Magnetocrystalline anisotropy energy: MAE (K)

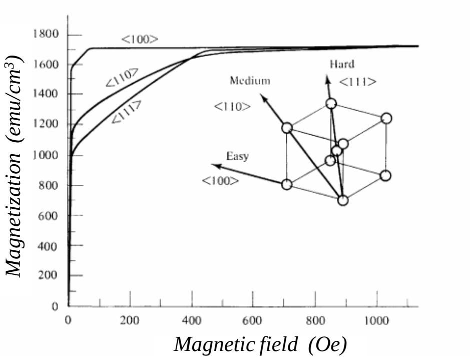
Define the space direction/s along which the magnetic moment prefer to align

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

Free magnetic atom: spatially isotropic $K = 0$

Fe bcc

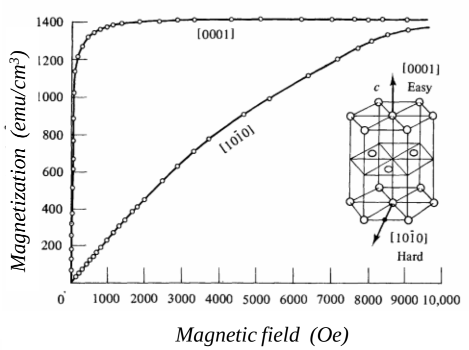
$$K_1 = 4.8 \times 10^4 \ J/m^3$$
$$= 2.4 \ \mu eV/atom$$



Co hcp

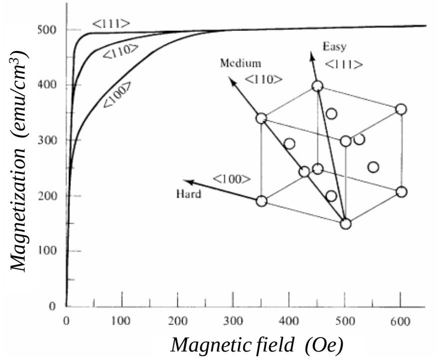
easy axis: (0001)

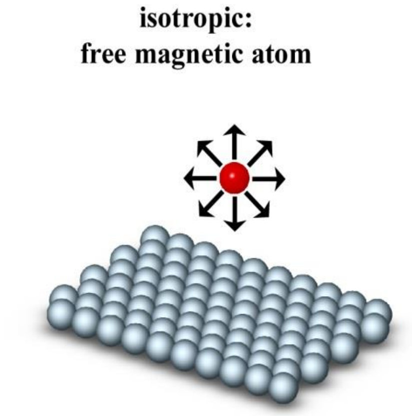
$$K_1 = 4.1 \times 10^5 \ J/m^3$$
$$= 45 \ \mu eV/atom$$

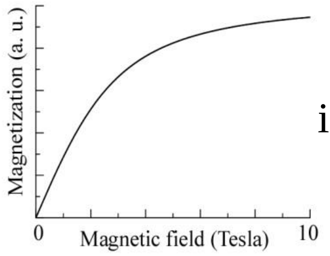


Ni fcc

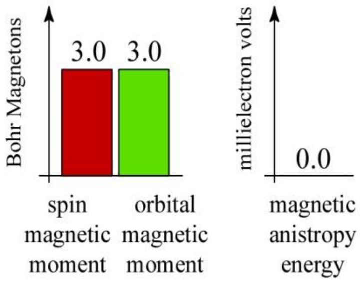
$$K_1 = -5.5 \times 10^3 \ J/m^3$$
$$= -0.3 \ \mu eV/atom$$





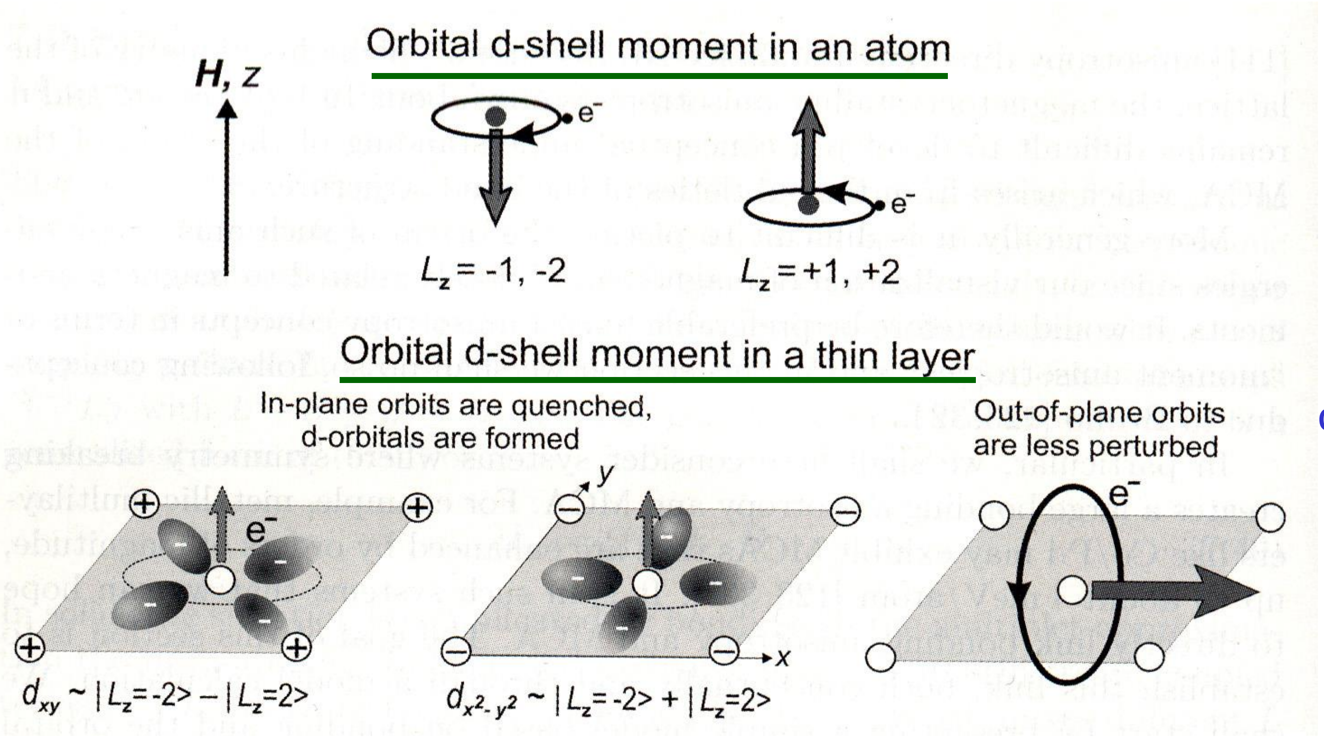


Direction independent



Co atoms

Orbital moment and anisotropic bonding: magnetization easy axis



Qualitative argument

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

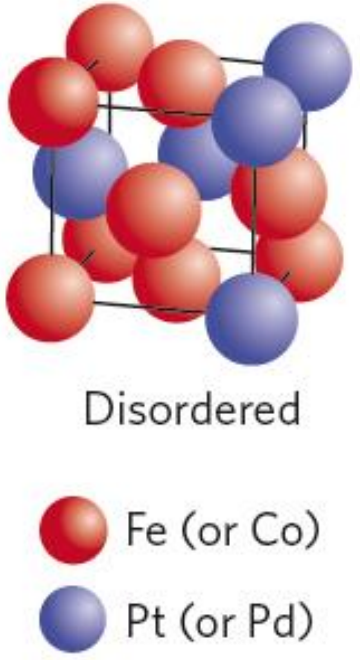
-d electron in a free atom. For an external magnetic field aligned along z the lowest energy state is L_z=-2.

