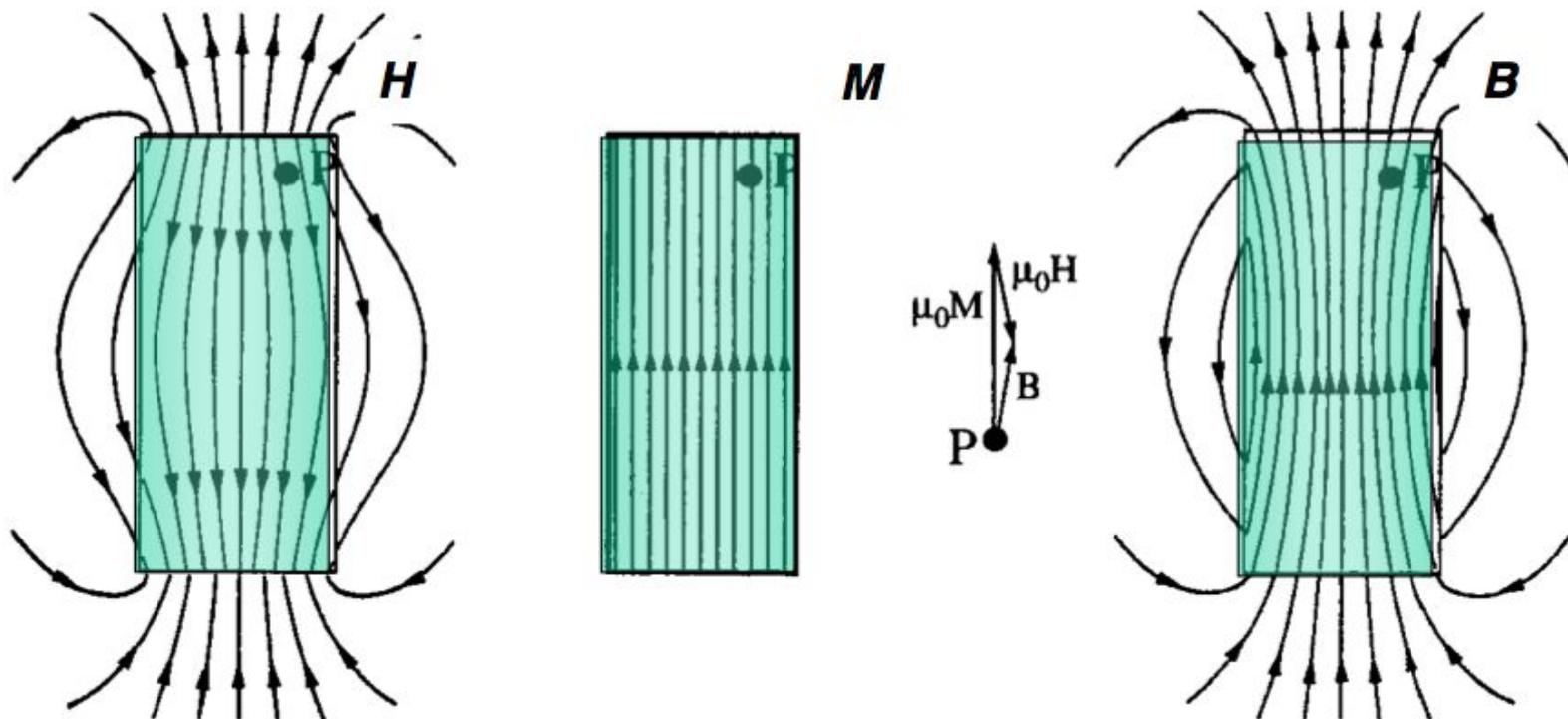


# An introduction to magnetism in three parts

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## Chapters of the three lectures

1. Maxwell equations
2. Quantum mechanics of magnetic moments
3. The crystal field and the spin-orbit interaction
4. Thermodynamics of non-interaction magnetic moments
5. The continuum model of magnetism
6. A closer look to the dipolar energy

## Literature

Soshin Chikazumi, Physics of Ferromagnetism  
Oxford University Press, 2<sup>nd</sup> edition, 672 pages (2009).

Detailed and easy to understand.

Stephen J. Blundell, Magnetism in Condensed Matter,  
Oxford University Press, 256 pages (2001).

Very easy to read, gives a condensed overview.

J.M.D. Coey, Magnetism and Magnetic Materials,  
Cambridge University Press, 628 pages (2010).

Extremely detailed and nicely illustrated book.  
Also available as e-book (b/w).

The four electromagnetic fields  $E$ ,  $D$ ,  $B$ , and  $H$ 

Symbol	Name	SI unit
$E$	electric field	$\left[\frac{V}{m}\right] = \left[\frac{N}{C}\right] = \left[\frac{kgm}{s^2 C}\right]$
$D$	electric displacement	$\left[\frac{C}{m^2}\right] = \left[\frac{Nm}{Vm}\right]$
$B$	magnetic flux density	$[T] = \left[\frac{Vs}{m^2}\right]$
$H$	magnetic field	$\left[\frac{A}{m}\right]$
$\epsilon_0$	permittivity = $8.854 \cdot 10^{-12}$	$\left[\frac{F}{m}\right] = \left[\frac{As}{Vm}\right] = \left[\frac{C^2}{Nm^2}\right]$
$\mu_0$	Permeability = $4\pi \cdot 10^{-7}$	$\left[\frac{N}{A^2}\right] = \left[\frac{Vs}{A}\right]$

In vacuum:

$$\mathbf{D} = \epsilon_0 \mathbf{E}$$

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B}$$

## Maxwell equations in matter

$$\nabla \mathbf{D} = \rho$$

Electrical charges are sources of D (not E)

$$\nabla \mathbf{B} = 0$$

Magnetic flux density is free of sources (not H)

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

Induction is caused by magnetic flux density (not H)

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}$$

Currents are sources for magnetic field (not B)

In matter:

$$\mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E}$$

$$\mathbf{H} = \frac{1}{\mu_0 \mu_r} \mathbf{B}$$

Matter acts oppositely on electrostatic and magnetostatic forces!

## CGS units – a must not do

Quantity	Symbol	SI unit	ESU unit	EMU unit	Gaussian unit
electric charge	$q$	1 C	$= (10^{-1} c) \text{ statC}$	$= (10^{-1}) \text{ abC}$	$= (10^{-1} c) \text{ Fr}$
electric current	$I$	1 A	$= (10^{-1} c) \text{ statA}$	$= (10^{-1}) \text{ abA}$	$= (10^{-1} c) \text{ Fr}\cdot\text{s}^{-1}$
electric potential voltage	$\phi$ $V$	1 V	$= (10^8 c^{-1}) \text{ statV}$	$= (10^8) \text{ abV}$	$= (10^8 c^{-1}) \text{ statV}$
electric field	$E$	1 V/m	$= (10^6 c^{-1}) \text{ statV/cm}$	$= (10^6) \text{ abV/cm}$	$= (10^6 c^{-1}) \text{ statV/cm}$
magnetic B field	$B$	1 T	$= (10^4 c^{-1}) \text{ statT}$	$= (10^4) \text{ Gs}$	$= (10^4) \text{ Gs}$
magnetic H field	$H$	1 A/m	$= (4\pi 10^{-3} c) \text{ statA/cm}$	$= (4\pi 10^{-3}) \text{ Oe}$	$= (4\pi 10^{-3}) \text{ Oe}$
magnetic dipole moment	$\mu$	1 A·m <sup>2</sup>	$= (10^3 c) \text{ statA}\cdot\text{cm}^2$	$= (10^3) \text{ abA}\cdot\text{cm}^2$	$= (10^3) \text{ erg/G}$
magnetic flux	$\Phi_m$	1 Wb	$= (10^8 c^{-1}) \text{ statT}\cdot\text{cm}^2$	$= (10^8) \text{ Mx}$	$= (10^8) \text{ G}\cdot\text{cm}^2$
resistance	$R$	1 $\Omega$	$= (10^9 c^{-2}) \text{ s/cm}$	$= (10^9) \text{ ab}\Omega$	$= (10^9 c^{-2}) \text{ s/cm}$
resistivity	$\rho$	1 $\Omega\cdot\text{m}$	$= (10^{11} c^{-2}) \text{ s}$	$= (10^{11}) \text{ ab}\Omega\cdot\text{cm}$	$= (10^{11} c^{-2}) \text{ s}$
capacitance	$C$	1 F	$= (10^{-9} c^2) \text{ cm}$	$= (10^{-9}) \text{ abF}$	$= (10^{-9} c^2) \text{ cm}$
inductance	$L$	1 H	$= (10^9 c^{-2}) \text{ cm}^{-1}\cdot\text{s}^2$	$= (10^9) \text{ abH}$	$= (10^9 c^{-2}) \text{ cm}^{-1}\cdot\text{s}^2$

