Magnetism

Two fundamental parameters

1) magnetic moment μ or magnetization (order parameter)

Define the intensity of the magnetic field generated by the system, via $\underline{H} = -\,\text{grad}\,(\underline{\mu}\cdot\underline{r}\,/r^3)$ and the intensity of the force acting on the system if immersed in a magnetic field, via $\underline{F} = \text{grad}\,(\underline{\mu}\cdot\underline{H})$
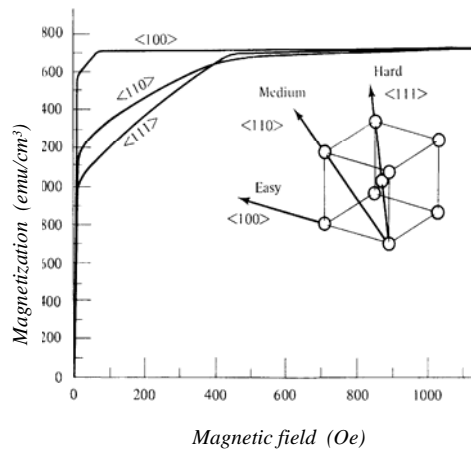
2) magnetic anisotropy energy K

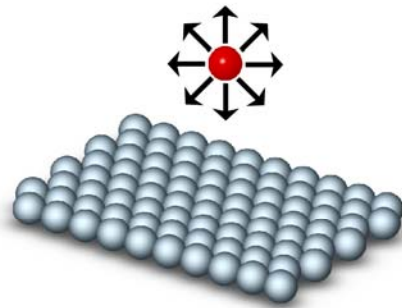Define the space direction/s along which the magnetic moment prefer to align

Fe bcc
easy axis: (100)
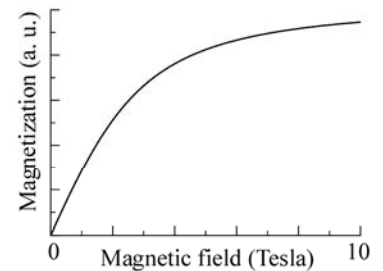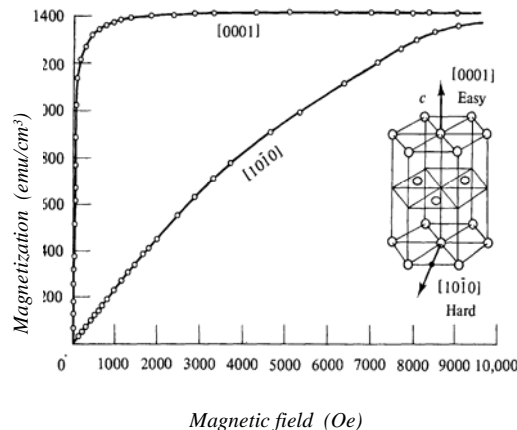
$K_1 = 4.8 \times 10^4 \ J/m^3$

$= 2.4 \ \mu eV/atom$

isotropic:
free magnetic atom

Co hcp
easy axis: (0001)

$K_1 = 4.1 \times 10^5 \ J/m^3$

$= 45 \ \mu eV/atom$
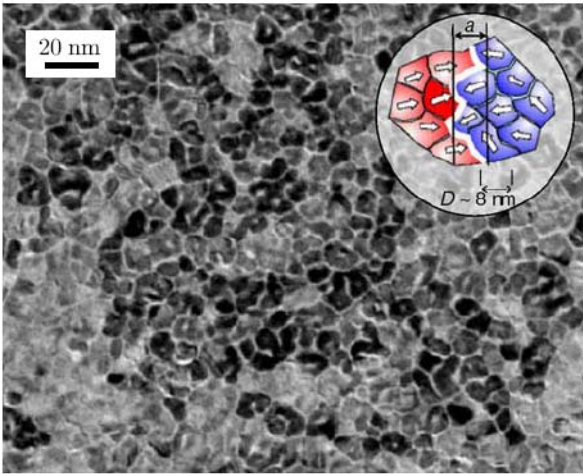

Bulk systems: K depends on the crystallographic structure

Complete isotropic
$K = 0$

Information storage in magnetic memory

20 nm

a

$D \sim 8$ nm

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

The bit size and shape is defined during writing by the head

GMR Read Sensor

Inductive Write Element

Collector pole

Write pole

d

W

t

N S N S N S N

Recording Medium

B

Soft Under layer

Exchange Break layer

a)

b)

The dream

Single particle bit

A. Moser, *et al.* J. Phys. D: Appl. Phys. **35**, R157 (2002).
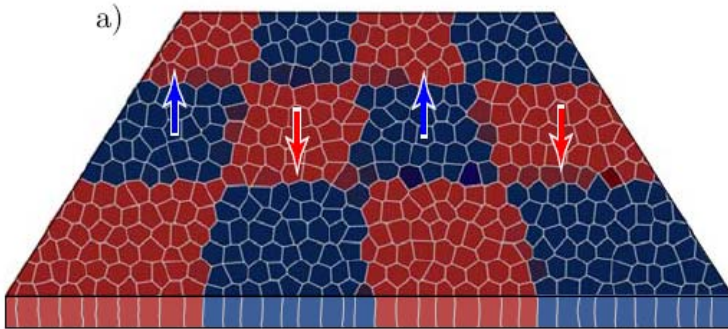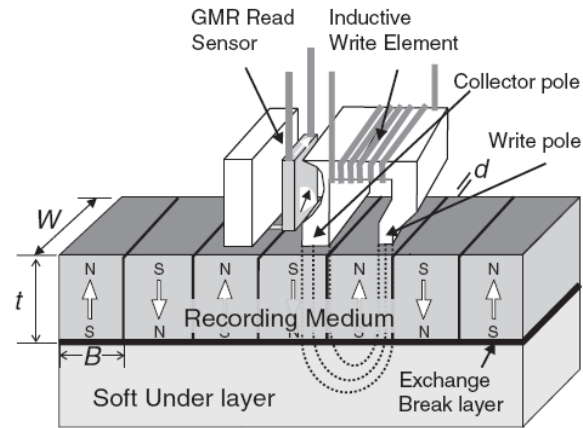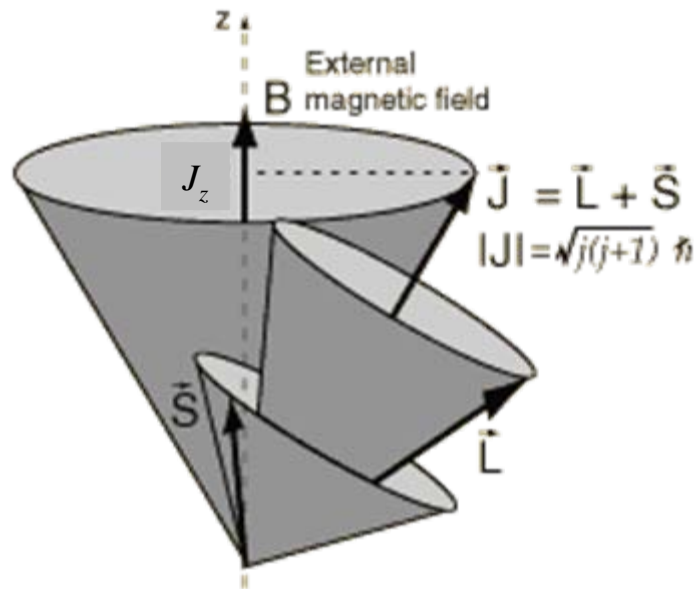
Atom in a magnetic field

$$\mathcal{H} = \sum_i \left(\frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_i) \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \mu_B B \frac{1}{\hbar} \sum_i (\ell_{z,i} + 2\, s_{z,i})$$

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

$$\mathcal{H}_{\ell s} = \sum_i \zeta(\vec{r}_i)\, \vec{\ell}_i \vec{s}_i$$

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

Orbital magnetism: $m_L = L\, \mu_B$
Spin Magnetism: $m_S = g_e\, S\, \mu_B = 2\, S\, \mu_B$
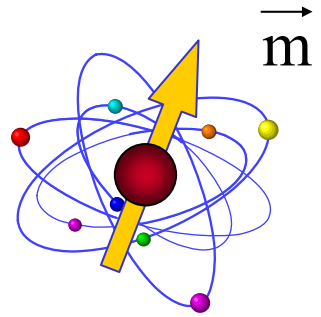Atomic magnetic moment: $m_{at} = \mu_B(L + g_e\, S) = g\, J_z\, \mu_B = g\, J\, \mu_B$

μ_B -> Bohr magneton
$g = 3/2 + [S(S+1) - L(L+1)]/(2J(J+1))$ is the Landé g-factor

Magnetism of an isolated atom

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

$\vec{m}$

Hund's rules:

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

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

Ground state of a 3d^7 ion (Co^{2+})

+2	+1	0	-1	-2
↑ ↓	↑ ↓	↑	↑	↑

$L = 3,\ S = 3/2,\ J = 9/2$
$m_L = L\,\mu_B = 3\ \mu_B$,
$m_S = g_e\,S\,\mu_B = 3\ \mu_B$,
$m_{at} = g\,J\,\mu_B = 6\ \mu_B$

Ground state of a 3d^5 ion (Mn^{2+})

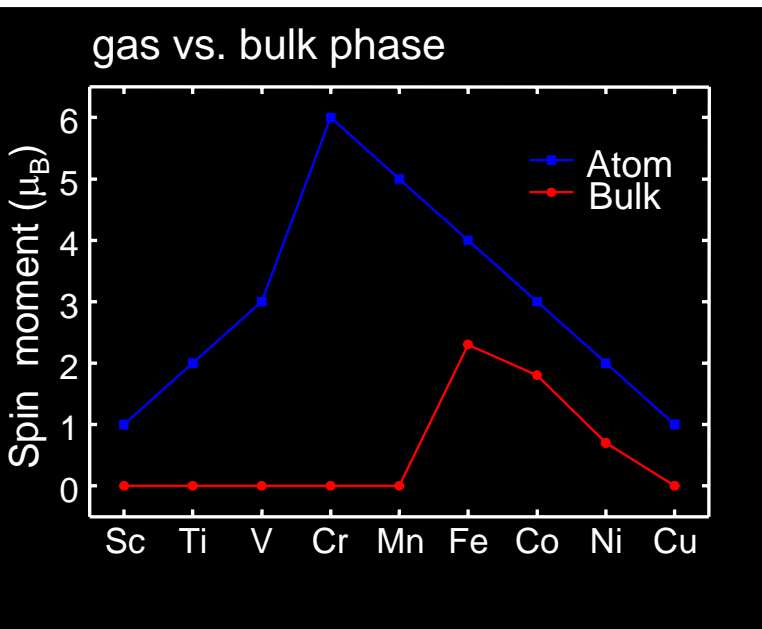| +2	+1	0	-1	-2
↑	↑	↑	↑	↑

$L = 0,\ S = 5/2,\ J = 5/2$
$m_L = L\,\mu_B = 0\ \mu_B$,
$m_S = g_e\,S\,\mu_B = 5\ \mu_B$,
$m_{at} = g\,J\,\mu_B = 5\ \mu_B$