- 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 braking 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

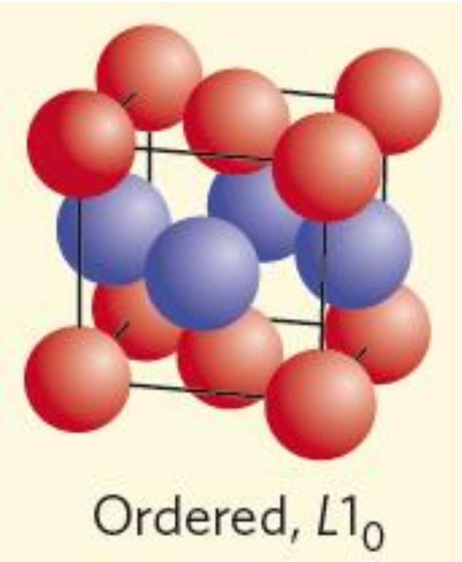
Example: L1$_0$ phase in FePt alloy

Low MAE



Ordering by annealing to about 600°C

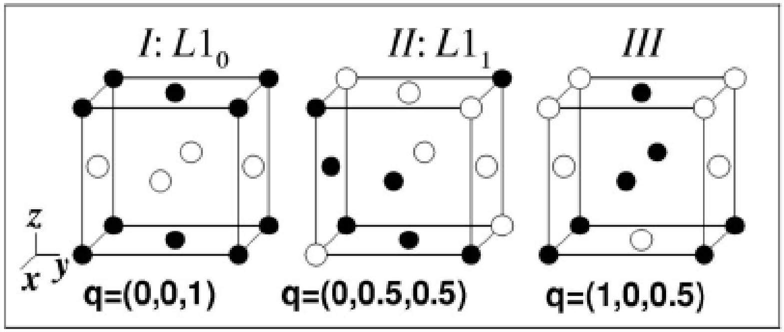
High MAE

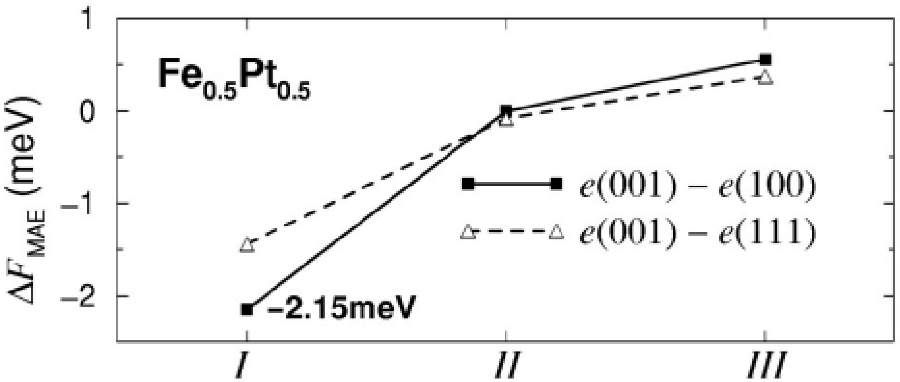


D. Alloyeau et al., Nat Mater. **8**, 940 (2009); Z.R. Day et al. Nano Lett. **1**, 443 (2001); S. Sun *et al.*, Science **287**, 1989 (2000)

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

CF tuning the MAE





Magnetocrystalline anisotropy in transition metals: theory

J. Phys.: Condens. Matter **10** (1998) 3239–3253. Printed in the UK PII: S0953-8984(98)86583-1

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 $|\boldsymbol{k},n,\sigma\rangle$ and eigenvalues $\varepsilon_{n,\sigma}(\boldsymbol{k})$

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

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

The intra-atomic spin–orbit interaction is given by

$$H_{\mathrm{so}} = \xi \sum_{\mu_1,\mu_2,\sigma_1,\sigma_2} \langle\mu_2,\sigma_2|\boldsymbol{L}\cdot\boldsymbol{S}|\mu_1,\sigma_1\rangle \sum_{\boldsymbol{k}} c^{\dagger}_{\mu_2,\sigma_2}(\boldsymbol{k})c_{\mu_1,\sigma_1}(\boldsymbol{k})$$

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

Magnetocrystalline anisotropy

H_{so} is a one-electron operator

diagonal in ***k*** (***k*** is conserved)

→

The only excited states are

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

$$\varepsilon_{n_1,\sigma_1}(\boldsymbol{k}) < \varepsilon_{\mathrm{F}} < \varepsilon_{n_2,\sigma_2}(\boldsymbol{k})$$

The excited state is an unoccupied state

In 3d metals $H_{\mathrm{so}} \approx$ 50-100 meV << band width ≈ 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 -> first order correction $<\mu\,|\,H_{\mathrm{so}}\,|\mu> = 0$

The second order correction is ≠ 0

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

$$\begin{aligned}\delta E = -\xi^2 \sum_{\theta} [& A(\theta,\uparrow,\uparrow)\langle \underline{\mu}_1,\uparrow|\boldsymbol{L}\cdot\boldsymbol{S}|\underline{\mu}_2,\uparrow\rangle\langle \mu_2,\uparrow|\boldsymbol{L}\cdot\boldsymbol{S}|\mu_1,\uparrow\rangle \\ & + A(\theta,\downarrow,\downarrow)\langle \underline{\mu}_1,\downarrow|\boldsymbol{L}\cdot\boldsymbol{S}|\underline{\mu}_2,\downarrow\rangle\langle \mu_2,\downarrow|\boldsymbol{L}\cdot\boldsymbol{S}|\mu_1,\downarrow\rangle \\ & - A(\theta,\uparrow,\downarrow)\langle \underline{\mu}_1,\uparrow|\boldsymbol{L}\cdot\boldsymbol{S}|\underline{\mu}_2,\downarrow\rangle\langle \mu_2,\downarrow|\boldsymbol{L}\cdot\boldsymbol{S}|\mu_1,\uparrow\rangle \\ & - A(\theta,\downarrow,\uparrow)\langle \underline{\mu}_1,\downarrow|\boldsymbol{L}\cdot\boldsymbol{S}|\underline{\mu}_2,\uparrow\rangle\langle \mu_2,\uparrow|\boldsymbol{L}\cdot\boldsymbol{S}|\mu_1,\downarrow\rangle]\end{aligned}$$

