \frac{1}{2}\ and\ g = 2$$



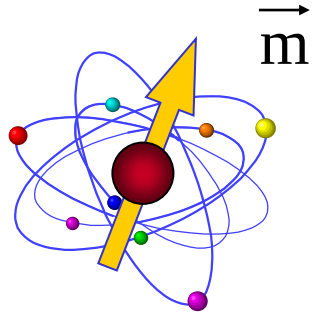


	tanh(x)	Occupation gr	Occupation ex
T = 0 or B = ∞	1	100%	0%
B = 0 or T = ∞	0	50%	50%
B = 0.55 $k_B T/\mu_B$	0.5	75%	25%

Hund's rules

Magnetism is given by:

1) The spin moments of the electrons
2) The orbital moments of the electrons
3) The filling of the atomic orbital



Hund's rules:

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

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

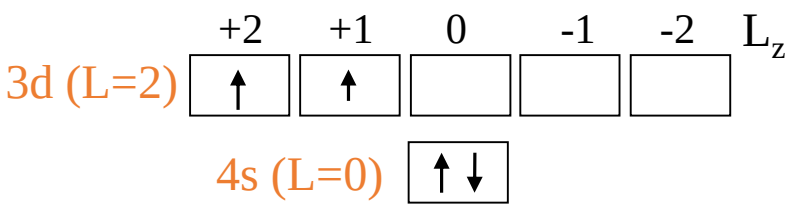
⟺ Coulomb repulsion V_{ee}

3) L and S couple parallel ($J=|L+S|$) if band more than half filled
   L and S couple antiparallel ($J=|L-S|$) if band less than half filled

⟺ Spin-orbit interaction

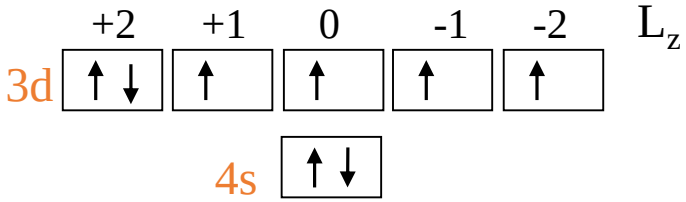
$Y_L^{L_z}$

Ground state of Ti (Ar $4s^2\ 3d^2$)



$L = 3, S = 1, J = 2$
$m_L = L\ \mu_B = 3\ \mu_B$,
$m_S = 2\ S\ \mu_B = 2\ \mu_B$,
$m_{at} = g\ J\ \mu_B = 1\ \mu_B$

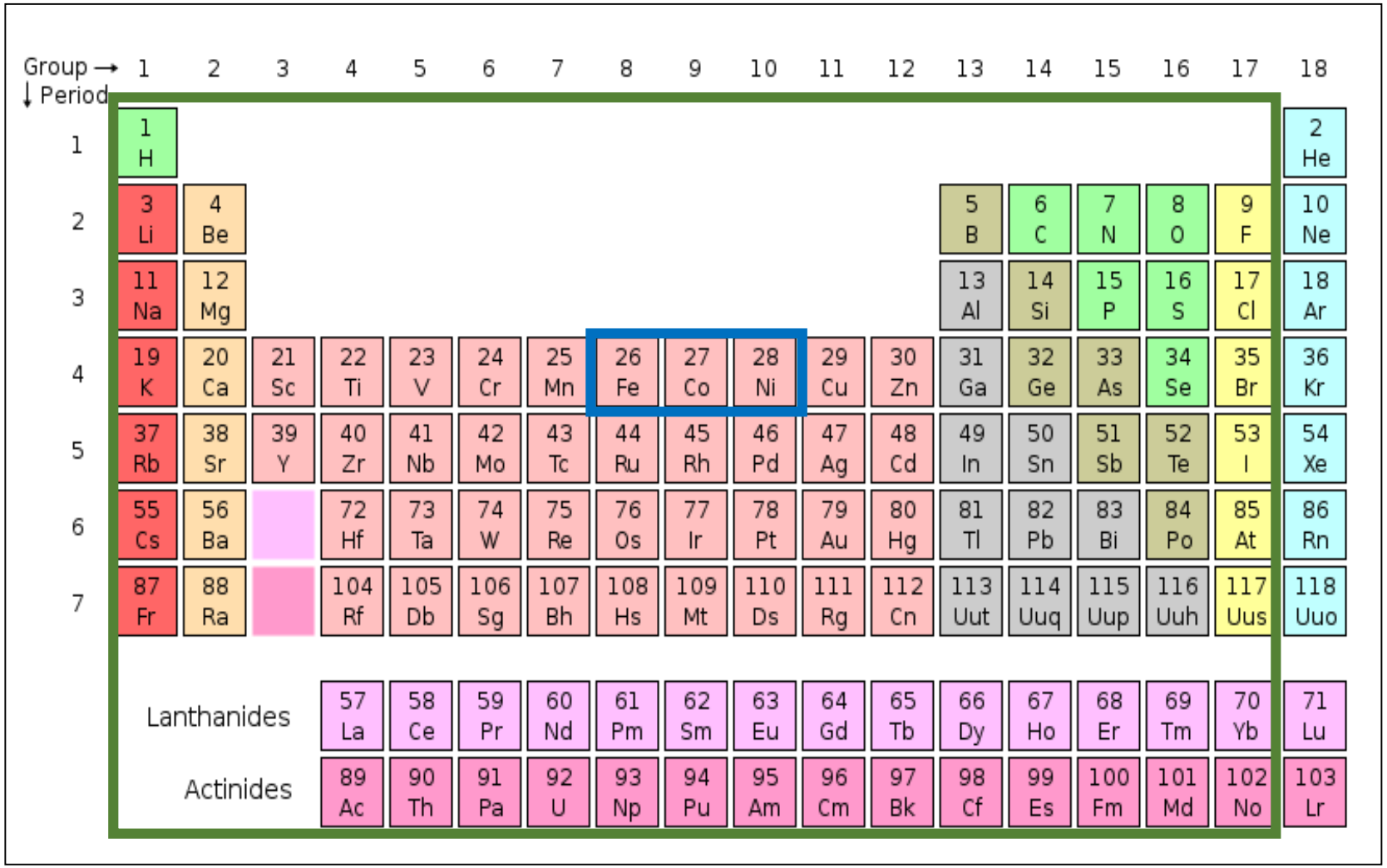
Ground state of Fe (Ar $4s^2\ 3d^6$)



$L = 2, S = 2, J = 4$
$m_L = L\ \mu_B = 2\ \mu_B$,
$m_S = 2\ S\ \mu_B = 4\ \mu_B$,
$m_{at} = g\ J\ \mu_B = 6\ \mu_B$