3d elements: gas and condensed matter phase

gas vs. bulk phase

mass-selected clusters in gas phase

N > 20 atoms

I.M.L. Billas, *et al.* Science **265**, 1682 (1994).
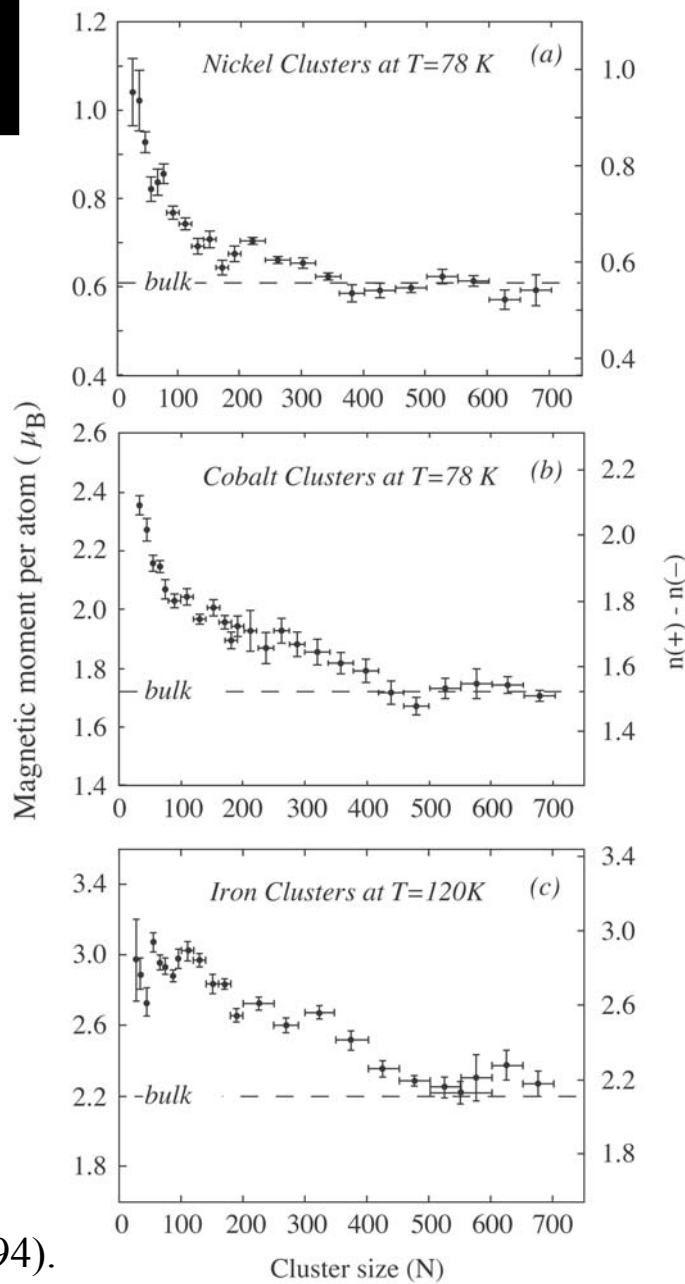
Bulk magnetism

Most atoms loose their magnetic moment when incorporated into a crystal (there are only few magnetic solids). The main reason is the delocalization of the electrons due to the overlap of the wave functions of neighboring atoms.

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

Experiments show that $3d$ ions in solids have $L \approx 0$, $J \approx S$ and $g = 2$.
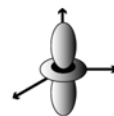
The crystal electric field produced by surrounding ions in a solid defines a particular set of (real) wave-functions for which the mean value of the orbital moment is zero (balance of $+/- m_L$).

d wave-functions in cubic symmetry

t_{2g}

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

The crystal field gives a reduction of the orbital moment depending on its symmetry and strength.
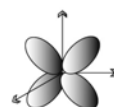
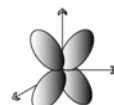 $d_{3z^2-r^2} = |0\rangle$

e_g

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

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

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

Localized magnetism -> 4f and 5f states of the rare heart
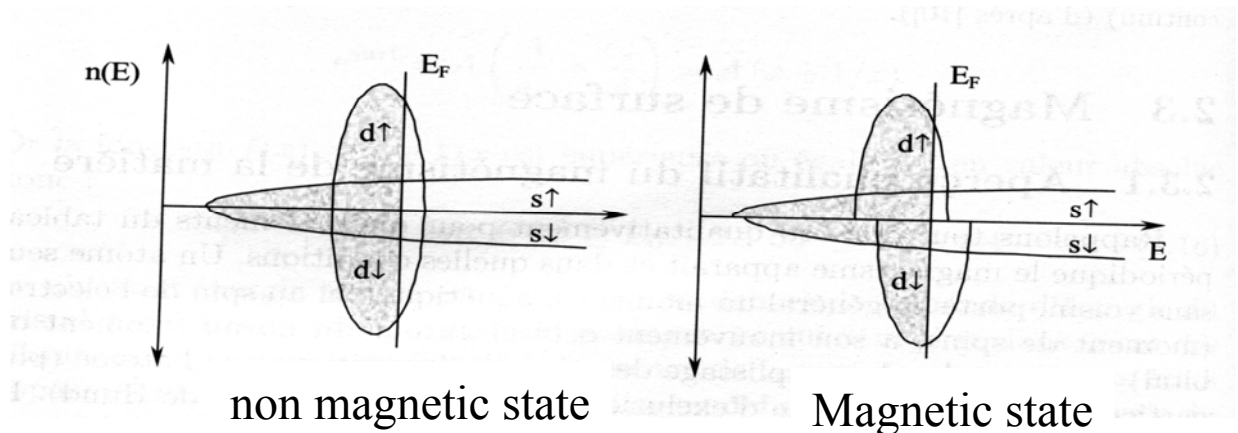Itinerant magnetism   -> 3d (4d, 5d) states of transition metals

Itinerant magnetism

Itinerant magnetism -> delocalized electrons -> electronic bands

Stoner Exchange interaction:
Is the energy necessary to reverse the
spin of one electron in the sea of all
the other electrons -> spin up – down
bands are shifted by $\delta = 1\text{-}2$ eV

$$\mathcal{H}_S = -1/2 \sum_{M,N} J_{M,N}\, \vec{S}_M \cdot \vec{S}_N,$$

non magnetic state   Magnetic state

Non magnetic state -> $n\uparrow = n\downarrow$

magnetic state -> splitting of electronic bands corresponding to
opposite spin direction -> $n\uparrow \neq n\downarrow$ (δ band shift)

Spontaneous magnet -> $\Delta E \approx n(E_F)\, \delta^2\, f(J) < 0$
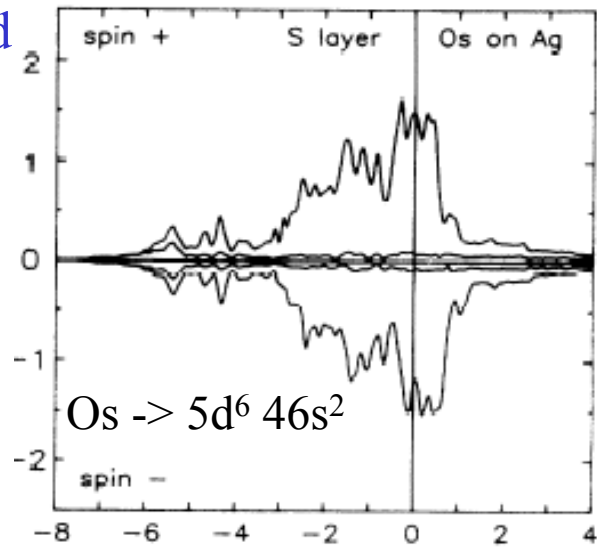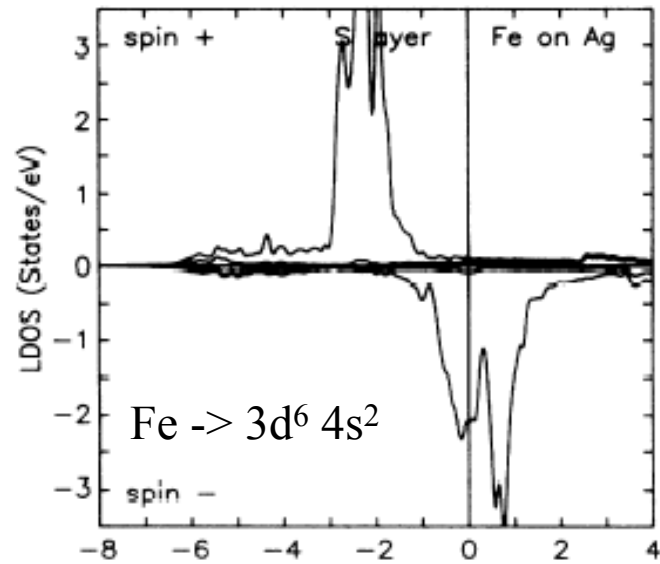Depends on $n(E_F)$, δ, and J

s bands are extended -> do not affect magnetism
d bands are localized -> their splitting determines the magnetism
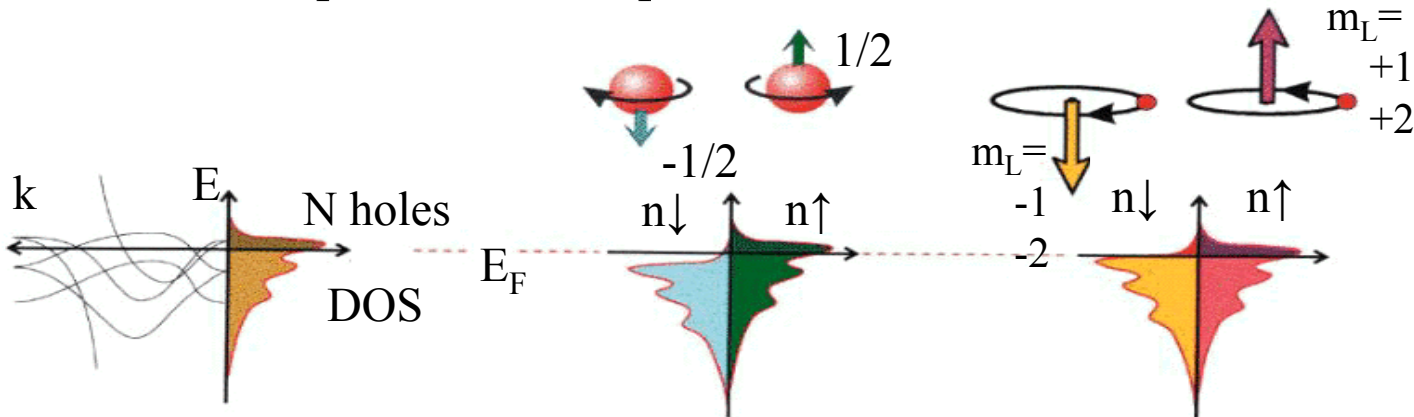
Fe is magnetic

Os is non-magnetic

d-band

spin +   S layer   Fe on Ag

LDOS (States/eV)