# 1. Maxwell equations

## Magnetic Periodic Table

1 <b>H</b> 1.00																	2 <b>He</b> 4.00						
3 <b>Li</b> 6.94 1 + 2s <sup>0</sup>	4 <b>Be</b> 9.01 2 + 2s <sup>0</sup>																	5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00 35	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99 1 + 3s <sup>0</sup>	12 <b>Mg</b> 24.21 2 + 3s <sup>0</sup>																	13 <b>Al</b> 26.98 3 + 2p <sup>0</sup>	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95
19 <b>K</b> 38.21 1 + 4s <sup>0</sup>	20 <b>Ca</b> 40.08 2 + 4s <sup>0</sup>	21 <b>Sc</b> 44.96 3 + 3d <sup>0</sup>	22 <b>Ti</b> 47.88 4 + 3d <sup>0</sup>	23 <b>V</b> 50.94 3 + 3d <sup>0</sup>	24 <b>Cr</b> 52.00 3 + 3d <sup>0</sup> 312	25 <b>Mn</b> 55.85 2 + 3d <sup>0</sup> 96	26 <b>Fe</b> 55.85 3 + 3d <sup>0</sup> 1043	27 <b>Co</b> 58.93 2 + 3d <sup>0</sup> 1390	28 <b>Ni</b> 58.69 2 + 3d <sup>0</sup> 629	29 <b>Cu</b> 63.55 2 + 3d <sup>0</sup>	30 <b>Zn</b> 65.39 2 + 3d <sup>10</sup>	31 <b>Ga</b> 69.72 3 + 3d <sup>10</sup>	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80						
37 <b>Rb</b> 85.47 1 + 5s <sup>0</sup>	38 <b>Sr</b> 87.62 2 + 5s <sup>0</sup>	39 <b>Y</b> 88.91 2 + 4d <sup>0</sup>	40 <b>Zr</b> 91.22 4 + 4d <sup>0</sup>	41 <b>Nb</b> 92.91 5 + 4d <sup>0</sup>	42 <b>Mo</b> 95.94 5 + 4d <sup>0</sup>	43 <b>Tc</b> 97.9	44 <b>Ru</b> 101.1 3 + 4d <sup>0</sup>	45 <b>Rh</b> 102.4 3 + 4d <sup>0</sup>	46 <b>Pd</b> 106.4 2 + 4d <sup>0</sup>	47 <b>Ag</b> 107.9 1 + 4d <sup>10</sup>	48 <b>Cd</b> 112.4 2 + 4d <sup>10</sup>	49 <b>In</b> 114.8 3 + 4d <sup>10</sup>	50 <b>Sn</b> 118.7 4 + 4d <sup>10</sup>	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 83.80						
55 <b>Cs</b> 132.9 1 + 6s <sup>0</sup>	56 <b>Ba</b> 137.3 2 + 6s <sup>0</sup>	57 <b>La</b> 138.9 3 + 4f <sup>0</sup>	72 <b>Hf</b> 178.5 4 + 5d <sup>0</sup>	73 <b>Ta</b> 180.9 5 + 5d <sup>0</sup>	74 <b>W</b> 183.8 6 + 5d <sup>0</sup>	75 <b>Re</b> 186.2 4 + 5d <sup>0</sup>	76 <b>Os</b> 190.2 3 + 5d <sup>0</sup>	77 <b>Ir</b> 192.2 4 + 5d <sup>0</sup>	78 <b>Pt</b> 195.1 2 + 5d <sup>0</sup>	79 <b>Au</b> 197.0 1 + 5d <sup>10</sup>	80 <b>Hg</b> 200.6 2 + 5d <sup>10</sup>	81 <b>Tl</b> 204.4 3 + 5d <sup>10</sup>	82 <b>Pb</b> 207.2 4 + 5d <sup>10</sup>	83 <b>Bi</b> 209.0	84 <b>Po</b> 209	85 <b>At</b> 210	86 <b>Rn</b> 222						
87 <b>Fr</b> 223	88 <b>Ra</b> 226.0 2 + 7s <sup>0</sup>	89 <b>Ac</b> 227.0 3 + 5f <sup>0</sup>																					
			58 <b>Ce</b> 140.1 4 + 4f <sup>0</sup> 13	59 <b>Pr</b> 140.9 3 + 4f <sup>0</sup>	60 <b>Nd</b> 144.2 3 + 4f <sup>0</sup> 19	61 <b>Pm</b> 145	62 <b>Sm</b> 150.4 3 + 4f <sup>0</sup> 105	63 <b>Eu</b> 152.0 2 + 4f <sup>0</sup> 90	64 <b>Gd</b> 157.3 3 + 4f <sup>0</sup> 292	65 <b>Tb</b> 158.9 3 + 4f <sup>0</sup> 229 221	66 <b>Dy</b> 162.5 3 + 4f <sup>0</sup> 179 85	67 <b>Ho</b> 164.9 3 + 4f <sup>0</sup> 132 20	68 <b>Er</b> 167.3 3 + 4f <sup>1</sup> 85 20	69 <b>Tm</b> 168.9 3 + 4f <sup>2</sup> 58	70 <b>Yb</b> 173.0 3 + 4f <sup>3</sup>	71 <b>Lu</b> 175.0 3 + 4f <sup>4</sup>							
			90 <b>Th</b> 232.0 4 + 5f <sup>0</sup>	91 <b>Pa</b> 231.0 5 + 5f <sup>0</sup>	92 <b>U</b> 238.0 4 + 5f <sup>0</sup>	93 <b>Np</b> 238.0 5 + 5f <sup>0</sup>	94 <b>Pu</b> 244	95 <b>Am</b> 243	96 <b>Cm</b> 247	97 <b>Bk</b> 247	98 <b>Cf</b> 251	99 <b>Es</b> 252	100 <b>Fm</b> 257	101 <b>Md</b> 258	102 <b>No</b> 259	103 <b>Lr</b> 260							

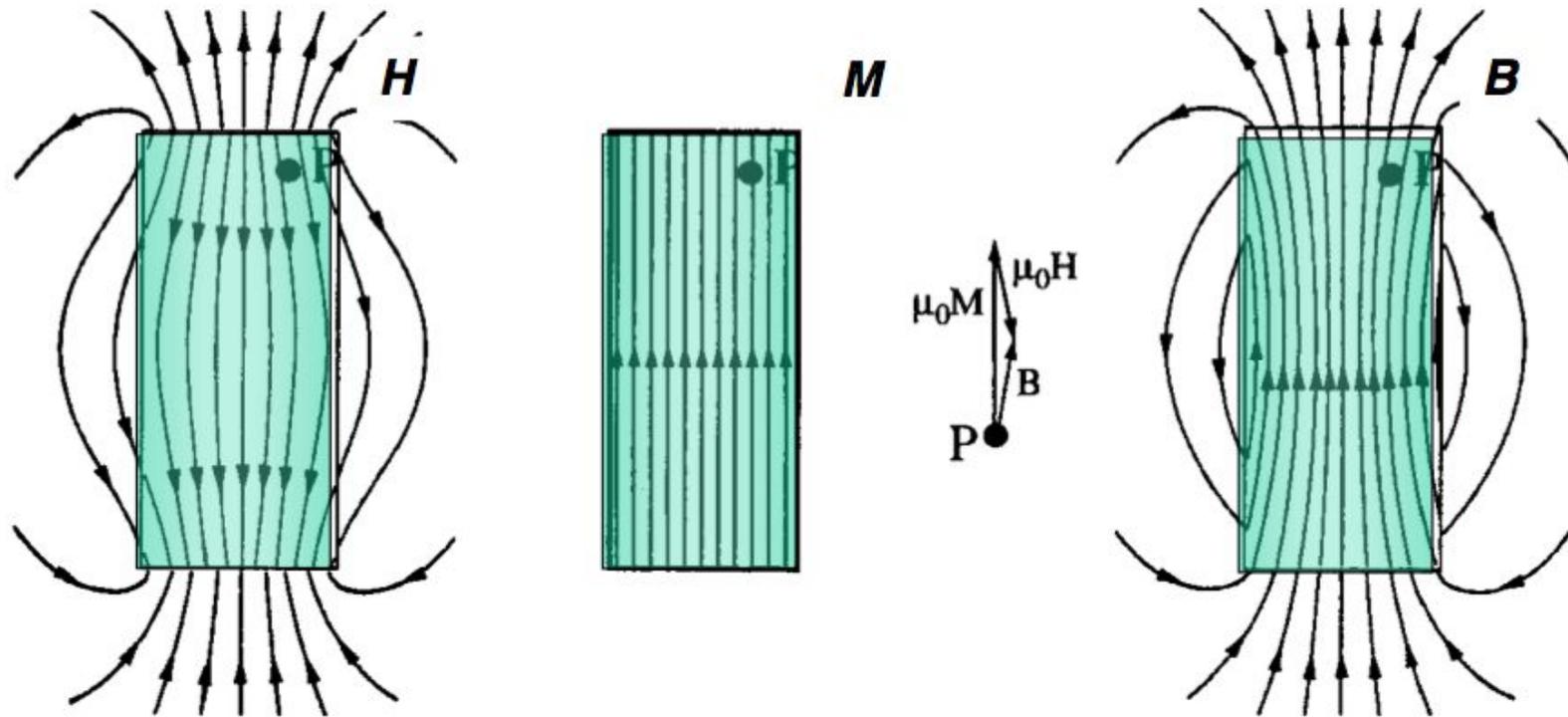
Atomic Number → 66 **Dy** ← Atomic symbol  
 Atomic weight → 162.5  
 Typical ionic charge → 3 + 4f<sup>0</sup>  
 Antiferromagnetic T<sub>N</sub>(K) → 179 85 ← Ferromagnetic T<sub>C</sub>(K)

- Nonmetal
- Metal
- Radioactive
- Diamagnet
- Paramagnet
- BOLD** Magnetic atom
- Ferromagnet T<sub>C</sub> > 290K
- Antiferromagnet with T<sub>N</sub> > 290K
- Antiferromagnet/Ferromagnet with T<sub>N</sub>/T<sub>C</sub> < 290 K

from: Coey

### The fields in and around a magnet

$$B = \mu_0(H + M) \rightarrow H = \frac{B}{\mu_0} - M$$



Outside the magnet:  $B$  and  $H$  are proportional,  $H$  is the stray field of the magnet  
Inside the magnet:  $B$ ,  $H$  and  $M$  are not parallel,  $H$  is the demagnetizing field

Qualitatively, the demagnetizing field opposes  $M$  and  $B$ .

from: Coey

### Magnetic susceptibility

Magnetization  $M$  : density of magnetic moments

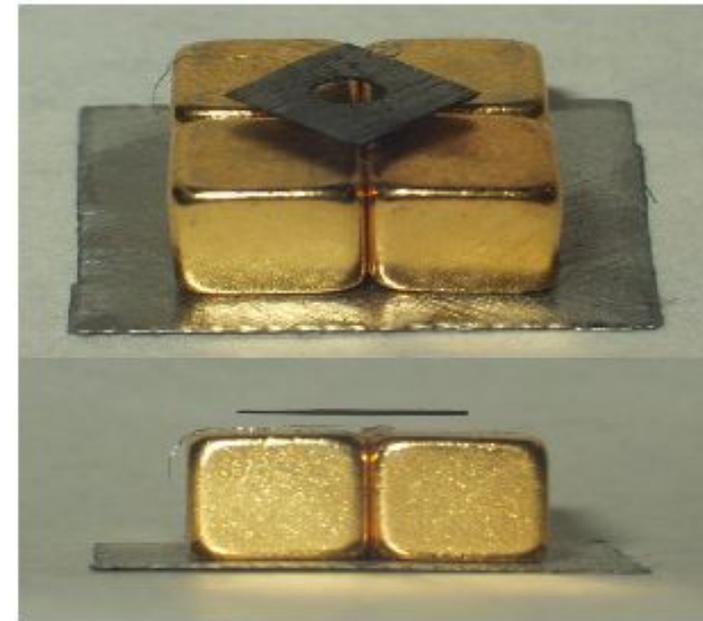
Inside matter:  $\vec{B} = \mu_0(\vec{H} + \vec{M})$ ,  $\mu_0 = 4\pi \times 10^{-7} \text{ Hm}^{-1}$

Magnetic susceptibility:  $\vec{M} = \frac{1}{\mu_0} \chi \vec{B} = \chi \vec{H}$

