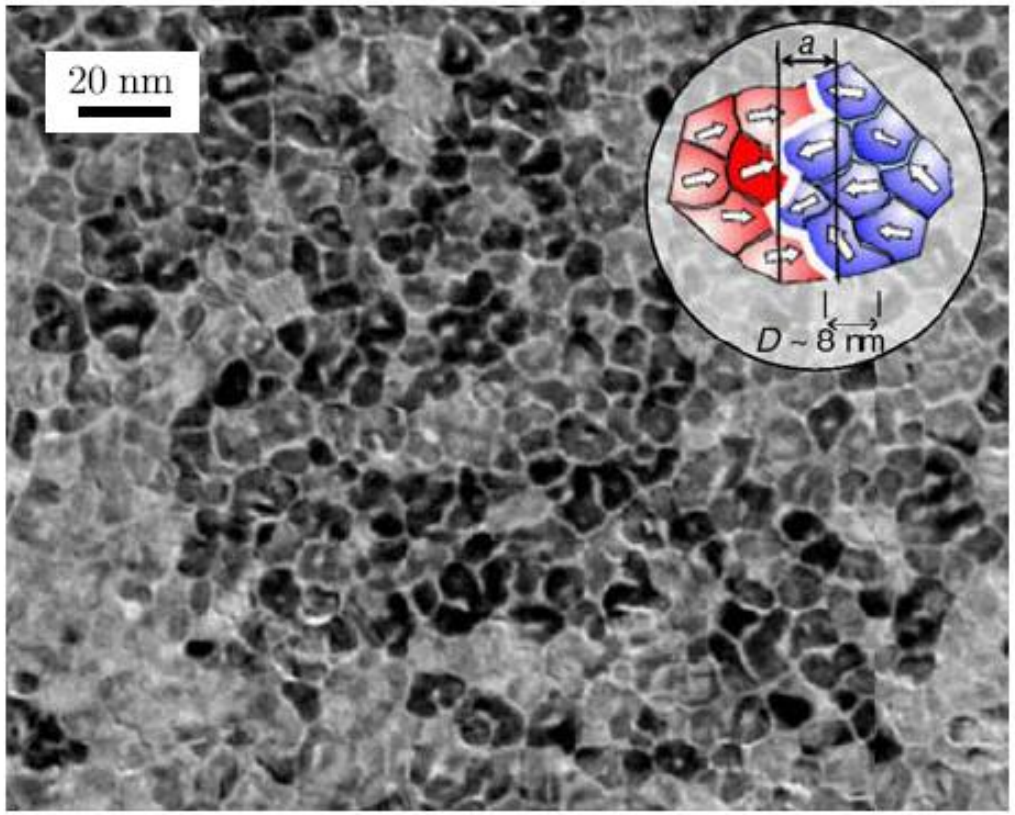
12

Magnetic anisotropy

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) …

Magneto-crystalline anisotropy energy (MAE)

Defines the direction(s) along which the magnetic moment prefers to align (together with the shape)

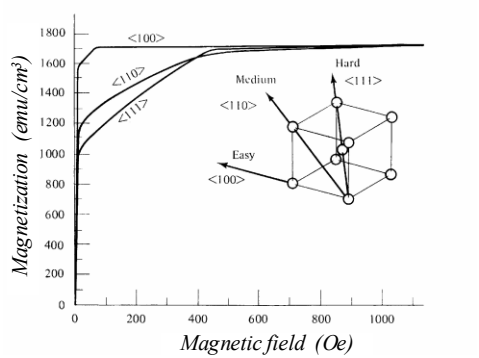
Bulk: MAE (K) depends on the crystal structure

Free magnetic atom: spatially isotropic ($K = 0$)

Fe bcc

$K_1 = 4.8 \times 10^4\ J/m^3$

$= 2.4\ \mu eV/atom$

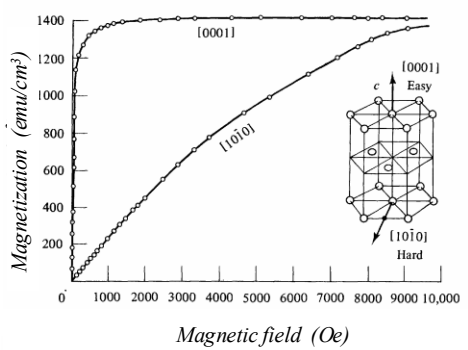


Co hcp

easy axis: (0001)

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

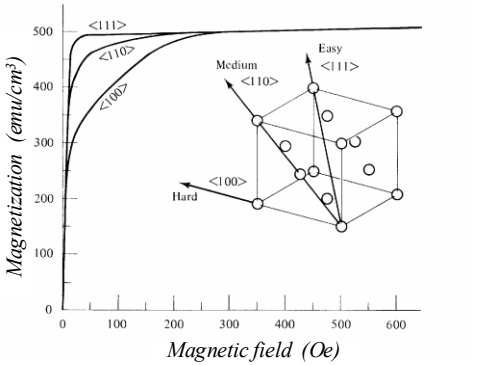
$= 45\ \mu eV/atom$

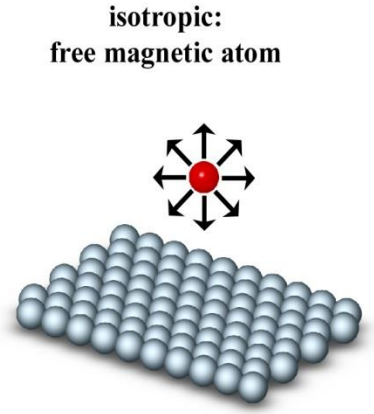


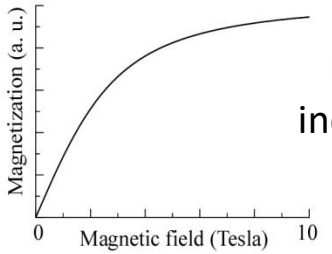
Ni fcc

$K_1 = -5.5 \times 10^3\ J/m^3$

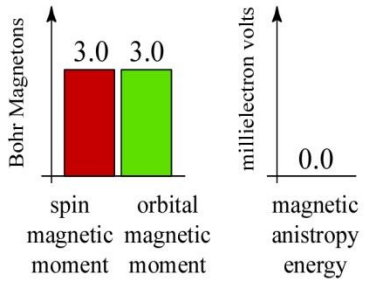
$= -0.3\ \mu eV/atom$





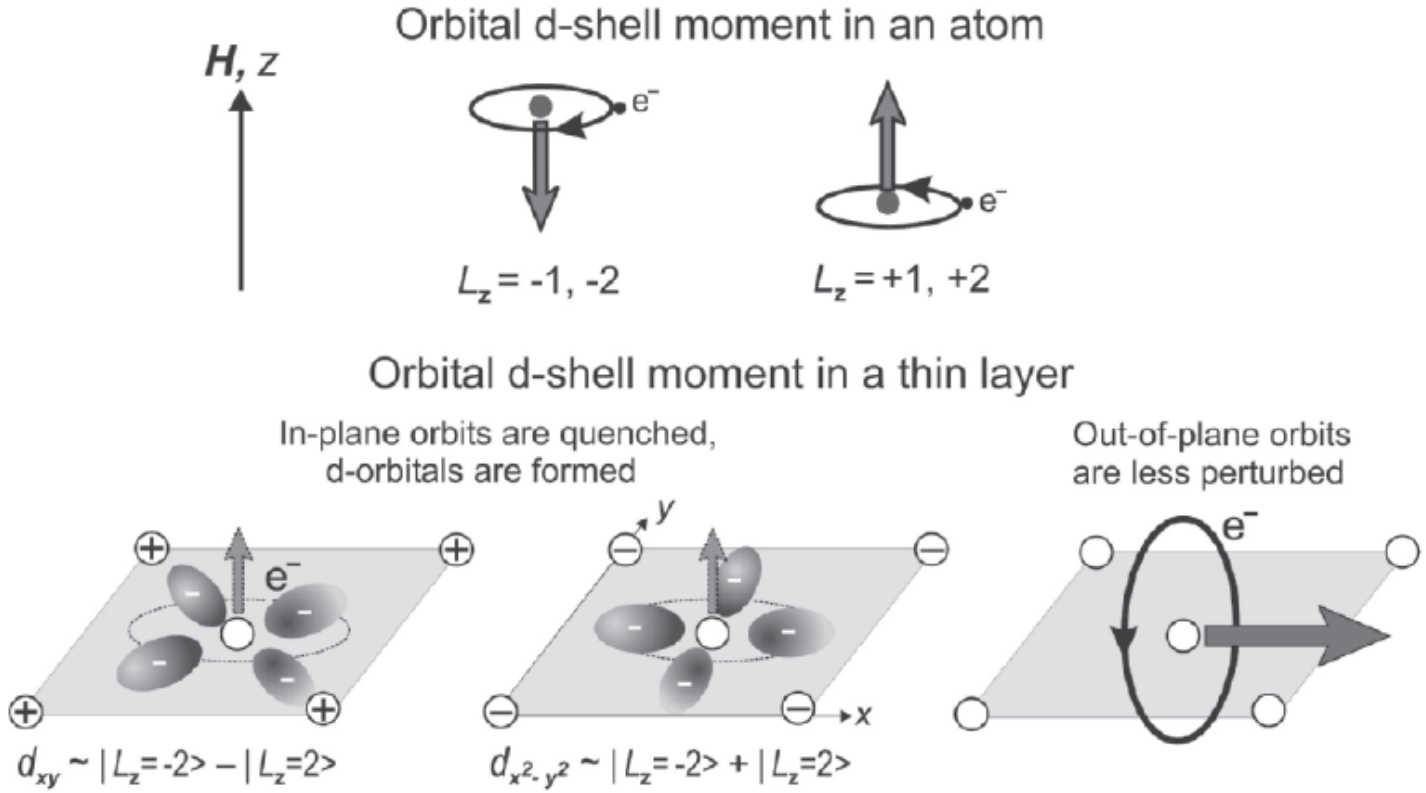


Direction independent



Co atoms

Origin of the MAE: Orbital moment and anisotropic bonds



d electron in a free atom.
Free orbital motion → atom with maximum L due to Hund's rules

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

Atom in a plane forming bonds with neighbouring atoms

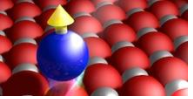
a) in-plane orbital motion frozen by bond → out-of-plane orbital moment is quenched

b) out-of-plane orbital motion unperturbed → in-plane orbital moment remains unquenched

The spin moment $\boldsymbol{S}$ is isotropic

However, spin-orbit coupling $(-\lambda\, \boldsymbol{S} \cdot \boldsymbol{L})$ **locks** the spin along the spatial direction having maximum $\boldsymbol{L}$

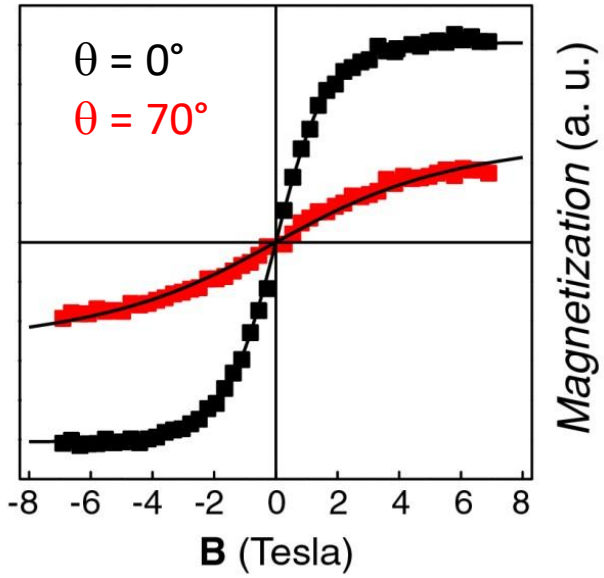
Magnetic anisotropy energy (MAE) $= -\lambda\, \boldsymbol{S} \cdot (\boldsymbol{L}_z - \boldsymbol{L}_{x,y}) = -\lambda\, \boldsymbol{S} \cdot \Delta \boldsymbol{L}$



MAE and orbital moment *vs.* cluster size

MAE originates from spin orbit coupling and anisotropic orbital bond: $K_{MAE} = \lambda\, S\, \Delta L$

