



*The Abdus Salam  
International Centre for Theoretical Physics*



**1855-9**

**School and Workshop on Highly Frustrated Magnets and Strongly  
Correlated Systems: From Non-Perturbative Approaches to  
Experiments**

*30 July - 17 August, 2007*

**Introduction to magnetism: basic concepts in magnetism, not specific to frustrated  
magnetism**

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**School on Highly frustrated magnetism and Strongly  
Correlated Systems  
30/07/07 – 07/08/07**

**Introduction to magnetism: basic concepts in magnetism, not  
specific to frustrated magnetism**

- Origin of magnetism: magnetism of atoms and ions**
- Atoms and ions in a crystal: crystal field, magneto-elastic effects**
- Exchange interactions: origin, different types of exchange**
- Magnetic ordering**
- Magnetism at finite temperature**



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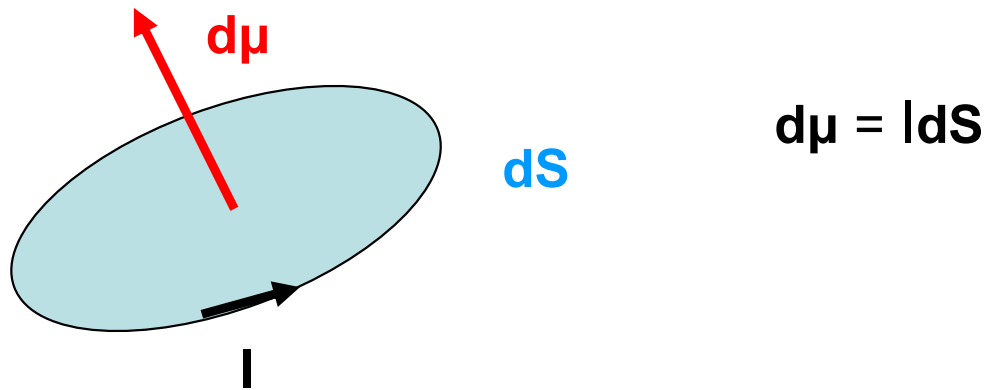
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# Magnetic moments: classical picture

## Orbital magnetism:

Magnetic moments created by a current loop



Electron motion around nucleus:

$$\mathbf{j}(\mathbf{r}') = -ev\delta(\mathbf{r}' - \mathbf{r})$$

$$\mathbf{m}_0 = \frac{1}{2} \int_{\mathbf{V}} (\mathbf{r} \times \mathbf{j}(\mathbf{r})) dV = \frac{e}{2} \mathbf{r} \times \mathbf{v} = \frac{e}{2m} \mathbf{L}_0$$

$\mathbf{L}_0 = \mathbf{r} \times m\mathbf{v}$  is the orbital angular momentum of the electron

**The orbital magnetic moment is proportional to the angular momentum**

# Atom with 1 electron: quantum picture

- potential  $V(\mathbf{r})$  has spherical symmetry
- eigenstates are also eigenstates of angular momentum

$$\vec{L} = -i\hbar \vec{r} \times \vec{\nabla}$$

- wave functions are characterized by 3 quantum numbers

- $\underline{n} = 1, 2, 3 \dots$ : electronic shell
- $\underline{l}, \underline{m}$  : orbital quantum numbers  
 $l = 0, 1, \dots, n-1$ : orbital quantum number (s, p, d, f.....)  
 $m = -l, -l+1, \dots, +l$ : quantification of  $L_z$

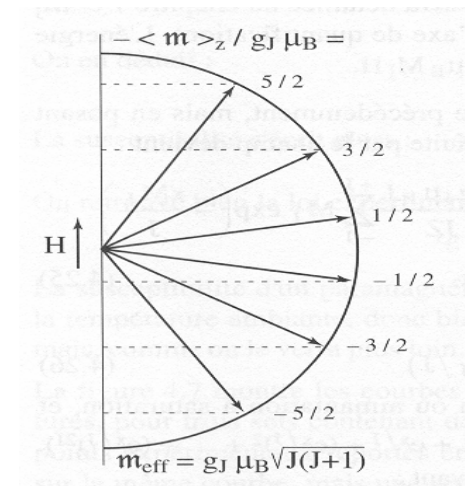
$$L^2 \Psi_{nlm} = \hbar^2 l(l+1) \Psi_{nlm}$$

$$L_z \Psi_{nlm} = \hbar m \Psi_{nlm}$$

Wave function:  $\Psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \varphi)$ ,  $R_{nl}(r) \propto \exp\left(-\frac{Zr}{na_0}\right)$

$Y_l^m(\theta, \varphi)$ : spherical harmonics

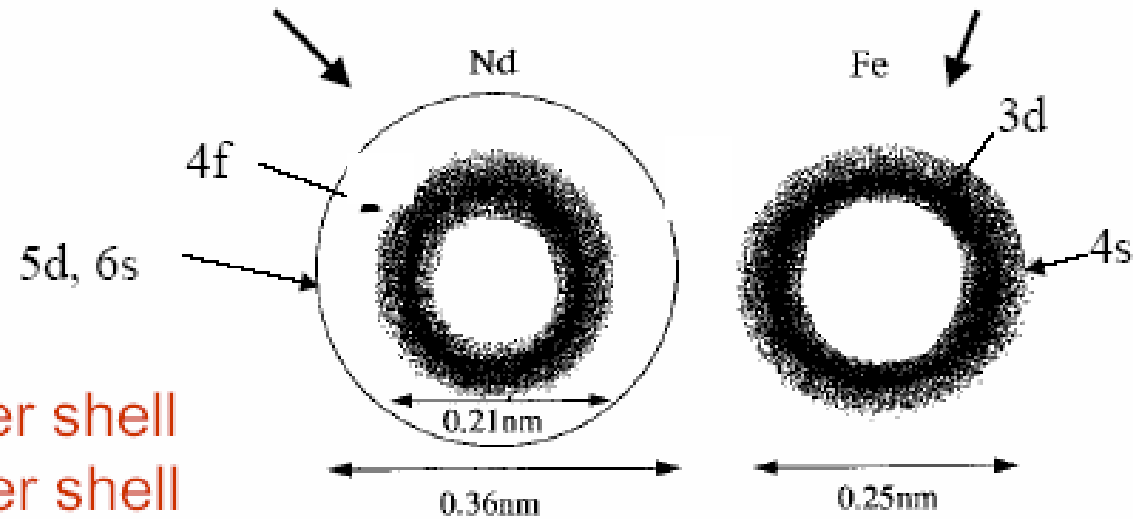
Energy: depends on n and l:  $E(n, l)$



# The 2 types of magnetic atoms:

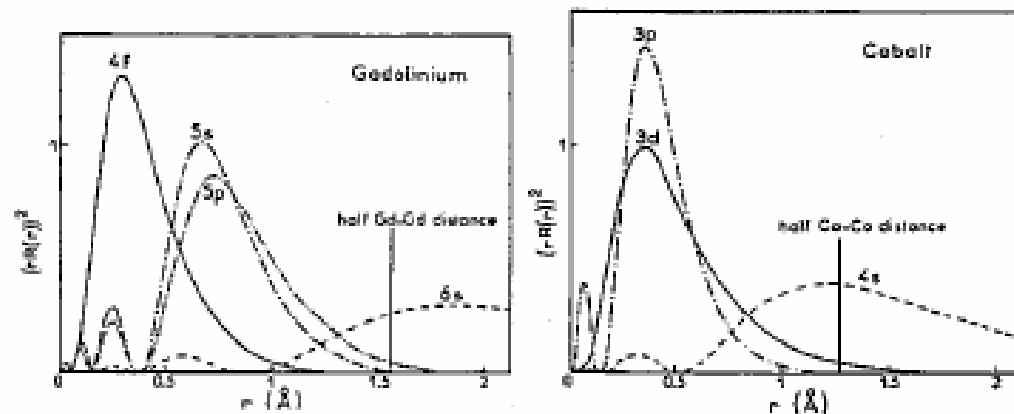
$$\Psi_{nlm} = R_{nl}(r)Y_l^m(\theta, \varphi) , R_{nl}(r) \propto \exp\left(-\frac{Zr}{na_0}\right)$$

Rare-earth element      Transition-metal element



4f electrons : inner shell  
3d electrons : outer shell

leads to very different behaviours



« radius » of wave function:  $r \propto na_0/Z$     Gd:  $Z = 64$  , Co :  $Z = 27$

## Spin and orbital moments

-orbital moment; magnetic moment due to orbital motion of electrons

$$\vec{\mu}_l = -(\hbar e/2m_e)\vec{L} = -\mu_B \vec{L}$$

-spin magnetic moment (classical picture: intrinsic motion of the electron around itself)

**S: spin kinetic moment**

$$\vec{\mu}_s = -(\hbar e/m_e)\vec{S} = -2\mu_B \vec{S}$$

-Spin S is quantized: **S=1/2, S<sub>z</sub>= ± 1/2 <S<sup>2</sup>> = S(S+1)= 3/4**

-Total magnetic moment:  $\vec{\mu}_l + \vec{\mu}_s = -\mu_B (\vec{L} + 2\vec{S})$

-Total moment is not colinear to total kinetic moment  $\vec{J} = \vec{L} + \vec{S}$  !

## Relativistic effects: spin-orbit coupling

Corrections of the order  $v/c$  and  $(v/c)^2$

$v/c \approx Z\alpha$  with  $\alpha = e^2/\hbar c \approx 1/137$

Spin-orbit coupling is important for heavy ions

Leading term in hamiltonian:  $H_{so} = \lambda \vec{L} \cdot \vec{S}$   
 $= \lambda/2 (J^2 - L^2 - S^2) \quad (\vec{J} = \vec{L} + \vec{S})$

with:  $\lambda = \frac{e\hbar^2}{2mc^2} \frac{1}{r} \frac{dV(r)}{dr}$   **$\lambda$  increases as  $Z^4$**

For a single electron  $J = L \pm 1/2$

**$J = L+S$  is a good quantum number.**

**But  $M = -\mu_B (L + 2S)$**



## Atoms with several electrons: Filling of the lowest energy levels $E_{nl}$ .

### Filling of the last shell obeys the following rules:

**1- Pauli principle:** 2 electrons cannot be in the same quantum state

s orbitals ( $l=0$ )  $\Rightarrow$  2 electrons ( $m=0, \sigma_z = \pm 1/2$ )

p states ( $l=1$ )  $\Rightarrow$  6 electrons ( $m=-1, 0, 1$ )

d states ( $l=2$ )  $\Rightarrow$  10 electrons .....

**2 – Wave function should be antisymmetric (orbital + spin)**

**3- Coulomb interactions between electrons**

$\Rightarrow$  **Hund's rules:**

- total spin  $S = S_1 + S_2 + \dots$  takes the largest possible value

- total orbital angular momentum  $L = L_1 + L_2 + \dots$  takes the largest possible value

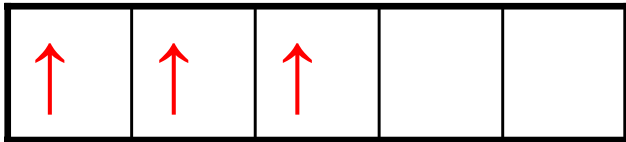
- spin-orbit coupling  $\lambda \vec{L} \cdot \vec{S}$        $J=L+S$  if  $\lambda < 0$  (shell more than half filled)  
 $J=L-S$  if  $\lambda > 0$  (shell less than half filled)

**Magnetism is due to unfilled shells only**

## Examples

Cr<sup>3+</sup>: 3d<sup>3</sup> - degeneracy of the configuration: 120

### Applications of Hund's rules



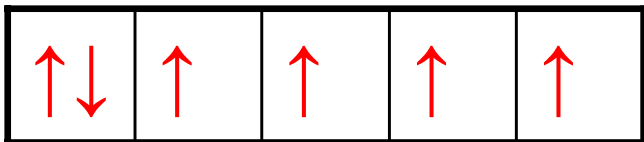
1<sup>st</sup> rule:  $S=3/2$

2<sup>nd</sup> rule:  $L=3$

S-O coupling:  $J = L-S = 3/2$  ( $\lambda > 0$ )

⇒ ground state degeneracy 4

Fe: 3d<sup>6</sup> - degeneracy: 210



$S = 2$ ,  $L = 2$ ,  $J = L+S = 4$  ( $\lambda < 0$ )

ground state degeneracy: 9

**Atomic state defined by  $L$ ,  $S$ ,  $J = L \pm S$  and  $M_J (= J_z)$   
degeneracy :  $2J + 1$**

## Coupling to magnetic field

$$H_p = -\vec{M} \cdot \vec{B} = \mu_B (\vec{L} + 2\vec{S}) \cdot \vec{B}$$

**B does not couple to J. However in weak field the multiplets are not mixed and interaction is:**

$$H_p \approx \mu_B (g_J \vec{J}) \cdot \vec{B} \quad g_J \text{ is the Landé factor}$$

