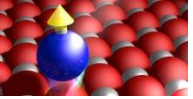
10

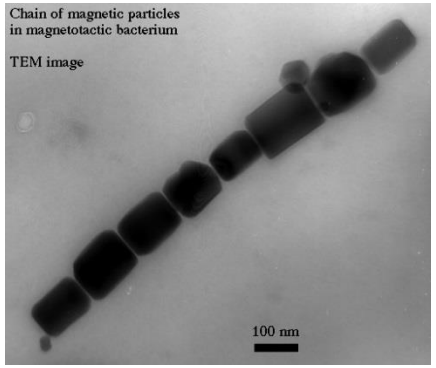
Magnetism at the nanoscale



Magnetism in Condensed Matter
S. Blundell
Oxford University Press

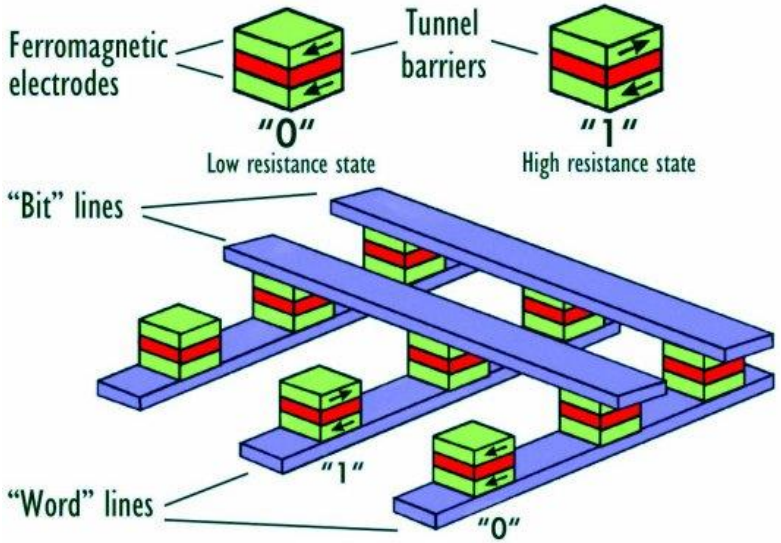
Magnetism
From Fundamentals to Nanoscale Dynamics
J. Stöhr and H.C. Siegmann
Springer

Nano-magnetism everywhere



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)].

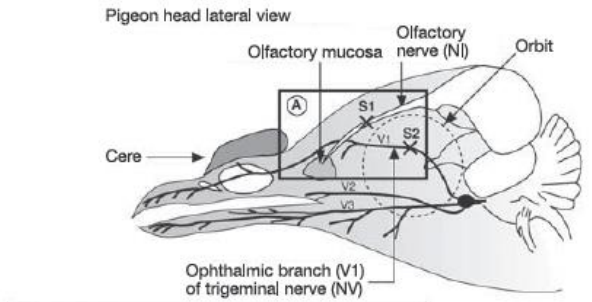
MRAM: Magnetic Random Access Memory

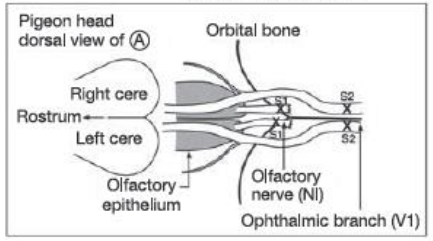


Magnetoreception and its trigeminal mediation in the homing pigeon

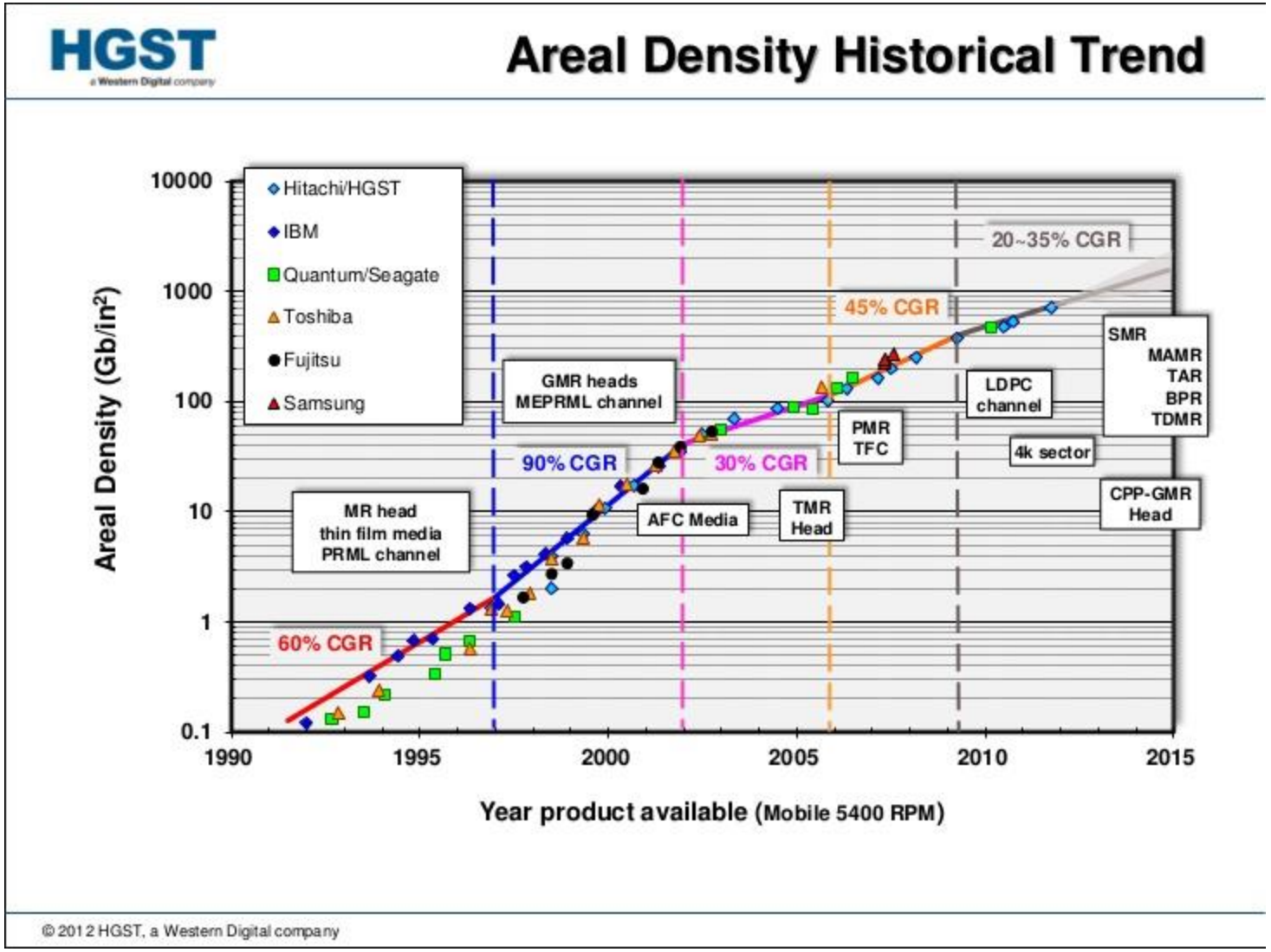
Cordula V. Mora[1]*, Michael Davison[2], J. Martin Wild[3] & Michael M. Walker[1]

Nature **432**, 508 (2004)