Spin does not depend too much on size



θ is the angle between the normal to the surface and the field B

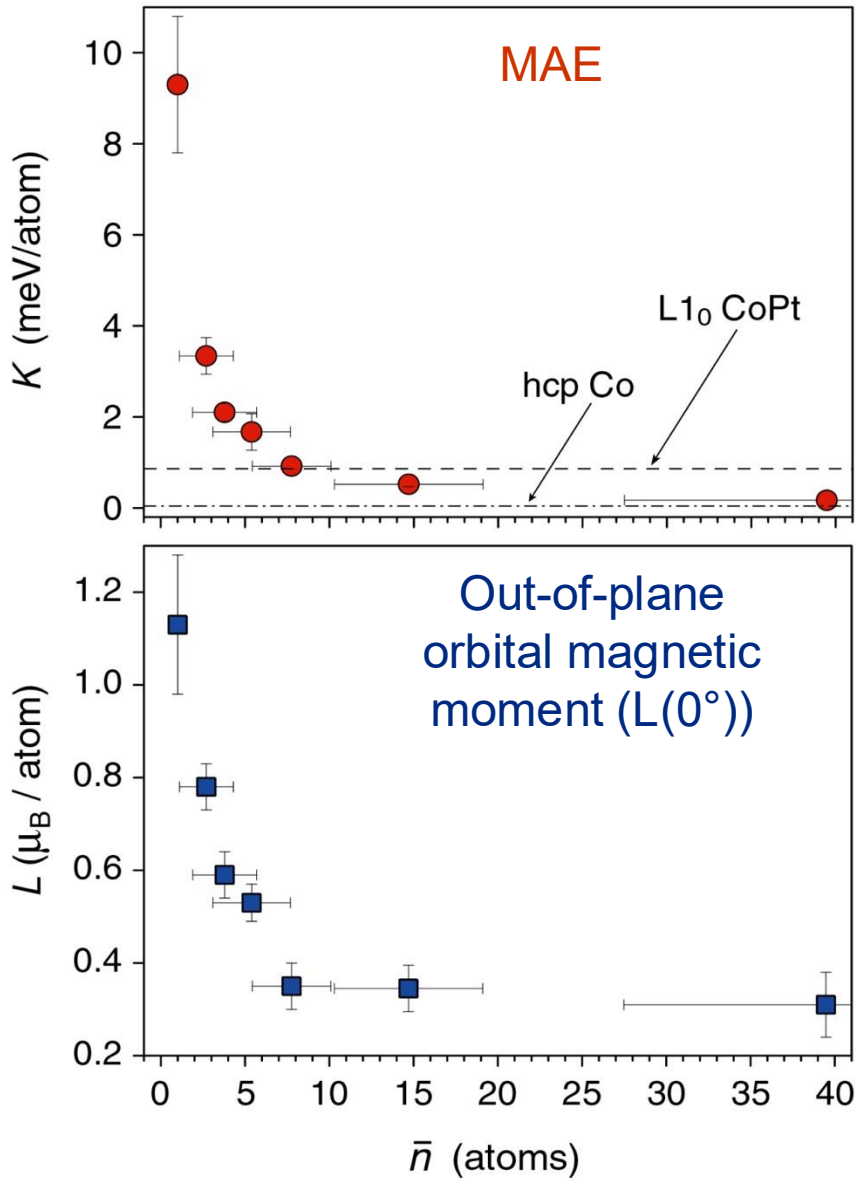
Using the XMCD (x-ray magnetic circular dichroism) technique, it is possible to measure L, S.

Fitting the magnetization curve knowing the adatom magnetic moment provides the MAE

Maximum theoretical value of the MAE for a Co atom:
Co: $S \approx 3/2; L \approx 3; \lambda \approx 20$ meV
MAE ≈ 90 meV

Hybridization between Co and Pt reduces L and thus the MAE

Co clusters on Pt(111) as a function of the size n

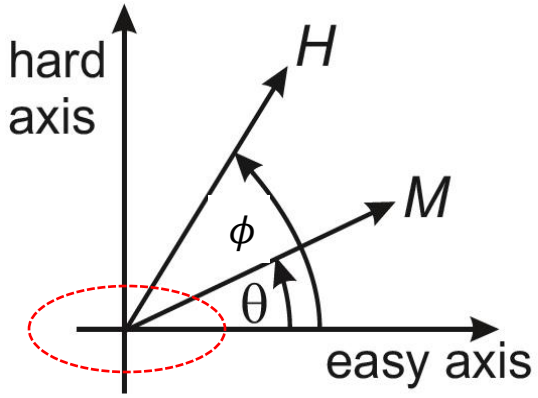


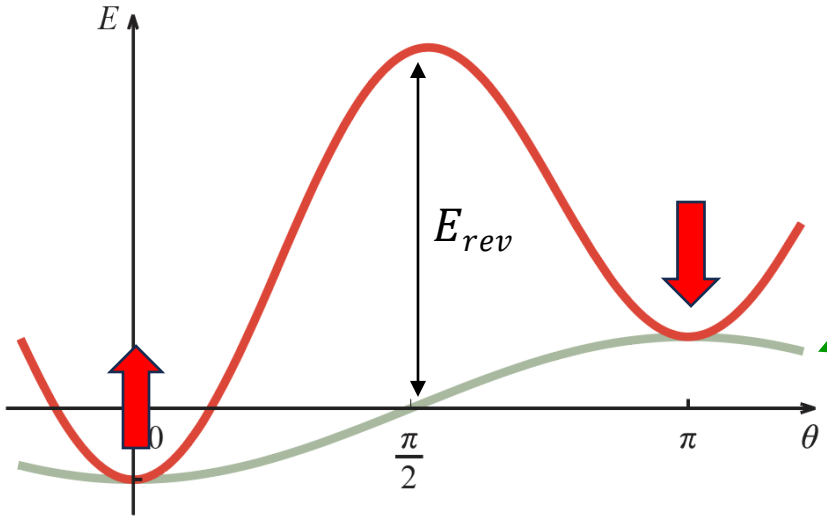
P. Gambardella *et al.*, Science **300**, 1130 (2003)

Macrospin (bit) magnetization

A bit is a binary system where 1 and 0 correspond to the magnetization being up or down

Magnetization along a defined axis: easy magnetization axis





Zeeman term (with ϕ=0)

anisotropy energy

$$E(\theta,\phi) = E_{rev}\sin^2(\theta) - \mu_0 MH\cos(\phi-\theta)$$

The energy has two minima, separated by a potential barrier

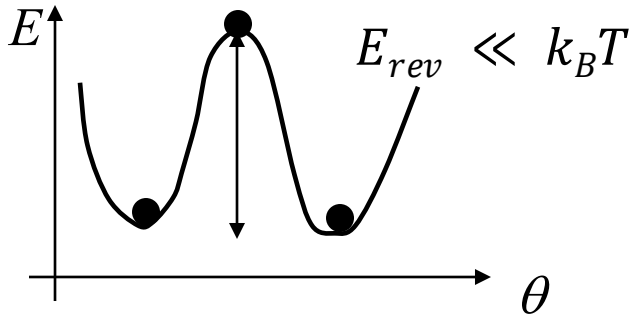
energy barrier for reversal E_{rev} = MAE (crystal field) + shape anisotropy energy assuming:
a) a single magnetic domain bit
b) coherent magnetization reversal (i.e. all spins in the bit turn at the same time)

Thermal stability of a macrospin (bit) magnetization

Exercise 12.1

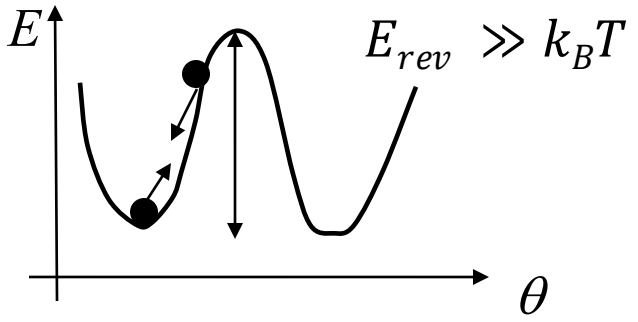
$$E(\theta) = E_{rev}\sin^2(\theta)$$

No magnetic field



the magnetization vector fluctuates

Information **can not** be stored



the magnetization vector cannot switch the versus

Information **can** be stored

Relaxation time = average time needed to jump from one minimum to the other:

$$\tau = \tau_0 \exp(E_{rev}/k_BT) \qquad \tau_0 \approx 10^{-10}\text{s}$$

τ = 1 year ⇒ $E_{rev} = 40\ k_BT \approx 1$ eV @ RT

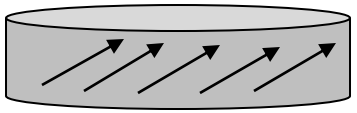
τ = 1 second ⇒ $E_{rev} = 23\ k_BT$

E_{rev} determines the thermal stability of the magnetization direction

Writing field: coherent magnetization reversal at T= 0 K

Stoner-Wohlfarth model : during the magnetization reversal all the atom spins in the particle stay aligned (macrospin)

hypothesys: all atoms contribute in the same way to the anisotropy energy: $E_{rev} = K_{atom}V$

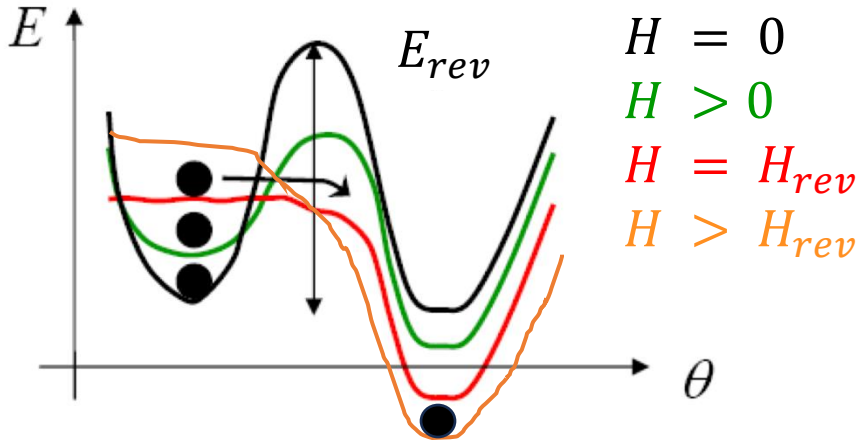


$$E(\theta,\phi) = E_{rev}\sin^2(\theta) - M\mu_0 H\cos(\phi-\theta)$$

$\frac{\partial E}{\partial \theta} = 0$ → direction of the magnetization

$\frac{\partial^2 E}{\partial \theta^2} = 0$ → reversal field H_{rev}

$$H_{rev} = \frac{2E_{rev}}{\mu_0 M} = \frac{2\,K_{atom}}{\mu_0\,\mu_{atom}}$$



H_{rev} is the field required to reverse the magnetization, i.e. to write a bit

Co in small cluster:
$K_{atom} \approx$ 1.2 meV
$\mu_{atom} \approx 2\mu_B = 2 \cdot 0.06$ meV/T

→ $B_{rev} = \mu_0 H_{rev} = 20$ T

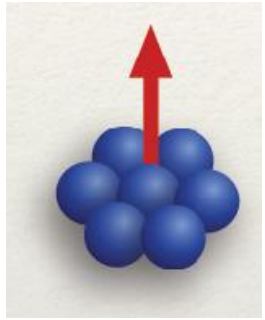
Macrospin: blocked and superparamagnetic states

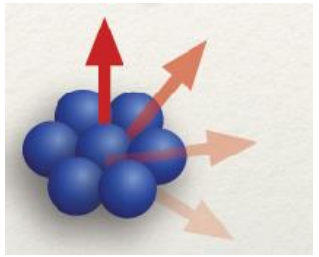
Exercise 12.2

Blocked state

Superparamagnetic state

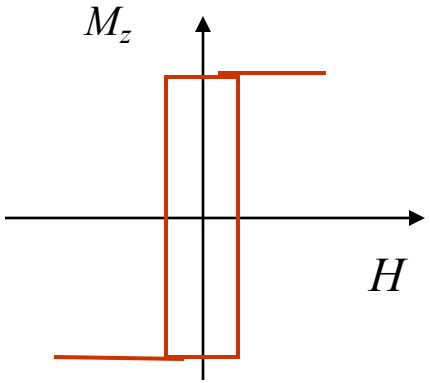
The system appears static when the relaxation time (τ) of the macrospin becomes much longer than the measuring time t



