

Stefano Rusponi, Raphael Butte

Objectives : Introduce students to the magnetic and electronic properties of nanostructures

Content:

- 1) Magnetism at the nanoscale :
 - a. Orbital and spin magnetic moment: from single atoms (0D) to thin films (2D) and bulk materials (3D)
 - b. Surface supported nanostructures: the effect of the supporting substrate on the cluster magnetic properties
 - c. magnetic anisotropy and the superparamagnetic limit in magnetic data storage
 - d. Exchange energy
 - e. Single atoms at surface
- 2) Electronics vs. spintronics :
 - a. 2D electron gas at heterogeneous semiconductor interfaces
 - b. A new 2D material: the electronic properties of graphene
 - c. Spin transport: spin valve, GMR and TMR
- 3) Epitaxial growth of metallic 2D nanostructures :
 - a. Cluster nucleation and aggregation: the importance of kinetics
 - b. Controlling shape and composition of 2D clusters grown by self assembly methods
 - c. Building clusters with specific magnetic properties
- 4) Semiconductor Materials for Photonics
 - a. Physical properties
 - b. Applications
- 5) Fabrication and Structural Properties of quantum dots
 - a. Epitaxial growth (Stranski-Krastanov and pyramidal quantum dots)
 - b. Chemically synthesized nanoparticles (CdSe quantum dots)
- 6) Electronic Properties of quantum dots
 - a. Quantum confinement effects (from 2D to 0D)
 - b. Electronic states: excitonic complexes (excitons, biexcitons, trions), dipole moment (Stark effect)
 - c. Exciton-phonon interactions (temperature dependent exciton linewidth), phonon wings, polaron complexes
 - d. Light-matter interaction in quantum dots (Purcell effect and strong-light-matter coupling)

Magnetism of nanostructures

Stefano Rusponi

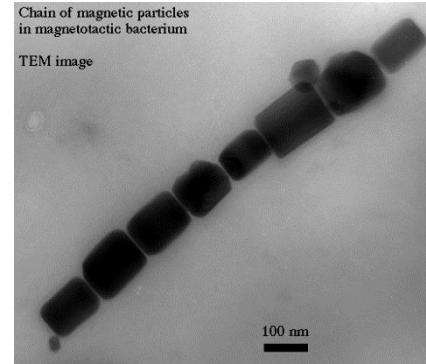
Institut de Physique (IPHYS)

École Polytechnique Fédérale de Lausanne (EPFL), Switzerland

- ❖ **Back to basics: magnetization sources and intrinsic parameters**
- ❖ **Understanding and controlling the magnetic properties of the nano world**

Copy of the slides can be found at the address
lns.epfl.ch -> [Lectures](#) -> [Magnetic and semiconducting nanostructures](#)

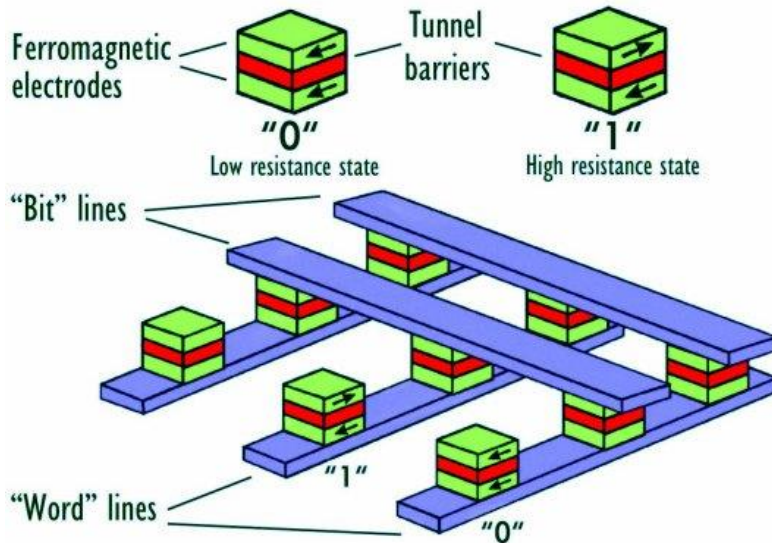
Credit Card



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)].

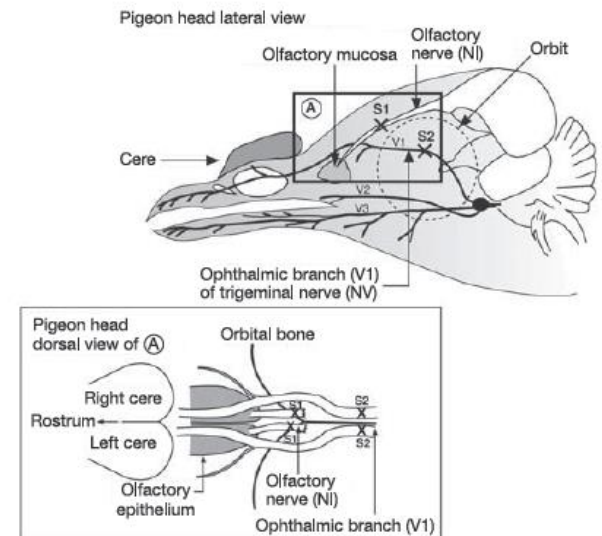
MRAM: Magnetic Random Access Memory



Magnetoreception and its trigeminal mediation in the homing pigeon

Cordula V. Mora^{1*}, Michael Davison², J. Martin Wild³
& Michael M. Walker¹

Nature **432**, 508 (2004)

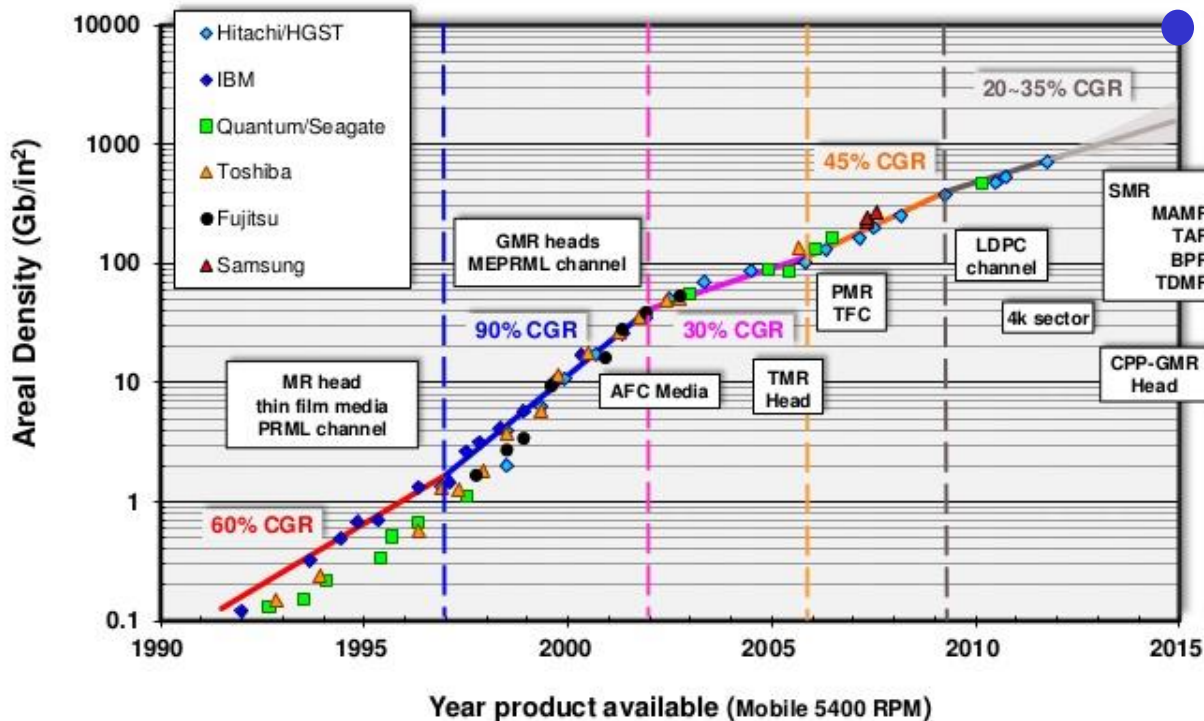


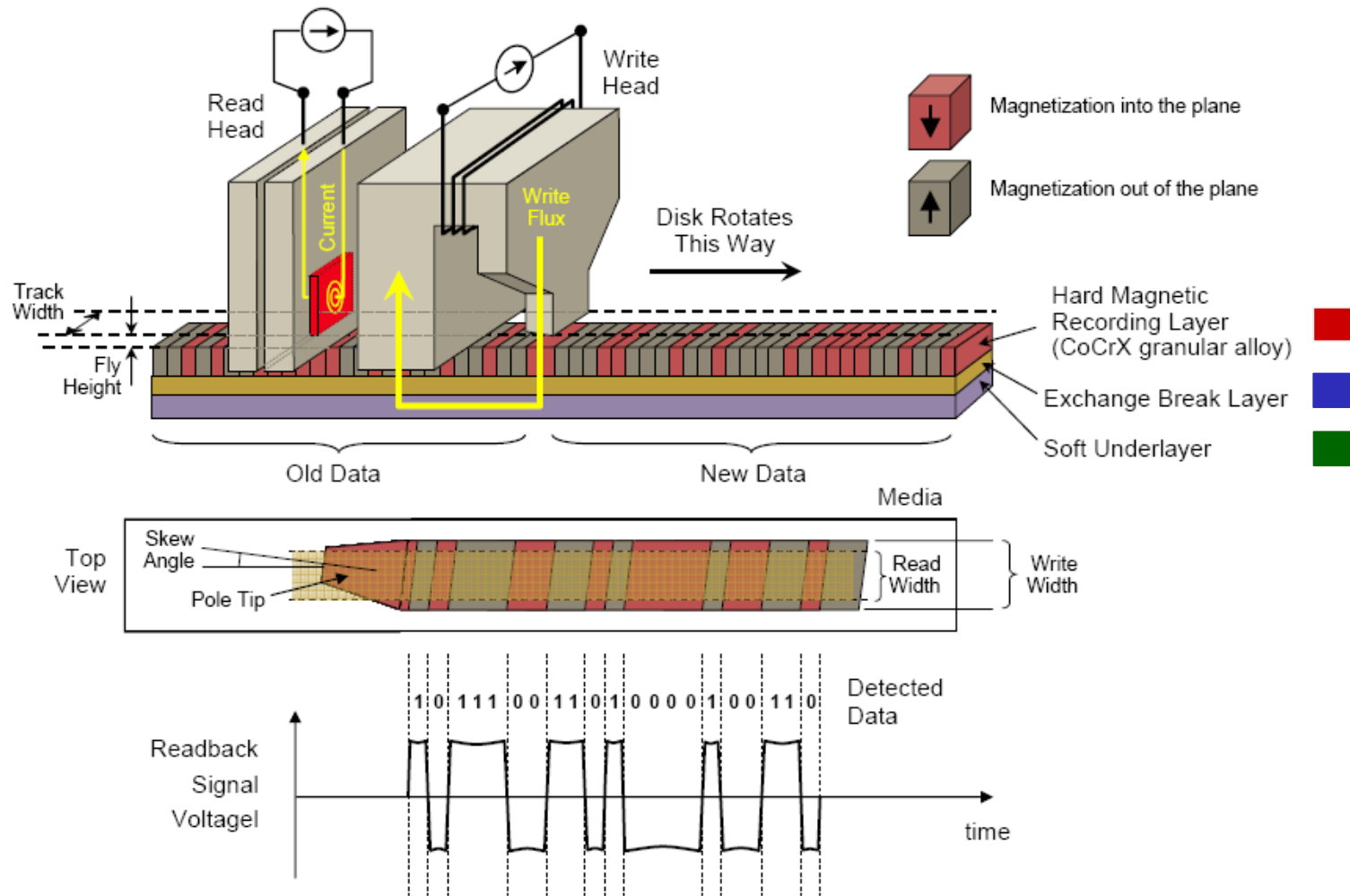
2015



HGST
a Western Digital company

Areal Density Historical Trend

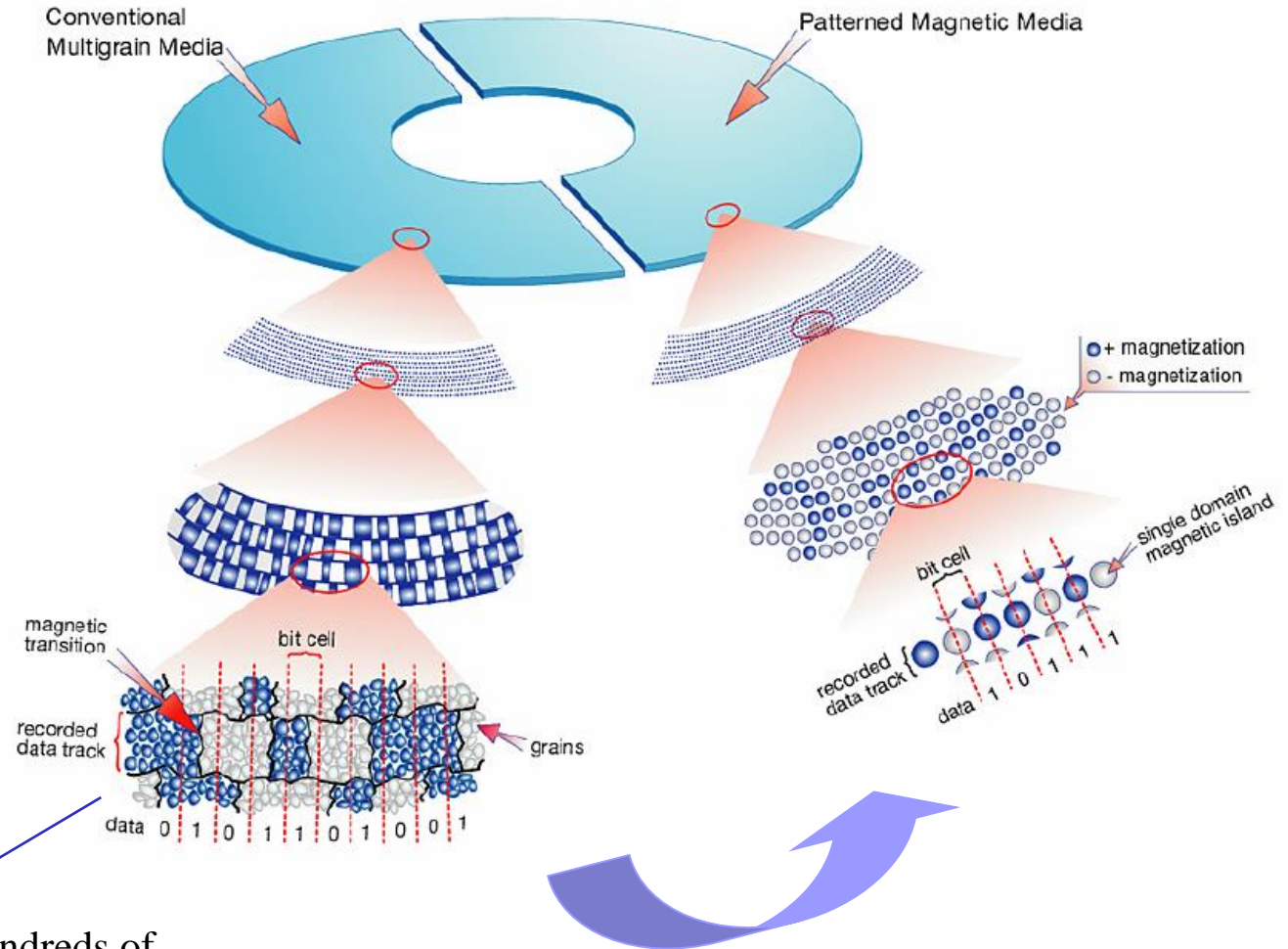




The writing-reading head is flying over the continuous magnetic media

Conventional Media vs. Patterned Media

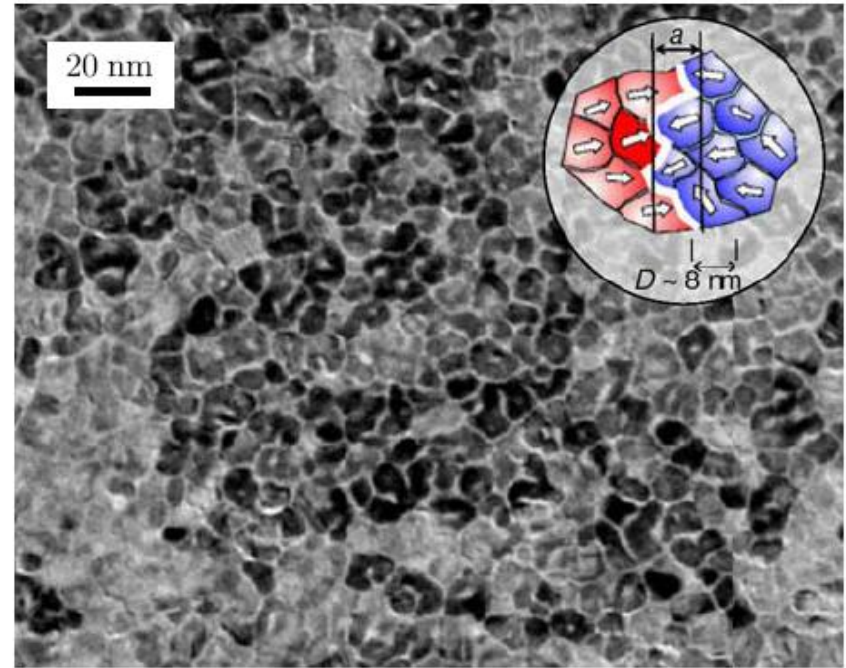
HITACHI
Inspire the Next



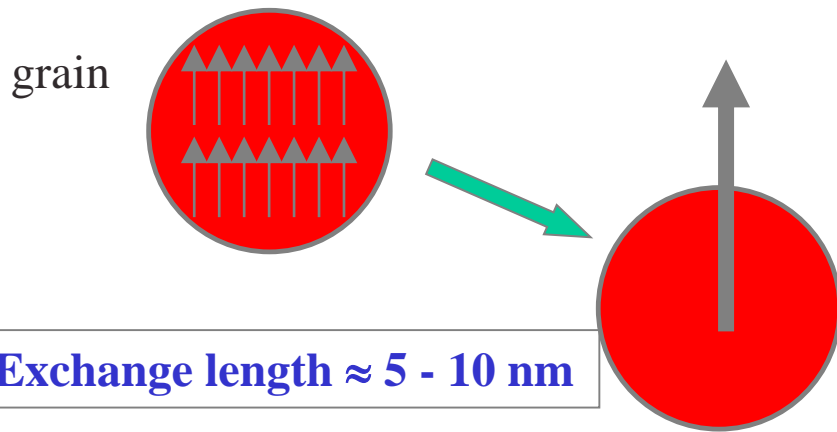
Each bit is made of a few hundreds of grains (to have a good signal to noise ratio). The bit size and shape is defined during writing by the writing head