Fe -> $3d^6\, 4s^2$

spin −

spin +   S layer   Os on Ag

Os -> $5d^6\, 46s^2$

spin −

S. Blugel Phys. Rev. Lett. **68**, 851 (1992)

Orbital and spin magnetic moments in bulk magnets

d-band occupation   Spin moment   Orbital moment

$m_L = +1$ $+2$

$1/2$

$-1/2$

$m_L = -1$ -2

k E N holes $n\downarrow$ $n\uparrow$ $n\downarrow$ $n\uparrow$

E_F DOS

Material	N holes
Fe	3.4
Co	2.5
Ni	1.5

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

m_{orb}
0.09
0.14
0.07

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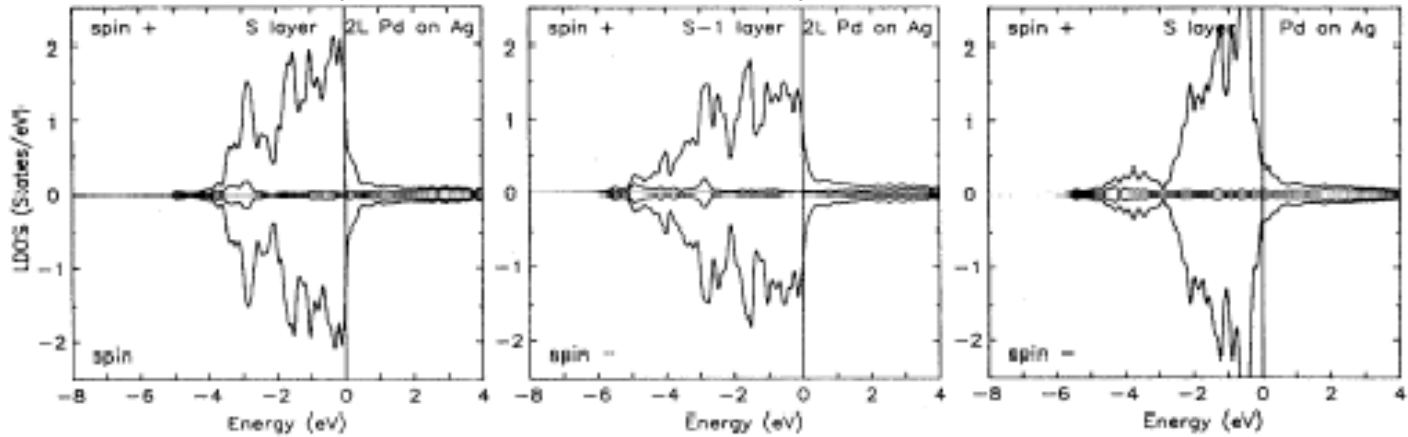
Surface magnetism

## Narrowing of the electronic band due to the broken symmetry at surface

2 ML Pd on Ag(001)
Surface layer

2 ML Pd on Ag(001)
Interface layer

1 ML Pd on Ag(001)

1) The Pd bi-layer bandwidth is wider than that of the mono-layer
Mean coordination in the bi-layer is larger than in the monolayer

2) Non magnetic elements in bulk state can become magnetic: Ex. Pd, Pt

3) The LDOS at the Fermi energy decreases moving from left to right
a)   The magnetic moment of the atoms in the surface layer of the 2 ML Pd film have a larger moment than the atoms in the interface layer
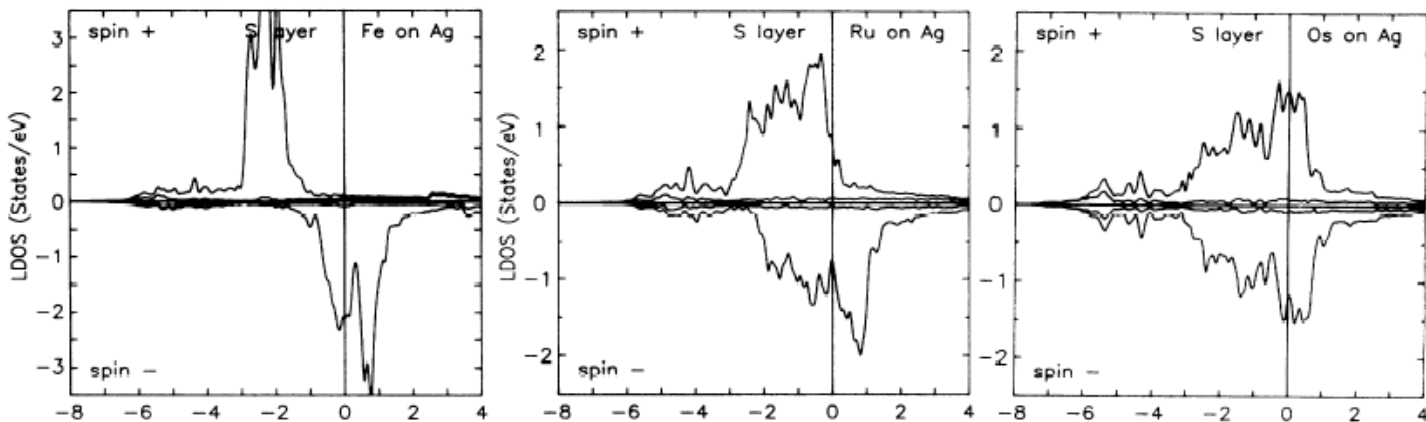b)   The magnetic moment is larger in the 2 ML film than in the 1 ML film
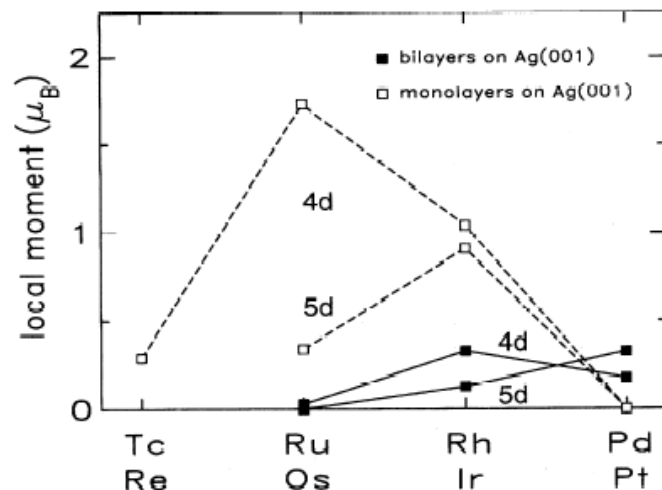
The electronic density at the Fermi level n(E_F) increases moving
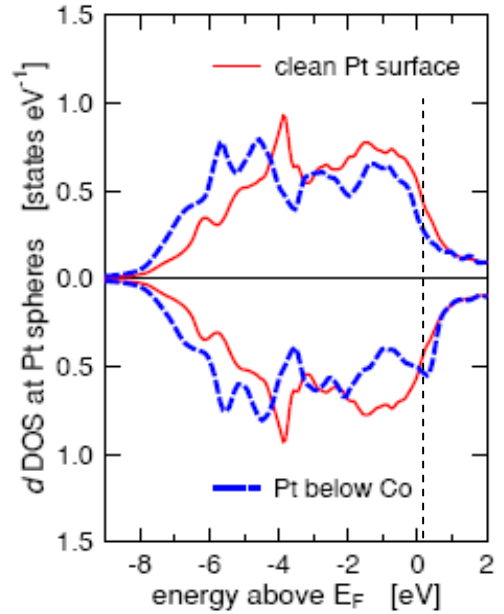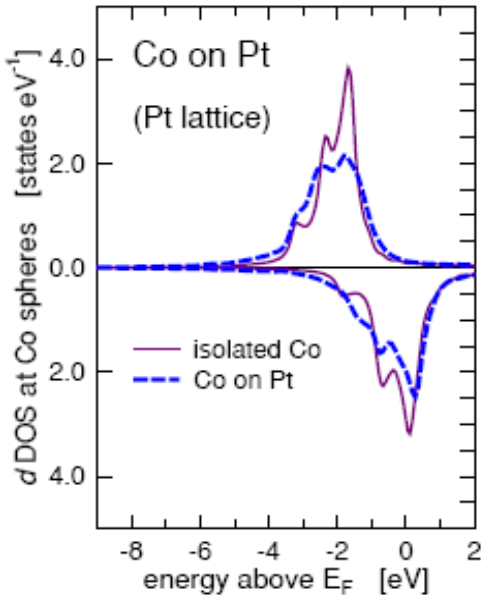from 5d to 4f elements

$$n(E_F) \sim 1/W$$
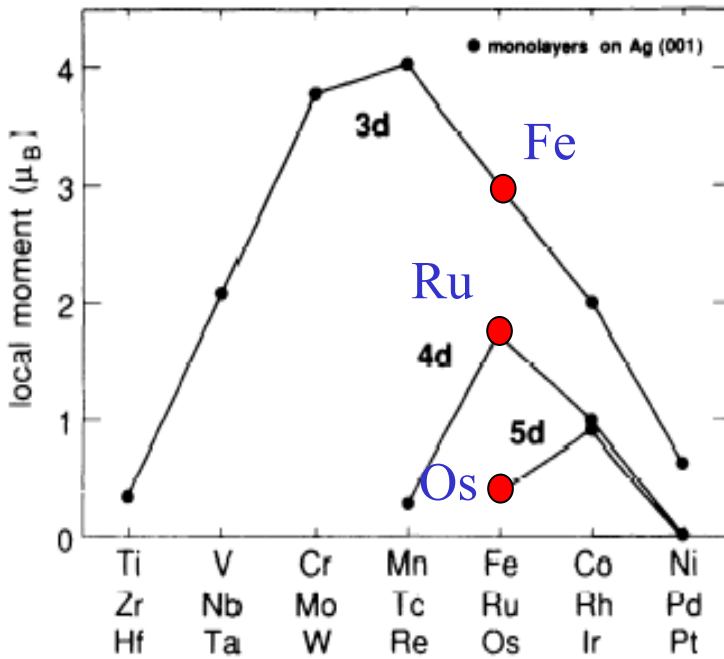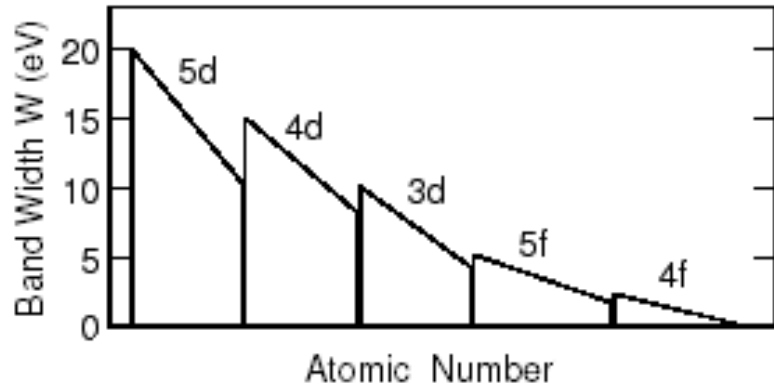
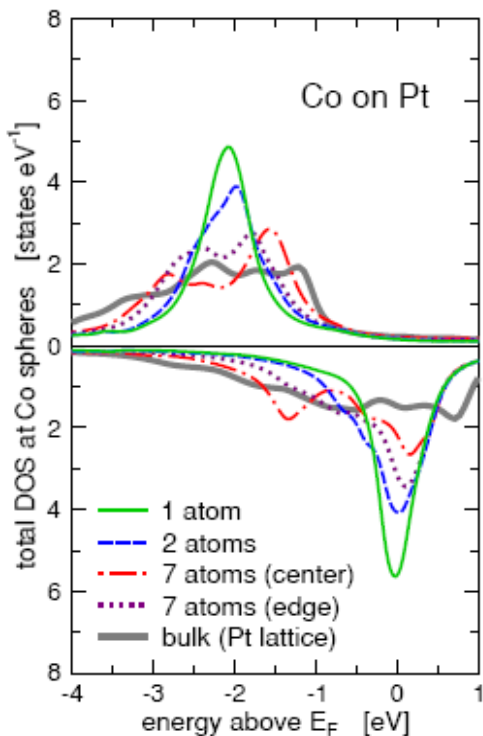Monolayer on Ag(001)

Co clusters on Pt(111)