Atomic scale *vs* bulk

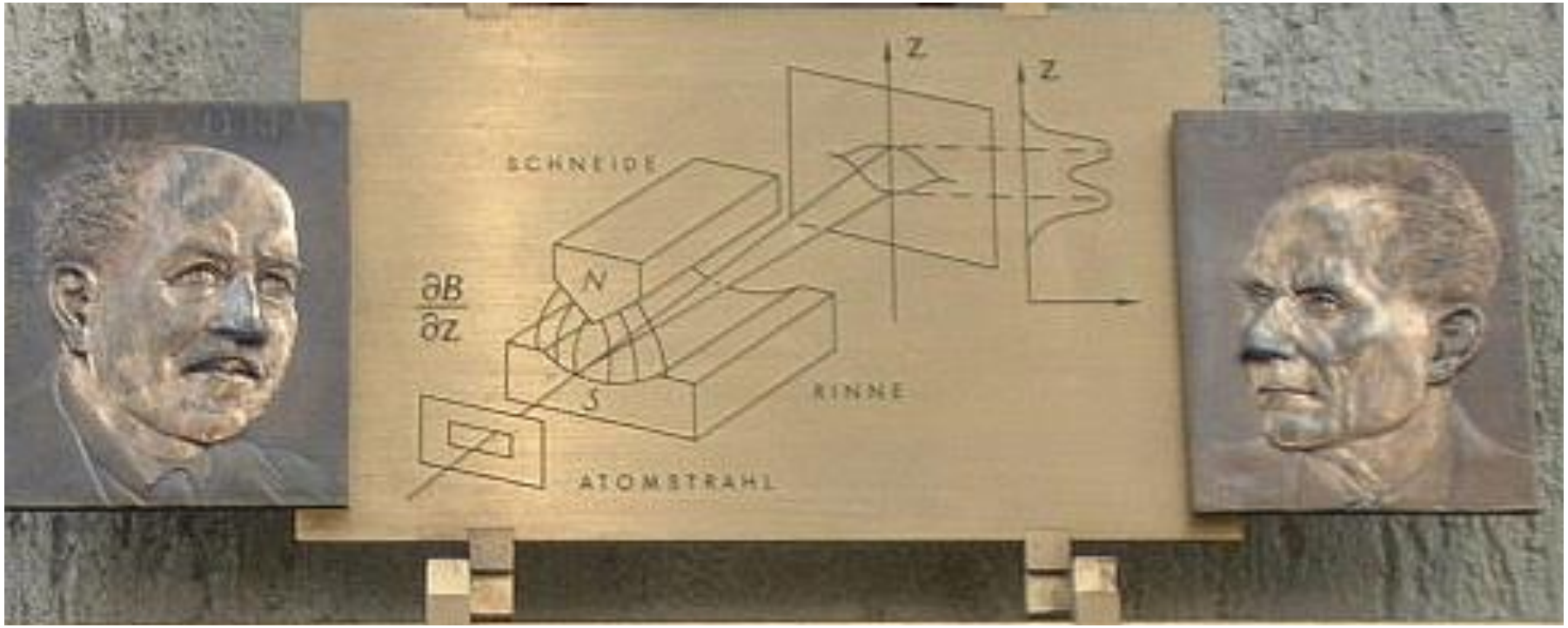
- Bulk (at room T): only a few elements (Fe, Co, and Ni) have a magnetic moment
- Atomic scale: all atoms except noble gas have a magnetic moment (due to unfilled electronic shells)



Stern-Gerlach experiment

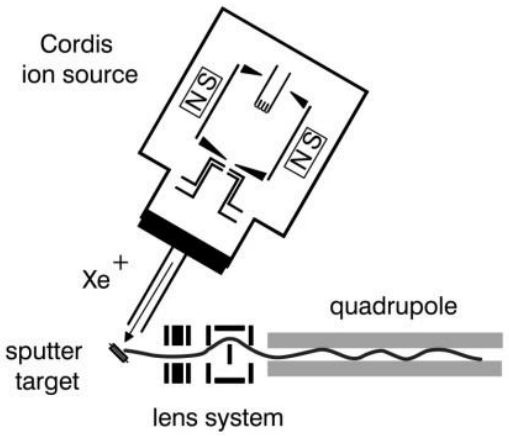
Beam of Ag atoms through a magnetic field

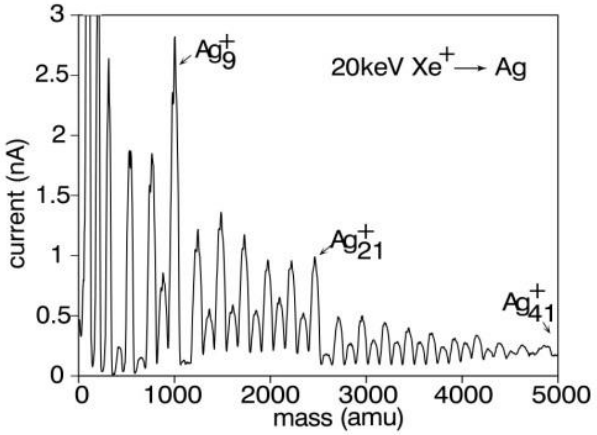
Ag: Kr $4d^{10}\ 5s^1$ → L=0; S=1/2, $S_z = J_z = \pm 1/2$

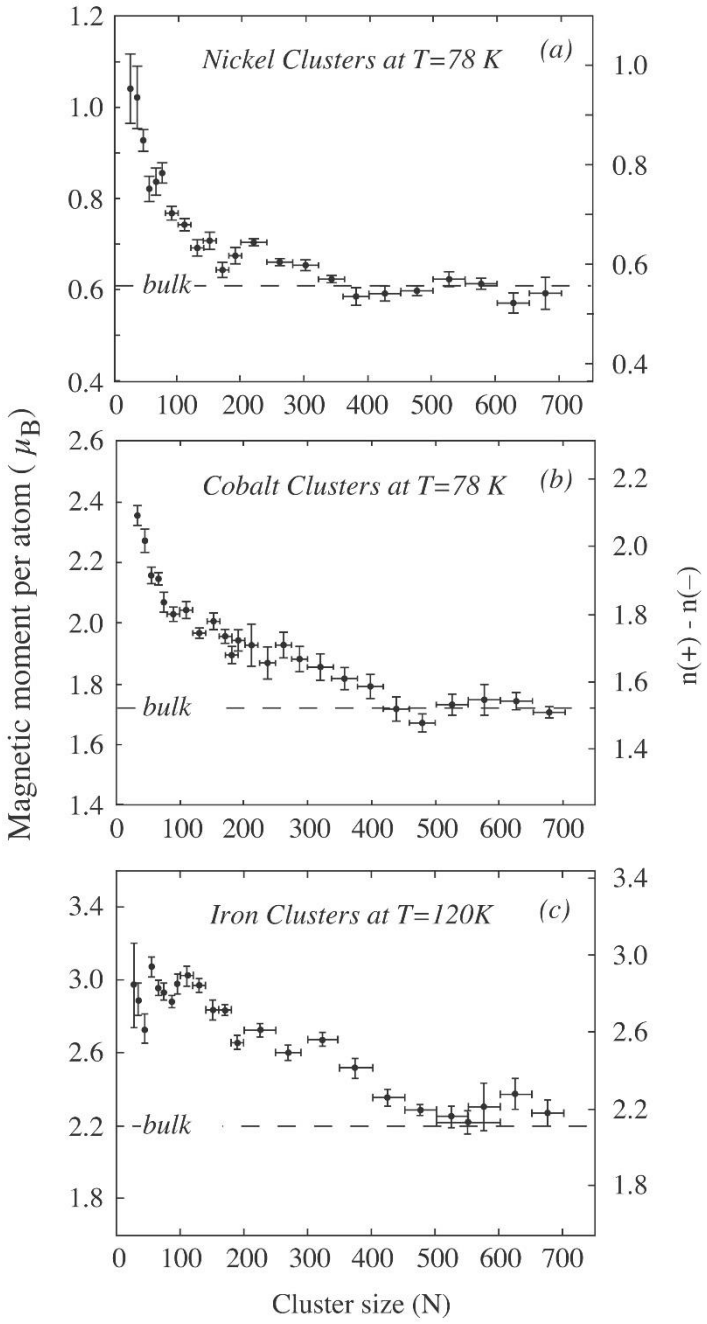


Ag atoms deviated depending on their spin moment

Stern-Gerlach experiment with clusters





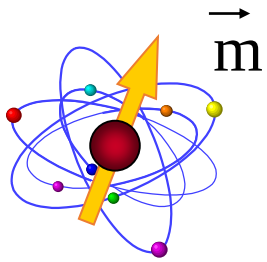


Below about 200 atoms per cluster the magnetic moment strongly increases with respect to bulk values

I.M.L. Billas, A. Châtelain, W.A. de Heer, Science 265, 1682 (1994).