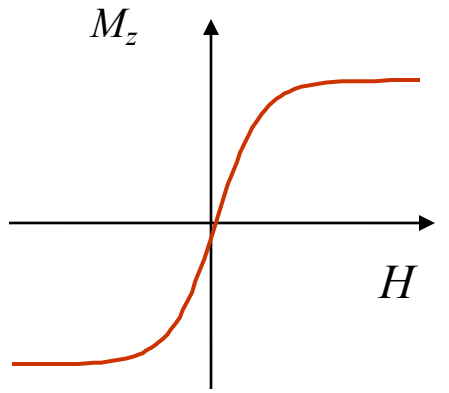


increasing temperature

The atom spins in the clusters are still coupled by exchange to form a macrospin.
The macrospin fluctuates similarly to the spin of a paramagnetic atom



$$\tau = \tau_0 \exp(E_{rev}/k_B T)$$



$$T_b = E_{rev} / (k_B \ln(\alpha t/\tau_0))$$

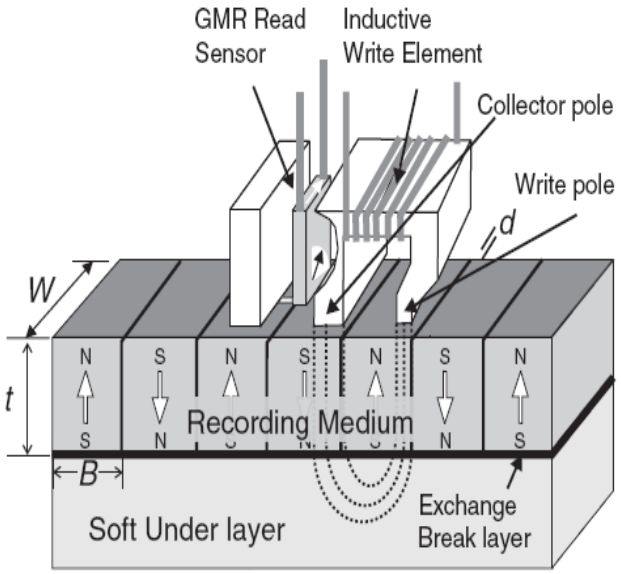
Blocking temperature T_b : a way to determine E_{rev} and therefore the anisotropy

Experiments: magnetic susceptibility measurements

FePt $L1_0$ phase for perpendicular recording

Perpendicular recording

HDD media: FePt in the $L1_0$ phase



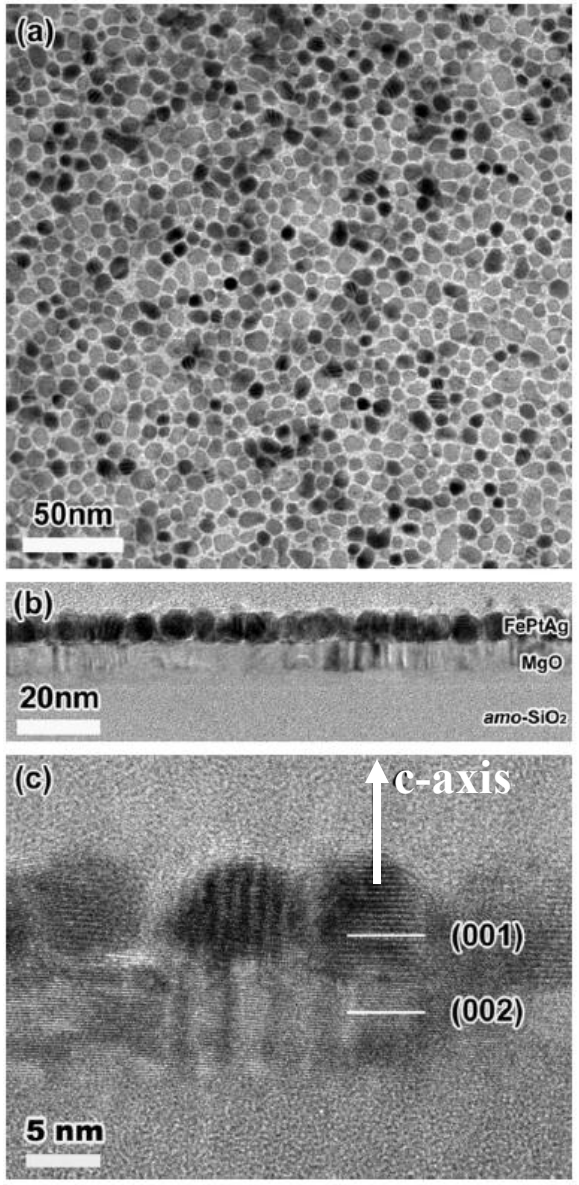


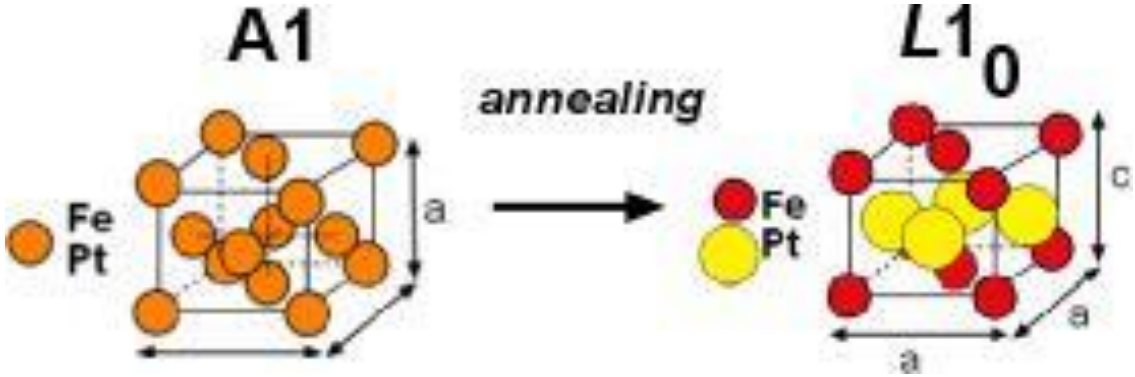
Fig. 8. (a) Bright field plane view image, (b) cross-sectional bright field image, and (c) cross-sectional high-resolution TEM image of the $(FePt)_{0.9}Ag_{0.1}$ –50vol%C film.

L. Zhang *et al.*, JMMM **322**, 2658 (2010)

Effect of crystal structure

Random distribution of Fe and Pt atoms

Ordered distribution of Fe and Pt atoms

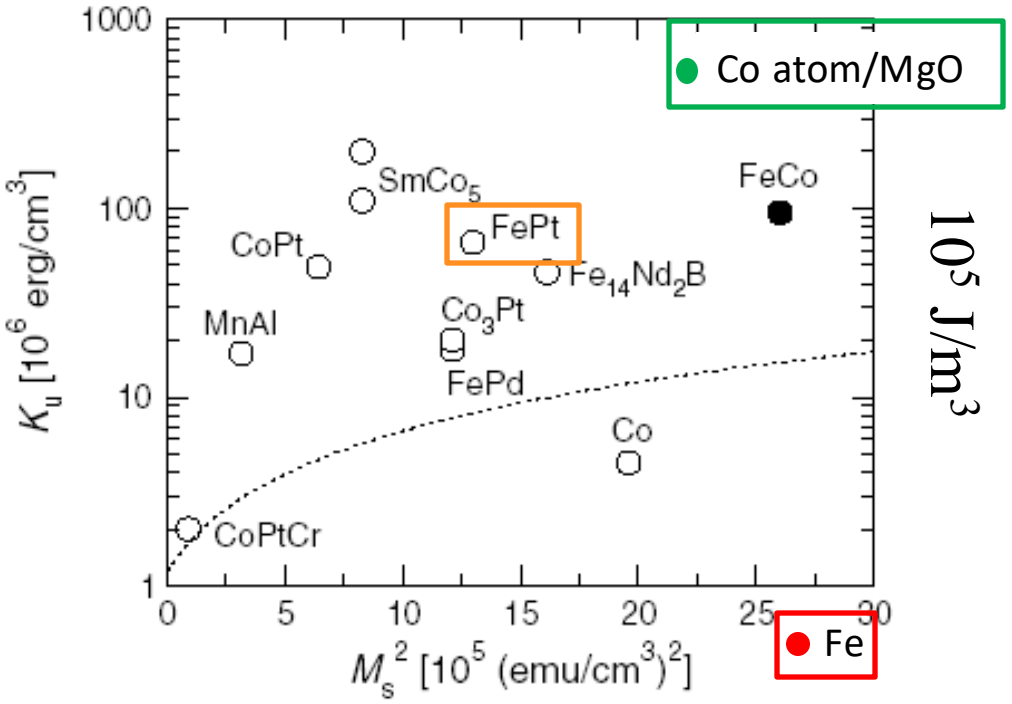


Basically isotropic

Strong easy axis along c-axis

In the alloy, every atom counts the same for the MAE (bulk property)

Why FePt in $L1_0$ phase and not simply Fe bcc?

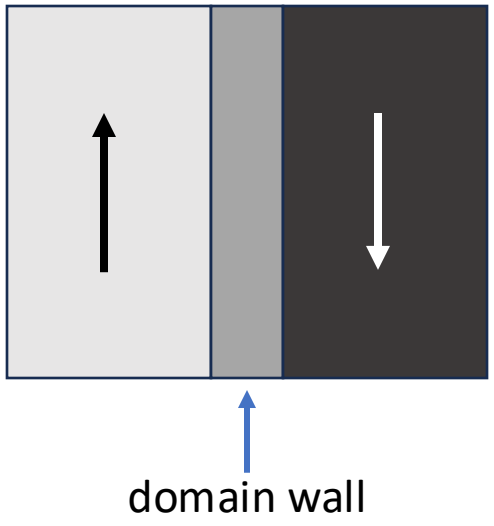


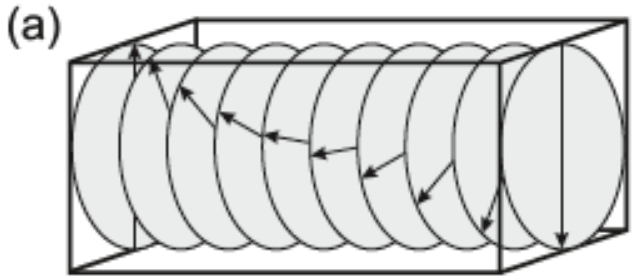
Storage media require materials with both:

- high K (to keep the magnetization orientation stable against thermal disorder)
- high M (to keep $H_{rev} = 2K\mathrm{V}/M$ within technological limit)

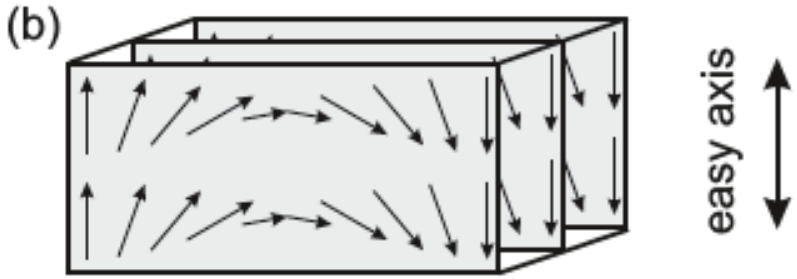
T. Burkert et al., *Phys. Rev. Lett.* 93, 027203 (2004).