The future: single particle per bit

TEM images of the magnetic layer in a MRAM. Each bit is made of a few hundreds of grains



All spins (μ_i) in the grain are ferromagnetically aligned



Exchange length $\approx 5 - 10$ nm

The grain (particle) can be described as a single **macrospin** $\mu = \sum_i \mu_i$

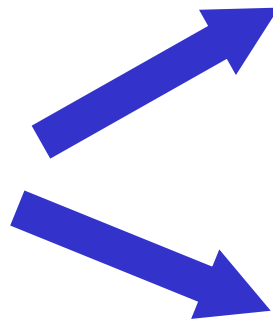
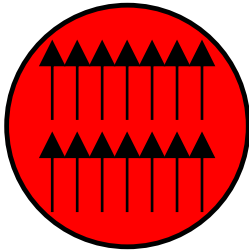
The macrospin direction change from grain to grain -> **magnetization easy axis (magnetic anisotropy)**

To have a net signal (magnetization) in one direction we have to mean over several grains

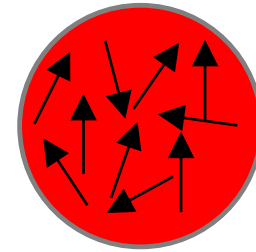
All spins in the grain **must be** ferromagnetically aligned

exchange energy J coupling spins

$$H_{exc} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

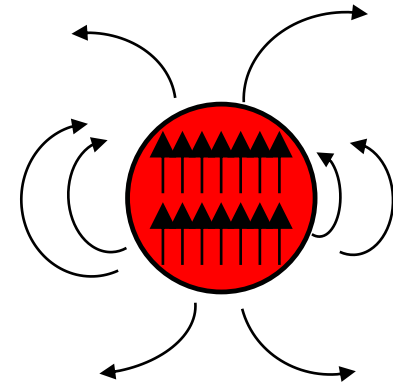
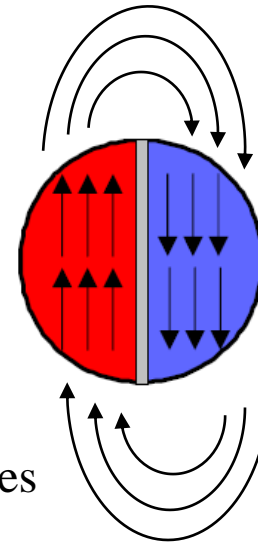


$$H_{exc} \ll kT$$



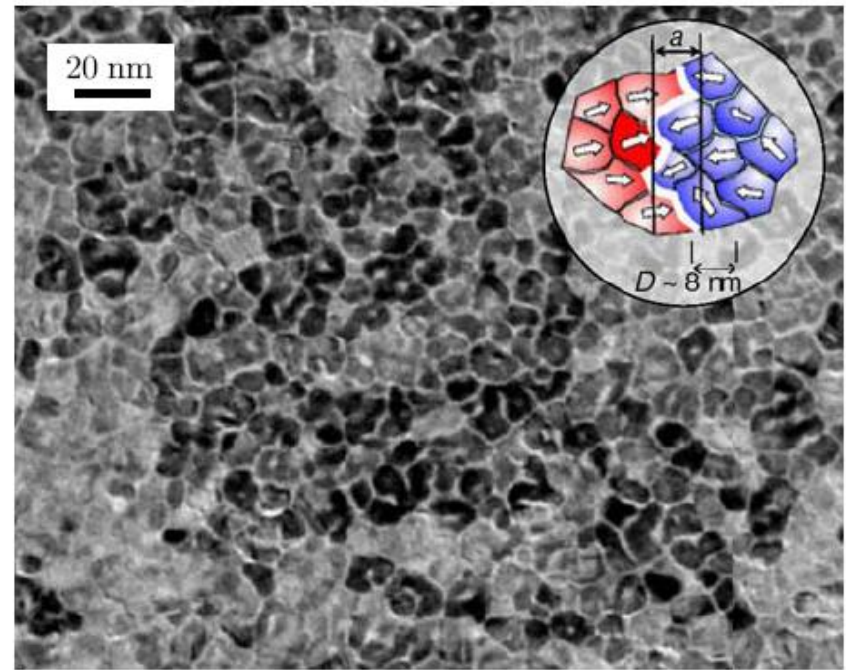
Coupling is destroyed and the net magnetic moment is zero

Domain formation -> cluster magnetic moment is strongly reduced

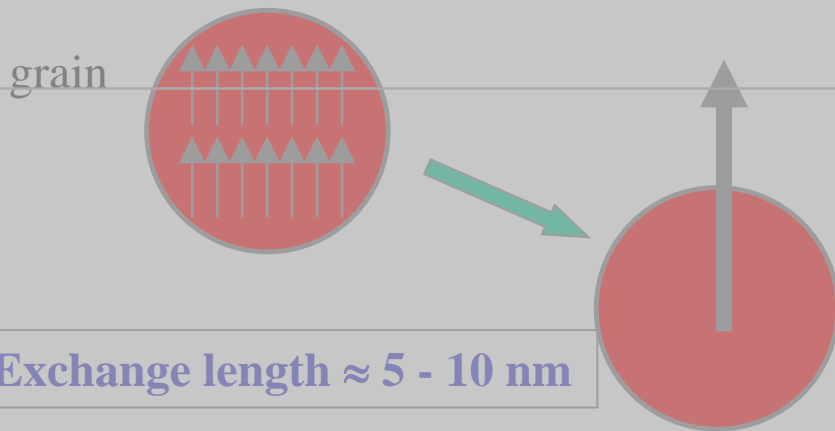


Gain in the **magnetostatic (shape) energy** at the expenses of the **exchange energy**

TEM images of the magnetic layer in a MRAM. Each bit is made of a few hundreds of grains



All spins (μ_i) in the grain are ferromagnetically aligned

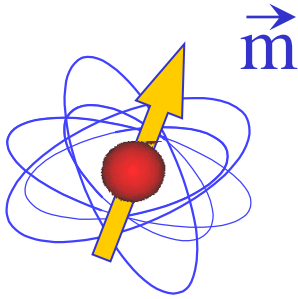


Exchange length $\approx 5 - 10$ nm

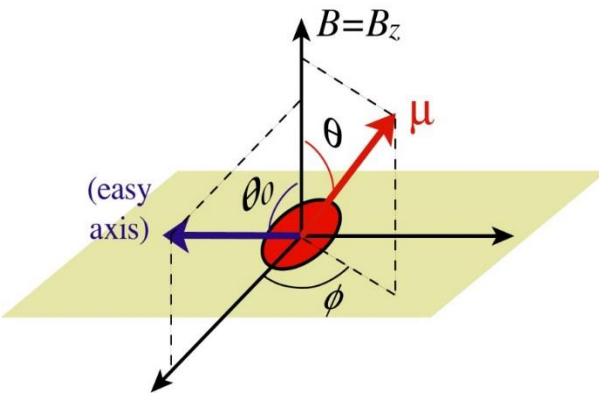
The grain (particle) can be described as a single **macrospin** $\mu = \sum_i \mu_i$

The macrospin direction change from grain to grain -> **magnetization easy axis (magnetic anisotropy)**

- To have a net signal (magnetization) in one direction we have to mean over several grains
- To write the bit we have to define (up or down) the magnetization direction

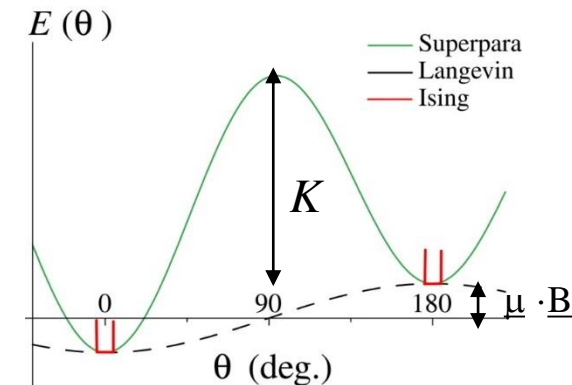


Free atom: the magnetic moment can point everywhere



Surface supported atom or cluster: due to the interaction with the neighbors the magnetic moment prefers to point along a specific direction

Magnetization along a defined axis:
easy magnetization axis



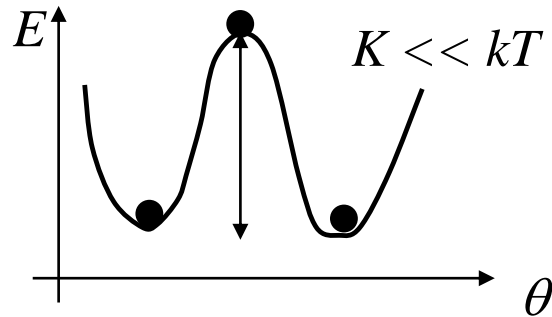
Magnetic anisotropy energy (MAE)

The MAE is the energy one needs to spend to reverse the magnetization (assuming a coherent magnetization reversal i.e. all spins turn at the same time)

$$E(\theta, \theta_0, \phi) = -\mu \cdot \mathbf{B} - K \cos^2(\text{easy} \cdot \mu)$$

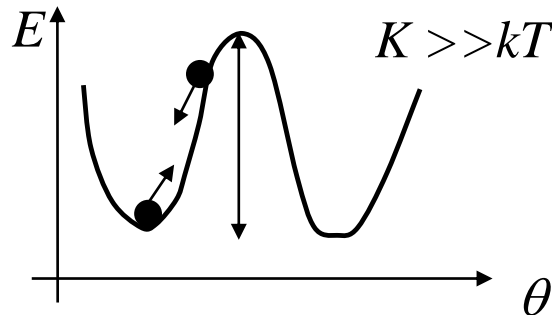
$B = 0$

$$E(\theta, \theta_0, \varphi) = -K \cos^2(\text{easy} \cdot \mu)$$



If $K \ll kT$ the magnetization vector isotropically fluctuates in the space.

Information can **not** be stored



If $K \gg kT$ the magnetization vector can not switch the versus

Information can be stored

Avg. time (relaxation time) taking to jump from one minimum to the other:

$$\tau = \tau_0 \exp(K/kT) \quad \tau_0 \approx 10^{-10} \text{s}$$

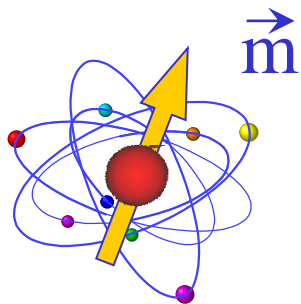
$\tau = 1 \text{ year}$	\longrightarrow	$K = 40 \text{ kT}$
$\tau = 1 \text{ second}$		$K = 23 \text{ kT}$

The MAE determines the thermal stability of the magnetization direction

Superparamagnetic limit: the particle MAE must be high enough to dominate the thermal fluctuations in order to be able to store information in the bit

**Intra-atomic exchange,
electron correlation effects:**

LOCAL (ATOMIC) MAGNETIC MOMENTS



d or *f* electrons

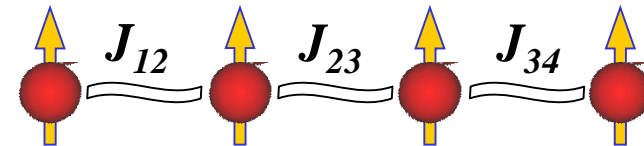


Hund's rules

Inter-atomic exchange:

MAGNETIC ORDER

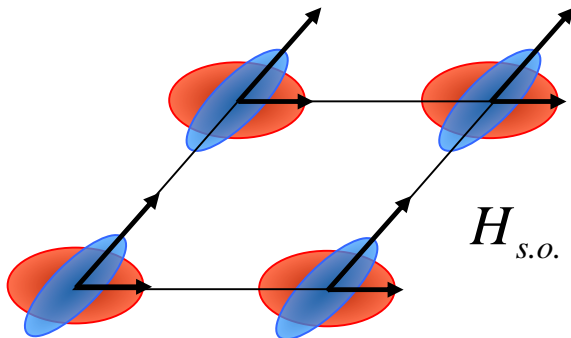
$$H_{exc} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



Spin-Orbit Coupling:

MAGNETOCRYSTALLINE ANISOTROPY:

K

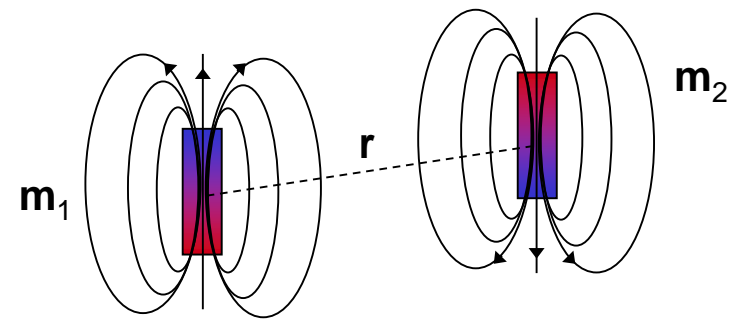


$$H_{s.o.} = \lambda \mathbf{L} \cdot \mathbf{S}$$

$$= \sum \xi \mathbf{s}_i \cdot \mathbf{l}_i$$

Dipolar Interaction:

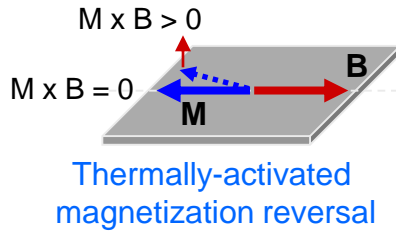
SHAPE ANISOTROPY



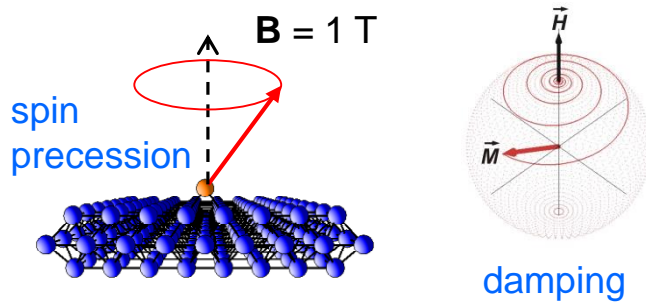
$$H_{dip} = \frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{r^3} - 3 \frac{(\mathbf{m}_1 \cdot \mathbf{r})(\mathbf{m}_2 \cdot \mathbf{r})}{r^5}$$

Time

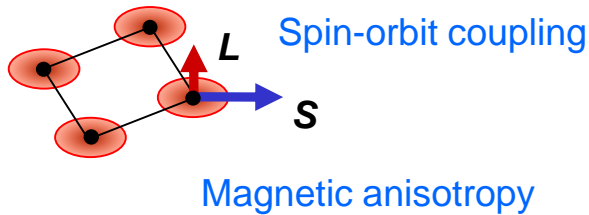
1 ns



100 ps



1 ps



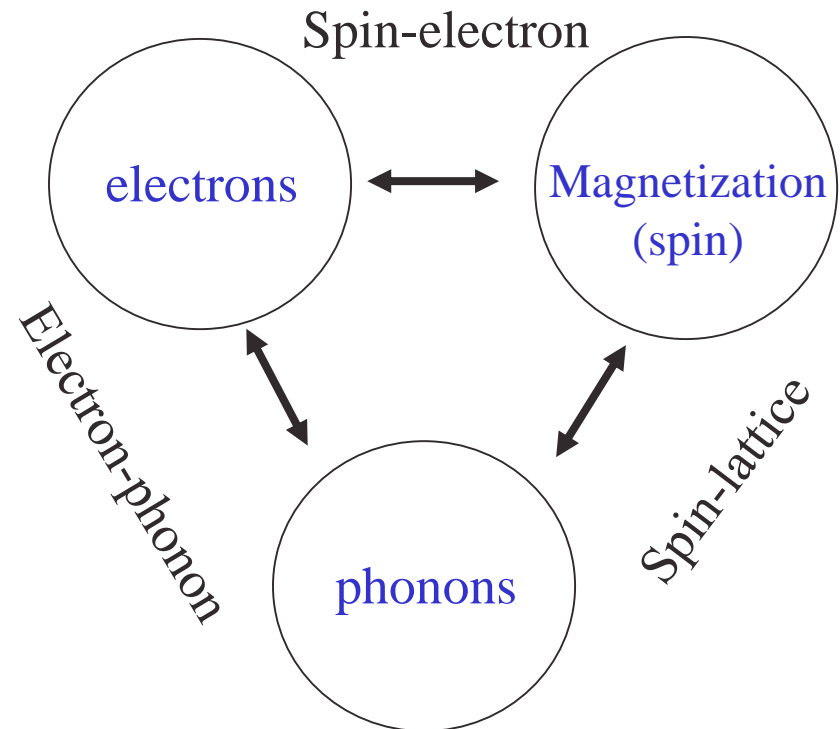
100 fs

10 fs

$t = \hbar/E$ where E is a characteristic energy

For example:
Spin-orbit coupling (SOC)
SOC = 10 meV
 $t = 100 \text{ fs}$

Interactions



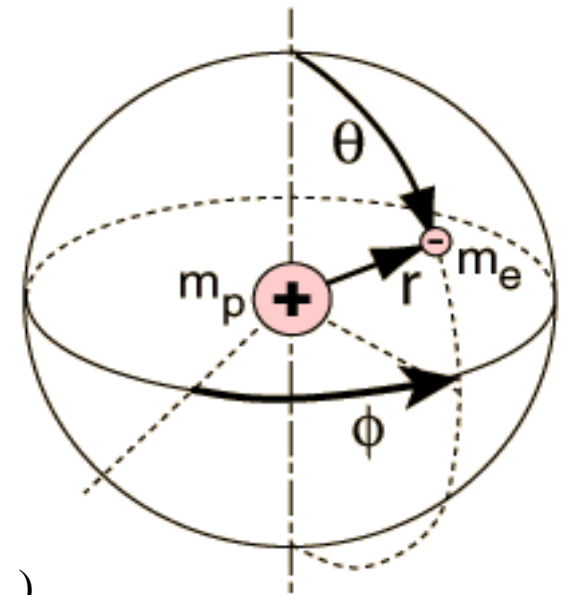
Not in this course

- [Stö06] -> J. Stöhr, and H.C. Siegmann, *Magnetism: from fundamentals to nanoscale dynamics* (Springer 2006)
- [Sko08] -> R. Skomski, *Simple models of Magnetism* (Oxford 2008)
- [Aha00] -> A. Aharoni, *Introduction to the theory of ferromagnetism* (Oxford university press 2000)
- [Plu01] -> M.L. Plumer, J. van Ek, and D. Weller, *The physics of ultra-high-density magnetic recording* (Springer 2001)
- [Bal62] -> C. J. Ballhausen, *Introduction to Ligand field theory* (McGraw-Hill 1962)
- [Fig00] -> B.N. Figgis, and M.A. Hitchman, *Ligand field theory and its applications* (Wiley-VCH 2000)
- [Bel89] -> G. M. Bell, and D. A. Lavis, *Statistical mechanics of lattice models* (Ellis Horwood limited 1989)

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

Example: the electron in a H atom $\rightarrow V_{\text{coulomb}} = -e^2/4\pi\epsilon_0 r$

In terms of the spherical coordinates r , θ , and ϕ the wave function takes the form $\Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$ 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.



