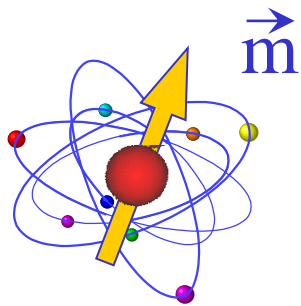


Intra-atomic exchange,
electron correlation effects:

LOCAL (ATOMIC) MAGNETIC MOMENTS



d or *f* electrons

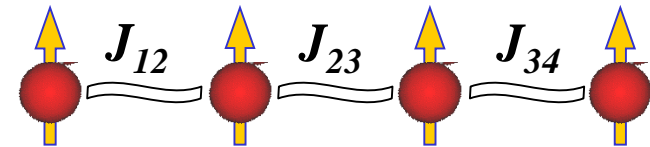


Hund's rules

Inter-atomic exchange:

MAGNETIC ORDER

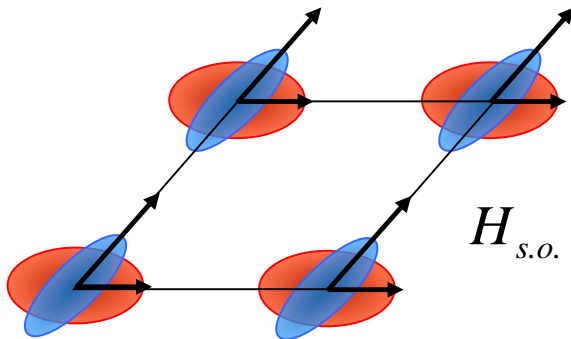
$$H_{exc} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



Spin-Orbit Coupling:

MAGNETOCRYSTALLINE ANISOTROPY:

K

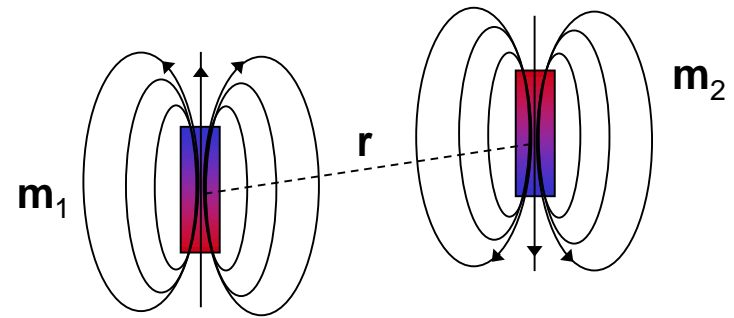


$$H_{s.o.} = \lambda \mathbf{L} \cdot \mathbf{S}$$

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

Dipolar Interaction:

SHAPE ANISOTROPY



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

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

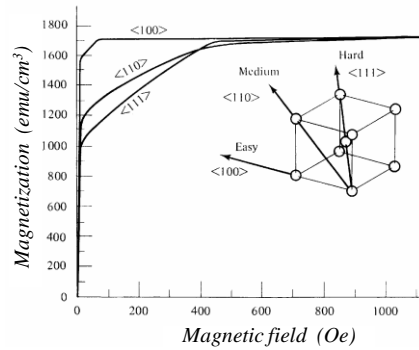
Bulk systems: the magnetic anisotropy energy
 K depends on the crystal structure

Free magnetic atom: spatially isotropic
 $K = 0$

Fe bcc

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

$$= 2.4 \text{ } \mu\text{eV/atom}$$

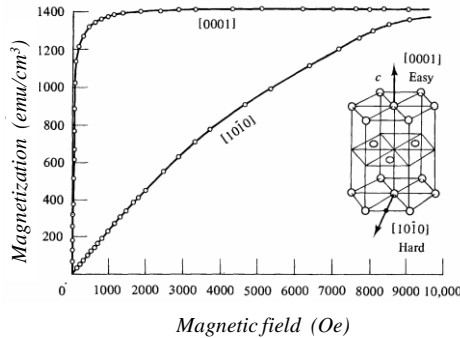


Co hcp

easy axis: (0001)

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

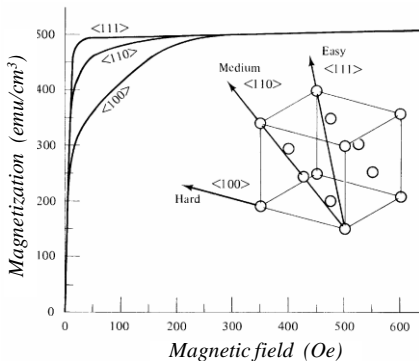
$$= 45 \text{ } \mu\text{eV/atom}$$



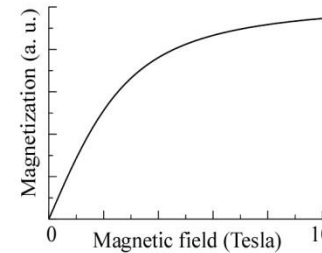
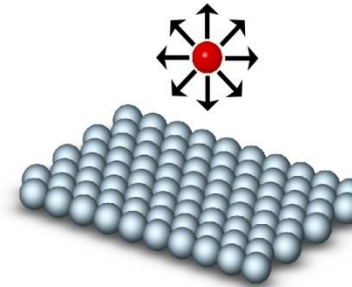
Ni fcc

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

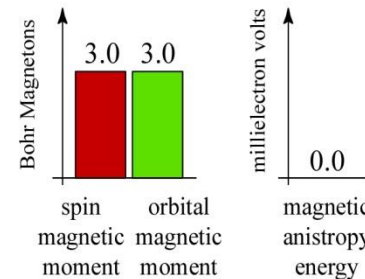
$$= -0.3 \text{ } \mu\text{eV/atom}$$



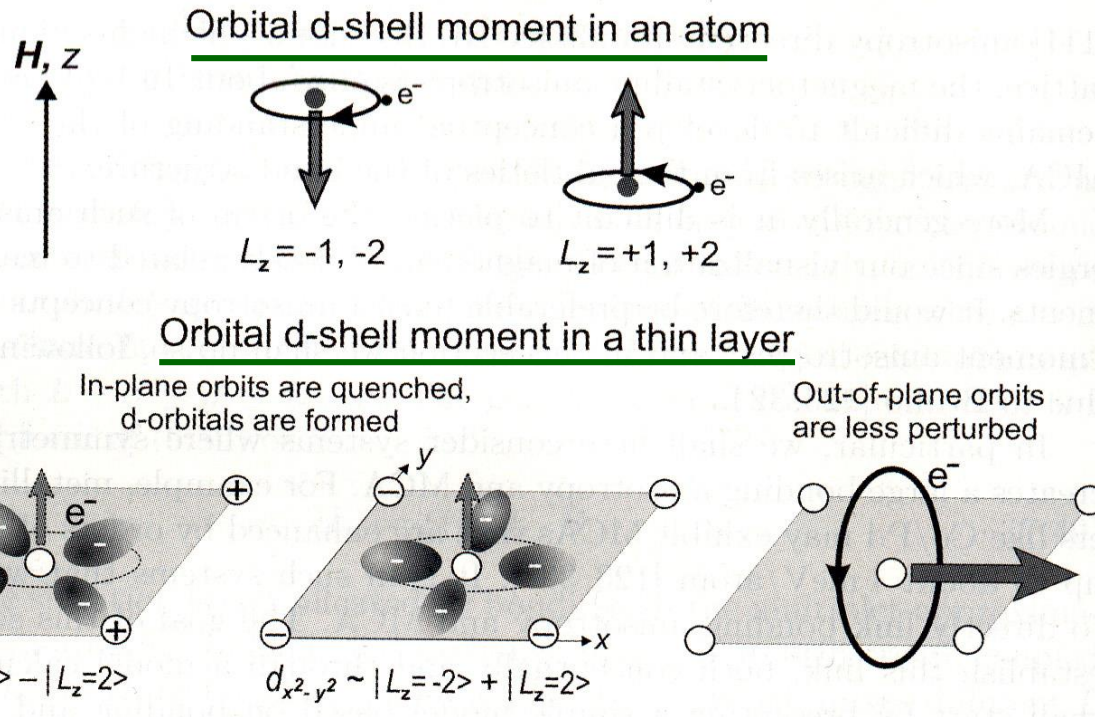
isotropic:
free magnetic atom



Direction
independent



Co atoms



Qualitative argument

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 $L_z = -2$.

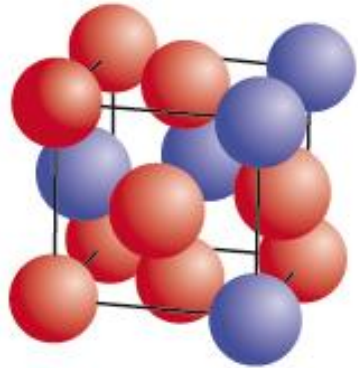
- **atom bonded to four atoms in a plane.**

a) in-plane 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 will be locked to the spatial direction along which L is maximum -> **easy axis**

Low MAE

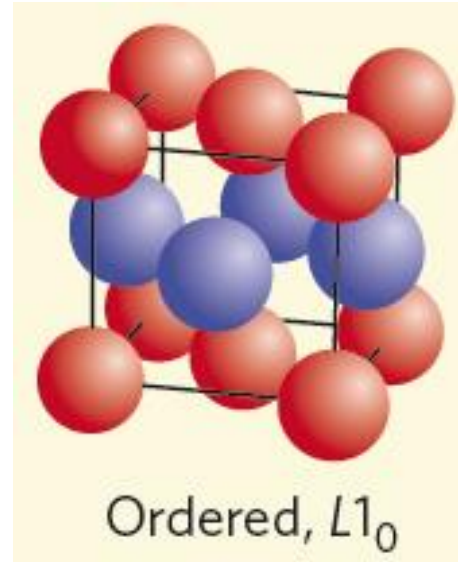


Disordered



Ordering by
annealing to
about 600°C

High MAE



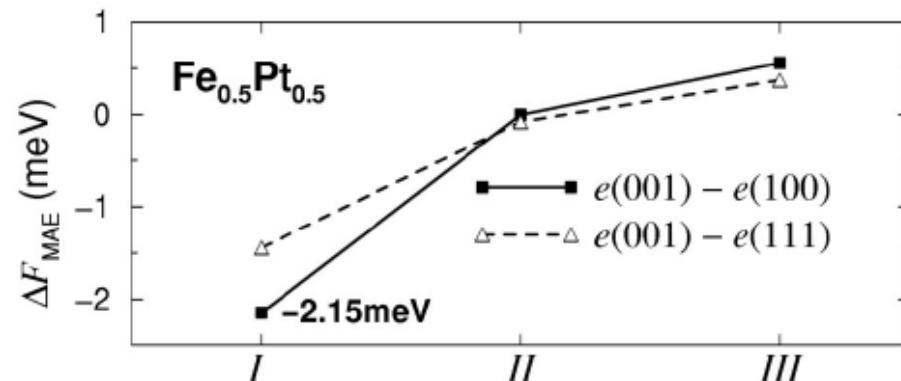
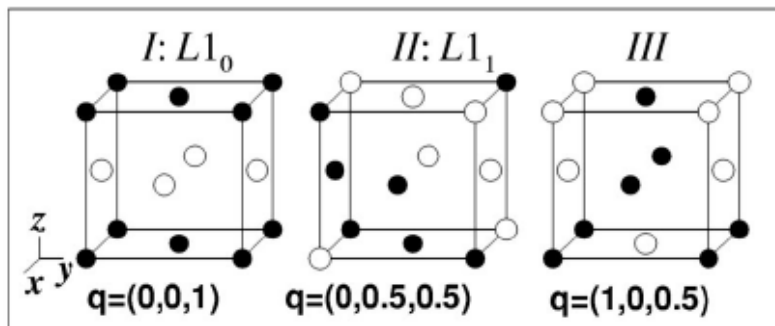
Ordered, $L1_0$

● Fe (or Co)
● Pt (or Pd)

D. Alloyeau et al., Nat Mater. **8**, 940 (2009); Z.R. Day et al. Nano Lett. **1**, 443 (2001); S. Sun *et al.*, Science **287**, 1989 (2000)

S. Ostanin *et al.* J. Appl. Phys. **93**, 453 (2003); S.S.A. Razeev *et al.*, Phys. Rev. Lett. **82**, 5369 (1999); J. Lyubina *et al.*, J. Phys.: Condens Matter **17**, 4157 (2005)

CF tuning the MAE



Microscopic origin of magnetocrystalline anisotropy in transition metal thin films

Gerrit van der Laan[†]

Daresbury Laboratory, Warrington WA4 4AD, UK

d band metal with eigenfunctions $|\mathbf{k}, n, \sigma\rangle$ and eigenvalues $\varepsilon_{n,\sigma}(\mathbf{k})$

$$|\mathbf{k}, n, \sigma\rangle = \sum_{\mu} a_{n,\mu,\sigma}(\mathbf{k}) |\mathbf{k}, \mu, \sigma\rangle$$

where \mathbf{k} is the electron wave vector, μ represents the d orbitals, σ is the spin, and $|\mathbf{k}, \mu, \sigma\rangle$ are the Bloch functions