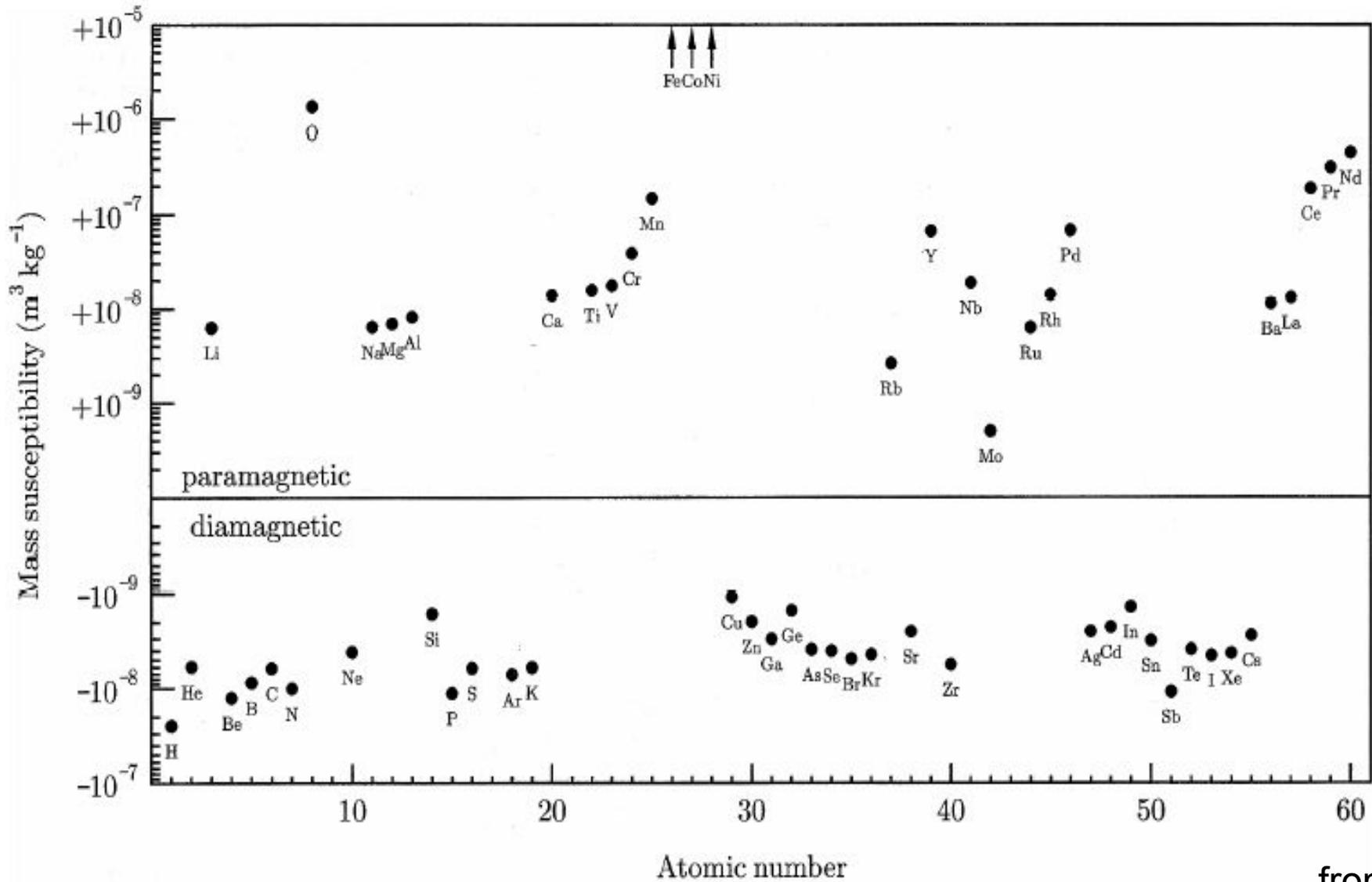
$\chi < 0$ : material is diamagnetic  
Diamagnetism is caused by induction currents of the orbiting electrons opposing the external field.

$\chi > 0$ : material is paramagnetic  
Paramagnetism is caused by orientation of local magnetic moments along the external field.

Graphite



### Magnetic Susceptibility



from: Blundell

## The magnetic moment of a bound electron

Magnetic moment of ring current (orbital moment)

$$\vec{\mu}_l = I \vec{A} = -e v \pi r^2 = \frac{-e}{2m} (m \omega r^2) = \frac{-e}{2m} \hbar \vec{l} = -\mu_B \vec{l}$$

Bohr magneton  $\mu_B = \frac{e \hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T}$

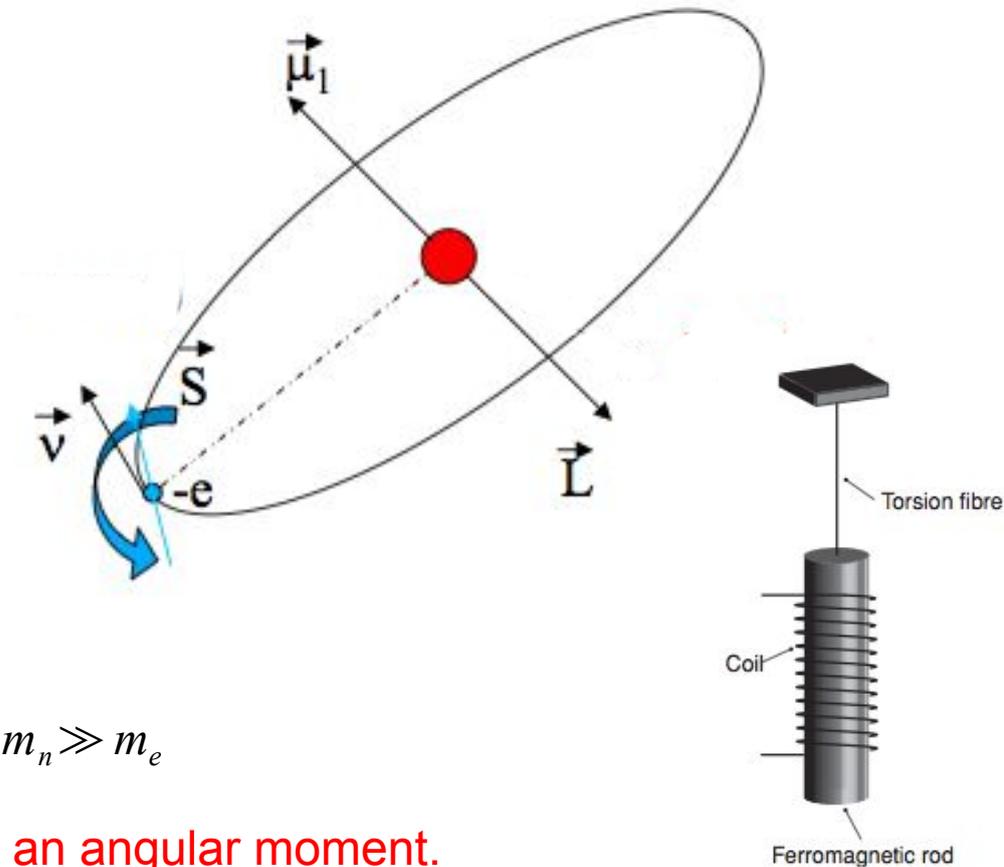
Magnetic moment of spin (spin moment)

$$\vec{\mu}_s = -\mu_B g \vec{s}$$

Landé factor of the electron  $g = 2.0023 \approx 2$

Magnetic moment of nucleus is neglected as  $m_n \gg m_e$

**Attention: The magnetic moment behaves like an angular momentum.**



## The magnetic moment of an atom

N electrons are filled into orbitals

Principal quantum number  $n = 1, 2, 3, \dots$  ( $K : n = 1, L : n = 2, M : n = 3 \dots$ )

Orbital quantum number  $l = 0, 1, \dots, n - 1$  ( $s : l = 0, p : l = 1, d : l = 2, f : l = 3$ )

Magnetic quantum number  $m_l = -l, -l + 1, \dots, l - 1, l$

Spin quantum number  $m_s = \pm \frac{1}{2}$

} z-components of l and s

Total magnetic moment of all electrons

$$\vec{\mu} = -\mu_B \sum_{i=1}^N \vec{l}_i + g \vec{s}_i = -g_{JLS} \mu_B \vec{J}$$

$$\vec{J} = \sum_{i=1}^N \vec{j}_i, \vec{j}_i = \vec{l}_i + \vec{s}_i$$

$$g_{JLS} = 1 + \frac{J(J+1)S(S+1) - L(L+1)}{2J(J+1)}$$

### Hund's rule

Due to Pauli's principle, a complete atomic shell has one electron for each spin and each magnetic state.

→ Both the total spin and orbital angular momentum vanish, as well as  $J$ .  
Complete shells have no magnetic moment.

An atom with an  $n^{\text{th}}$  incomplete shell and orbital momentum  $L$  can be in  $2(2L+1)$  degenerate states, if we neglect Coulomb interaction between the electrons and spin orbit interaction.

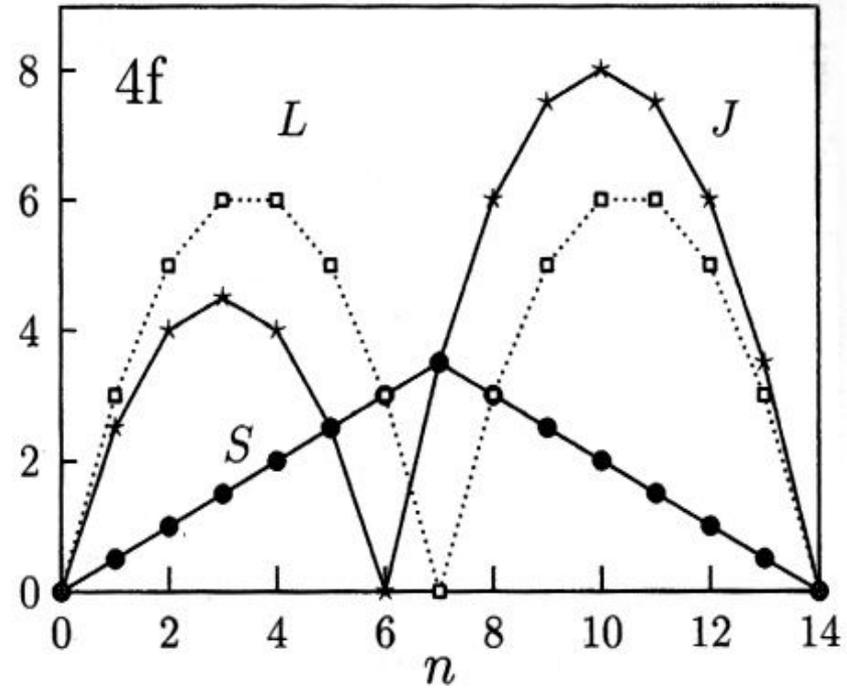
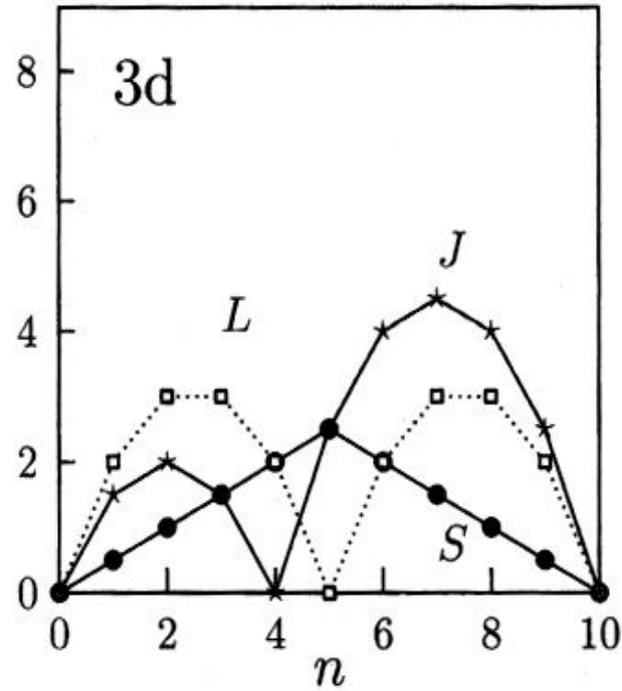
Taking into account both interactions, the states split up and a unique ground state is established that determines the magnetic moment.

Hund's rules describe how to fill in the electrons for weak spin-orbit interaction.

### Hund's rule

1. Hund's rule: **Ground state has maximal S**,  
because two electrons with opposite spin are allowed to be in the same orbital (magnetic state), i.e. close to each other (Pauli's principle), causing a large Coulomb repulsion.
2. Hund's rule: **Ground state has maximal L**,  
because Coulomb repulsion is smaller, if electrons orbit in the same rotation sense (sign of magnetic quantum number) around the nucleus.
3. Hund's rule: **For less than half filled shells  $J=|L-S|$  and for more  $J=|L+S|$** ,  
because spin-orbit interaction is given by  $\lambda \vec{L} \vec{S}$ , in which  $\lambda$  changes sign from positive to negative at half filled shell.