- $R(r)$ \rightarrow principal quantum number $n = 1, 2, 3, \dots$ (K, L, M,..)
- $\Theta(\theta)$ \rightarrow orbital quantum number $l = 0, 1, 2, \dots, n-1$
- $\Phi(\phi)$ \rightarrow magnetic quantum number $m = -l, -(l-1), \dots, l-1, l$
- $\uparrow \downarrow$ \rightarrow spin quantum number $m_s = \pm 1/2$

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

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

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

Spin-orbit interaction:

Interaction of the spin of an electron with the magnetic field generated by its own orbital motion

Orbital magnetism:

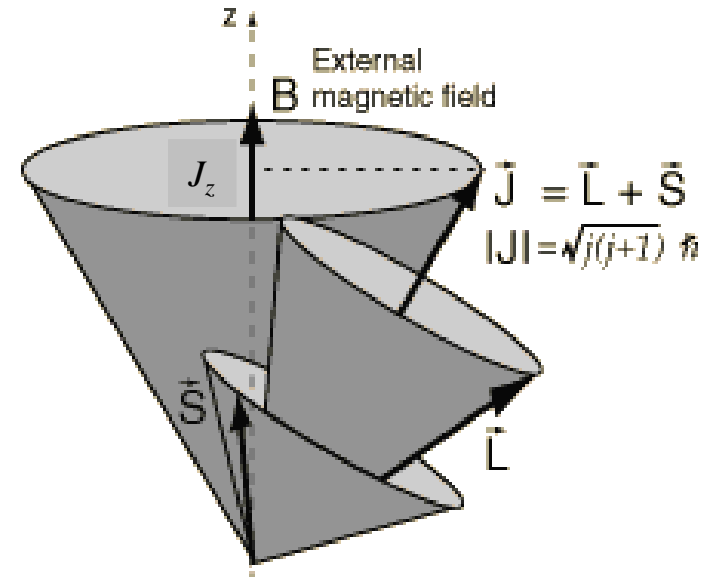
$$m_L = -L \mu_B$$

Spin Magnetism:

$$m_S = -g_e S \mu_B = -2 S \mu_B$$

Atomic magnetic moment:

$$m_{\text{at}} = -\mu_B (\mathbf{L} + g_e \mathbf{S})$$



The expectation value of \mathbf{m}_{at} in the field direction is

$$\begin{aligned} \mathbf{m}_J &= (1/B) \langle \text{LSJJ}_z | (\mathbf{m}_L + \mathbf{m}_S) \cdot \mathbf{B} | \text{LSJJ}_z \rangle = \\ &= m_B \langle \text{LSJJ}_z | \mathbf{L}_z + 2\mathbf{S}_z | \text{LSJJ}_z \rangle = \mu_B g_J \mathbf{J}_z \end{aligned}$$

$\mu_B \rightarrow$ Bohr magneton; $\mu_B = 0.058 \text{ meV/T}$; $g = 3/2 + [S(S+1) - L(L+1)] / (2J(J+1))$ is the Landé g-factor

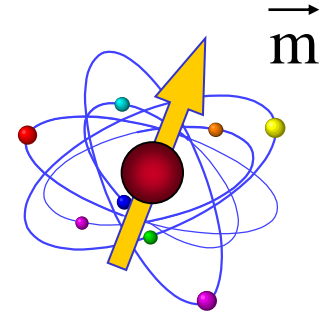
High magnetic field limit ($m_J B > \xi LS$): Paschen-Back effect

$$\begin{aligned} \mathbf{m}_{\text{at}} &= (1/B) \langle \text{LSM}_L \text{M}_S | -(\mathbf{m}_L + \mathbf{m}_S) \cdot \mathbf{B} | \text{LSM}_L \text{M}_S \rangle = \\ &= m_B \langle \text{LSM}_L \text{M}_S | \mathbf{L}_z + 2\mathbf{S}_z | \text{LSM}_L \text{M}_S \rangle = \mu_B (\mathbf{M}_L + 2\mathbf{M}_S) \end{aligned}$$

3d transition metals
 $\xi = 50 - 100 \text{ meV} \rightarrow B > 50 \text{ T}$

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:

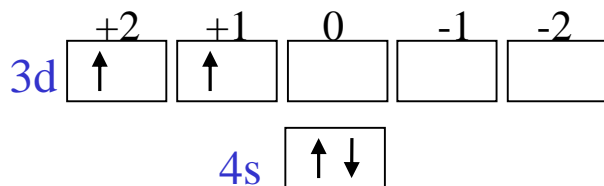
1) Total spin $S = \sum_i s_i$ maximized

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

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

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



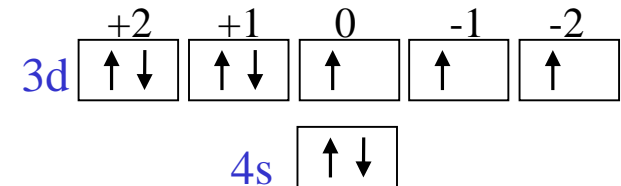
$$L = 3, S = 1, J = 2$$

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

$$m_S = g_e S \mu_B = 2 \mu_B,$$

$$m_{at} = g J \mu_B = 1 \mu_B$$

Ground state of Co ($3d^7 4s^2$)



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

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

$$m_S = g_e S \mu_B = 3 \mu_B,$$

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

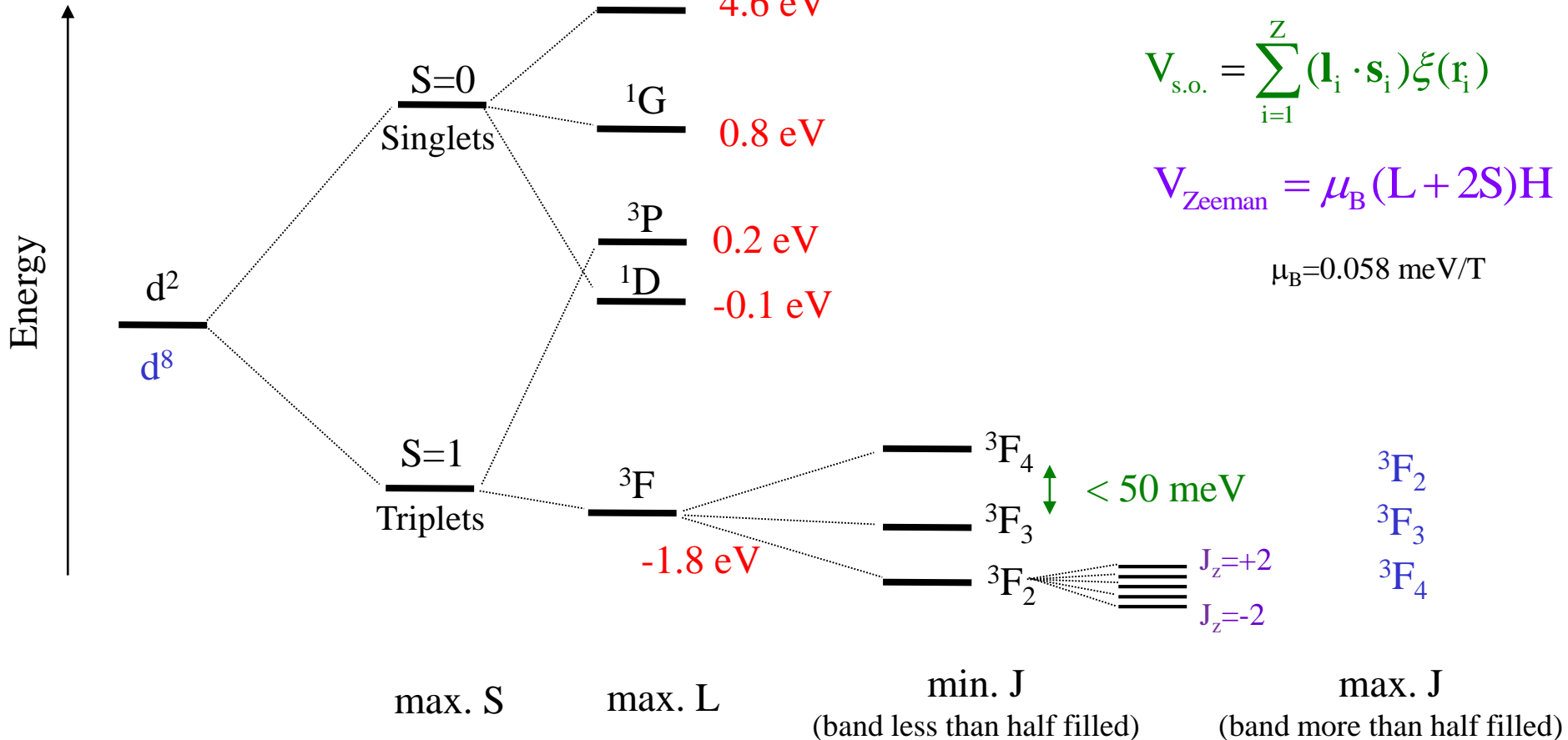
Energy spectrum (3d metals)

$$V_{e-e} = \sum_{i < j}^Z \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|^2}$$

$$V_{s.o.} = \sum_{i=1}^Z (\mathbf{l}_i \cdot \mathbf{s}_i) \xi(\mathbf{r}_i)$$

$$V_{Zeeman} = \mu_B (L + 2S) H$$

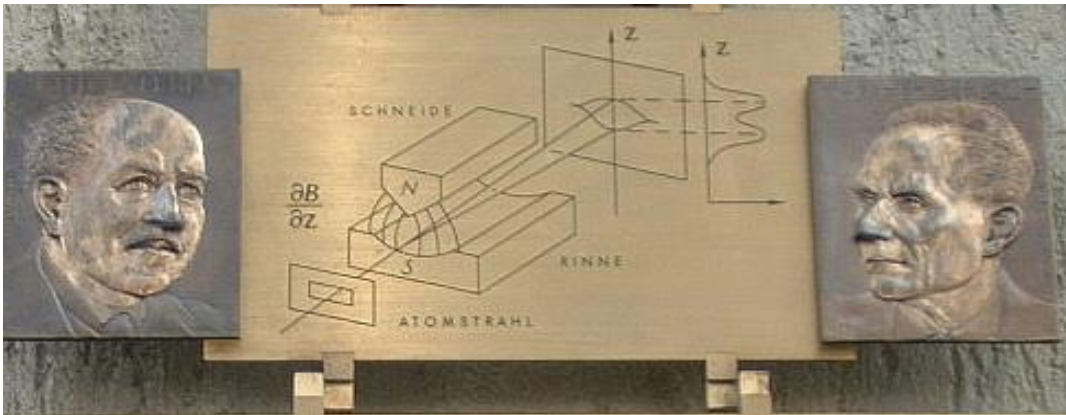
$$\mu_B = 0.058 \text{ meV/T}$$



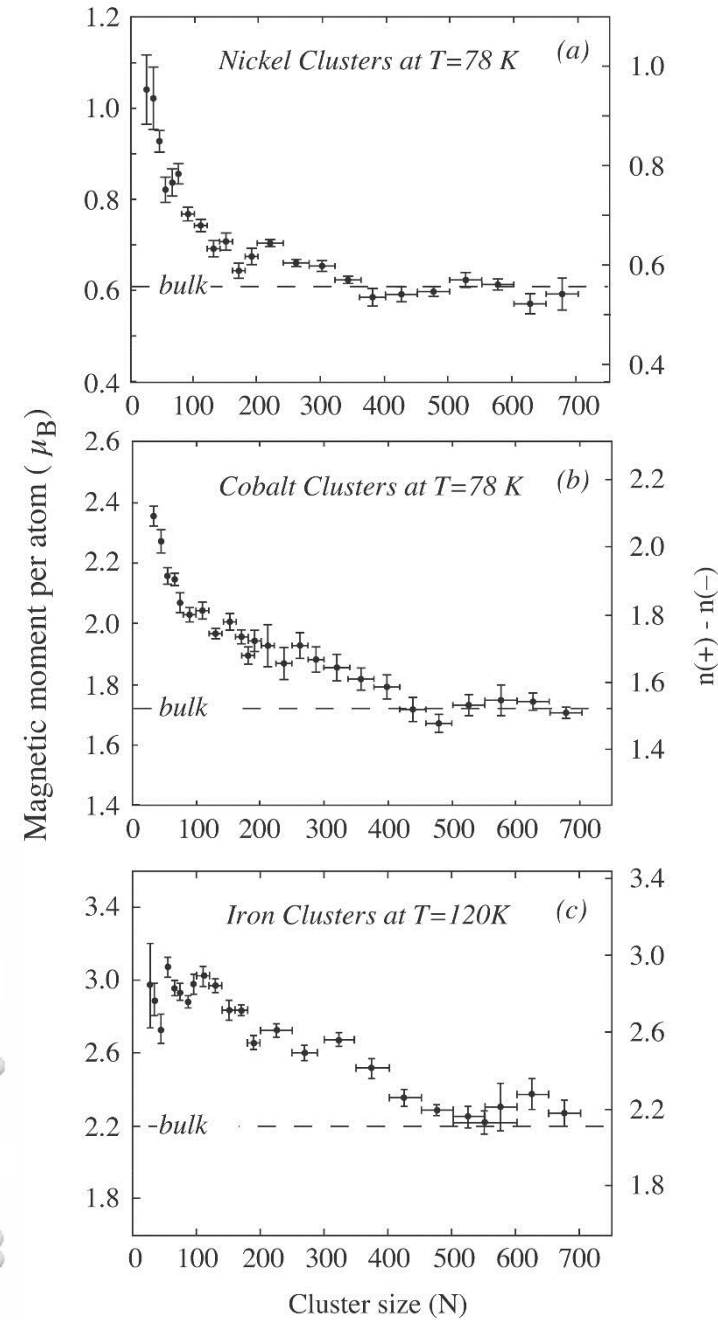
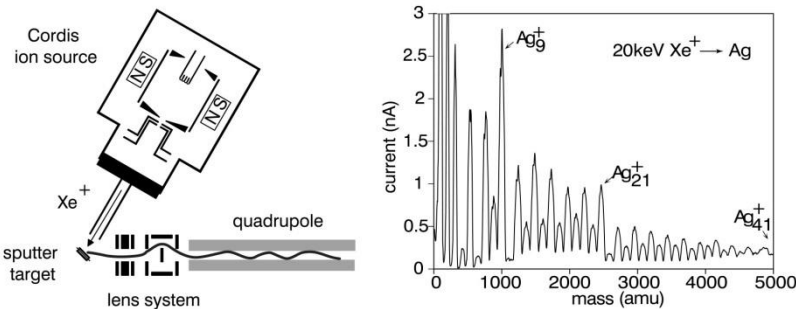
Multiplets terms: $^{2S+1}X_J$ with $X = S, P, D, F, G, H, I, \dots$ for $L = 0, 1, 2, 3, 4, 5, 6, \dots$