→ majority to majority state

→ minority to minority state

→ Spin-flip transitions

$$A(\theta,\sigma_1,\sigma_2) \equiv \int_{\varepsilon_1<\varepsilon_{\mathrm{F}}<\varepsilon_2} \frac{\mathrm{d}\varepsilon_1\,\mathrm{d}\varepsilon_2}{\varepsilon_2-\varepsilon_1}\sum_{\boldsymbol{k}} n_{\mu_1,\underline{\mu}_1,\sigma_1}(\boldsymbol{k},\varepsilon_1)\,n_{\mu_2,\underline{\mu}_2,\sigma_2}(\boldsymbol{k},\varepsilon_2)$$

$$\theta = \mu_1, \underline{\mu}_1, \mu_2, \underline{\mu}_2$$

Magnetocrystalline anisotropy

$$\delta E \approx \underbrace{-\frac{1}{4}\xi\,\hat{\boldsymbol S}\cdot[\langle \boldsymbol L^{\downarrow}\rangle - \langle \boldsymbol L^{\uparrow}\rangle]} + \underbrace{\frac{\xi^2}{\Delta E_{\rm ex}}\left[\frac{21}{2}\hat{\boldsymbol S}\cdot\langle \boldsymbol T\rangle + 2\langle (L_\zeta S_\zeta)^2\rangle\right]}$$

Majority to majority
Minority to minority

Spin-flip transitions

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

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

$\Delta E_{\rm ex}$ is the exchange splitting between majority and minority states

K = δE(H//z) - δE(H//x or y)

energy difference between two magnetization directions

If majority states completely full

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

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

Actually

$$K = \alpha\frac{\xi}{4}\Delta \mathrm{L} = \alpha\frac{\xi}{4}(\mathrm{L}_z - \mathrm{L}_{x,y})$$

$$\alpha \approx 0.2 - 0.25$$

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

MAE *vs.* ΔL in complex systems

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

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)

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

sum over all **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 $5d^{10}\ 6s^{1}$ -> negligible S and L ->

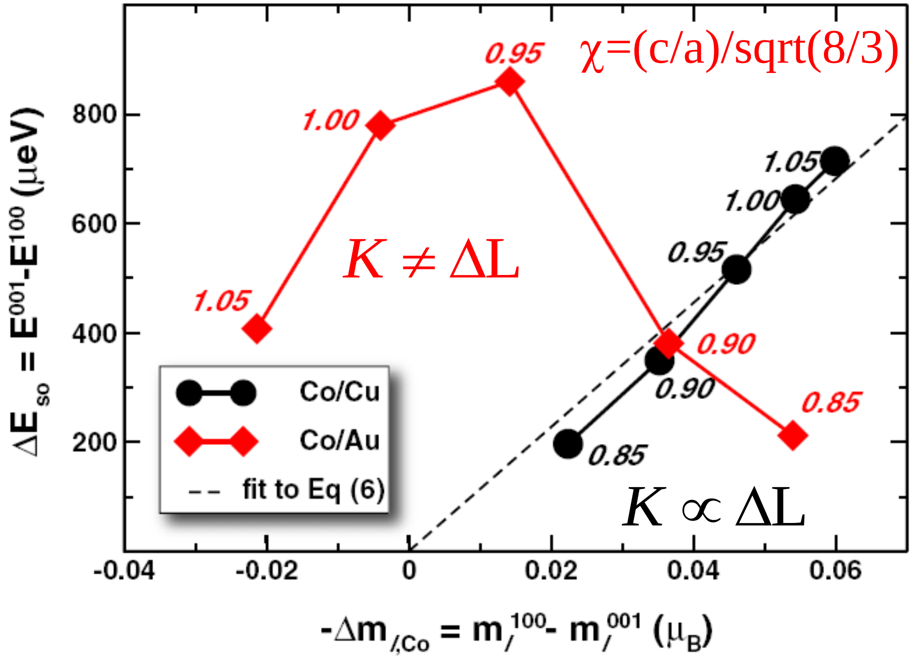
a) S and L can be not zero due to orbital hybridization

b) very high spin-orbit constant ζ about 600 meV

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

C. Andersson *et al.* Phys. Rev. Lett. **99**, 177207 (2007)

Calculation as a function of the deformation parameter χ



Magnetocrystalline anisotropy: band structure

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

$$L_+ = L_x + L_y \qquad L_- = L_x - L_y$$

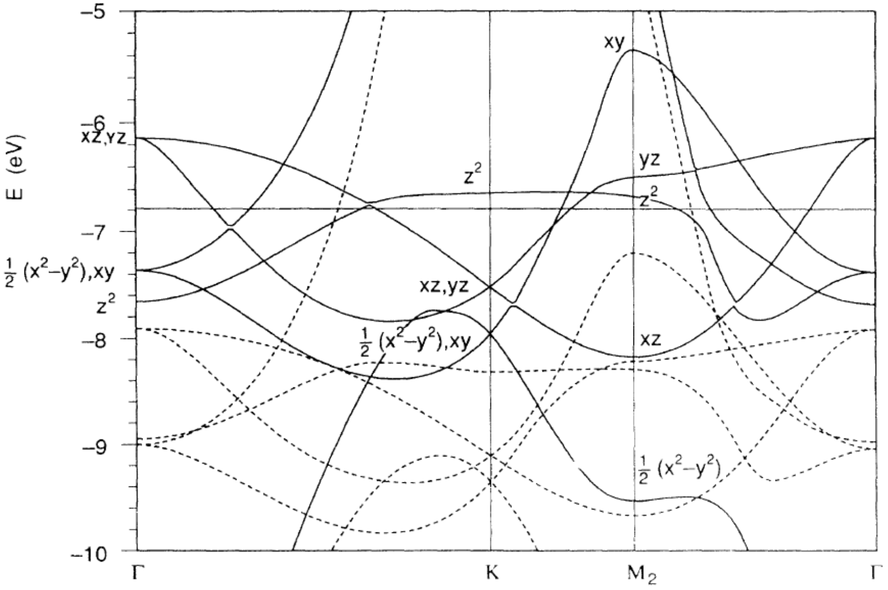
$$\mathcal{H}^{SO}(\hat{\mathbf{n}}) = \frac{\xi}{2}\begin{pmatrix} \hat{\mathbf{n}} \cdot \mathbf{l} & \hat{\mathbf{n}}_\perp \cdot \mathbf{l} + \frac{1}{2}(l_- - l_+) \\ \hat{\mathbf{n}}_\perp \cdot \mathbf{l} - \frac{1}{2}(l_- - l_+) & -\hat{\mathbf{n}} \cdot \mathbf{l} \end{pmatrix}$$