High density magnetic recording: the rush to the nano



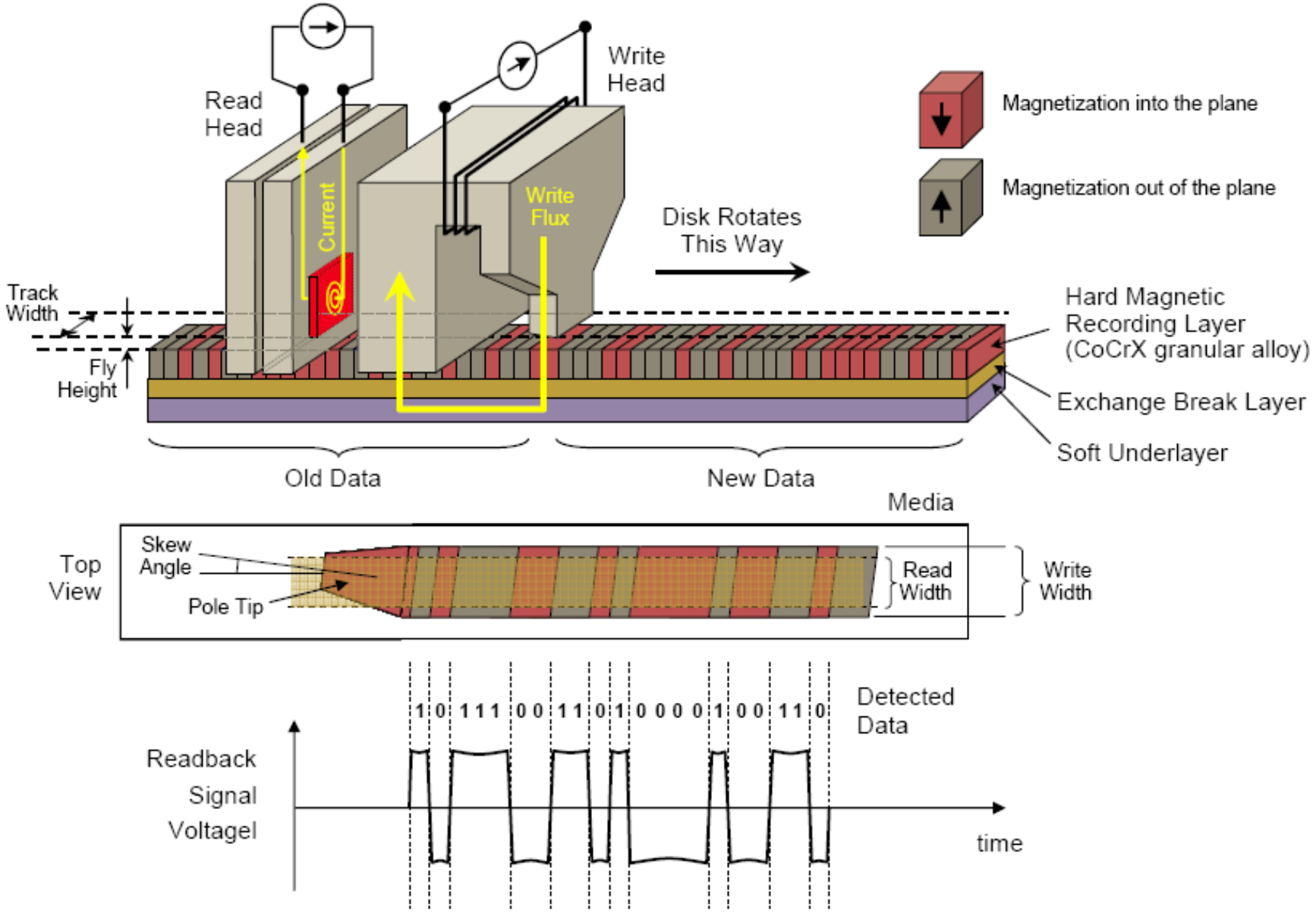
2025

28TB on 10 platters
→ 1.0-1.5 Tb/in^2

20-25 nm pitch

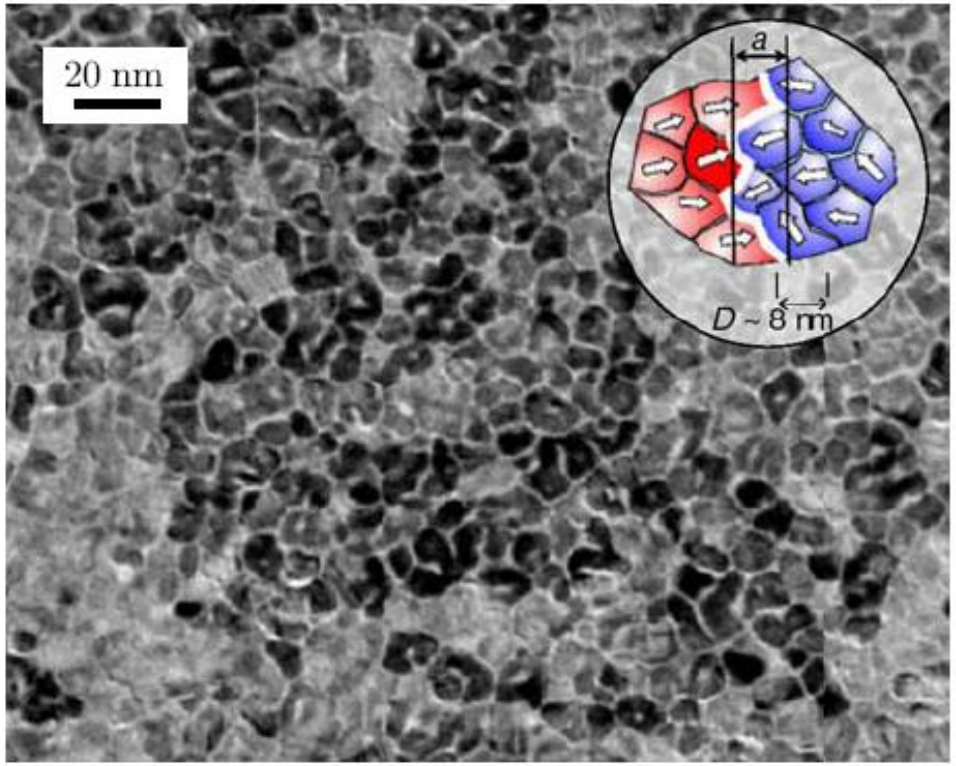
For large scale storage, SSDs are four to five times more expensive per gigabyte than HDDs
HDDs are more reliable for long-term data recovery

The recording mechanism in an HDD: a condensate of concepts



The storage media

TEM images of CoCrPt recording layer with in-plane magnetization.

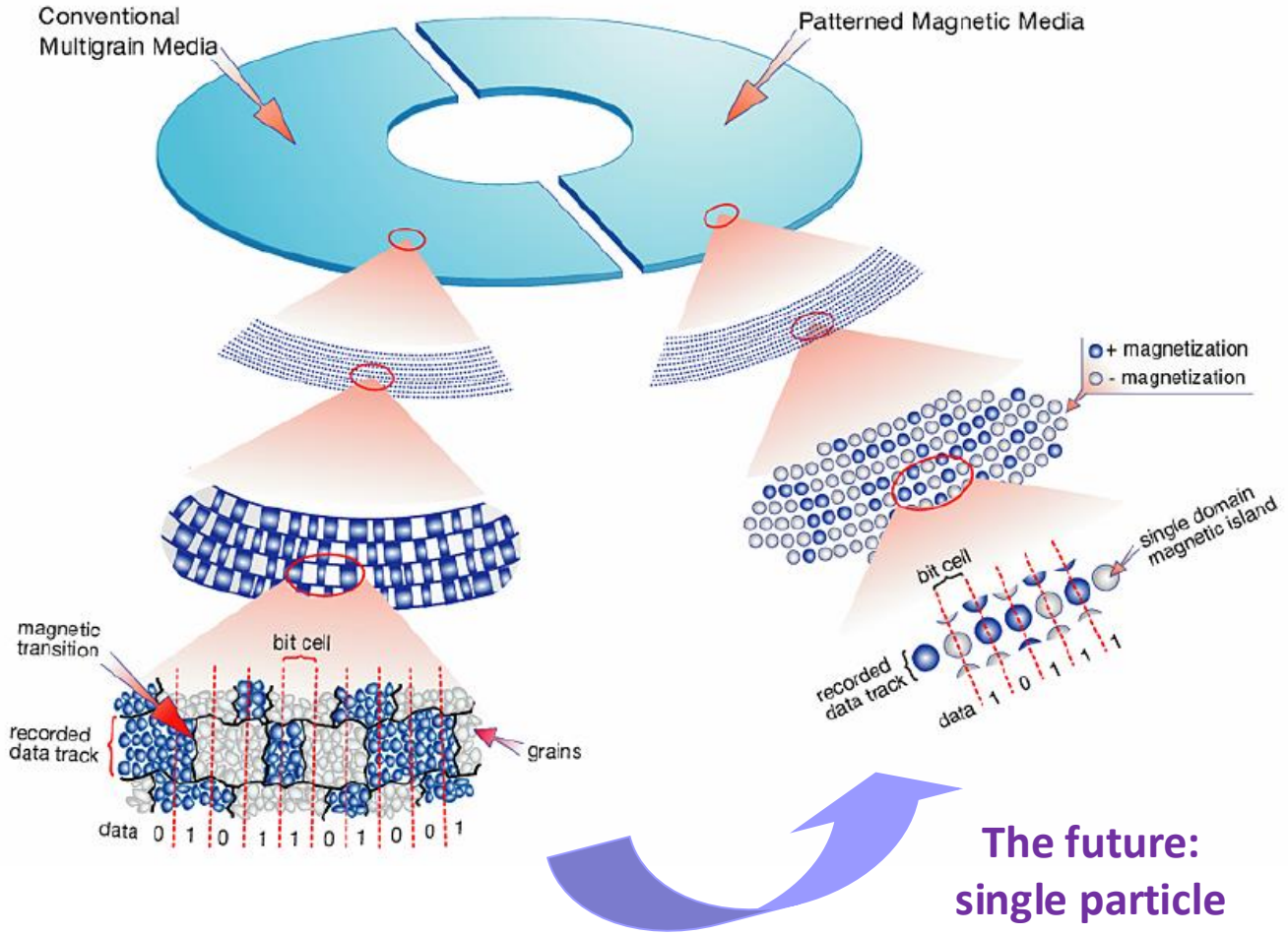


The inset sketches two bits. Each bit consist of several tens of grains. The bit size and shape is defined during the head writing process