Co monomer

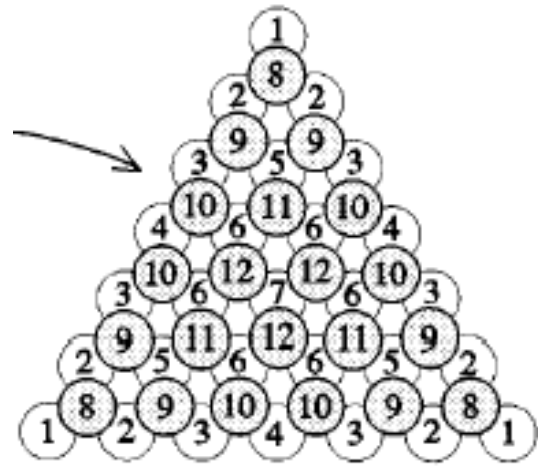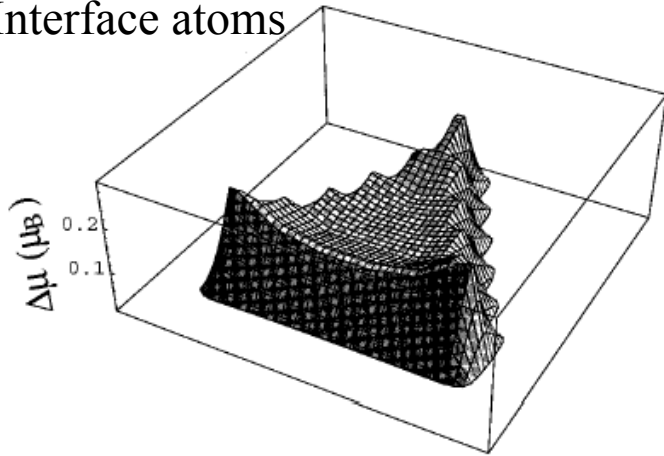Note: asymmetry in the Pt LDOS at E_F when covered by Co-> induced magnetic moment

Size dependence

Reduced asymmetry by increasing the cluster size -> reduced magnetic moment

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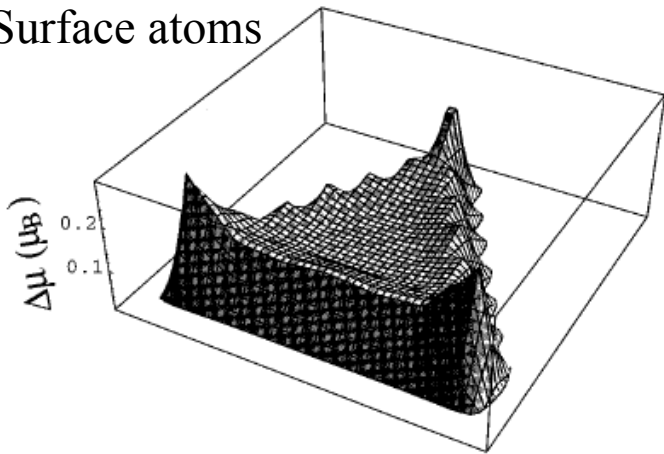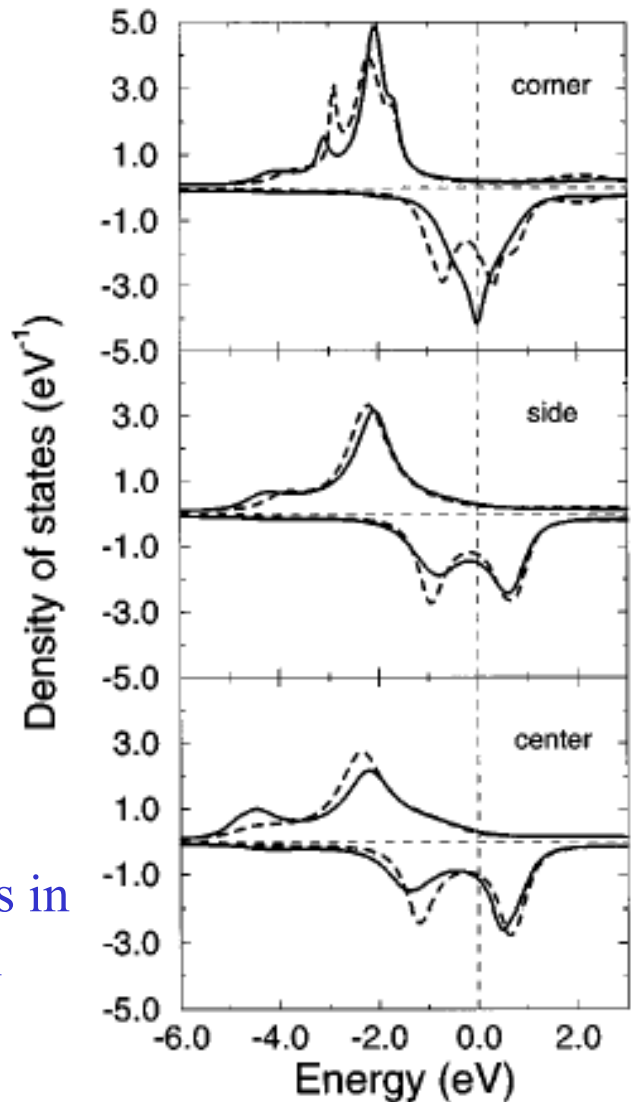
Cluster magnetism

Two atomic layer high Co islands
on Cu(111)

Interface atoms

Surface atoms

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

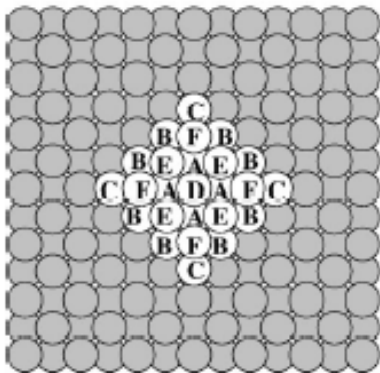J. Izquierdo *et al.* Phys. Rev. B **55**, 445 (1997)

Cluster magnetism
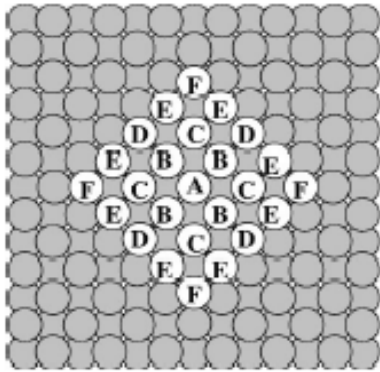
Site	A	B	C	D	E	F
$\mu(\mu_B)$	1.53	1.61	1.66	1.66	1.72	1.80

$<\mu> = 1.69\ \mu_B$

Co/Cu(100)

J. Izquierdo *et al.* Phys. Rev. B **63**, 140413 (2001)

Site	A	B	C	D	E	F
$\mu(\mu_B)$	1.15	1.46	1.67	1.52	1.65	1.64

$<\mu> = 1.51\ \mu_B$
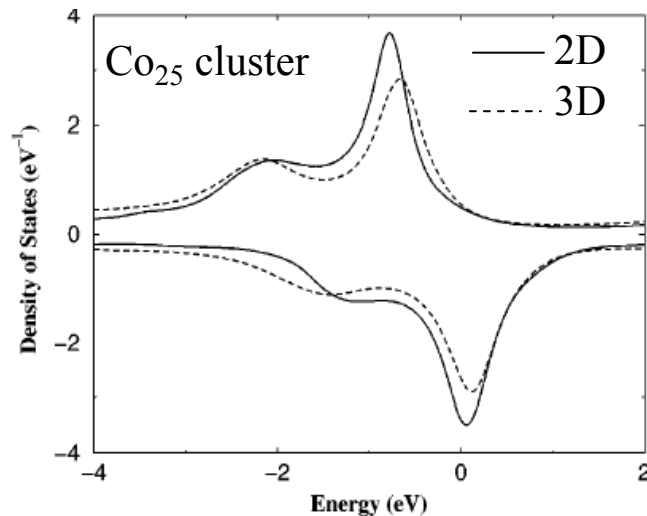
In general:
- Narrowing of the d band at surface -> increased m_S
- Larger m_s -> larger m_L due to the spin-orbit coupling
- Symmetry breaking at surface -> removal of the m_L quenching
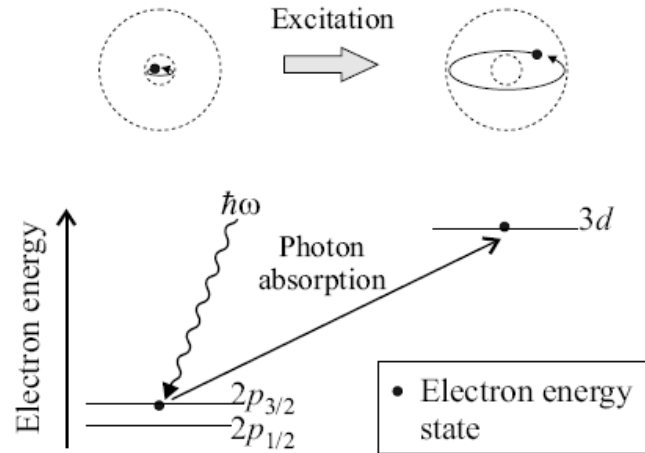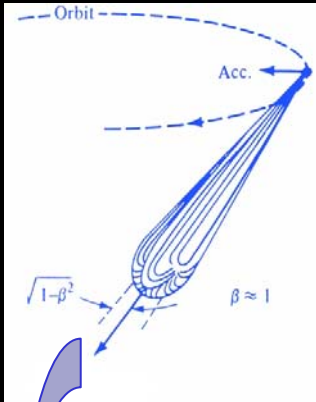
XMCD: X-rays Magnetic Circular Dichroism

Two step model:
1) spin-polarized photoelectrons are created by using circularly polarized x-rays
2) these polarized photoelectrons are used to analyze the spin-split final density of states, thus the valence band acts as a spin-sensitive detector.

XAS of 3d elements

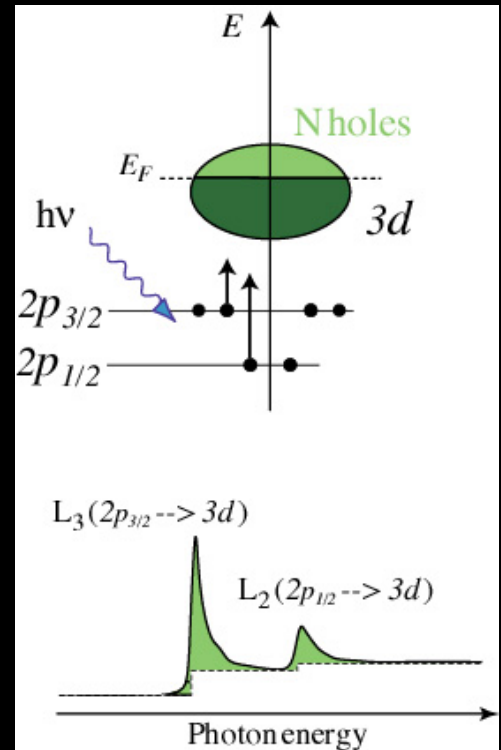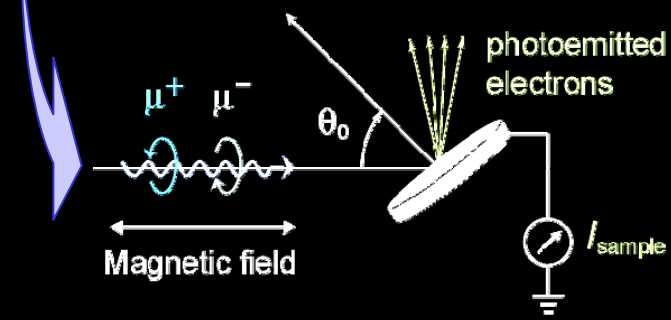relativistic electrons

Variable energy polarized x-rays

x-ray monochromator

μ⁺ μ⁻

θ₀

photoemitted electrons

Magnetic field

I_{sample}

Photons transfer their angular momentum to the excited photoelectrons through the spin-orbit interaction