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

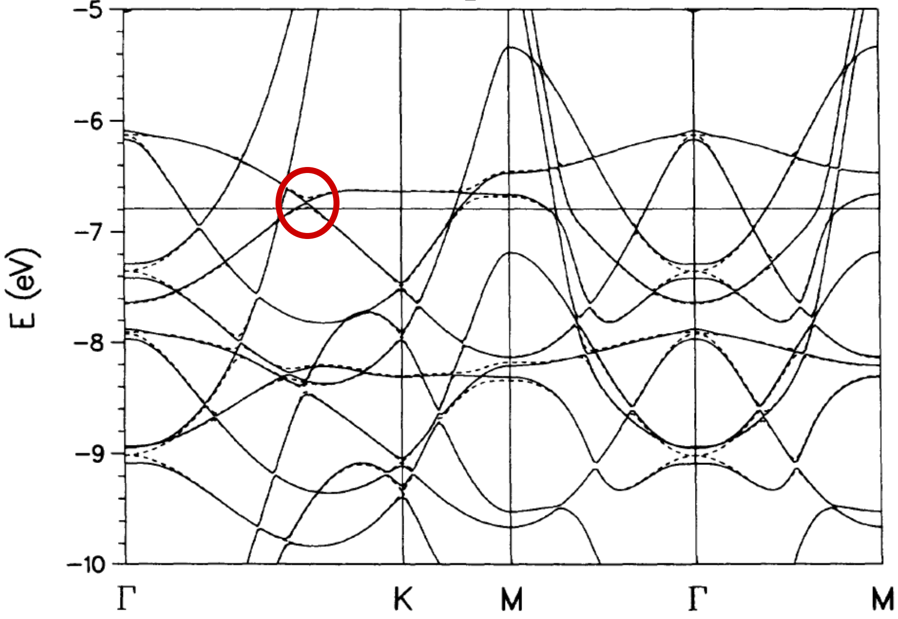
Free-standing Co monolayer

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)

G.H.O. Daalderop *al*. Phys. Rev. B **50**, 9989 (1994);

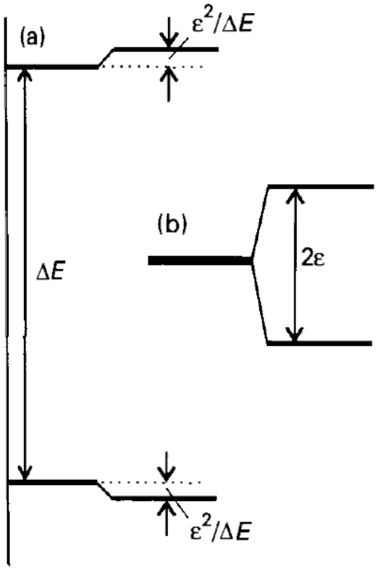
Magnetocrystalline anisotropy: degenerate case

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)

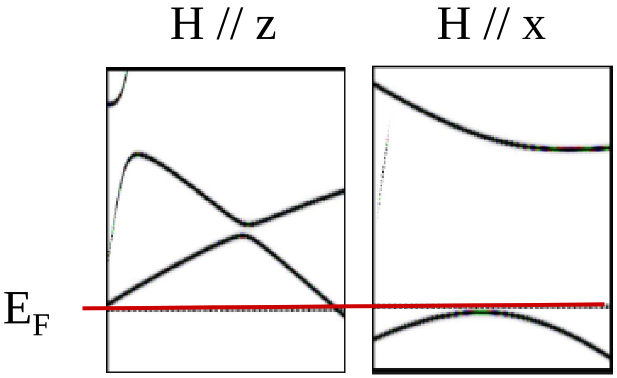
The correct formula becomes $\delta E = \varepsilon$ with $\varepsilon = \langle 1|H_{soc}|2\rangle$

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

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



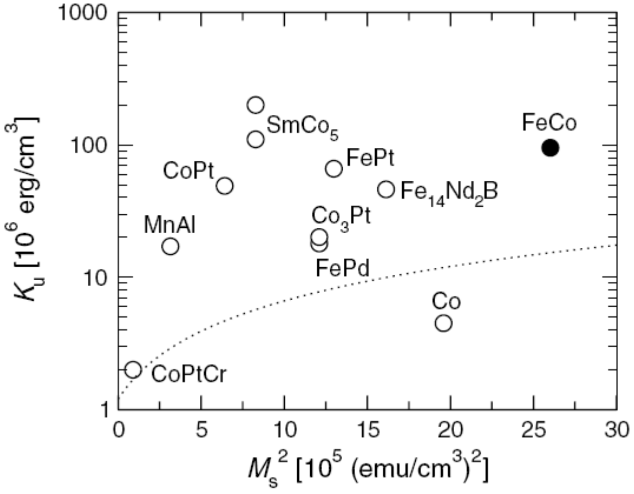
Degenerate states close to E_F can give huge contributions to the MAE



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

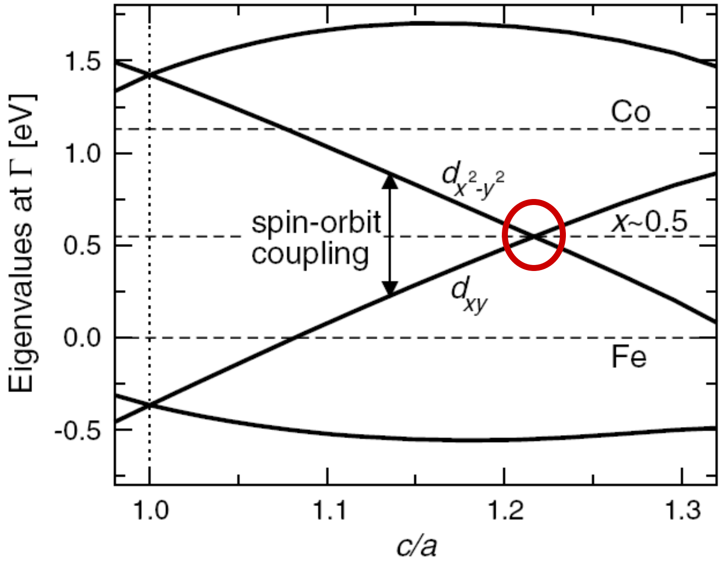
Example: FeCo bulk

Enhanced MAE for the composition and c/a distortion at which the d_{x2-y2} and d_{xy} states cross.