Hund's rule



Sidenote: Half filled shells have  $L=0$  and shells with one less electron have  $J=0$ .

from: Blundell

Hund's rule

Example: Fe 3d<sup>6</sup>

						half					
						full					
1. Hund's rule	$m_s :$	$1/2$	$1/2$	$1/2$	$1/2$		$-1/2$	$-1/2$	$-1/2$	$-1/2$	$-1/2$
2. Hund's rule	$m_l :$	2	1	0	-1		2	1	0	-1	-2
3. Hund's rule	J :		L-S					L+S			

Spectroscopic term  $(2S+1)L_J$

$$3d^6 = {}^5D_6$$

$$S = 1/2(5-1) = 2$$

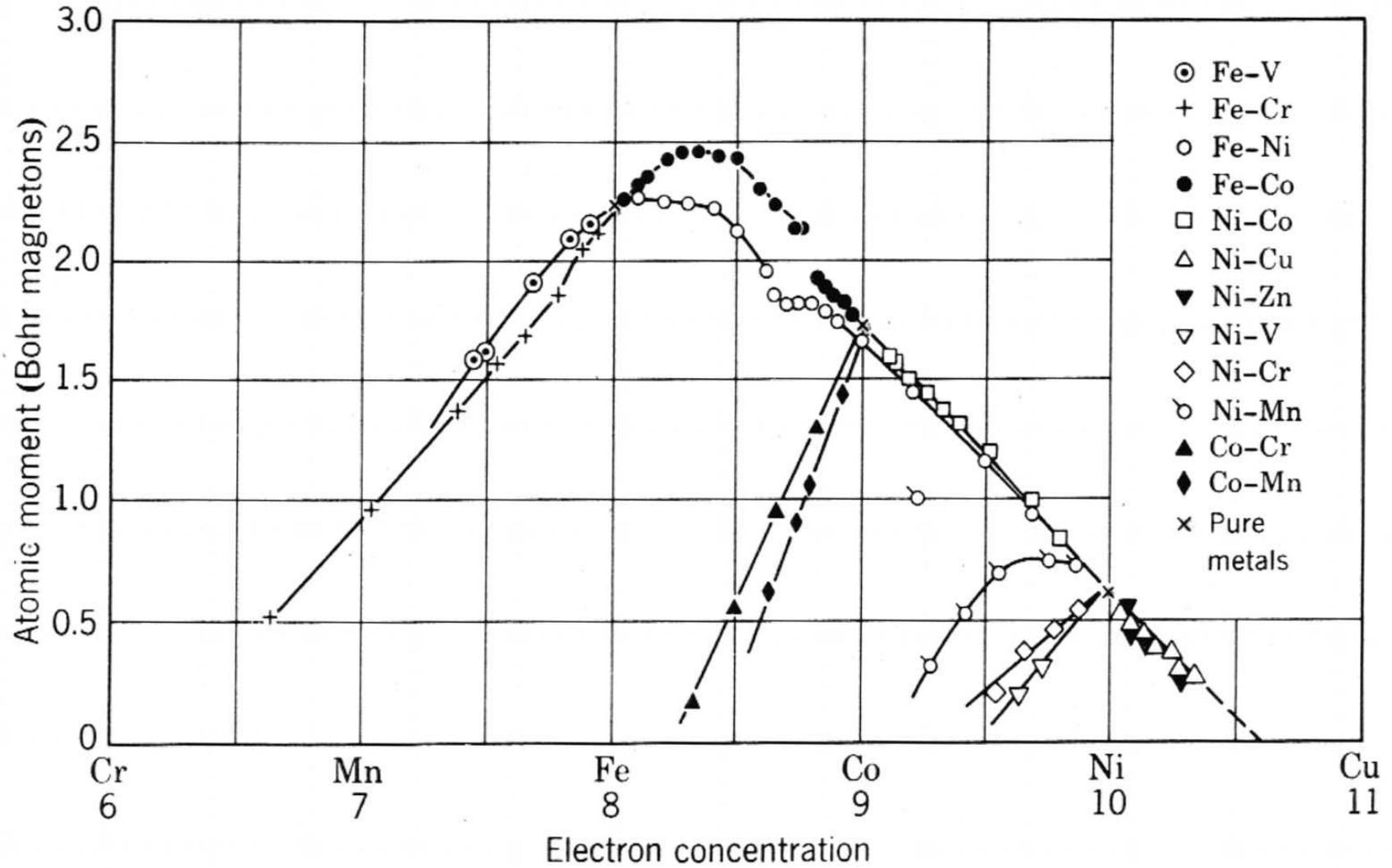
$$L = 0+2 = 2$$

$$J = |L+S| = 4$$

$$\mu = 6\mu_B$$

bcc Fe with 2 atoms per unit cell of  $(286 \text{ pm})^3$  leads to  $M = 12 \mu_B / (286 \text{ pm})^3 = 4,75 \text{ MA/m}^2$   
 But experimental value is  $1.71 \text{ MA/m}^2$

### Slater-Pauling curve

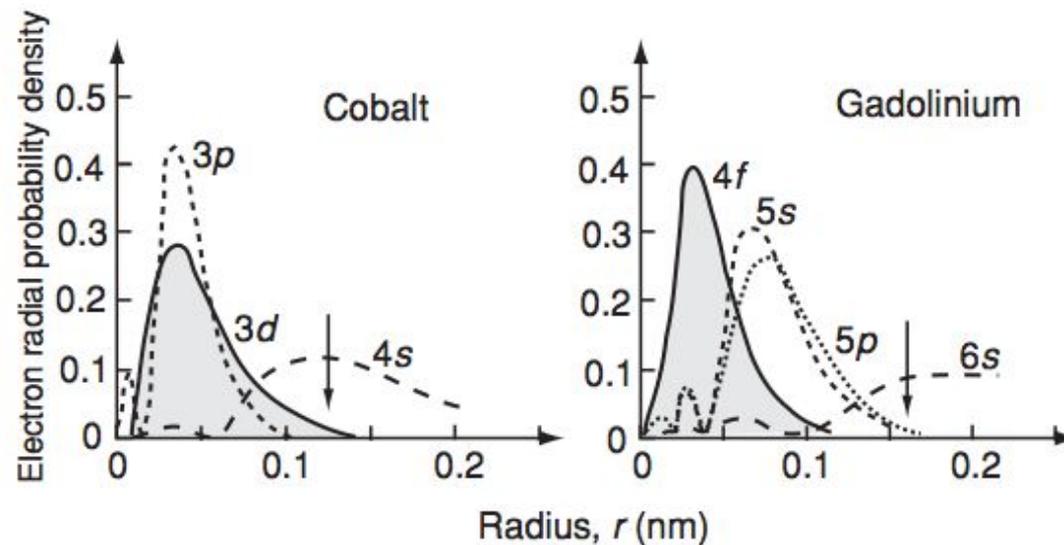


### Problems with Hund's rules

- Hund's rule assumes that the spin-orbit interaction is a small correction
- works well for 3d and 4f, where we get l-s coupling, but is only an approximation
  - fails for heavier elements, where we get j-j coupling
- Experimental values for atoms in the gas phase slightly deviate from Hund's rules

Hund's rule assumes free atoms (isotropic situation)

- in a crystal, neighbouring atoms break continuous rotation symmetry, which effects L
  - electrons may delocalize and form bands, which effects S
- Effects are very strong for 3d but almost negligible for 4f elements.



from Coey

### The crystal field

The electric fields of neighboring atoms can perturb the centro-symmetric potential of the free atom.

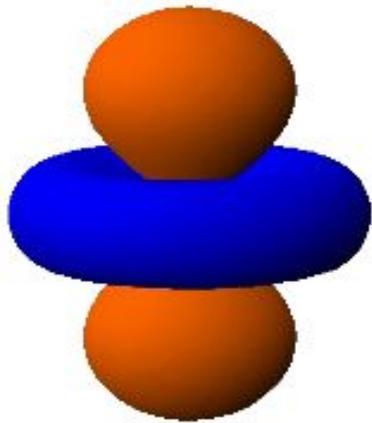
The new orbital eigenstates are thus mixtures of the free atom eigenstates.

If crystal field is not too strong, the orbital states in the presence of a crystal field are states with a good  $L^2$  but not with a good  $L_z$ .

More details will be given by Kuzmin

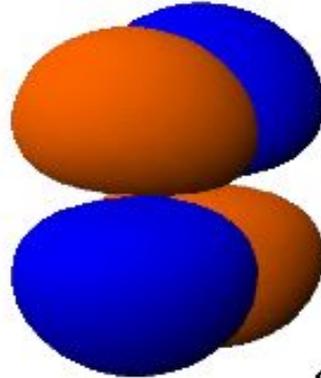
The orbital states in a cubic crystal field

$m = 0$

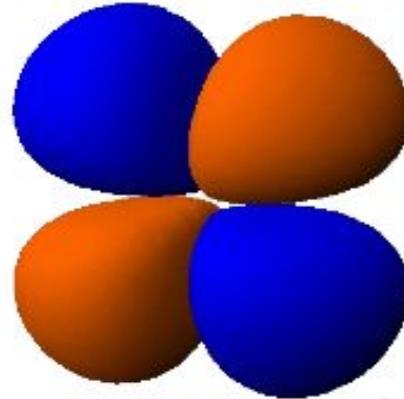


$$d_{z^2} = Y_{20}$$

$m = \pm 1$

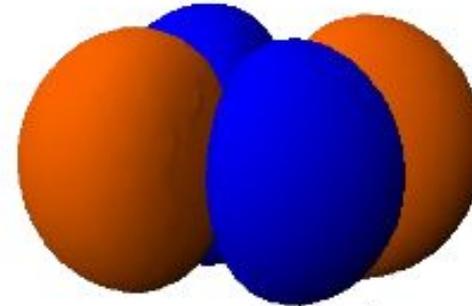


$$d_{yz} = \frac{i}{\sqrt{2}}(Y_{21} - Y_{2-1})$$

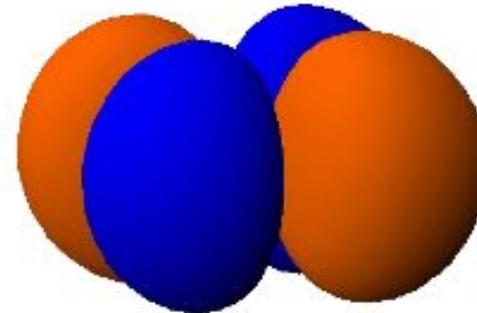


$$d_{xz} = \frac{1}{\sqrt{2}}(-Y_{21} + Y_{2-1})$$

$m = \pm 2$



$$d_{xy} = \frac{i}{\sqrt{2}}(Y_{22} - Y_{2-2})$$



$$d_{x^2 - y^2} = \frac{1}{\sqrt{2}}(Y_{22} + Y_{2-2})$$

## Quenching of the orbital moment

While  $L^2$  is not influenced  $\langle d_{xy} | L^2 | d_{xy} \rangle = L(L+1)$

$L_z$  is quenched  $\langle d_{xy} | L_z | d_{xy} \rangle = \frac{1}{2} (\langle Y_{22} | L_z | Y_{22} \rangle + \langle Y_{2-2} | L_z | Y_{2-2} \rangle) = \frac{1}{2} (2-2) = 0$

So, if you apply a magnetic field along z, you see to first order no magnetic moment along z. In second order perturbation theory, you see eventually an orbital moment.