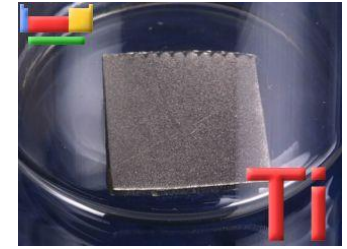
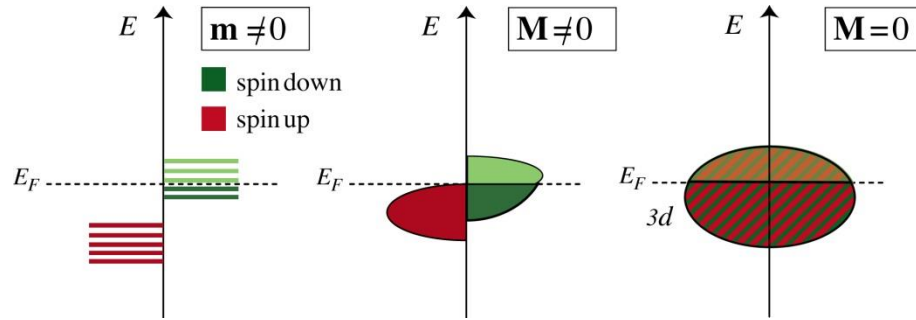
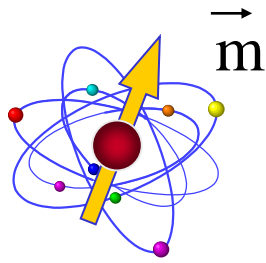
Stern-Gerlach experiment on Ag atoms

Ag: $4d^{10} 5s^1$ \rightarrow $L=0; S=1/2$

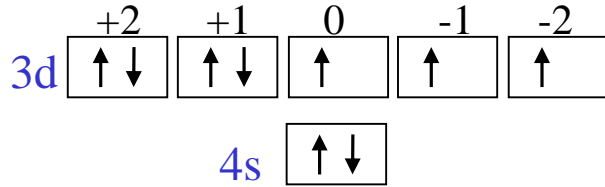


Stern-Gerlach experiment on clusters





Ground state of Co ($3d^7 4s^2$)



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

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

$$m_S = g_e S \mu_B = 3 \mu_B,$$

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

1) Band formation

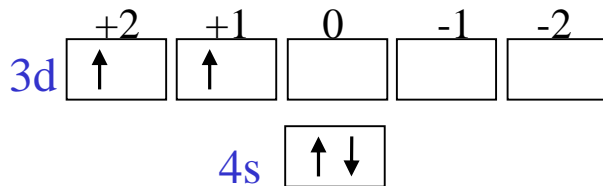
2) Crystal field

$$H = H_{atom} + H_{Field}$$

$$H_{Field} = -e\phi(r)$$

The crystal electric field produced by surrounding ions in a solid defines a particular set of (real) **wave-functions** for which the mean value of the orbital moment is zero

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



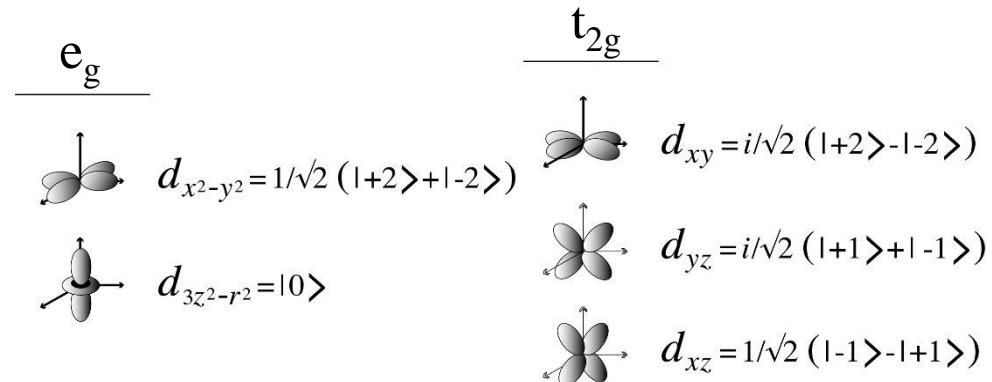
$$L = 3, S = 1, J = 2$$

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

$$m_S = g_e S \mu_B = 2 \mu_B,$$

$$m_{at} = g J \mu_B = 1 \mu_B$$

d wave-functions in cubic symmetry $\rightarrow L \approx 0$

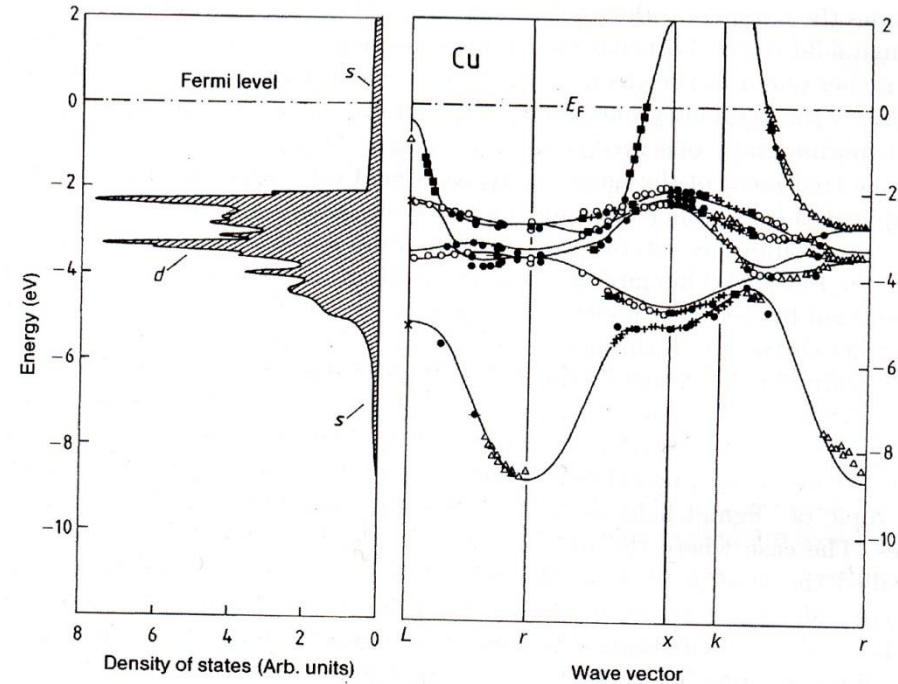
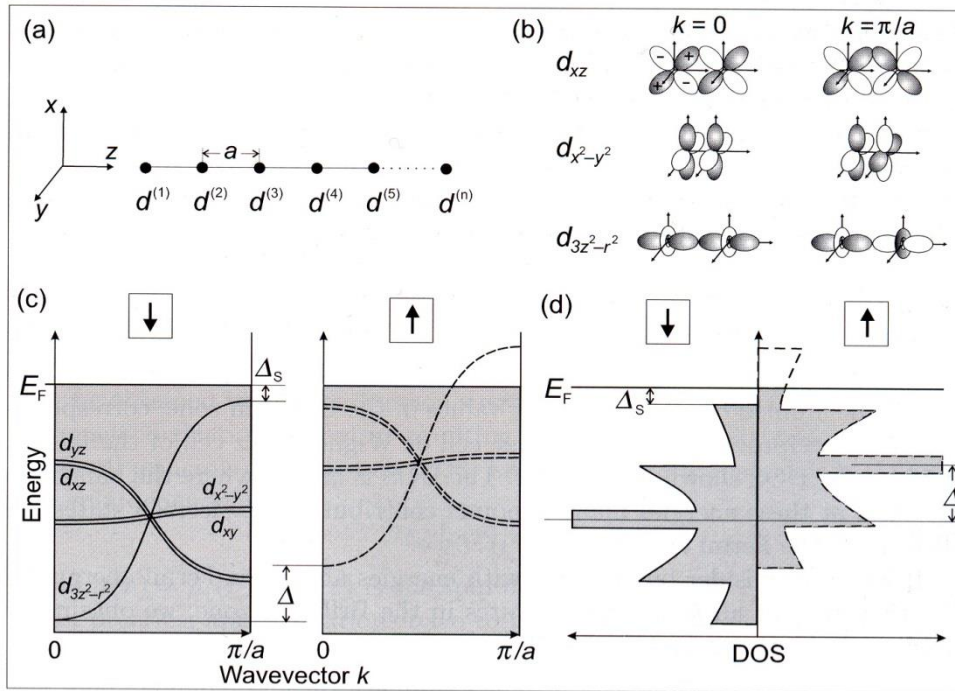


The periodic potential of a crystal breaks up the atom states and redistributes the valence electrons in Bloch states \rightarrow the quantum numbers nlm are replaced by the band index n and the wave vector k (and of course the spin)

[Stö06]

Ideal chain

Cu crystal



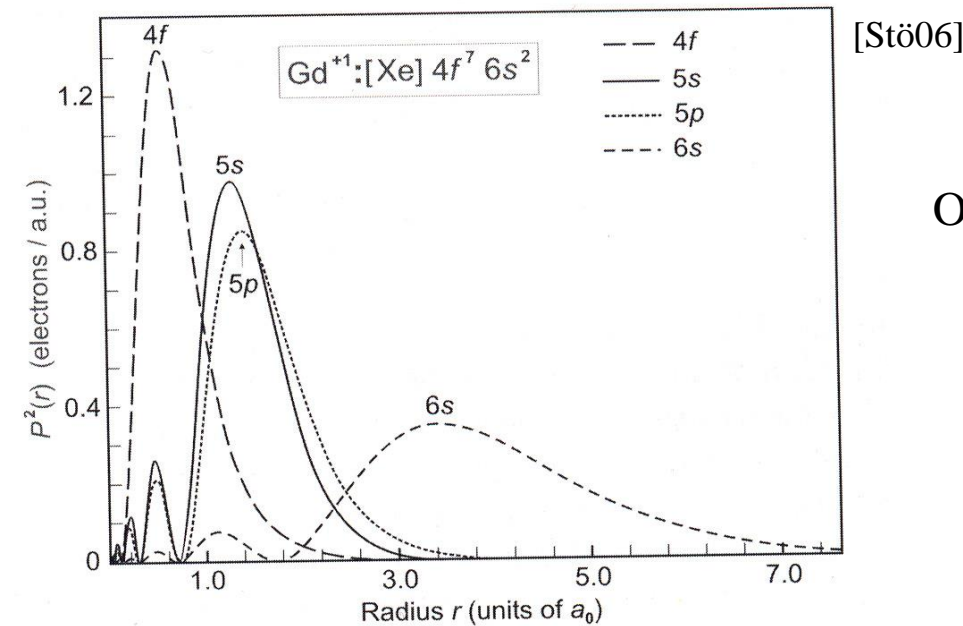
In band theory combining orbitals on different atoms corresponds to the formation of Bloch functions which, for the case of a linear chain of n atoms, are written as:

$$\phi_j(\mathbf{k}) = \sum_n d_j(n) e^{i\mathbf{k}\cdot n\mathbf{a}}$$

$$d_j = d_{xy}, d_{xz}, d_{x^2-y^2}, \dots$$

For $k=0$ $\phi_j(0) = \sum_n d_j(n)$

For $k=\pi/a$ $\phi_j(\pi/a) = \sum_n d_j(n) e^{i\pi n} = \sum_n (-1)^n d_j(n)$

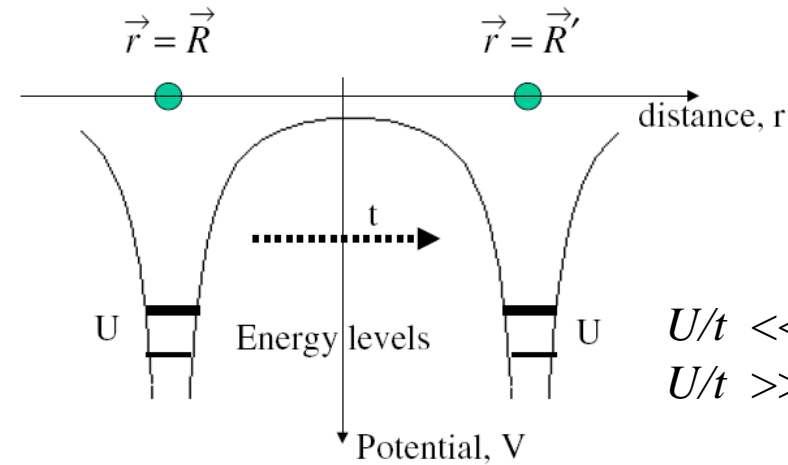


Only the external 6s electrons are delocalized but they contribute only marginally to the Gd magnetism !!!!!

Magnetism quantum theory has been developed from two opposite starting points:

- a) **The localized model:** each electron remains localized or correlated with a determined atom. The **intra-atomic $e^- - e^-$ interactions are large** and determine the magnitude of the localized magnetic moment on each lattice site. In contrast, the inter-atomic $e^- - e^-$ interactions are much smaller and compete with the thermal disorder to establish the magnetic ordering
- b) **The band model (itinerant):** each magnetic carrier is itinerant through the solid (due to the wave function overlapping), moving in the average potential of the other electrons and ions. In this case, the electron levels form energy bands and the weak $e^- - e^-$ interactions stabilize the ordered magnetic moments

f states in rare earth are well localized but d states in metals are poorly localized !!!!!!



U -> coulomb repulsion for electrons on the same atoms
 t -> hopping energy

$U/t \ll 1$ -> independent and delocalized electrons
 $U/t \gg 1$ -> localized electrons

$$H_{\text{Hub}} = -t \sum_{\sigma=\uparrow\downarrow} (c_{1\sigma}^* c_{2\sigma} + c_{2\sigma}^* c_{1\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow})$$

Hopping from atom 1 to atom 2
 conserving the spin

Coulomb repulsion U of electrons with opposite spin on the same atom

$c_{i\sigma}^*$ creates an electron with spin σ on atom i

$n_{i\sigma}$ gives the number of electron with spin σ on atom i

example

The Hubbard model for the hydrogen molecule

The Anderson impurity model describes a localized state, the 3d-state, interacting with delocalized electrons in a conduction band.

Ground state Ψ_0 and operators a^+ annihilate or a create a specific electron.

For example, an electron can hop from the 3d-states to a state in the (empty) conduction band, i.e. $|\Psi_0 a_{3d}^+ a_{ck}\rangle$, where a_{ck} indicates an electron in the conduction band with reciprocal-space vector k .

$$H_{\text{AIM}} = \varepsilon_{3d} a_{3d}^\dagger a_{3d} + U_{dd} a_{3d}^\dagger a_{3d} a_{3d}^\dagger a_{3d} + \sum_k \varepsilon_{vk} a_{vk}^\dagger a_{vk} + t_{v3d} \sum_k (a_{3d}^\dagger a_{vk} + a_{vk}^\dagger a_{3d})$$

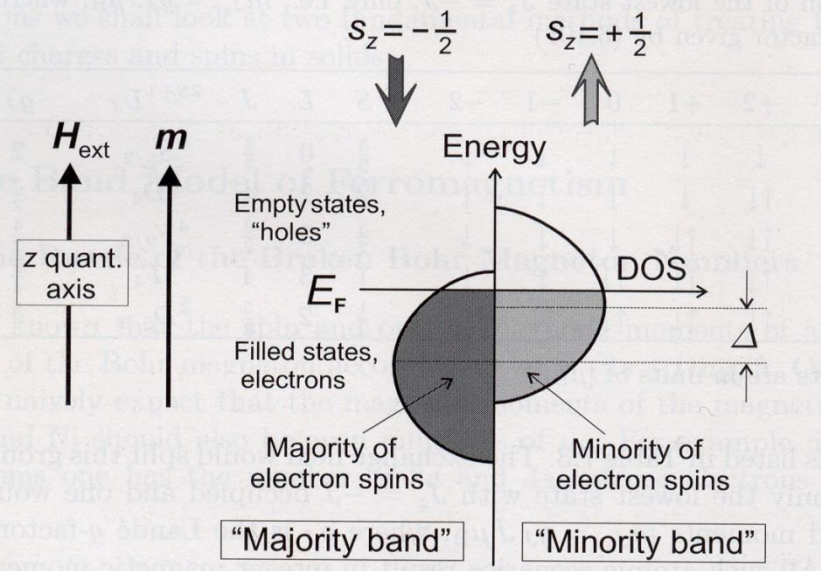
These four terms represent, respectively, the 3d-state, the correlation of the 3d-state, the valence band and the coupling of the 3d-states with the valence band

Coordination Chemistry Reviews 249 (2005) 31–63

Review

Multiplet effects in X-ray spectroscopy

Stoner model for 3d band and nomenclature



Stoner Exchange interaction Δ :

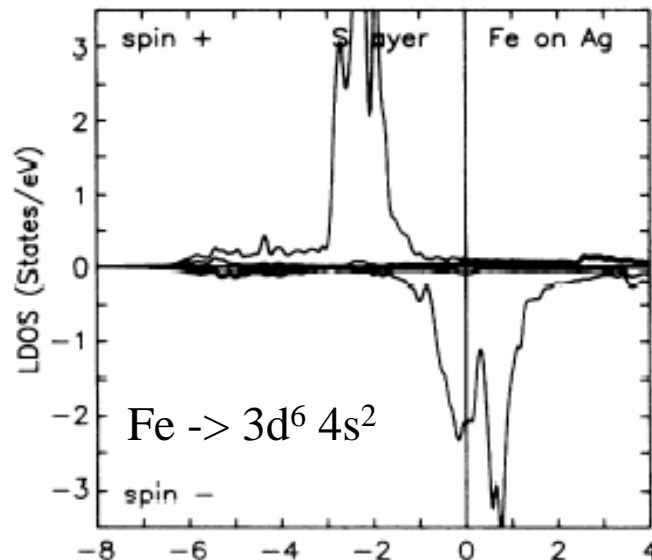
Is the energy necessary to reverse the spin of one electron in the sea of all the other electrons \rightarrow spin up – spin down bands are shifted by $\Delta = 1-2$ eV

$$\langle s_z \rangle = \frac{\hbar}{2} (N_e^\uparrow - N_e^\downarrow)$$

$$s_z^\uparrow = +\frac{\hbar}{2}; \quad s_z^\downarrow = -\frac{\hbar}{2}$$

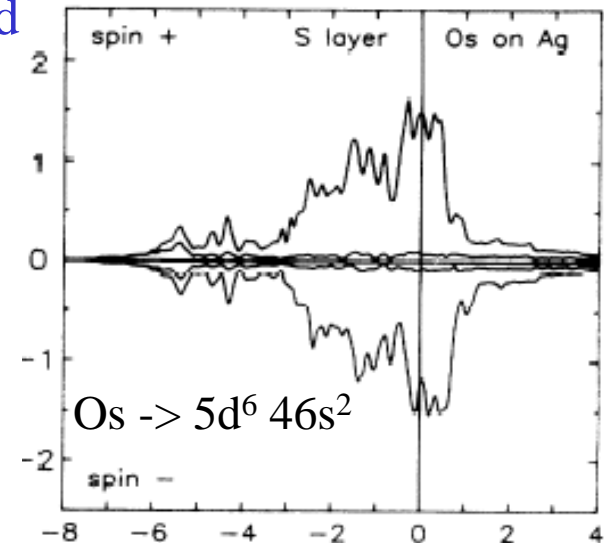
$$|m| = -2\mu_B \langle s_z \rangle / \hbar$$