Domain walls





Bloch wall
The rotation of the magnetization occurs in a plane parallel to the plane of the domain wall



Néel wall
The rotation of the magnetization occurs in a plane perpendicular to the plane of the domain wall

Competition:
exchange energy → infinite wall width
(parallel alignement favored, stiffness)

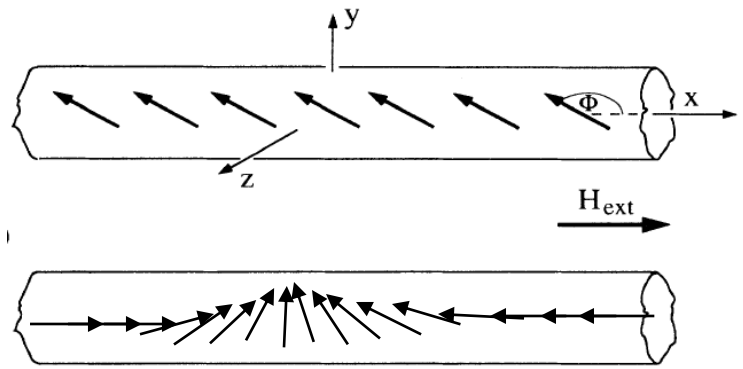
but

anisotropy energy → small wall width
(specific direction preferred)

→ **finite domain wall width**

Coherent vs. incoherent magnetization reversal

Wire with length L, section W, lattice parameter a.
Each atom contributes with K to the anisotropy energy



Coherent reversal: $E_{rev} = K\,L\,W$

Reversal by domain wall creation and propagation: $E_{rev} = 4\,W\sqrt{AK}$

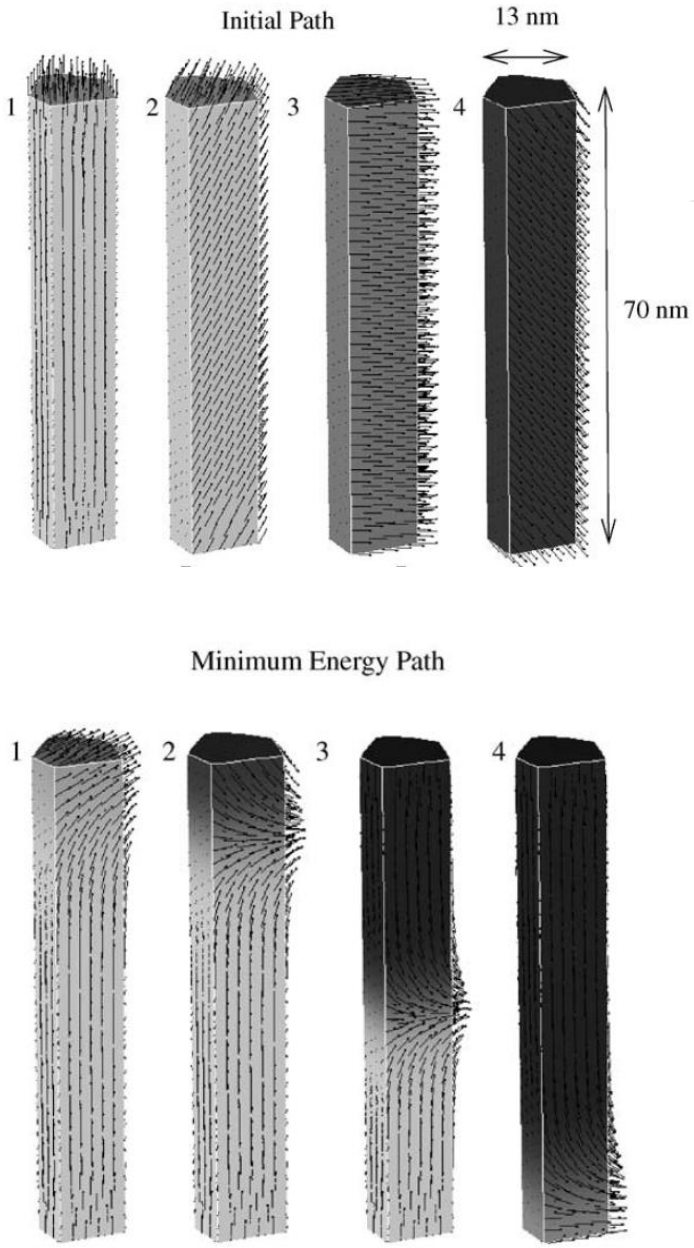
$A = 2J_{ex}S^2/a$ is called "stiffness"

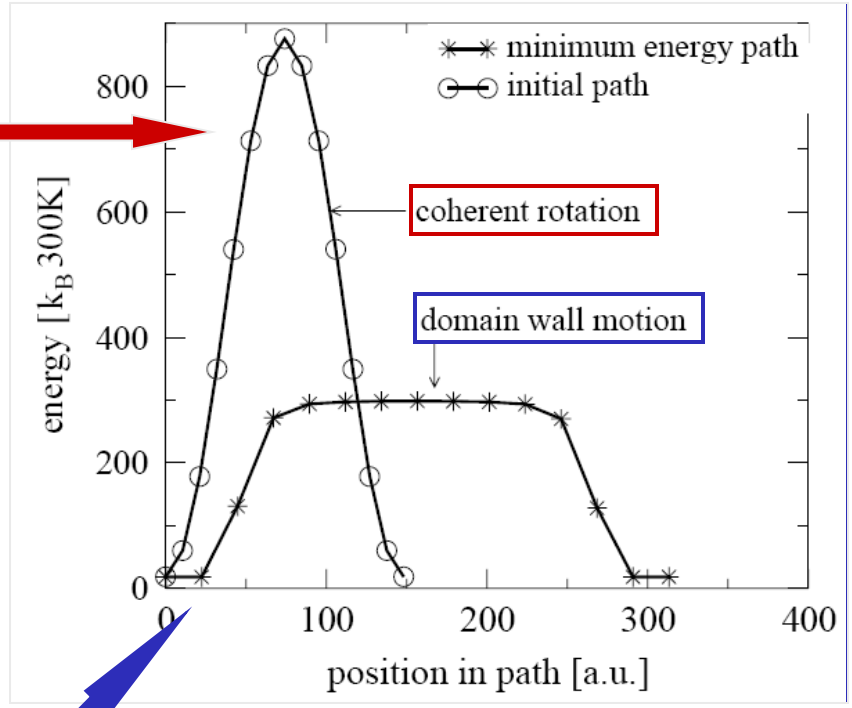
Domain wall propagation is favored if:

$$L > 4\sqrt{A/K}$$

H.-B. Braun Phys. Rev B **50**, 16502 (1994); H.-B. Braun Phys. Rev B **50**, 16485 (1994);
H.-B. Braun Phys. Rev Lett. **71**, 3557 (1993); H.-B. Braun J. Appl. Phys. **85**, 6172 (1999)

Particle shape affects magnetization reversal





Domain wall creation and propagation costs less energy than coherent rotation

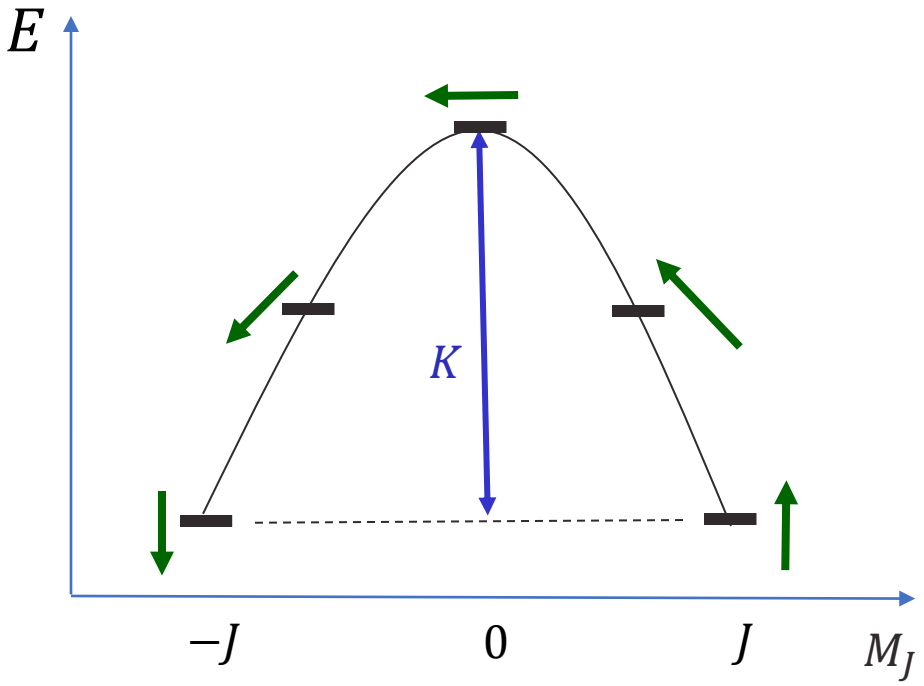
R. Dittrich *et al.* J. Magn. Magn. Matter. **250**, L12 (2002)

MAE: classical *vs.* quantum objects

Ideal uniaxial case: crystal field with C_∞ symmetry along z direction

Quantum:

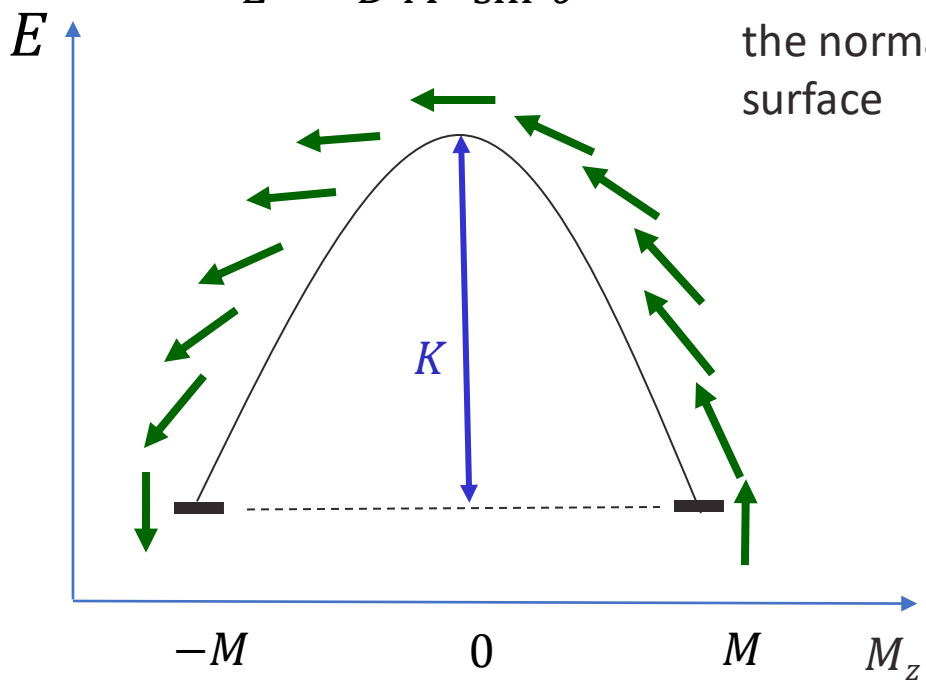
$\mathcal{H} = D\, J_z{}^2$



Only a discrete number $(2J + 1)$ of states is available

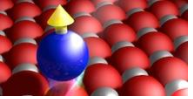
Classical:

$E = D\, M^2 \sin^2\theta$



Continuous magnetization rotation

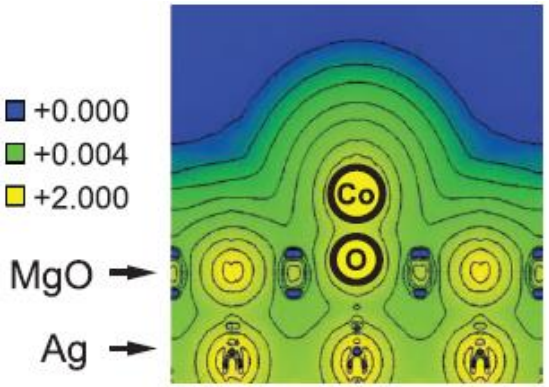
θ is the angle between the **macrospin** $\boldsymbol{M}$ and the normal to the surface

