Exchange and ordering in magnetic materials

Claudine Lacroix, Institut Néel, Grenoble

1-Origin of exchange

2- Exchange in insulators: superexchange and Goodenough-Kanamori rules

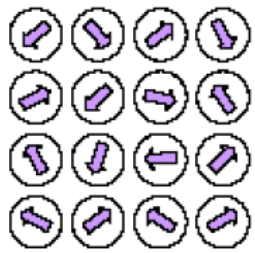**3- Exchange in metals: RKKY, double exchange, band magnetism**

4- Magnetic ordering: different types of orderings, role of dimensionality, classical vs quantum spins
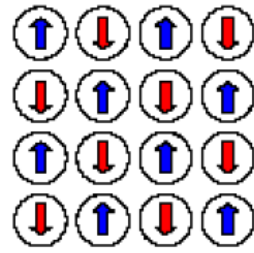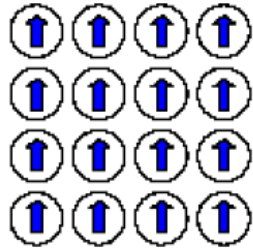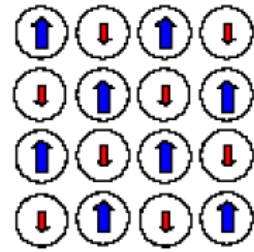
Various types of ordered magnetic structures:

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

Various microscopic mecanisms for <u>exchange interactions</u> in solids:

-Localized / itinerant spin systems

-Short / long range

-Ferro or antiferro

$$H = -\sum_{ij} J_{ij}\, \vec{S_i}.\vec{S_J}$$

2

Exchange and ordering in magnetic materials

1-Origin of exchange

2- Exchange in insulators:superexchange and Goodenough-Kanamori rules

3- Exchange in metals: RKKY, double exchange, band magnetism

4- Magnetic ordering: different types of orderings, role of dimensionality, classical vs quantum spins

Origin of exchange interactions: - electrostatic interactions

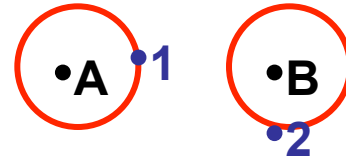- Pauli principle

Interatomic exchange: Hydrogen molecule

Exchange interactions are due to Coulomb repulsion of electrons

Hamiltonian of 2 H nuclei (A, B) + 2 electrons (1,2):

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

$H_0 = p^2/2m + U(r)$

H_{int}: Coulomb interaction

•A •1 •B
•2

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

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

$\Rightarrow$ **either φ symmetric, χ antisymmetric**
or φ antisymmetric, χ symmetric
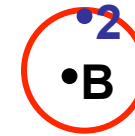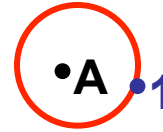
Spin wave-functions:

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

Triplet state: symmetric (S=1) $\frac{1}{\sqrt{2}}(|\uparrow\downarrow> +|\downarrow\uparrow>), |\uparrow\uparrow>, |\downarrow\downarrow>$ $S_z = 0, \pm1$

Energy difference comes from the orbital part $<\varphi |H_{int}| \varphi>$ (<u>no spin in the hamiltonian!</u>)

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

- **Eigenfunctions** of total hamiltonian

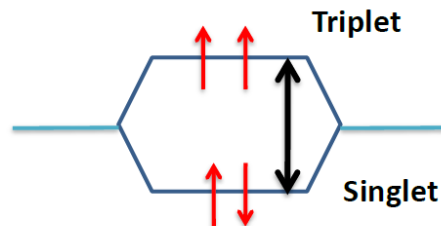**Symmetric wave function:** (associated with S=0)

$$\varphi_S(r_1, r_2) = \frac{1}{\sqrt{2}} (\psi_A(r_1)\psi_B(r_2) + \psi_A(r_2)\psi_B(r_1))$$