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

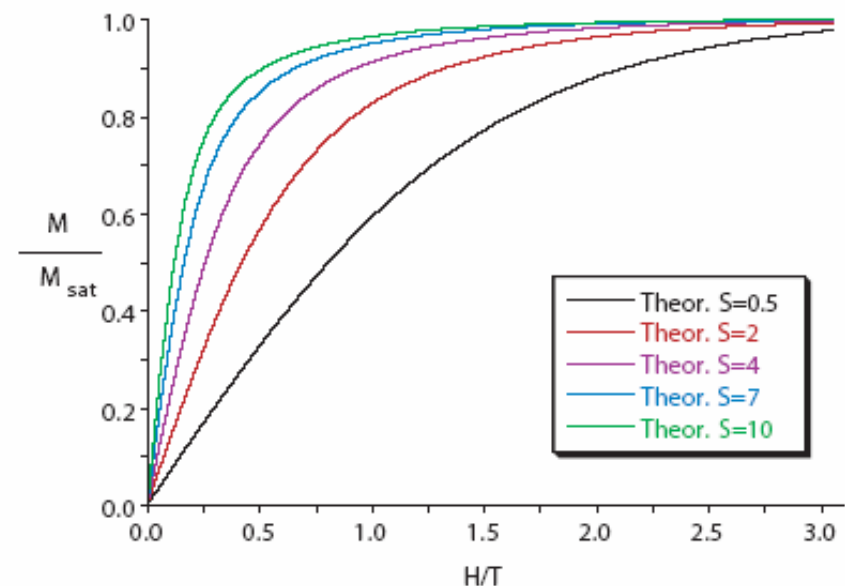
**Magnetization is given by the Brillouin function:**

$$M = M_0 B_J \left( \frac{M_0 B}{kT} \right), \quad M_0 = g_J \mu_B J$$

**At low field: Curie susceptibility**

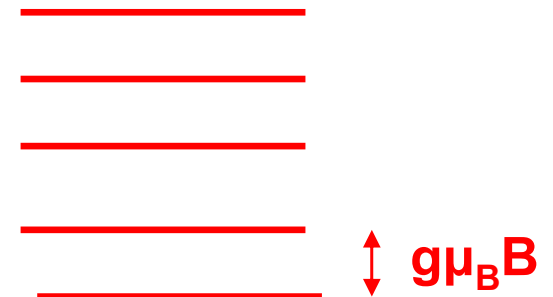
$$\chi = \frac{M}{B} = \frac{C}{T}, \quad C = (g_J \mu_B)^2 \frac{J(J+1)}{kT}$$

$$m_{\text{eff}} = g_J \mu_B \sqrt{J(J+1)}$$



## Partition function for a magnetic moment in a field:

Energy:  $E(J_z) = g\mu_B B J_z$   $J_z = -J, -J+1, \dots, +J$



$$Z = \sum \exp(-E(J_z)/kT)$$

$$= \exp(gBJ\mu_B/kT) + \exp(g(B(J-1))\mu_B/kT) + \dots$$

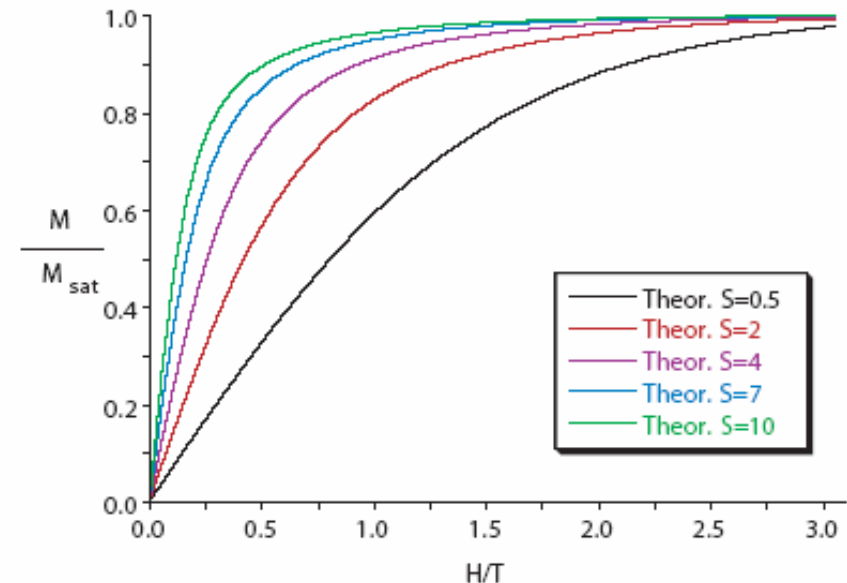
$$+ \exp(gB(-J+1)\mu_B/kT) + \exp(-gBJ\mu_B/kT)$$

For  $J=1/2$ :  $Z = 2 \cosh(gB\mu_B/2kT)$

## Magnetization:

$$\langle M \rangle = \frac{1}{Z} \sum_{J_z} gJ\mu_B J_z \exp\left(-\frac{gJ\mu_B J_z B}{kT}\right)$$

$$= g\mu_B J B J \left(\frac{g\mu_B B}{kT}\right)$$



## Magnetic moments in a magnetic field: 2 effects:

- Interaction of the magnetic moments with the applied field

Zeeman energy:  $E = -\mathbf{M} \cdot \mathbf{B} \Rightarrow \mathbf{M} = \chi \mathbf{B}$  (paramagnet)

- Motion of electron charge in a magnetic field : Lorentz force

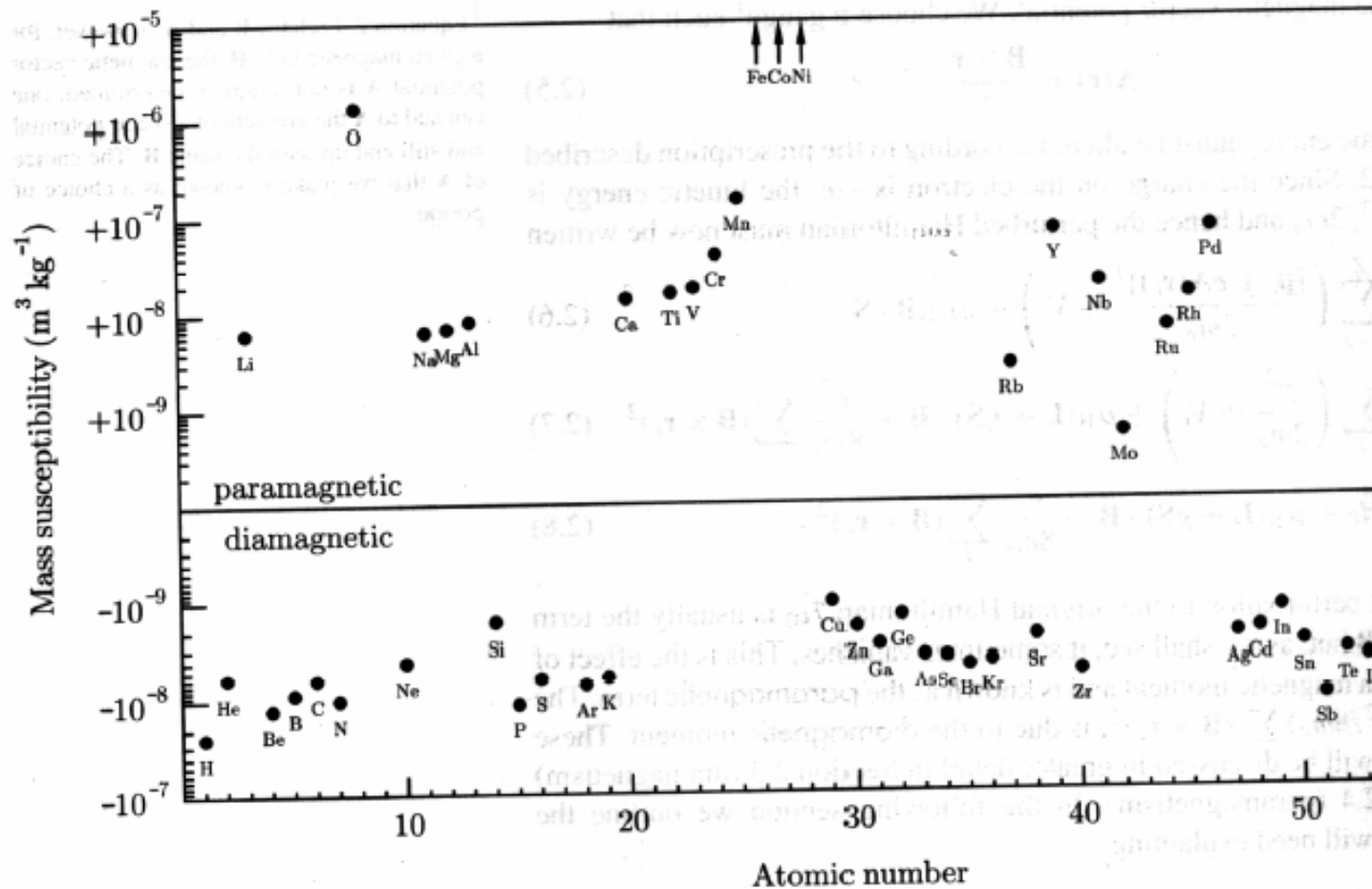
$$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B}) \quad \text{with } \vec{B} = \vec{\nabla} \times \vec{A} \quad (\vec{A} : \text{potential vector})$$

kinetic energy of electron:  $E = p^2/2m$  , with  $p = mv - eA$

In magnetic systems Zeeman effect dominates  $\Rightarrow$  paramagnetism, ferromagnetism...

in non-magnetic systems Lorentz force only  $\Rightarrow$  diamagnetism, Landau levels

# Magnetic behavior of the elements of periodic table



Susceptibility  $M/B$  for the elements of periodic table  
 (Fe, Co and Ni are ferromagnetic and  $M \neq 0$  in zero field)

## Diamagnetism: due to effect of B on the orbital motion

If **B** is constant and // to z-axis, then a possible choice of potential vector **A** is:

$$\mathbf{A}(\mathbf{r}) = \frac{\mathbf{B} \times \mathbf{r}}{2} = \frac{1}{2}(-B_y, B_x, 0)$$

kinetic energy:

$$E = \frac{p^2}{2m} = \frac{(m\mathbf{v} - e\mathbf{A})^2}{2m} = \frac{mv^2}{2} + \Delta E$$

$$\Delta E = -e\langle \mathbf{v} \cdot \mathbf{A} \rangle + \frac{e^2}{2m} \langle \mathbf{A}^2 \rangle$$

The 1<sup>st</sup> term vanishes since  $\langle \mathbf{A} \rangle = 0$

The 2<sup>nd</sup> term: 
$$\frac{e^2 B^2}{8m} \langle x^2 + y^2 \rangle = \frac{e^2 B^2}{12m} \langle r^2 \rangle$$

Magnetization:  $\mathbf{M} = -\frac{\partial E}{\partial \mathbf{B}}$  is opposite to magnetic field

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

**79 out of the first 103 elements are magnetic in atomic state**

**Non-magnetic atoms: - filled shells (Zn, Yb)**

**-  $J = L - S = 0$  (Sm, W)**

**Only a few of them are magnetic in solid state (15)**



H																He	
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

**Only 15 elements are magnetically ordered in the solid state: d and f elements**



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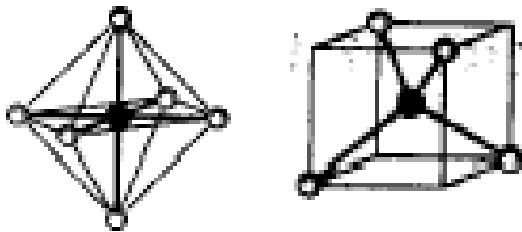
# Magnetic ions and atoms in a crystal: crystal field

In a solid: the potential has no spherical symmetry

Cubic crystal:  $V_c = V_0(x^4 + y^4 + z^4)$

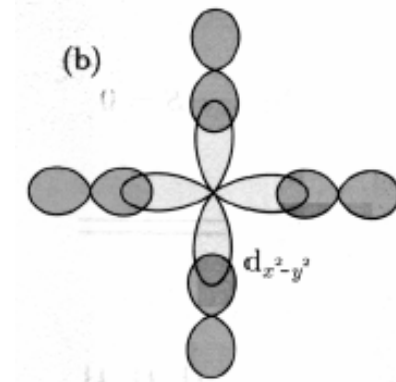
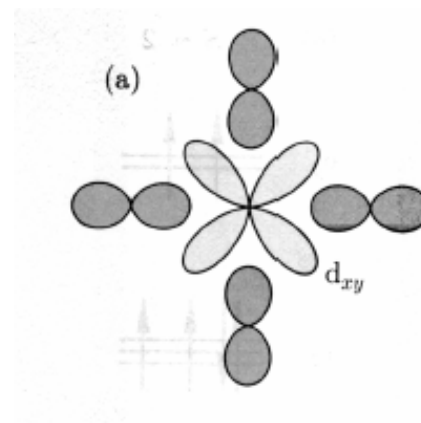
1-dimensional system:  $V_c = V_0 z^2$