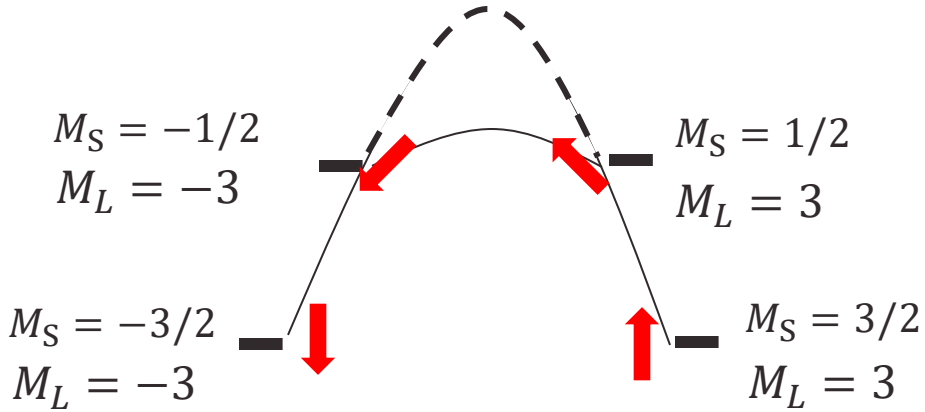


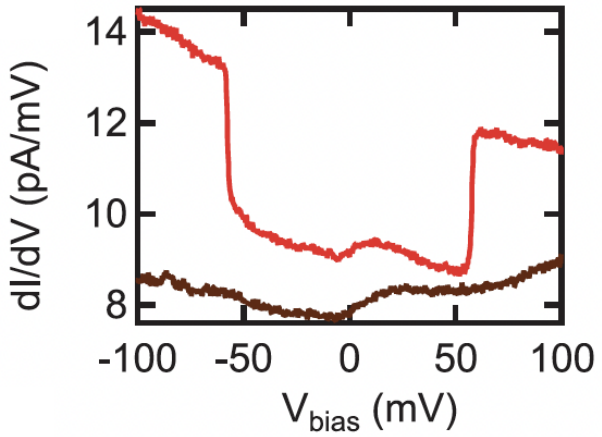
MAE limit in 3d metal atoms

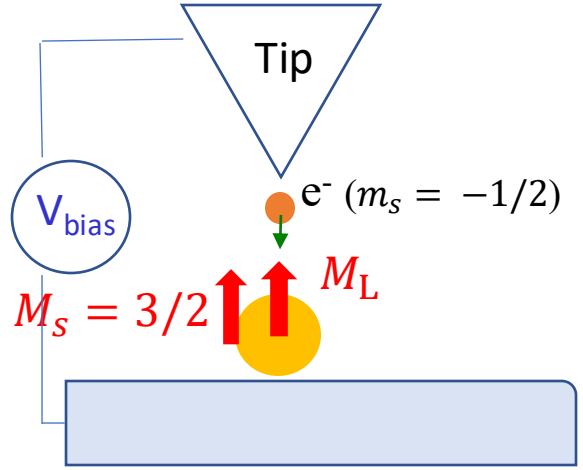
Co atom on MgO adsorbs on top of oxygen and forms a strong uniaxial bond (almost C_∞), generates a strong out-of-plane anisotropy

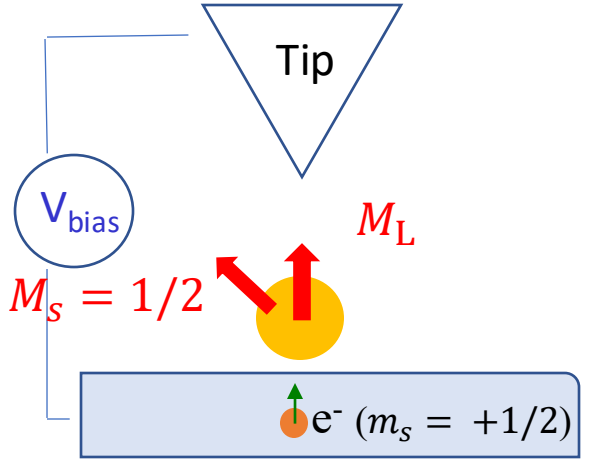
From XMCD:
Co preserves atomic values of both L and S: $L = 2.9,\ S = 3/2$











Spin-flip transitions that leave L unchanged

$$\Delta E = \lambda \Delta S M_L \approx 20 \cdot 1 \cdot 2.9 \approx 60 \text{ meV}$$

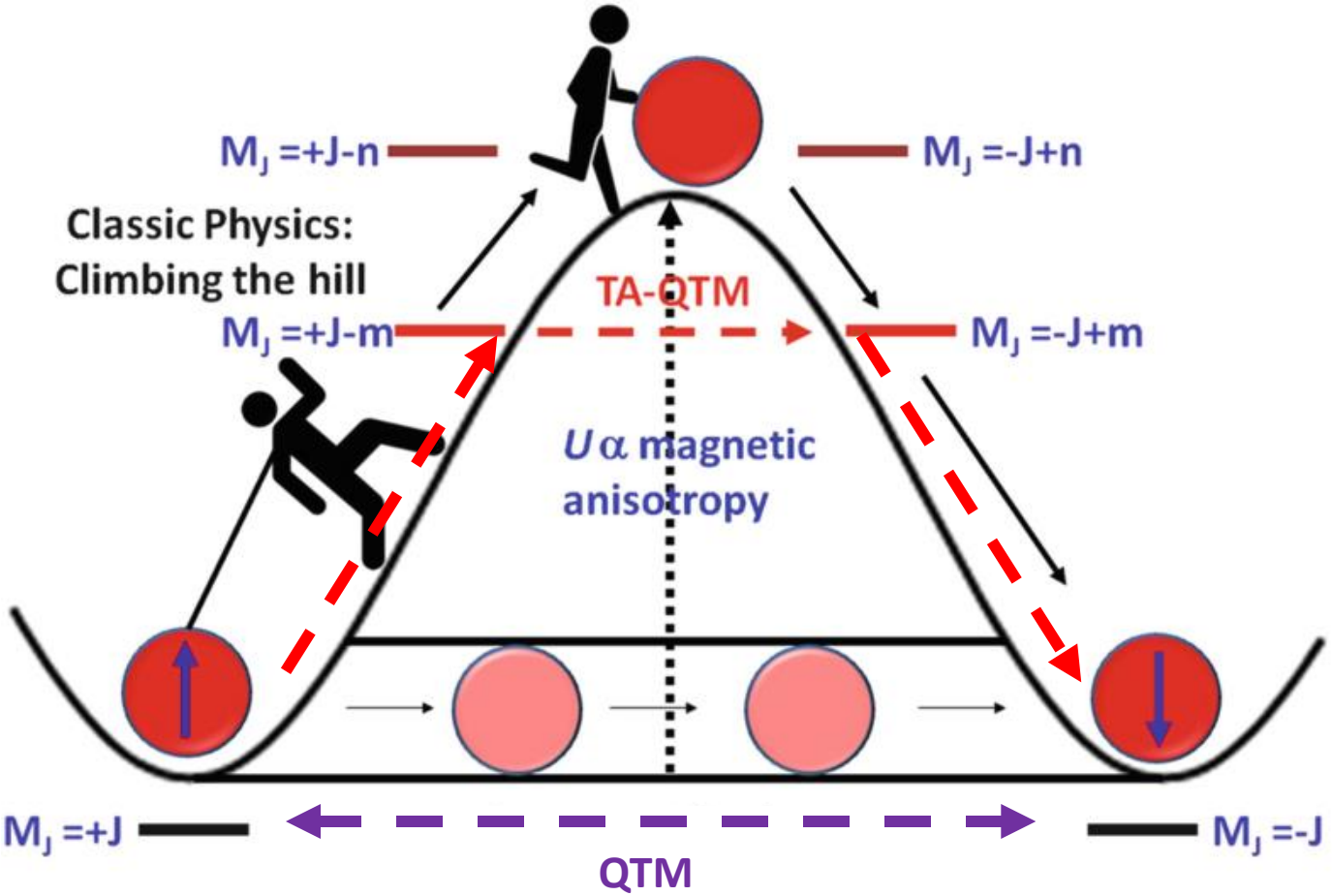
I. Rau *et al.*, Science **344**, 988 (2014)

Quantum tunneling of magnetization (QTM)

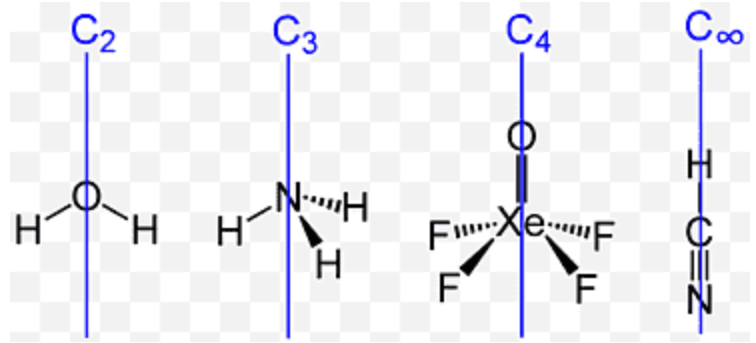
Real case: crystal field with C_n symmetry

Reversal via: QTM

TA-QTM



Ex.: crystal field with C_n symmetry



TA-QTM: thermal assisted QTM

W. Wernsdorfer, C. R. Chimie **11,** 1086 (2008)

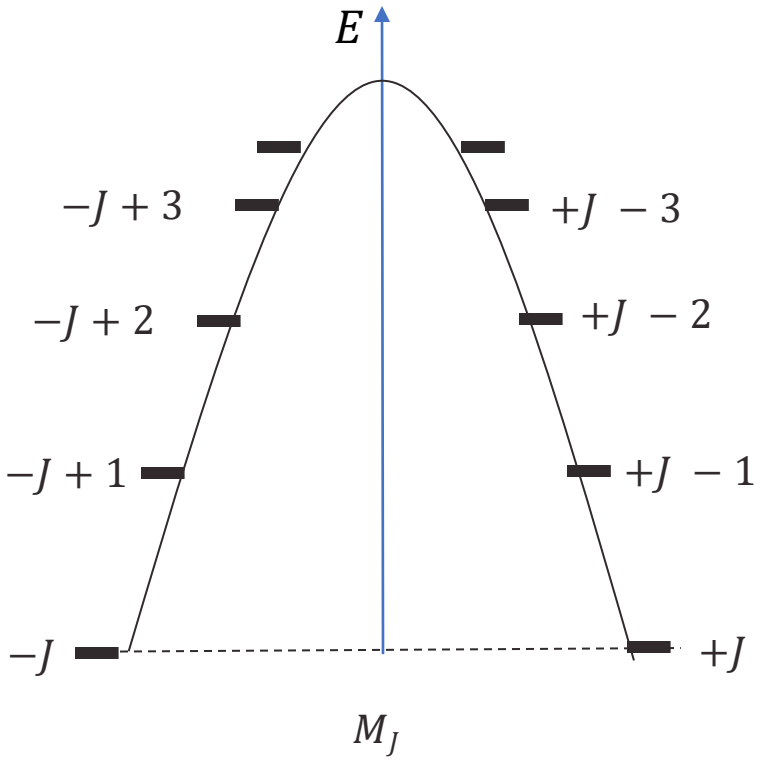
Level splitting induced by crystal field

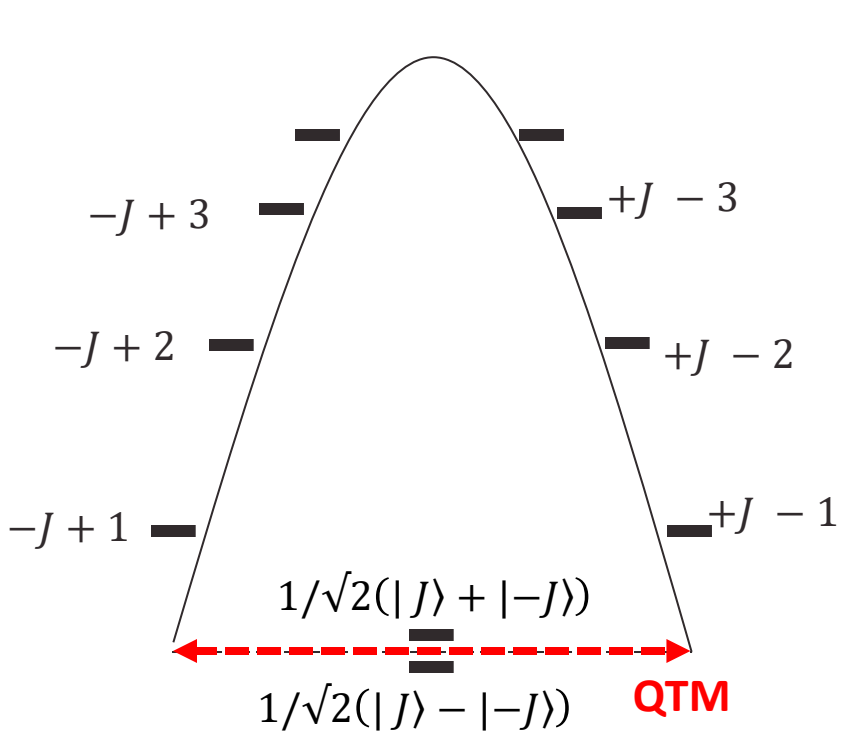
C$_\infty$ symmetry: $\mathcal{H} = D\,J_z{}^2$