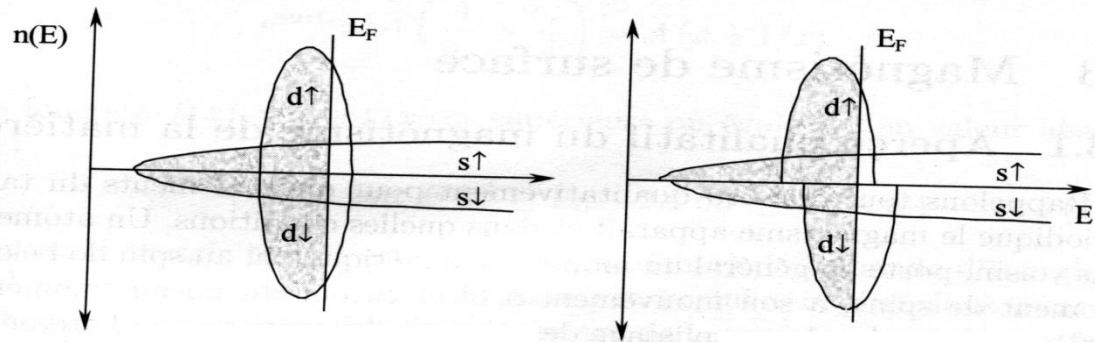
Fe is magnetic



Os is non-magnetic

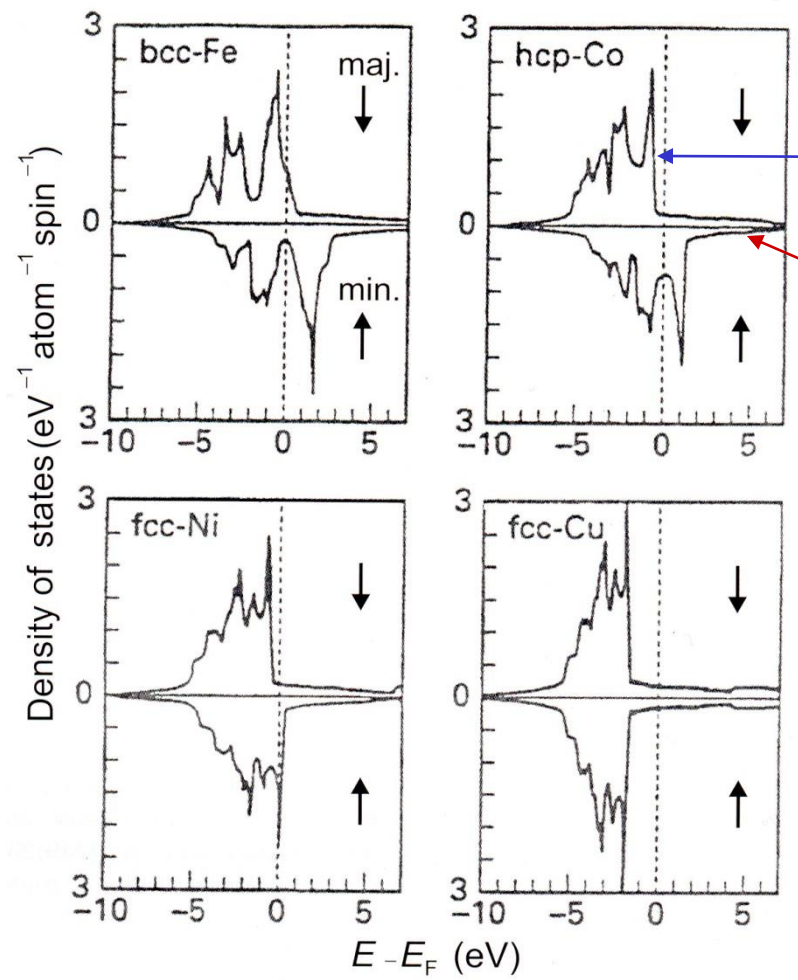
d-band





non magnetic state

Magnetic state

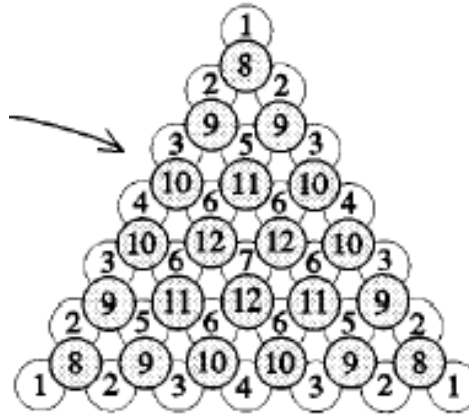


d band

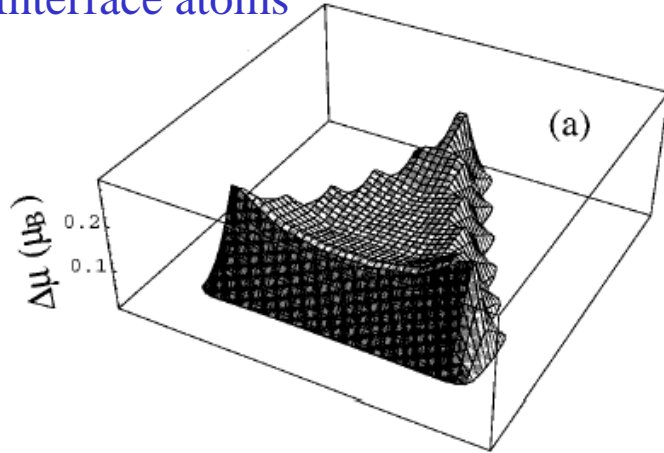
s band

- s, p bands are extended (band width about 10 eV)-> contribute by about 5%
- d bands are narrow (band width about 3 eV)-> their splitting determines the magnetism

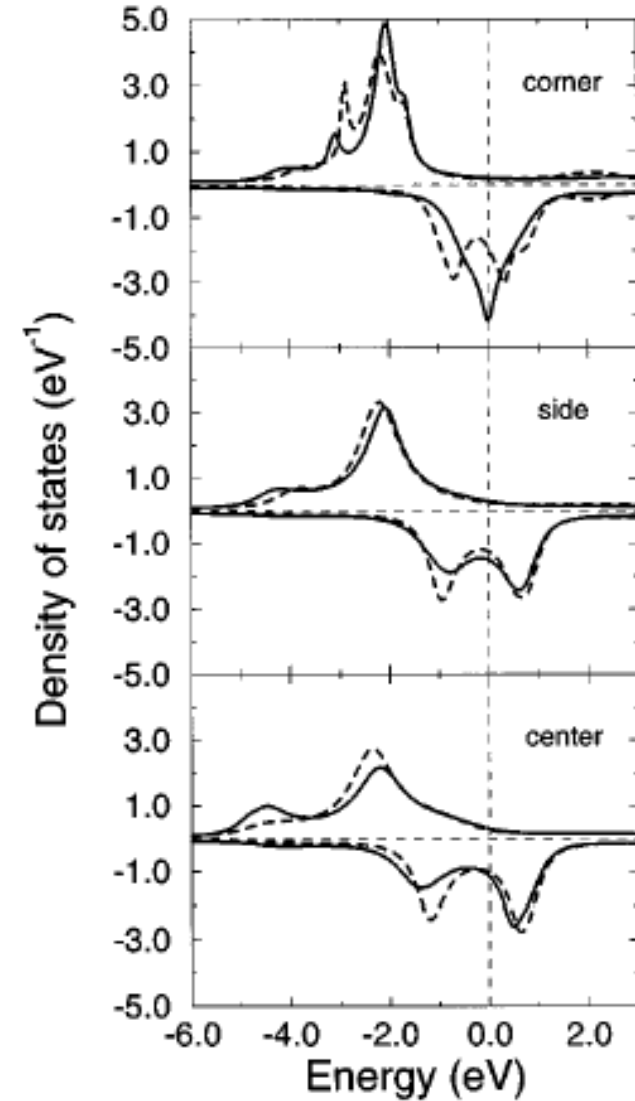
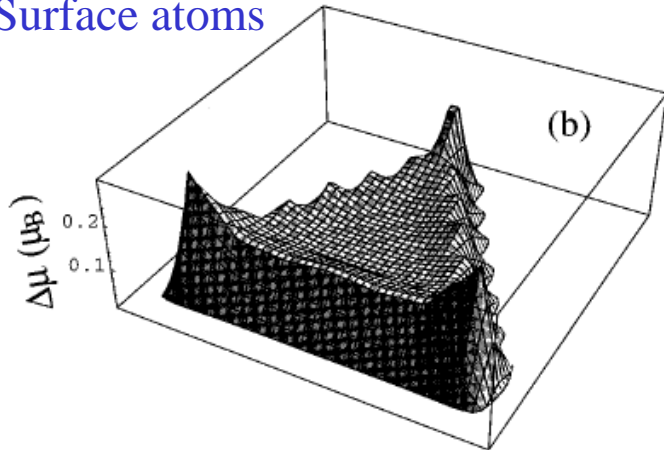
Two atomic layer high Co island
on Cu(111)



Interface atoms

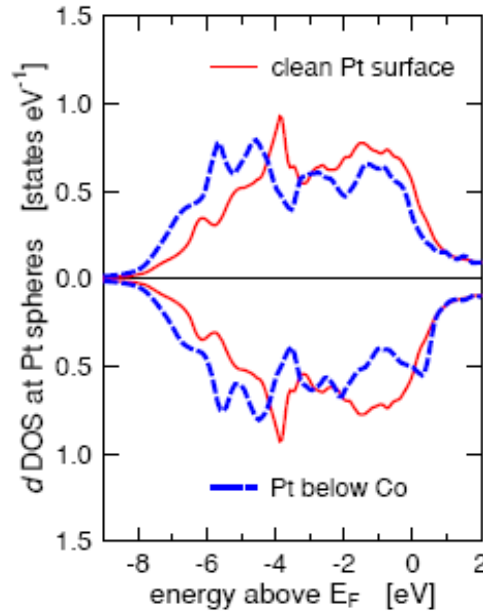
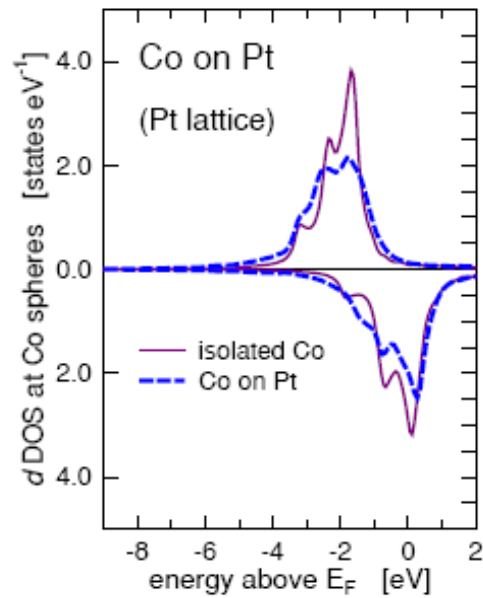


Surface atoms

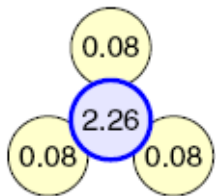


The magnetic moment of the atoms in the island
depends on the local coordination

Co monomer interaction with the substrate



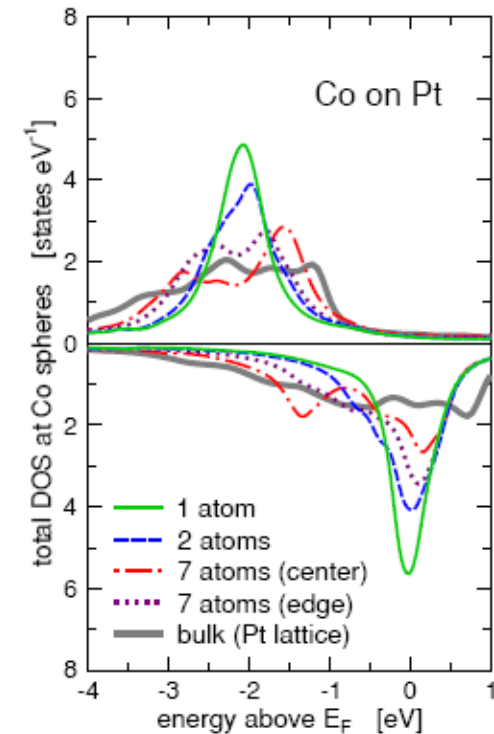
Asymmetry in the Pt LDOS at E_F when covered by Co \rightarrow induced magnetic moment in the Pt(111)



● Co atom
● Pt atom

Size dependence

Reduced asymmetry by increasing the cluster size \rightarrow reduced magnetic moment



The interaction of the atomic electronic shell with the surrounding atoms (crystal field) locks the atomic orbital moment to the crystal structure (symmetry)

In the ligand (crystal) field theory the effect of the surrounding atoms is described by an effective potential (localized electrons)

$$H_{CF} = H_{atom} + H_{Field}$$

$$H_{Field} = -e\phi(r)$$

For example for an octahedral crystal field we get

$$\phi(r) = \sum_{i=1}^6 eZ_i / r_i$$

H_{Field} can be developed in series of the spherical harmonics -> because H_{Field} does not depend on the spin, the 3d wave functions (or a linear combination of them) are eigenfunctions of H_{CF}