1 bit ≈ 50 grains

Conventional Media vs. Patterned Media

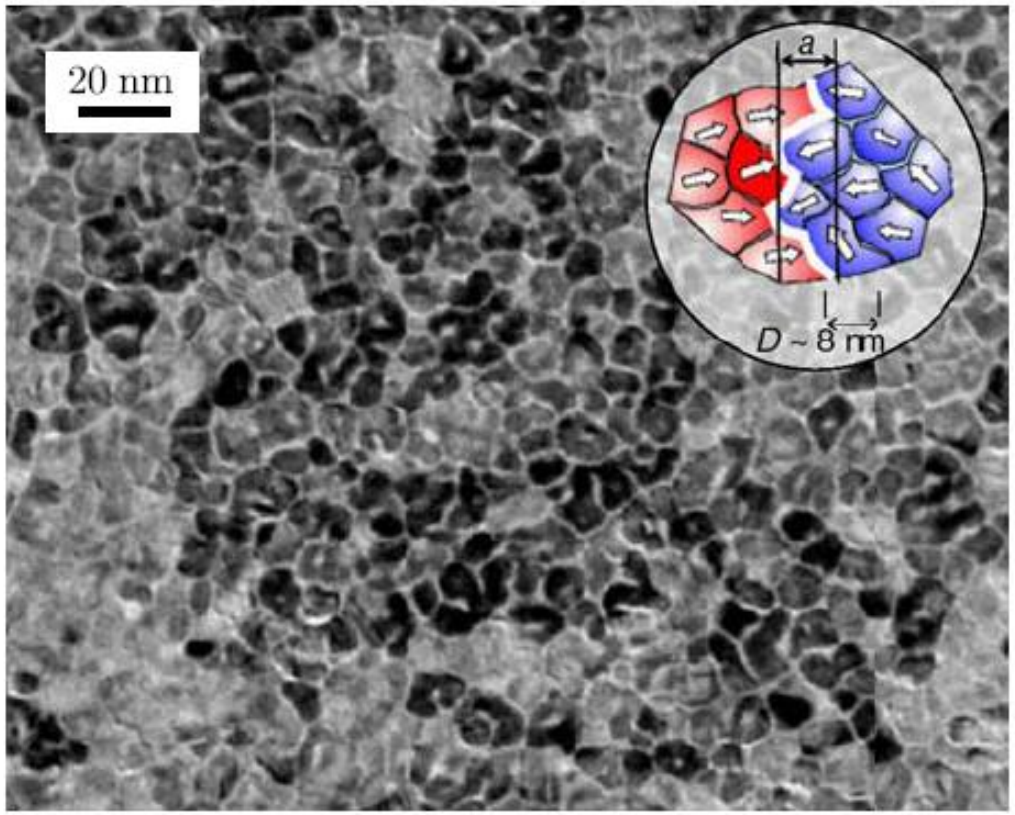
HITACHI
Inspire the Next



The future: single particle per bit

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 looking at this picture

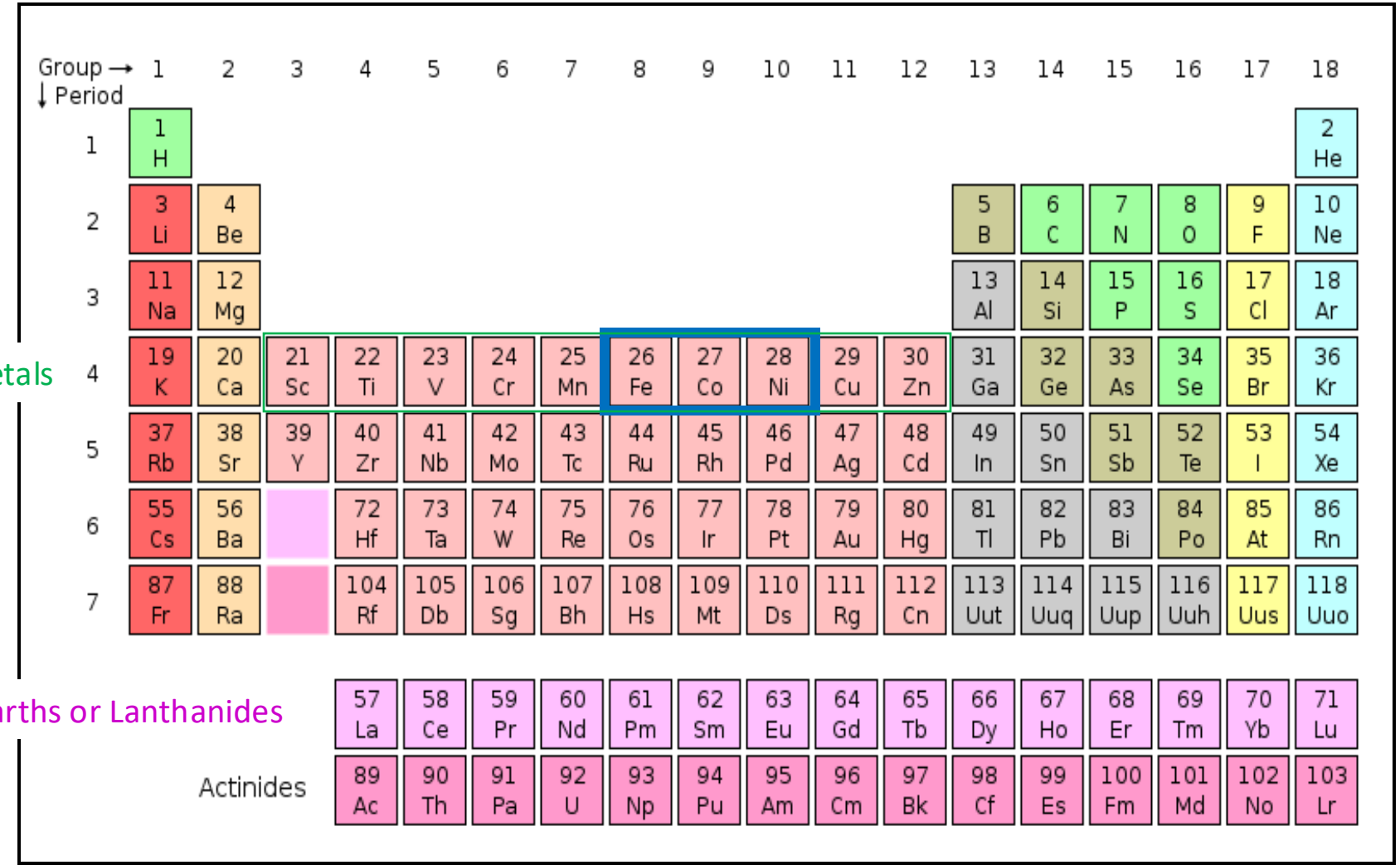


CoCrPt recording layer

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

Origin of the magnetic moment (or magnetization)

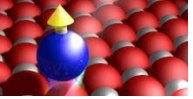
- Observation: at ambient conditions only a few elements (Fe, Co, and Ni) have a magnetic moment
- Is this true also at the nanoscale?
- Does this mean that only these 3 elements can be used in a recording media?
- SmCo is the strongest magnet at ambient conditions: why we need Sm, if Sm is not a magnet?



3d transition metals

$[Ar]\ 4s^2\ 3d^N$

$[Xe]\ 4f^N\ 6s^2$



Many-electron atom

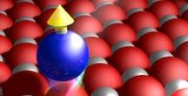
All the electrons interact with one another, analytical solution not possible
Orbital approximation, single electron Hamiltonian → electron configuration $(n,\ l)$
Pauli exclusion principle → max two electrons per orbital
$\mathcal{H}_0$ from hydrogenic Hamiltonian, putting Z electrons

Additional terms:
V_{ee} Coulomb interaction that describes the repulsion between electrons
V_{so} spin-orbit coupling, orbital and spin angular momentum are not independent
V_{Zee} Zeeman interaction if a magnetic field is applied

$$\mathcal{H}_{atom} = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m_e} + eV(r_i)\right) + \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|} + \sum_{i=1}^{Z} \xi_{nl}(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i + \frac{\mu_B}{\hbar}(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{B} = \mathcal{H}_0 + V_{ee} + V_{so} + V_{Zee}$$

$$\boldsymbol{S} = \sum_{i=1}^{Z} \boldsymbol{s}_i \qquad \boldsymbol{L} = \sum_{i=1}^{Z} \boldsymbol{l}_i$$

$$V_{SO} = \lambda \boldsymbol{L} \cdot \boldsymbol{S} \qquad \lambda = \pm \frac{\zeta_{nl}}{2S}$$



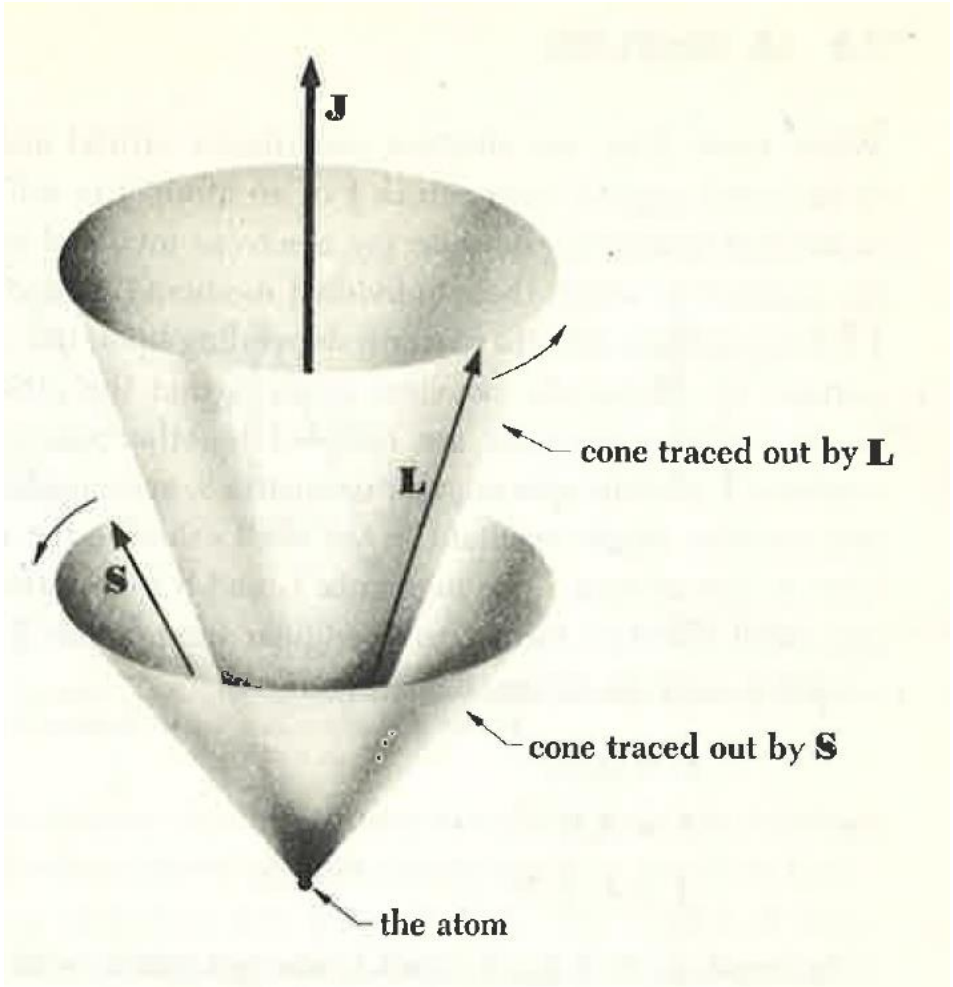
Interactions: orders of magnitude

$$\mathcal{H}_{atom} = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m_e} + eV(r_i)\right) + \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|} + \sum_{i=1}^{Z} (\boldsymbol{l}_i \cdot \boldsymbol{s}_i)\, \xi_{nl}(r_i) + \frac{\mu_B}{\hbar} (\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{B} = H_{Coul} + V_{ee} + V_{so} + V_{Zee}$$

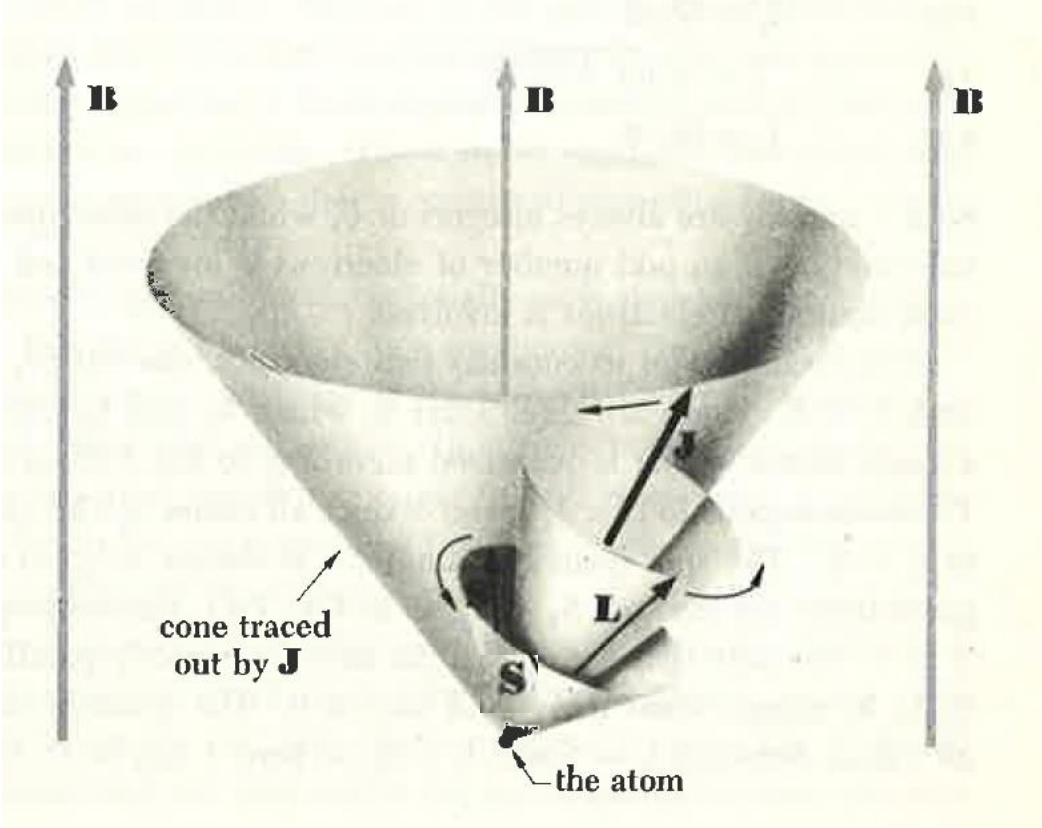
interaction term	3d transition metals	4f rare earths
V_{ee}	1 eV	1 eV
V_{SO}	50 - 100 meV	300 - 500 meV
$V_{Zee}\ (B = 1\mathrm{T})$	0.1 - 0.2 meV	0.1 - 0.6 meV