The intra-atomic spin–orbit interaction is given by

$$H_{\text{SO}} = \xi \sum_{\mu_1, \mu_2, \sigma_1, \sigma_2} \langle \mu_2, \sigma_2 | \mathbf{L} \cdot \mathbf{S} | \mu_1, \sigma_1 \rangle \sum_{\mathbf{k}} c_{\mu_2, \sigma_2}^{\dagger}(\mathbf{k}) c_{\mu_1, \sigma_1}(\mathbf{k})$$

c^{\dagger} and c are creation and annihilation operators

H_{so} is a one-electron operator
diagonal in \mathbf{k} (\mathbf{k} is conserved)



The only excited states are

$$|ex\rangle = c_{n_2, \sigma_2}^\dagger(\mathbf{k}) c_{n_1, \sigma_1}(\mathbf{k}) |gr\rangle$$

$$\varepsilon_{n_1, \sigma_1}(\mathbf{k}) < \varepsilon_F < \varepsilon_{n_2, \sigma_2}(\mathbf{k}) \quad \text{The excited state is an unoccupied state}$$

In 3d metals $H_{so} \approx 50-100$ meV \ll band width $\approx 1-5$ eV (due to the Coulomb repulsion and crystal field)

Spin-orbit can be treated as a perturbation

The d orbitals have $L = 0 \rightarrow$ first order correction $\langle \mu | H_{so} | \mu \rangle = 0$

The second order correction is $\neq 0$

$$\delta E = \sum_{ex} \frac{\langle gr | H_{so} | ex \rangle \langle ex | H_{so} | gr \rangle}{E_{gr} - E_{ex}}$$

$$\delta E = -\xi^2 \sum_{\theta} [A(\theta, \uparrow, \uparrow) \langle \underline{\mu}_1, \uparrow | \mathbf{L} \cdot \mathbf{S} | \underline{\mu}_2, \uparrow \rangle \langle \mu_2, \uparrow | \mathbf{L} \cdot \mathbf{S} | \mu_1, \uparrow \rangle \quad \rightarrow \text{majority to majority state}$$

$$+ A(\theta, \downarrow, \downarrow) \langle \underline{\mu}_1, \downarrow | \mathbf{L} \cdot \mathbf{S} | \underline{\mu}_2, \downarrow \rangle \langle \mu_2, \downarrow | \mathbf{L} \cdot \mathbf{S} | \mu_1, \downarrow \rangle \quad \rightarrow \text{minority to minority state}$$

$$- A(\theta, \uparrow, \downarrow) \langle \underline{\mu}_1, \uparrow | \mathbf{L} \cdot \mathbf{S} | \underline{\mu}_2, \downarrow \rangle \langle \mu_2, \downarrow | \mathbf{L} \cdot \mathbf{S} | \mu_1, \uparrow \rangle$$

$$- A(\theta, \downarrow, \uparrow) \langle \underline{\mu}_1, \downarrow | \mathbf{L} \cdot \mathbf{S} | \underline{\mu}_2, \uparrow \rangle \langle \mu_2, \uparrow | \mathbf{L} \cdot \mathbf{S} | \mu_1, \downarrow \rangle] \quad \rightarrow \text{Spin-flip transitions}$$

$$A(\theta, \sigma_1, \sigma_2) \equiv \int_{\varepsilon_1 < \varepsilon_F < \varepsilon_2} \frac{d\varepsilon_1 d\varepsilon_2}{\varepsilon_2 - \varepsilon_1} \sum_{\mathbf{k}} n_{\mu_1, \underline{\mu}_1, \sigma_1}(\mathbf{k}, \varepsilon_1) n_{\mu_2, \underline{\mu}_2, \sigma_2}(\mathbf{k}, \varepsilon_2) \quad \theta = \mu_1, \underline{\mu}_1, \mu_2, \underline{\mu}_2$$

$$\delta E \approx \underbrace{-\frac{1}{4}\xi \hat{S} \cdot [\langle L^\downarrow \rangle - \langle L^\uparrow \rangle]}_{\text{Majority to majority, Minority to minority}} + \underbrace{\frac{\xi^2}{\Delta E_{\text{ex}}} \left[\frac{21}{2} \hat{S} \cdot \langle T \rangle + 2 \langle (L_\xi S_\xi)^2 \rangle \right]}_{\text{Spin-flip transitions}}$$

Majority to majority
Minority to minority

Spin-flip transitions

$$T = \hat{S} - 3\hat{r}(\hat{r} \cdot S)$$

Anisotropy of the spin moment (for ex. due to an anisotropy of the electron charge distribution)

ΔE_{ex} is the exchange splitting between majority and minority states

$$K = \delta E(H//z) - \delta E(H//x \text{ or } y)$$

energy difference between two magnetization directions

If majority states completely full

$$K = \frac{\xi_{\text{s.o.}}}{4} \Delta L + O\left(\frac{\xi_{\text{s.o.}}^2}{\Delta E_{\text{ex}}}\right)$$

P. Bruno, PRB **39**, 865 (1989);
G. van der Laan, JPCM **10**, 3239 (1998).

Actually

$$K = \alpha \frac{\xi}{4} \Delta L = \alpha \frac{\xi}{4} (L_z - L_{x,y})$$

$$\alpha \approx 0.2 - 0.25$$

J. Stöhr, J. Magn. Magn. Mater **200**, 470 (1999);

The factor α is necessary to find a good agreement between XMCD and other magnetometer measurements.
Discrepancy probably due to spin-flip term and not perfectly spin-split bands

$$\Delta E_{so} = \sum_{qss'} \Delta E_q^{ss'} = \sum_{qss'} \{E_q^{ss'}(\hat{n}_1) - E_q^{ss'}(\hat{n}_2)\}$$

The MAE (between two magnetization directions n_1 and n_2) can be written as a sum over atomic species, q , and as a double sum over the spin indices, s (occupied), and s' (unoccupied)

$$E_q^{ss'}(\hat{n}) = - \sum_{\mathbf{k}ij} \sum_{q'} \sum_{\{m\}} n_{\mathbf{k}is, qm, q'm'} n_{\mathbf{k}js', q'm'', qm'''} \frac{\langle qms | \mathcal{H}_{so}(\hat{n}) | qm'''s' \rangle \langle q'm''s' | \mathcal{H}_{so}(\hat{n}) | q'm's \rangle}{\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}i}}$$

sum over all \mathbf{k} points in the Brillouin zone, all occupied states i , all unoccupied states j , all sites in the unit cell q' and magnetic quantum numbers $\{m\}$

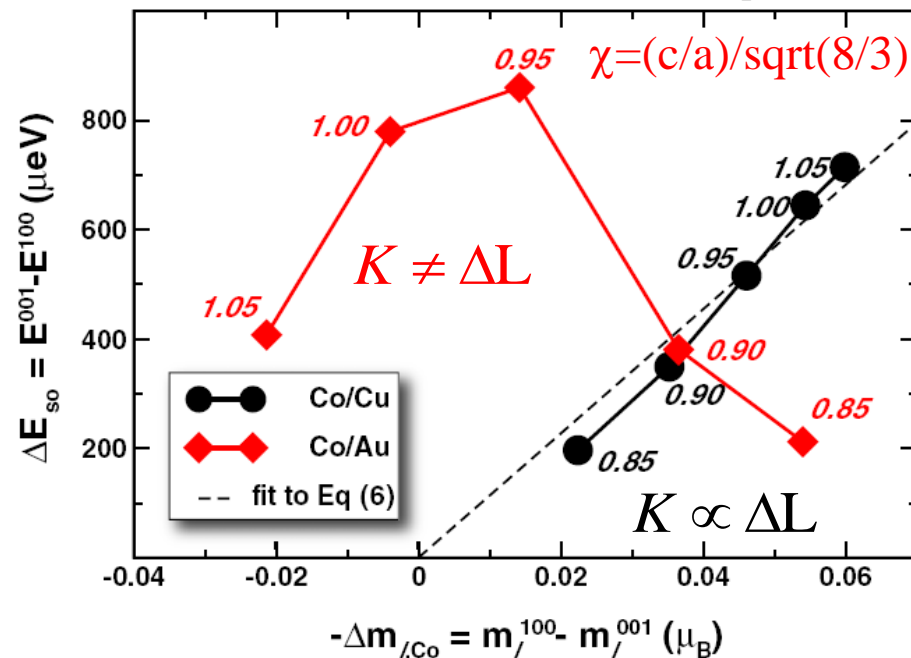
sum over all sites gives off-site contributions ($q \neq q'$) through the spin-orbit scattering (or coupling) at other sites.

Au is $5d^{10} 6s^1 \rightarrow$ negligible S and L \rightarrow

- a) S and L can be not zero due to orbital hybridization
- b) very high spin-orbit constant ζ about 600 meV

The magnetization easy axis does not always coincide with the largest orbital moment

Calculation as a function of the deformation parameter χ



$$\mathbf{L} \cdot \mathbf{S} = L_z S_z + \frac{1}{2} (L_+ S_- + L_- S_+)$$

$$L_+ = L_x + iL_y \quad L_- = L_x - iL_y$$



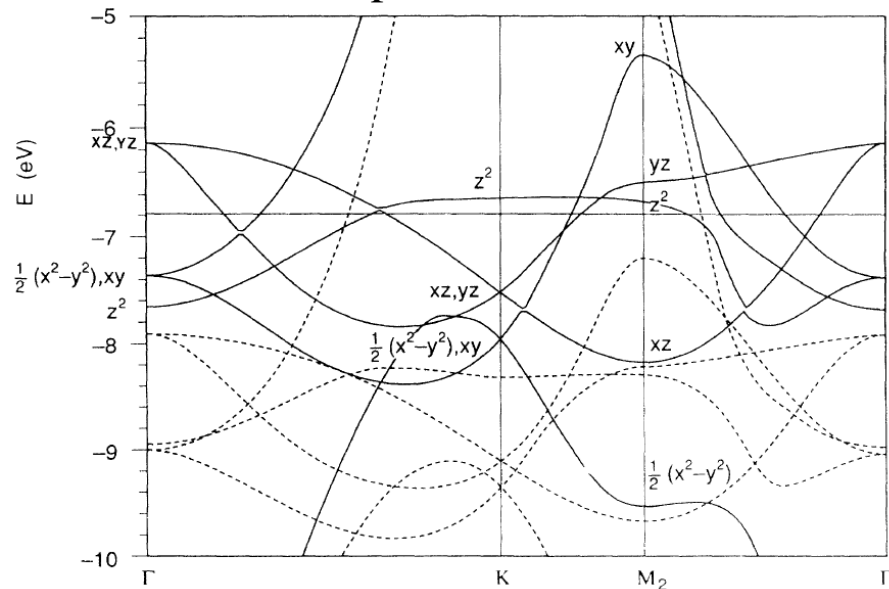
$$\mathcal{H}^{\text{SO}}(\hat{\mathbf{n}}) = \frac{\xi}{2} \begin{pmatrix} \hat{\mathbf{n}} \cdot \mathbf{l} & \hat{\mathbf{n}}_{\perp} \cdot \mathbf{l} + \frac{1}{2}(l_- - l_+) \\ \hat{\mathbf{n}}_{\perp} \cdot \mathbf{l} - \frac{1}{2}(l_- - l_+) & -\hat{\mathbf{n}} \cdot \mathbf{l} \end{pmatrix}$$

H_{so} depends on the direction of the magnetization

L -> quantization axis is due to the Crystal Field
S -> quantization axis is due to the external field H

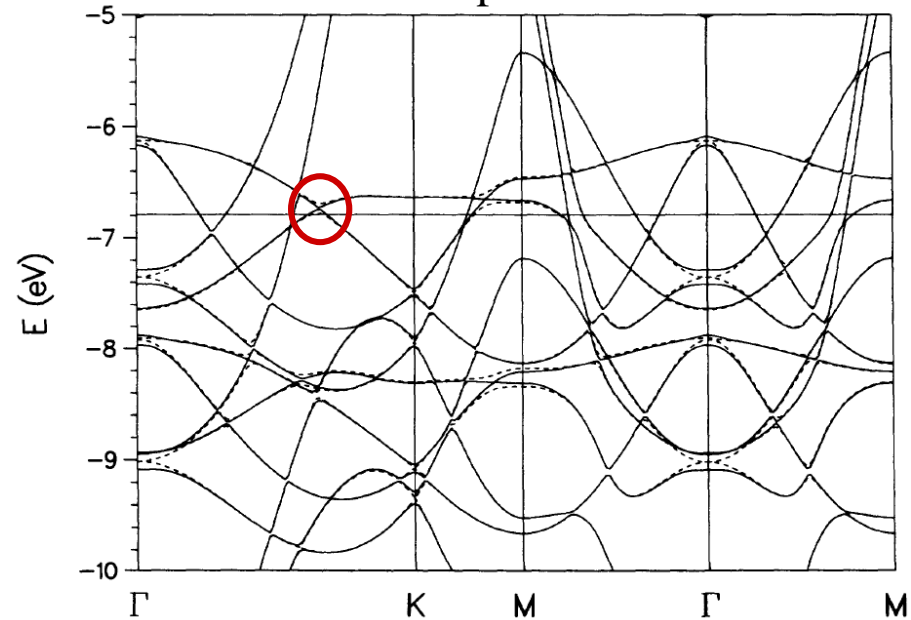
Free-standing Co monolayer

Spin-orbit off



Majority spin (dashed) and minority spin (solid)