Atom *vs* bulk

atom



CF = 0
(the 3d orbitals
are degenerate)

d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{xy}, $d_{3z^2-r^2}$

N.B.: $d_{3z^2-r^2} \Leftrightarrow d_{z^2}$

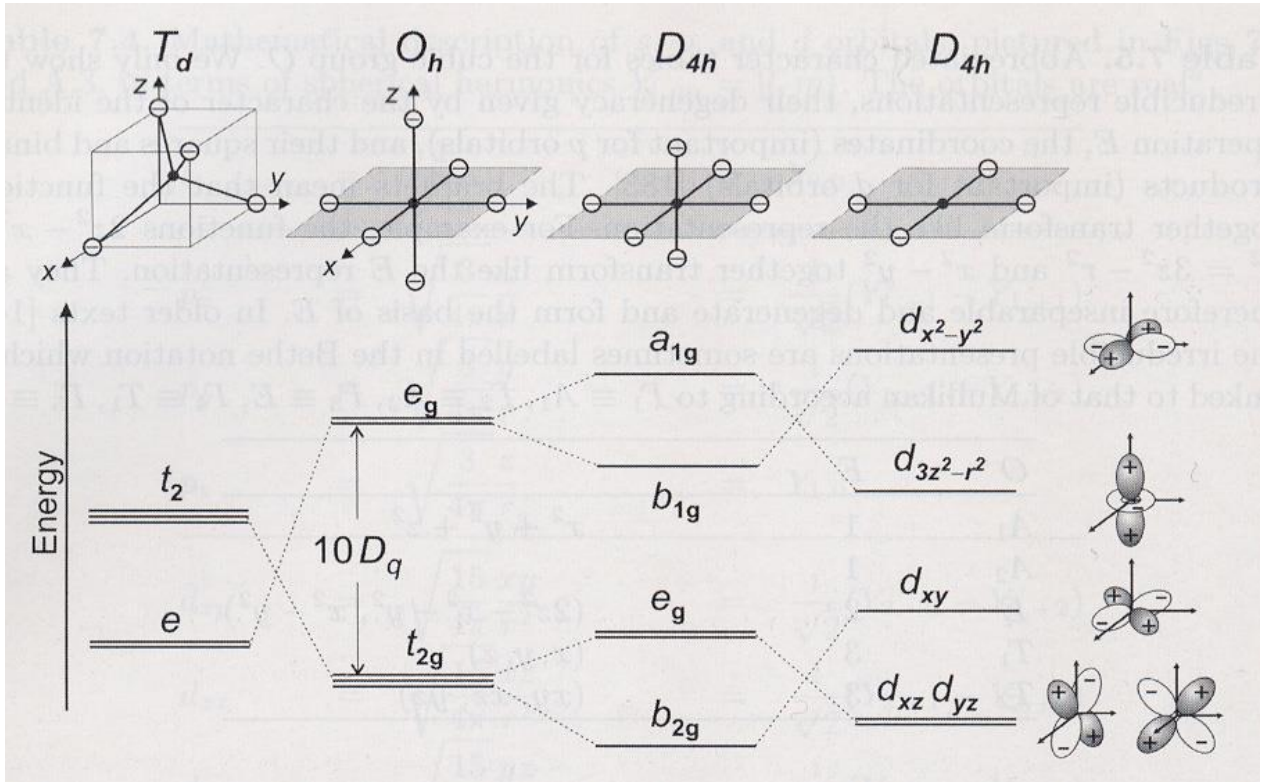
bulk

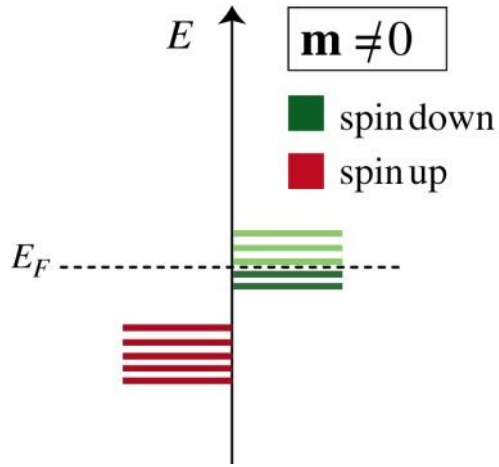
1) Crystal field (CF) : bond formation
Broken orbital degeneracy

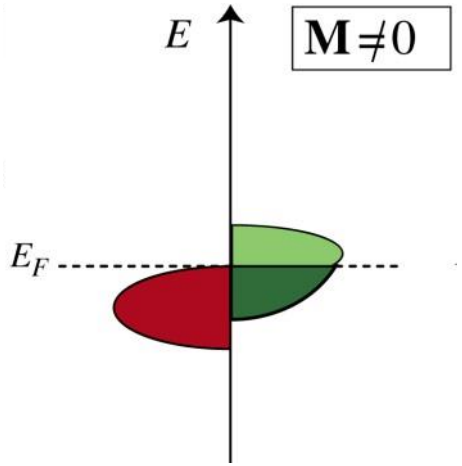
$\Leftrightarrow$

2) Electronic band formation

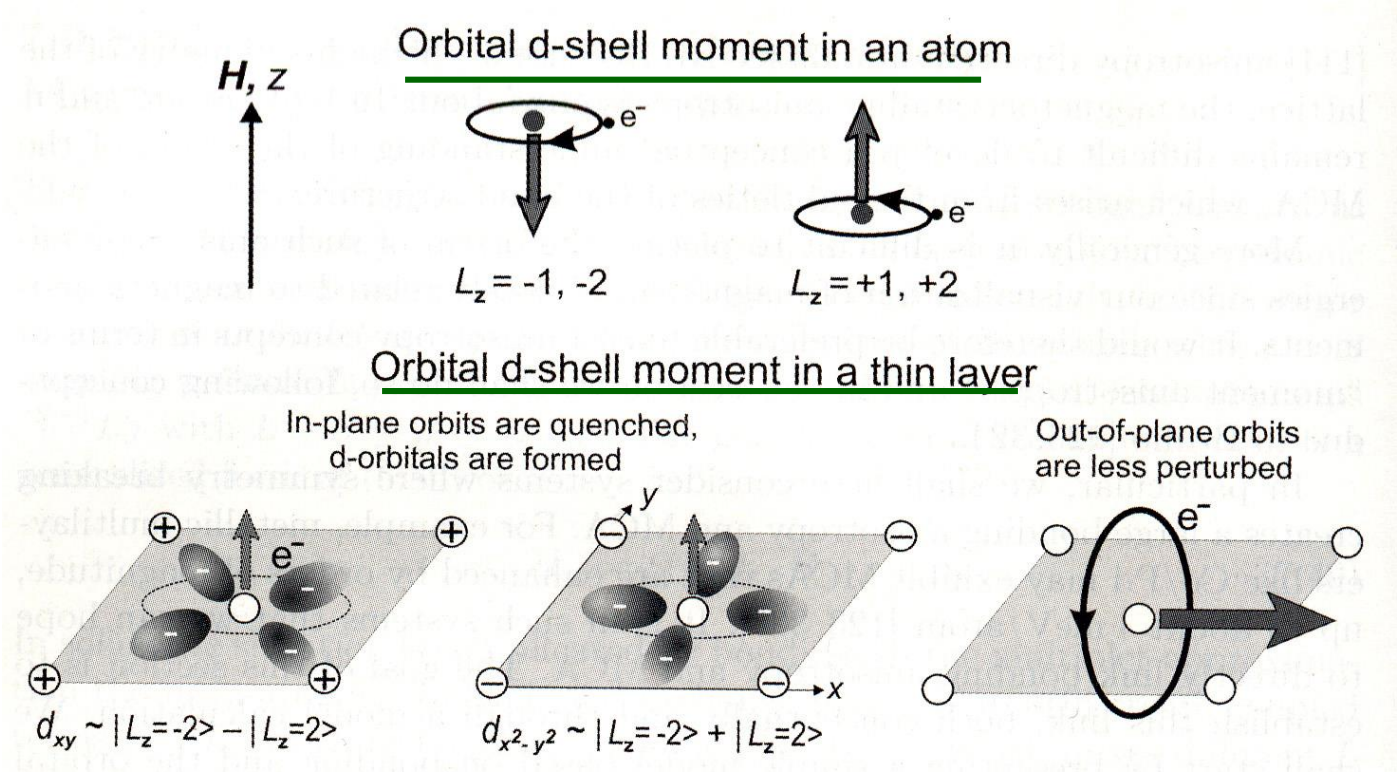
$d_{xz} = a\, Y_2^1 + b\, Y_2^{-1}$ $\quad$ $d_{xy} = a\, Y_2^{-2} - b\, Y_2^2$