Origin of the crystal field: electrostatic interaction of the electronic charge density with the neighbouring ions

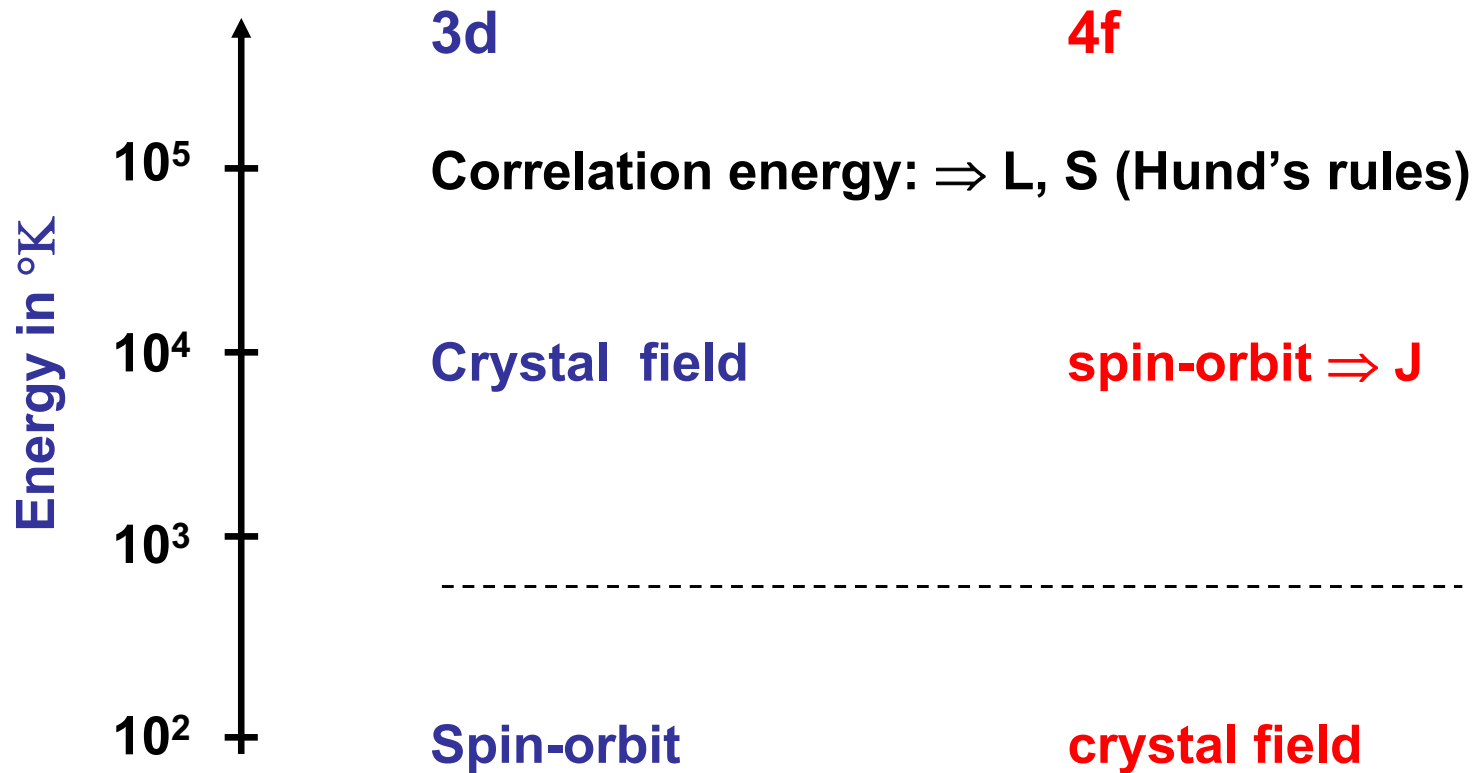


2 cubic environments: octahedral and tetrahedral

In octahedral environment  $xy$  orbital is lower in energy than  $x^2-y^2$



## Order of magnitude of the energies involved:



-3d electrons less localized than 4f: crystal field larger in 3d than in 4f

-Spin orbit coupling  $\propto Z^4$ : larger in 4f than in 3d

-In 3d ions : crystal field  $\gg$  spin-orbit: orbital moment is reduced (or quenched)

-In 4f ions: spin-orbit  $\gg$  crystal field: the ground state multiplet (J) is splitted by crystal field

Crystal field for 4f ions: crystal field is a perturbation on the ground state multiplet defined by J

For a 1-dimensional crystal field:  $V_c = BJ_z^2$

**J=4, B>0 (4f<sup>2</sup>: Pr<sup>3+</sup>)**



**Ground state J<sub>z</sub>=0**

**« non- magnetic »**

**J=5/2, B<0 (4f<sup>1</sup>: Ce<sup>3+</sup>)**



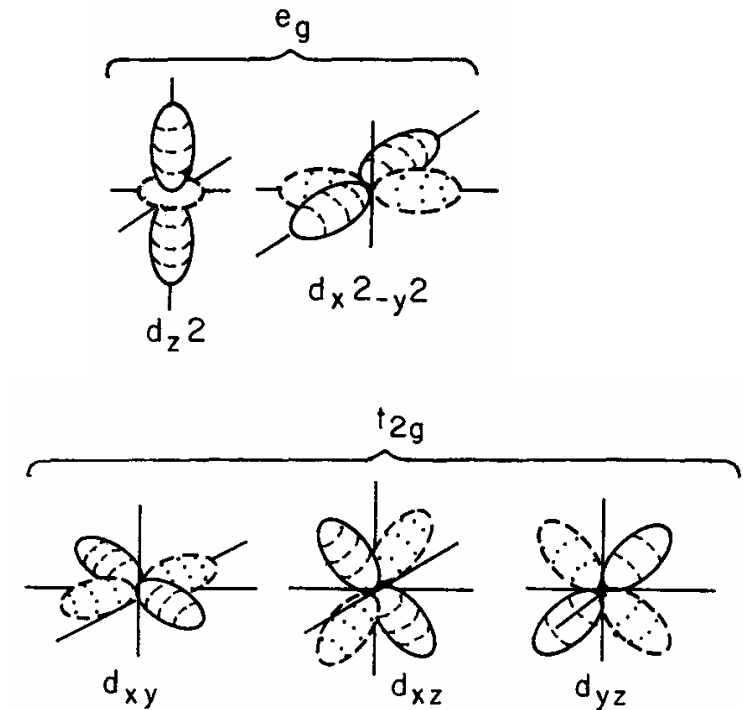
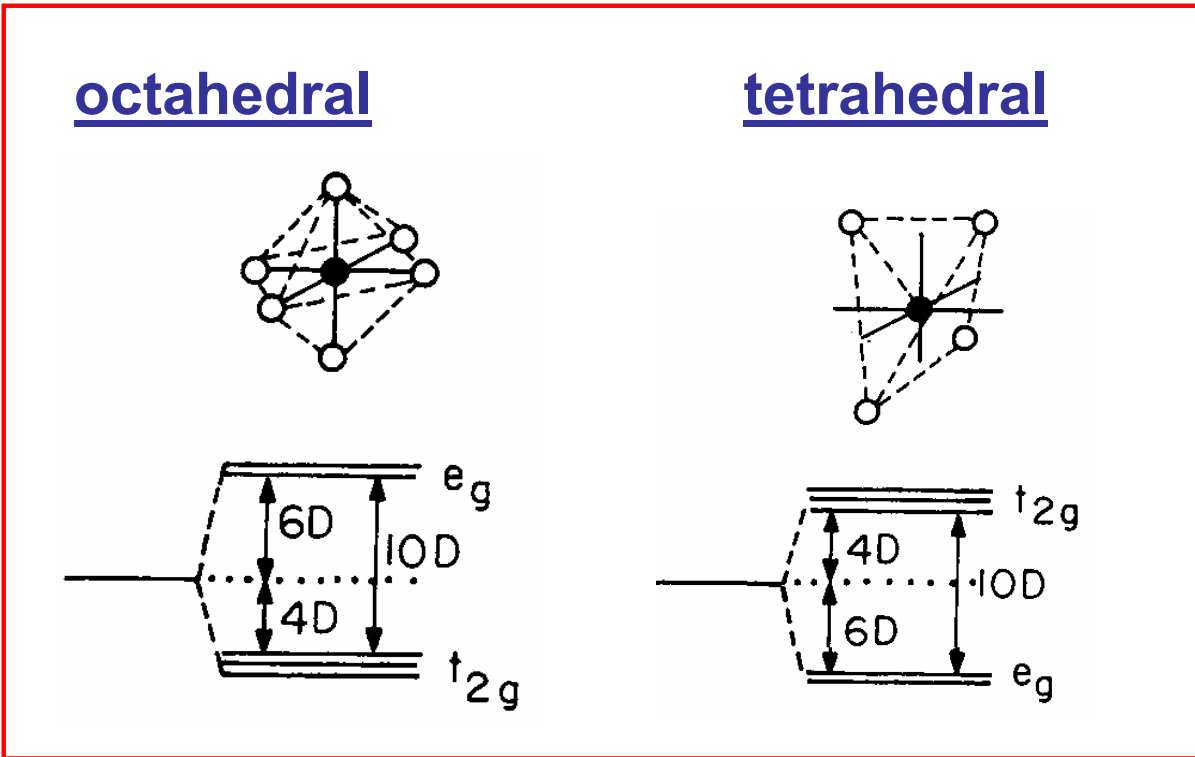
**ground state: J<sub>z</sub>=± 5/2**

**Ising-like**

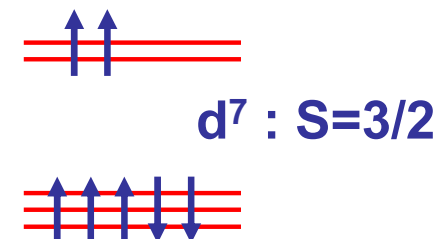
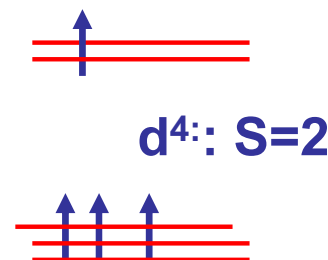
# Crystal field for 3d ions : cubic crystal field

Crystal field potential:  $V_c = V_0(x^4 + y^4 + z^4 - 3/5r^4)$

d orbitals are splitted in 2 groups:  $e_g$  and  $t_{2g}$ ; 2 cases:



Filling of the d-orbitals following 1st Hund's rule (S maximum)



## Quenching of orbital magnetic moment:

Wave functions of  $e_g$  states:  $\frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2})$  and  $Y_2^0$

No orbital magnetism:

$$\left\langle e_g^1 \left| L_\alpha \right| e_g^2 \right\rangle = 0, \alpha = x, y, z$$

$t_{2g}$  states:  $\frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2})$ ,  $\frac{1}{\sqrt{2}}(Y_2^1 - Y_2^{-1})$ , and  $\frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1})$

Diagonal matrix elements of  $L_\alpha$  vanish, only off-diagonal elements:  
 $\Rightarrow$  «reduced» orbital moment

In cubic symmetry orbital magnetism is either quenched ( $e_g$ ) or reduced ( $t_{2g}$ ):  $L$  is not given by Hund's rule

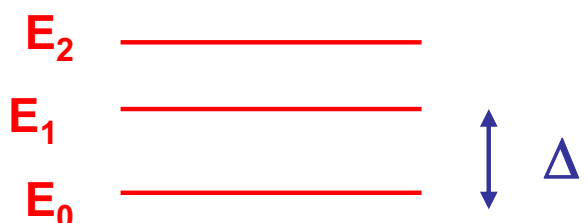
Spin-orbit coupling is a smaller effect, acting mainly in  $t_{2g}$  states

Single ion anisotropy: due to crystal field + spin orbit

3d ion: spin orbit coupling is a perturbation

$$\langle \mathbf{0} | \vec{L} | \mathbf{0} \rangle = \mathbf{0} \Rightarrow \langle \mathbf{0} | \lambda \vec{L} \cdot \vec{S} | \mathbf{0} \rangle = \mathbf{0} \Rightarrow \text{no effect to 1st order}$$

2<sup>nd</sup> order perturbation:

$$\Delta E = - \sum \frac{\langle \mathbf{0} | \lambda \vec{L} \vec{S} | n \rangle \langle n | \lambda \vec{L} \vec{S} | \mathbf{0} \rangle}{E_n - E_0} = - \sum_{\alpha\beta} \Lambda_{\alpha\beta} S_\alpha S_\beta \quad \Delta E \approx \frac{\lambda^2}{\Delta}$$