XMCD theory: basic idea

Photon-electron interaction: dipole approximation

$$H_{int}(0,t) \approx \underline{r} \cdot \underline{\varepsilon}_q \left[a_k \exp(-i\omega_k t) + c.c. \right]$$

The dipole operator $P_q^1 = \underline{r} \cdot \underline{\varepsilon}_q$ can be written in terms of Racah's tensor operators (where $Y_{l,m}$ are the spherical harmonics)

$q = 0$ -> linear polarization
$q = +/- 1$ -> circular polarization

$$P_{\pm 1}^{(1)} = \mp \frac{1}{\sqrt{2}} (x \pm iy) = r C_{\pm 1}^{(1)} = r\sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}$$

$$P_0^{(1)} = z = r C_0^{(1)} = r\sqrt{\frac{4\pi}{3}} Y_{1,0}$$

The photon absorption generates a transition from an initial core level to a final level close to the Fermi level (note that the spin is not affected)

$$|i\rangle = R_i(r) \, |c, m_c; s = \tfrac{1}{2}, m_s\rangle \quad \longrightarrow \quad |f\rangle = R_f(r) \, |l, m_l; s = \tfrac{1}{2}, m_s\rangle$$

$\langle l, m \lvert C_{\pm 1}^{(1)} \rvert l-1, m\mp 1\rangle$	$= \sqrt{\dfrac{(l\pm m)(l\pm m-1)}{2(2l-1)(2l+1)}}$	$\langle l, m \lvert C_{\pm 1}^{(1)} \rvert l+1, m\mp 1\rangle$	$= -\sqrt{\dfrac{(l\mp m+2)(l\mp m+1)}{2(2l+3)(2l+1)}}$
	$= \sqrt{\dfrac{l(l-1)\pm(2l-1)m+m^2}{2(2l-1)(2l+1)}}$		$= -\sqrt{\dfrac{l(l+3)\mp(2l+1)m+m^2}{2(2l+3)(2l+1)}}$
$\langle l, m \lvert C_0^{(1)} \rvert l-1, m\rangle$	$= \sqrt{\dfrac{l^2-m^2}{(2l-1)(2l+1)}}$	$\langle l, m \lvert C_0^{(1)} \rvert l+1, m\rangle$	$= \sqrt{\dfrac{(l+1)^2-m^2}{(2l+3)(2l+1)}}$

Table 1.3: Electric dipole matrix elements $\langle l, m_l \lvert C_q^{(1)} \rvert c, m_c\rangle$ in the one electron model. The matrix elements are non-vanishing when $c = l-1$ (left column) or $c = l+1$ (right column), and when $m_c + q = m_l$. q denotes the state of polarization of the photons which mix the states $|l, m_l\rangle$ and $|c, m_c\rangle$.

Remember: things become easily complicate. For example, if spin-orbit interaction is not negligible the (L, m_L, S, m_S) is not the good basis and you have to use the (L, S, J, m_J) basis
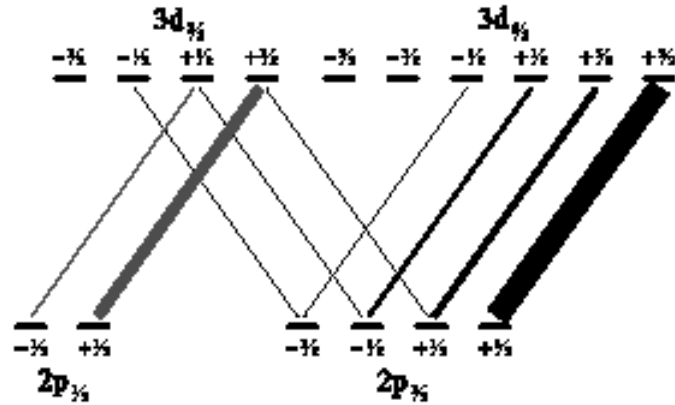
Right ($\Delta m = +1$) and Left ($\Delta m = -1$) circularly polarized photons create photoelectrons with opposite spins.
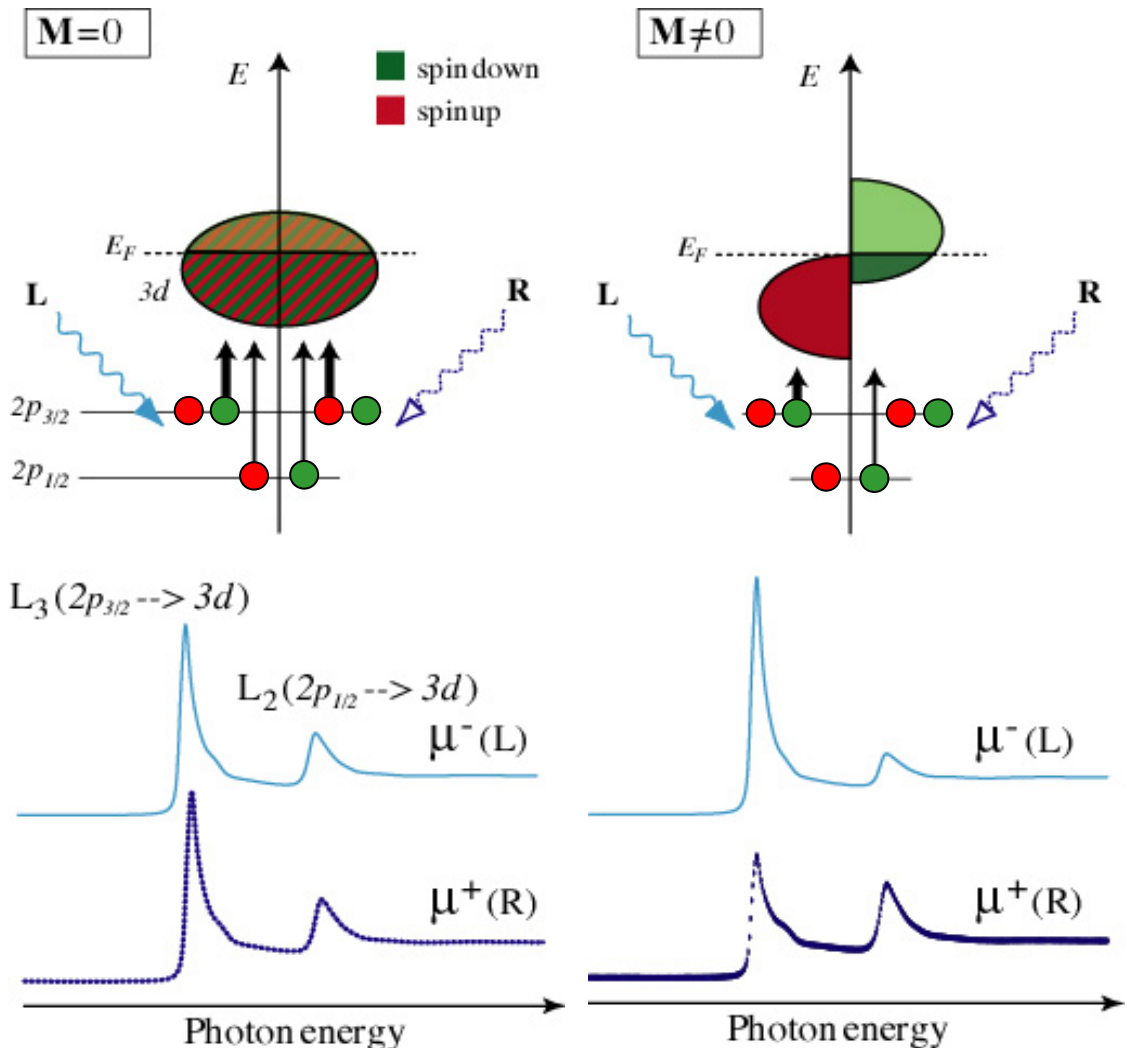
Since:

$$p_{3/2} \text{ (L+S coupling)}$$
$$p_{1/2} \text{ (L-S coupling)}$$

The spin polarization of the photoelectrons generated by circularly polarized light is opposite at the L_3 and L_2 edges

Transition probability represented by the line thickness for right circularly polarized x-rays. For clarity the transitions to the 4s levels are neglected (account for less than 5%)

Sum Rules

Separate determination of orbital and spin moment
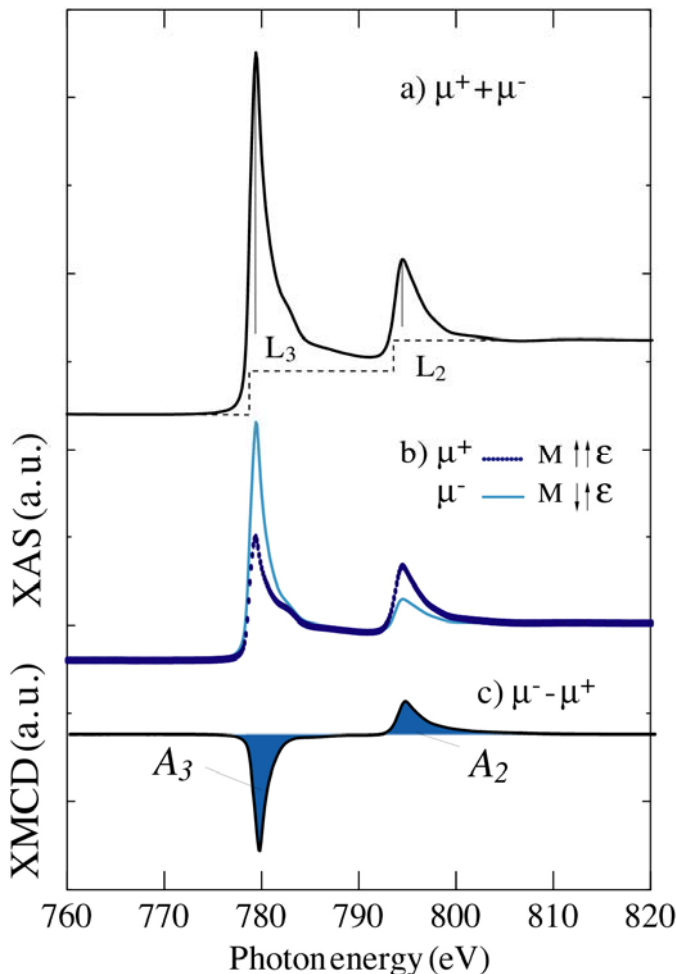(actually their projections along the ligth propagation direction)

$$m_S = -3 \, n_h \, \mu_B \, (A_3 - 2A_2) + m_T$$
$$m_L = -2 \, n_h \, \mu_B \, (A_3 + A_2)$$

Where A_3 (A_2) is the XMCD measured at the L_3 (L_2) edge, n_h is the number of unoccupied d state (number of holes) and m_T is the magnetic spin dipole moment ($\underline{T} = \underline{S} - 3 \, \underline{r} \, (\underline{r} \cdot \underline{S})$).
These rules hold only for itinerant magnetism

30 ML Co/Pt(997)

a) $\mu^+ + \mu^-$

L_3 L_2

b) μ^+ ...... M $\uparrow\uparrow\varepsilon$
   μ^- —— M $\downarrow\uparrow\varepsilon$

c) $\mu^- - \mu^+$

A_3 A_2

XAS (a.u.)   XMCD (a.u.)

760 770 780 790 800 810 820
Photon energy (eV)

XMCD: the difference between the XAS spectrum acquired with R and L polarized light

Operatively:
1) Measure of the XAS spectra with light polarized R and L in a saturating external magnetic field
2) For fcc and bcc crystallographic structures a magic angle (~57°) for the photon incidence exists at which $m_T = 0$
3) XMCD acquired at different angles gives m_s, m_L, and m_T

B. Thole et al., Phys. Rev. Lett. 68, 1943 (1992)
P. Carra et al., Phys. Rev.Lett. 70, 694 (1993)
J. Stöhr and H. König, Phys. Rev. Lett. 75, 3748 (1995).