Spin-orbit on



M // z (solid) and M // x (dashed)

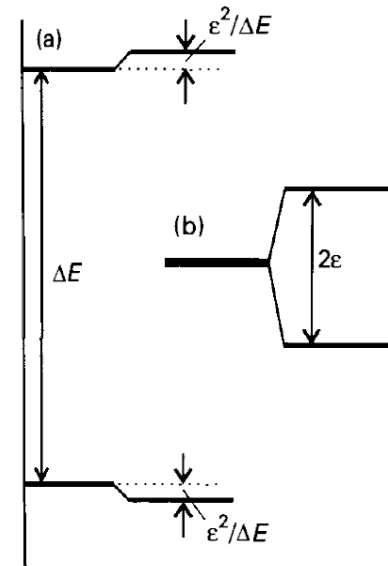
Including H_{so} the magnetization rotation splits degenerate states -> change of the system energy -> Easy axis = axis returning the lowest energy (x in the present case)

When two or more states are degenerate the previous second order perturbation expression for H_{so} is not valid (you can find infinite value for δE)

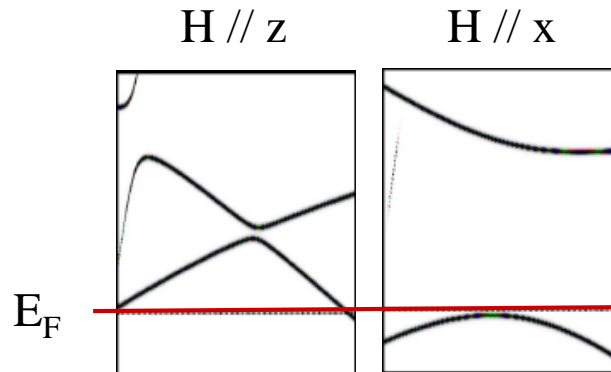
The correct formula becomes $\delta E = \varepsilon$ with $\varepsilon = \langle 1 | H_{soc} | 2 \rangle$

Degenerate states see a much larger shift in energy than non degenerate states:

- Degenerate split $\rightarrow 2\varepsilon$
- Non degenerate split $\rightarrow 2\varepsilon^2/\Delta E$ (since $\Delta E = (E_{ex} - E_{gr}) \gg \varepsilon$)

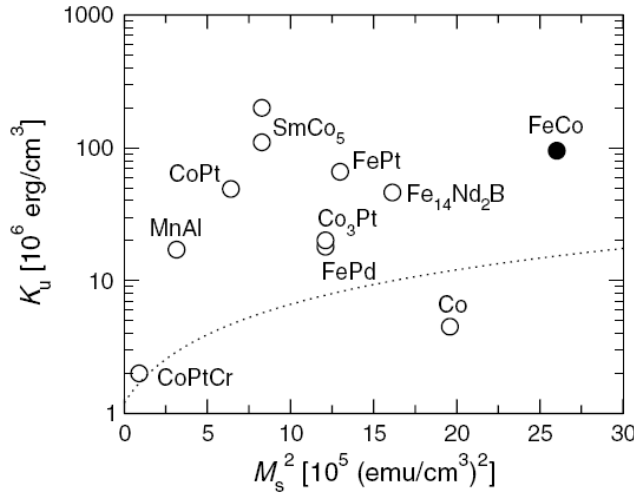


Degenerate states close to E_F can give huge contributions to the MAE

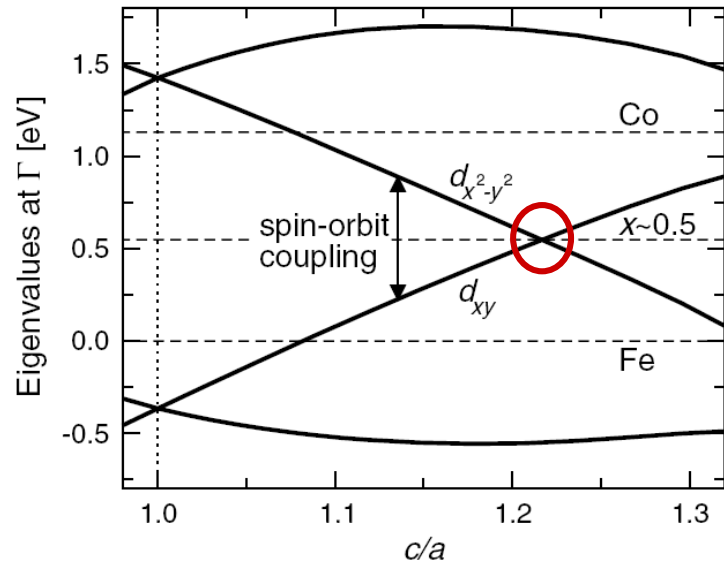


Spin-orbit splits the degenerate states in such a way that one state is shifted below E_F and the second one is shifted above E_F when $H // x$

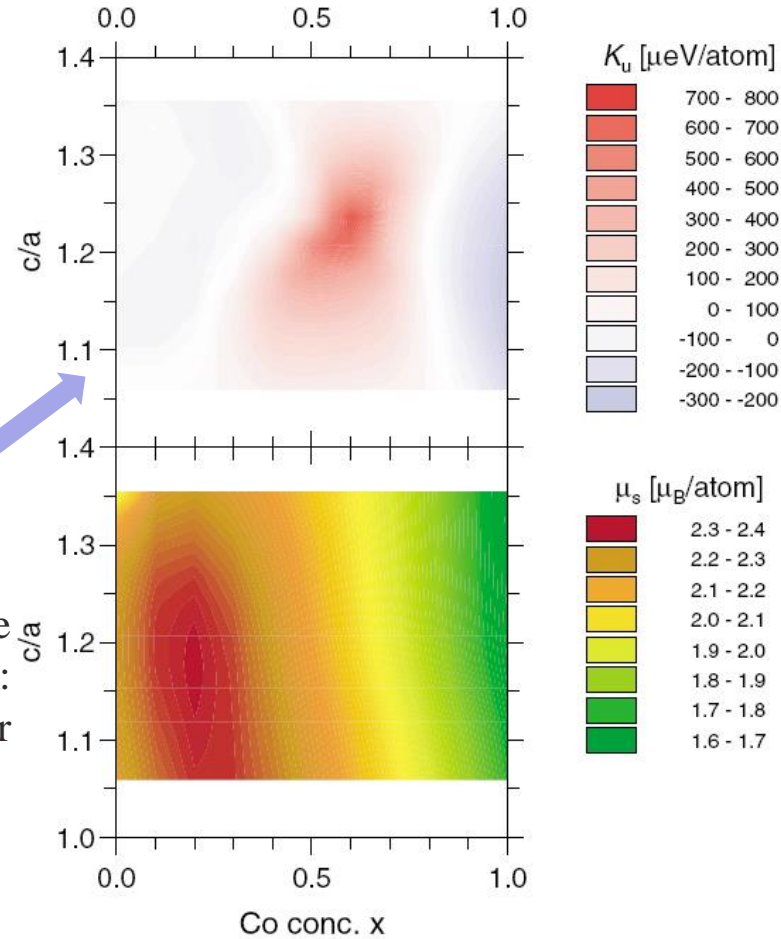
Enhanced MAE for the composition and c/a distortion at which the $d_{x^2-y^2}$ and d_{xy} states cross.



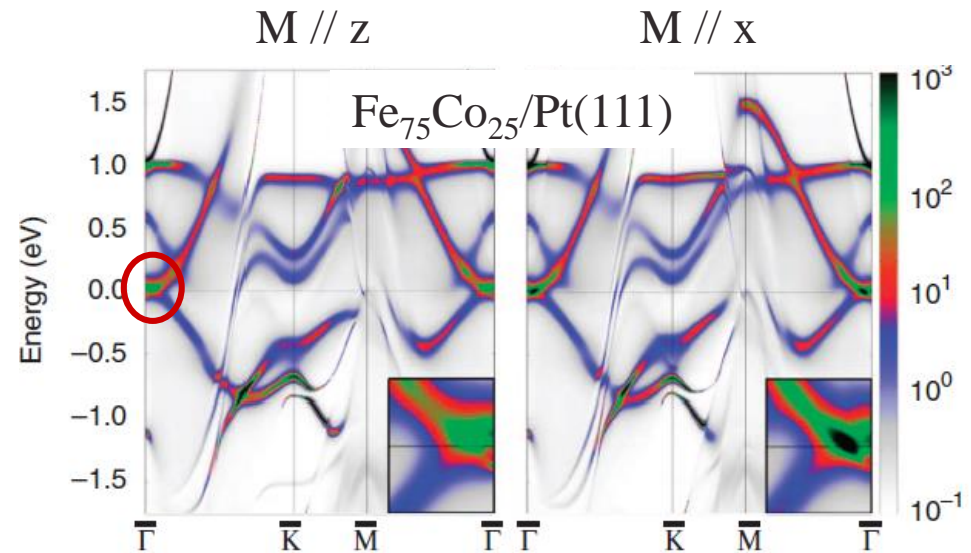
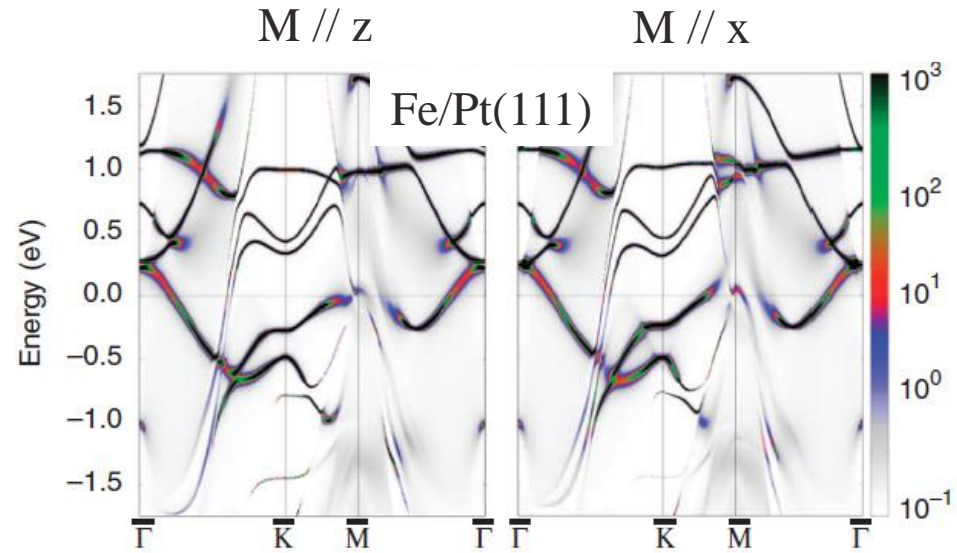
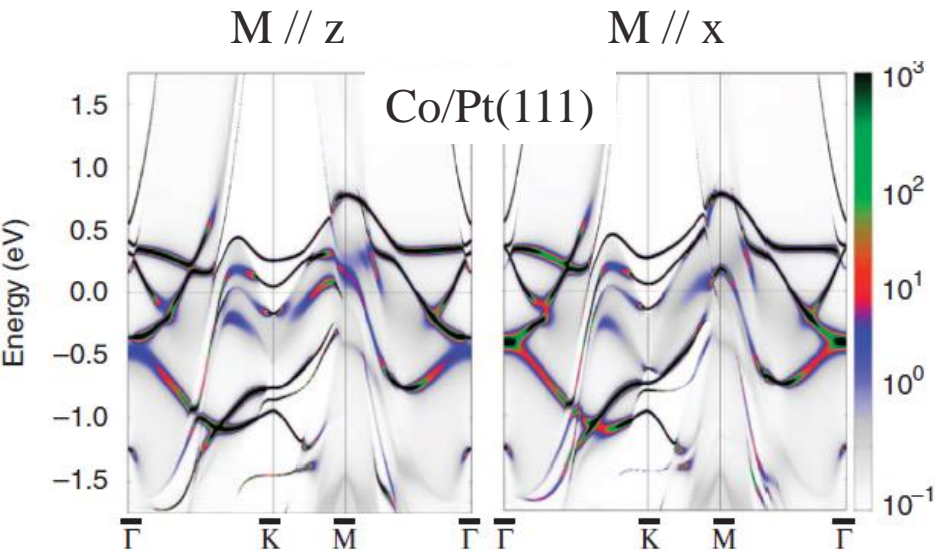
FeCo bcc $\rightarrow K = 1\text{-}2 \mu\text{eV/atom}$
 FeCo bct $\rightarrow K = 0.8 \text{ meV/atom}$



Spin orbit split these two degenerate states: maximum MAE for $c/a = 1.2$ and $x = 0.5$