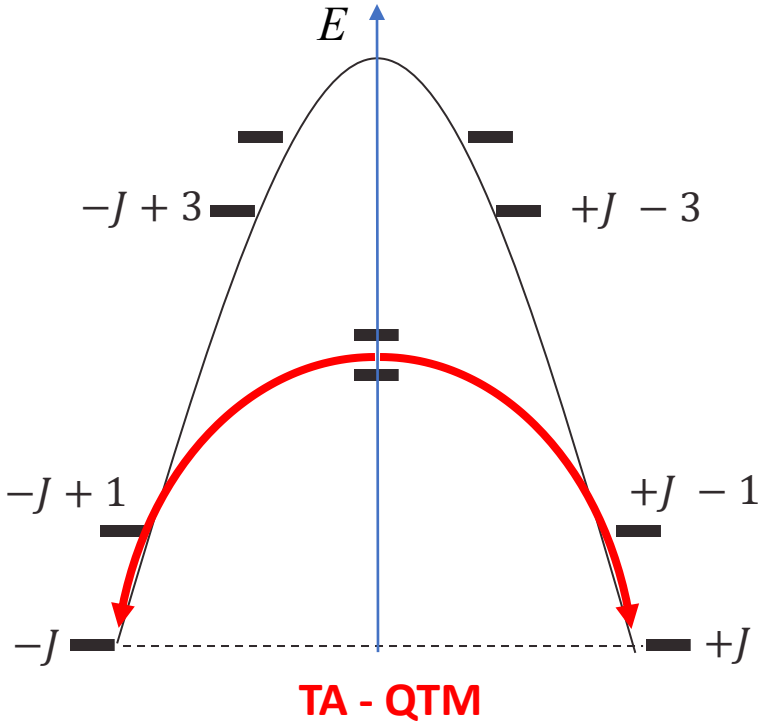
Pure M_J states → No QTM

C_n symmetry: $E = D\,J_z{}^2 + \alpha\,(J_+{}^n + J_-{}^n)$

$J_\pm{}^n$ operators mix states satisfying $M_J - M_{J'} = nk$ (k integer) → QTM or TA-QTM





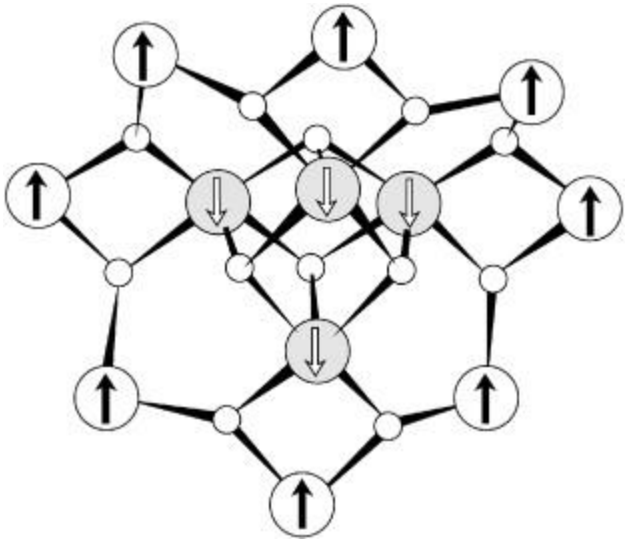


In case of QTM, a net magnetization cannot be stabilized in the ground state (the ground state is a superposition of spin-up and spin-down states) → the particle or atom cannot be a bit.
But it's a prototype of a qubit (superposition state)!

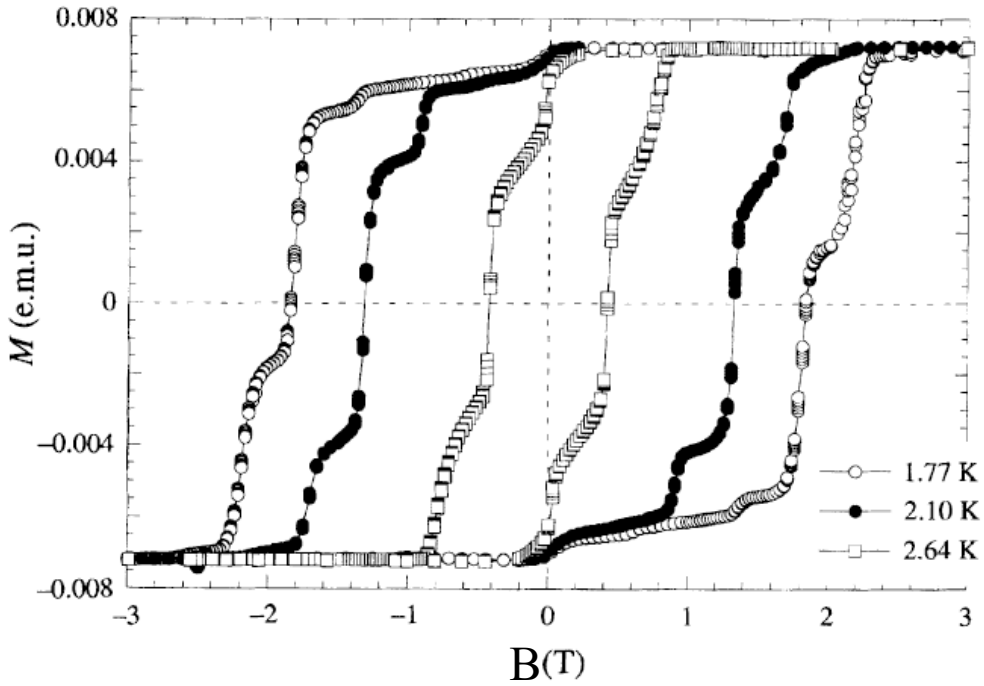
Quantum tunneling of magnetization in Mn_{12}-acetate

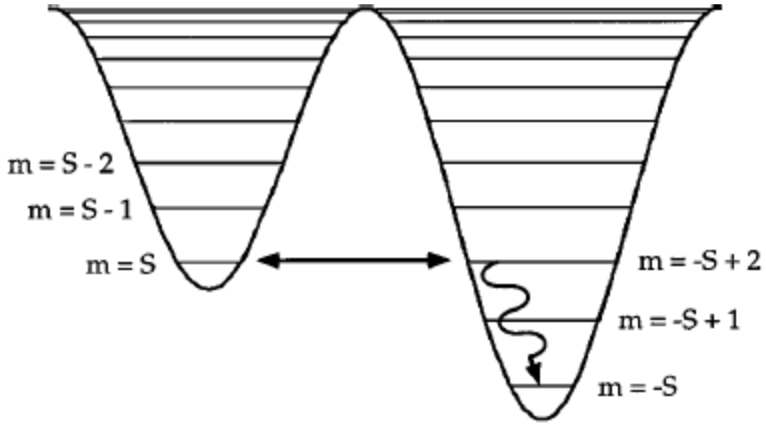
Exercise 12.3

Single molecule magnet:
Mn_{12}-acetate



Mn atoms have $S = 5/2,\ L = 0$
8 Mn pointing up; 4 Mn pointing down
Total $J = S = 10$





QTM when states with opposite M_J are degenerate

here $M_J = M_S$ is called m

L. Thomas *et al.* Nature **383**, 145 (1996)
J. R. Friedman *et al.* Phys. Rev. Lett. **76**, 3830 (1996)

Spectroscopy

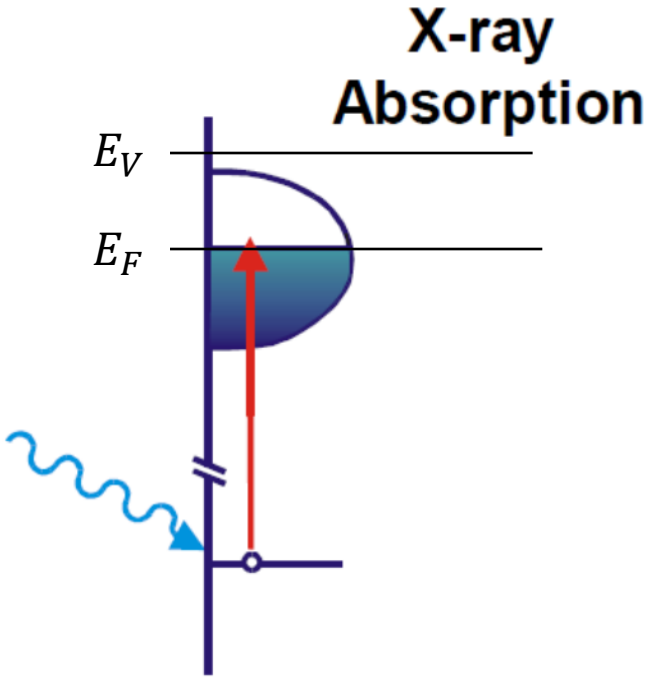
Band structure	ARUPS (ARPES)
Chemical composition	XPS, Auger
Magnetism	XAS, XMCD
Bond orientation	XLD
Structure modification	EXAFS
…	
…	
…	

XAS *vs.* XPS

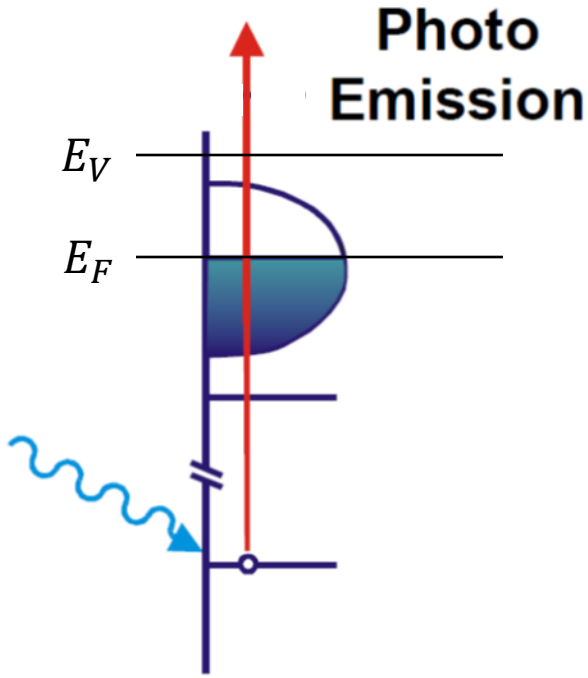
XAS
Incoming phonons with **tuned energy**

Maximum absorption for resonant excitation from a core level to a valence state

XAS
X-ray absorption spectroscopy



XPS
X-ray photoelectron spectroscopy



Different detection schemes
Total electron yield TEY → surface sensitive
Transmission yield TY → bulk sensitive
Fluorescence yield FY → bulk sensitive

X-ray absorption process: Selection rules

The transition probability per unit time from an initial state i to a final state f (Fermi's golden rule)

$$w_{i\to f} = \frac{2\pi}{\hbar}|\langle f|\mathcal{H}_{int}|i\rangle|^2\delta(\varepsilon_f - \varepsilon_i - \hbar\omega)$$

$\hbar\omega$ energy required to excite the electron from initial to final state

x-ray absorption intensity per atom, in the electron dipole approximation

$$I = 4\pi^2\frac{e^2}{\hbar c}\hbar\omega\left|\langle f|\hat{\mathcal{E}}\cdot\mathbf{r}|i\rangle\right|^2$$

$\hat{\mathcal{E}}$ unit electric field vector

$\boldsymbol{r} = x\hat{\boldsymbol{e}}_x + y\hat{\boldsymbol{e}}_y + z\hat{\boldsymbol{e}}_z$ electron position

dipole operator: it can be expressed in terms of spherical harmonics $Y_{1,m}$;
Which $Y_{1,m}$? It depends on the photon spin *i.e.* on the polarization of light (left, right, linear)

Focusing on the angular part of the electronic states: the matrix elements consist of integrals involving the product of spherical harmonics