Higher order terms in high symmetry environment (cubic):  $\Delta E \propto \frac{\lambda^4}{\Delta^3}$

Energy depends on the direction of magnetization:

i.e.  $-DS_z^2$  with  $D > 0$  or  $< 0$

Rare earth ions: similar form  $\Delta E = \sum_{\alpha\beta} \Lambda_{\alpha\beta} J_\alpha J_\beta$

Order of magnitude: for cubic 3d metals: a few °K  
for rare earth:  $10^2$  to  $10^3$  °K



## High spin- low spin states (transition metals)

### Example of $\text{Fe}^{2+}$ ( $d^6$ configuration) in a cubic crystal field



-If large crystal field, all  $t_{2g}$  states are filled  $\Rightarrow S=0$  (low spin)

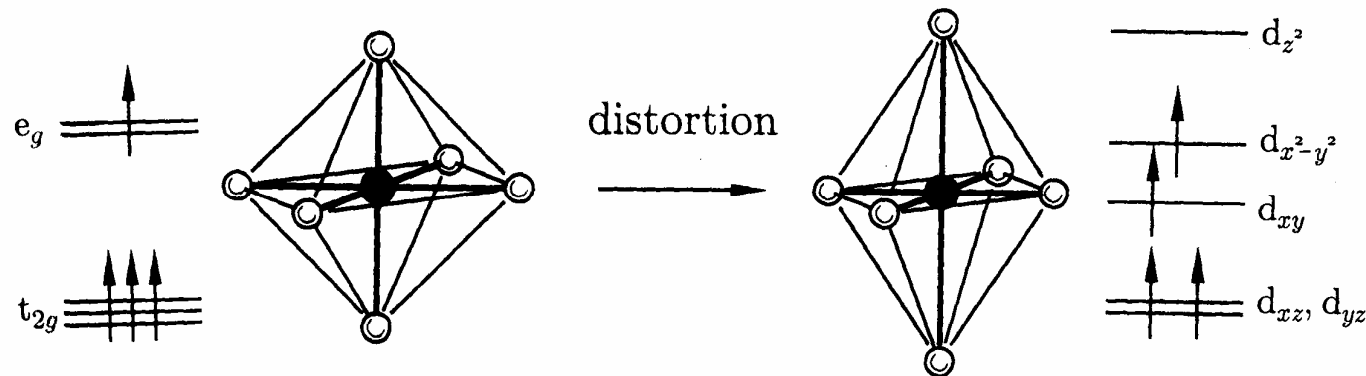


**1<sup>st</sup> Hund's rule is violated!**

## Coupling to the lattice deformation: Jahn-Teller effect

If orbital ground state is degenerate, then lowering of energy by crystal distortion is possible

Example:  $e_g$  electron in a distorted cubic crystal field



Tetragonal distortion removes the degeneracy of  $e_g$  electron

Distortion:  $\varepsilon \Rightarrow$  elastic energy  $E_{el} = A\varepsilon^2$

$\Rightarrow$  variation of crystal field energy  $\Delta = B\varepsilon$

Minimum of energy:  $\varepsilon = -A/2B$

spontaneous distortion; no orbital degeneracy in the ground state

## Magnetism of atoms and ions:

- **most of isolated atoms and ions are magnetic:**

total spin  $S$ , total orbital momentum  $L$  and  $J = L \pm S$   
determined by Hund's rules and spin-orbit coupling

- **Ions in a solid:**

- crystal field effect modifies the ground state
- big differences between 3d and 4f ions

- **Other interactions may be important:** anisotropy, Jahn-Teller effect, magneto-elastic interactions ...

- **Magnetism of solids:** magnetic moments are interacting  $\Rightarrow$  magnetic ordering

H																He	
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
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			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

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## Origin of exchange interactions:

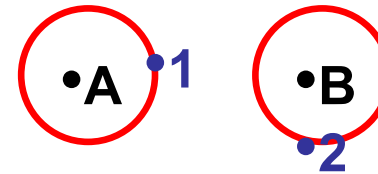
- electrostatic interactions
- Pauli principle

## Interatomic exchange: Hydrogen molecule

**Exchange interactions are due to Coulomb repulsion of electrons**

Hamiltonian of 2 H nuclei (a, b) + 2 electrons (1,2):

$$H = H_0(r_1-R_a) + H_0(r_2-R_B) + H_{\text{int}}$$



$H_{\text{int}}$ : Coulomb interaction between

- the 2 H nuclei
- the 2 electrons
- each electron with the 2<sup>nd</sup> nucleus

**2 possibilities for the total electronic spin: S=0 or S=1**

Wave function of the 2 electrons:  $\Psi(1,2) = \varphi(\vec{r}_1, \vec{r}_2)\chi(\sigma_1, \sigma_2)$

$\varphi(\vec{r}_1, \vec{r}_2)$  : orbital part

$\chi(\sigma_1, \sigma_2)$  : spin part

**Pauli principle: wave function  $\Psi(1,2)$  should be antisymmetric**

**$\Rightarrow$  either  $\varphi$  symmetric,  $\chi$  antisymmetric  
or  $\varphi$  antisymmetric,  $\chi$  symmetric**

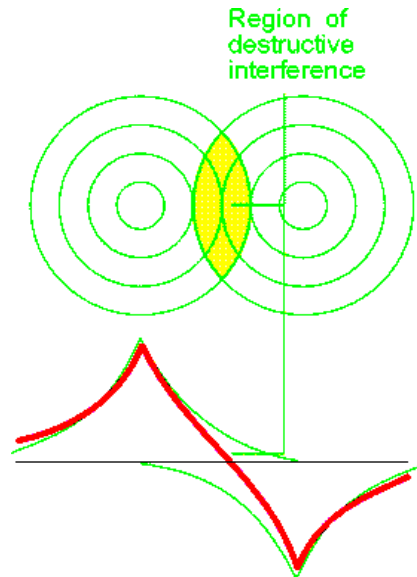
**Spin wave functions:**

**Singlet state: antisymmetric:  $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$   $S=0$**

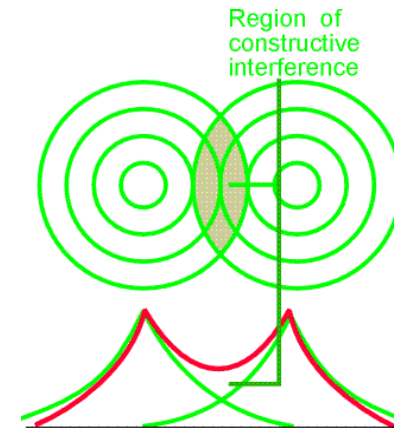
**Triplet state: symmetric (S=1)  $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle); |\uparrow\uparrow\rangle; |\downarrow\downarrow\rangle$   $S_z = 0, \pm 1$**

**Energy difference comes from the orbital part  $\langle\varphi|H_{\text{int}}|\varphi\rangle$**

If  $S=1$ , wave function is antisymmetric in real space



If  $S=0$ , wave function is symmetric in real space



Charge distribution is different  $\Rightarrow$  electrostatic energy is different

$$\Delta E = 2 \frac{U I^2 - J}{1 - I^2}$$

where  $I$  is overlap of the 2 wave functions,  $U$  is the Coulomb energy, and  $J$  is exchange

Effective interaction between the 2 spins:

$$-J_{12} \vec{S}_1 \cdot \vec{S}_2 = -\frac{J_{12}}{2} (\vec{S}_1 + \vec{S}_2)^2 + J_{12} S(S+1) \text{ and } J_{12} = \Delta E$$

$J_{12} < 0$  for  $H_2$  molecule: ground state is singlet  $S=0$



**In H<sub>2</sub> molecule: direct exchange due to overlap between 2 atomic orbitals**

**In solids: direct exchange is also present but small because d and f orbitals are localized:**

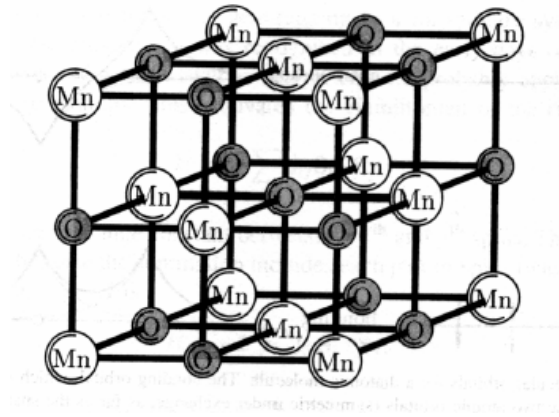
$$J_{12} \propto \int dr_1 dr_2 \Phi_1^*(r_1) \Phi_2^*(r_2) V(r_{12}) \Phi_1(r_2) \Phi_2(r_1)$$

**Indirect mechanisms are usually larger:**

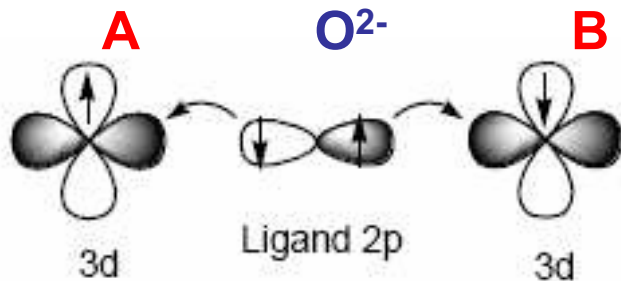
- Superexchange (short range, ferro or AF)**
- RKKY (long range, oscillating sign)**
- Double exchange (ferro)**
- Itinerant magnetic systems**

Superexchange: in many materials (oxydes), magnetic atoms are separated by non-magnetic ions (oxygen)

⇒ Indirect interactions through Oxygen



MnO: Mn<sup>2+</sup> are separated by O<sup>2-</sup>



- Effective hopping between A and B:  $t_{AB}$

- 2<sup>nd</sup> order perturbation in  $t_{AB}$ :

$$\uparrow \quad \uparrow \quad \Rightarrow \quad \Delta E = 0$$

$$\uparrow \quad \downarrow \quad \Rightarrow \quad \Delta E = -2t_{AB}^2/U$$

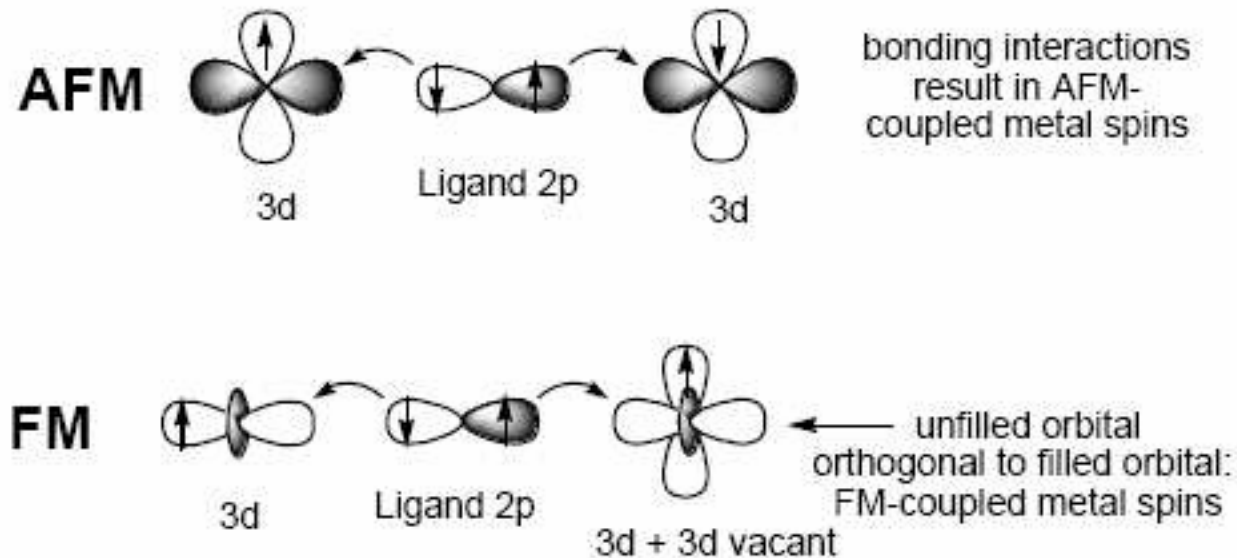
correction depends on the relative spin orientation