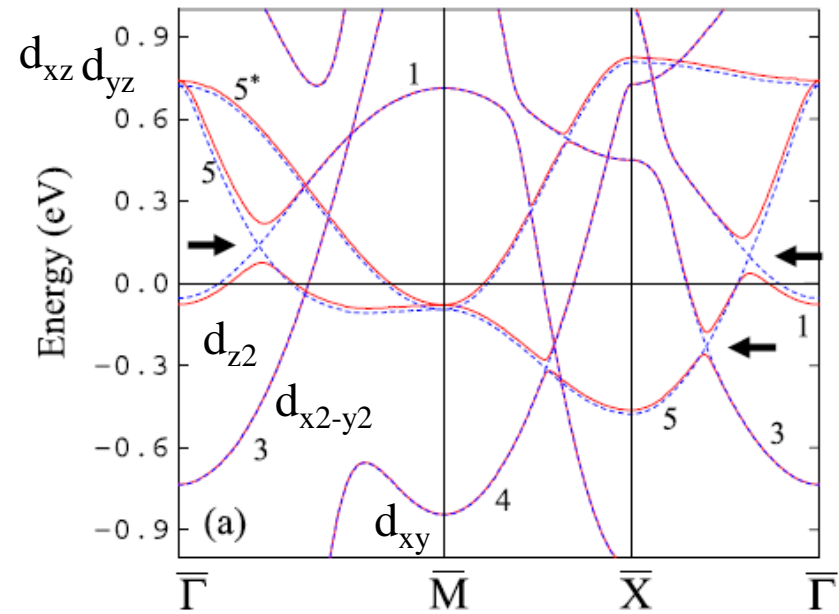


Calculated d-orbitals spin-down eigenvalues at the Γ point as a function of c/a ratio. The Fermi energies of Fe, Co, and Fe_{0.5}Co_{0.5} are indicated by dashed lines



1) Degenerate d_{xy} and $d_{x^2-y^2}$ orbitals at Fermi level for $\text{Fe}_{75}\text{Co}_{25}$ \rightarrow chance of having large MAE

2) Splitting of the d_{xy} and $d_{x^2-y^2}$ orbitals \rightarrow gain in energy when $M // z$
 $\rightarrow z$ is the easy axis with large MAE

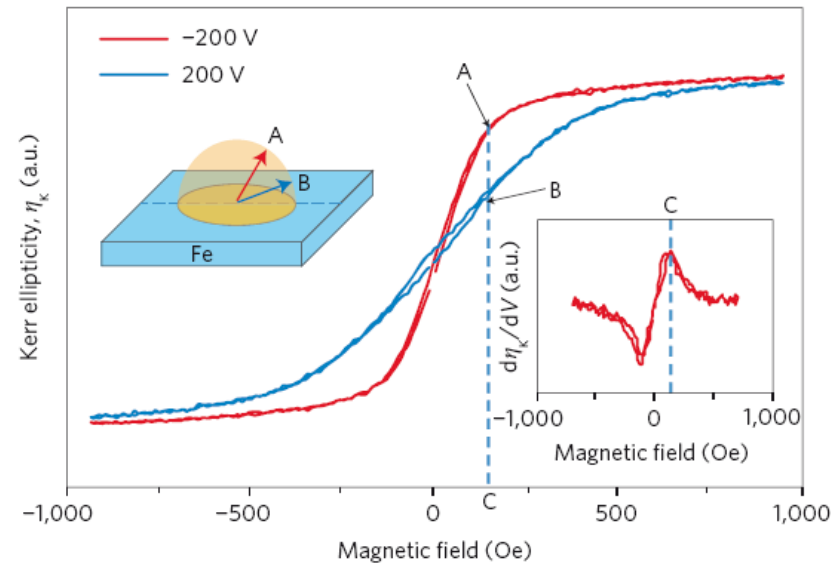
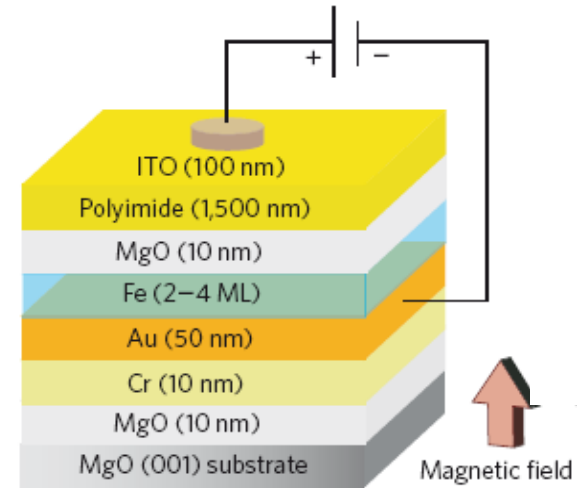


minority-spin band for an Fe(001) monolayer in an external electric field of zero (dotted lines) and 1 eV/Å (solid lines).

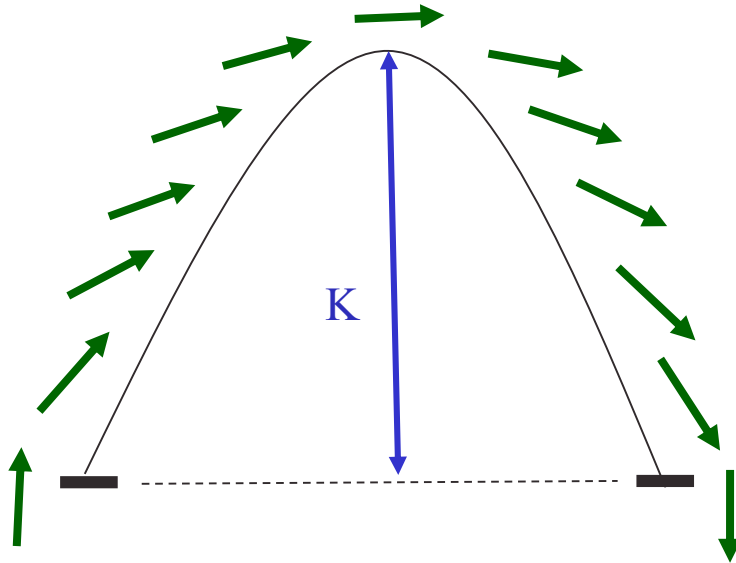
$E = 0$ represent the Fermi energy. Arrows indicate band gaps induced by the electric field.

Electric field $\rightarrow Y_0^1$ symmetry

$$\langle l' m' | Y_0^1 | l m \rangle \neq 0 \quad \text{when } l' = l + 1 \text{ and } m' = m$$

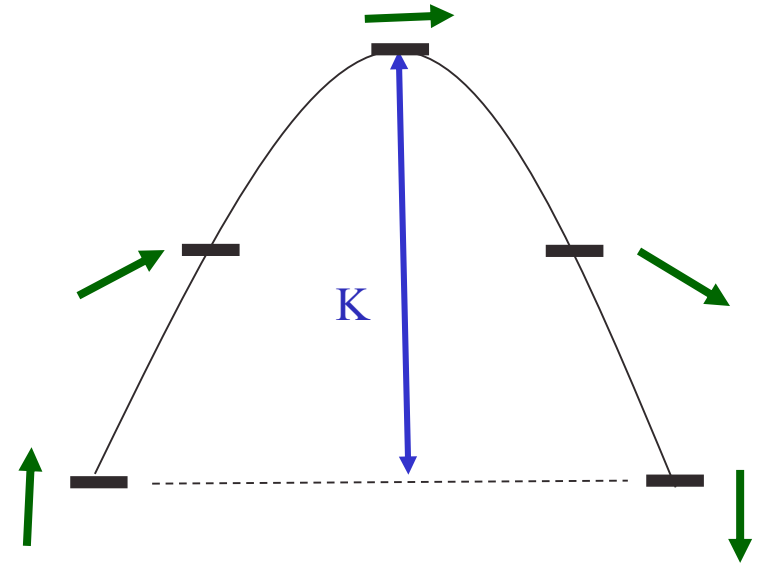


Classic



Continuous magnetization rotation:
To reverse the magnetization must rotate and pass through the hard axis direction

Quantum



Only a discrete number of states are available

Transition metals $H = H_{e-e} + H_{CF} + H_{SOC} + H_{Zeeman}$

$$\mathcal{H}_{sp-orb} = \lambda \mathbf{L} \cdot \mathbf{S} \quad \mathcal{H}_Z = \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} \quad |\Gamma, \gamma\rangle |S, M_S\rangle \quad \text{Basis in a crystal field} \\ (\Gamma \text{ is the orbital part})$$

$$\mathcal{H}_{eff} = \langle \Gamma, \gamma | \mathcal{H}_{sp-orb} + \mathcal{H}_Z | \Gamma, \gamma \rangle$$

$$= 2\mu_B \mathbf{H} \cdot \mathbf{S} - \sum_{\Gamma', \gamma'} \frac{|\langle \Gamma', \gamma' | \mu_B \mathbf{H} \cdot \mathbf{L} + \lambda \mathbf{L} \cdot \mathbf{S} | \Gamma, \gamma \rangle|^2}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}$$

Second order perturbation theory

$$\mathcal{H}_{eff} = 2\mu \mathbf{H} \cdot \mathbf{S} - 2\mu_B \lambda \sum_{\mu, \nu} A_{\mu\nu} S_\mu H_\nu - \lambda^2 \sum_{\mu, \nu} A_{\mu\nu} S_\mu S_\nu - \mu_B^2 \sum_{\mu, \nu} H_\mu H_\nu \Lambda_{\mu\nu}$$

$$A_{\mu\nu} = \sum_{\Gamma', \gamma'} \frac{\langle \Gamma, \gamma | L_\mu | \Gamma', \gamma' \rangle \langle \Gamma', \gamma' | L_\nu | \Gamma, \gamma \rangle}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}$$

$$\mathcal{H}_{eff} = \sum_{\mu, \nu} (\mu_B g_{\mu\nu} H_\mu S_\nu - \lambda^2 A_{\mu\nu} S_\mu S_\nu - \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu)$$

$$g_{\mu\nu} = 2(\delta_{\mu\nu} - \lambda A_{\mu\nu})$$

$\Lambda_{\mu\nu}$ reflects the symmetry of the crystal. The spin Hamiltonian must also display this symmetry; for example, in a cubic crystal $\Lambda_{xx} = \Lambda_{yy} = \Lambda_{zz}$. Thus the anisotropy term reduces to a constant.

For axial symmetry $\Lambda_{xx} = \Lambda_{yy} = \Lambda_{\perp}$ and $\Lambda_{zz} = \Lambda_{\parallel}$

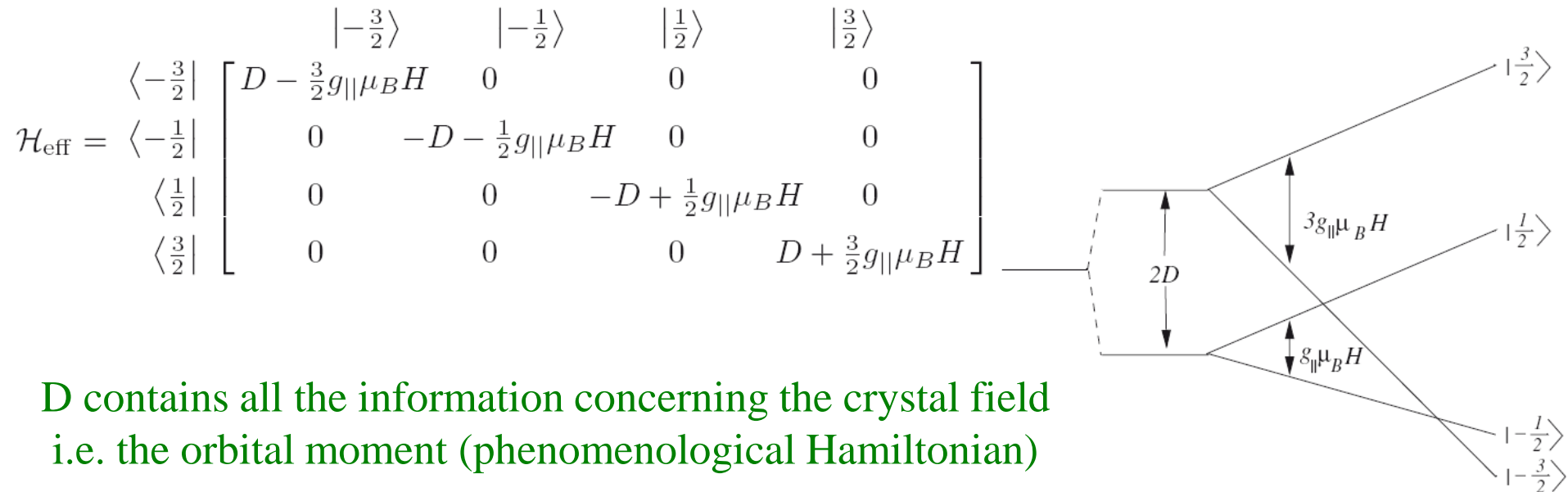


Neglecting $\mu_B^2 \Lambda_{\mu\nu} H_{\mu} H_{\nu}$

$$\mathcal{H}_{\text{eff}} = g_{\parallel} \mu_B H_z S_z + g_{\perp} \mu_B (H_x S_x + H_y S_y) + D [S_z^2 - \frac{1}{3} S(S+1)] + \frac{1}{3} S(S+1) (2 \Lambda_{\perp} + \Lambda_{\parallel}) \lambda^2, \quad D = \lambda^2 (\Lambda_{\parallel} - \Lambda_{\perp})$$