Antisymmetric wave function (associated with S=1)

$$\varphi_A(r_1, r_2) = \frac{1}{\sqrt{2}} (\psi_A(r_1)\psi_B(r_2) - \psi_A(r_2)\psi_B(r_1))$$

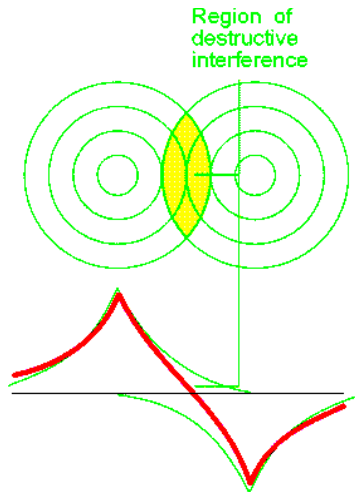-**Interaction energy:** $\quad \Delta E_S = \langle \varphi_S | H_{int} | \varphi_S \rangle$

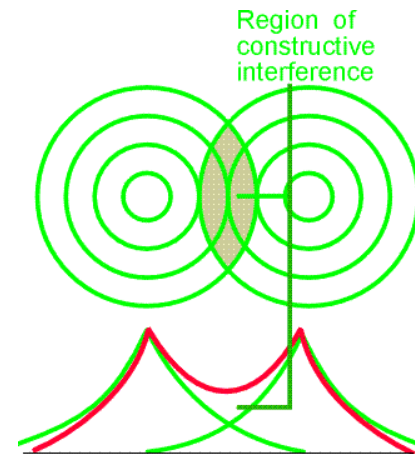$$\Delta E_A = \langle \varphi_A | H_{int} | \varphi_A \rangle$$

$$\Delta E_A - \Delta E_S = E(S=1) - E(S=0)$$

$\Delta E_A \neq \Delta E_S \implies$ **singlet and triplet have different energies**

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

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

Region of destructive interference

Region of constructive interference

Charge distribution is different ⇒ electrostatic energy is different

Effective interaction between the 2 spins:

$$\Delta E = \Delta E_A - \Delta E_S = \Delta E(S=1) - \Delta E(S=0)$$

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

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

In H_2 molecule: <u>direct exchange</u> due to overlap between 2 atomic orbitals

In solids: direct exchange is also present:

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

$(\rightarrow J_D)$

<u>But indirect mecanisms</u> are usually larger:

-Superexchange (short range, ferro or AF)

-RKKY (long range, oscillating sign)

-Double exchange (ferro)

-Itinerant magnetic systems

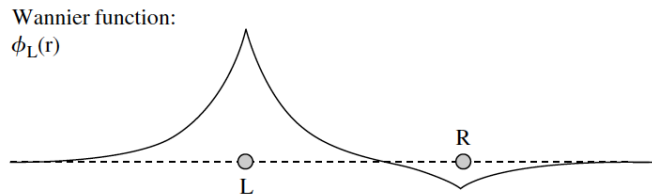Exchange results always from competition between kinetic energy (delocalization) and Coulomb repulsion
Hybridization (d-d, f-spd, d-sp…) is necessary

Calculation of exchange using with Wannier functions (R. Skomski)

Atomic wave function:
$\phi_1(r)$

Wannier function:
$\phi_L(r)$
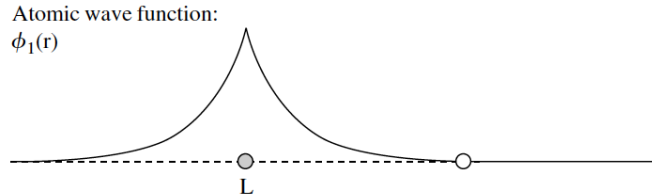
Atomic wave functions are not orthogonal