Quenching of the orbital moment due to bond formation



the orbital moment arises from the electron precession (Y_l^m)

-> bond formation stops the precession

A strong directional bonding generates a reduction in the component of L perpendicular to the bond direction

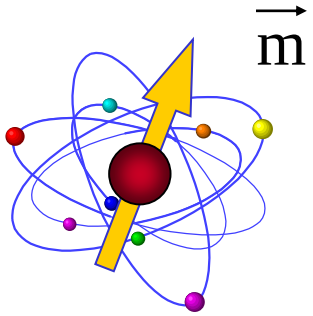
- atom bonded to four atoms in a plane.

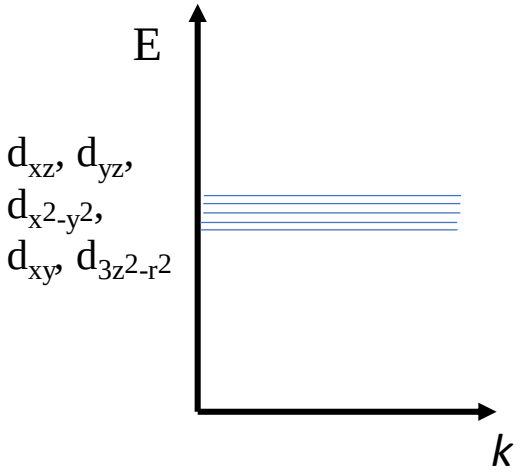
-a) The *d* electron will form a standing wave with a spatial shape depending on the distribution of the electronic charge on the neighbouring atoms (i.e. orbital motion frozen by the formation of bonds with the neighbouring atoms) -> out-of-plane orbital moment is quenched

b) The orbital motion perpendicular to the bonding plane is less perturbed by the bonds -> in-plane orbital moment will stay unquenched ->

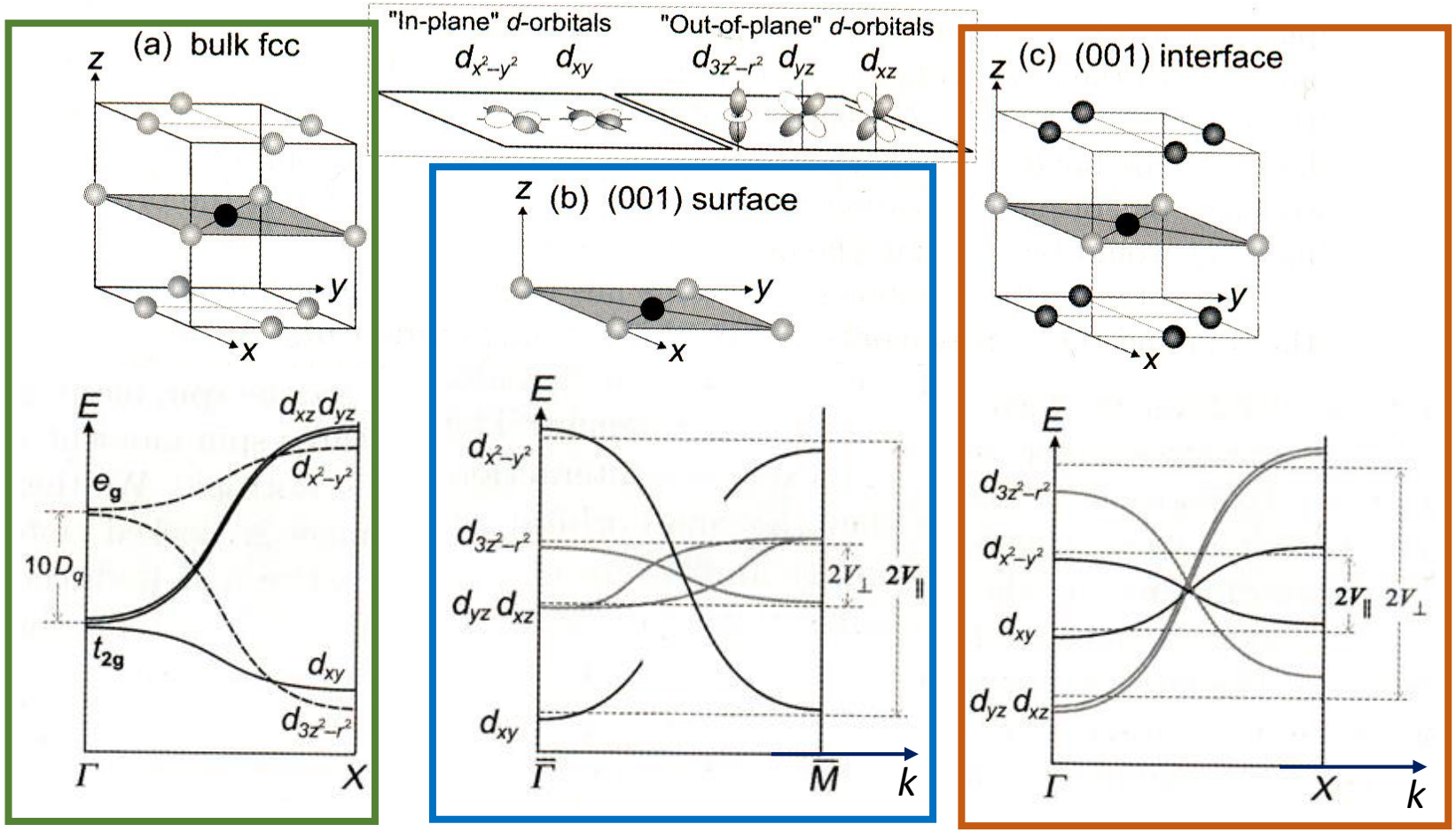
symmetry breaking implies anisotropic orbital moments