Effective Heisenberg interaction:  $J_{AB} = -2 \frac{t_{AB}^2}{U}$

## Characteristics of superexchange :

-Short range interaction: A and B should be connected by an Oxygen ion

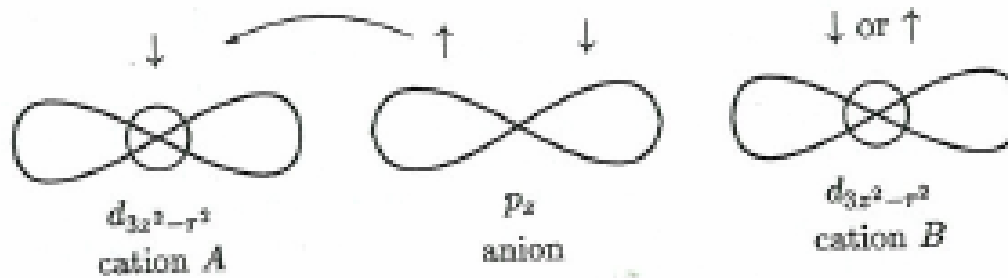
-Can be ferro or antiferromagnetic:



-depends on orbital occupation, A-O-B angle

- usually AF

## Calculation of superexchange in perturbation in $t_{AO}$ and $t_{BO}$



Hybridization:  $p_z$  wave function is mixed with  $d_{z^2}$  orbitals

- If antiparallel configuration of A and B,  $p_{z\uparrow}$  hybridize only with A:

$$|p_{z\uparrow}\rangle' = \frac{|p_{z\uparrow}\rangle + b|d_{A\uparrow}\rangle + b|d_{B\uparrow}\rangle}{\sqrt{1+b^2}}$$

- If A and B are parallel:  $p_{z\uparrow}$  hybridize with A and B, but no hybridization for  $p_{z\downarrow}$

$$|p_{z\uparrow}\rangle' = \frac{|p_{z\uparrow}\rangle + b|d_{A\uparrow}\rangle}{\sqrt{1+b^2}}, \text{ with } b \propto \frac{\langle p_z | V | d_A \rangle}{\epsilon_p - \epsilon_d}$$

Energy of the 2 configurations:

$$E_{\uparrow\uparrow} = E_0 - \frac{2b^2}{1+2b^2} (\epsilon_d - \epsilon_p) \quad E_{\uparrow\downarrow} = E_0 - \frac{2b^2}{1+b^2} (\epsilon_d - \epsilon_p)$$

$$E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = 2b^4 (\epsilon_d - \epsilon_p) = \frac{2t_{AO}^4}{\epsilon_d - \epsilon_p}$$

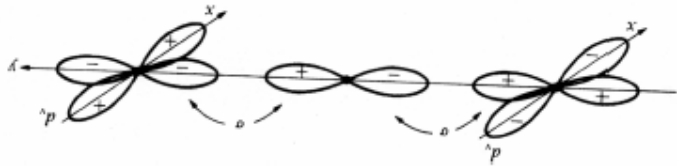
## Sign and value of superexchange depends on:

- The angle M - O - M
- The d orbitals involved in the bond

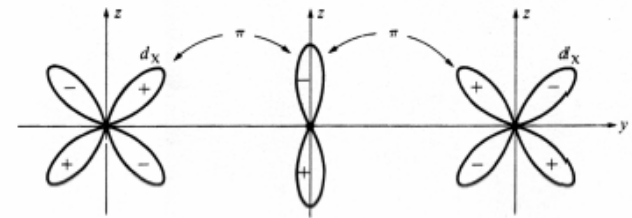
Some examples:

### Antiferromagnetic superexchange

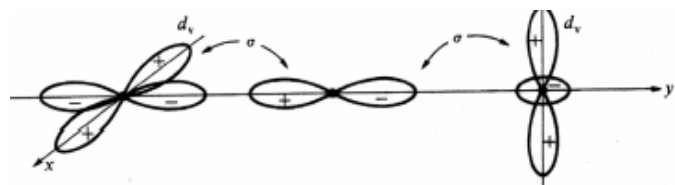
Strong:



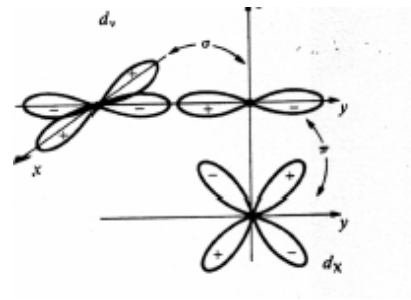
weak:



### Ferromagnetic



2 different orbitals



90° coupling

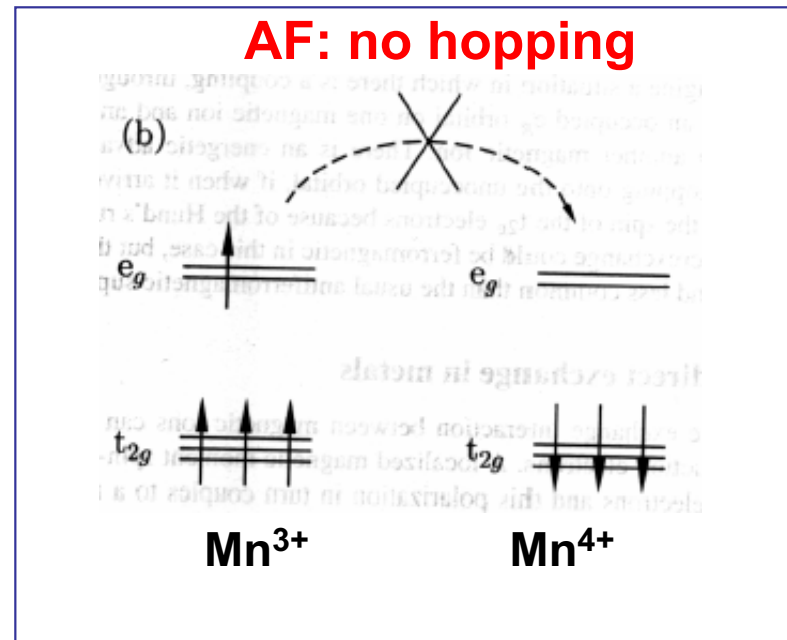
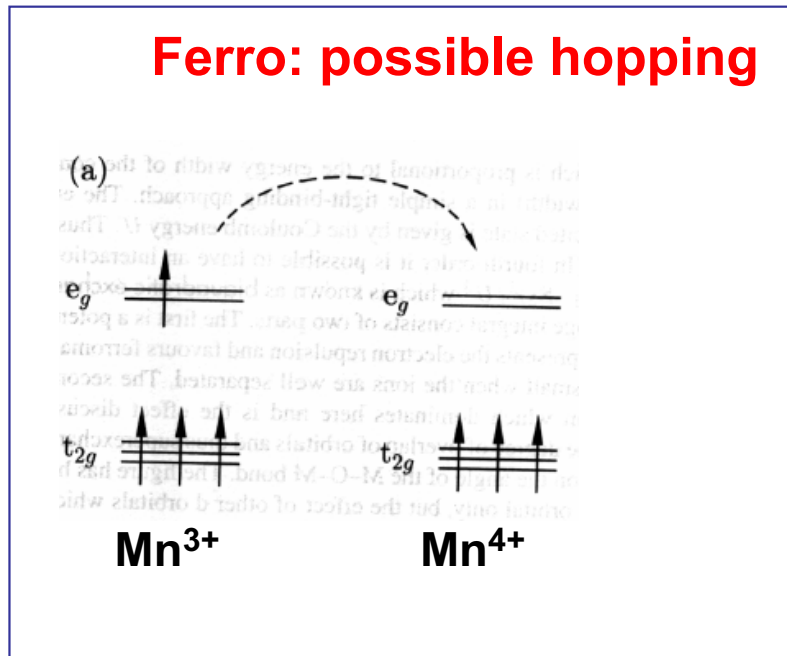
# Double exchange in 3d metals

Metallic systems are often mixed valence: example of manganites:

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ : coexistence of  $\text{Mn}^{4+}$  (3 electrons,  $S=3/2$ )

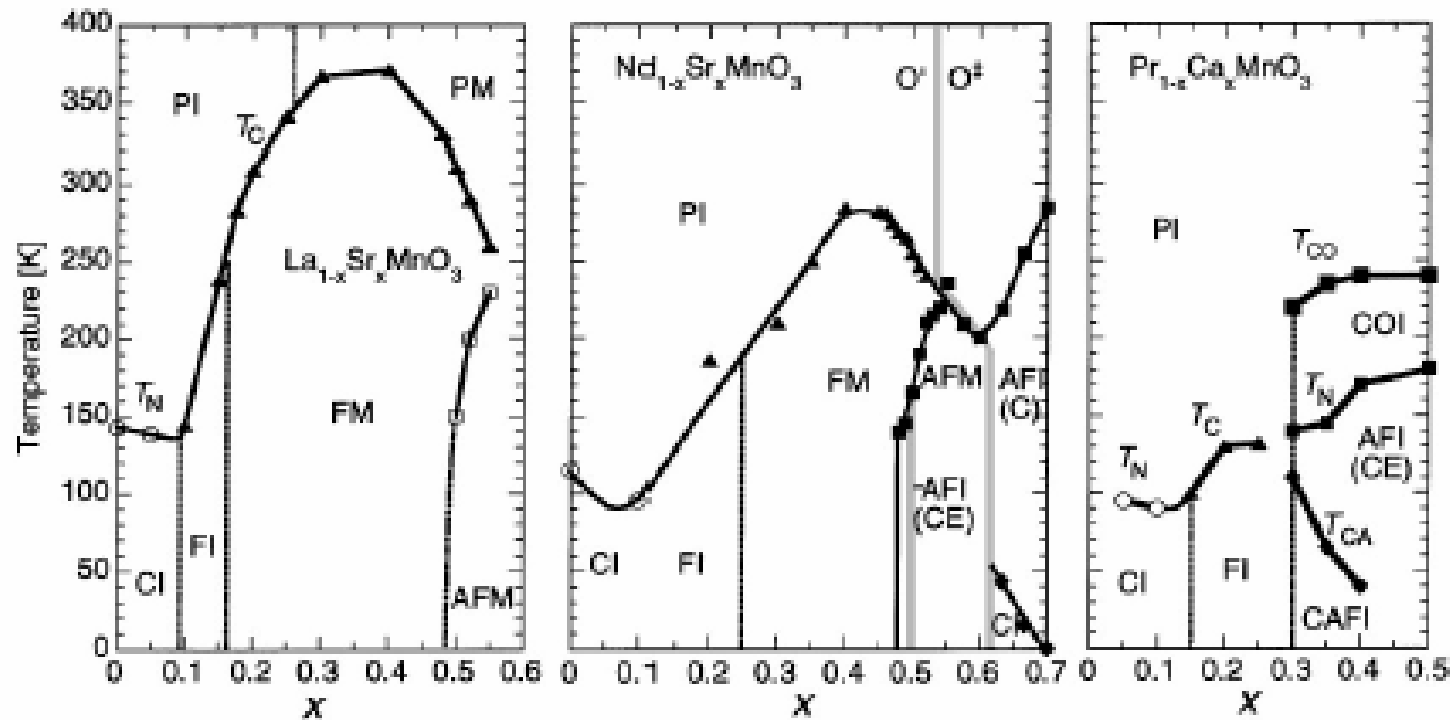
and  $\text{Mn}^{3+}$  (4 electrons,  $S=2$ , localized spin  $3/2 + 1$  conduction electron in  $e_g$  band)

spin  $3/2 + 1$  conduction electron in  $e_g$  band)



**Ferromagnetic interaction due to local Hund's coupling -  $J \mathbf{S}_i \cdot \boldsymbol{\sigma}_i$**   
**Short range interaction**

## Phase diagram of (La,Sr)MnO<sub>3</sub>, (Nd,Sr)MnO<sub>3</sub>, (Pr,Ca)MnO<sub>3</sub>



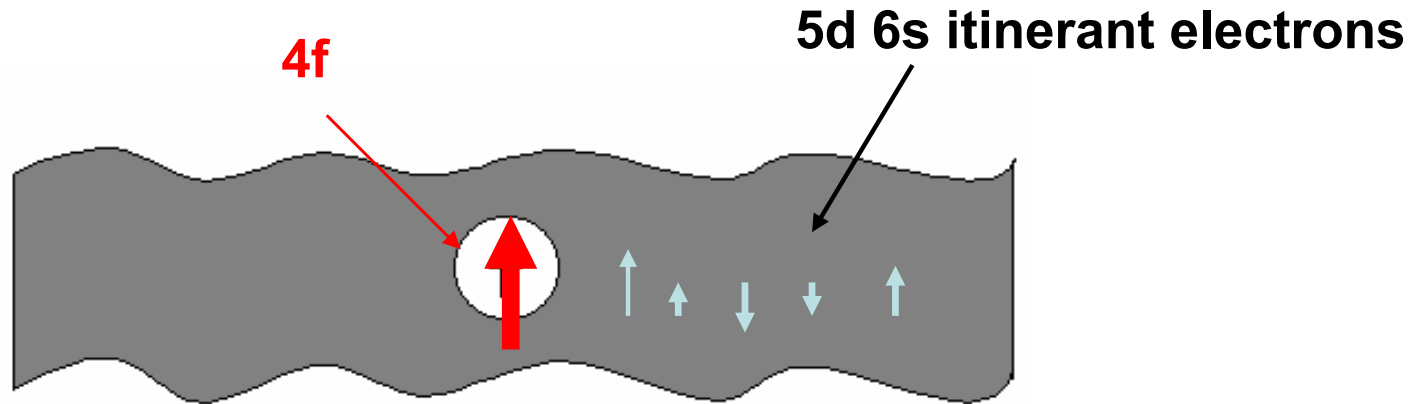
PI: paramagnetic insulating  
PM: paramagnetic metal  
CI: spin canted insulating