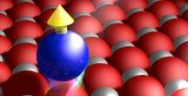
L and ***S*** are coupled

No external ***B*** field: the total ***J*** is conserved in magnitude and direction, ***L*** and ***S*** precess around the the direction of the resultant ***J***



External ***B*** field applied: ***J*** precesses about the direction of ***B***





From angular momentum to magnetic moment

Exercise 10.1

Total magnetic moment operator

$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S$$

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(g_L \boldsymbol{L} + g_S \boldsymbol{S}) \qquad g_L = 1 \qquad g_S = 2$$

g-factors for orbital and spin magnetic moments (similar to classical gyromagnetic ratio)

With spin-orbit coupling, $\boldsymbol{S}$ and $\boldsymbol{L}$ don't correspond to good quantum numbers anymore, but $\boldsymbol{J}$ does.
In the presence of a magnetic field, the component of the magnetic moment parallel to $\boldsymbol{J}$ is conserved, but the component perpendicular to $\boldsymbol{J}$ is not.
We can write the operator total magnetic moment operator as

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar} g_J \boldsymbol{J} \qquad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

g_J is the Landé g-factor
it describes the projection of $\boldsymbol{L} + 2\boldsymbol{S}$ onto $\boldsymbol{J}$

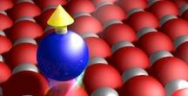
$$\mu_B = \frac{e\,\hbar}{2\,m_e} = 0.058 \text{ meV T}^{-1}$$ Bohr magneton

In the limit of a weak magnetic fied $\boldsymbol{B}$, defining the quantization axis z, the magnetic moment along z is

$$\mu_z = \frac{1}{B}\langle L\,S\,J\,M_J|(\boldsymbol{\mu}_L + \boldsymbol{\mu}_S)\cdot\boldsymbol{B}|L\,S\,J\,M_J\rangle$$

$$= -\frac{\mu_B}{\hbar}\langle L\,S\,J\,M_J|L_z + 2S_z|L\,S\,J\,M_J\rangle = -\frac{\mu_B}{\hbar} g_J \langle L\,S\,J\,M_J|J_z|L\,S\,J\,M_J\rangle = -\mu_B\, g_J M_J$$

frequently indicated simply as μ



Magnetic moment of free atoms in field

Hund's rules to find the **ground state**:

1) Total spin $\boldsymbol{S} = \sum_i \boldsymbol{s}_i$ maximized ($\Rightarrow S = M_S$ max)

2) Total orbital momentum $\boldsymbol{L} = \sum_i \boldsymbol{l}_i$ maximized ($\Rightarrow L = M_L$ max)

$\Leftrightarrow$ Coulomb repulsion V_{ee}

3) Total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$

$\boldsymbol{L}$ and $\boldsymbol{S}$ parallel ($J = L + S$) if subshell more than half filled

$\boldsymbol{L}$ and $\boldsymbol{S}$ antiparallel ($J = |L - S|$) if subshell less than half filled

$\Leftrightarrow$ Spin-orbit interaction V_{SO}

Ti: [Ar] $3d^2\ 4s^2$

Only the 3d subshell is partially occupied

m_l	$+2$	$+1$	0	-1	-2
m_s	$\uparrow$	$\uparrow$			

$M_S = 1 \rightarrow S = 1$

$M_L = 3 \rightarrow L = 3$

subshell less than half-filled $\rightarrow J = L - S = 2$

$$\mu_z = -g_J M_J\ \mu_B = -\frac{2}{3} 2\ \mu_B = -\frac{4}{3}\ \mu_B$$

Fe: [Ar] $3d^6\ 4s^2$

Only the 3d subshell is partially occupied

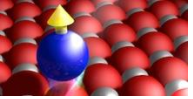
m_l	$+2$	$+1$	0	-1	-2
m_s	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$

$M_S = 2 \rightarrow S = 2$

$M_L = 2 \rightarrow L = 2$

subshell more than half-filled $\rightarrow J = L + S = 4$

$$\mu_z = -g_J M_J\ \mu_B = -\frac{3}{2} 4\ \mu_B = -6\ \mu_B$$



Zeeman interaction

Atom described by quantum numbers $|L\ S\ J\ M_J\rangle$ with M_J assuming $2J+1$ values between $-J$ and $+J$

At $B = 0$ T the $2J+1$ values are degenerate in energy

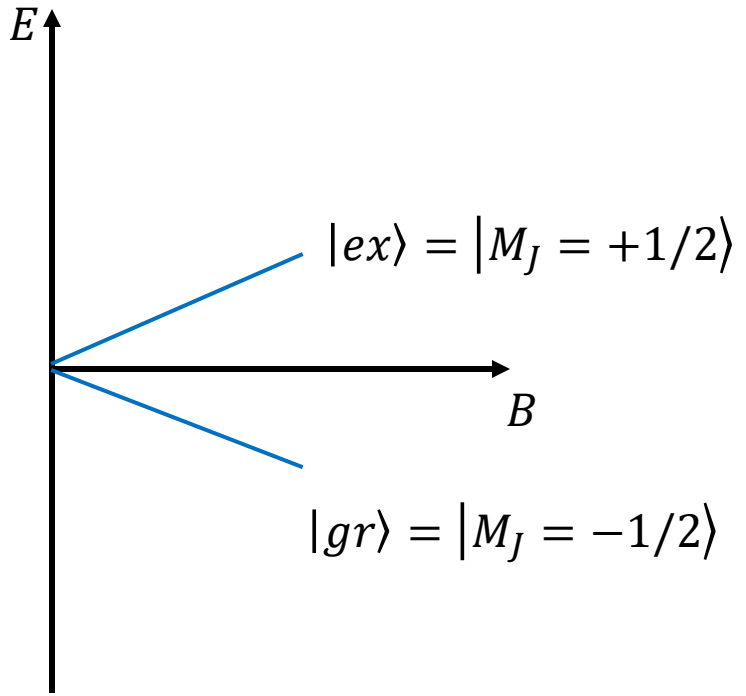
At $B \neq 0$ T the $2J+1$ states split: Zeeman splitting

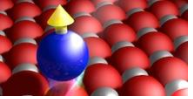
$$H_{Zee} = g_J\ \mu_B\ \boldsymbol{J} \cdot \boldsymbol{B}/\hbar$$

$$E(M_J) = g_J \mu_B M_J\ B$$

Example: atom with $J = 1/2$

two energy levels: $\pm g_J\ \mu_B\ M_J\ B$





Magnetism of an isolated atom at finite temperature

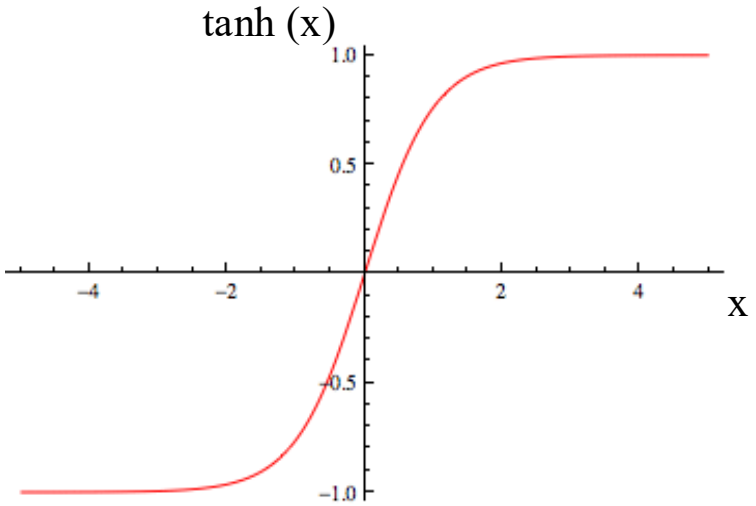
Boltzmann factor: expresses the relative probability that a quantum state of energy E to be occupied at temperature T

$$\exp\left(-E_{M_J}/k_B T\right) = \exp\left(-M_J\, g_J\, \mu_B\, B\, /\, k_B T\right)$$

The net magnetic moment is given by the contribution of all occupied states: in this cas with only two states of opposite magnetization we have:

$$\mu(B,T) = \mu^{\uparrow} - \mu_{\downarrow} = |M_J|\, g_J\, \mu_B \left(\frac{e^x}{e^x + e^{-x}} - \frac{e^{-x}}{e^x + e^{-x}}\right) = |M_J|\, g_J\, \mu_B\, tanh(x) \qquad x = \frac{M_J\, g_J\, \mu_B B}{k_B T}$$

$$\mu(B,T) = \mu_B\, tanh\left(\frac{\mu_B B}{k_B T}\right) \qquad \text{with} \quad |M_J| = \frac{1}{2} \quad \text{and} \quad g_J = 2$$