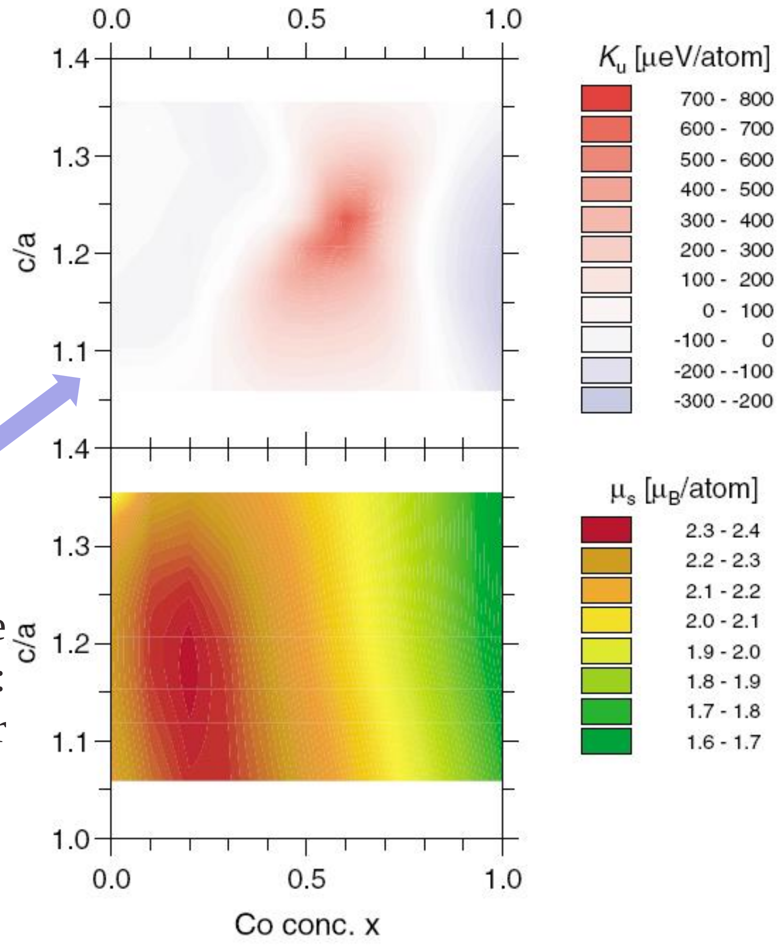
FeCo bcc -> K= 1-2 μeV/atom

FeCo bct -> K= 0.8 meV/atom



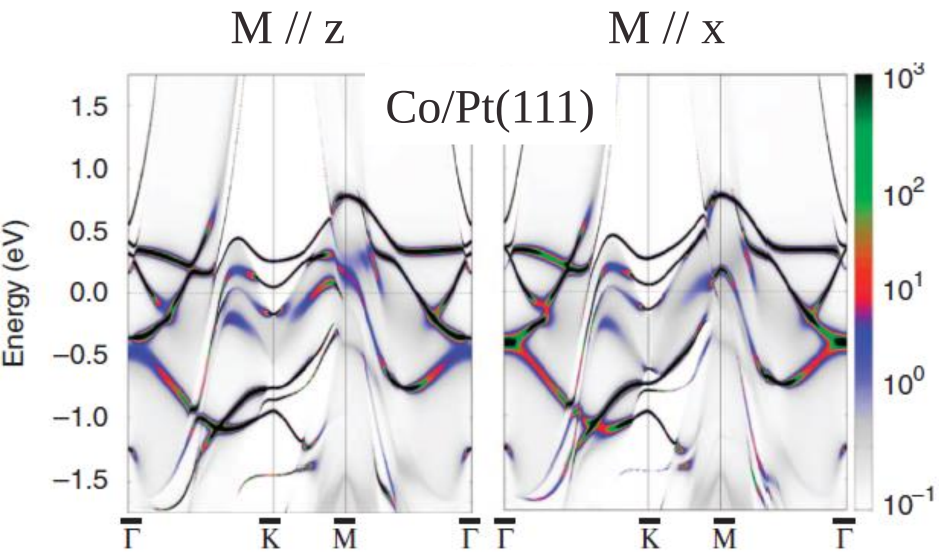
Calculated d-orbitals spin-down eigenvalues at the Γ point as a function of c/a ratio. The Fermi energies of Fe, Co, and $Fe_{0.5}Co_{0.5}$ are indicated by dashed lines

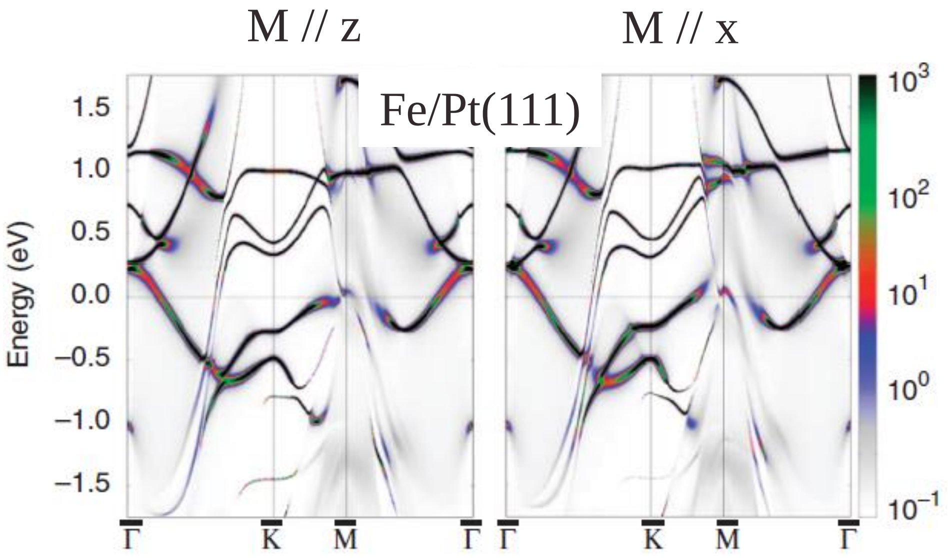
Spin orbit split these two degenerate states: maximum MAE for c/a = 1.2 and x = 0.5



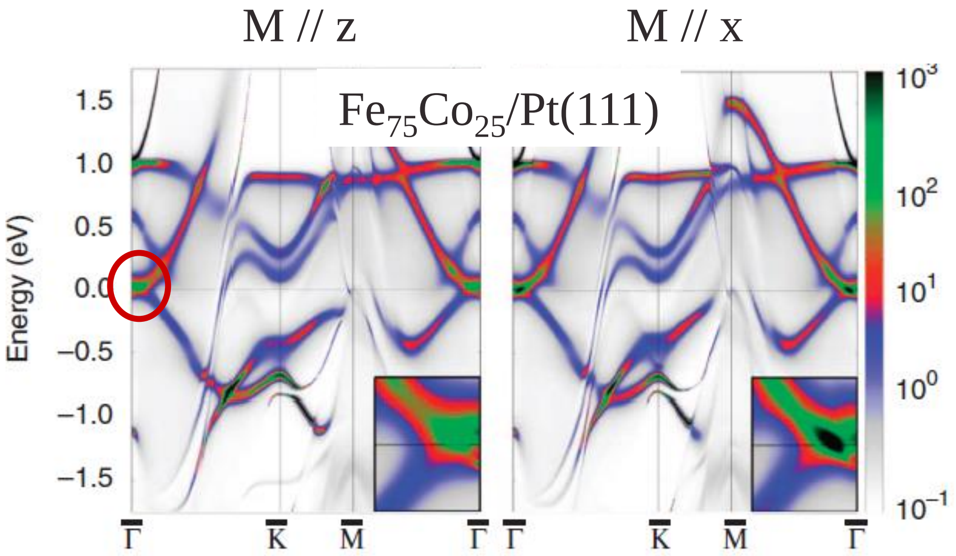
T. Burkert *et al.* Phys. Rev. Lett. **93**, 027203 (2004);