In general, the way in which H_{Field} is treated depends on the element

$$H_{field} < \lambda LS < V_{e-e}$$

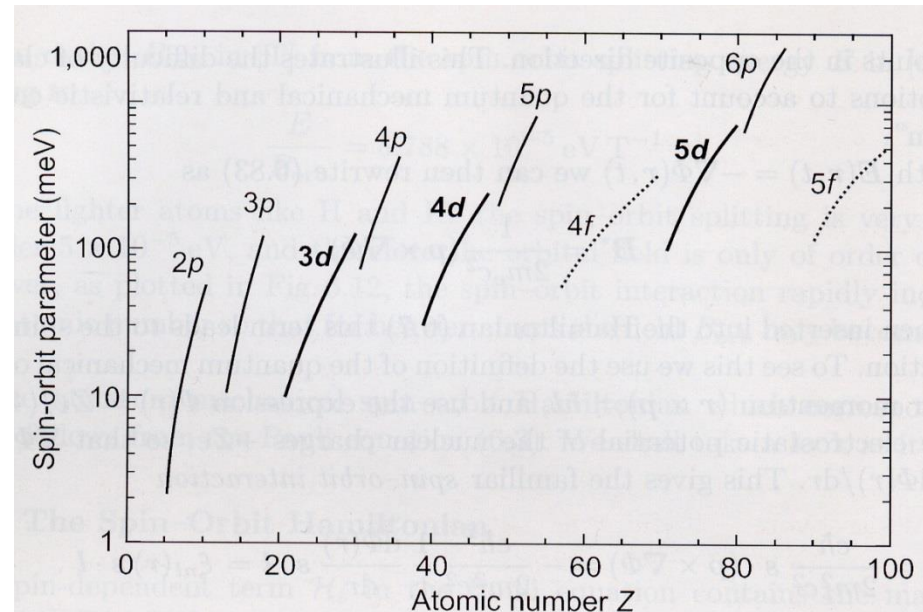
Rare earths

$$\lambda LS < H_{field} < V_{e-e}$$

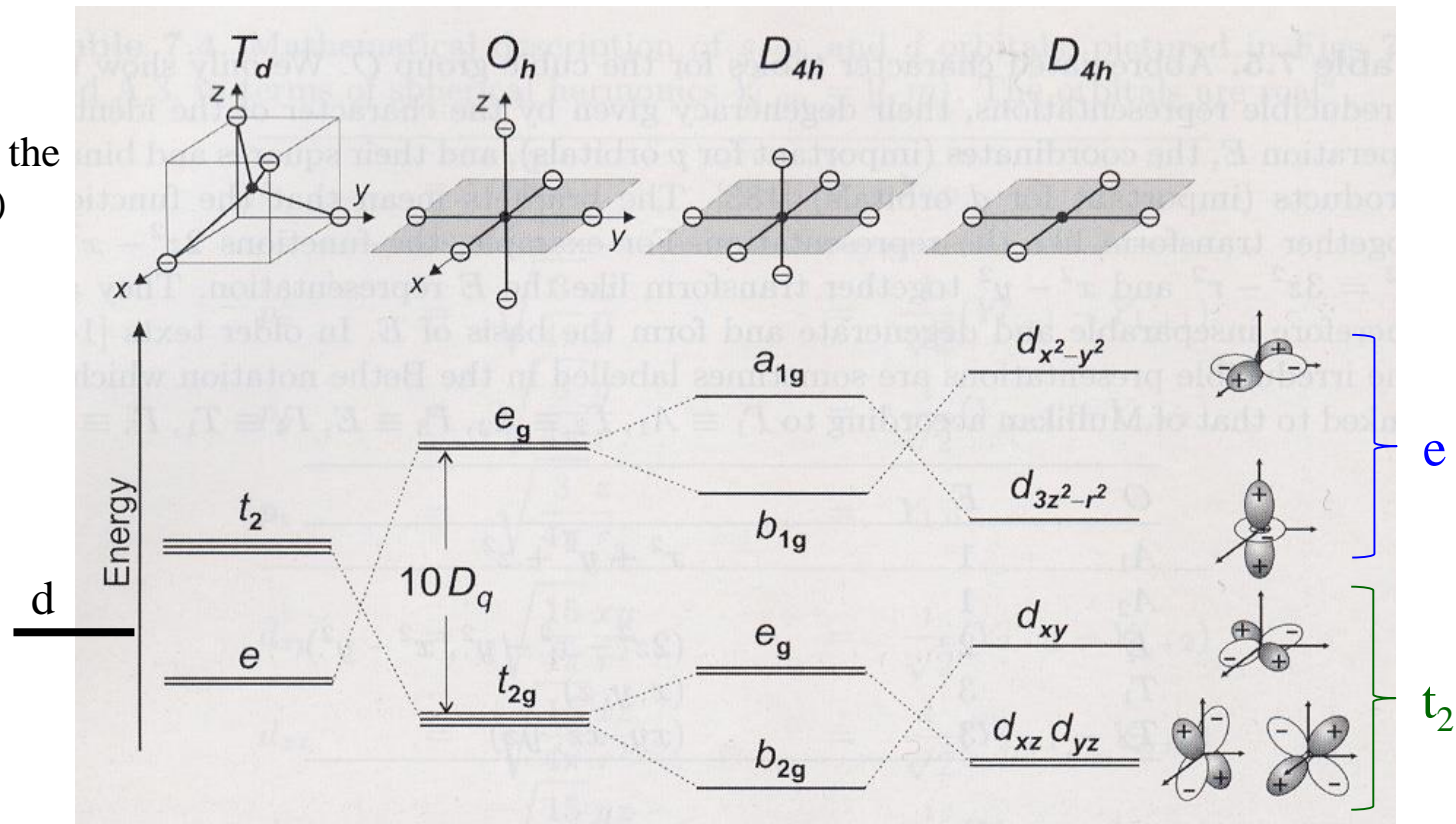
Transition metals 3d

$$\lambda LS < V_{e-e} < H_{field}$$

metals 4d-5d



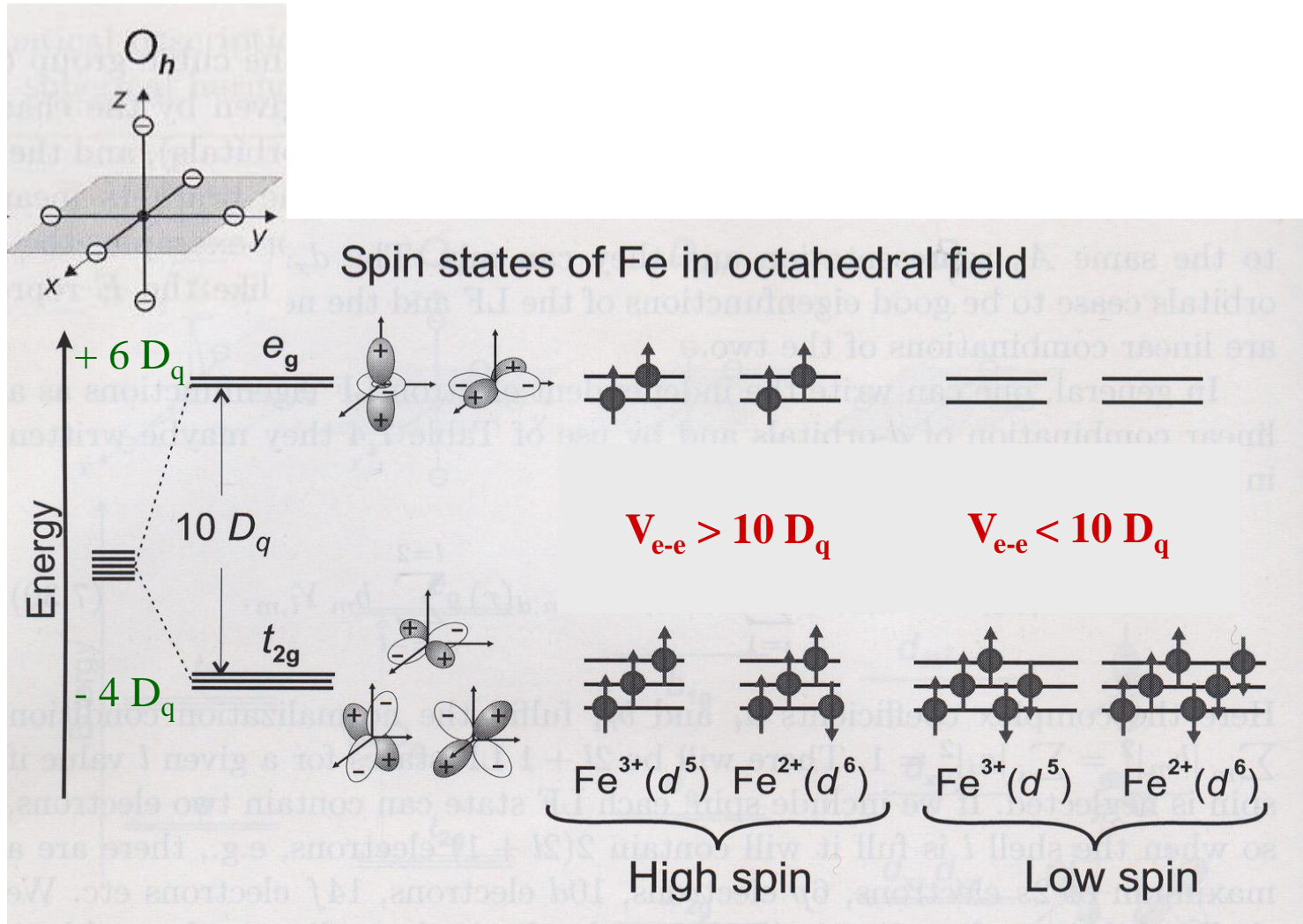
$10D_q$ gives the strength of the CF (historical notation)



Qualitative arguments: the central atom orbitals pointing toward the ligand positions are higher in energy than those orbitals avoiding the ligand positions (Coulomb repulsion).

The t_{2g} orbitals point towards the centres of the cube faces while the e_g orbitals point towards the centres of the cube edges.

In T_d symmetry the latter points are closer to the ligands by a factor $\sqrt{2}$



The orbital occupation (and then the spin S) depends on the relative strength of the electron-electron interaction V_{e-e} and the crystal field $10 D_q$

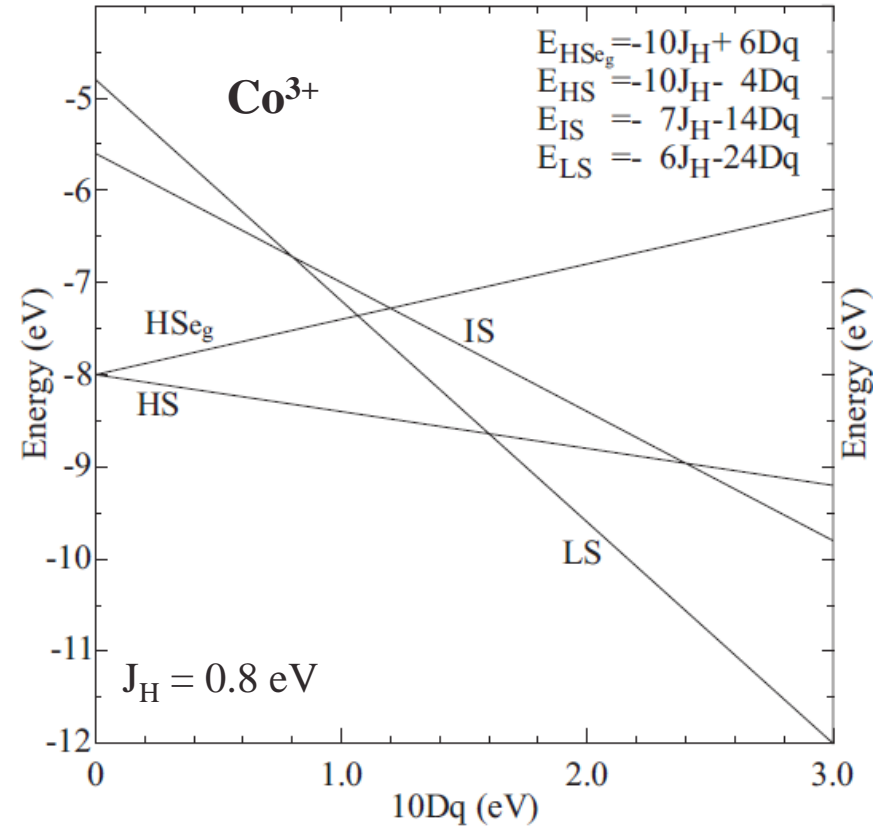
The simplest approximation to describe the electron-electron interaction:

- U is the repulsive Coulomb energy between each pair of electrons
- J_H is the attractive Hund's rule exchange interaction between each pair of electrons with parallel spin (1st Hund's rule).

For high CF the low spin state becomes favorable

	Low Spin	Intermediate Spin	High Spin
Co⁴⁺ d⁵	$S=1/2$ 	$S=3/2$ 	$S=5/2$
Co³⁺ d⁶	$S=0$ 	$S=1$ 	$S=2$
Co²⁺ d⁷	$S=1/2$ 		$S=3/2$

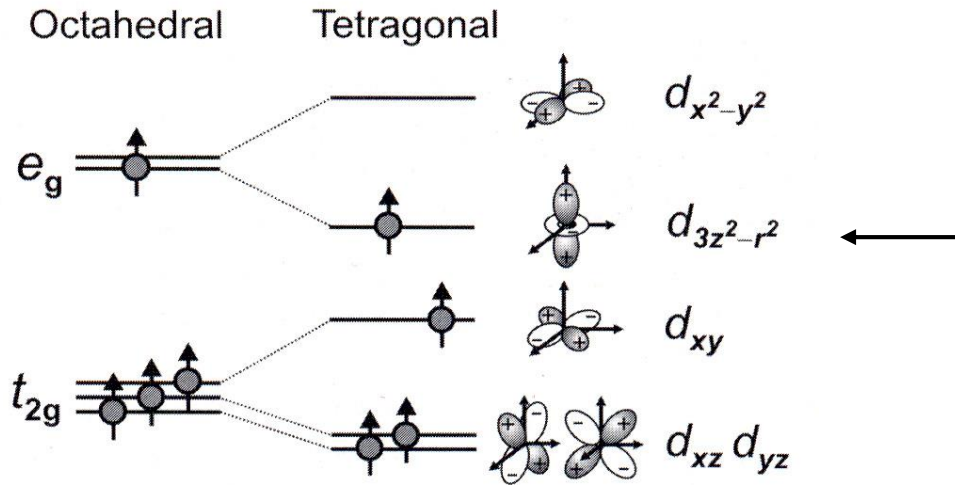
Possible valences and spin states of the Co ion in octahedral symmetry. The d shell is split into a t_{2g} and e_g sub-shell.



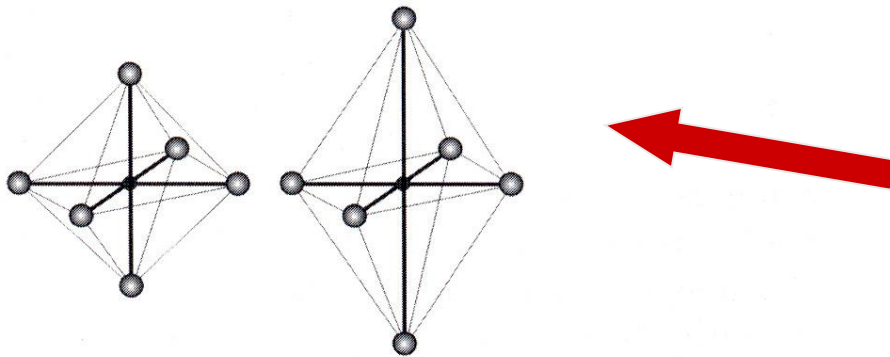
- HS -> 10 electron pairs ($-10 J_H$), 2 electrons in e_g ($+2 \cdot 6D_q$) and 4 electrons in t_{2g} ($-4 \cdot 4D_q$) -> $E_{HS} = -10 J_H - 4D_q$
- LS -> 2 times (up and down) 3 electron pairs ($-6 J_H$), and 6 electrons in t_{2g} ($-6 \cdot 4D_q$) -> $E_{LS} = -6 J_H - 24D_q$

The electron-electron repulsion energy is U times the number of electron pairs found minus J_H times the number of pairs of electrons with parallel spin

Jahn-Teller effect for $Mn^{3+} (d^4)$



This orbital reduces the energy because it is pointing toward the oxygen atoms



Mn^{3+} in the centre of an oxygen octahedron

The system lower the total energy by a tetragonal distortion

Material	N holes	m_s^{tot}	m_s^{d}	m_s^{sp}	m_{orb}
Fe	3.4	2.19	2.26	-0.07	0.09
Co	2.5	1.57	1.64	-0.07	0.14
Ni	1.5	0.62	0.64	-0.02	0.07

	$n_{3d}+n_{4s}$	$n_{3d}(\downarrow)$	$n_{3d}(\uparrow)$	$n_{4s}(\downarrow)$	$n_{4s}(\uparrow)$	$h_{3d}(\downarrow)$	$h_{3d}(\uparrow)$	$m (\mu_B)$
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 \downarrow and \uparrow bands for 3d elements (n – electrons, h – holes)

- Qualitative argument: in an isolated atom, the electrons can freely rotate about the core \rightarrow the orbital moment arises from this processional motion (Y_1^m) \rightarrow bond formation stops the processional motion

- Formal argument: the orbital moment associated to the d orbitals is zero

For ex.: $d_{xz} = 2^{-1/2} (Y_2^{-1} - Y_2^{+1})$ or $d_{yz} = i 2^{-1/2} (Y_2^{-1} + Y_2^{+1})$

However $\int d_{xz}^* L_z d_{yz} d\tau = \hbar$; $\int d_{xy}^* L_z d_{x^2-y^2} d\tau = 2\hbar$

A rotation by $2\pi/8$ about the z axis transforms $d_{x^2-y^2}$ in d_{xy} (and vice versa), and a rotation of $2\pi/4$ transforms d_{xz} in d_{yz} . $d_{3z^2-r^2}$ cannot be transformed in any other orbitals by a rotation about the z axis, thus no contribution to orbital moment in z direction

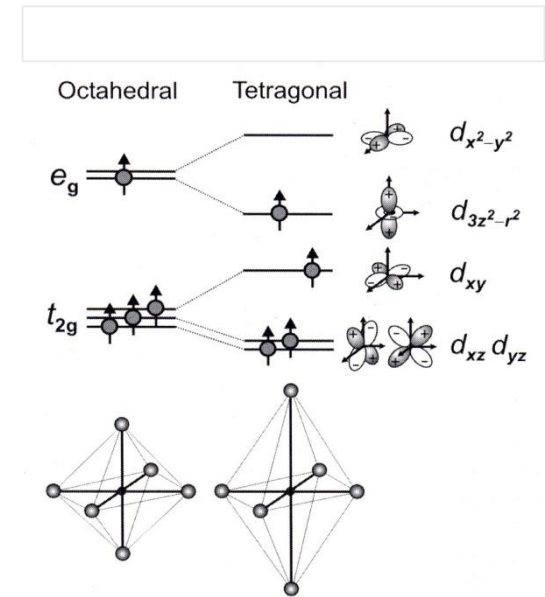
Orbital moment is associated to transformation by rotation of pairs of orbitals. This holds only if:

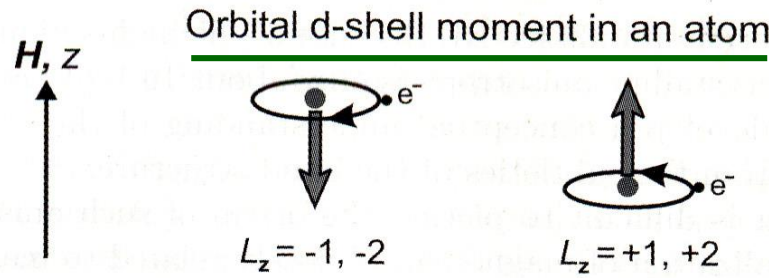
- a) the two states of the pair are degenerate
- b) There must not be an electron in the second orbital with the same spin as that in the first orbital

Ex:

- in the tetrahedral or octahedral symmetry the $d_{x^2-y^2}$ in d_{xy} are split and hence do not contribute to the orbital moment (as a consequence of point a)

- in octahedral symmetry the $3d^3$ or $3d^5$ configurations have $L=0$ (as a consequence of point b one can not rotate d_{xz} onto d_{yz})



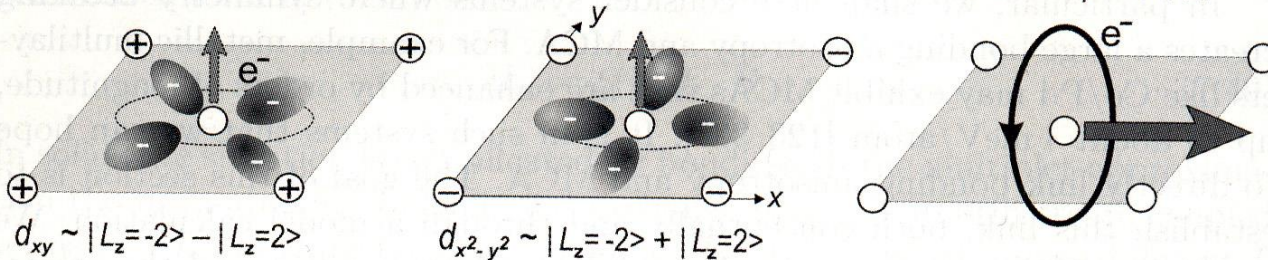


Qualitative argument

Orbital d-shell moment in a thin layer

In-plane orbits are quenched,
d-orbitals are formed

Out-of-plane orbits
are less perturbed



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

- **d electron in a free atom.** For an external magnetic field aligned along z the lowest energy state is $L_z = -2$.