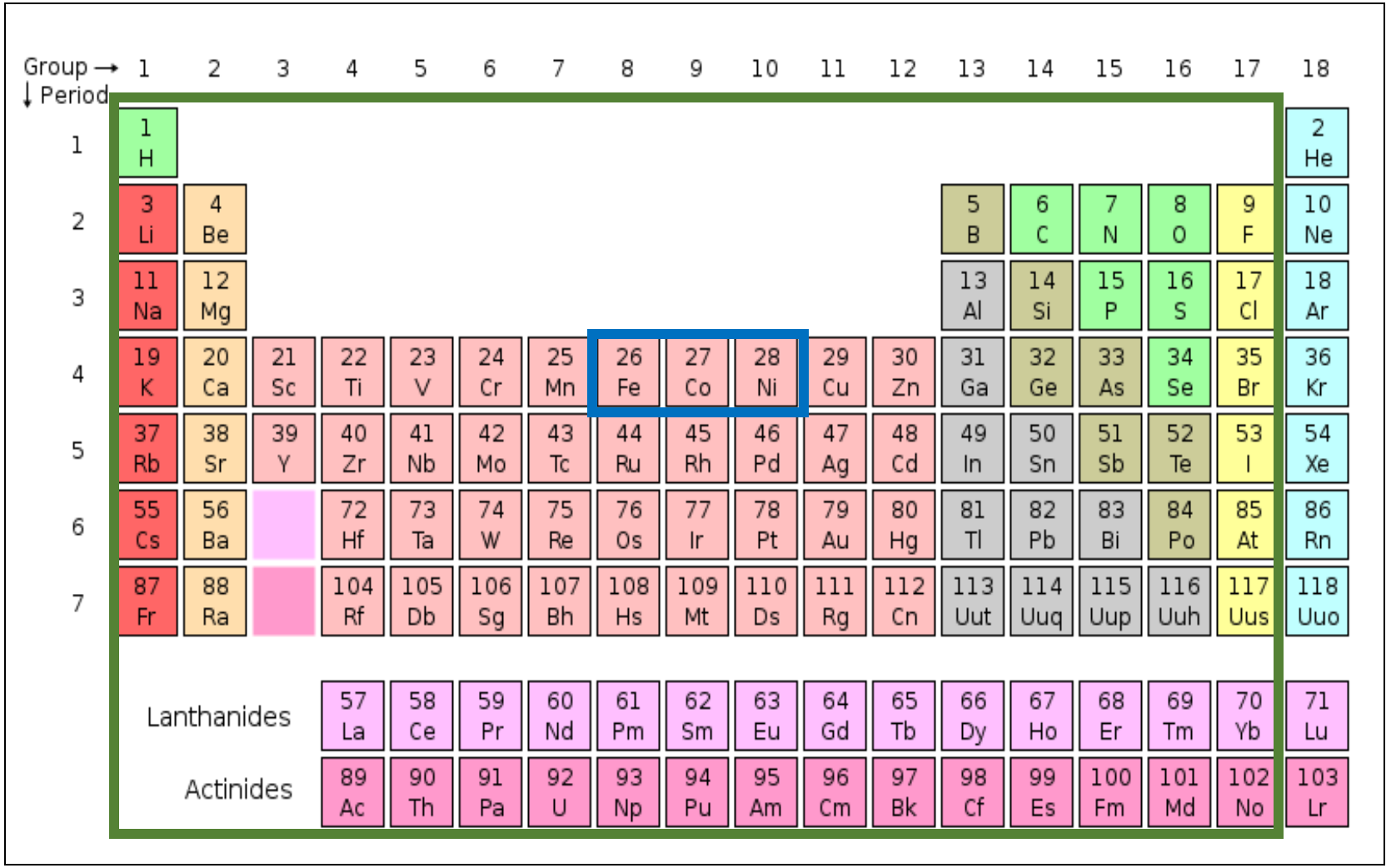


	tanh(x)	Occupation gr	Occupation ex
T = 0 or B = ∞	1	100%	0%
B = 0 or T = ∞	0	50%	50%
B = 0.55 k_BT/μ_B	0.5	75%	25%

Isolated atoms *vs.* bulk

Bulk (at room T): only a few elements (Fe, Co, and Ni) have a magnetic moment

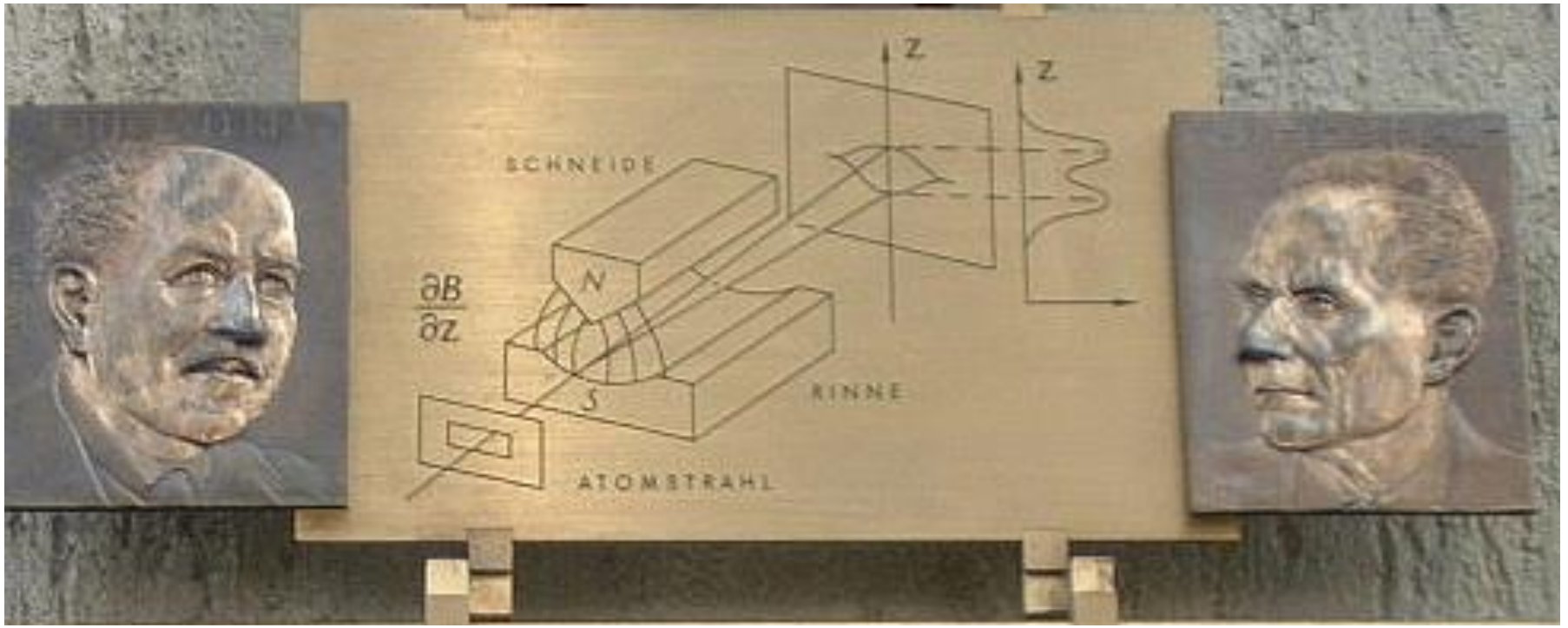
Atoms: all atoms except noble gas have a magnetic moment



Stern-Gerlach experiment (1922)

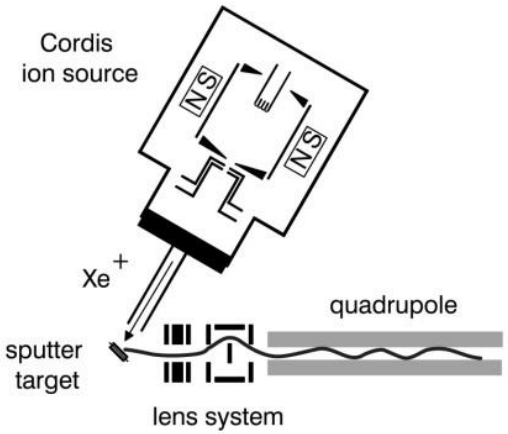
Beam of Ag atoms through a non-uniform magnetic field

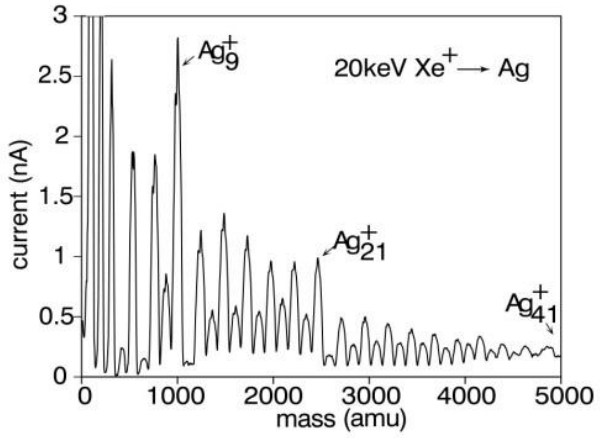
Ag: [Kr] $4d^{10}\ 5s^1$ ⟹ $L = 0;\ S = 1/2,$ $M_S = M_J = \pm 1/2$

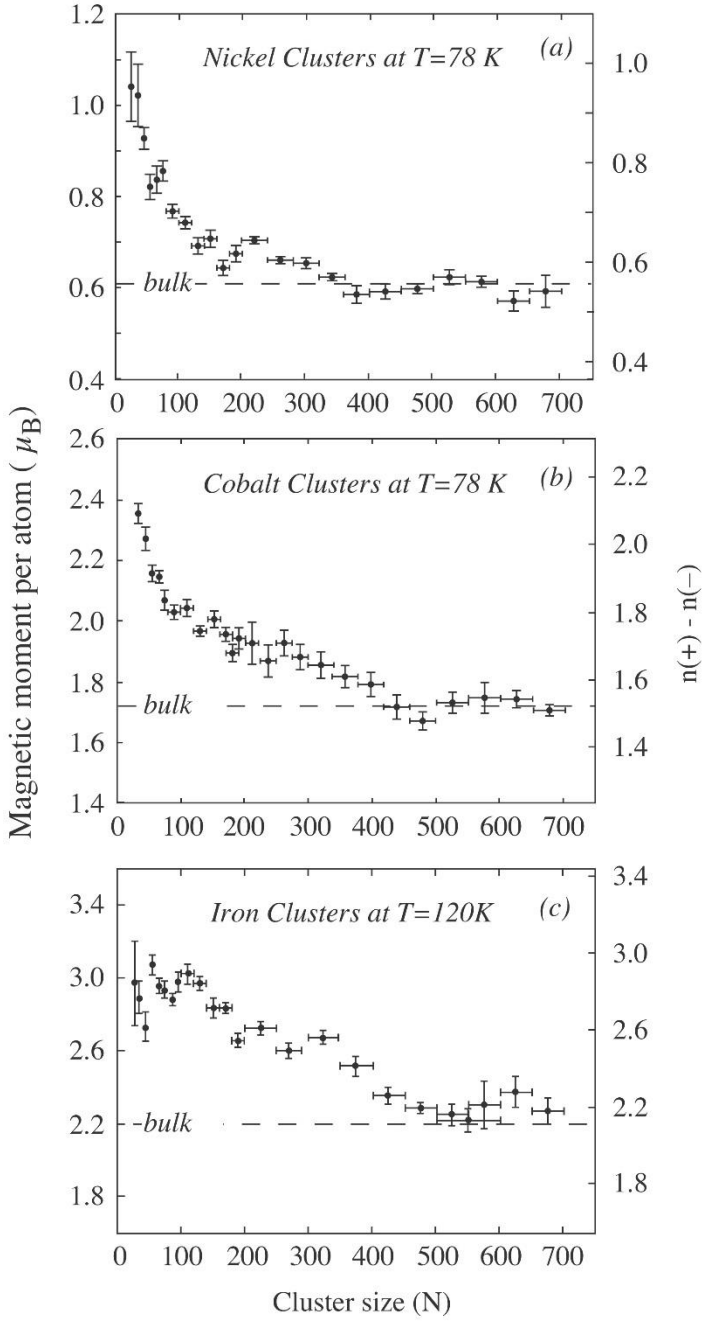


Ag atoms deviate depending on their spin moment

Stern-Gerlach experiment with clusters

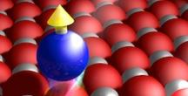






Below about 200 atoms per cluster, the magnetic moment strongly increases with respect to bulk values and tends to the gas-phase atom value