Perturbation:  $V_i = \mu_B L_i B_i$   $\mu_i^o = \frac{-\delta E^o}{\delta B_i}$   $\langle L_i \rangle = \frac{\delta E^o}{\mu_B \delta B_i}$

$$\vec{L} = \sum_n^{\text{excited}} \left( \frac{-2\mu_B B_x |\langle \psi_0 | L_x | \psi_n \rangle|^2}{E_n - E_0} \vec{x} - \frac{2\mu_B B_y |\langle \psi_0 | L_y | \psi_n \rangle|^2}{E_n - E_0} \vec{y} - \frac{2\mu_B B_z |\langle \psi_0 | L_z | \psi_n \rangle|^2}{E_n - E_0} \vec{z} \right)$$

$\Psi_n$  : multi-electron wave function

## Quenching of the orbital moment

A closer look:

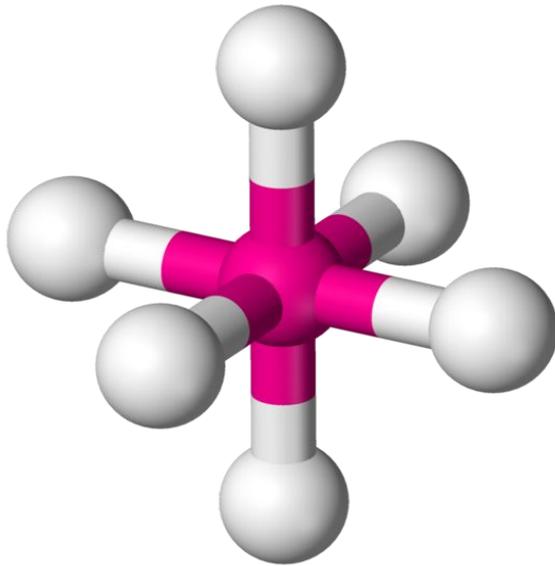
$$\vec{L} = \sum_n^{\text{excited}} \left( \frac{-2\mu_B B_x |\langle \psi_0 | L_x | \psi_n \rangle|^2}{E_n - E_0} \vec{x} - \frac{2\mu_B B_y |\langle \psi_0 | L_y | \psi_n \rangle|^2}{E_n - E_0} \vec{y} - \frac{2\mu_B B_z |\langle \psi_0 | L_z | \psi_n \rangle|^2}{E_n - E_0} \vec{z} \right)$$

$L_z$  can only be caused by mixing of states that contain same  $L_z$  components

$$d_{xz}, d_{yz} \quad \text{and} \quad d_{xy}, d_{x^2-y^2}$$

$L_x$  or  $L_y$  can only be caused by mixing of states that contain  $L_z$  components that differ by one as  $L_x$  and  $L_y$  can be written as superpositions of  $L^-$  and  $L^+$ .

## Crystal field splitting in an octahedral crystal field



$$e_g: \begin{aligned} e_1 &= d_{z^2} = Y_{20} \\ e_2 &= d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_{22} + Y_{2-2}) \end{aligned}$$

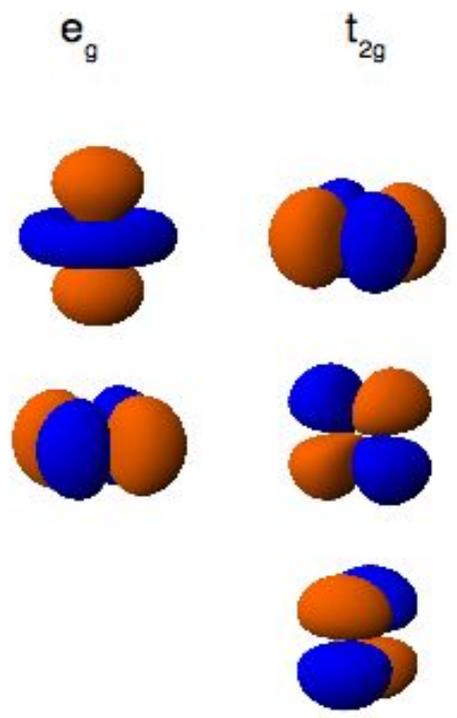
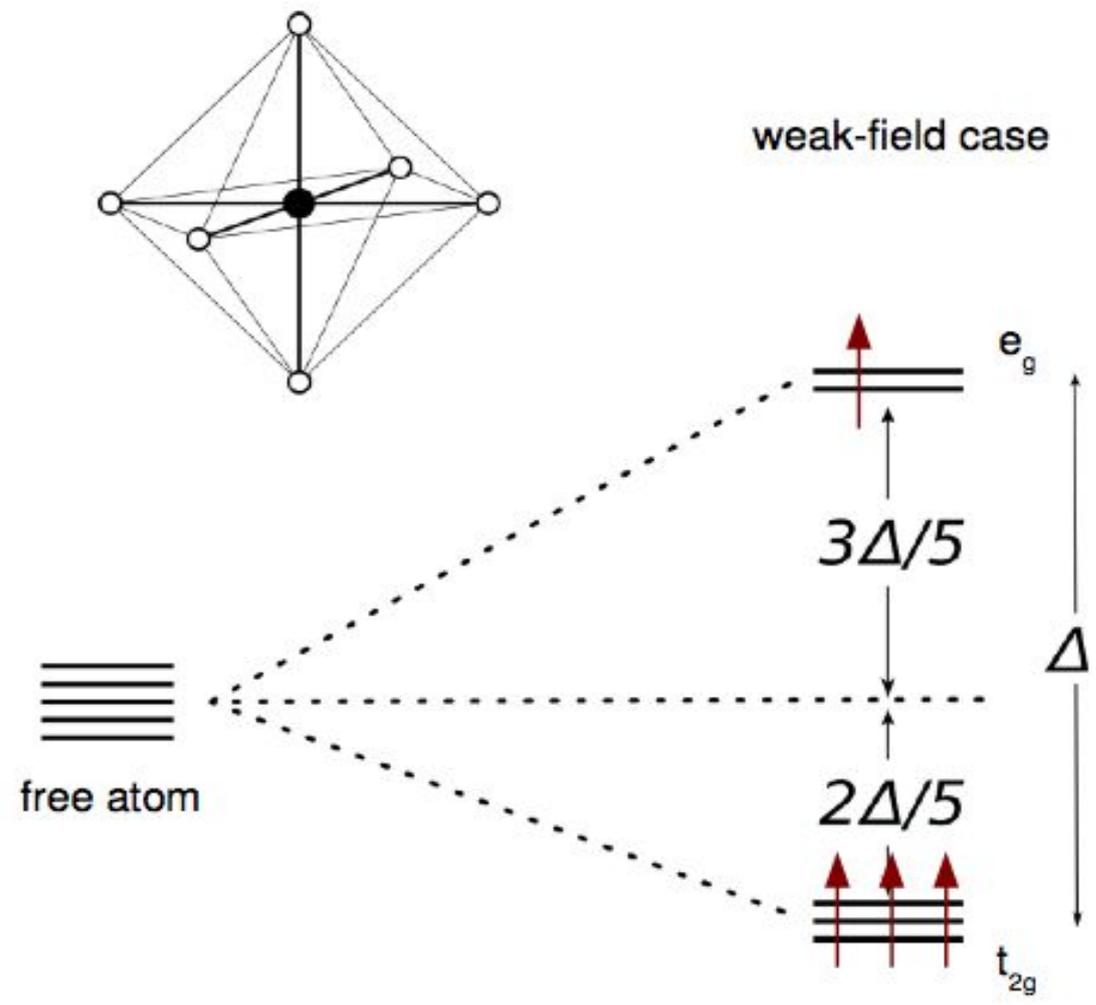
fully quenched

$$t_{2g}: \begin{aligned} t_1 &= \frac{1}{\sqrt{2}}(d_{xz} - id_{yz}) = Y_{2-1} \\ t_2 &= \frac{1}{\sqrt{2}}(-id_{xz} + d_{yz}) = Y_{21} \end{aligned}$$

partially quenched

$$t_3 = d_{xy} = \frac{-i}{\sqrt{2}}(Y_{22} - Y_{2-2})$$

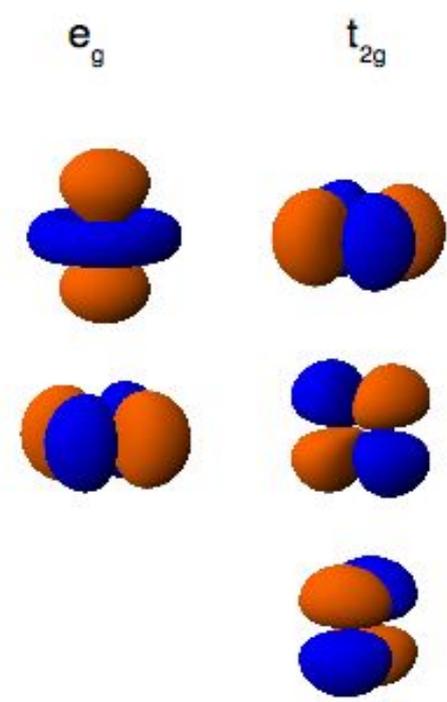
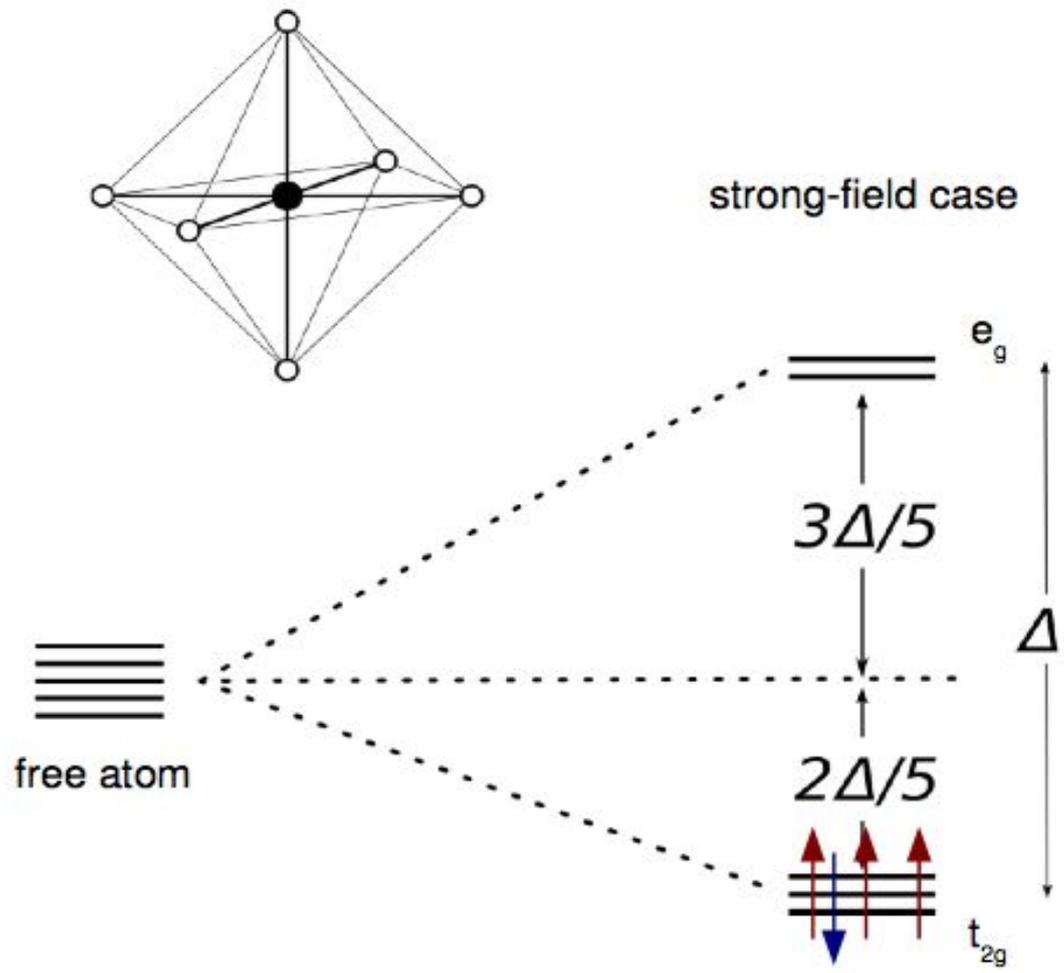
Weak octahedral crystal field



L quenched.