- **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) -> The out-of-plane orbital moment is quenched

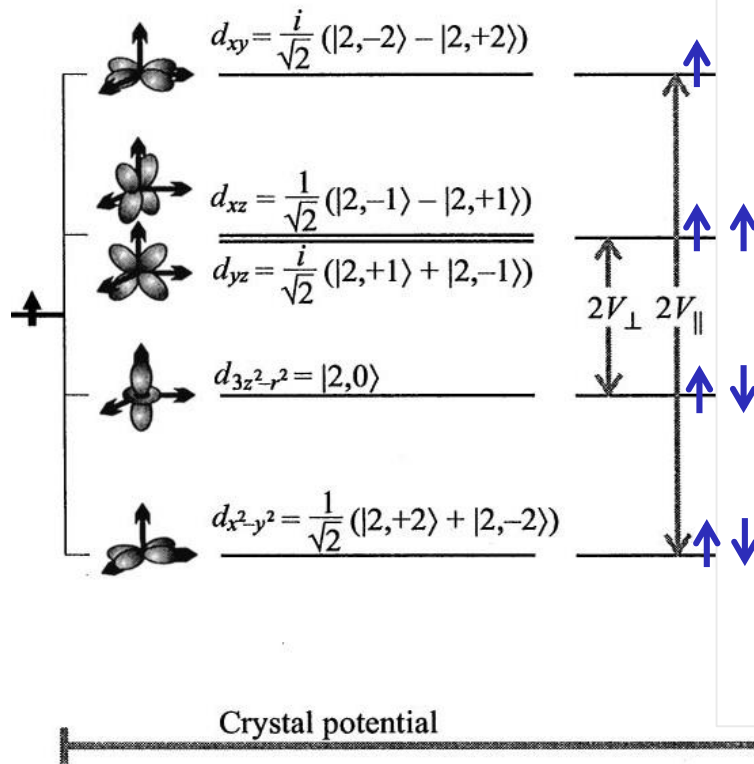
b) The orbital motion perpendicular to the bonding plane is less perturbed by the bonds -> in-plane orbital moment will stay unquenched -> **symmetry breaking implies anisotropic orbital moments**

- **The spin moment S is isotropic.** However, due to the spin-orbit coupling the spin moment is locked to the spatial direction along which L is maximum -> **easy axis**

Example: Co monolayer on Cu(100)

Co is a transition metal with electronic configuration given by $4s^2 3d^7$

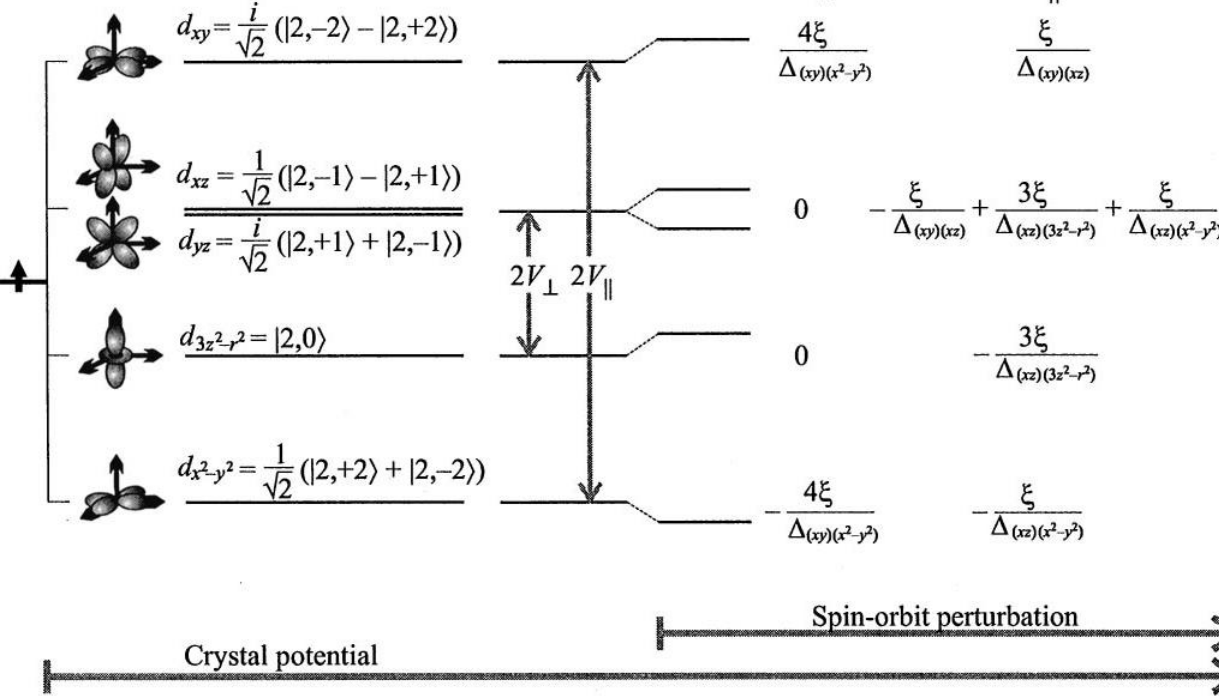
Assuming no charge transfer between Co and Cu the crystal field splitting gives the following energy scheme



$L = 0$ because:

- $d_{3z^2-r^2}$ gives no contribution to L
- d_{xy} and $d_{x^2-y^2}$ can not transform one in the other because not degenerate
- d_{xz} and d_{yz} can not transform one in the other because have the same spin

Crystal field splitting for a Co monolayer on Cu(100)



Theoretical basis

- Pure d orbitals are split (about 1 eV) by crystal field -> L=0
- Spin-orbit coupling (about 50 meV) mixes the pure d-orbitals creating new (first-order) states with non zero (but small) orbital moment

Spin-orbit is a perturbation: (assuming the spin down band completely full)

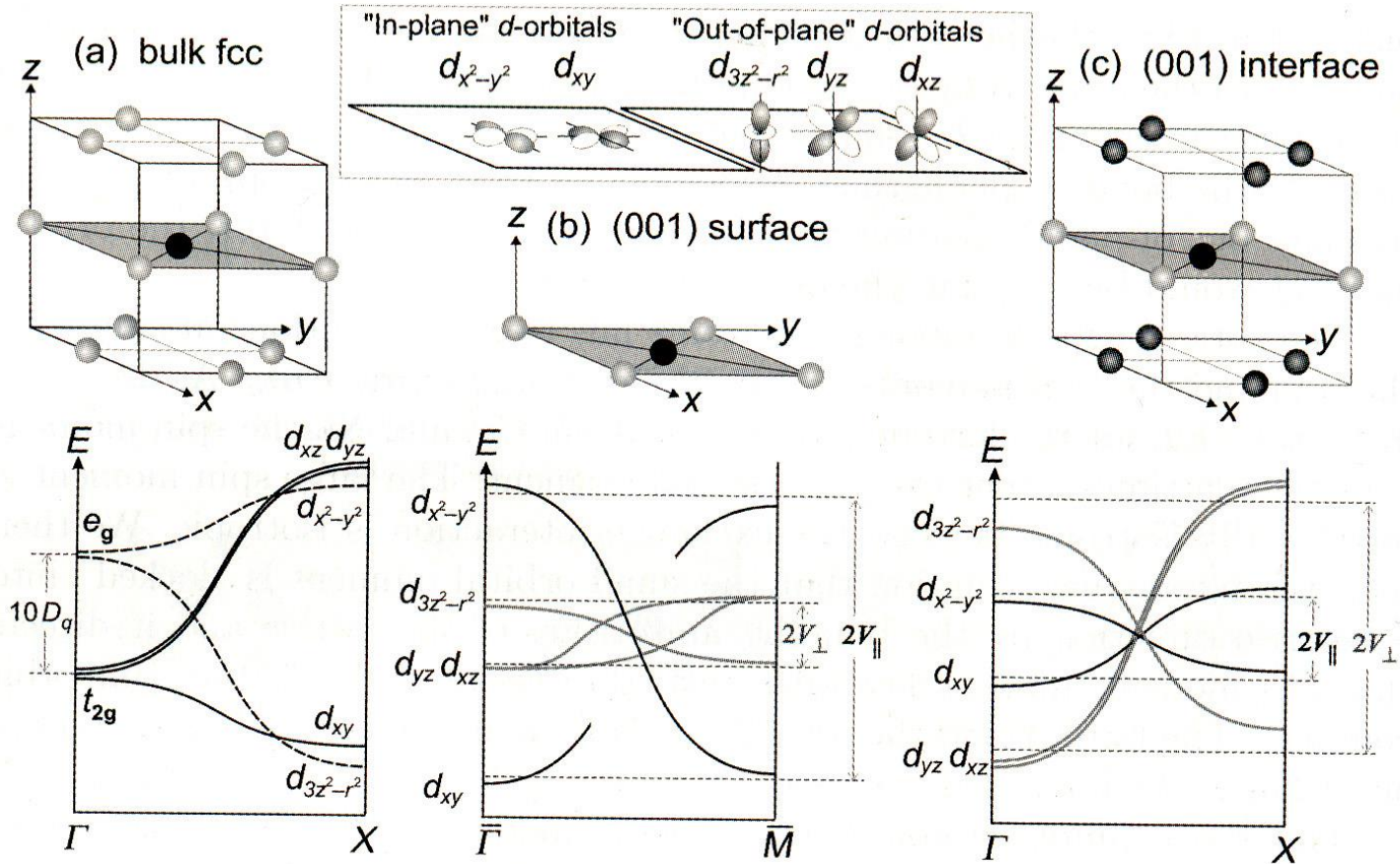
Matrix elements $\langle d_n | \mathbf{e} \cdot \mathbf{L} | d_m \rangle$

	$\langle zx $	$\langle yz $	$\langle xy $	$\langle x^2 - y^2 $	$\langle 3z^2 - r^2 $
$ zx\rangle$	0	$-i\hat{e}_z$	$i\hat{e}_x$	$-i\hat{e}_y$	$i\sqrt{3}\hat{e}_y$
$ yz\rangle$	$i\hat{e}_z$	0	$-i\hat{e}_y$	$-i\hat{e}_x$	$-i\sqrt{3}\hat{e}_x$
$ xy\rangle$	$-i\hat{e}_x$	$i\hat{e}_y$	0	$2i\hat{e}_z$	0
$ x^2 - y^2\rangle$	$i\hat{e}_y$	$i\hat{e}_x$	$-2i\hat{e}_z$	0	0
$ 3z^2 - r^2\rangle$	$-i\sqrt{3}\hat{e}_y$	$i\sqrt{3}\hat{e}_x$	0	0	0

$$\langle L_{\alpha}^n \rangle \approx \zeta \sum_m \frac{\left| \langle d_n^+ | L_{\alpha} | d_m^+ \rangle \right|^2}{E_n - E_m}$$

example

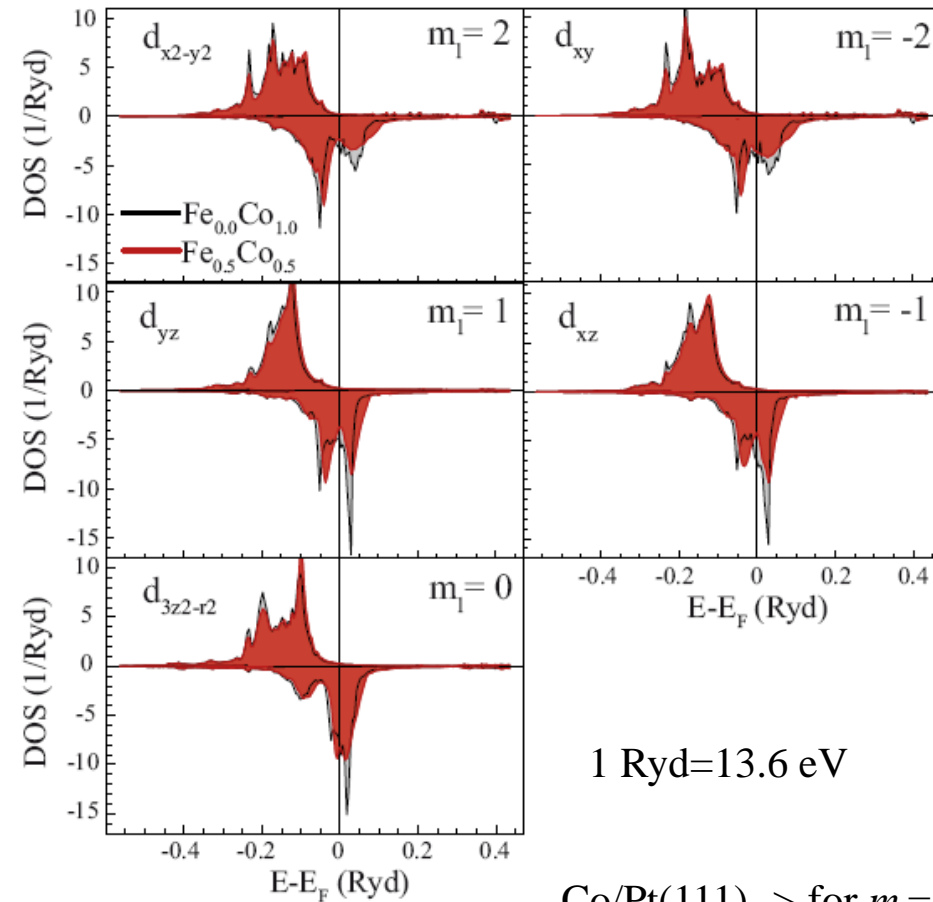
$$\langle L_x^{xy} \rangle \approx \xi \sum_m \frac{\left| \langle d_{xy}^+ | L_x | d_m^+ \rangle \right|^2}{E_{xy} - E_m} = \frac{\xi \left| \langle d_{xy}^+ | iL_x | d_{xz}^+ \rangle \right|^2}{E_{xy} - E_{xz}} = \frac{\xi}{E_{xy} - E_{xz}}$$



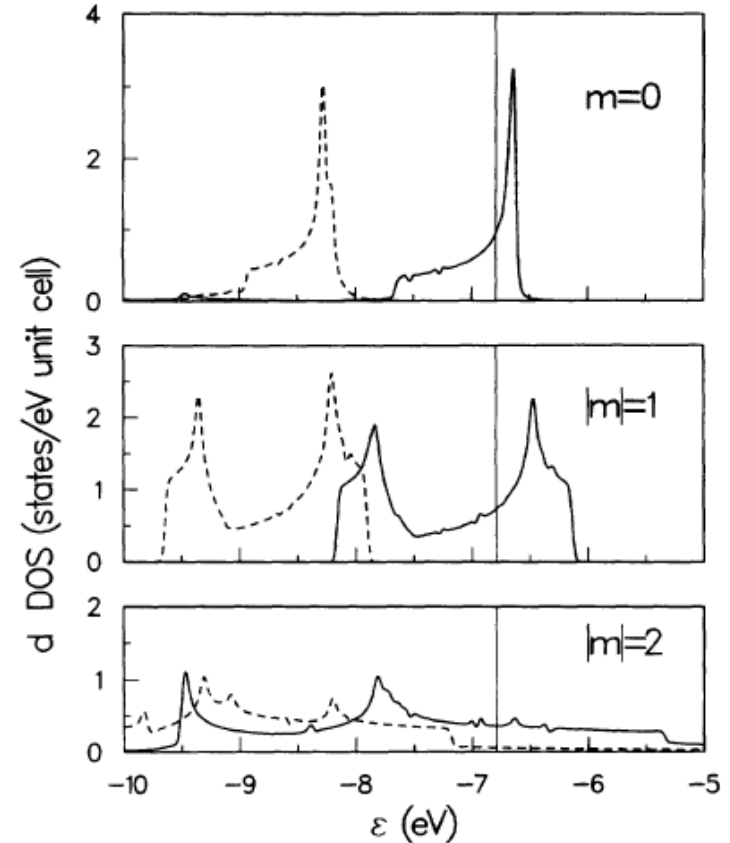
The band width is correlated to the crystal field strength

- b) **free-standing monolayer**: only the in-plane d-orbitals feel the bonding and then show splitting and dispersion in the (E,k) space while the out-of-plane d-orbitals stay mostly unperturbed
- c) in a **multilayer** with stronger out-of-plane than in-plane bonds the situation is reversed
- 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

Co/Pt(111)



Free-standing

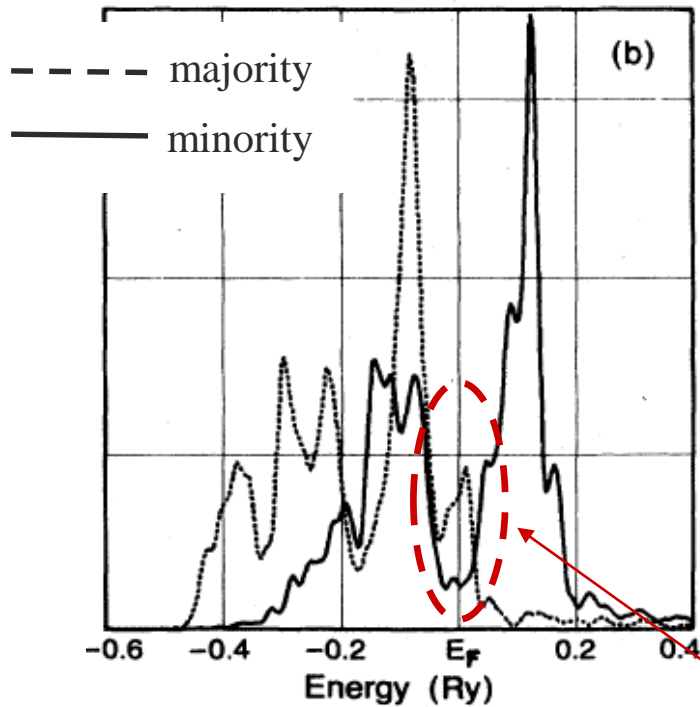


Co/Pt(111) \rightarrow for $m_l=1$ and $m_l=0$ the DOS widths are about 3 and 4 eV larger than in the free-standing Co monolayer; for $m_l=2$ there is no sizeable difference.