Example:
$$\left|\iint \sin\theta\, d\theta\, d\phi\, Y_{2,2}^*\sqrt{\frac{4\pi}{3}}\, Y_{1,1}\frac{1}{\sqrt{3}}Y_{1,0}\right|^2 = \frac{4}{15}$$

final state operator initial state

dipole selection rules

$$\Delta l = \pm 1$$
$$\Delta m_l = 0, \pm 1$$

with

$$\Delta s = 0$$
$$\Delta m_s = 0$$

polarization dependent

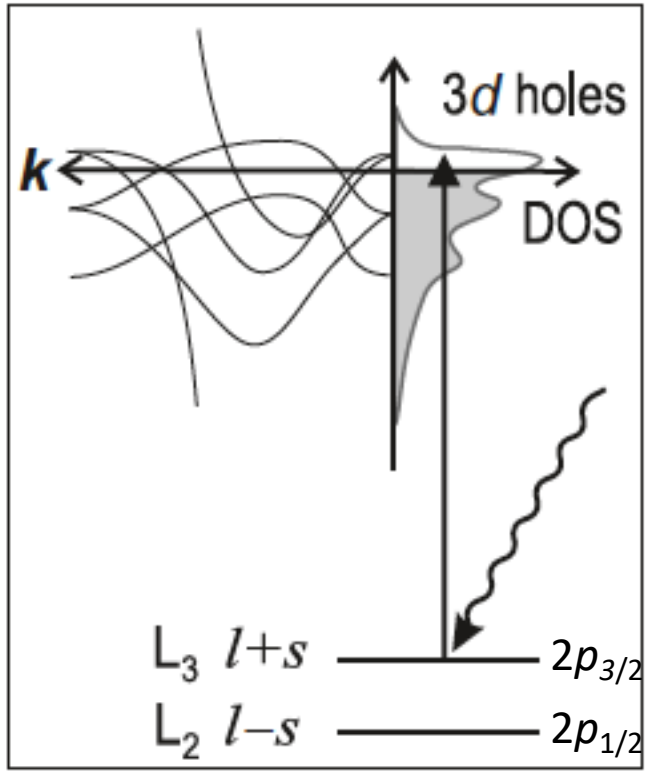
XAS: example of L_2, L_3 edges

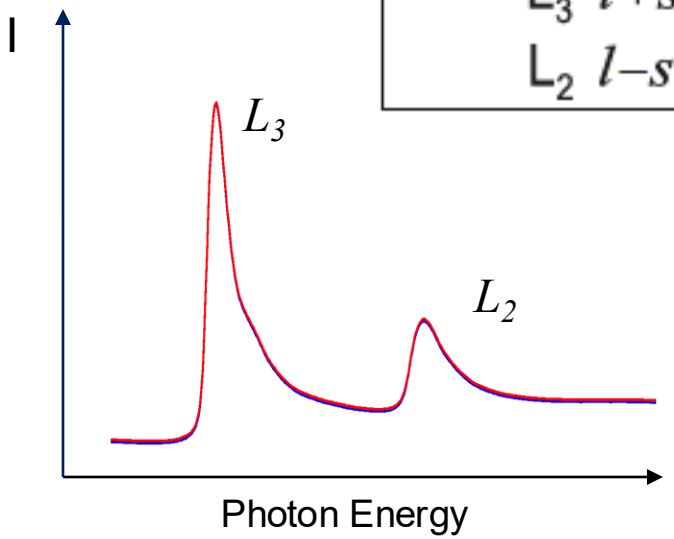
2p levels (6 electrons)
each electrons has $l = 1$, and $s = 1/2$
total angular momentum for each electron:
$j = l + s, \ldots |l - s| \quad \rightarrow \quad j = 3/2, 1/2$
The basis describing the states is $|l, s, j, m_j\rangle$

Due to spin-orbit coupling, the states with $j = 1/2$ (L_2 edge) have a different energy than the ones with $j = 3/2$ (L_3 edge)

The antiparallel configuration ($2p_{1/2}$) is energetically favorable, i.e. has higher binding energy, therefore it requires higher photon energy to be reached

Intensity ratio related to degeneracy $(2j + 1)$
(branching ratio)

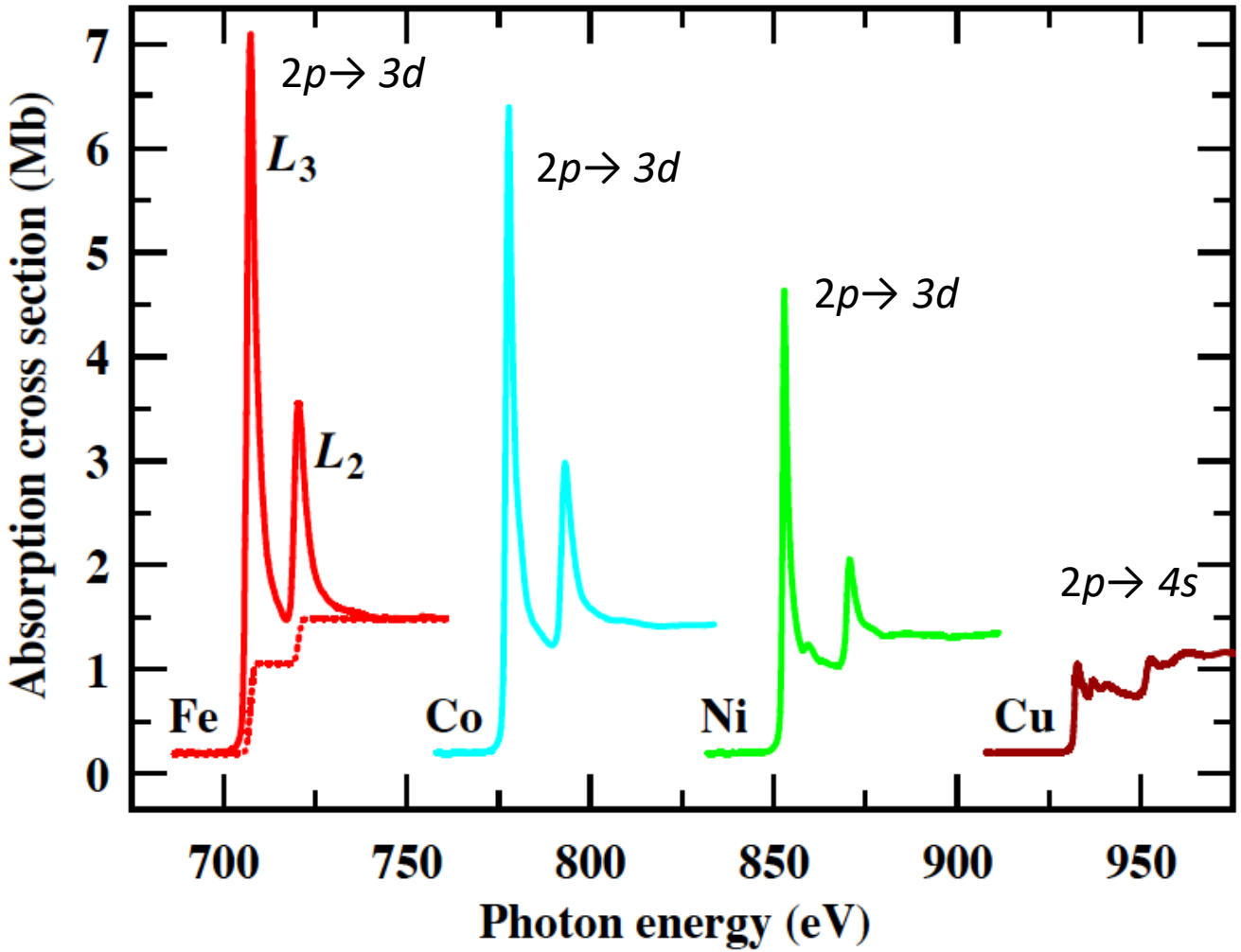




XAS element sensitivity

Exercise 12.4

26	55.847	27	58.9332	28	58.70	29	63.546
2,3		2,3		2,3		2,1	
3135		3201		3187		2836	
1809		1768		1726		1357.6	
7.86	Fe	8.90	Co	8.90	Ni	8.96	Cu
$[Ar]3d^6 4s^2$		$[Ar]3d^7 4s^2$		$[Ar]3d^8 4s^2$		$[Ar]3d^{10} 4s^1$	
Iron		Cobalt		Nickel		Copper	



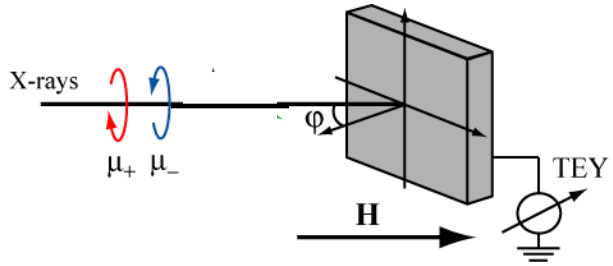
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$
26 Fe	7112	844.6†	719.9†	706.8†
27 Co	7709	925.1†	793.2†	778.1†
28 Ni	8333	1008.6†	870.0†	852.7†
29 Cu	8979	1096.7†	952.3†	932.7

For Fe, Co, Ni, the signal is dominated by the 2p → 3d transition

For Cu, the 3d states are fully occupied (except for some weak hybridization), the signal corresponds to 2p → 4s

The observed intensity reflects the empty DOS states between E_F and E_V

XMCD: X-ray magnetic circular dichroism



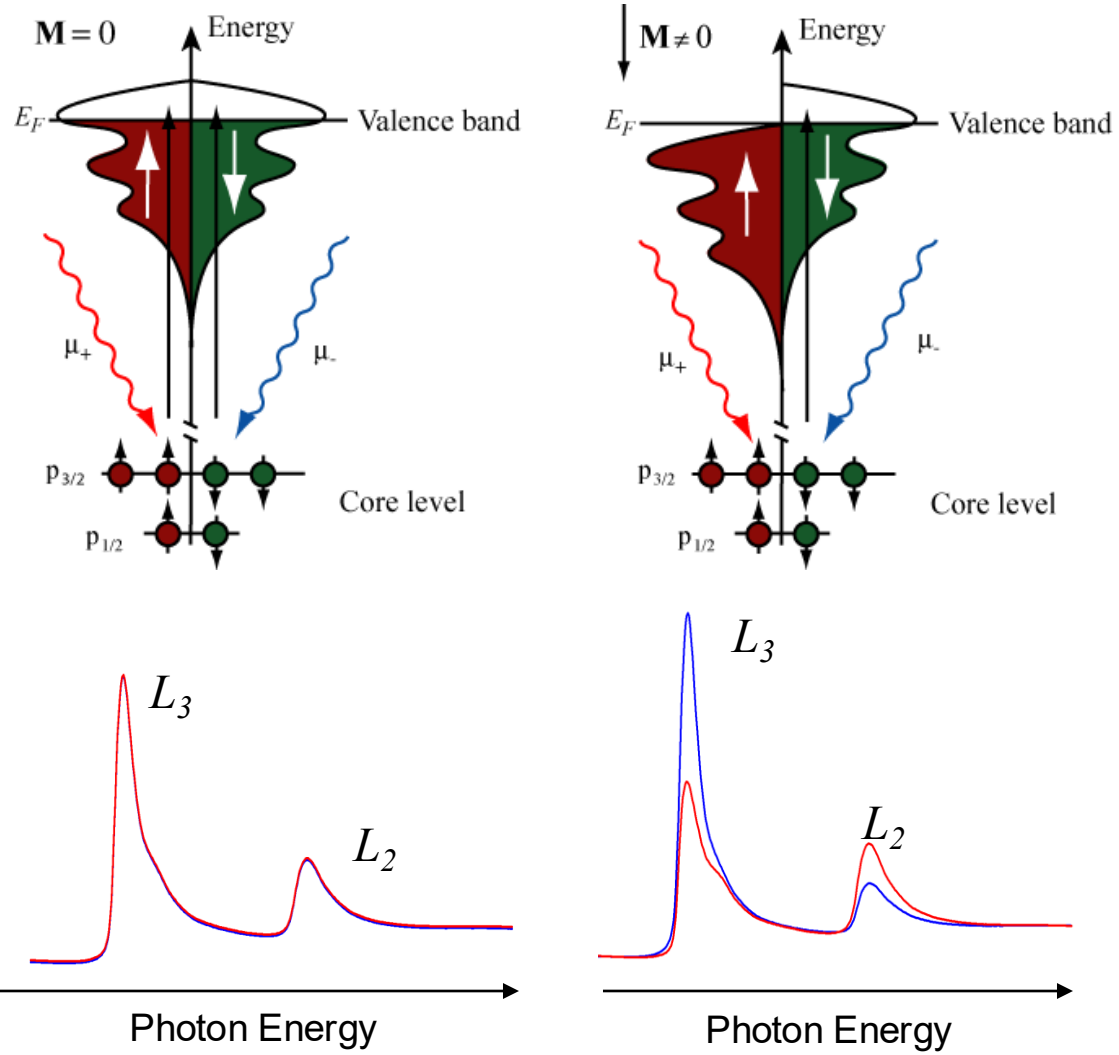
The XMCD, defined as the intensity difference between antiparallel and parallel orientations of the sample magnetization and the incident photon spin, is directly proportional to the atomic magnetic moment.