Hund's rules hold: S=2

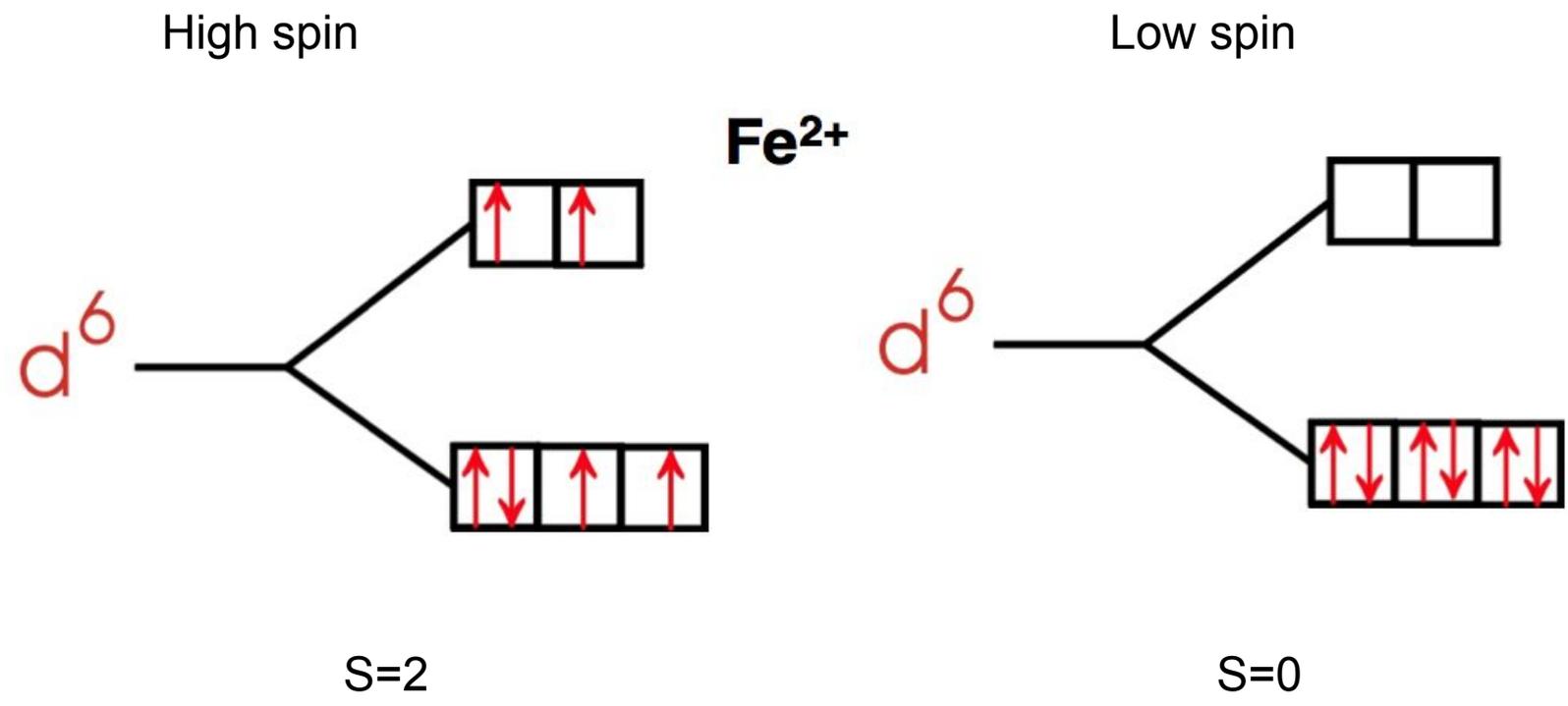
### Strong octahedral crystal field



Degenerate ground state!  
L is not fully quenched.

Hund's rules fail:  $S=1$

### High-spin low-spin transitions



## Comparison between theory and experiment

**Table 4.6.** The 4f ions. The paramagnetic moment  $m_{eff}$  and the saturation moment  $m_0$  are in units of  $\mu_B$ 

$4f^n$		$S$	$L$	$J$	$g$	$m_0 = gJ$	$m_{eff} = g\sqrt{J(J+1)}$	$m_{eff}^{exp}$
1	Ce <sup>3+</sup>	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	2.14	2.54	2.5
2	Pr <sup>3+</sup>	1	5	4	$\frac{4}{5}$	3.20	3.58	3.5
3	Nd <sup>3+</sup>	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{8}{11}$	3.27	3.52	3.4
4	Pm <sup>3+</sup>	2	6	4	$\frac{3}{5}$	2.40	2.68	
5	Sm <sup>3+</sup>	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	0.71	0.85	1.7
6	Eu <sup>3+</sup>	3	3	0	0	0	0	3.4
7	Gd <sup>3+</sup>	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	8.9
8	Tb <sup>3+</sup>	3	3	6	$\frac{3}{2}$	9.0	9.72	9.8
9	Dy <sup>3+</sup>	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{5}$	10.0	10.65	10.6
10	Ho <sup>3+</sup>	2	6	8	$\frac{5}{4}$	10.0	10.61	10.4
11	Er <sup>3+</sup>	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	9.0	9.58	9.5
12	Tm <sup>3+</sup>	1	5	6	$\frac{7}{6}$	7.0	7.56	7.6
13	Yb <sup>3+</sup>	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	4.0	4.53	4.5

**Table 4.7.** The 3d ions.  $m_{eff}$  is in units of  $\mu_B$ 

$3d^n$		$S$	$L$	$J$	$g$	$m_{eff} = g\sqrt{J(J+1)}$	$m_{eff} = g\sqrt{S(S+1)}$	$m_{eff}^{exp}$
1	Ti <sup>3+</sup> , V <sup>4+</sup>	$\frac{1}{2}$	2	$\frac{3}{2}$	$\frac{4}{5}$	1.55	1.73	1.7
2	Ti <sup>2+</sup> , V <sup>3+</sup>	1	3	2	$\frac{2}{3}$	1.63	2.83	2.8
3	V <sup>2+</sup> , Cr <sup>3+</sup>	$\frac{3}{2}$	3	$\frac{3}{2}$	$\frac{2}{5}$	0.78	3.87	3.8
4	Cr <sup>2+</sup> , Mn <sup>3+</sup>	2	2	0			4.90	4.9
5	Mn <sup>2+</sup> , Fe <sup>3+</sup>	$\frac{5}{2}$	0	$\frac{5}{2}$	2	5.92	5.92	5.9
6	Fe <sup>2+</sup> , Co <sup>3+</sup>	2	2	4	$\frac{3}{2}$	6.71	4.90	5.4
7	Co <sup>2+</sup> , Ni <sup>3+</sup>	$\frac{3}{2}$	3	$\frac{9}{2}$	$\frac{4}{3}$	6.63	3.87	4.8
8	Ni <sup>3+</sup>	1	3	4	$\frac{5}{4}$	5.59	2.83	3.2
9	Cu <sup>2+</sup>	$\frac{1}{2}$	2	$\frac{5}{2}$	$\frac{6}{5}$	3.55	1.73	1.9

Orbital moments

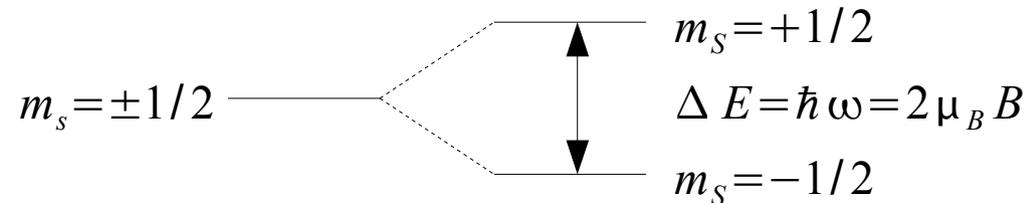
Fe: 0.09  $\mu_B$ Co: 0.15  $\mu_B$ Ni: 0.05  $\mu_B$ 

From Coey

## The Zeeman energy and the Brillouin function

Interaction between paramagnetic moment and magnetic field in z-direction:

$$J=1/2, L=0, S=1/2$$

$$E_Z = -\vec{\mu} \cdot \vec{B} = m_J g_{JLS} \mu_B B \quad m_s = \pm 1/2$$


With partition function  $Z$ , the expectation value of  $m_J$  can be calculated