Ex: $S=3/2$ and $\mathbf{H} = (0,0,H) \rightarrow \mathcal{H} = g_{\parallel} \mu_B H_z S_z + D S_z^2$

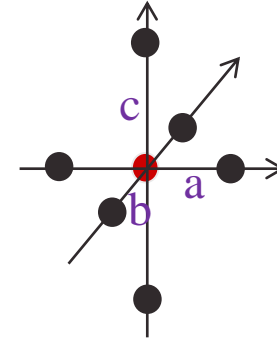
$D > 0$



D contains all the information concerning the crystal field i.e. the orbital moment (phenomenological Hamiltonian)

In general Λ_{xx} , Λ_{yy} , and Λ_{zz} are different (distorted octahedral symmetry)

$$H = g_{\parallel} \mu_B H_z S_z + D[S_z^2 - 1/3 S(S+1)] + E(S_x^2 - S_y^2)$$



$$D = -\lambda^2/\Delta E (-1/2 \Lambda_{xx} - 1/2 \Lambda_{yy} + \Lambda_{zz}) \sim \lambda^2/\Delta E (L_{\parallel} - L_z)$$

$$E = -\lambda^2/\Delta E (1/2 \Lambda_{xx} - 1/2 \Lambda_{yy}) \sim \lambda^2/\Delta E (L_x - L_y)$$

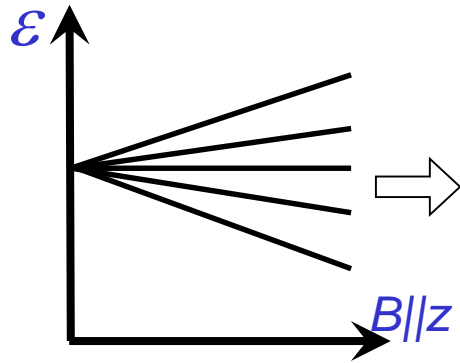
D and E parameters, which determine the energy splitting, are proportional to:

- a) orbital anisotropy
- b) Spin-orbit constant

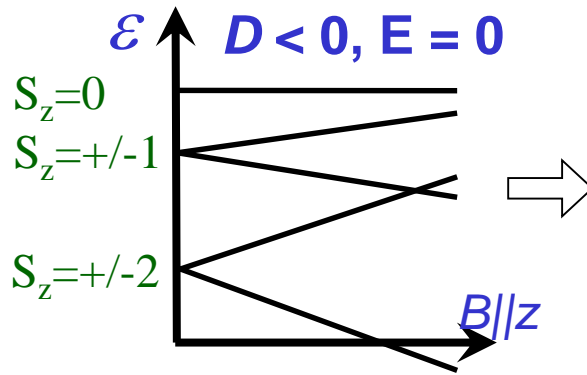
N.B.:

- 1) Actually L and S are not always good quantum numbers (J is better). In addition hybridization between different atoms can complicate things.
- 2) Thus, in the previous equations **S should be considered as a sort of effective spin operator S^*** to be determined by fitting the data.
- 3) However, assuming negligible hybridization and CF quenching the orbital moment $\rightarrow S^* \sim S$

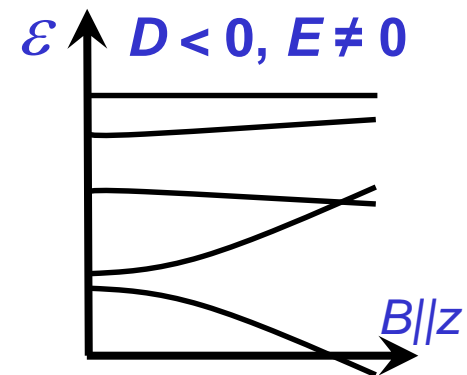
Energy spectrum: ex. $S = 2$



CF = 0

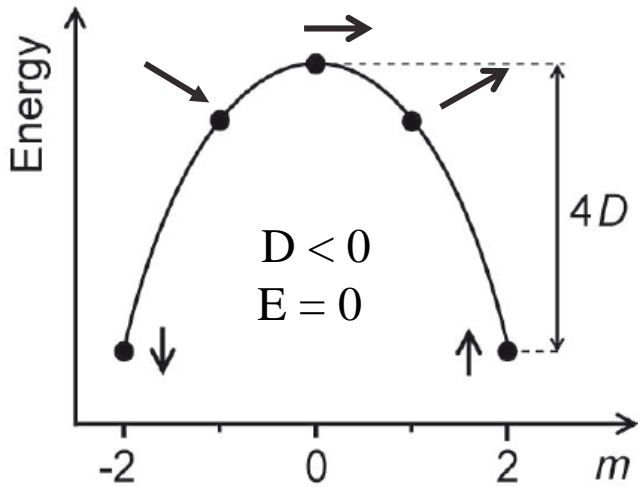


CF different from 0

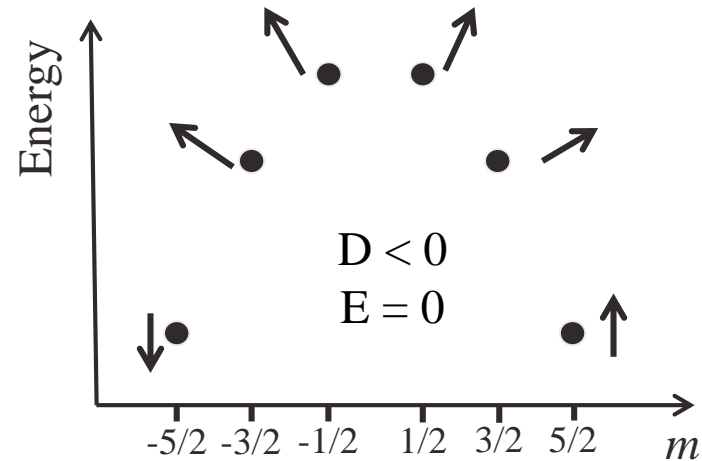


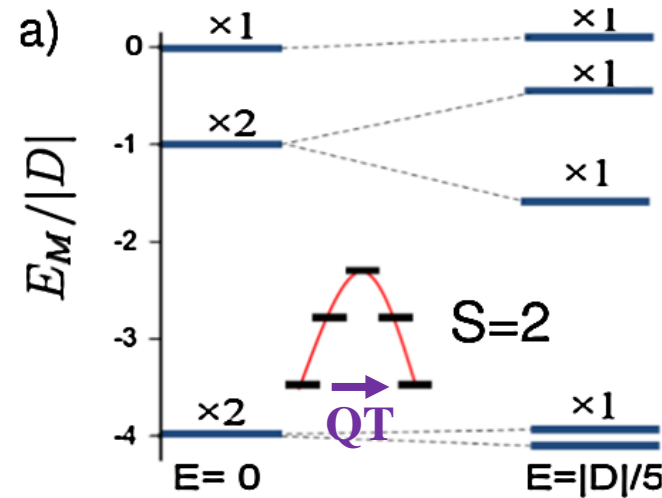
Energy barrier for spin reversal (K_r): case $E=0$

$K_r = DS^2$ (S integer)



$K_r = D(S^2 - 1/4)$ (S half-integer)





$E (S_x^2 - S_y^2) = E (S_+^2 + S_-^2) \rightarrow$ quantum tunneling (QT)
 $S_+^2 (S_-^2)$ operator couples state $S_z = 2$ with $S_z = 0$ and
 $S_z = 0$ with $S_z = -2$

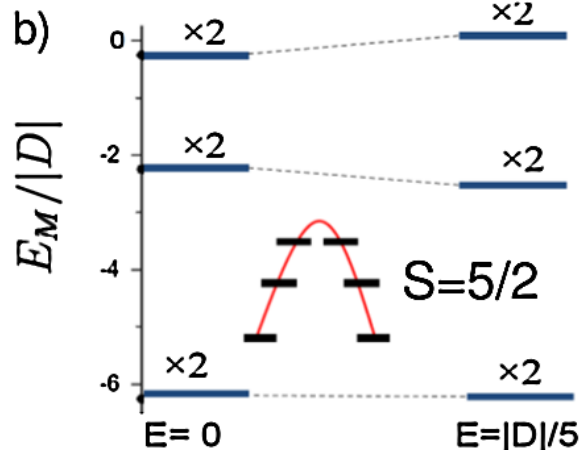
No net magnetic
moment



Can not be a bit

$D = -1.55$ meV, and $E = 0.31$ meV

Eigenstate	$ +2\rangle$	$ +1\rangle$	$ +0\rangle$	$ -1\rangle$	$ -2\rangle$	Eigenvalues
$B = 0$ T						
ψ_0	0.697	0	-0.166	0	0.697	-6.93 meV
ψ_1	0.707	0	0	0	-0.707	-6.74 meV
ψ_2	0	0.707	0	-0.707	0	-3.08 meV
ψ_3	0	0.707	0	0.707	0	-0.58 meV
ψ_4	0.117	0	0.986	0	0.117	0.19 meV



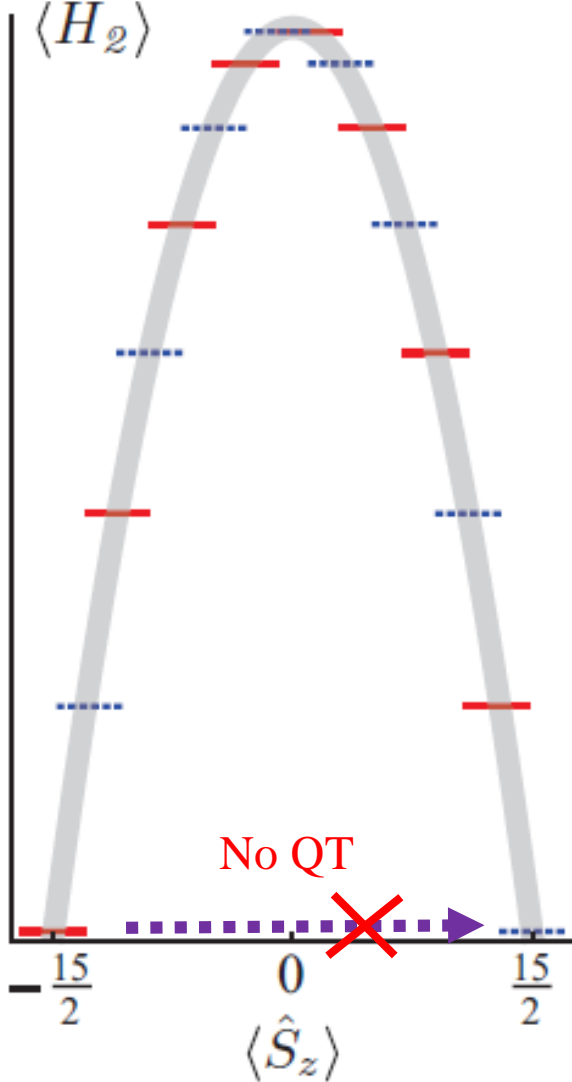
Ground state is
twofold degenerate
($S_z = \pm 5/2$)



Can be a bit

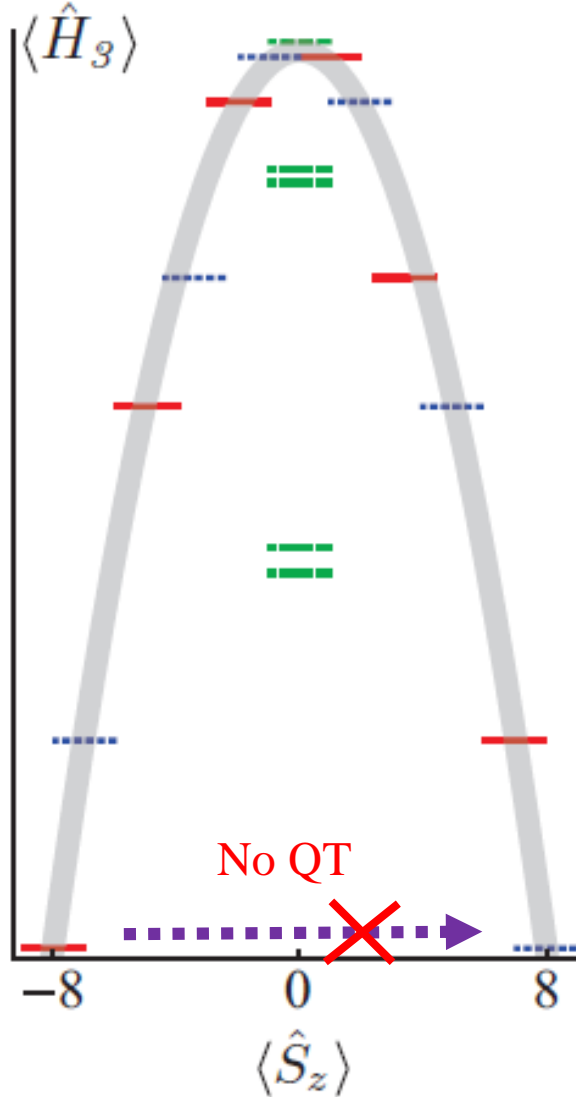
C_{2v} CF symmetry

$$\hat{H}_2 = D_2 \hat{S}_z^2 + \tilde{B} \hat{S}_z + E_2 (\hat{S}_+^2 + \hat{S}_-^2)$$