$$\langle \Psi_A | \Psi_B \rangle = S \neq 0$$

Wannier wave functions are orthogonal

$$\langle \Psi_R | \Psi_L \rangle = 0$$

2 electrons wave function with $S_z=0$ (↑↓ pair)

$$\Psi(\mathbf{r}, \mathbf{r}') = c_I \phi_L(\mathbf{r}) \phi_L(\mathbf{r}') + c_{II} \phi_L(\mathbf{r}) \phi_R(\mathbf{r}') + c_{III} \phi_R(\mathbf{r}) \phi_L(\mathbf{r}') + c_{IV} \phi_R(\mathbf{r}) \phi_R(\mathbf{r}')$$

$$E\Psi = \mathbf{H}_o(\mathbf{r})\Psi + \mathbf{H}_o(\mathbf{r}')\Psi + V_C(\mathbf{r}, \mathbf{r}')\Psi$$

H_0 : 1-electron hamiltonian $\quad H_o(\mathbf{r}) = -\hbar^2 \nabla^2 / 2m + V_o(\mathbf{r}) + V_o(|\mathbf{r} - \mathbf{R}|)$

V_c : Coulomb interactions

$$\Psi(\mathbf{r}, \mathbf{r}') = c_{\mathrm{I}}\phi_{\mathrm{L}}(\mathbf{r})\phi_{\mathrm{L}}(\mathbf{r}') + c_{\mathrm{II}}\phi_{\mathrm{L}}(\mathbf{r})\phi_{\mathrm{R}}(\mathbf{r}') + c_{\mathrm{III}}\phi_{\mathrm{R}}(\mathbf{r})\phi_{\mathrm{L}}(\mathbf{r}') + c_{\mathrm{IV}}\phi_{\mathrm{R}}(\mathbf{r})\phi_{\mathrm{R}}(\mathbf{r}')$$

Coulomb integral:

$$U = \int \int \phi_{\mathrm{L}}^{*}(\mathbf{r})\phi_{\mathrm{L}}^{*}(\mathbf{r}')V_{\mathrm{C}}(\mathbf{r}, \mathbf{r}')\phi_{\mathrm{L}}(\mathbf{r})\phi_{\mathrm{L}}(\mathbf{r}')\, dV\, dV'$$
$$= \int \int n_{\mathrm{L}}(\mathbf{r})V_{\mathrm{C}}(\mathbf{r}, \mathbf{r}')n_{\mathrm{L}}(\mathbf{r}')\, dV\, dV'$$

(**Coulomb energy of 2 electrons on the same atom**)

Exchange integral

$$J_{\mathrm{D}} = \int \int \phi_{\mathrm{L}}^{*}(\mathbf{r})\phi_{\mathrm{R}}^{*}(\mathbf{r}')V_{\mathrm{C}}(\mathbf{r}, \mathbf{r}')\phi_{\mathrm{R}}(\mathbf{r})\phi_{\mathrm{L}}(\mathbf{r}')\, dV\, dV'$$

$$H = 2E_{\mathrm{o}} + \begin{pmatrix} U & t & t & J_{\mathrm{D}} \\ t & 0 & J_{\mathrm{D}} & t \\ t & J_{\mathrm{D}} & 0 & t \\ J_{\mathrm{D}} & t & t & U \end{pmatrix}$$