Ni/Pt multilayers
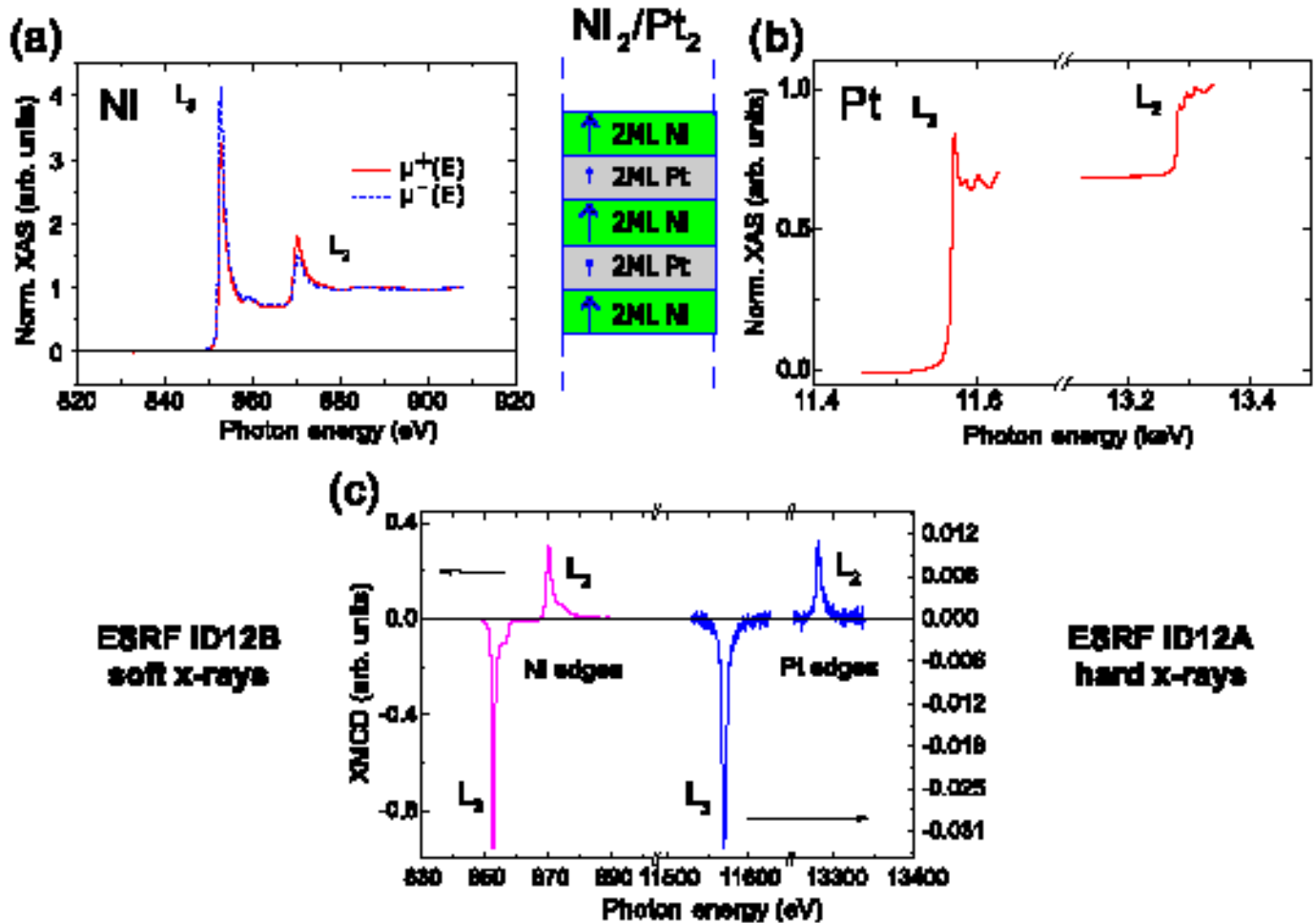
X-ray absorption spectra for a Ni_2–Pt_2 multilayer: (*a*) x-ray absorption coefficients for R ($\mu^+(E)$) and L ($\mu^-(E)$) circularly polarized x-rays at the Ni $L2,3$ edges in the soft x-ray range, (*b*) isotropic XAS at the Pt $L2,3$ edges in the hard x-ray regime, (*c*) XMCD spectra at the Ni and Pt $L2,3$ edges

XMCD $\neq$ 0 -> Ni is magnetic (as usual), but also Pt is magnetic

F. Wihelm et al., *Phys. Rev. Lett.* 85, 413 (2000)
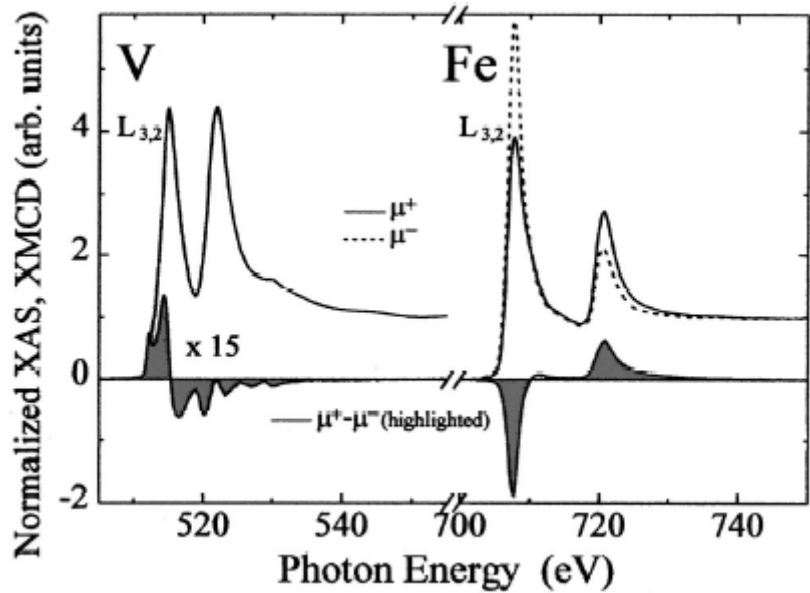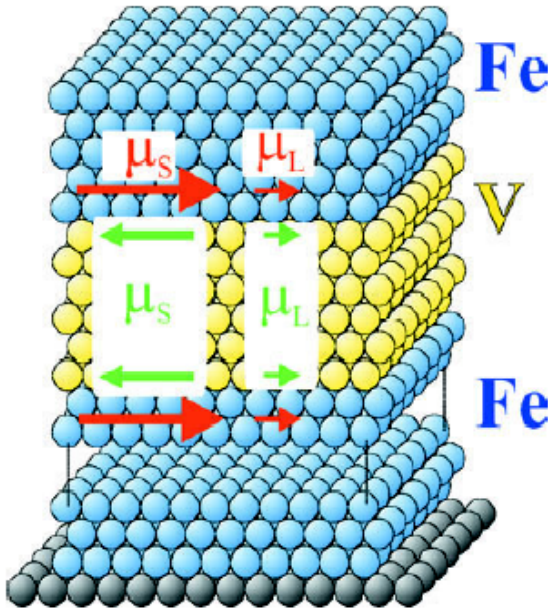
Fe/V/Fe(110) trilayer

Normalized XAS of L (dashed line) and R (solid line) circularly polarized light and the XMCD at the $L_{2,3}$ edges of V and Fe for a Fe/V4 /Fe(110) trilayer.
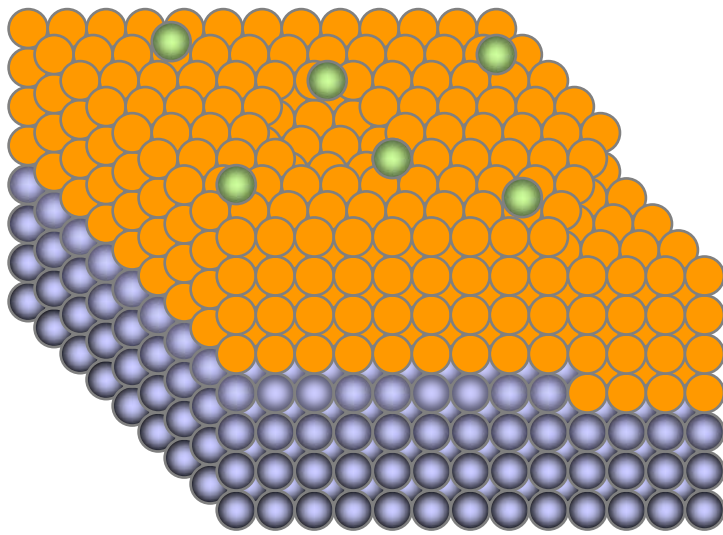
Antiferromagnetic coupling: XMCD signal for V and Fe have opposite signs

The induced magnetic moment in the V atoms strongly reduces with increasing the V thickness

Sum rules can not be applied due to overlapping between $2p^{1/2}$ and $2p^{3/2}$ states

A. Scherz *et al.,* J. Appl. Phys. **91**, 8
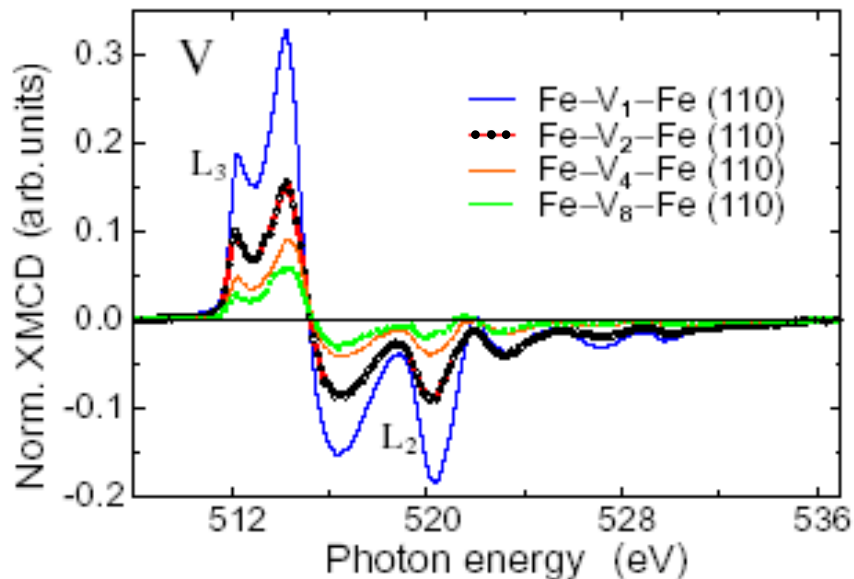
Single atoms on metals surfaces

Fe, Co atoms (<0.01 ML)