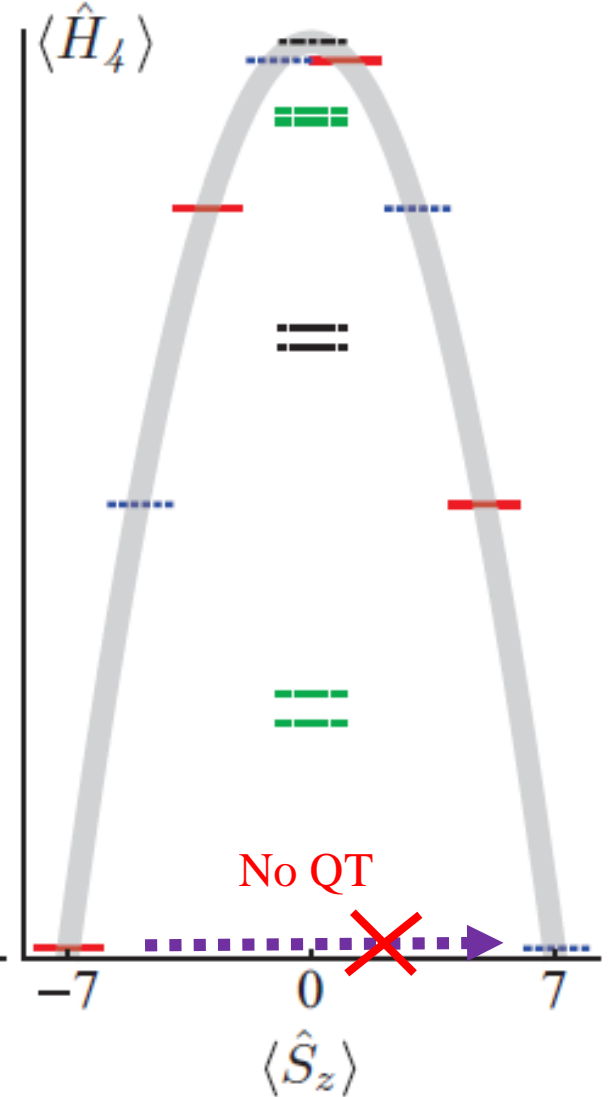
C_{3v} CF symmetry

$$\hat{H}_3 = D_3 \hat{S}_z^2 + \tilde{B} \hat{S}_z + E_3 (\hat{S}_z (\hat{S}_+^3 + \hat{S}_-^3) + (\hat{S}_+^3 + \hat{S}_-^3) \hat{S}_z)$$



C_{4v} CF symmetry

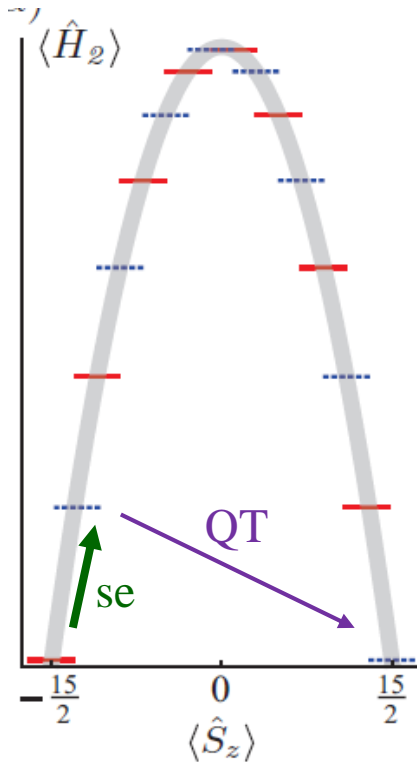
$$\hat{H}_4 = D_4 \hat{S}_z^2 + \tilde{B} \hat{S}_z + E_4 (\hat{S}_+^4 + \hat{S}_-^4)$$



No QT -> magnetization preserved without external perturbation

C_{2v} CF symmetry + interaction with conduction electron

$$H_2 = B S_z + D_2 S_z^2 + E_2 (S_+^2 + S_-^2) + J_0 S_z \sigma_z + 1/2 J_0 (S_+ \sigma_- + S_- \sigma_+)$$



The interaction with the conduction electrons can induce transitions with $\Delta S = +/- 1$: single electron transition (se)

In this case we observe a rotation of the magnetization

Another source of destabilization are the phonons:
 $\Delta S = +/- 1, 2$

Magnetization is stable only if QT, electron and phonon transitions are forbidden

Reaching the magnetic anisotropy limit of a 3d metal atom

I. Rau *et al.*, Science **344**, 988 (20014)

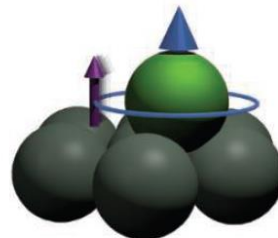
Ileana G. Rau,^{1*} Susanne Baumann,^{1,2*} Stefano Rusponi,³ Fabio Donati,³ Sebastian Stepanow,⁴ Luca Gragnaniello,³ Jan Dreiser,^{3,5} Cinthia Piamonteze,⁵ Frithjof Nolting,⁵ Shruba Gangopadhyay,¹ Oliver R. Albertini,^{1,6} Roger M. Macfarlane,¹ Christopher P. Lutz,¹ Barbara A. Jones,¹ Pietro Gambardella,^{4,†} Andreas J. Heinrich,^{1,†} Harald Brune^{3,†}

Designing systems with large magnetic anisotropy is critical to realize nanoscopic magnets. Thus far, the magnetic anisotropy energy per atom in single-molecule magnets and ferromagnetic films remains typically one to two orders of magnitude below the theoretical limit imposed by the atomic spin-orbit interaction. We realized the maximum magnetic anisotropy for a 3d transition metal atom by coordinating a single Co atom to the O site of an MgO(100) surface. Scanning tunneling spectroscopy reveals a record-high zero-field splitting of 58 millielectron volts as well as slow relaxation of the Co atom's magnetization. This striking behavior originates from the dominating axial ligand field at the O adsorption site, which leads to out-of-plane uniaxial anisotropy while preserving the gas-phase orbital moment of Co, as observed with x-ray magnetic circular dichroism.

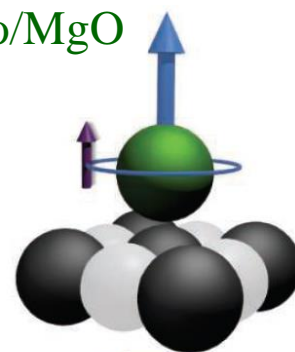
Free Co



Co/Pt(111)



Co/MgO



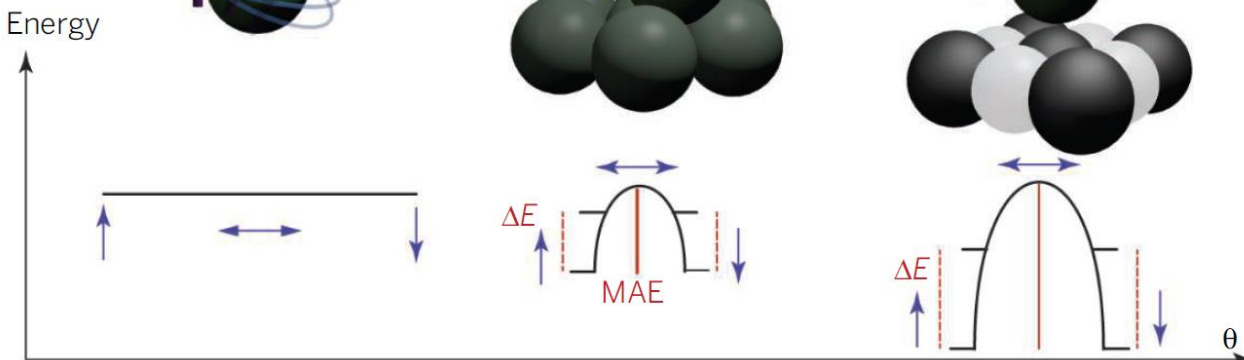
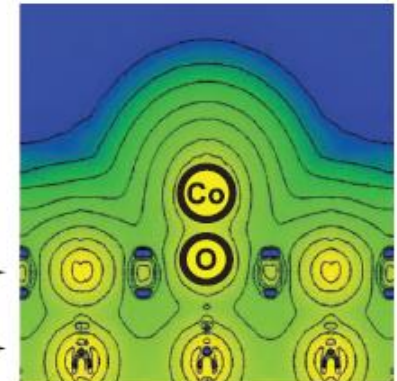
■ +0.000

■ +0.004

■ +2.000

MgO →

Ag →

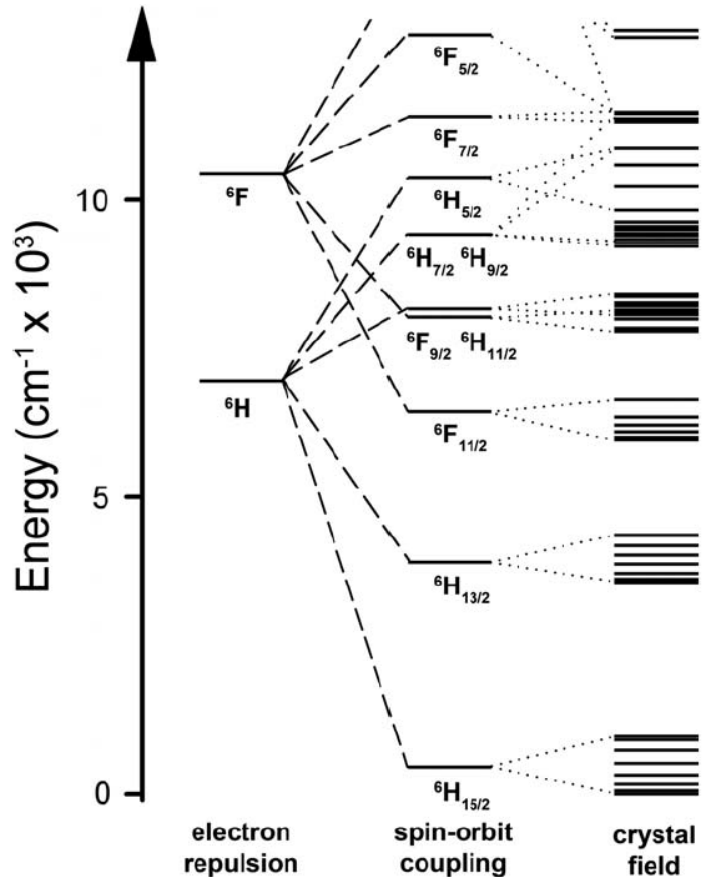


A. A. Khajetoorians and J. Wiebe, Science **344**, 976 (20014)

$$\text{Rare earths: } H = H_{e-e} + H_{\text{SOC}} + H_{\text{CF}} + H_{\text{Zeeman}}$$

The CF removes the $(2J + 1)$ -fold degeneracy of the ground state

Dy³⁺ (6s⁰ 4f⁹)

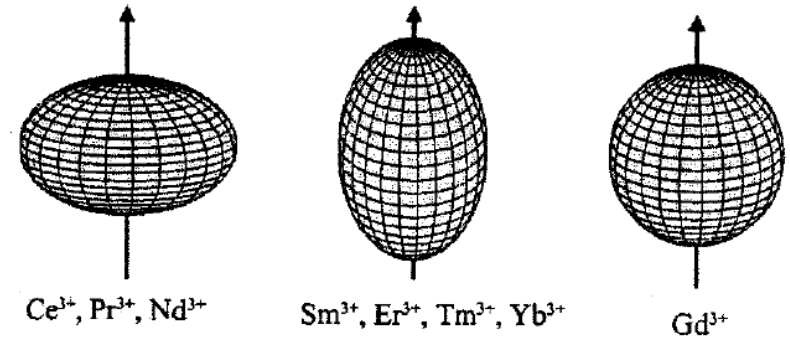
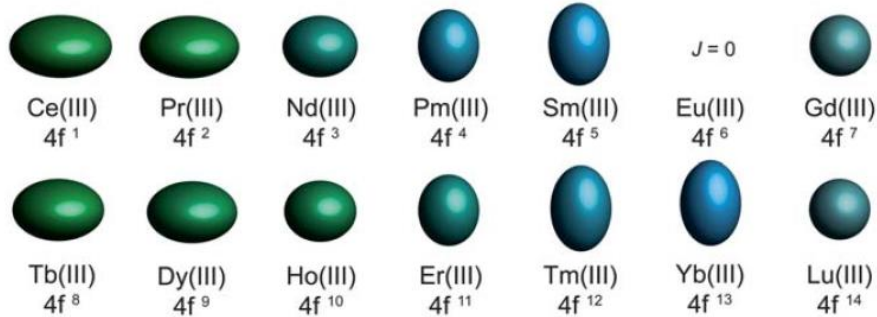