Ligand field: larger DOS width \rightarrow stronger bonding \rightarrow smaller L perpendicularly to the bond

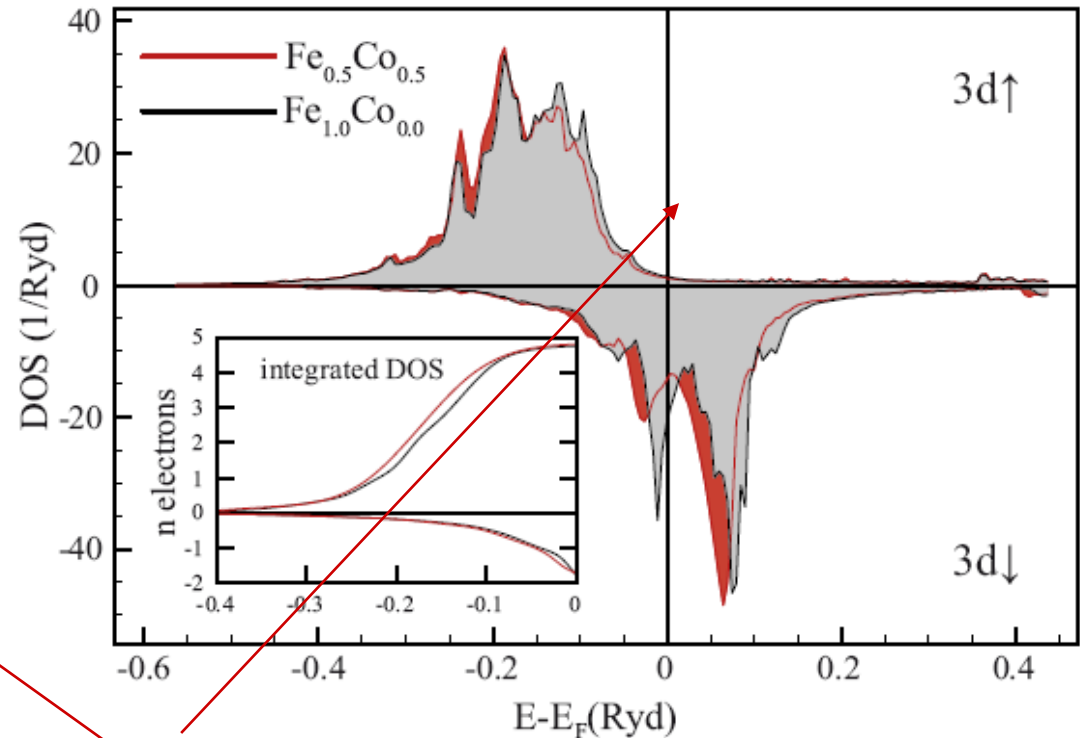
$m_l=1$ and $m_l=0$ correspond to out-of-plane orbitals (bonds) \rightarrow stronger out-of-plane bonds in Co/Pt(111) \rightarrow reduced in plane orbital moment in comparison with the free-standing case

Bulk Fe



minority state (solid line), majority states (dashed line)

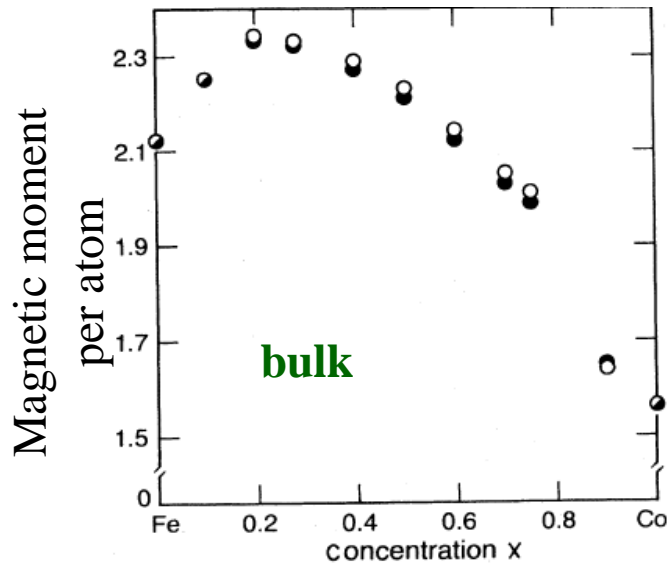
monolayer



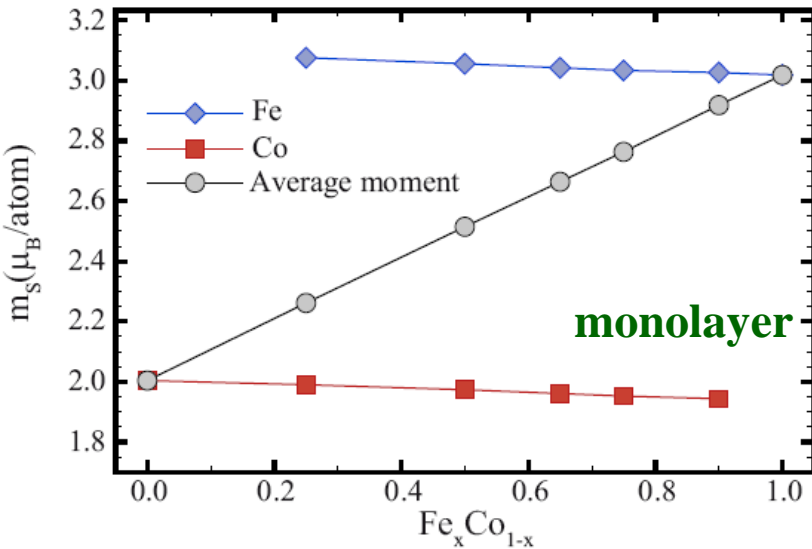
Peak in the majority states is missing and minority states are shifted at higher energy (the largest fraction of minority states is above Fermi level)

Bulk Fe is a soft magnet (majority states are not completely full) while is a strong magnet in the monolayer -> low dimensionality increased the band splitting

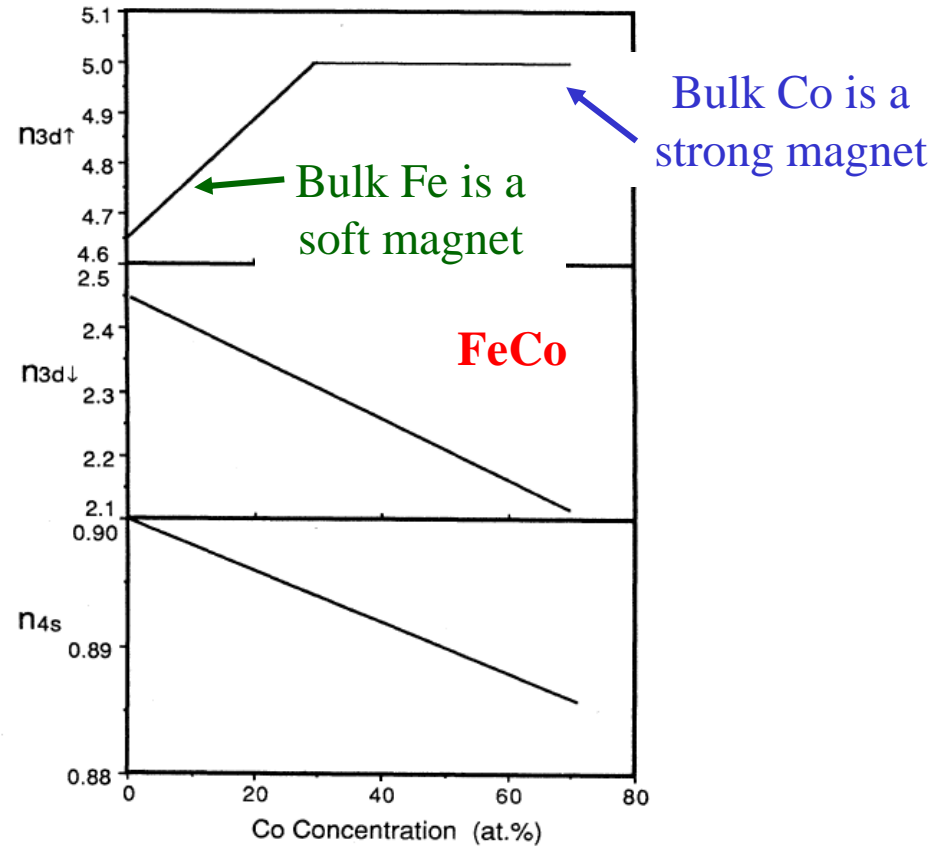
Fe spin magnetic moment is larger in monolayer (about 3 μ_B) than in bulk (about (2.2 μ_B))



Redistribution of $3d\downarrow$ electrons to the $3d\uparrow$ states at the Fe sites while adding Co up to a concentration of about 30%. After the maximum magnetization value, the total number of $3d\uparrow$ electrons remains constant, whereas the number of $3d\downarrow$ electrons increases in order to accommodate the additional electrons coming from Co

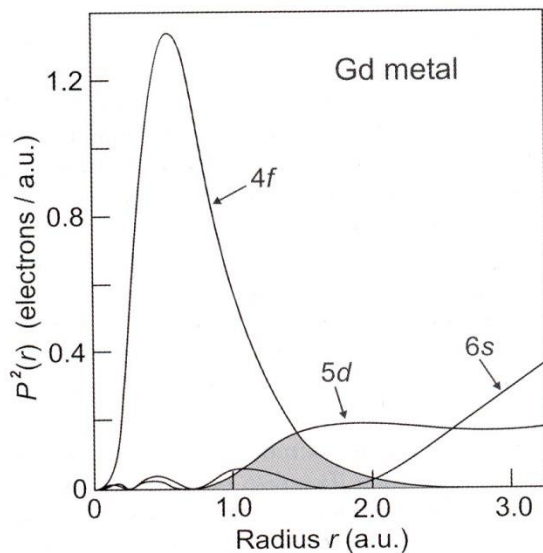


In monolayer regime both Fe and Co are strong magnets: moment increase linearly with 3d electrons



L. Pauling, Phys. Rev. **54**, 899 (1938); H.H. Hamdeh *et al.*, Phys. Rev. B **39**, 11233 (1989); R.H. Victora *et al.*, Phys. Rev. B **30**, 259 (1984); G. Moulas *et al.*, Phys. Rev. B **78**, 214424 (2008).

Electronic configuration: $Xe\ 6s^2\ 4f^N$
(exception for Gd $6s^1\ 5d^1\ 4f^7$)



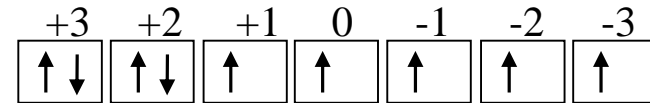
4f states are strongly localized ->
do not participate to bonding
CF ~ 10 meV
SOC ~ 200 meV



Coulomb repulsion ~ 1-10 eV

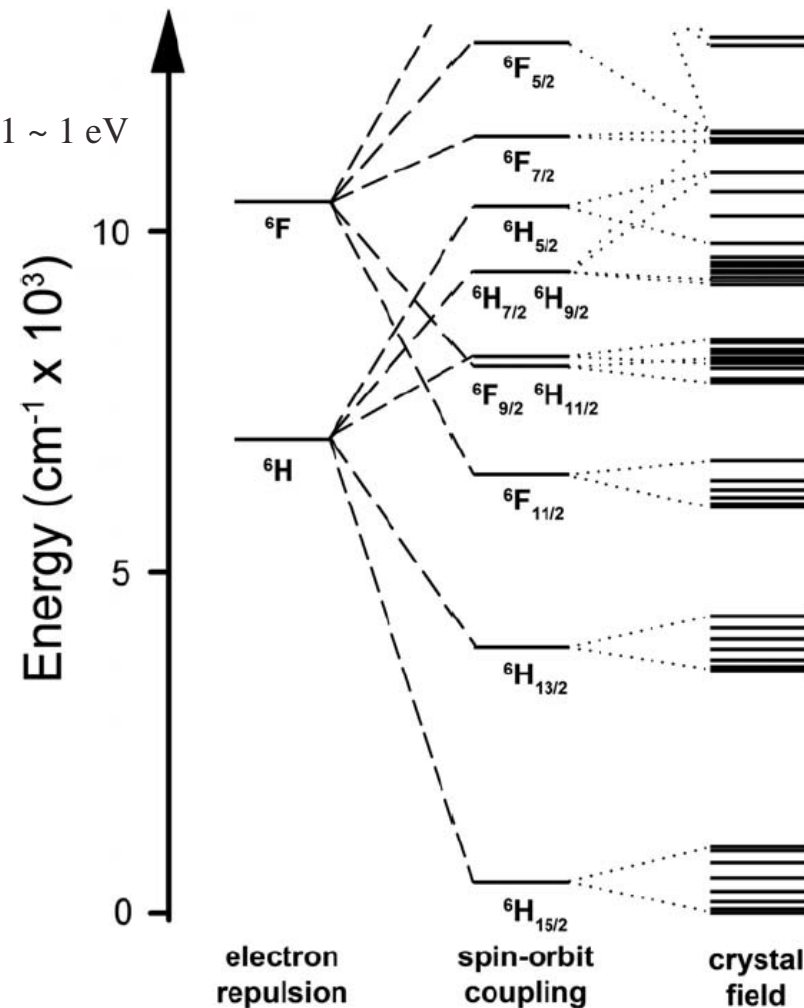
- Magnetic moment defined by the 4f states
- L unquenched (small CF for the 4f, Hund's rules hold)

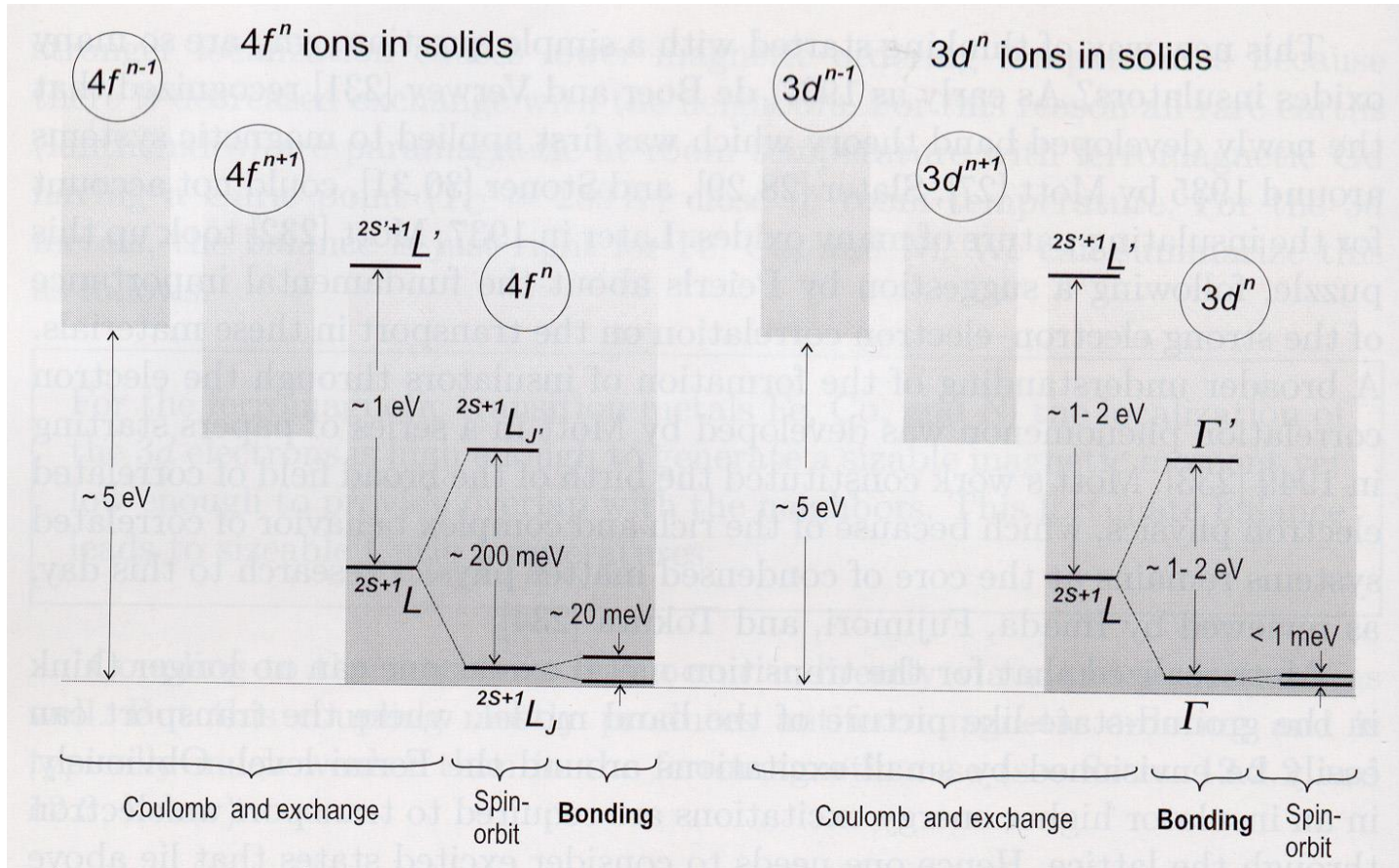
$Dy^{3+}\ (6s^0\ 4f^9)$



$L=5; S=5/2 \rightarrow$ ground state ${}^6H_{15/2}$

8000 $cm^{-1} \sim 1\ eV$





$$H_{\text{field}} < \lambda LS$$

Rare earths

Bonding = CF

$$\lambda LS < H_{\text{field}} < V_{e-e}$$

Transition metals 3d

$$\lambda LS < V_{e-e} < H_{\text{field}}$$

metals 4d-5d