Dipole selection rules, for 3d transition metals

$$\Delta l = \pm 1, \Delta s = 0 \qquad 2\mathrm{p} \rightarrow \begin{matrix} 3\mathrm{d} \\ 4\mathrm{s} \end{matrix}$$

$\Delta m_l = +1$ right circular

$\Delta m_l = -1$ left circular

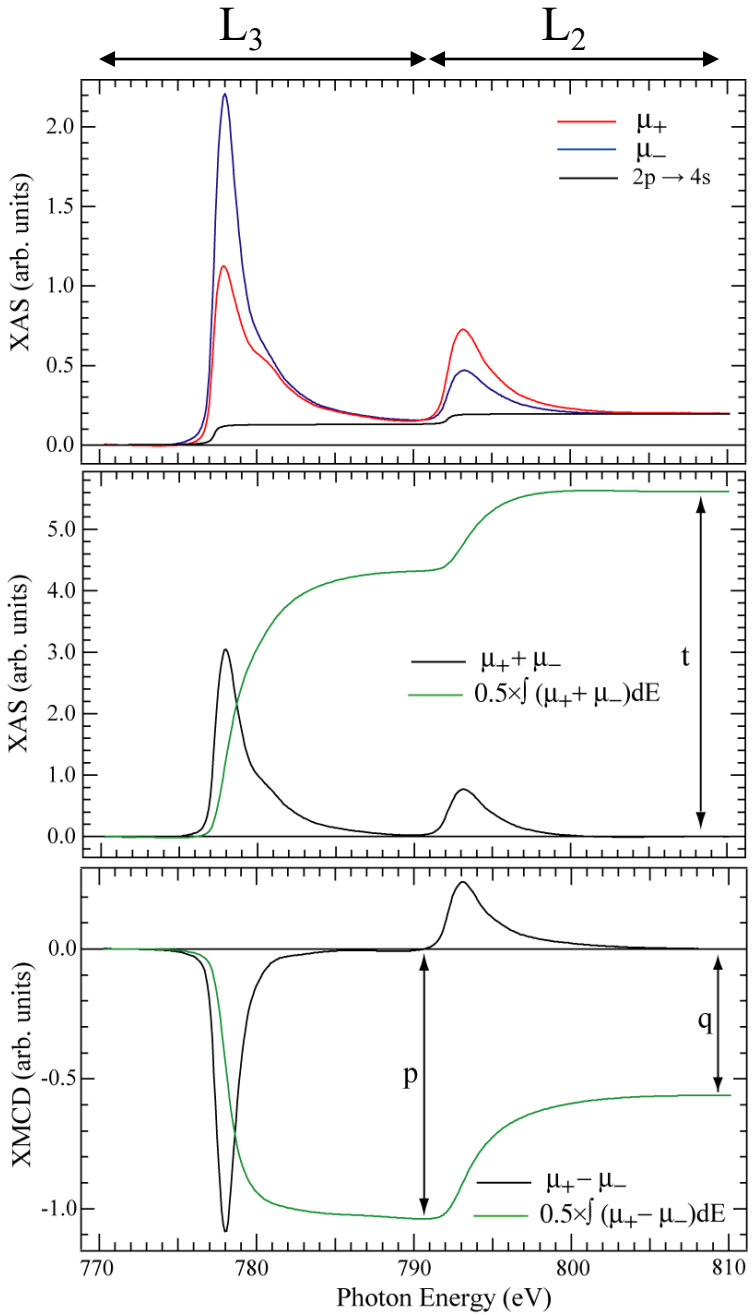


Conservation of angular momentum: transfer of the photon angular momentum to the excited electron. If the photoelectron is excited from a spin-orbit split core level, the angular momentum of the photon can be transferred in part to the spin through the spin-orbit coupling.

Measuring S and L momenta via XMCD sum rules

Exercise 12.5

Ex.: 1 layer Co on Rh(111)



Sum rules for 3d transition metals:

$$L = -\frac{4}{3} h_d \frac{\int_{L3+L2} (\mu_+ - \mu_-) dE}{\int_{L3+L2} (\mu_+ + \mu_-) dE} = -\frac{4}{3} h_d \frac{q}{t}$$

$$S + 7D = -h_d \frac{6\int_{L3} (\mu_+ - \mu_-) dE - 4\int_{L3+L2} (\mu_+ - \mu_-) dE}{\int_{L3+L2} (\mu_+ + \mu_-) dE}$$

$$= -h_d \frac{6p - 4q}{t}$$

Here the notation is

$I\mu_+ \rightarrow \mu_+$

$I\mu_- \rightarrow \mu_-$

L: orbital angular momentum

S: spin angular momentum

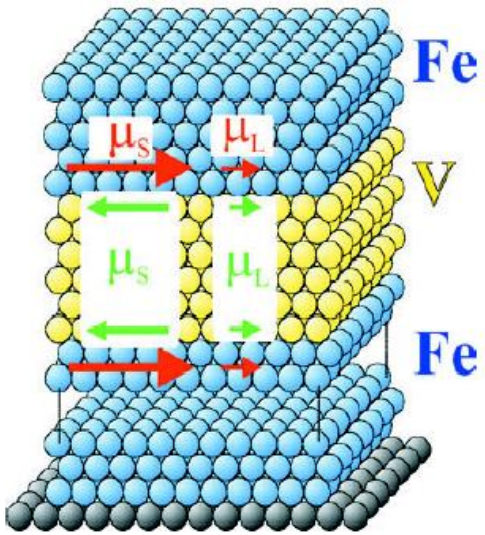
D: magnetic spin dipole

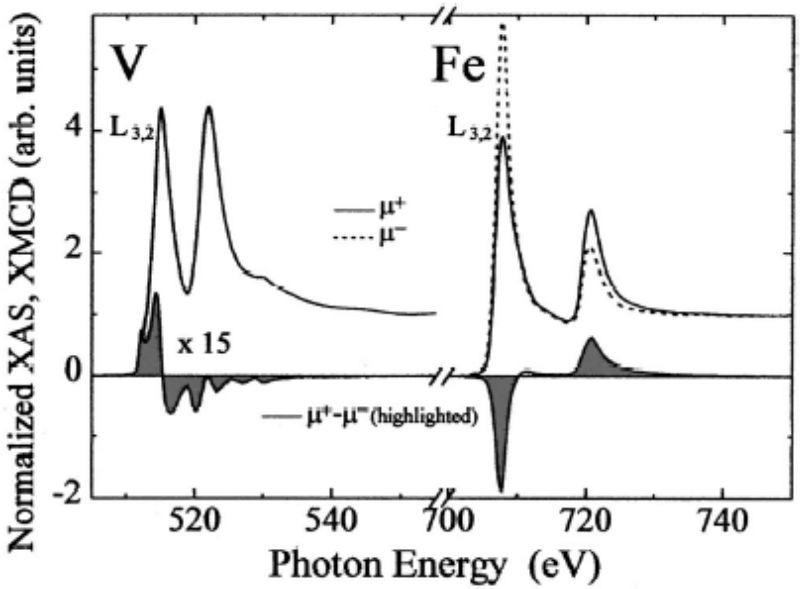
h_d : number of d-holes (empty states) in the valence band (frequently unknown, requires input from theory)

L, *S* in units of μ_B / atom (μ_L, μ_S)

B. T. Thole *et al.* PRL **68**, 1943 (1992)
P. Carra *et al.* PRL **70**, 694 (1993)

Element-resolved magnetism

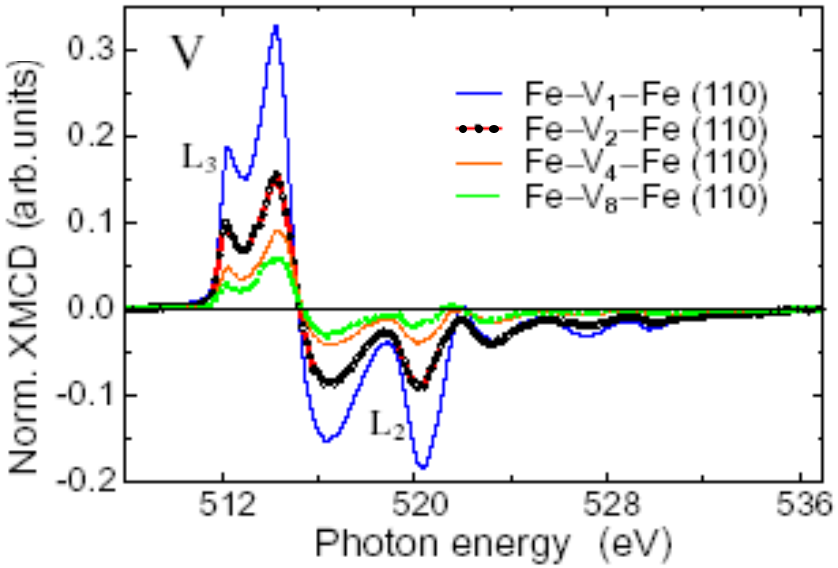




Normalized XAS of left (dashed line) and right (solid line) circularly polarized light and the XMCD at the $L_{2,3}$ edges of V and Fe for a Fe/V4 /Fe(110) structure.

1) Stronger magnetic moments in Fe compared to V
2) 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

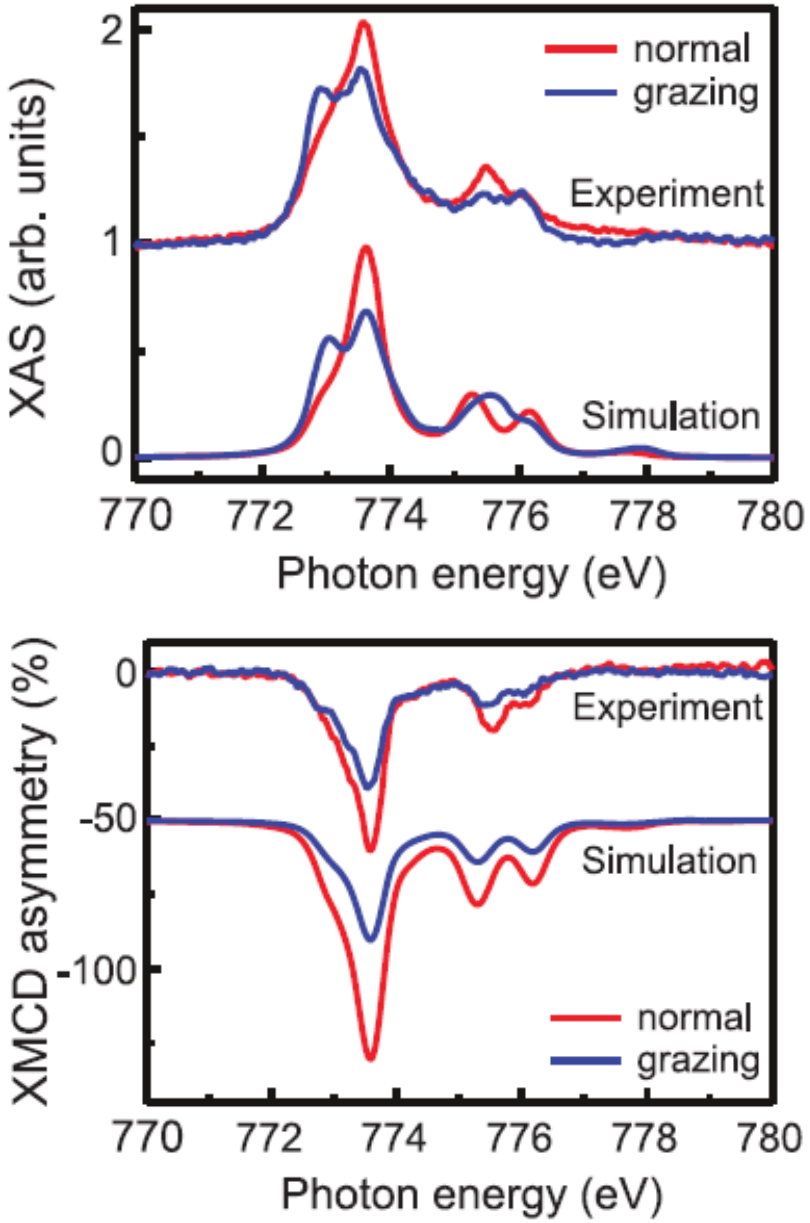


A. Scherz *et al.,* J. Appl. Phys. **91**, 8760 (2002)

XMCD of Co atoms adsorbed on MgO/Ag(100)

B = 7 T and T = 2 K

L_3edge



Magnetization easy axis:
out-of-plane (XMCD signal larger at normal incidence than grazing incidence)

spectra with multi-peaks:
atomic-like valence states

atomic-like orbital moments (from sum rules):
$\mu_{\mathrm{L}} = 2.9\ \mu_B$

The CF with C_∞ symmetry preserves pure L_z states
→ atomic-like orbital moment → high MAE

Rau *et al. Science* 988, **344** (2014)