FI: ferromagnetic insulating  
FM: ferromagnetic metal

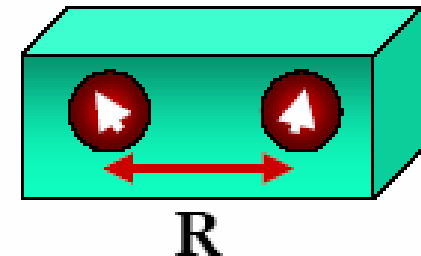
**Competition between: superexchange, double exchange, charge ordering, orbital ordering**

## RKKY interactions (rare earths):

- In rare earth, 4 f states are localized  $\Rightarrow$  no overlap with neighboring sites
- 4f states hybridize with conduction band (6s, 5d)  $\Rightarrow$  long range interactions



Interaction between 2 RE ions at distance  $R$ : transmitted by conduction electrons

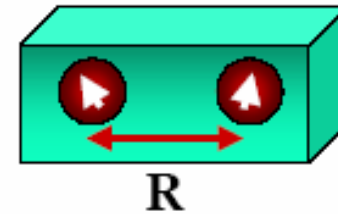




## Microscopic mechanism:

-Local interaction  $J$  between 4f spin  $S_i$  and conduction electron spin density  $\sigma(r)$ :  $-J(R_i-r)S_i \cdot \sigma(r)$

- $J(R_i-r)$  is local:  $J\delta(R_i-r)$



-Field acting on the itinerant spin  $\sigma(R_i)$ :  $h_i \propto JS_i$

- Induced polarization of conduction electrons at all sites:  $m_j = \chi_{ij} h_i$   
where  $\chi_{ij}$  is the generalized (non-local) susceptibility

-Effective field at site  $j$  on spin  $S_j$ :  $h_j \propto Jm_j = J^2 \chi_{ij} S_i$

-Interaction energy between  $S_i$  and  $S_j$ :

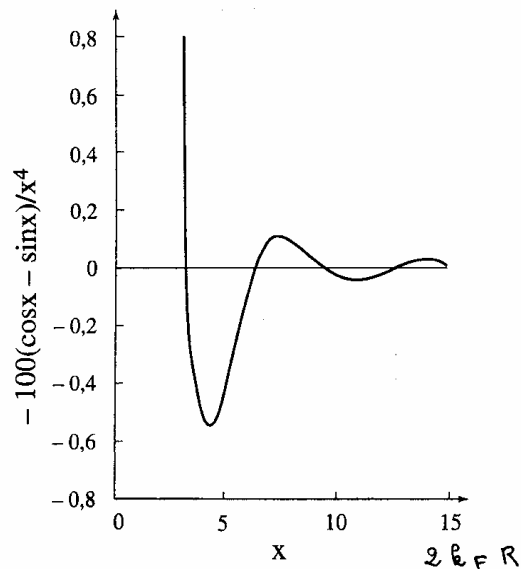
$$E_{ij} \propto J^2 \chi_{ij} S_i \cdot S_j = J(R_i - R_j) S_i \cdot S_j$$

## Exchange interaction between 2 rare earth ions:

$$J(R_i - R_j) \approx J^2 \rho(E_F) \frac{\cos(2k_F(R_i - R_j))}{(R_i - R_j)^3}$$

**J = local exchange**

**$\rho(E_F)$  = conduction electron density of states**

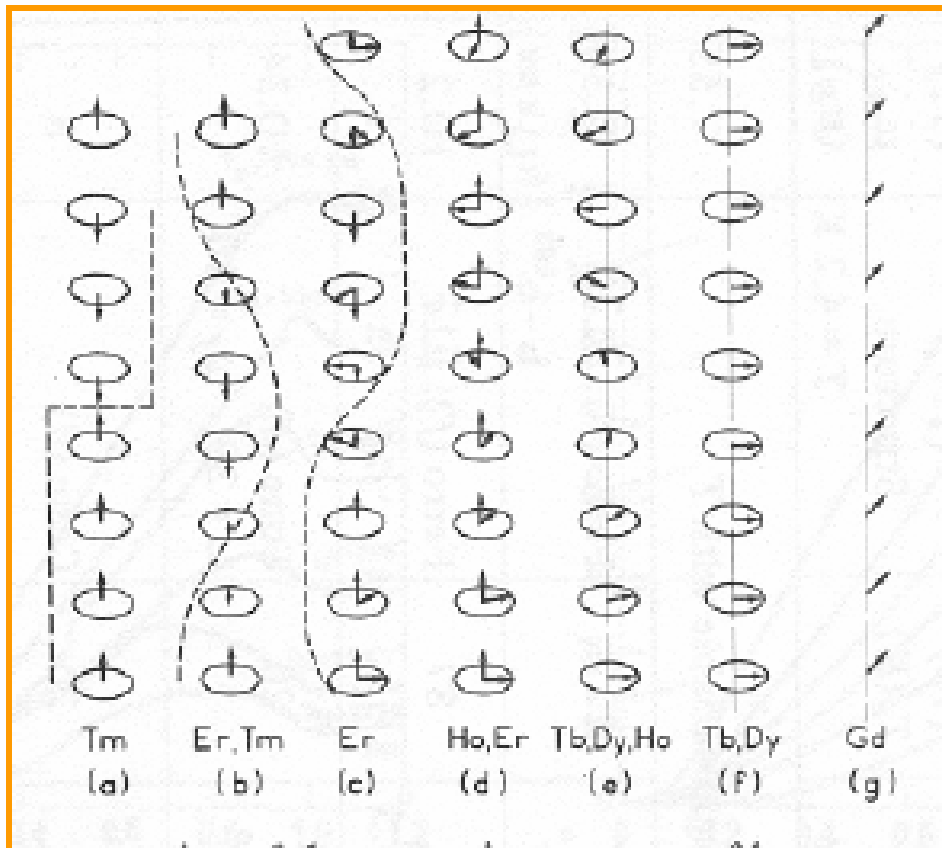


**- Interaction is long range:  
characteristic length  $\approx 1/2k_F$**

**-Oscillating interaction:**

$$J(r) \propto \frac{-x \cos x + \sin x}{x^4}, \quad x = 2k_F r$$

## Magnetic structures of rare-earth metals:



**Large variety of structures:  
Ferro, AF, helicoidal....**

**Long range + oscillating**

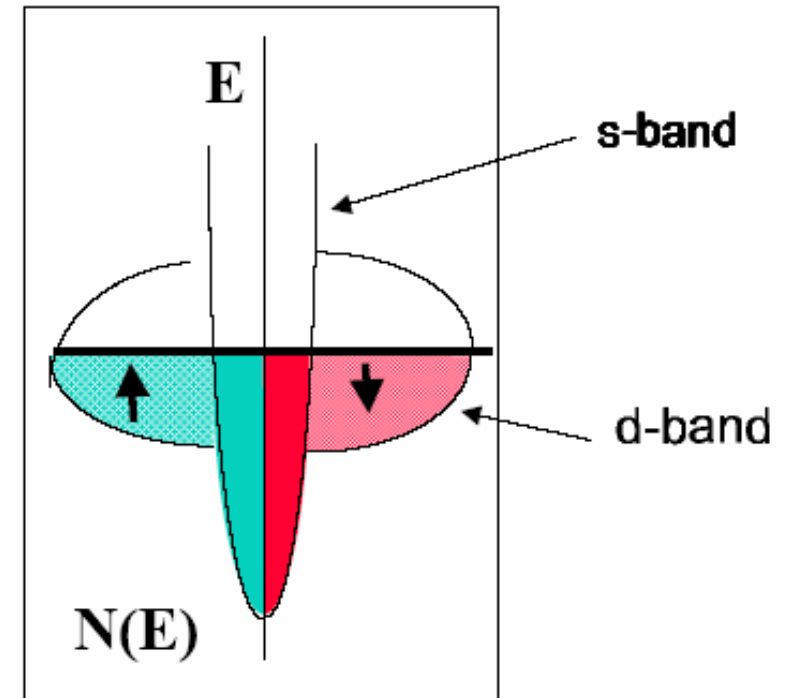
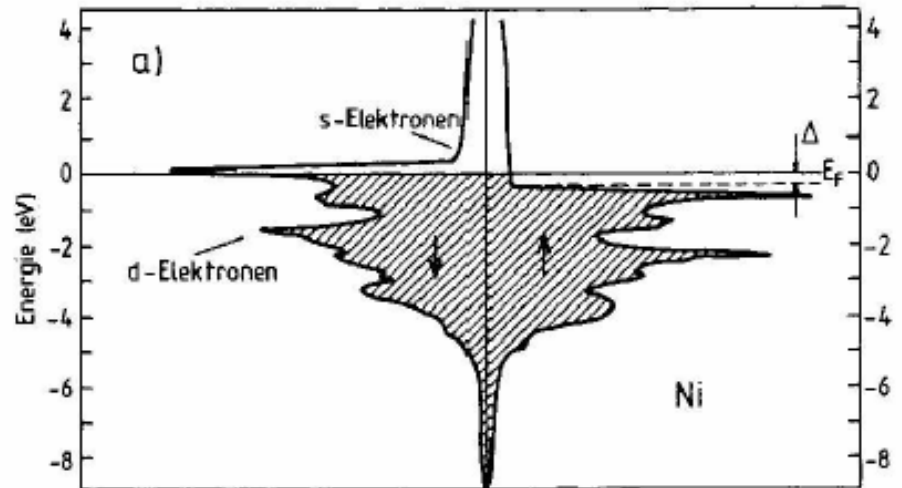
**In 3D systems:**  $J(r) \propto \frac{\cos(2k_F r)}{r^3}$

**in 2D:**  $J(r) \propto \frac{\sin(2k_F r)}{r^2}$

**in 1D:**  $J(r) \propto \frac{\cos(2k_F r)}{r}$

# Magnetism of 3d metals: due to itinerant character of 3 d electrons

## Band structure of Ni



d electrons form a narrow band (few eV)

Description of d electrons: Hubbard model

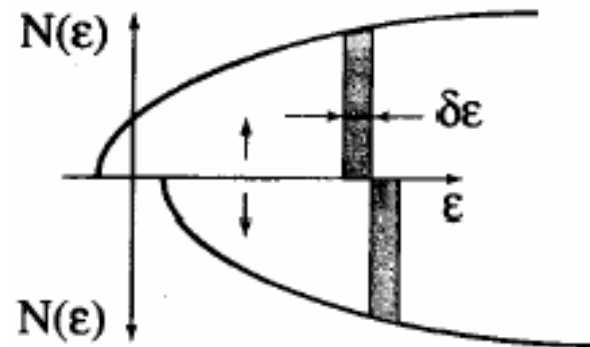
-band energy + Local Coulomb repulsion with  $U \approx W$  (few eV)

$$\sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + U n_{i\downarrow} n_{i\downarrow}$$

## Pauli susceptibility of band electrons:

Magnetic field  $B$  splits the  $\downarrow$  and  $\uparrow$  spin bands:  $\delta\varepsilon = \mu_B B$

Induced magnetization:  $M = \mu_B (N_{\uparrow} - N_{\downarrow}) = 2\mu_B \rho(E_F) \delta E$



Decrease of magnetic energy: 
$$E_M = U n_{\uparrow} n_{\downarrow} = U \left( \frac{N}{2} + \rho(E_F) \delta E \right) \left( \frac{N}{2} - \rho(E_F) \delta E \right)$$
$$= U \frac{N^2}{4} - U (\rho(E_F) \delta E)^2$$