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



Quenching of orbital moment

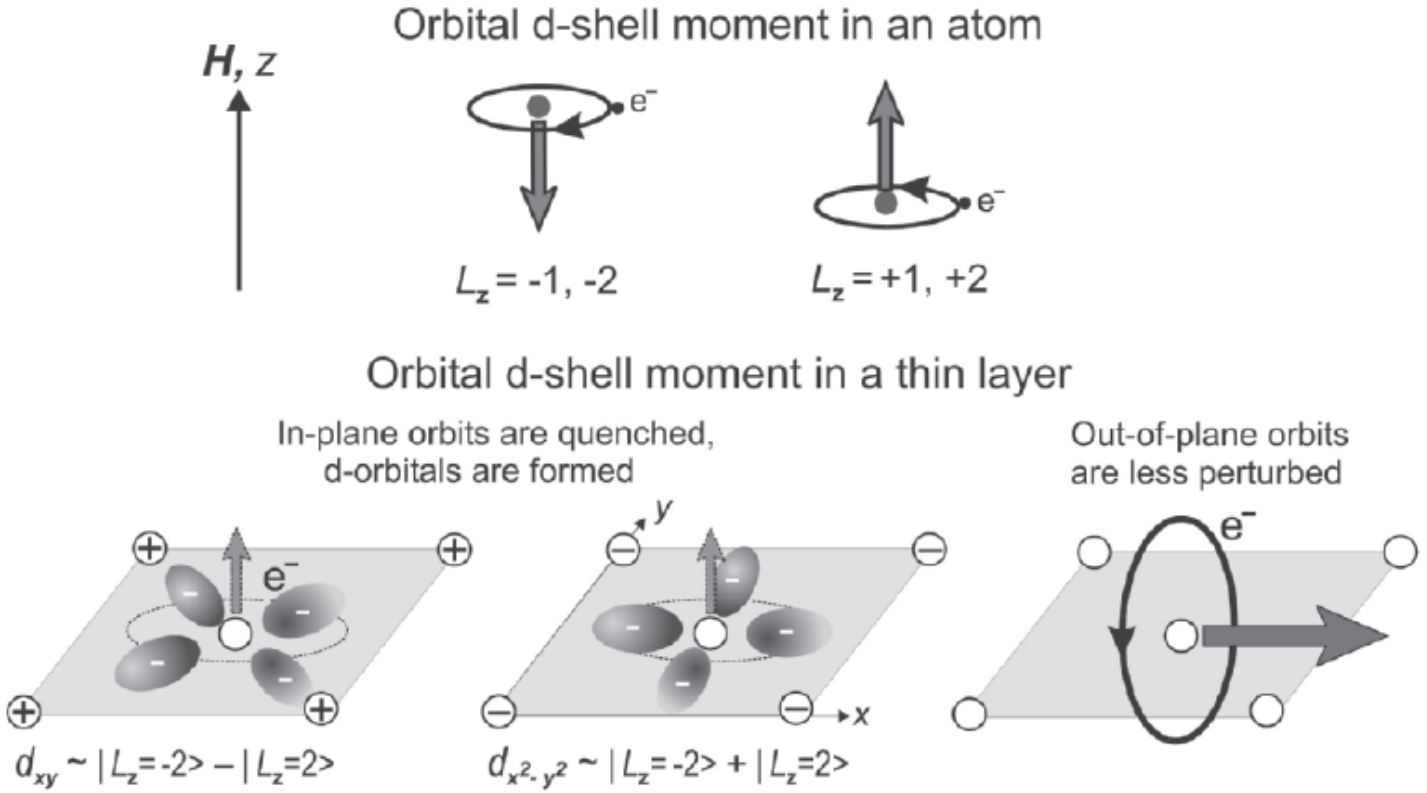
Suppression of the orbital contribution to the magnetic moment

Origin:

- crystal field and covalent bonds (main effect in semiconductors, insulators, oxides)
- electron delocalization and band formation (in metals)

This effect reduces the orbital angular momentum so that it does not contribute to the overall magnetism, which is then dominated by the spin magnetic moment.

Quenching of orbital moment due to bond formation



the orbital moment L 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

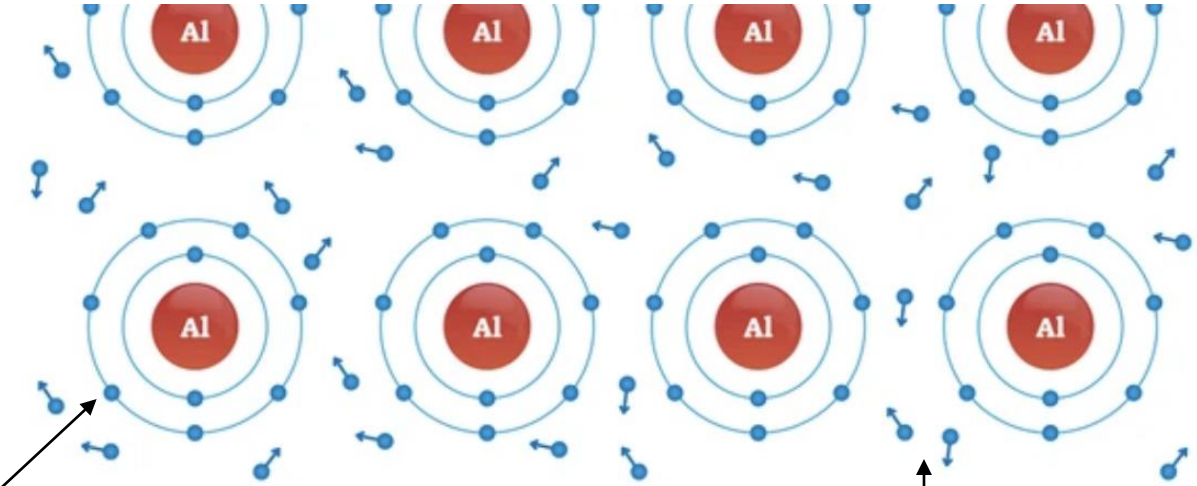
The central atom binds to four atoms in a plane.

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 **reduced** and **anisotropic** orbital moment

Quenching of orbital moment due to electron delocalization

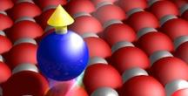


core electrons
similar to free atom case, full shells

conduction electrons
delocalized, “sea” of electrons

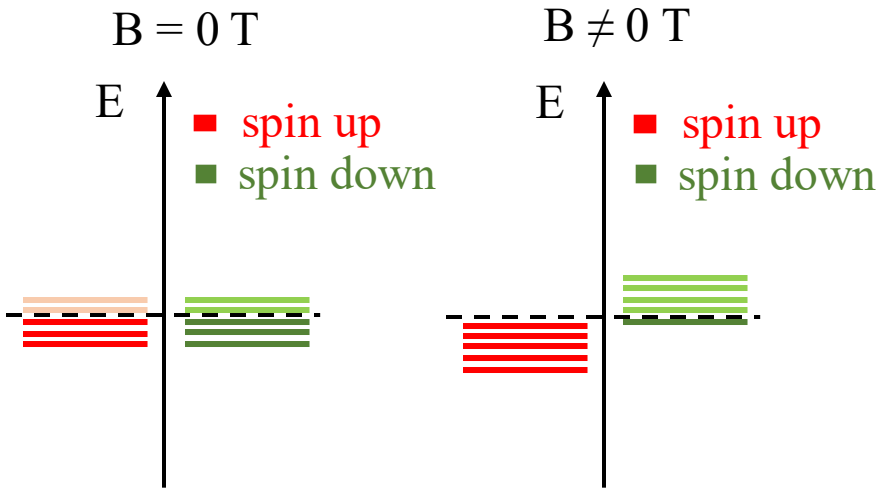
The delocalization significantly alters the electronic wave functions, and there are no more “circular” orbits → the orbital magnetic moment is strongly suppressed.

Electrons in d bands are intermediate (delocalized but not as much as s or p electrons)