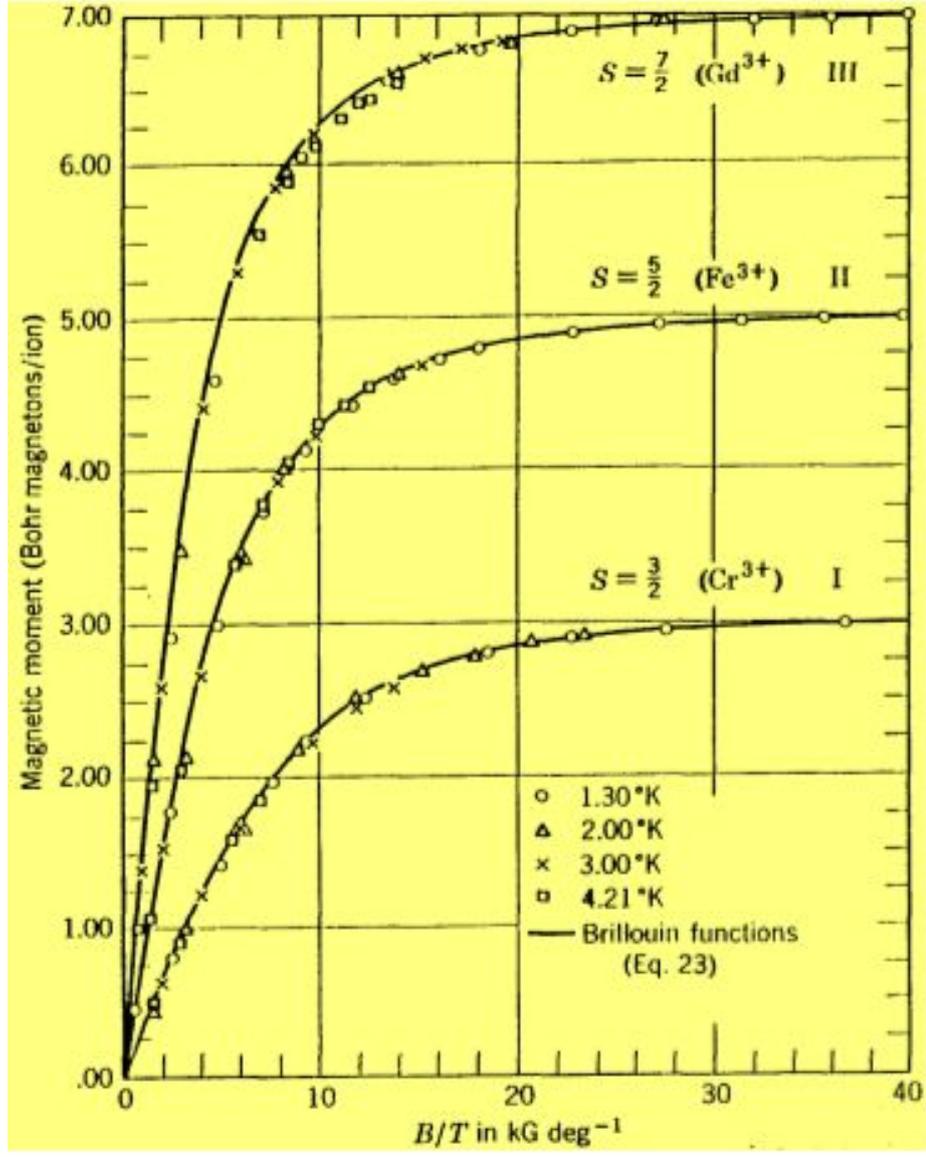
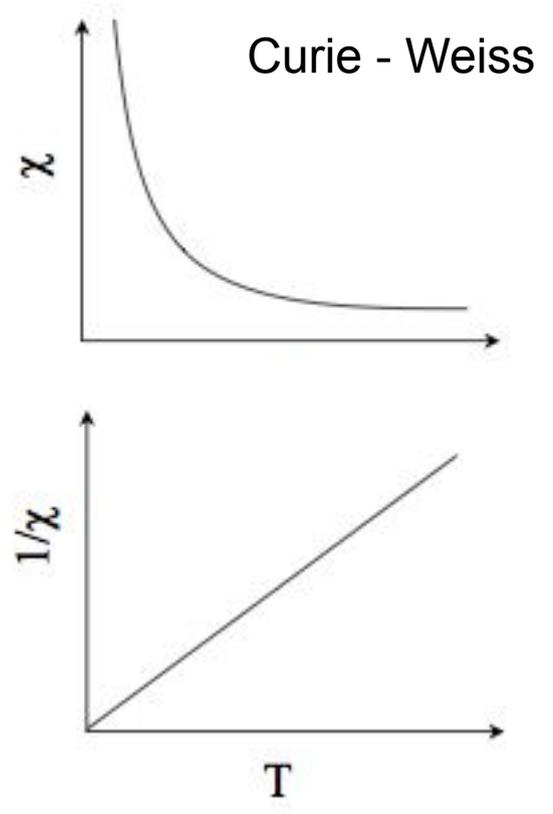
$$Z = \sum_{m_J=-J}^{+J} e^{m_J g_{JLS} \mu_B B / k_B T}$$

$$\langle m_J \rangle = -k_B T \frac{d \ln(Z)}{d B} = g_{JLS} \mu_B J \times B_J(g_{JLS} \mu_B J B / k_B T)$$

The Zeeman energy and the Brillouin function

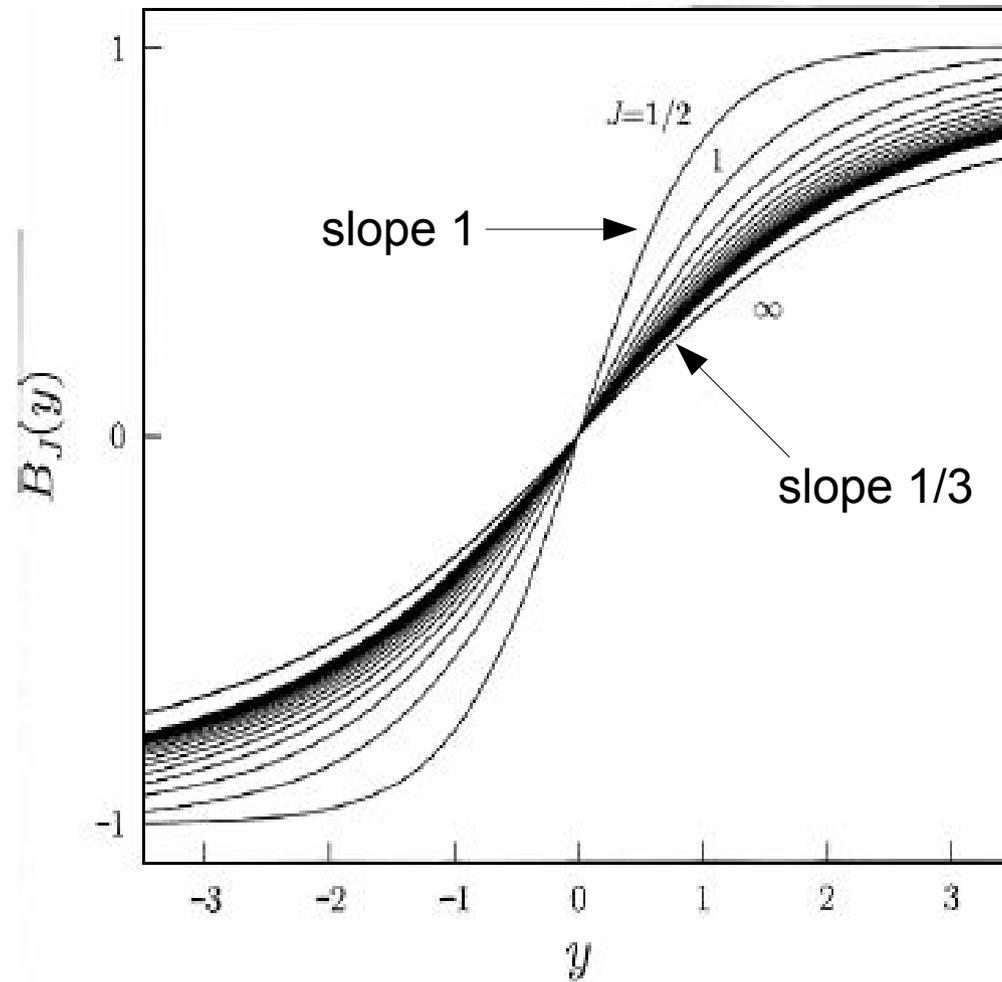
$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right)$$

$$y = \frac{g \mu_B J B}{k_B T}$$



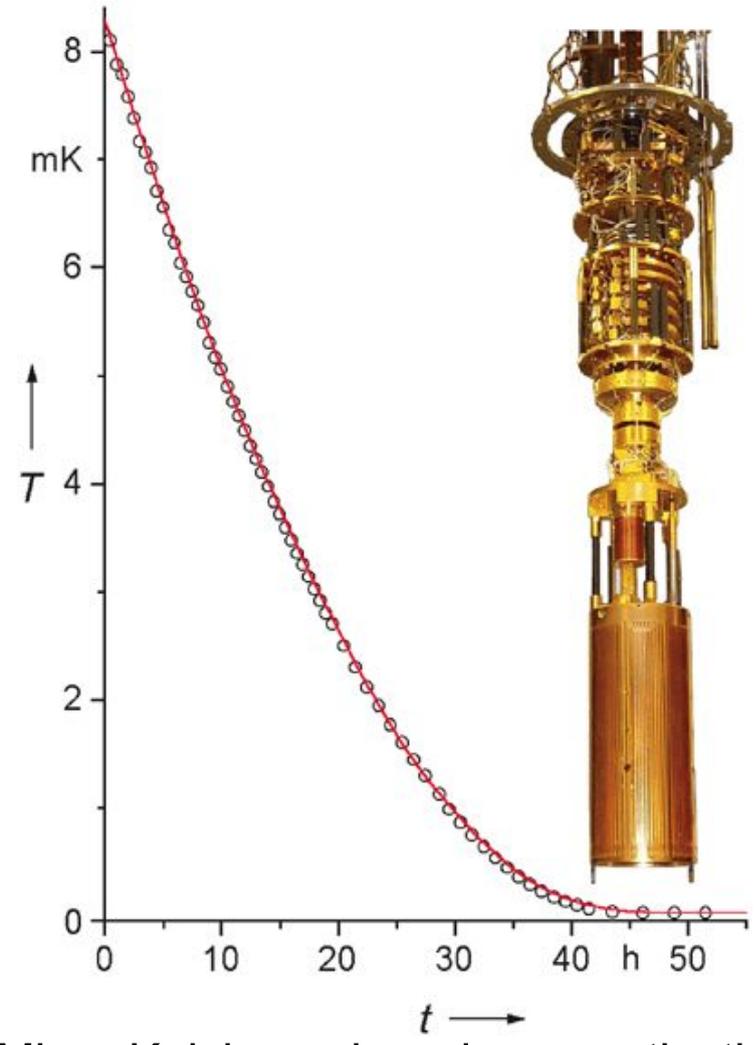
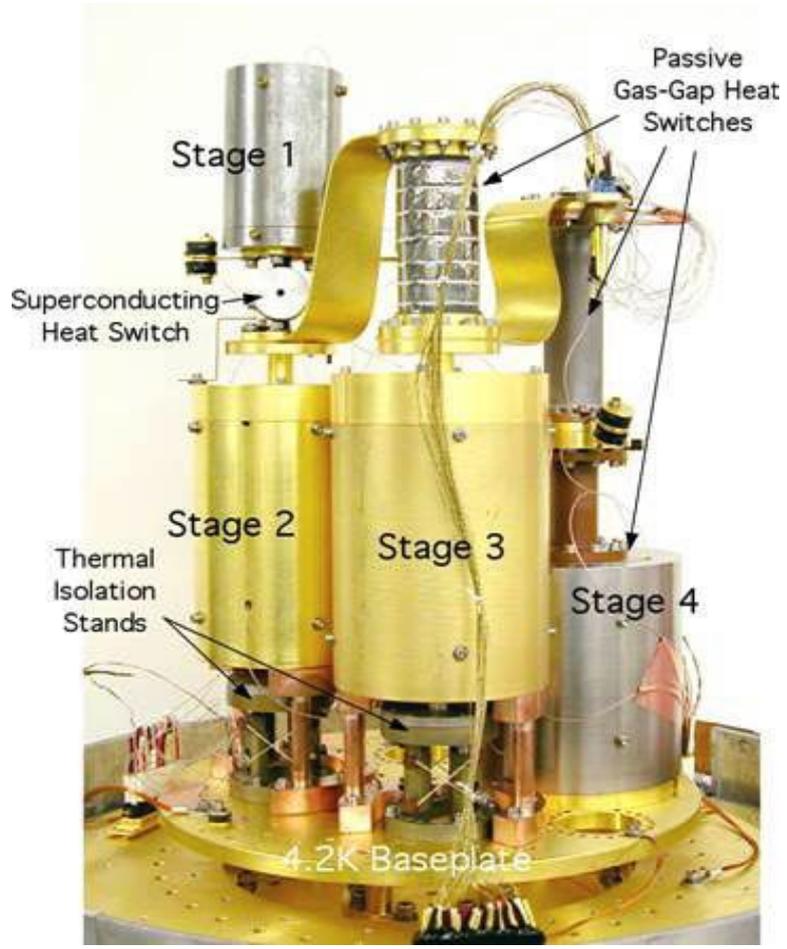
from: Kittel

## The Brillouin Function



from: Blundell

### Adiabatic demagnetization



NASA: X-ray calorimeter of the international X-ray observatory

PTB: Micro-Kelvin nuclear demagnetization of Cu

### Continuum model of magnetism

Atomic picture of individual quantum-mechanical moments is not feasible for even moderate numbers of atoms.