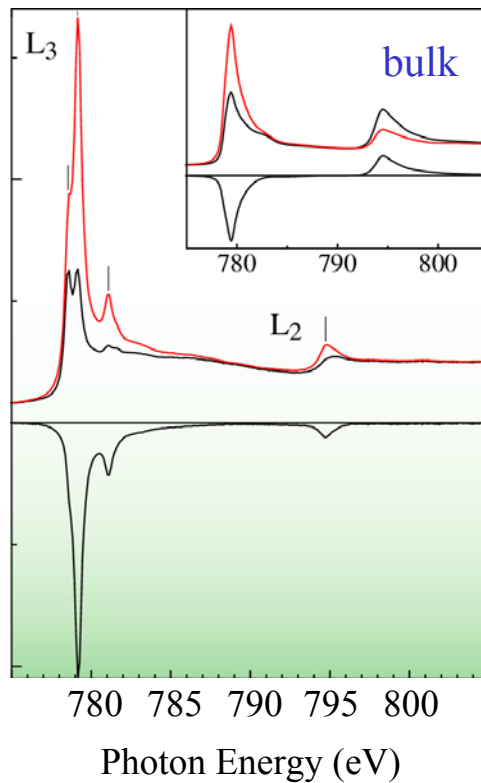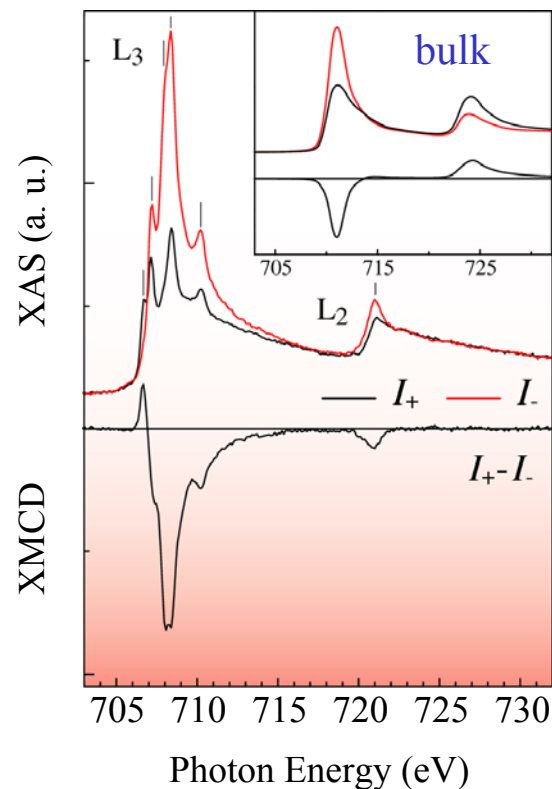Cs, K, Na, or Li film

Cu(100)

$T = 10$ K, B = 7 Tesla

Fe/K

Co/K

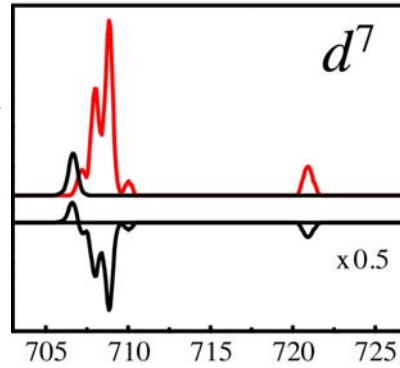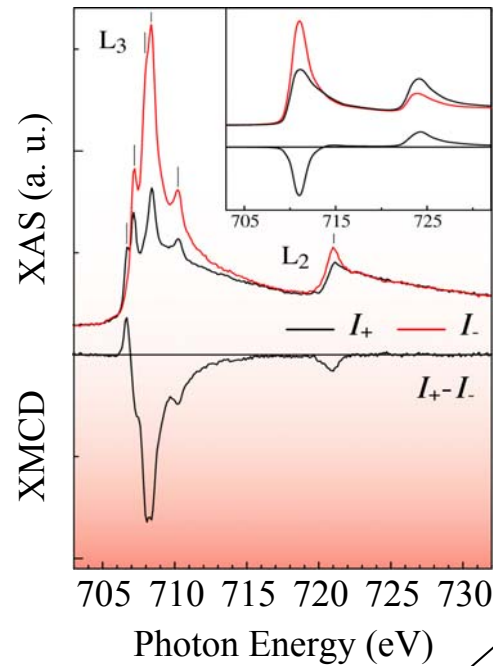The spectra do not depend on the magnetic field direction ->
K = 0

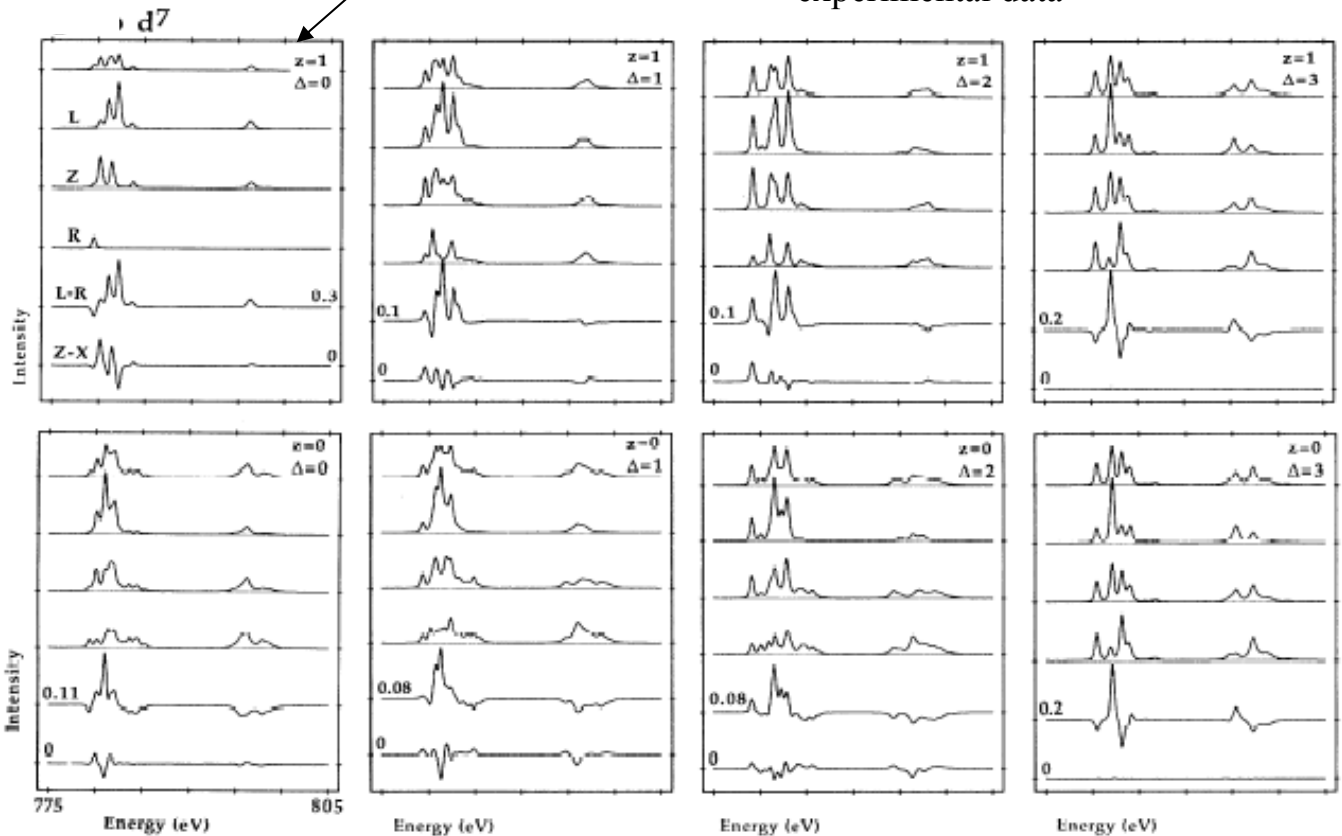# Atomic like behavior: soft interaction with the substrate

Iron

Fe atom: $d^6 \rightarrow d^7$
$m_L = 2 \, \mu_B \rightarrow 3 \, \mu_B$
$m_S = 4 \, \mu_B \rightarrow 3 \, \mu_B$

Co atom: $d^7 \rightarrow d^8$
$m_L = 3 \, \mu_B \rightarrow 3 \, \mu_B$
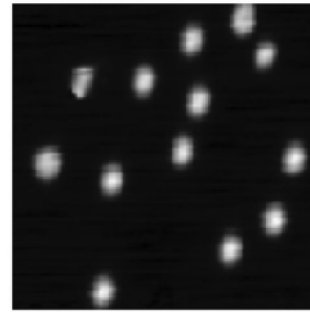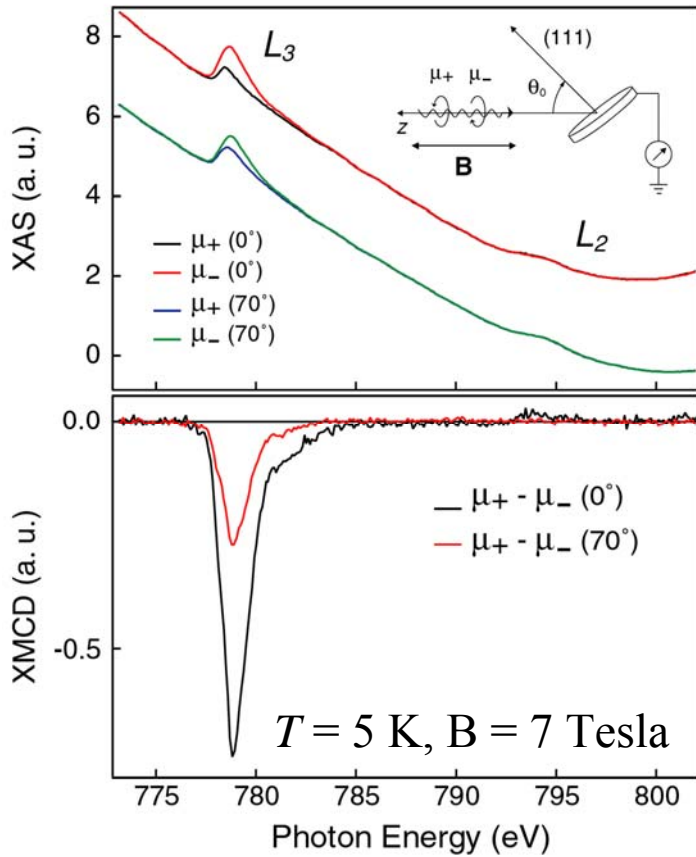$m_S = 3 \, \mu_B \rightarrow 2 \, \mu_B$

Note: in the simulation L – R is plotted in place of the R – L of the experimental data

XAS spectra for $3d^6 \rightarrow 2p^5 \, 3d^7$ transitions with (z = 1) and without (z = 0) spin-orbit interactions
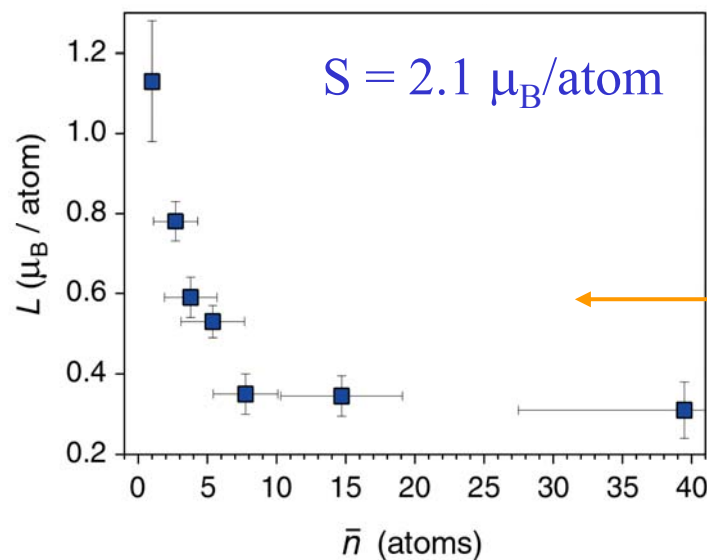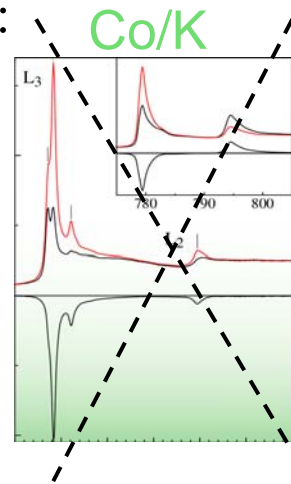
G. Van der Laan *et al.*, Phys. Rev. B **43**, 13401 (1991)