Example: FeCo monolayer





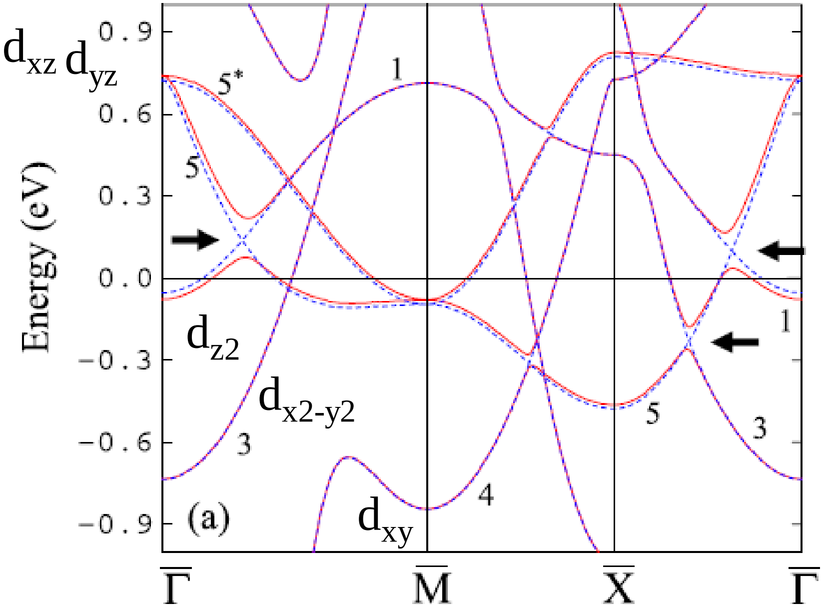
1) Degenerate d_{xy} and d_{x2-y2} orbitals at Fermi level for $Fe_{75}Co_{25}$ -> chance of having large MAE



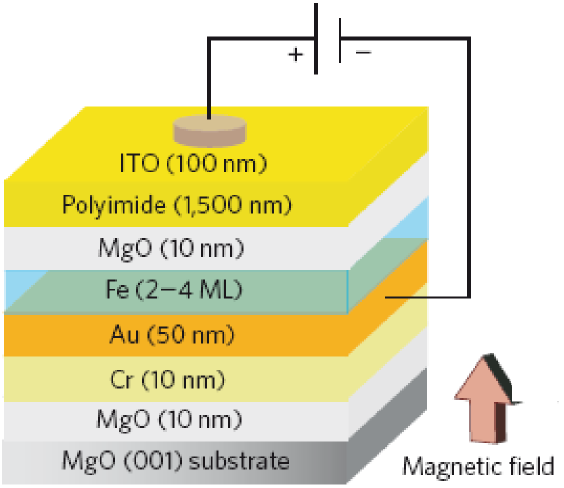
2) Splitting of the d_{xy} and d_{x2-y2} orbitals -> gain in energy when M // z -> z is the easy axis with large MAE

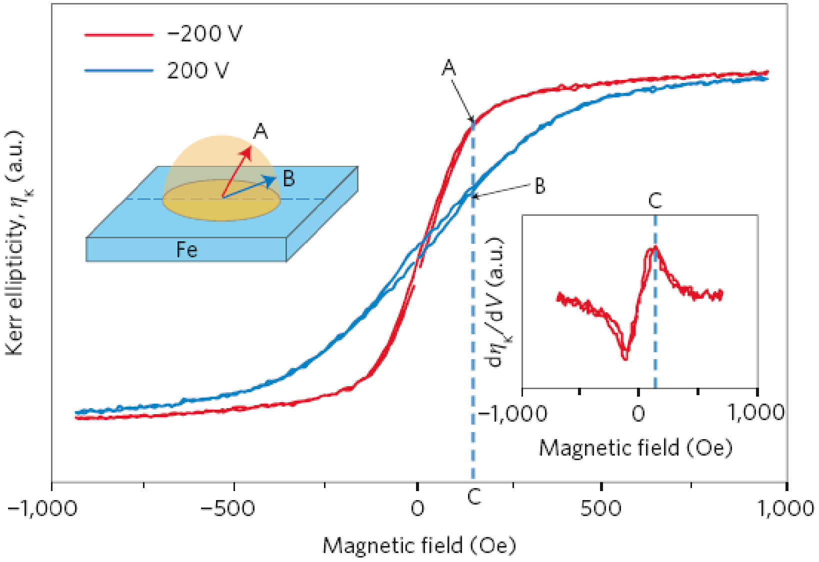
S. Ouazi *et al.* Nat. Commun. **3**, 1313 (2012); G. Moulas et al. Phys. Rev. B, **78**, 214424 (2008)

MAE modification by an external electric field



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 -> Y_0^1 symmetry

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

K. Nakamura *et al.* Phys. Rev. Lett. **102**, 187201 (2009); T. Maruyama *et al.*, Nature Nanotech.. **4**, 158 (2009)

Spin Hamiltonian: transition metals

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

$$\mathcal{H}_{\mathrm{sp-orb}} = \lambda \boldsymbol{L} \cdot \boldsymbol{S} \qquad \mathcal{H}_Z = \mu_B (\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{H} \qquad |\Gamma,\, \gamma\rangle |S,\, M_S\rangle$$

Basis in a crystal field
(Γ is the orbital part)

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

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

Second order perturbation theory

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

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

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

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

R. M. White, *Quantum theory of magnetism*, Springer (2007)

Spin Hamiltonian: transition metals

$\Lambda_{\mu\nu}$ 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 $\Lambda_{zz} = \Lambda_{//}$

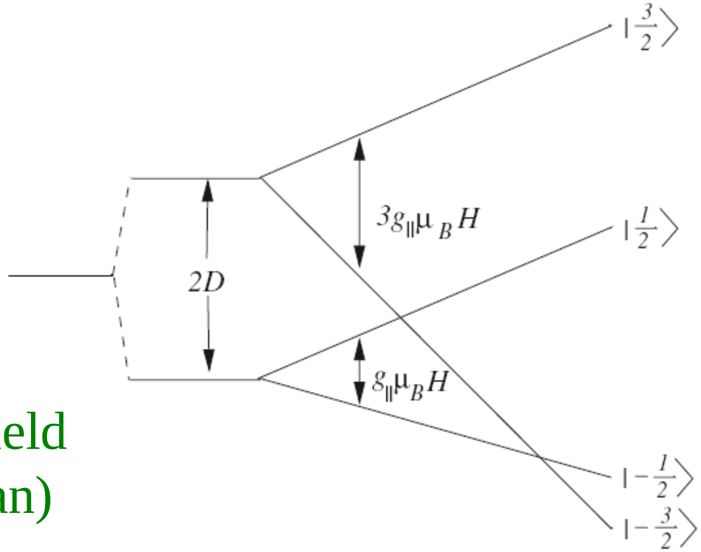
Neglecting $\mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu$

$$\mathcal{H}_{\mathrm{eff}} = g_{||}\mu_B H_z S_z + g_{\perp}\mu_B (H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)]$$

$$+\frac{1}{3}S(S+1)\left(2\wedge_{\perp} + \Lambda_{||}\right)\lambda^2 \,, \qquad D = \lambda^2(\wedge_{||} - \wedge_{\perp})$$