E_0: atomic energy

t: hopping integral

Solutions for the eigenstates

$$|1\rangle = \frac{1}{\sqrt{2}}|LR\rangle - \frac{1}{\sqrt{2}}|RL\rangle$$

$$|2\rangle = \frac{1}{\sqrt{2}}|LL\rangle - \frac{1}{\sqrt{2}}|RR\rangle$$

$$|3\rangle = \frac{\sin\chi}{\sqrt{2}}(|LL\rangle + |RR\rangle) + \frac{\cos\chi}{\sqrt{2}}(|LR\rangle + |RL\rangle)$$
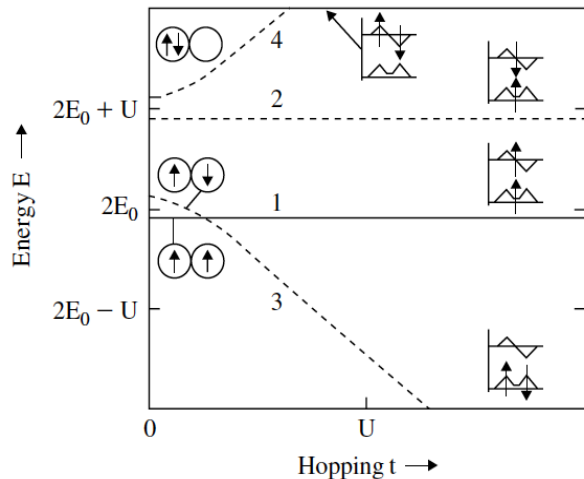
$$|4\rangle = \frac{\cos\chi}{\sqrt{2}}(|LL\rangle + |RR\rangle) - \frac{\sin\chi}{\sqrt{2}}(|LR\rangle + |RL\rangle)$$

$$E_1 = 2E_o - J_D$$

$$E_2 = 2E_o + U - J_D$$

$$E_3 = 2E_o + \frac{U}{2} + J_D - \sqrt{4t^2 + \frac{U^2}{4}}$$

$$E_4 = 2E_o + \frac{U}{2} + J_D + \sqrt{4t^2 + \frac{U^2}{4}}$$

Ground state for $J_D > 0$:

- **Small t/U: state 1 ($S_z = 0$, $S = 1$)**
- **Large t/U: state 3 ($S_z = 0$, $S = 0$)**

Exchange:

$$\frac{1}{2}(E_1 - E_3) = J_D + \frac{U}{4} - \sqrt{t^2 + \frac{U^2}{16}}$$

Exchange:

$$\frac{1}{2}(E_1 - E_3) = J_D + \frac{U}{4} - \sqrt{t^2 + \frac{U^2}{16}}$$

2 contributions:

- J_D (direct exchange)

- contribution of the kinetic energy t

At small t/U $$J = J_D - \frac{2t^2}{U}$$

J_D can be >0 or <0,
kinetic term is antiferromagnetic (superechange)

Exchange results always from competition between kinetic energy (delocalization) and Coulomb repulsion
Hybridization (d-d, f-spd, d-sp…) is necessary

12

Exchange and ordering in magnetic materials

1-Origin of exchange

2- Exchange in insulators:superexchange and Goodenough-Kanamori rules

3- Exchange in metals: RKKY, double exchange, band magnetism

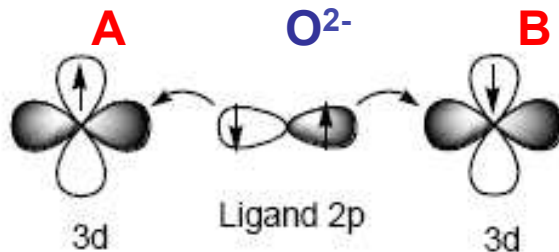4- Magnetic ordering: different types of orderings, role of dimensionality, classical vs quantum spins

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

$\Rightarrow$ **Indirect interactions through Oxygen**
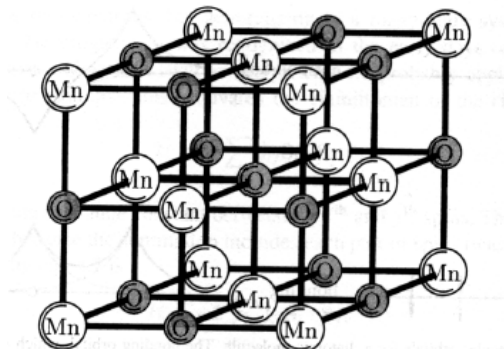
MnO: Mn^{2+} are separated by O^{2-}