Band width *vs.* bond formation





atom:
quantized, degenerate orbitals



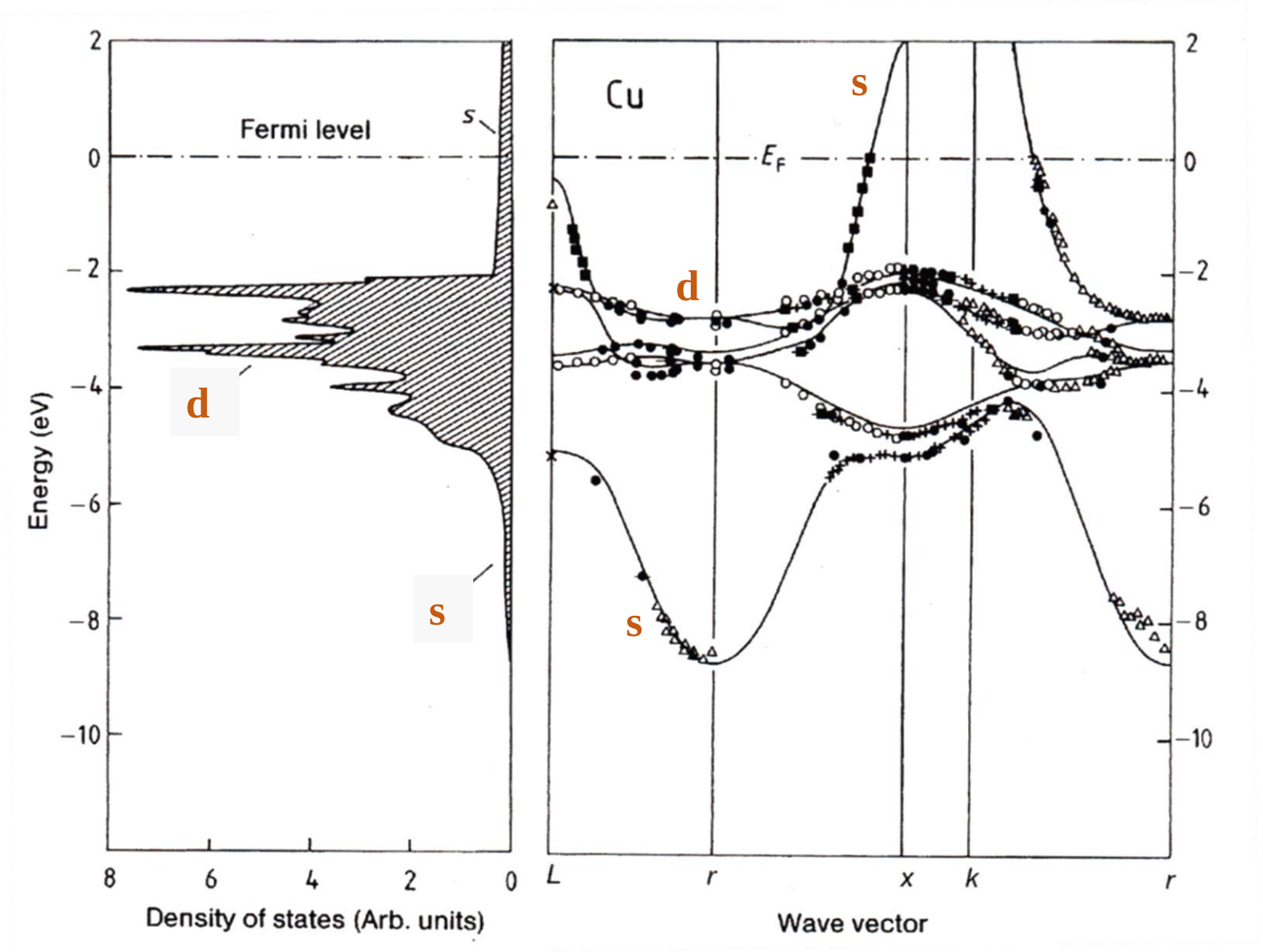
Bulk: bands form due to overlapping of the wave functions of closed atoms. Band width is correlated to the crystal field strength

-b) free-standing monolayer: mainly the in-plane d-orbitals feel the bonding and then show big splitting and dispersion in the (E,k) space while the out-of-plane d-orbitals stay mostly unperturbed -> L_z quenched

-c) in a multilayer with stronger out-of-plane than in-plane bonds, the situation is reversed -> $L_{x,y}$ quenched

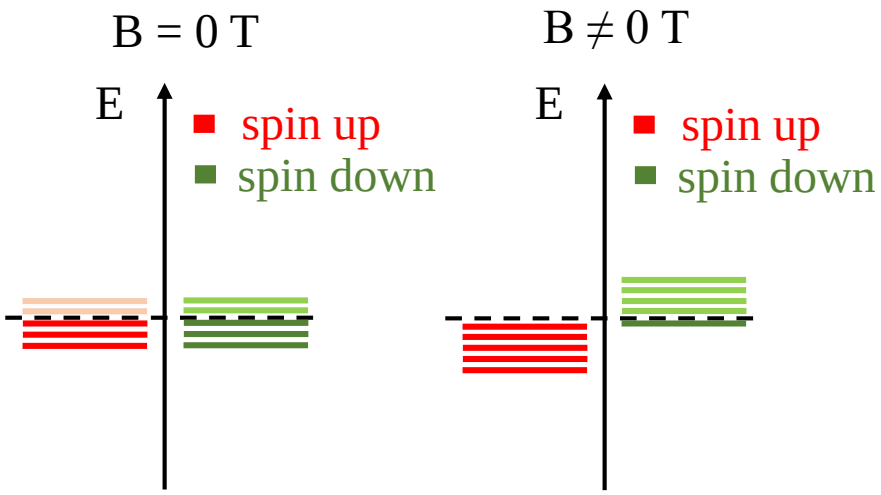
-a) in a cubic structure in-plane and out-of-plane bonds have similar strength and then the dispersion of the d-orbitals is similar -> $L_{x,y,z}$ quenched