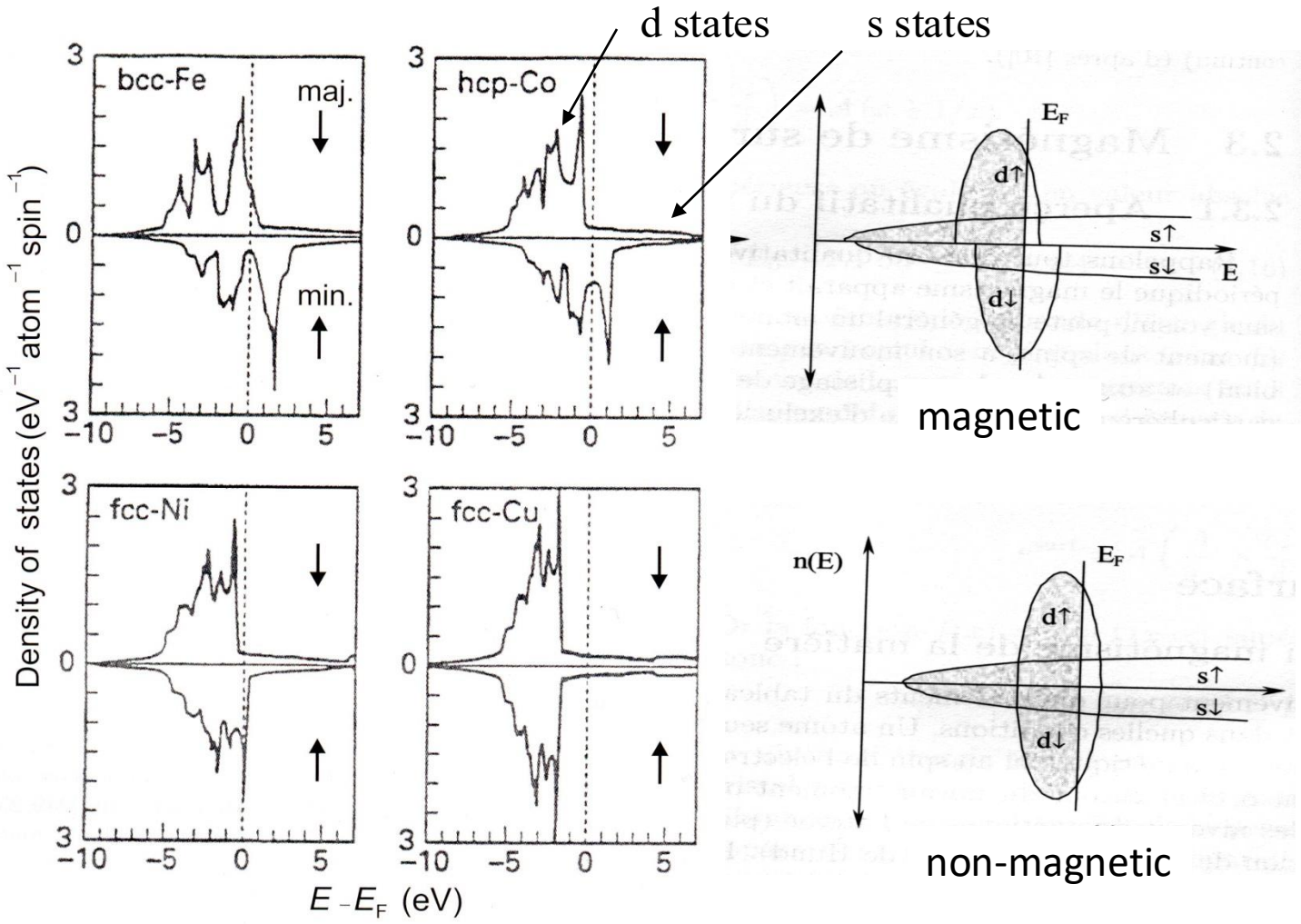
Spin: free atom *vs.* bulk

Atom



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

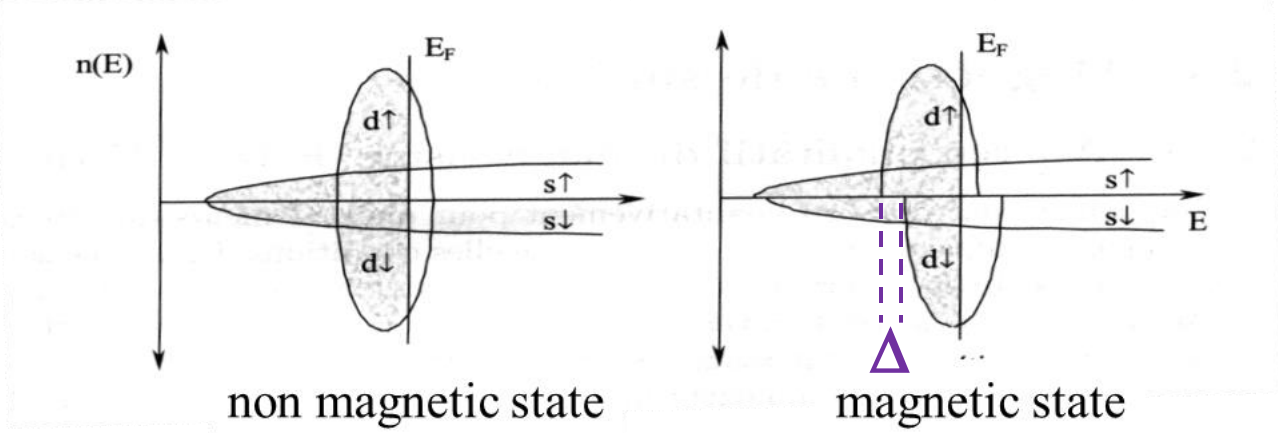
Bulk



Due to electron-electron interaction, spontaneous magnetization can appear even in absence of an external magnetic field.

Stoner model for spontaneous magnetization: exchange splitting

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



$n(E)$: density of states

Coulomb interaction: $V_{ee}\, N_{up}\, N_{dw}$

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

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

Each band shifts by $\Delta/2$ in opposite directions;
N_{up} (N_{dw}) increases (decreases) by $dN = n(E_F)\,\Delta/2$.
Gain (loss) in energy is = $dN\,\Delta/2$

Kinetic energy variation = $\frac{\Delta}{2}\left(dN_{up} - dN_{dw}\right) = \frac{\Delta}{2}\left[n(E_F)\frac{\Delta}{2} - \left(-n(E_F)\frac{\Delta}{2}\right)\right] = \frac{\Delta^2}{2}n(E_F)$

Coulomb (e-e) interaction variation = $V_{ee}\left[\frac{N^2}{4} + n(E_F)\frac{\Delta}{2}\frac{N}{2} - n(E_F)\frac{\Delta}{2}\frac{N}{2} - \frac{\Delta^2}{4}n^2(E_F)\right] - V_{ee}\frac{N^2}{4} = -V_{ee}\frac{\Delta^2}{4}n^2(E_F)$

Total electron energy variation $dE = \frac{\Delta^2}{2}n(E_F) - V_{ee}\frac{\Delta^2}{4}n^2(E_F) = \frac{\Delta^2}{2}n(E_F)\left(1 - \frac{V_{ee}}{2}n(E_F)\right)$

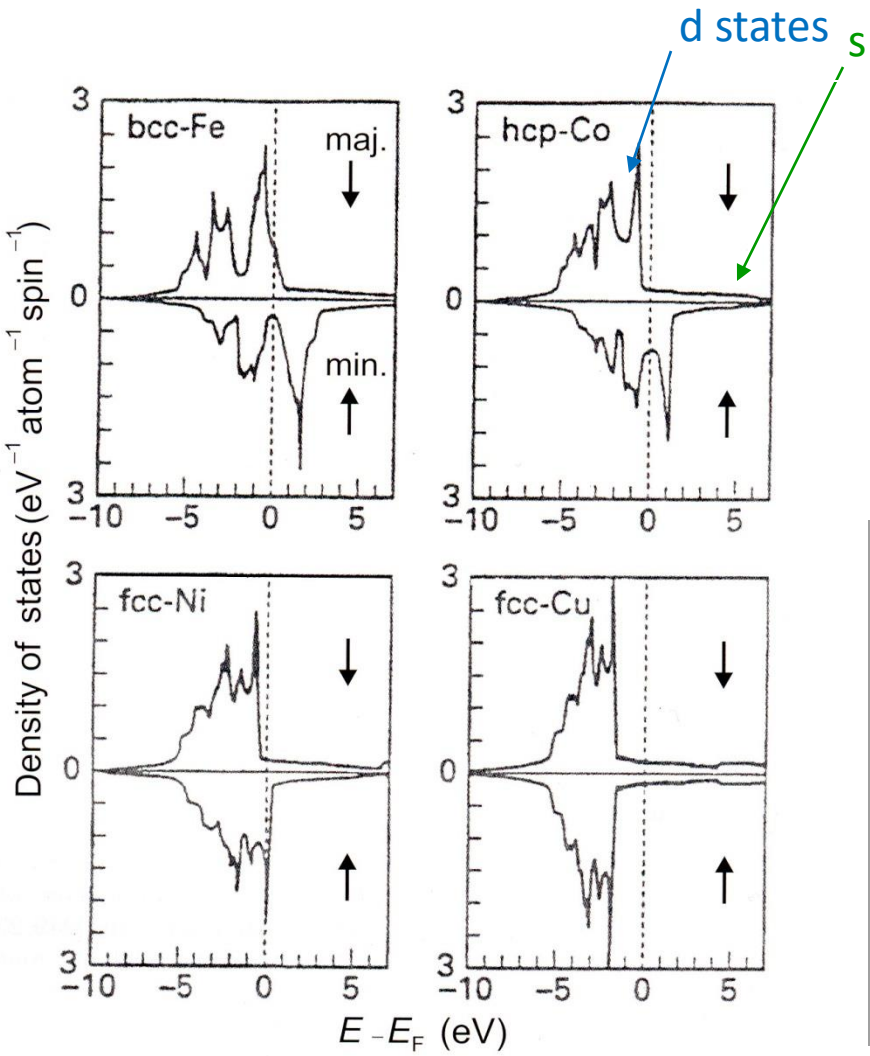
If $dE < 0$ spontaneous magnetism appears: $1 - \frac{V_{ee}}{2}n(E_F) < 0$ **(Stoner criterion)**

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

St&Sie06; S. Blugel Phys. Rev. Lett. **68**, 851 (1992)

Spin: transition metals

Exercise 10.2



s, p bands are extended (band width about 10 eV) → contribution of 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 gas phase case

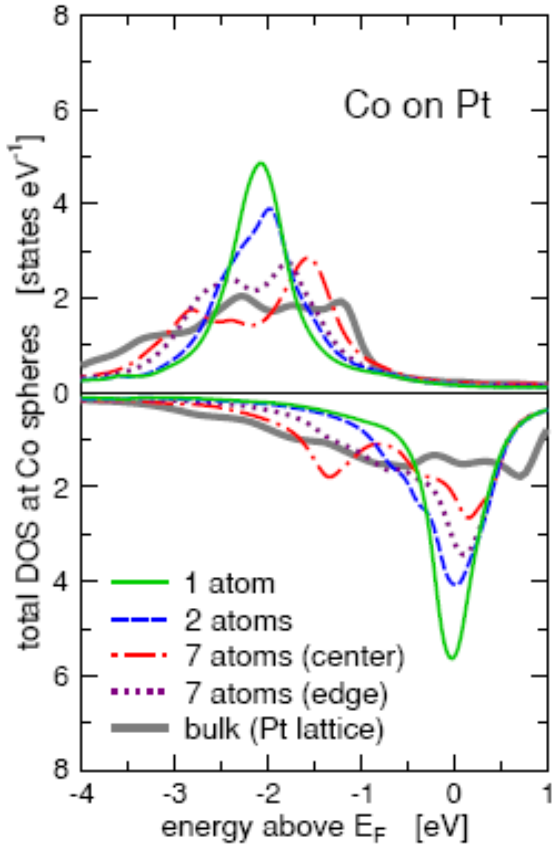
	$n_{3d}+n_{4s}$	$n_{3d}(\downarrow)$	$n_{3d}(\uparrow)$	$n_{4s}(\downarrow)$	$n_{4s}(\uparrow)$	$h_{3d}(\downarrow)$	$h_{3d}(\uparrow)$	μ (μ_B)
Cr	6	2.7	2.7	0.3	0.3	2.3	2.3	0
Mn	7	3.2	3.2	0.3	0.3	1.8	1.8	0
Fe	8	4.8	2.6	0.3	0.3	0.2	2.4	2.2
Co	9	5.0	3.3	0.35	0.35	0.0	1.7	1.7
Ni	10	5.0	4.4	0.3	0.3	0.0	0.6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