Example: Already a cube of  $3 \times 3 \times 3$  Gd atoms, each with  $J=7/2$ , build a Hilbert space of  $(2J+1)^{3 \times 3 \times 3} = 8^{27} \approx 2.417.851.639.229.260.000.000.000$  states.

Is there a classical equation of the magnetization that captures the main aspects?

Solution: **Take the limit of slow variations of the direction of magnetization of neighboring atoms and construct a continuous vector field of a classical magnetization.**

$$\mathbf{M} = \mathbf{M}(\mathbf{r})$$

Zeeman energy then turns into:  $E_Z = - \int \mathbf{M}(\mathbf{r}) \mathbf{B}_{ext} d\mathbf{r}$

## Direct exchange interaction between two electrons

Quantum mechanical system with two electrons : total wave function must be antisymmetric under exchange of the two electrons, as electrons are fermions.

$$\Psi(1,2) = -\Psi(2,1)$$

Wave function of electron is a product of spatial and spin part:  $\Psi(1) = \Psi(r_1) \times \vec{\sigma}(1)$

For antiparallel spins (singlet):  $\sigma(1,2) = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow)$       antisymmetric

For parallel spins (triplet) :  $\sigma(1,2) = \uparrow\uparrow, \frac{1}{\sqrt{2}} (\uparrow\downarrow + \downarrow\uparrow), \downarrow\downarrow$       symmetric

→ Spatial part of wave function has opposite symmetry to spin part

## Direct exchange interaction between two electrons

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} (\Psi_a(r_1)\Psi_b(r_2) + \Psi_a(r_2)\Psi_b(r_1)) \quad \text{symmetric for singlet}$$

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} (\Psi_a(r_1)\Psi_b(r_2) - \Psi_a(r_2)\Psi_b(r_1)) \quad \text{antisymmetric for triplet}$$

For the antisymmetric wave function :  $\Psi(r_1, r_2) = -\Psi(r_2, r_1)$

In case  $r_1 = r_2$  follows :  $\Psi(r, r) = 0$

→ Coulomb repulsion is lower for antisymmetric spatial wave function and thus its energy is lower than that of the symmetrical spatial wave function

Exchange interaction between two spins: difference of the coulomb energy due to symmetry

$$E_S - E_T = 2 \int \Psi_a^*(r_1)\Psi_b^*(r_2) \frac{e^2}{4\pi\epsilon_0|r_1-r_2|} \Psi_a(r_2)\Psi_b(r_1) dr_1 dr_2$$

### Direct exchange between localized electrons

$$J = \frac{E_S - E_T}{2}, E_{ex} = -2J \vec{S}_1 \vec{S}_2$$

$J > 0$  : parallel spins are favoured (ferromagnetic coupling)

$J < 0$ : antiparallel spins are favoured (antiferromagnetic coupling)

Heisenberg model for N spins:  $E = - \sum_{i,j=1}^N J_{ij} \vec{S}_i \vec{S}_j$

As electrons are assumed as localized, wave functions decay quickly and mainly nearest neighbors contribute to exchange.

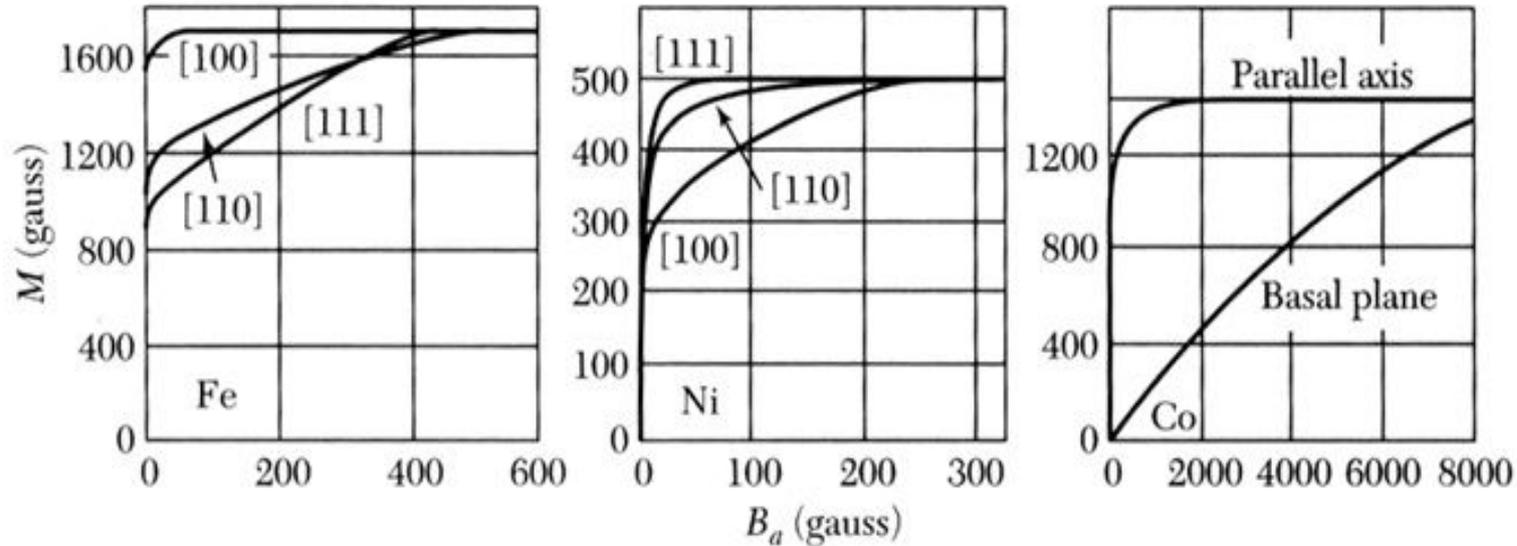
Nearest neighbor Heisenberg model:  $E = - \sum_{i,j \text{ NN}} J \vec{S}_i \vec{S}_j$

### Continuum description of exchange

Quantum mechanics:  $\hat{H}_{ex} = -2 \sum_{ij} J_{ij} \hat{S}_i \hat{S}_j$

Continuum description:  $E_{ex} = A \int (\nabla \mathbf{m}(\mathbf{r}))^2 d\mathbf{r} = A \int [(\nabla m_x)^2 + (\nabla m_y)^2 + (\nabla m_z)^2] d\mathbf{r}$

Easy and hard magnetic directions



$$K_1 = 5.48 \times 10^4 \text{ J/M}^2 \quad K_1 = -1.26 \times 10^4 \text{ J/m}^2 \quad K_1 = 7.66 \times 10^5 \text{ J/m}^2$$

$$10^4 \text{ J/m}^2 \approx 1 \mu \text{ eV/atom}$$

Along easy axis of magnetization the sample can be saturated with small fields.  
 Along the hard axis higher fields are necessary.

Cubic crystal:  $E_A = K_1 (m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2) + K_2 (m_x^2 m_y^2 m_z^2) + K_3 (m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2)^2 + \dots$

Hexagonal crystal:  $E_A = K_1 \sin(\theta)^2 + K_2 \sin(\theta)^4 + K_3 \cos(6\phi) \sin(\theta)^6 + \dots$



## The basics of micromagnetism

In micromagnetism, the magnetic moments of a ferromagnet are approximated by a continuous vector field of variable direction but constant length.

A stable magnetic state is a local minimum of the energy functional of this vector field.

$$\vec{M}(\vec{r}) = |M| \vec{m}(\vec{r})$$

Zeeman energy density :  $E_Z(\vec{r}) = -\mu_0 M \vec{H}_{ext} \vec{m}(\vec{r})$

Exchange energy density :  $E_{ex}(\vec{r}) = A (\vec{\nabla} \vec{m}(\vec{r}))^2$

Anisotropy energy density :  $E_A(\vec{r}) = f(\vec{m}(\vec{r}))$

Dipolar energy density :  $E_D(\vec{r}) = \int_V \frac{\mu_0 M}{2} \frac{\vec{m}(\vec{r}) \vec{\nabla}' \cdot (\vec{m}(\vec{r}') (\vec{r}' - \vec{r}))}{4\pi |\vec{r} - \vec{r}'|^3} d\vec{r}'$

Total energy :  $E = \int_V (E_Z(\vec{r}) + E_{ex}(\vec{r}) + E_A(\vec{r}) + E_D(\vec{r})) d\vec{r}$

## The basics of micromagnetism

If we neglect the non local dipolar energy, the energy density is given by local properties. To minimize the exchange energy, the vector field homogeneously points in one direction. The direction is chosen to minimize the Zeeman and anisotropy energy. The magnet is in the single domain state.

Basically all complexity of the magnetic structures of magnets is caused by the complex dipolar energy.

$$H_D(\vec{r}) = -M \int_V \frac{\vec{\nabla}' \cdot (\vec{m}(\vec{r}')(\vec{r}' - \vec{r}))}{4\pi |\vec{r} - \vec{r}'|^3} d\vec{r}' = - \int_V \frac{\rho(\vec{r}')(\vec{r}' - \vec{r})}{4\pi |\vec{r} - \vec{r}'|^3} d\vec{r}' + \int_S \frac{\sigma(\vec{r}')(\vec{r}' - \vec{r})}{4\pi |\vec{r} - \vec{r}'|^3} d\vec{r}'$$

where  $\rho$  is the magnetic volume charge density and  $\sigma$  is the magnetic surface charge density

$$\rho(\vec{r}) = -M \vec{\nabla} \cdot \vec{m}(\vec{r})$$

$$\sigma(\vec{r}) = M \vec{m}(\vec{r}) \cdot \vec{n}(\vec{r})$$

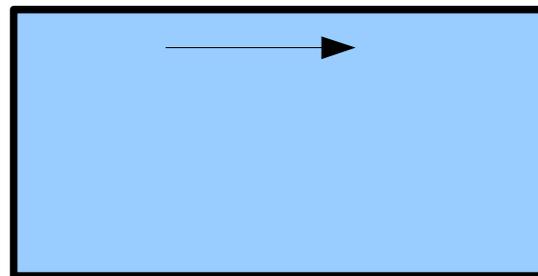
### The basics of micromagnetism

In case the dipolar energy is the dominant energy, the ground state configuration will avoid both volume and surface magnetic charges.

Volume charges are created e.g. by head-to-head or tail-to-tail configurations.



Surface charges can be avoided, if magnetization is always tangential to edge of sample.



Dipolar energy depends on shape of sample → shape anisotropy