3d wave functions hybridize with p wave function of O^{2-}

In the antiferromagnetic configuration, electrons of atoms A and B can both hybridize with 1 p-electron of O^{2-}: gain of kinetic energy

➔ **energy depends on the relative spin orientation**

14

Superexchange: due to hybridization

$d_{3z^2-r^2}$
cation A

p_z
anion

$d_{3z^2-r^2}$
cation B

↑   ↑&↓   ↓ or ↑
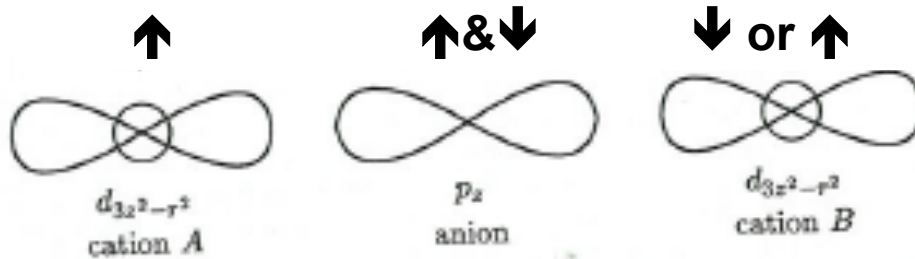
Hybridization: p_z wave function is mixed with d_{z2} orbitals

-If A and B antiparallel, $p_{z\uparrow}$ hybridize with A
$p_{z\downarrow}$ hybridize with B

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

Energy difference of the 2 configurations:

$$\Delta E = E_{\uparrow\uparrow} - E_{\uparrow\downarrow} \, \alpha \, \frac{b^4}{\varepsilon_d - \varepsilon_p}$$

where *b* is the hybridization

15

An effective model :

-1 orbital atoms with Coulomb repulsion
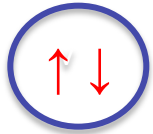
↑↓   **When 2 electrons in the same orbital: energy U**

- **2 atoms with 1 electron**

A ↑   ↓ **B**

- **Effective hopping between A and B t_{AB}**
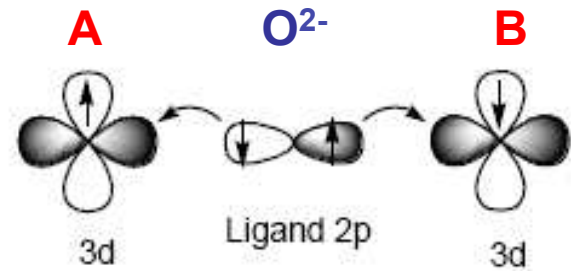
- 2nd order perturbation in t_{AB}:

↑ ↑ $\Rightarrow$ $\Delta E = 0$

↑ ↓ $\Rightarrow$ $\Delta E = -2t_{AB}^2/U$

energy depends on the relative spin orientation
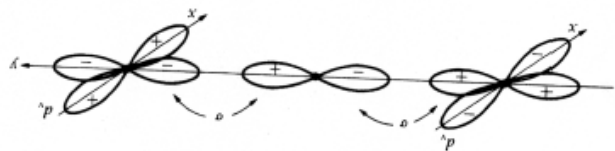
Effective Heisenberg interaction: $J_{AB} = -2\dfrac{t_{AB}^2}{U}$

Sign and value of superexchange depends on:

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

Some examples (Goodenough-Kanamori rules):
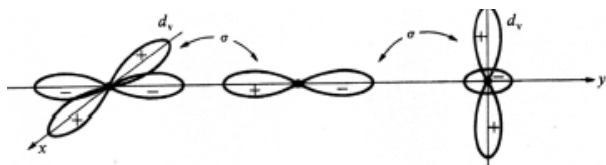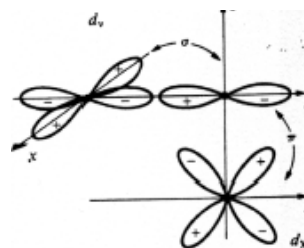
Antiferromagnetic superexchange
Strong: **weak:**
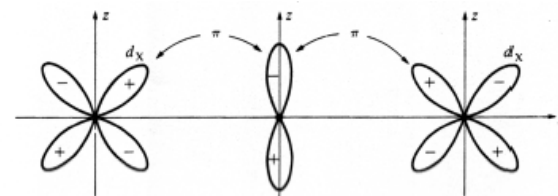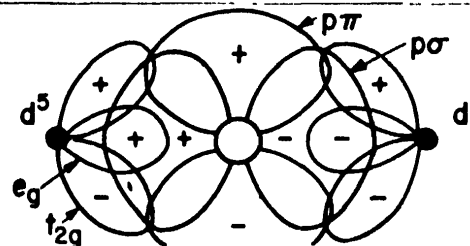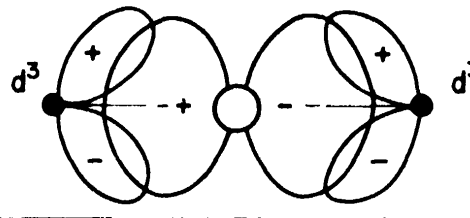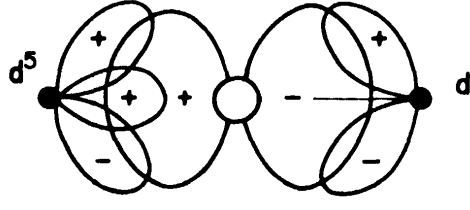

Ferromagnetic

90° coupling

2 diiferent orbitals

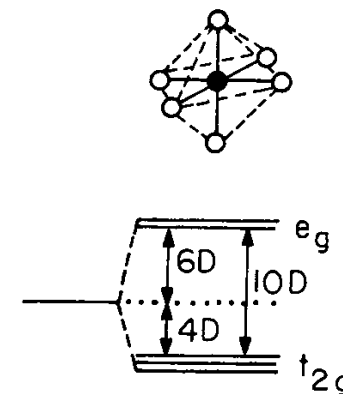| CASE	OUTER-ELECTRON CONFIGURATION	CORRELATION SUPEREXCHANGE		DELOCALIZATION SUPEREXCHANGE		SUM	STRENGTH °K (OXIDES)
		$p\sigma$	$p\pi$	$p\sigma$	$p\pi$		
#1	d^5 ... d^5	STRONG ↑↓	WEAK ↑↓	STRONG ↑↓	WEAK ↑↓	↑↓	~750
#2	d^3 ... d^3	WEAK TO MODERATE ↑↓	WEAK ↑↓	—	WEAK ↑↓	↑↓	≲300
#3	d^5 ... d^3	MODERATE ↑↑	WEAK ↑↓	MODERATE ↑↑	WEAK ↑↓	↑↓	~400

Fig. 42. Three possible 180° cation-anion-cation interactions between octahedral-site cations. (The $p\pi$ orbitals are not indicated in the diagrams for cases 2 and 3.)

d^5: Mn^{2+}, Fe^{3+} ; d^3: Cr^{3+}, V^{2+}

18

Goodenough: Magnetism and the chemical bond (1963)

<u>Caracteristics of superexchange</u> :

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

-Can be ferro or antiferromagnetic: usually AF, but not always

-depends on   - orbital occupation (nb of 3d-electrons, e_g or
                 t_{2g} character)
                 - A-O-B angle