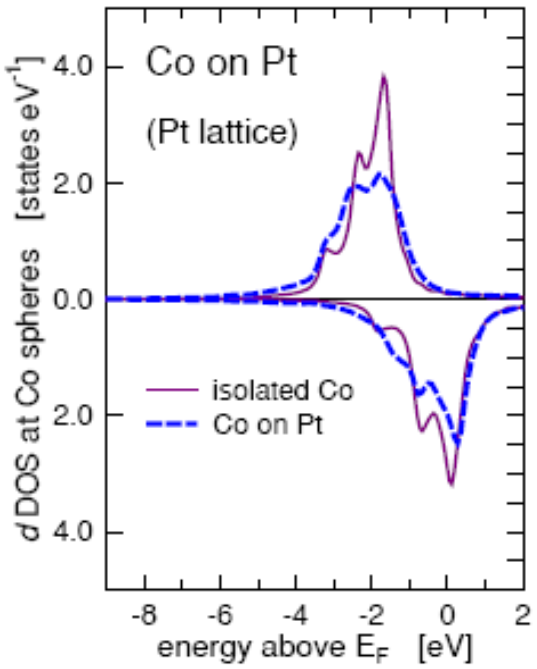
Example: Co on Pt(111)

Size dependence



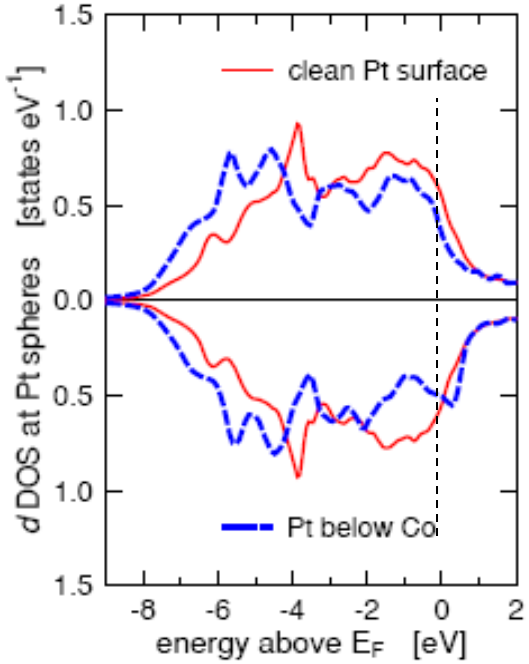
Increasing the cluster size (i.e. bond number), the DOS becomes broader

Hybridization effect



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

Co monolayer

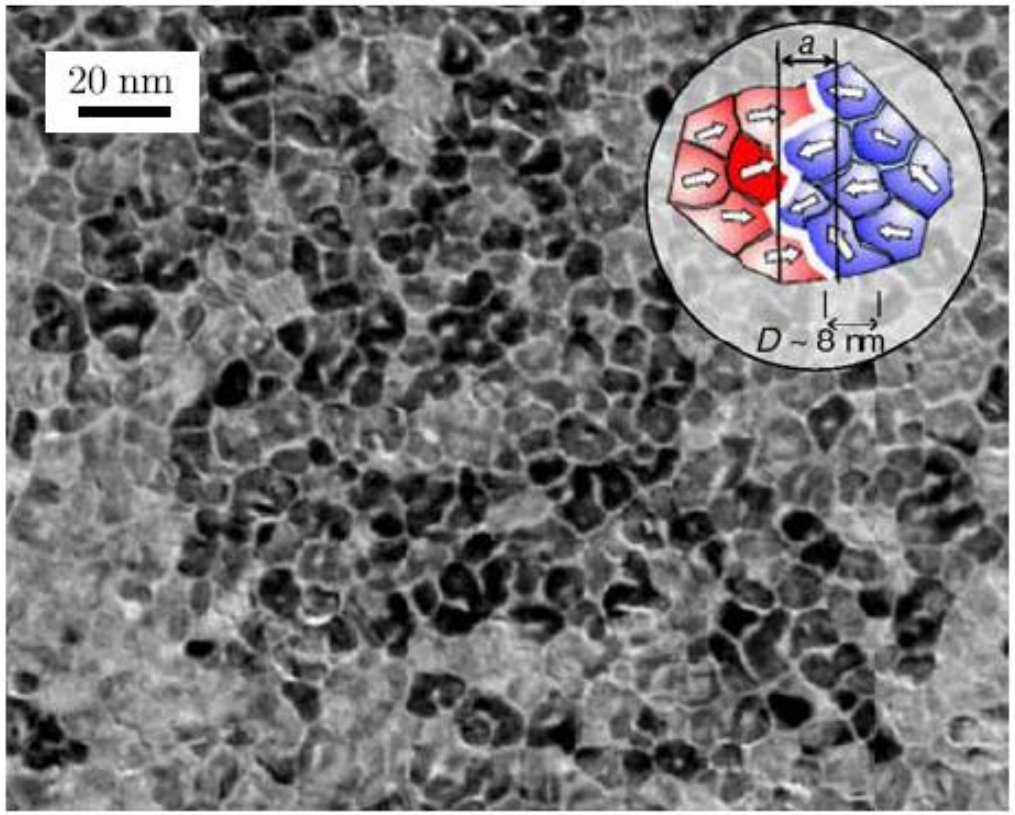


Asymmetry in the Pt DOS at E_F when covered by Co → induced magnetic moment

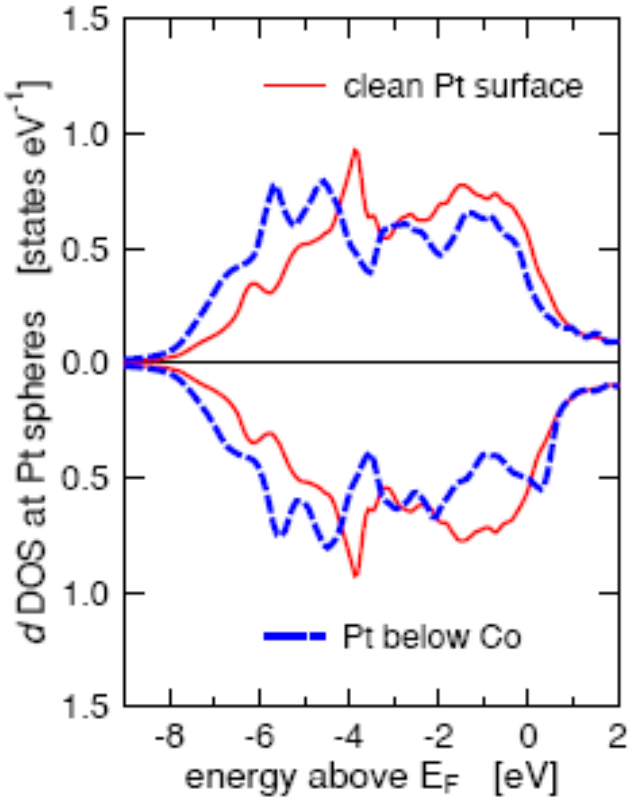
O. Sipr *et al.* J. Phys.: Condens. Matter. 19, 096203 (2007)

Magnetization in a multi-element cluster

CoCrPt recording layer

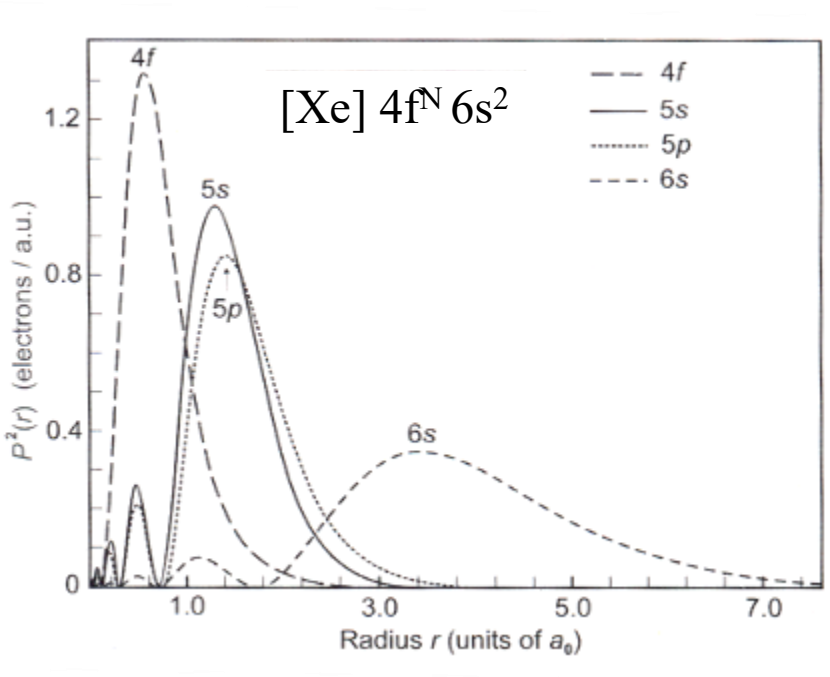


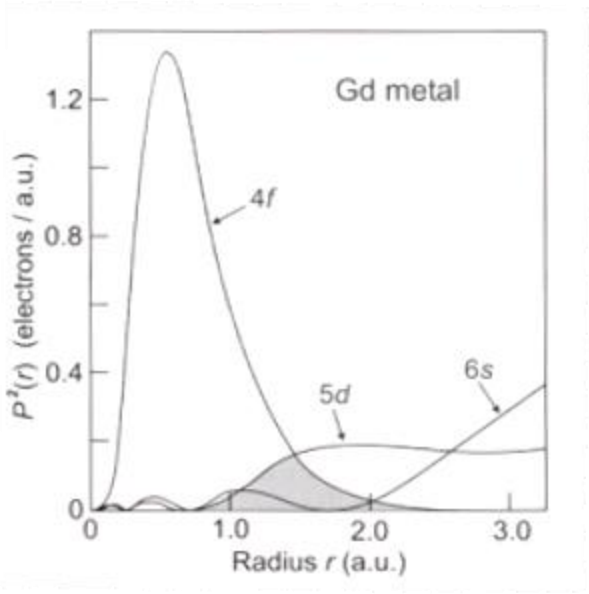
Pt covered by a Co monolayer



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

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 at the core → the 4f electrons do not participate to bonds

L unquenched

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

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 that can participate to bonds