Co/Pt(111)

Isolated atoms

$T = 5$ K, B = 7 Tesla

STM image 85 x 85 Å²

The spectrum depends on the magnetic field direction -> K ≠ 0 (anisotropic system)

Bulk stile spectrum: sum rules

$m_L \sim \mu_B \; (A_3 + A_2)$

Co/K

S = 2.1 μ$_B$/atom

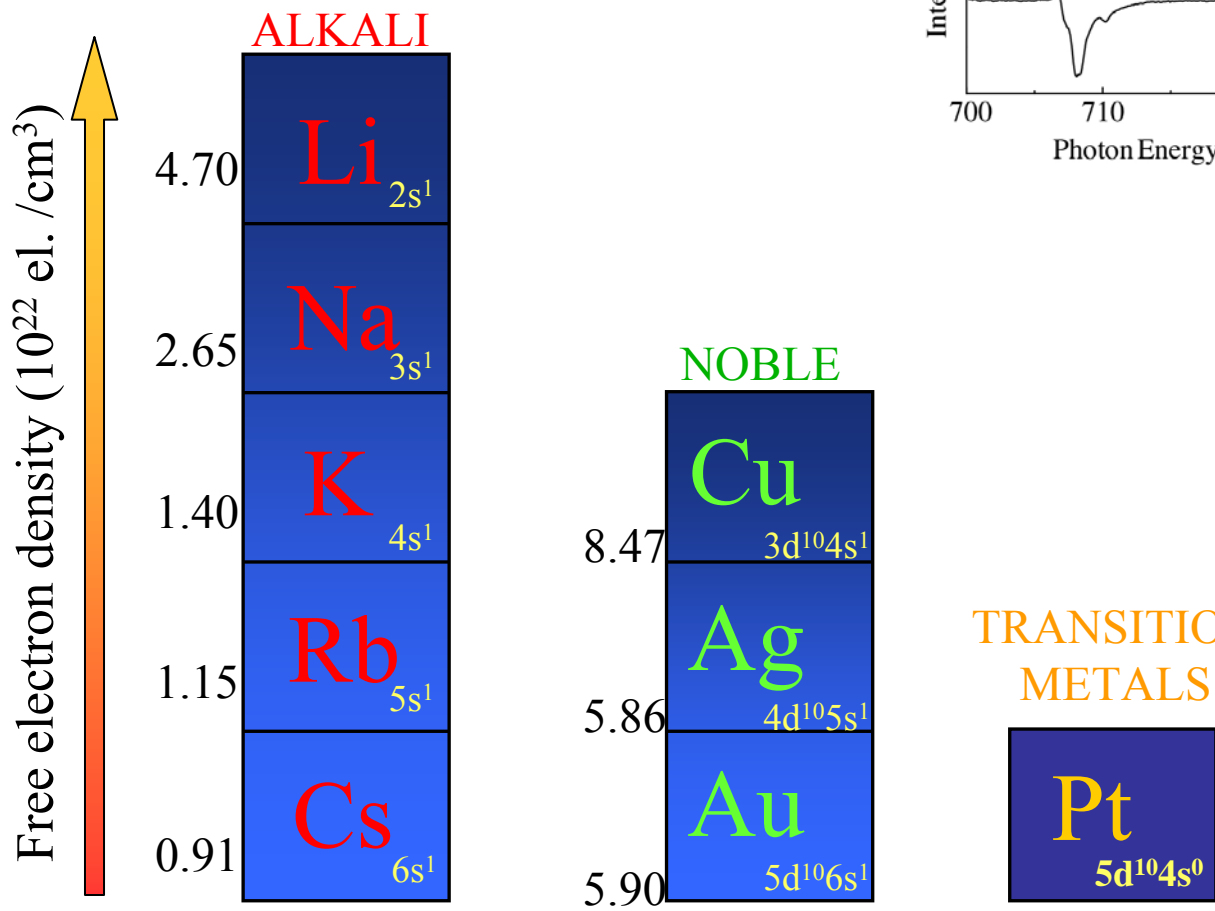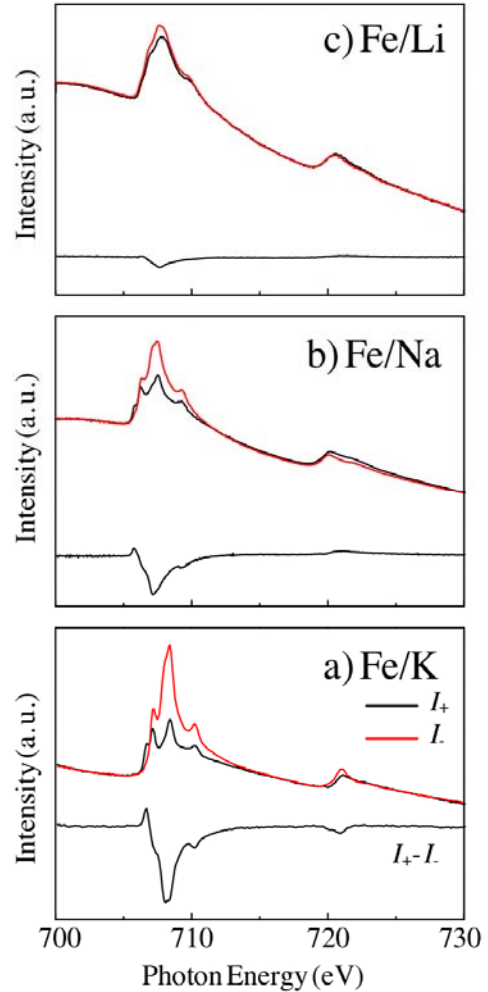The orbital moment strongly decreases by increasing the cluster size -> **coordination effect**
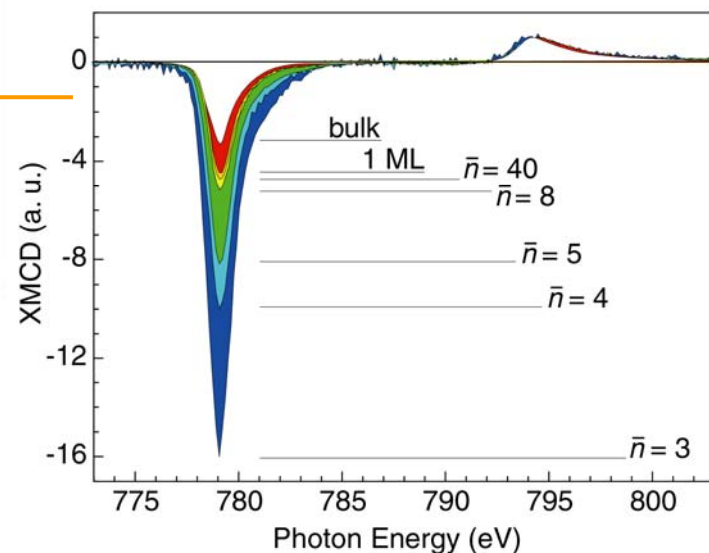
Interaction with the substrate

The interaction strength depends on the electronic state of the substrate

The interaction influences both:
1) atomic magnetic moment
2) Magnetic anisotropy energy

Evolution toward the bulk spectrum

c) Fe/Li

b) Fe/Na

a) Fe/K
— I_+
— I_-

$I_+ - I_-$

Intensity (a.u.)

Photon Energy (eV)

Free electron density (10^{22} el. /cm^3)

ALKALI

4.70	Li $2s^1$
2.65	Na $3s^1$
1.40	K $4s^1$
1.15	Rb $5s^1$
0.91	Cs $6s^1$

NOBLE

8.47	Cu $3d^{10}4s^1$
5.86	Ag $4d^{10}5s^1$
5.90	Au $5d^{10}6s^1$

TRANSITION METALS

Pt $5d^{10}4s^0$
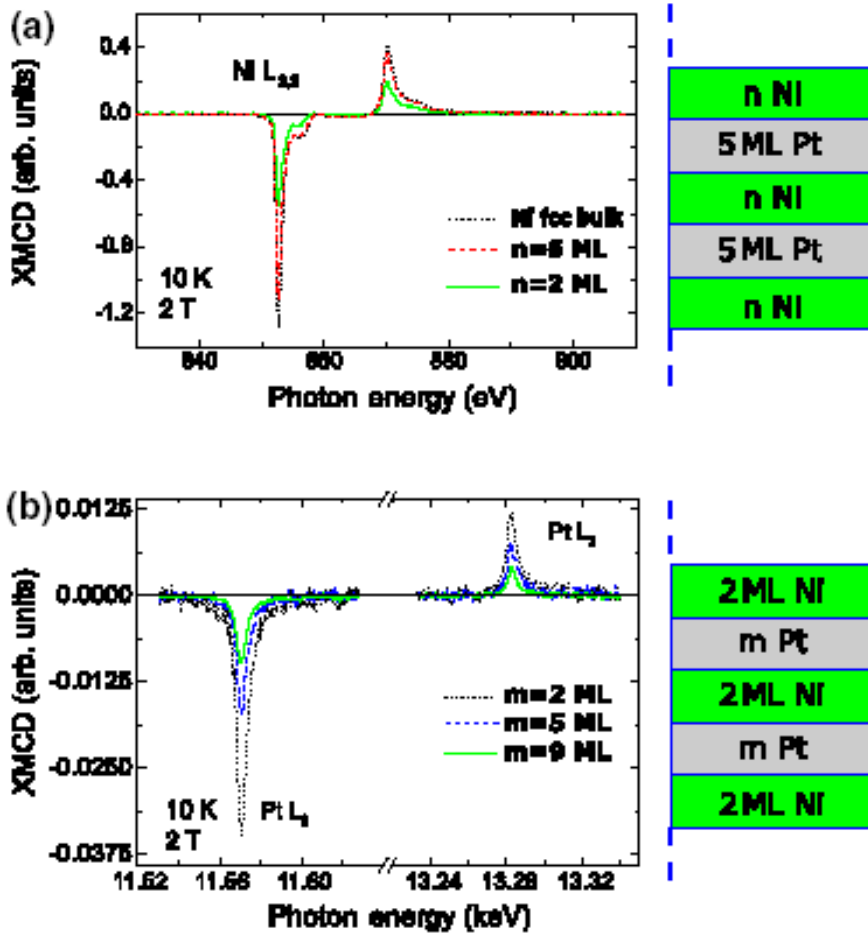
(*a*) XMCD at the Ni $L_{2,3}$ edges for two multilayers with constant Pt thickness (5 ML) and variable Ni thickness (Ni$_n$–Pt$_5$). (*b*) Pt $L_{2,3}$ edge XMCD for three multilayers with constant Ni thickness (2 ML) and variable Pt thickness (Ni$_2$–Pt$_m$)

n (ML)	m (ML)	μ_{Ni} (μ_B/atom)	μ_{Pt} (μ_B/atom)
2	5	0.24	0.09
2	2	0.39	0.17
6	5	0.47	0.17
6	2	0.49	0.29
13	5	0.54	0.21
Bulk Ni		0.61 [18]	

XMCD data for the average total magnetic moment of Ni and Pt. The induced moments are larger for thin Pt and thick Ni layers. The Ni magnetic moment is always reduced compared to the bulk (see the last row). The effect is stronger for thin Ni separated by thick Pt layers. The error bars are typically of about 10%.