Ex: S=3/2 and H = (0,0,H) -> H = $g_{||}\mu_B H_z S_z + D[S_z^2 - 1/3\, S(S+1)]$ D > 0

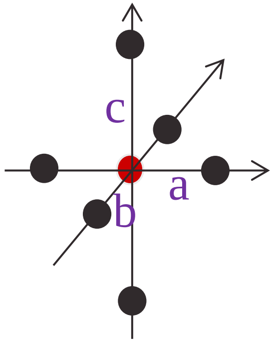
$$\mathcal{H}_{\mathrm{eff}} = \begin{array}{c} \\ \langle -\frac{3}{2}| \\ \langle -\frac{1}{2}| \\ \langle \frac{1}{2}| \\ \langle \frac{3}{2}| \end{array} \begin{array}{c} \begin{array}{cccc} \quad |-\frac{3}{2}\rangle \quad & \quad |-\frac{1}{2}\rangle \quad & \quad |\frac{1}{2}\rangle \quad & \quad |\frac{3}{2}\rangle \quad \end{array} \\ \begin{bmatrix} D - \frac{3}{2}g_{||}\mu_B H & 0 & 0 & 0 \\ 0 & -D - \frac{1}{2}g_{||}\mu_B H & 0 & 0 \\ 0 & 0 & -D + \frac{1}{2}g_{||}\mu_B H & 0 \\ 0 & 0 & 0 & D + \frac{3}{2}g_{||}\mu_B H \end{bmatrix} \end{array}$$



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

Spin Hamiltonian: transition metals

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.

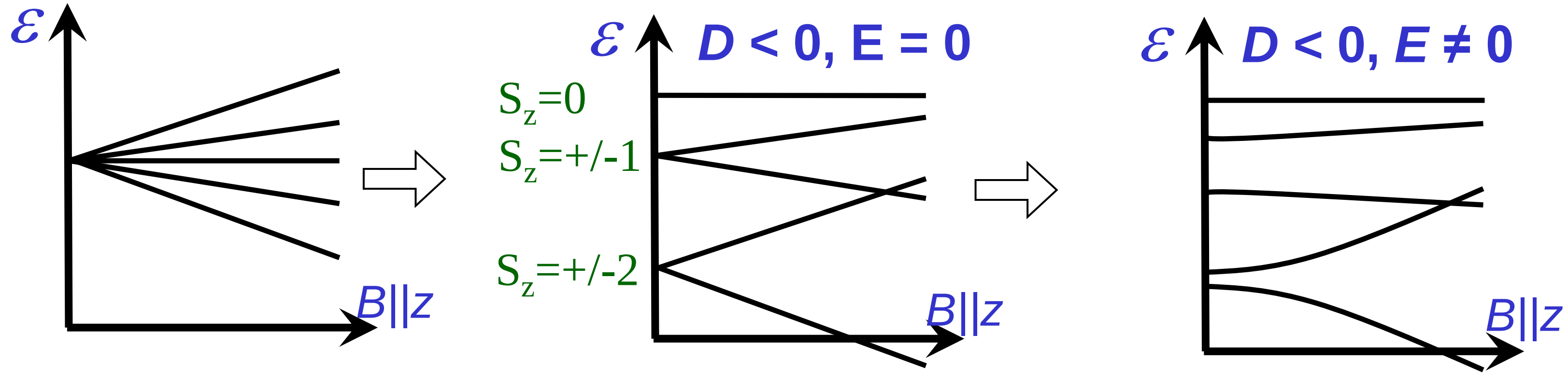
2) Thus, in the previous equations S should be considered as a sort of effective spin operator S* to be determined by fitting the data.

3) However, assuming negligible hybridization and CF quenching the orbital moment -> S*~S

T. Schuh *et al*. Phys. Rev. B **84**, 104401 (2011); D. Dai *et al*., J. Comput. Chem. **29**, 2187 (2008)

Spin Hamiltonian: energy spectrum

Energy spectrum: ex. S = 2

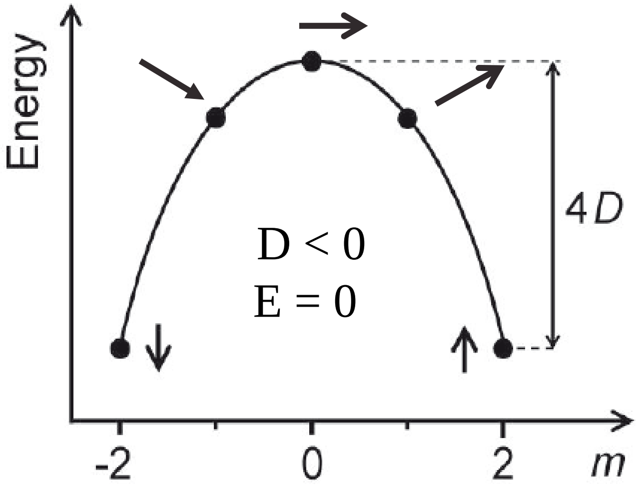


CF = 0

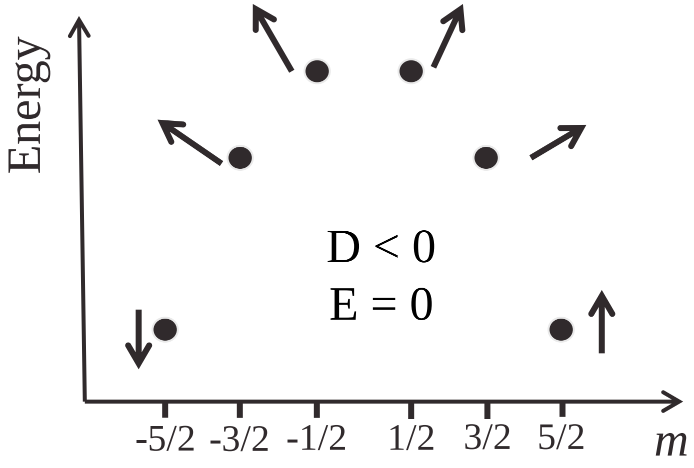
CF different from 0

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

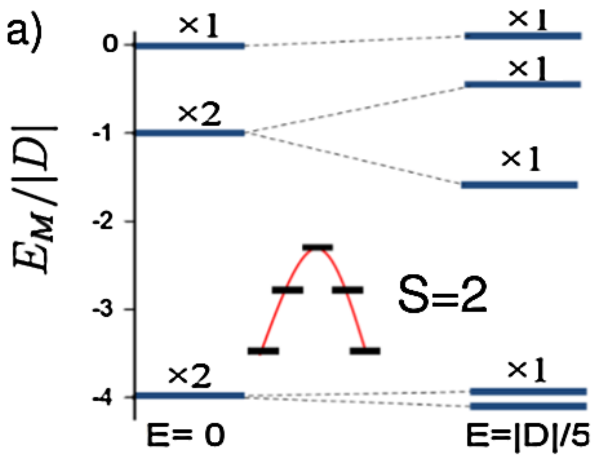
$K_r = DS^2$ (S integer)