L and S are mixed by SOC -> CF acts on a basis $|J, M_J\rangle$

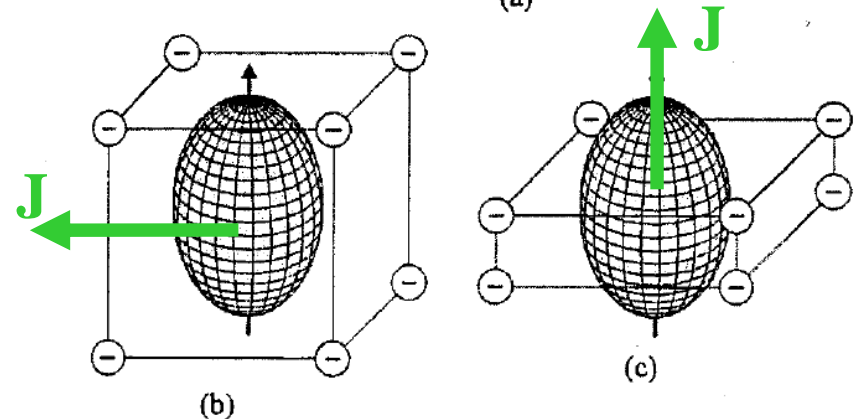
In the rare earth case the CF is only a perturbation
-> $S^* \sim J$

4f-shell electron distribution

(for $J_z = J$)



(a)

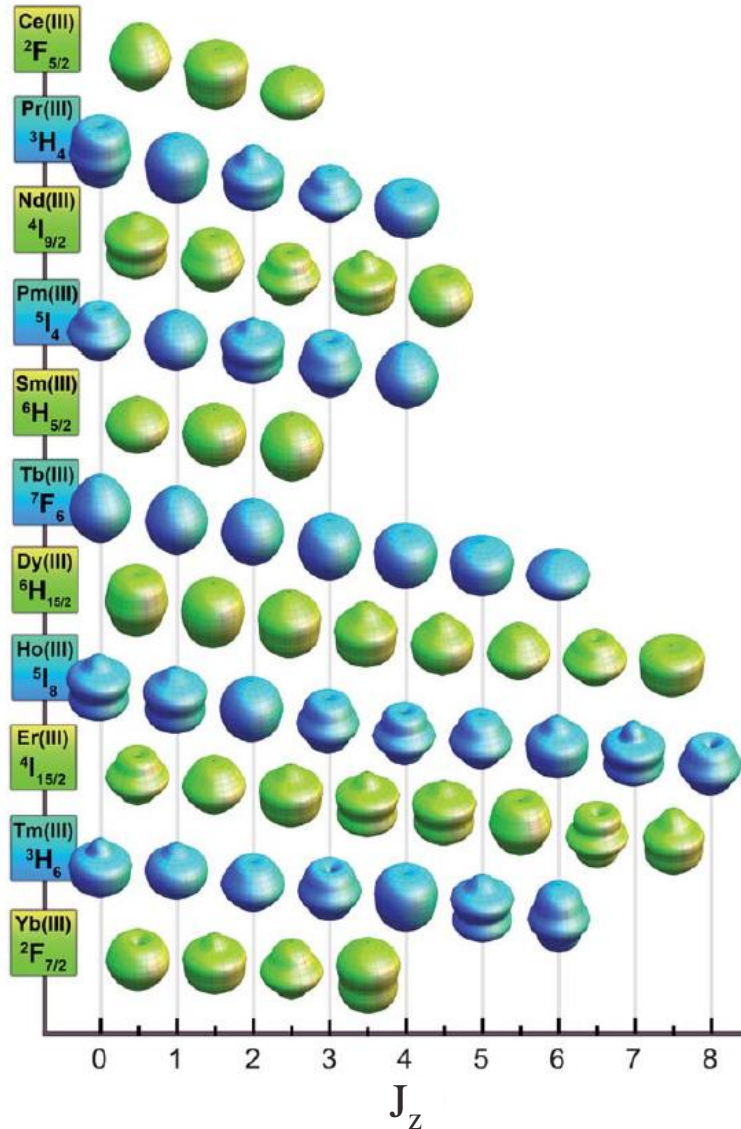


Anisotropy is due to the **electrostatic interaction** with the surrounding charges

4f charge density for J_z states composing the lowest spin-orbit coupled (J) state. If $CF = 0$, all m_J states for each lanthanide ion are degenerate



CF determines the J_z ground state



Gas phase

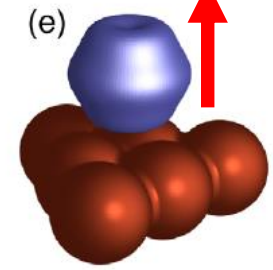
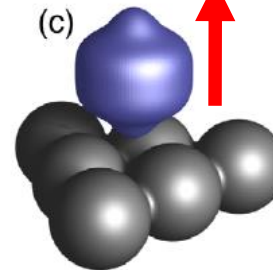
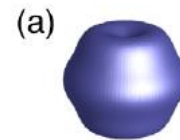
On Pt(111)

On Cu(111)

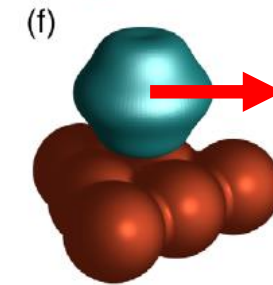
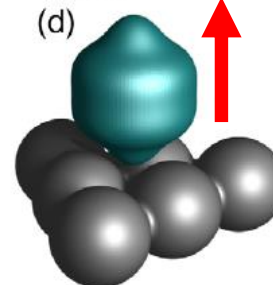
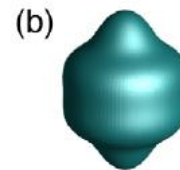
$J_z = 8$

$J_z = 6$

$J_z = 7.5$



Ho



$J_z = 7.5$

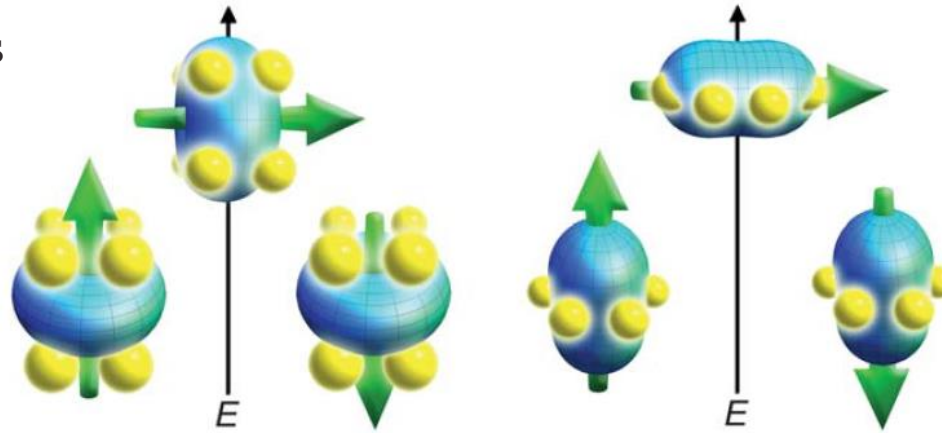
$J_z = 6.5$

$J_z = 1.0$



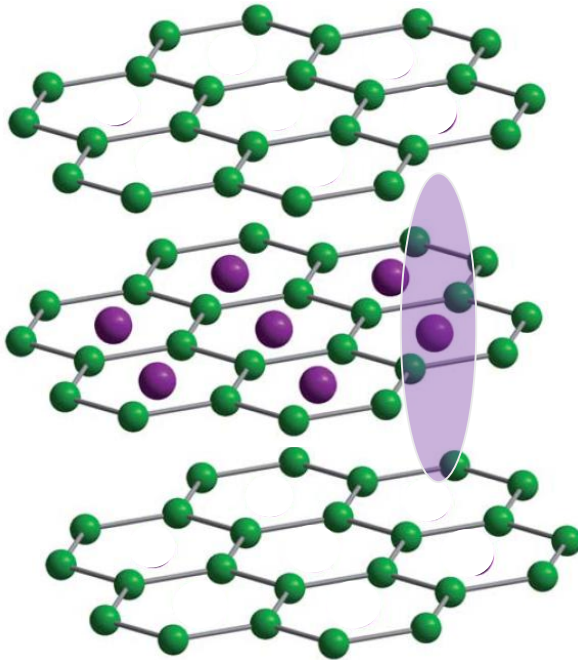
The arrow indicates the easy axis

Ground state configurations
for oblate and prolate 4f
electron distribution

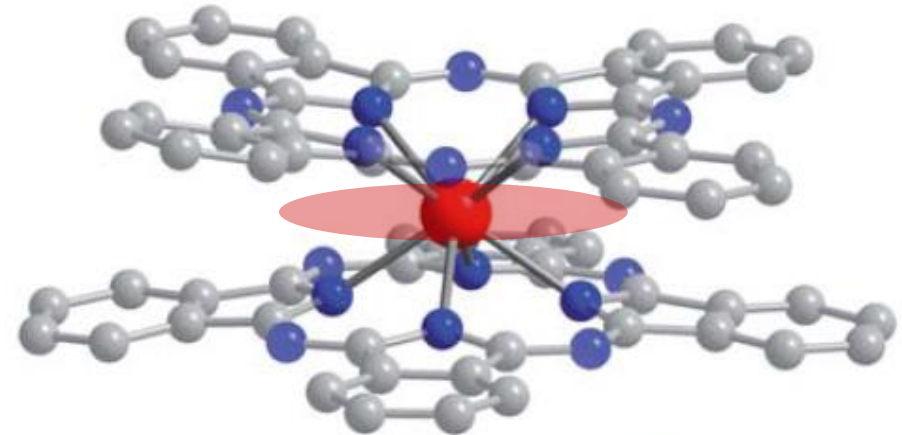


J. D. Rinehart et al., Chem.
Sci. 2, 2078 (2011);

SmCo₅



TbPc₂



The prolate 4f electron distribution of Sm
prefers to point the empty center of the hexagon

The oblate 4f electron distribution of
Tb prefers to stay in between the two
Pc planes

CF hamiltonian

$$\hat{H}_{\text{eff}} = E_0 + E_Z + \sum_{n=2}^{\text{even}} \sum_{m=0}^n B_n^m \hat{O}_n^m + \sum_{n=2}^{\text{even}} \sum_{m=1}^n C_n^m \hat{\Omega}_n^m$$

O_n^m and Ω_n^m with $n = 6$ for rare earth
($n = 4$ for transition metals)

They are the Stevens

operators describing the CF in terms of

J_z, J_+ and J_-

Ex:

$$O_2^0 = 3J_z^2 - J(J+1); B_2^0 = D/3$$

$$O_2^2 = \frac{1}{2}(J_+^2 + J_-^2); B_2^2 = 2E$$

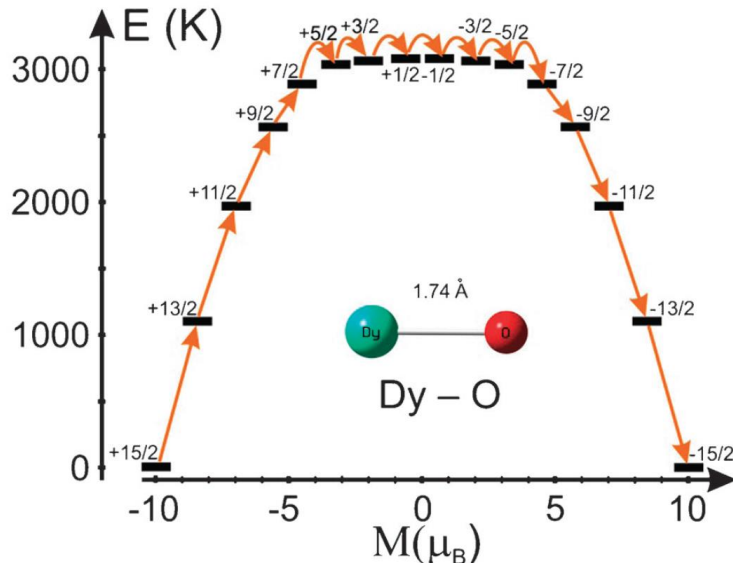
$$O_4^3 = \frac{1}{4} [J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3) J_z]; O_4^4 = \frac{1}{2}(J_+^4 + J_-^4);$$

Depending on the CF symmetry can exist terms coupling J and $-J$ ground states via J_+ (J_-) operator \rightarrow quantum tunneling \rightarrow no stable magnetization

We can increase the

single-ion anisotropy by judiciously choosing the coordination environment of the lanthanide ion.