-   Very common in oxides or sulfides

<u>Goodenough-Kanamori rules: empirical but most of the time   correct</u>

Exchange and ordering in magnetic materials

1-Origin of exchange

2- Exchange in insulators:superexchange and Goodenough-Kanamori rules

3- Exchange in metals: RKKY, double exchange, band magnetism

4- Magnetic ordering: different types of orderings, role of dimensionality, classical vs quantum spins
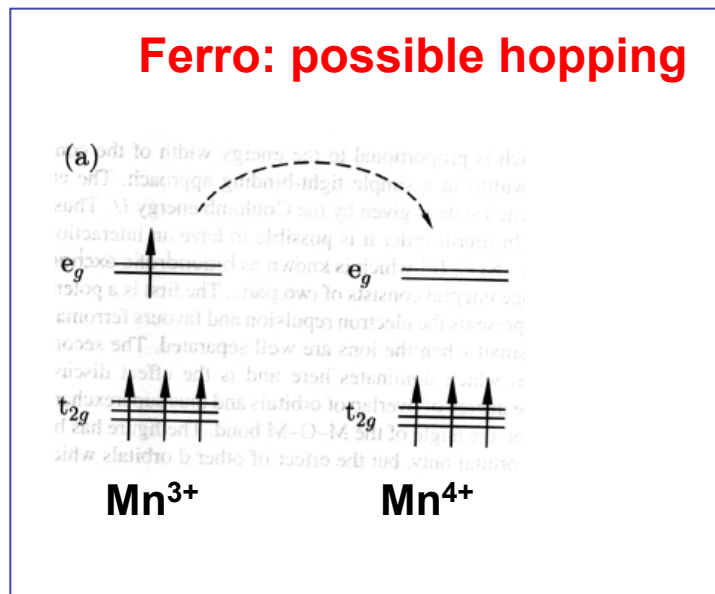
Double exchange in 3d metals

Metallic systems are often mixed valence: example of manganites:
$La_{1-x}Ca_xMnO_3$: coexistence of Mn^{4+} (3 electrons, S=3/2)
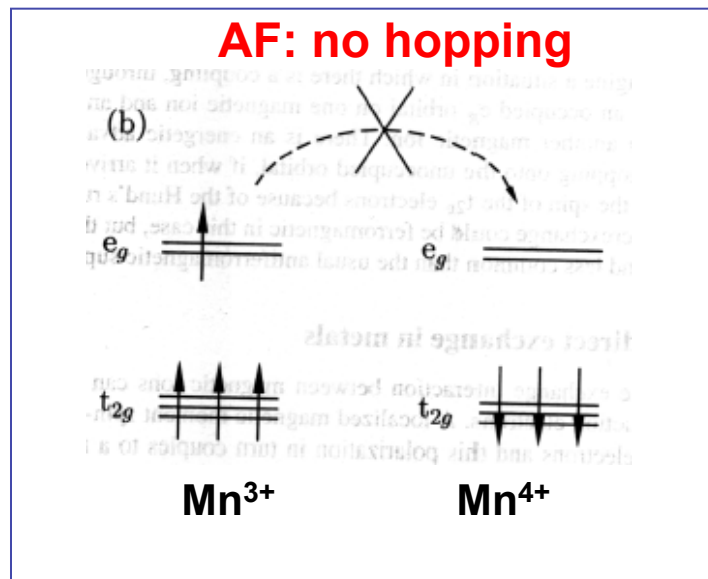and Mn^{3+} (4 electrons, S=2 , localized spin
3/2 + 1 conduction electron in e_g band)
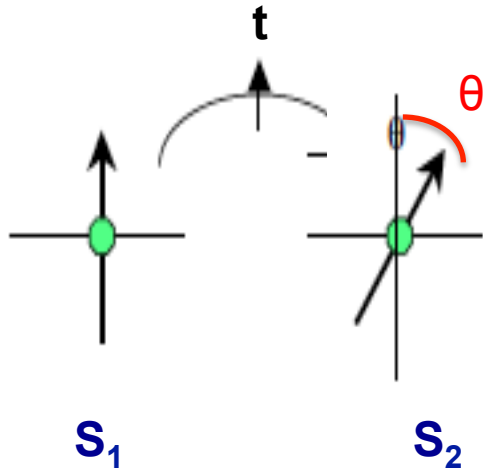