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



Quantum tunneling for E ≠ 0: integer *vs.* half integer spin

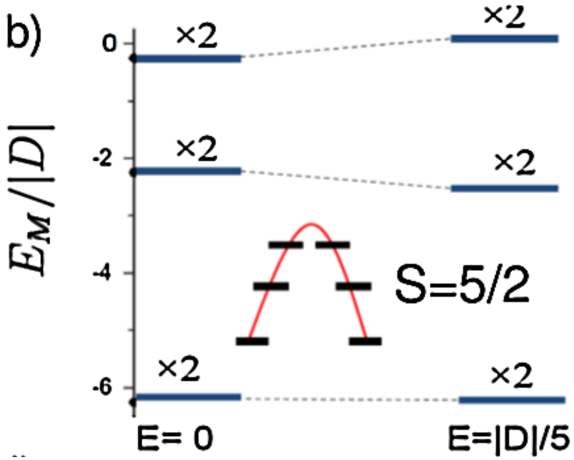


E ($S_x^2-S_y^2$) = E ($S_+^2+S_-^2$) -> quantum tunneling
S_+ (S_-) operator couples state $S_z = 2$ with $S_z = 0$ and $S_z = 0$ with $S_z = -2$

No net magnetic moment → **Can not be a bit**

D = –1.55 meV, and E = 0.31 meV

Eigenstate	|+2⟩	|+1⟩	|+0⟩	|−1⟩	|−2⟩	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



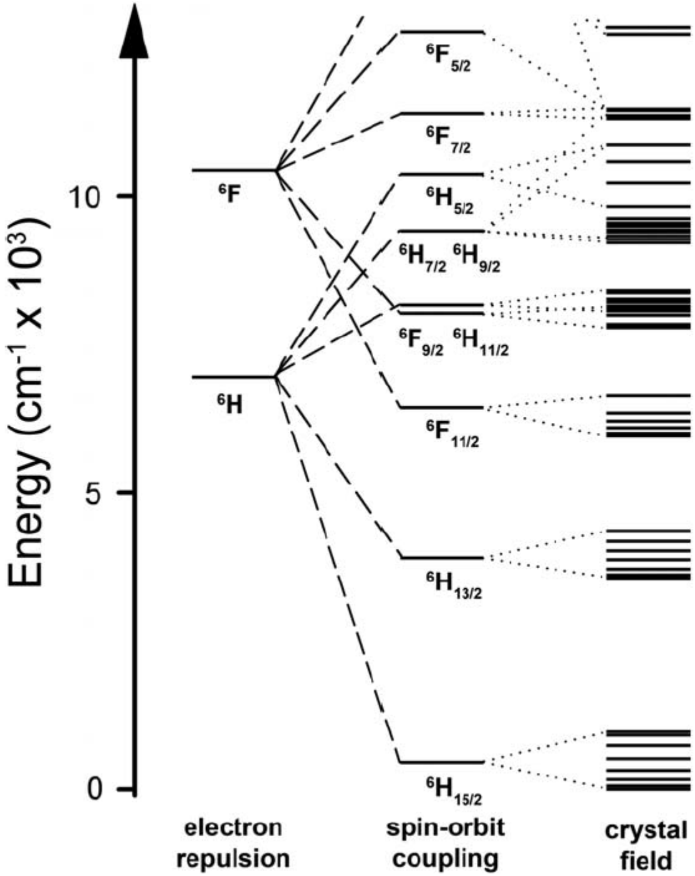
Ground state is twofold degenerate (S_z= +/- 5/2) → **Can be a bit**

F.Delgado *et al.*, Phys. Rev. Lett. **108**, 196602 (2012)

Spin Hamiltonian: rare earths

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

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



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

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

In the rare earth case the CF only perturb the orbital moment ->
S*~J

J. D. Rinehart *et al*., Chem. Sci. **2**, 2078 (2011); L. Ungur *et al*., Phys. Chem. Chem. Phys **13**, 20086 (2011)

Spin Hamiltonian: rare earths

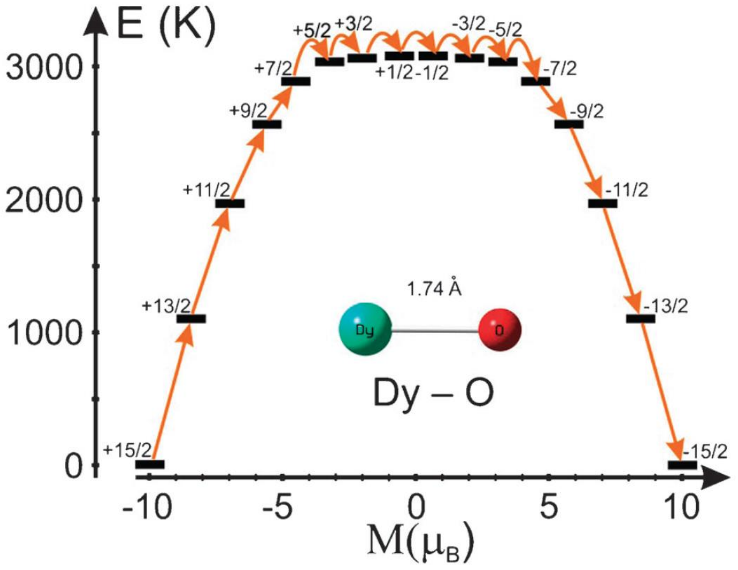
CF hamiltonian

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

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: $O_2^0 = 3J_z^2 - J(J+1)$; $B_2^0 = D/3$
$O_2^2 = ½(J_+^2 + J_-^2)$; $B_2^2 = 2E$
$O_4^3 = ¼\,[J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)\,J_z]$; $O_4^4 = ½(J_+^4 + J_-^4)$;

Depending on the CF symmetry can exist terms coupling J and –J ground states via J_+ (J_-) operator -> quantum tunneling -> 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 -> -9/2 -> -3/2 -> 3/2 -> 9/2-> 15/2

Axial CF -> only O_2^0 term ->
no quantum tunneling

A.Abragam and B. Bleaney, Electron *paramagnetic resonance of transitions ions*, Clarendon press, Oxford (1970); J. D. Rinehart et al., Chem. Sci. 2, 2078 (2011);