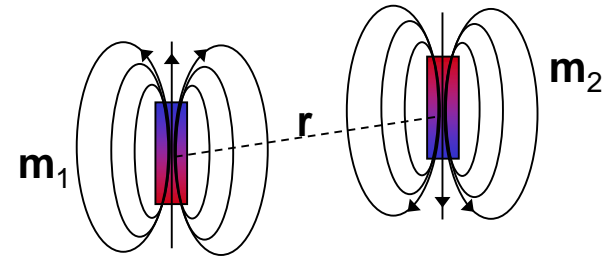
Ex.: CF with a significant O_4^3 (C_{3v}) term is not convenient for Dy^{3+} ($J = 15/2$) because J_+^3 links $-15/2 \rightarrow -9/2 \rightarrow -3/2 \rightarrow 3/2 \rightarrow 9/2 \rightarrow 15/2$



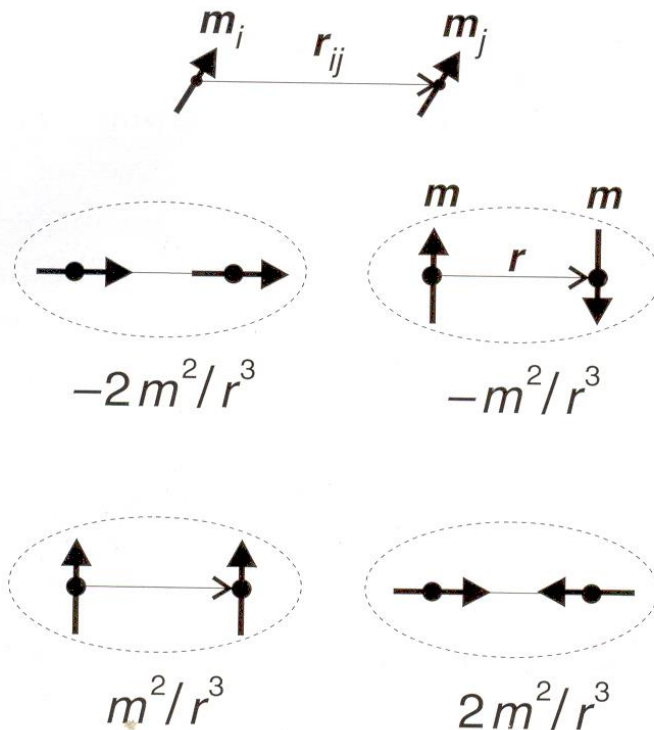
Axial CF \rightarrow only O_2^0 term \rightarrow no quantum tunneling

Long range interaction between magnetic moments

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



m_1 and m_2 can be the magnetic moments of two atoms in a particle or the moments of two particles



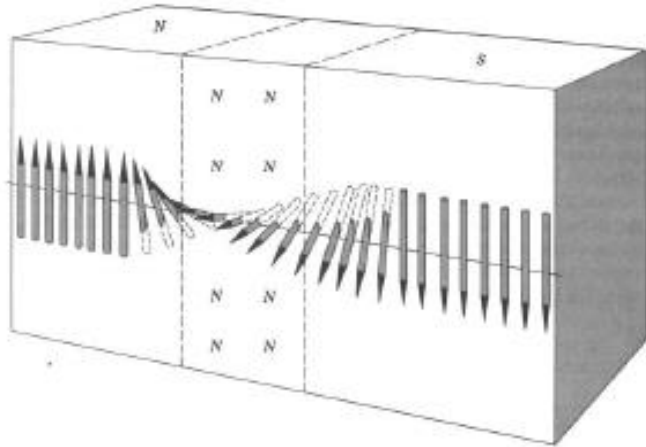
In out-of-plane configuration the dipolar interaction is reduced

The magnetic configurations are determined by the competition, at a local scale, of four different energies:

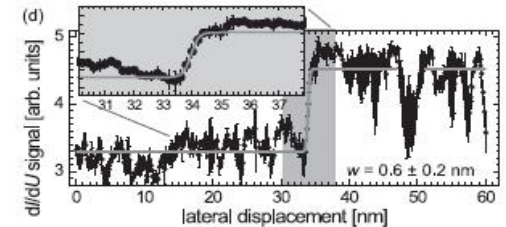
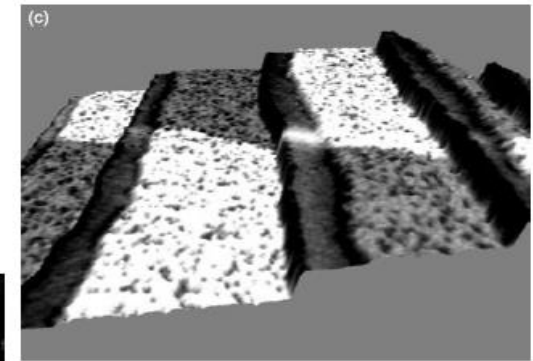
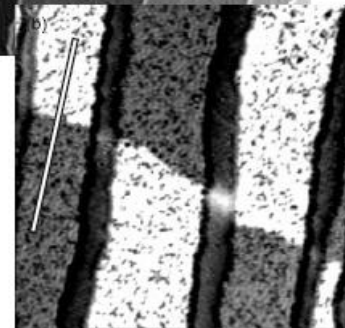
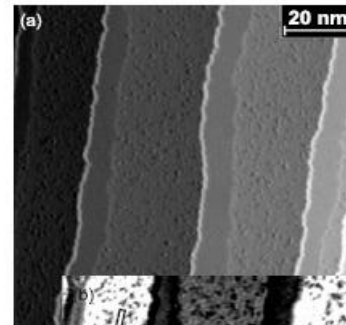
Zeeman, **exchange**, **magnetocrystalline anisotropy**, and **dipolar coupling**.

$$E = -\mu_0\mu\mathbf{H}\sum_i \mathbf{m}_i - J\sum_{\langle i,j \rangle} \mathbf{m}_i \cdot \mathbf{m}_j - \sum_i k_i(\mathbf{m}_i \cdot \mathbf{e}_i)^2 - \frac{\mu_0\mu^2}{8\pi} \sum_{i,j \neq i} \left[\frac{3(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{\mathbf{m}_i \mathbf{m}_j}{r_{ij}^3} \right],$$

exchange, magnetocrystalline energy -> short range
dipolar energy -> long range

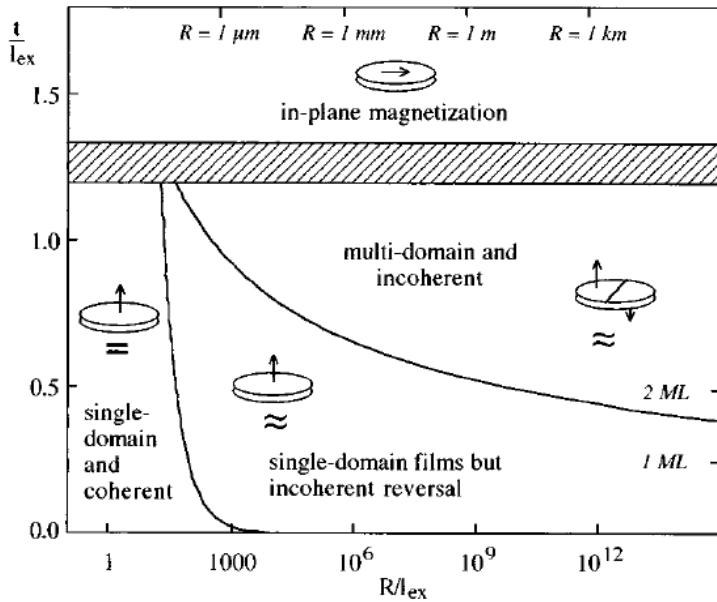


Structure of a domain wall between two ferromagnetic domains with opposite orientation of the local magnetization (180° wall)



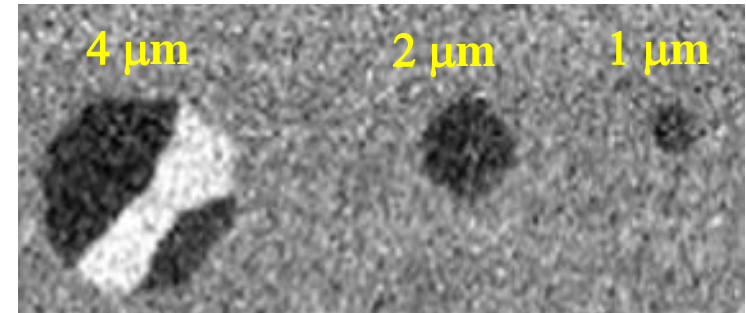
SP-STM of 1.3 monolayers Fe / stepped W(110)

Magnetic phase diagram for ultrathin films with perpendicular anisotropy ($l_{ex} = 2\text{nm}$)

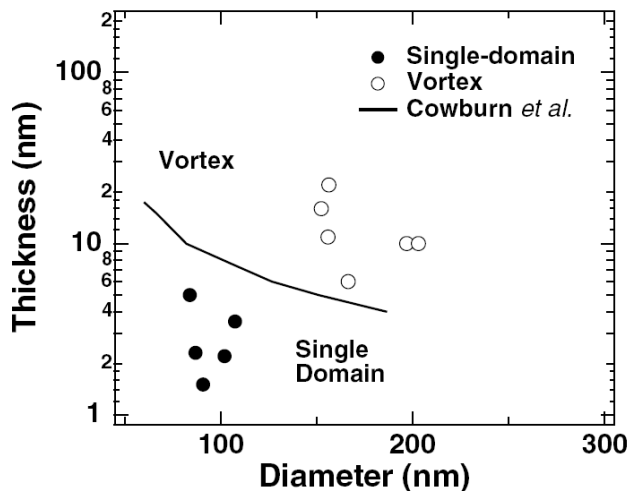


R. Skomski et al. Phys.Rev. B **58**, 3223 (1998)
A. Vaterlaus et al. J. Magn. Magn. Mater. **272-276**, 1137 (2004)

magnetic domain pattern of perpendicularly magnetized ultra-thin Fe particles grown on Cu(0 0 1)



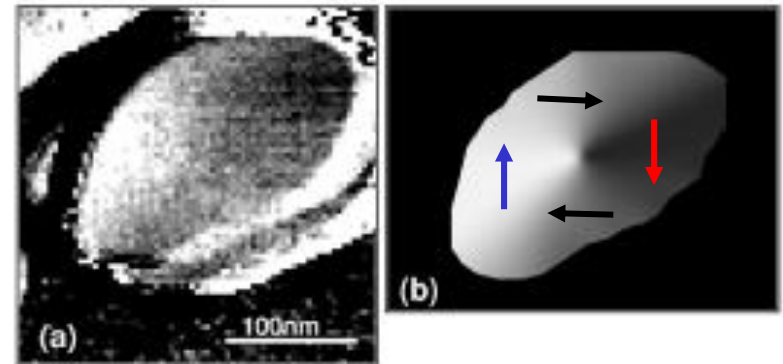
Magnetic phase diagram for ultrathin particles with in-plane anisotropy (Fe/W(001))



magnetic domain pattern of in-plane magnetized ultra-thin Fe particles grown on W(0 0 1)

SP-STM

Calculated vortex



R. Skomski et al. Phys.Rev. Lett. **91**, 127201 (2003)

$$E_{dip} = -\frac{\mu_0}{2} \int \mathbf{M} \cdot \mathbf{H}_{dem} dV$$

$$\mathbf{H}_{dem} = -\mathbf{D}\mathbf{M}$$

Pushes the magnetization \mathbf{M} along the longer side of the nanostructure:

Cylinder $\rightarrow \mathbf{M} \parallel$ axis

Disk $\rightarrow \mathbf{M} \parallel$ disk surface

Sphere:

$$D = \begin{bmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{bmatrix}$$

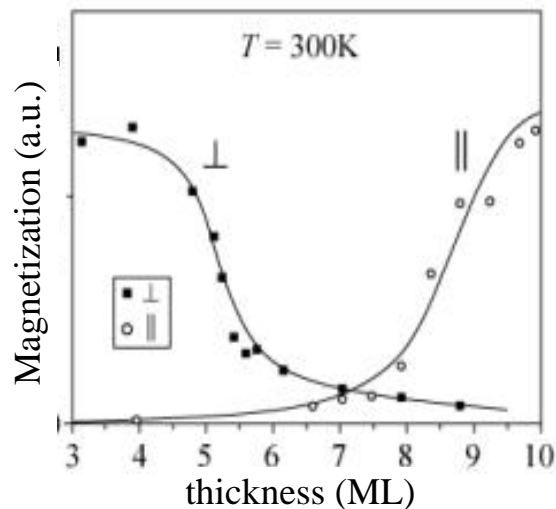
∞ -Cylinder:

$$D = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

∞ -Plane (thin film):

$$D = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Co/Pt(111)



Orientation and shape of Co magnetic domains