How to read density of states and band dispersion: example of Cu crystal



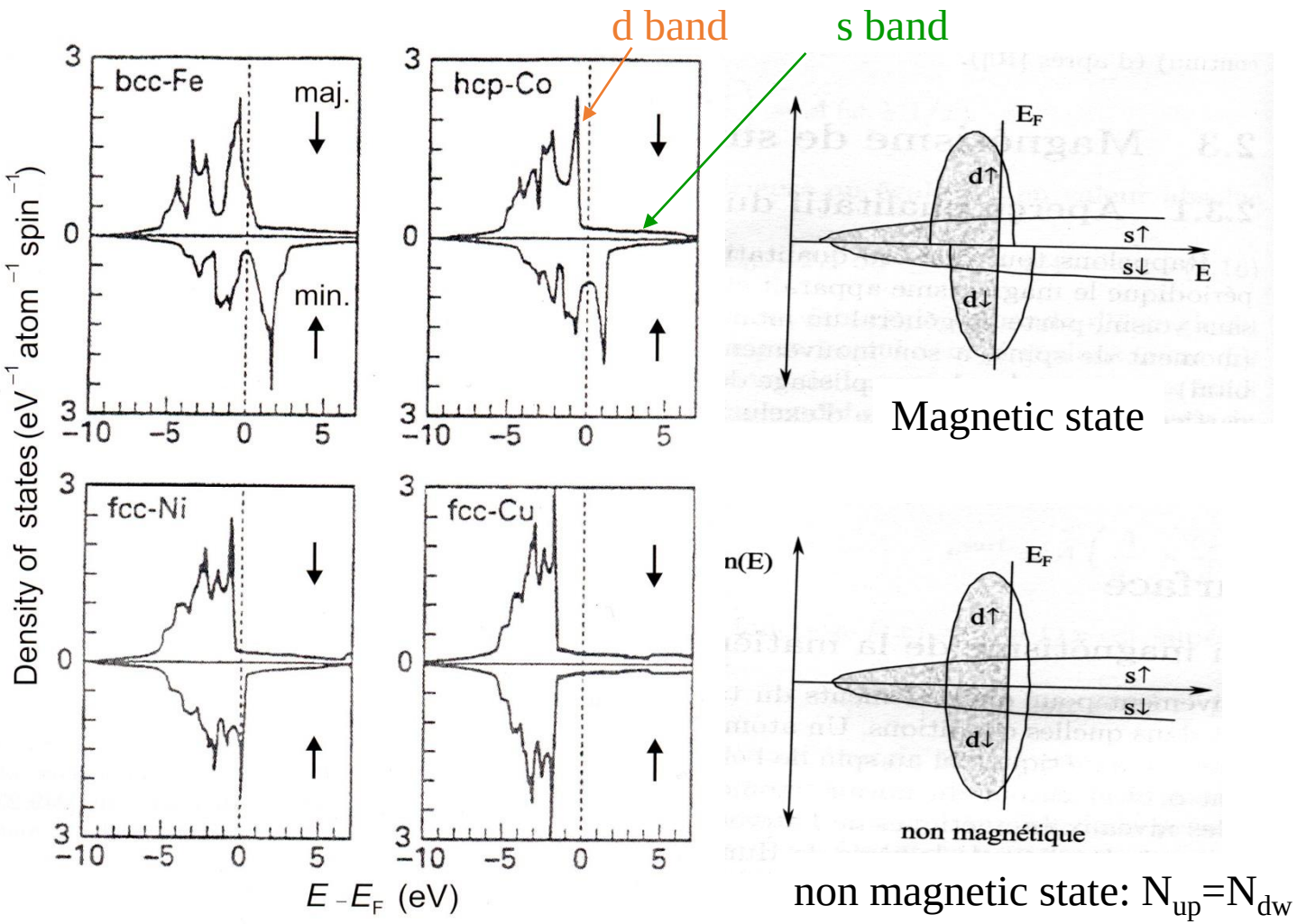
Spin: atom *vs* bulk

Free standing atom



The orbitals are degenerate. Only when the quantization axis is defined (for example by applying an external field) we measure the spin defined by the Hund's rules

Bulk

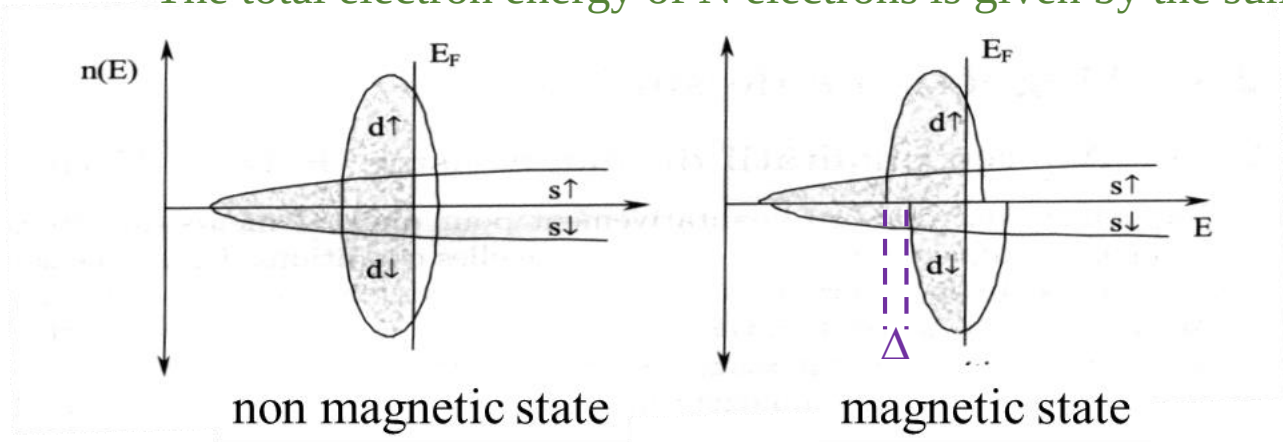


non magnetic state: $N_{up}=N_{dw}$

Due to electron-electron interaction, spontaneous magnetization can appear even in absence of an external magnetic field (band splitting).
The quantization axis is provided by the crystal structure

Stoner model for spontaneous magnetization

The total electron energy of N electrons is given by the sum of the energies of all occupied states



Coulomb interaction:
$V_{ee}\ N_{up}\ N_{down}$

$N_{up} = N/2$
$N_{down} = N/2$

$N_{up} = N/2 + n(E_F)\ \Delta/2$
$N_{down} = N/2 - n(E_F)\ \Delta/2$

Each band shifts by $\Delta/2$ in opposite directions;
$n(E_F)$ is the electron density at E_F

Kinetic electron energy variation = $n(E_F)\ \Delta/2 * \Delta/2 - (-n(E_F)\ \Delta/2 * \Delta/2) = 1/2\ n(E_F)\ \Delta^2$

Coulomb (e-e) interaction variation = $-1/4\ V_{ee}\ n^2(E_F)\ \Delta^2$

Total electron energy change $dE = 1/2\ n(E_F)\ \Delta^2 - 1/4\ V_{ee}\ n^2(E_F)\ \Delta^2 = 1/2\ n(E_F)\ \Delta^2\ (1 - 1/2\ V_{ee}\ n(E_F))$

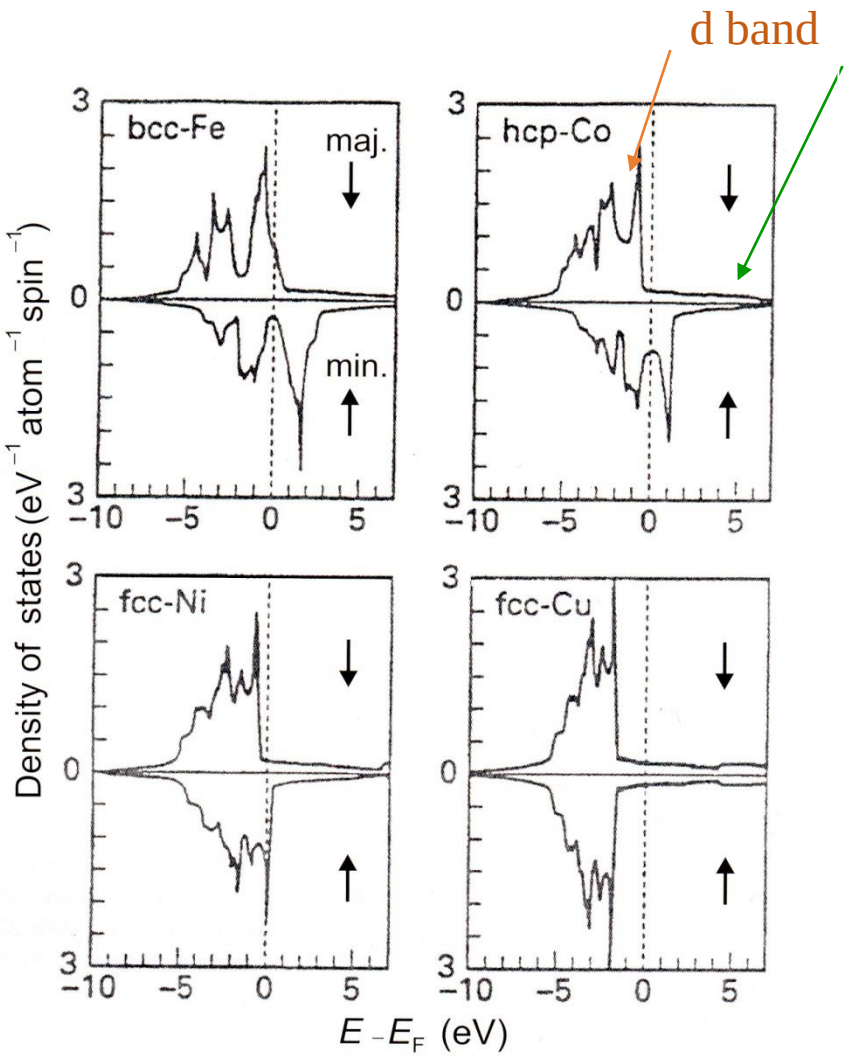
If $dE < 0$ spontaneous magnetism appears -> $1 - 1/2\ V_{ee}\ n(E_F) < 0$ (Stoner criterion)