Increase of kinetic energy:  $\Delta E_C = \rho(E_F) (\delta E)^2$

Zeeman energy:  $E_Z = -MB = -2\mu_B \rho(E_F) B \delta E$

Resulting magnetic moment:  $M = \frac{2\mu_B^2 \rho(E_F)}{1 - U\rho(E_F)} B$

Susceptibility:  $\chi = \frac{\chi_{\text{Pauli}}}{1 - U\rho(E_F)}$

Susceptibility is enhanced by the Stoner factor

Paramagnetic state becomes unstable

when  $U\rho(E_F) > 1$

- large  $U$

- or large density of states at the

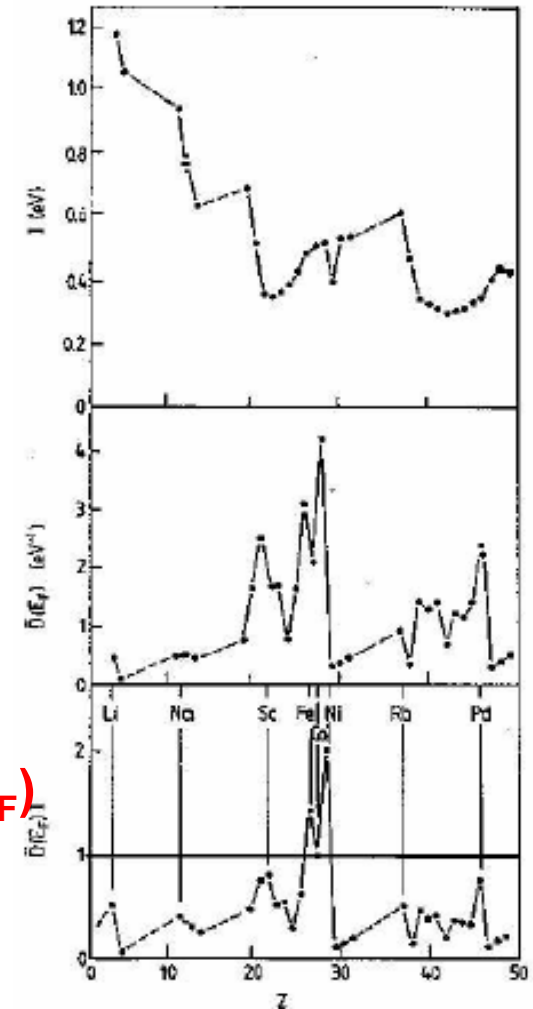
Fermi level

Stoner criterion is satisfied only for the 3d elements

$U$

$\rho(E_F)$

$U\rho(E_F)$

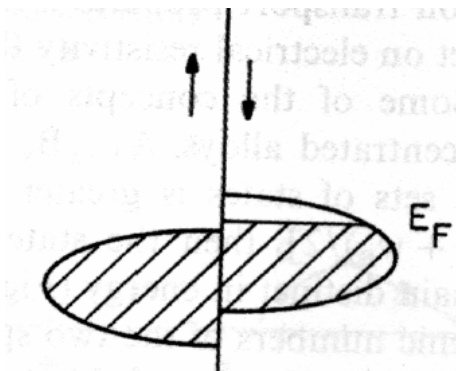


## Itinerant ferromagnetism:

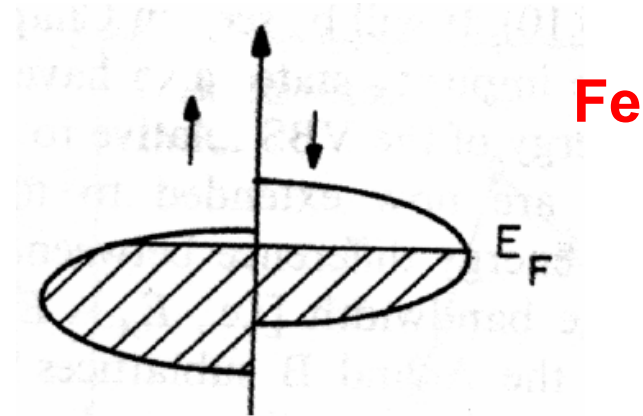
When the Stoner criterion is satisfied  $U\rho(E_F) > 1$  ferromagnetism can be stabilized

Origin of magnetism: Coulomb interaction  $U$

## Strong / weak ferromagnets



Ni



Fe

Magnetic moments are non-integer

For pure transition metals: Fe  $\rightarrow m_0 \approx 2.2 \mu_B / \text{atom}$

Co  $\rightarrow m_0 \approx 1.8 \mu_B / \text{atom}$

Ni  $\rightarrow m_0 \approx 0.64 \mu_B / \text{atom}$

# Hubbard model in the large U limit: Mott transition

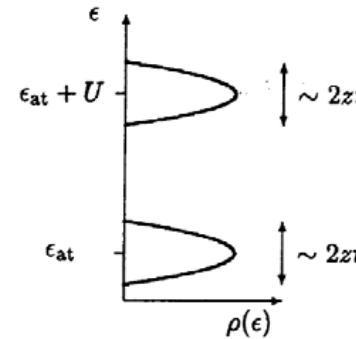
$$H = \sum \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + U \sum n_{i\uparrow} n_{i\downarrow}$$

$\epsilon_k$ : band structure; bandwidth  $W$  ;  $U$ : local Coulomb repulsion

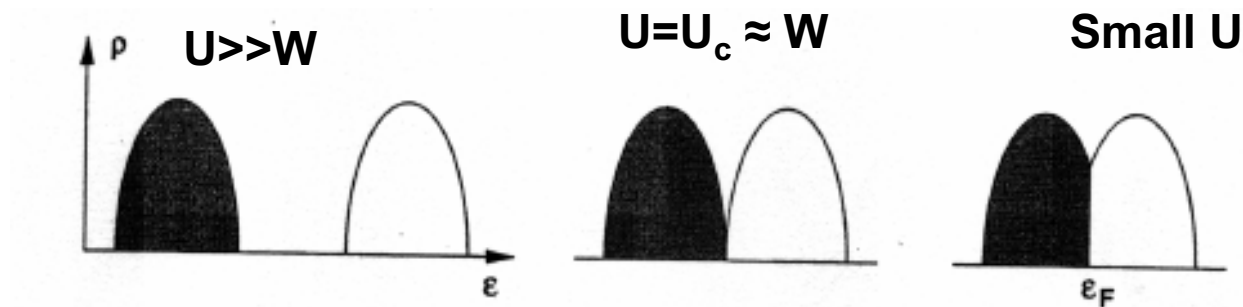
If  $U$  is large ( $\gg$  bandwidth), double occupation forbidden

“atomic limit”:  $W = 0$

Hubbard subbands ( $W \ll U$ )



Mott transition: occurs for half filled band





**Magnetic moments for itinerant systems strongly depend on their environment and interactions:**

**Magnetic moment of Fe determined by atomic rules:**

$$m_0 = g_J \mu_B J, \quad m_{\text{eff}} = g_J \mu_B (J(J+1))^{1/2}$$

$$\text{Fe}^{3+}: 3d^5 \quad L=0, S=5/2, J=5/2, g_J=2, \quad m_0 = 5\mu_B, \quad m_{\text{eff}} = 5.9$$

$$\text{Fe}^{2+}: 3d^6, L=2, S=2, J=4, g_J=3/2, \quad m_0 = 6\mu_B, \quad m_{\text{eff}} = 6.7$$

**Fe-compounds:**

- FeO (Fe<sup>2+</sup>):  $m_{\text{eff}} = 5.33$  → partial quenching of orbital moment (if total quenching, spin only magnetism →  $m_{\text{eff}} = 4.9$ )

$$\gamma\text{Fe}_2\text{O}_3 (\text{Fe}^{3+}): m_0 = 5 \mu_B$$

$$\alpha\text{-Fe (metal): } m_0 = 2.2 \mu_B$$

$$\text{YFe}_2: m_0 = 1.45 \mu_B$$

YFe<sub>2</sub>Si<sub>2</sub> : Fe is non-magnetic

$$\text{Fe surface: } m_0 = 2.8 \mu_B$$

The various exchange mechanisms can usually be described by an effective exchange hamiltonian :

$$H = - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

$J_{ij}$  can be long or short range, positive or negative

It results from the the Coulomb interactions between electrons

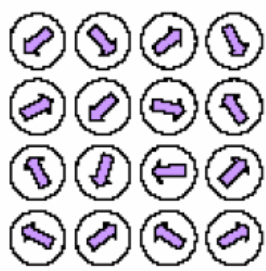
It is an interaction between spins: if the magnetic moment is given by  $J$  instead of  $S$  ( $L \neq 0$ ), interaction can be rewritten as:  $H = - \sum_{ij} J'_{ij} \vec{J}_i \cdot \vec{J}_j$

If  $J = L+S$ , and  $L+2S = g_J J$ , then  $S = (g_J - 1)J$   
and  $J'_{ij} = (g_J - 1)^2 J_{ij}$

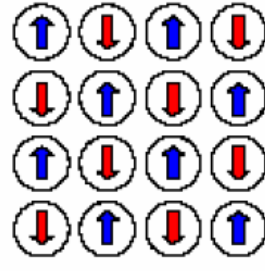
# Various microscopic mechanisms for exchange interactions in solids:

- Localized / itinerant spin systems
- Short / long range
- Ferro or antiferro

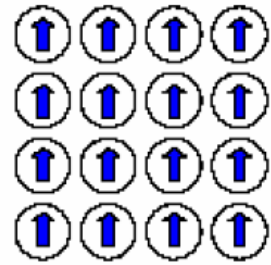
## Various types of ordered magnetic structures:



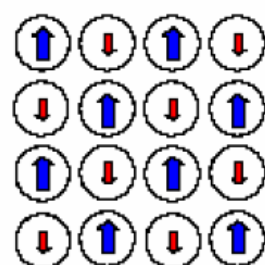
Paramagnetic



Antiferromagnetic



Ferromagnetic



Ferrimagnetic

### Ferromagnets

$T_c$

Fe	1043 K
Co	1394 K
Ni	631 K
Gd	293 K

### Antiferromagnets

	$T_N$
CoO	293K
NiO	523K

**Type of magnetic order depends on the interactions**

**Also spin glasses, spin liquids... : no long range magnetic order**



**School on Highly frustrated magnetism and Strongly  
Correlated Systems  
30/07/07 – 07/08/07**

**Introduction to magnetism: basic concepts in magnetism, not  
specific to frustrated magnetism**

- Origin of magnetism: magnetism of atoms and ions**
- Atoms and ions in a crystal: crystal field, magneto-elastic effects**
- Exchange interactions: origin, different types of exchange**
- Magnetism at finite temperature**

## The molecular field approximation

$$H = - \sum_{ij} I_{ij} \vec{S}_i \cdot \vec{S}_j - \sum_i g\mu_B \vec{S}_i \cdot \vec{B} = - \sum_i \vec{S}_i (g\mu_B \vec{B} + \sum_j I_{ij} \vec{S}_j)$$

Each magnetic moment is in an effective field

$$\vec{B}_i = \vec{B} + \sum_j \frac{I_{ij}}{g\mu_B} \vec{S}_j$$

external field + field created by the neighboring moments

Approximation:  $S_j$  is replaced by its average  $\langle S_j \rangle = S$  (T)

Then  $B_i = B + zM$ , ( $z =$  number of nearest neighbors,  $M = g\mu_B S$ )

Simple problem: magnetic moment in a uniform field  $B_{\text{eff}}$  : Brillouin function

$$\langle M \rangle = M_0 B_J \left( \frac{g\mu_B B_{\text{eff}}}{kT} \right)$$

$B_{\text{eff}}$  depends on  $M$ :  
selfconsistent equation

## Predictions of mean field theories:

-  $T < T_c$   $M(T)$  calculated selfconsistently

$$- T_c = 2zI J(J+1)/3k_B$$

At low  $T$ :  $M(T) - M_0 \propto \exp(-2T_c/T)$

Near  $T_c$ :  $M(T) \propto (T_c - T)^{1/2}$

-  $T > T_c$  susceptibility: Curie Weiss law

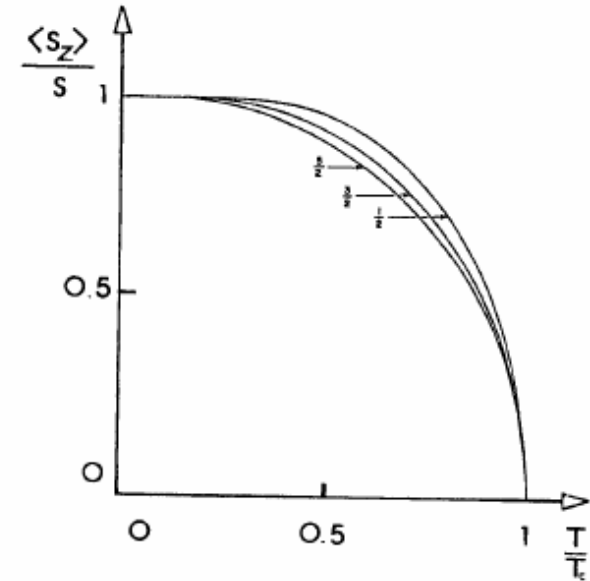
$$\chi = \frac{C}{T - T_c}$$

Deviations at low  $T$ :  $M(T)/M_0 = 1 - AT^{3/2}$  (ferromagnet)

$1 - AT^2$  (Antiferromagnet)

Deviations near  $T_c$ :  $M(T)/M_0 = (T_c - T)^\beta$  with  $\beta < 0.5$

Deviations above  $T_c$ :  $\chi(T) \propto (T - T_c)^\gamma$  with  $\gamma > 1$



At low temperature: thermal variation is dominated by spin waves

Collective excitations of magnetic moments:

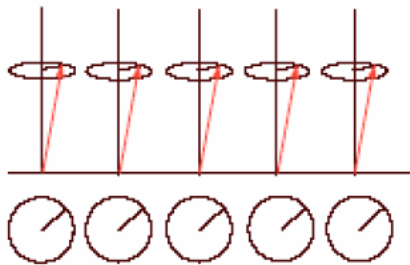
Ground state:  $\uparrow \uparrow \uparrow \uparrow \uparrow \dots$

Spin wave: linear combination of :  $\uparrow \uparrow \downarrow \uparrow \uparrow$

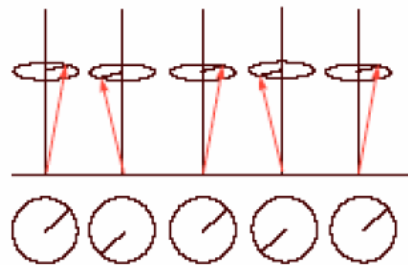
This is not an eigenstate :  $S_i^+ S_j^-$  induces correlated spin flips

Energy of spin waves:  $E(k) = \hbar\omega(k) = 2S(I(0) - I(k))$

$$I(k) = \sum_{ij} I(r_i - r_j) e^{ik(r_i - r_j)}$$

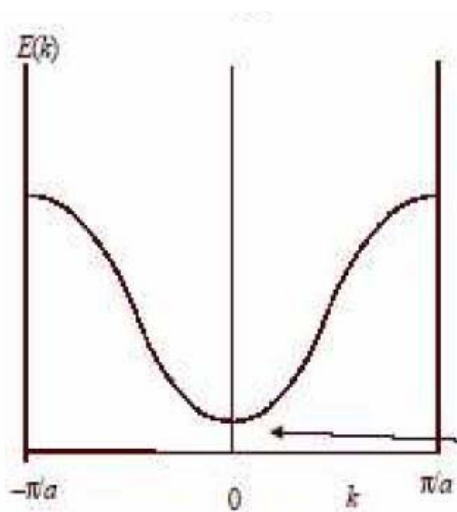


$k = 0$



$k = \pi/a$

Spin waves excitations: low energy cost



In ferromagnets: at low k:

$$E(k) \approx zI S(ka)^2$$

In antiferromagnets: spin wave energies

$$E(k) \propto zIS \sin(ka)$$

Magnetization at low T :  $M(T) = M_0 -$  number of excited spin waves

$$N_{sw} = \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle = \sum_{\mathbf{k}} \frac{1}{e^{E(\mathbf{k})/T} - 1}$$

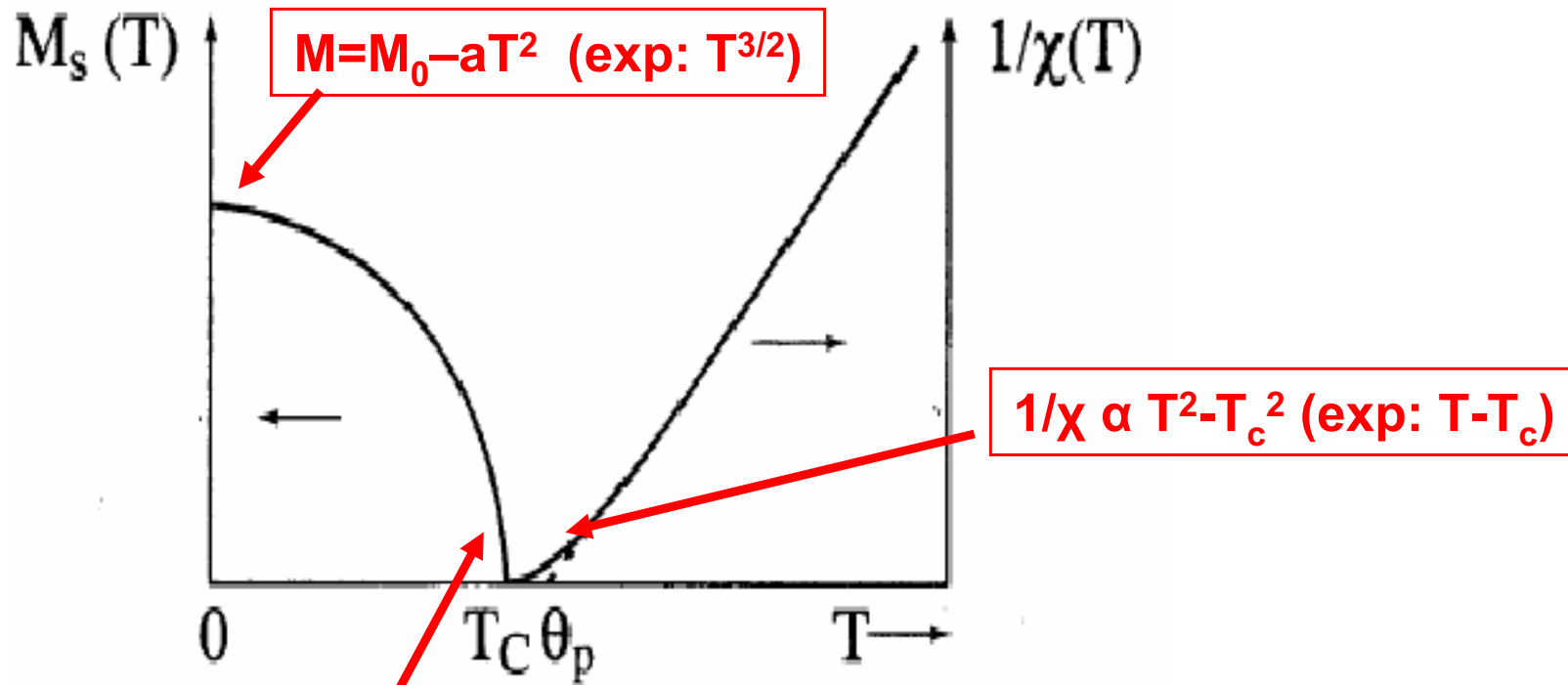
⇒ in a ferromagnet: magnetization  $M(T)/M_0 = 1 - AT^{3/2}$

in antiferromagnet:  $1 - AT^2$

If gap in the spin wave spectrum (i.e. anisotropy), behavior is different:  $\exp(-\Delta/T)$



## Itinerant systems: Stoner theory at finite temperature:



$$M = M_0 - aT^2 \quad (\text{exp: } T^{3/2})$$

$$1/\chi \propto T^2 - T_c^2 \quad (\text{exp: } T - T_c)$$

$$M = b(T_c - T)^{1/2} \quad (\text{exp: } (T_c - T)^\beta)$$

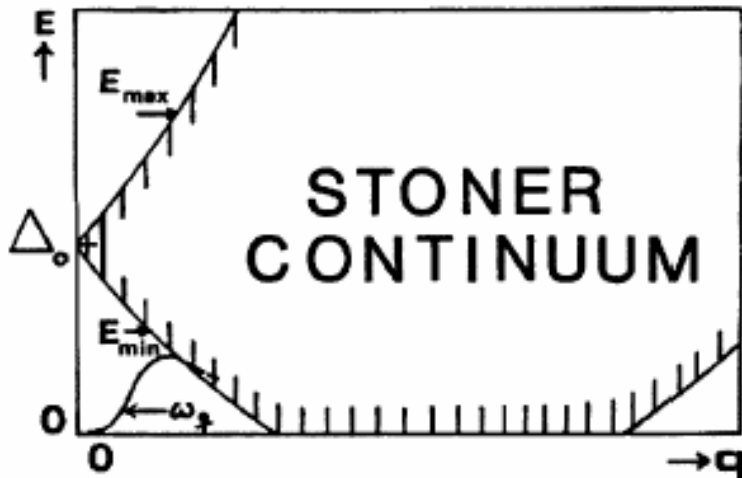
Order of magnitudes for  $T_c$ :  
Fe: 1040 (Stoner: 4400-6000)  
Co: 1400 (Stoner: 3300-4800)  
Ni: 630 (Stoner: 1700-2900)

# 4- magnetism at finite temperature

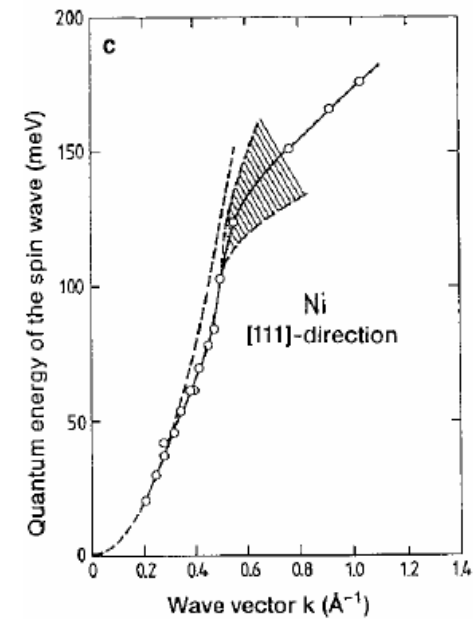
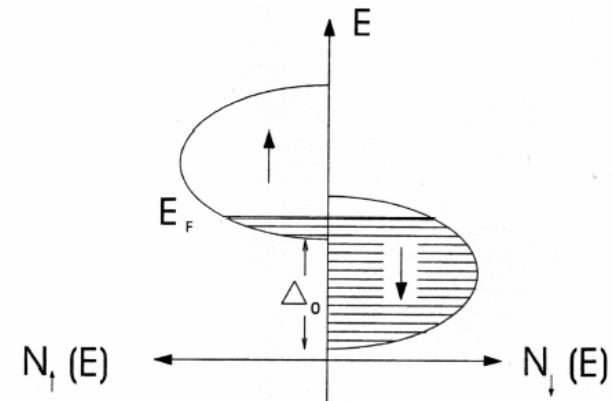
## Spin waves also exist in itinerant ferromagnets:

2 types of excitations:

- Stoner excitations: transition from a filled  $\uparrow$  state to an empty  $\downarrow$  state: gap  $\Delta_0$  at  $q=0$ ; continuum at  $q \neq 0$
- Collective excitations: spin waves



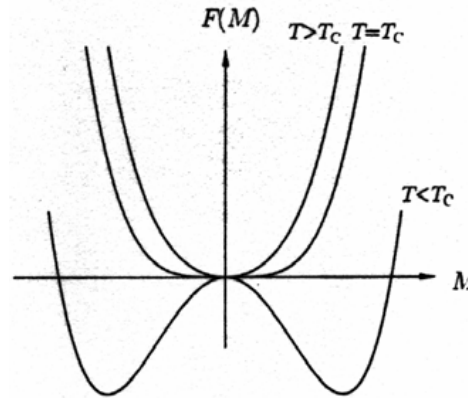
**Magnetic excitations in Ni ( $\Delta_0 \approx 100\text{meV}$ )**



## Temperature effects: Landau expansion

Free energy near  $T_c$  can be expanded in powers of  $M$ :

$$F(M) = F_0 + a(T)M^2 + b(T)M^4 + c(T)(\vec{\nabla} M)^2 - MH$$



- If uniform magnetization:  $T_c$  is determined by  $a(T_c) = 0$

→  $a(T) = a_0(T - T_c)$  and:

$$M(T) = \frac{a_0(T_c - T)^{1/2}}{2b}$$

- Near  $T_c$ , large fluctuations of  $M$ :  $\vec{\nabla} M \neq 0$  → critical region

Correlation length:  $\xi$  becomes large:

$$S_i S_j \propto \exp(-R_{ij}/\xi) \quad \xi(T) \approx (T_c - T)^{-\nu}$$

## Critical exponents

they depend on

- the type of interactions (Heisenberg, X-Y, Ising...)
- the dimensionality of the system

$$M(T) \propto (T_c - T)^\beta, \chi(T) \propto (T - T_c)^{-\gamma}$$

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	D=1	D=2	D=3	Mean field	
Heisenberg	No ordering		$\beta = 0.36$ $\gamma = 1.39$	$\beta = 1/2$ $\gamma = 1$	
X-Y			$\gamma = \infty$ Kosterlitz- Thouless		$\beta = 0.35$ $\gamma = 1.32$
Ising			$\beta = 1/8$ $\gamma = 7/4$		$\beta = 0.32$ $\gamma = 1.24$

**Deviations from mean field indicate short range correlations near  $T_c$**

# Summary

## « Usual » magnetic systems:

- The magnetic moments of atoms and ions determined by atomic rules: values of  $L$ ,  $S$ ,  $J$
- In a solid: environment should be taken into account (crystal field, anisotropy)
- Interactions between ions due to exchange interactions: long or short range, positive or negative
- Usually long range magnetic ordering of the moments due to exchange: Néel temperature
- Also valid for metals

## What is different in frustrated or low dimensional materials?

- Low dimensionality: strong fluctuations (spin waves) prevent long range ordering
- Frustrated lattices: geometry prevents long range ordering