It depends on V_{ee} and $n(E_F)$ (both are material dependent)

N.B.: The electron-nucleus interaction (distance) is not affected by the band splitting

St&Sie-2006; S. Blugel Phys. Rev. Lett. **68**, 851 (1992)

Spin: transition metals



- s, p bands are extended (band width about 10 eV) -> contribute by about 5% to the spin moment

- d bands are narrow (band width about 3 eV) -> their splitting strongly affects the magnetism

Redistribution of electrons in the different bands: spin is smaller than in the isolated freestanding case

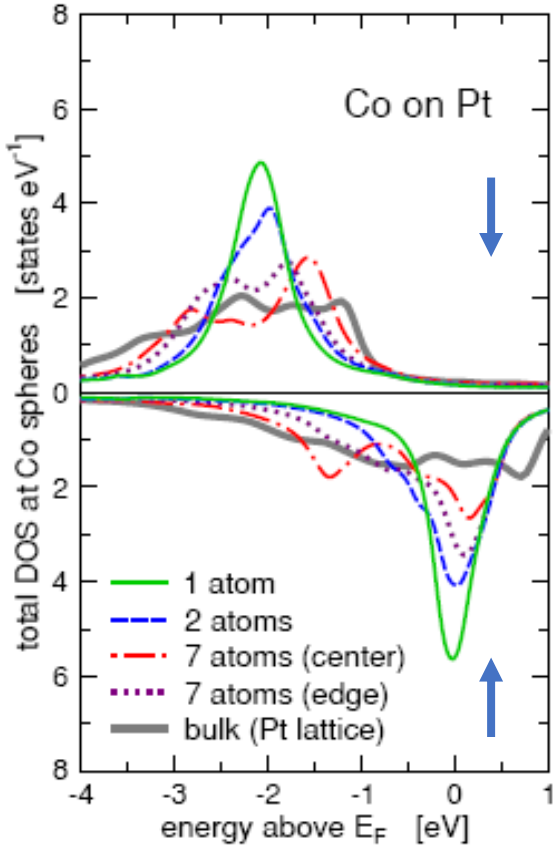
	$n_{3d}+n_{4s}$	$n_{3d}(\downarrow)$	$n_{3d}(\uparrow)$	$n_{4s}(\downarrow)$	$n_{4s}(\uparrow)$	$h_{3d}(\downarrow)$	$h_{3d}(\uparrow)$	m (μ_B)
Cr	6	2.7	2.7	0.3	0.3	2.3	2.3	0
Mn	7	3.2	3.2	0.3	0.3	1.8	1.8	0
Fe	8	4.8	2.6	0.3	0.3	0.2	2.4	2.2
Co	9	5.0	3.3	0.35	0.35	0.0	1.7	1.7
Ni	10	5.0	4.4	0.3	0.3	0.0	0.6	0.6
Cu	11	5.0	5.0	0.3	0.3	0.0	0.0	0

Filling of the ↓ and ↑ bands for 3*d* elements (*n* – electrons, *h* – holes)

J. Stöhr and R. Nakajima, IBM J. Res. Develop. 42, 1998; O. Eriksson et al., Phys. Rev. B 42, 2707 (1990).

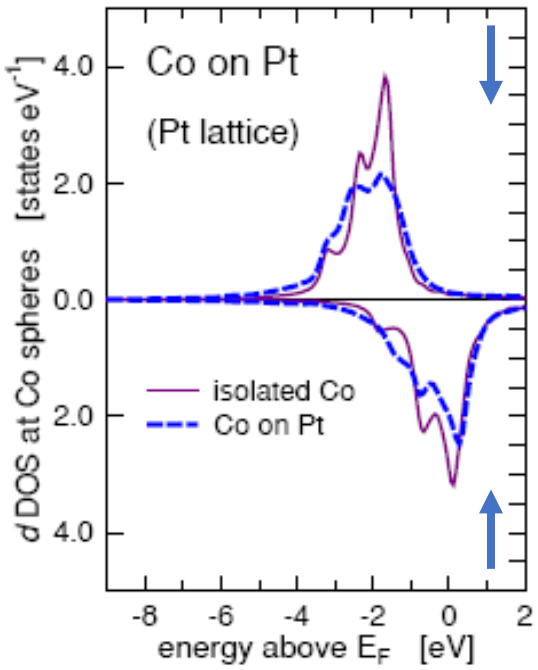
Hybridization: Co on Pt(111) as an example

Size dependence



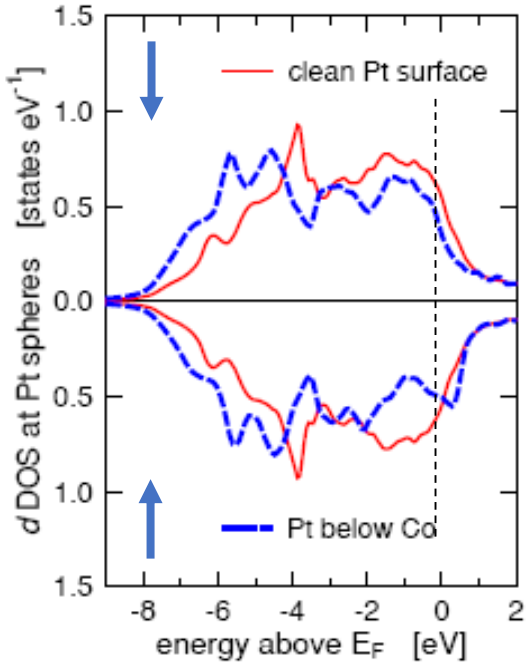
- Band splitting
- Increasing the cluster size (i.e. bond number), DOS becomes broader

Hybridization effect



The Co DOS becomes broader due to hybridization (bond formation) with the Pt substrate

Co monolayer

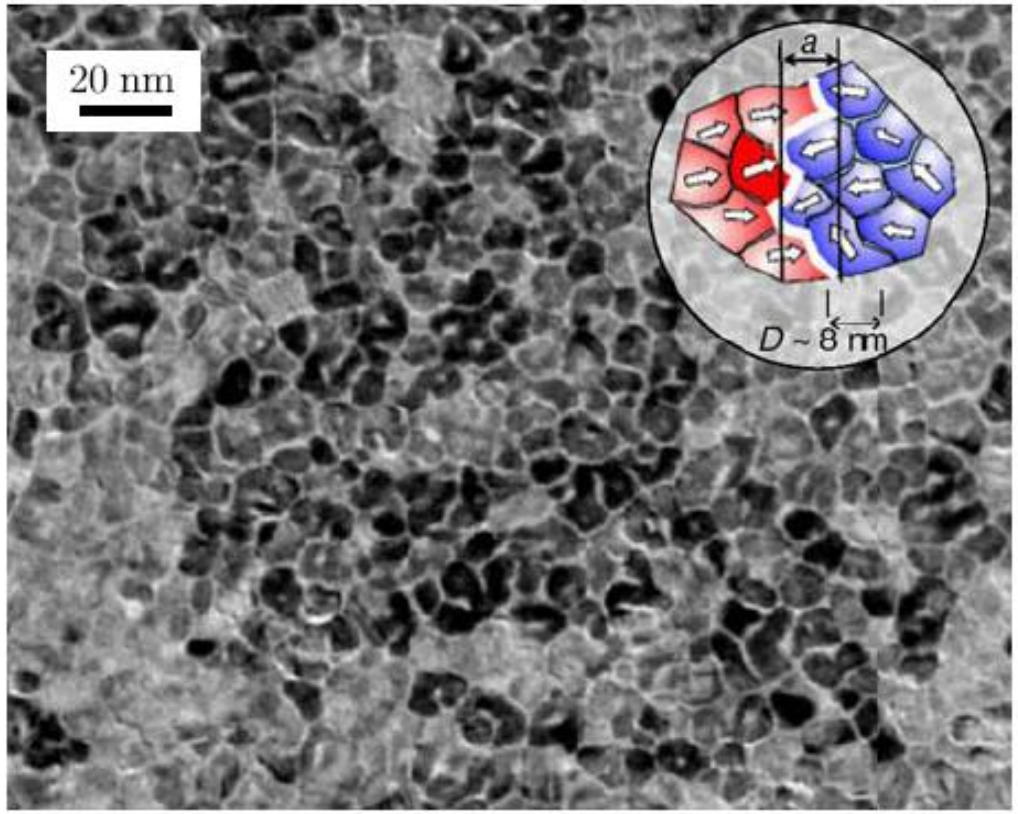


Asymmetry in the Pt DOS at E_F when covered by Co-> induced magnetic moment

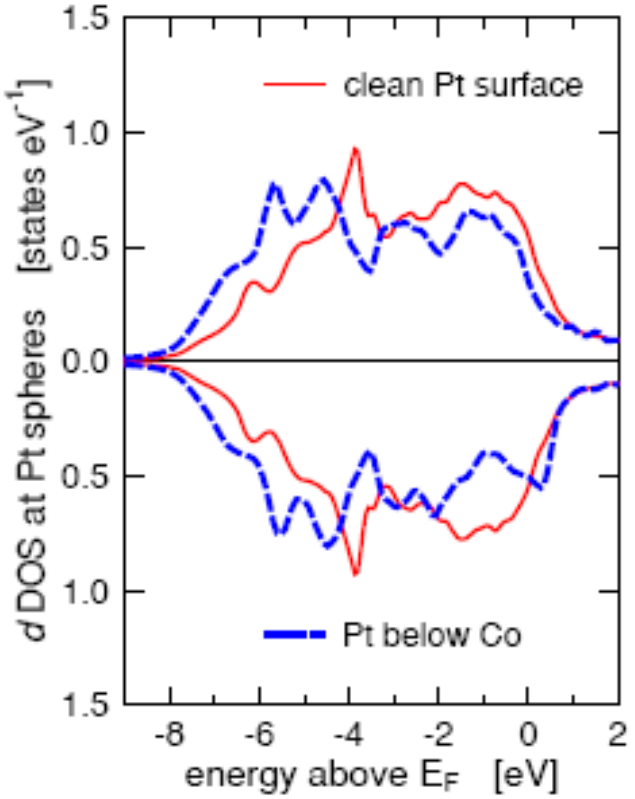
O. Sipr *et al.* J. Phys.: Condens. Matter. 19, 096203 (2007)

Magnetization in a multi-element cluster

CoCrPt recording layer



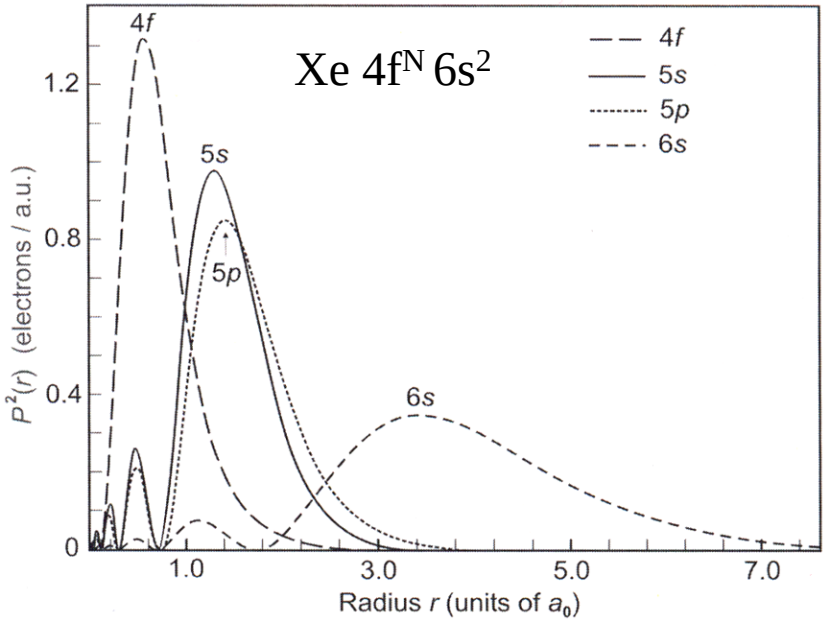
Pt covered by a Co monolayer

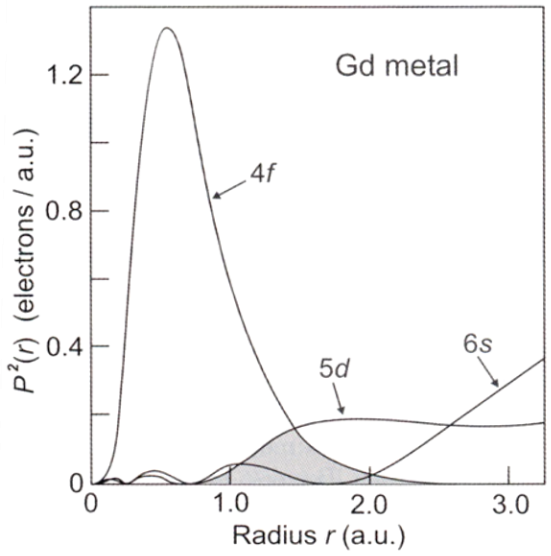


In a cluster, the Pt DOS is narrower and due to hybridization with Co can develop a non negligible magnetic moment

Rare earth magnetism

Electronic configuration in atomic case: Xe $4f^{N}\,6s^{2}$
(exception for Gd: Xe $4f^{7}\,5d^{1}\,6s^{2}$)





Radial distribution of the different orbitals

4f states are strongly localized around the nucleus ->
do not participate to bonds

- Magnetic moment defined by the 4f states (Hund's rules hold)

- L unquenched

The difference between atomic and bulk case is the electronic configuration.
In bulk, rare earths have the configuration Xe $4f^{N-1}\,5d^{1}\,6s^{2}$ with the 3 electrons in the outer shells participating to bond formation