Ferro: possible hopping

AF: no hopping

Ferromagnetic interaction due to local Hund's coupling $- J_H S_i.s_i$
For large J_H : $E_F - E_{AF} \propto - t$ (hopping energy)

Toy model: 2 spins + conduction electron

$$H = -J_H\left(\vec{S_1}.\vec{\sigma_1} + \vec{S_2}.\vec{\sigma_2}\right) - t\sum_{\sigma}\left(c_{1\sigma}^+ c_{2\sigma} + h.c.\right)$$

$$H= \begin{bmatrix} -JS/2 & 0 & -t & 0 \\ 0 & +JS/2 & 0 & -t \\ -t & 0 & -JS/2\cos\theta & -JS/2\sin\theta \\ 0 & -t & -JS/2\sin\theta & +JS/2\cos\theta \end{bmatrix}$$
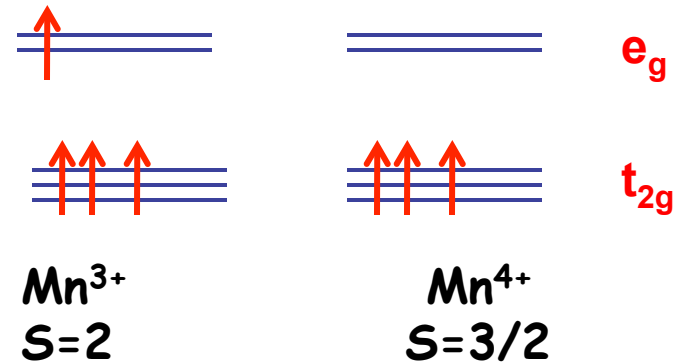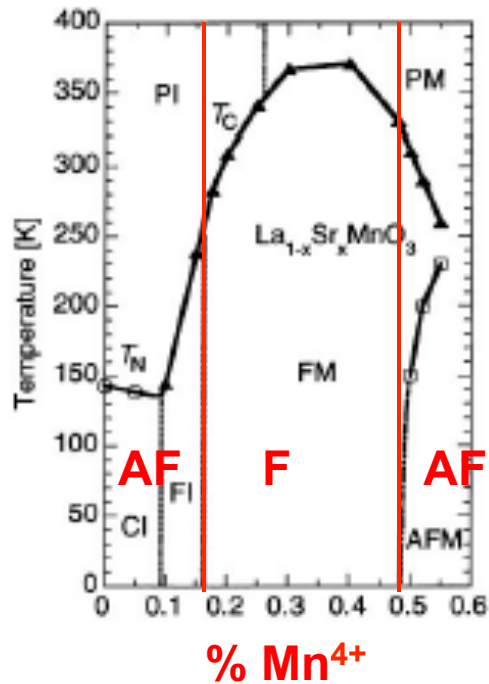
Lowest eigenvalue: $E = -\sqrt{(JS/2)^2 + t^2 + JSt\left|\cos\dfrac{\theta}{2}\right|}$

Small t/J: $-\dfrac{JS}{2} - t\cos\dfrac{\theta}{2}$ **small J/t:** $-t - \dfrac{JS}{2}\cos\dfrac{\theta}{2}$

Exchange energy (E(θ=π)-E(θ=0)) is given either by t or by J

But it is not of Heisenberg type $S_1.S_2$ (cos(θ/2), not cosθ)

22

Phase diagram of manganites

% Mn^{4+}

Mn^{3+}
S=2

Mn^{4+}
S=3/2

e$_g$

t$_{2g}$

Neighboring ions:

-2 Mn^{3+} ions: superexchange (AF)

-2 Mn^{4+} ions: superexchange (AF)

- Mn^{3+} - Mn^{4+}: double exchange (F)

Competition between: superexchange, double exchange
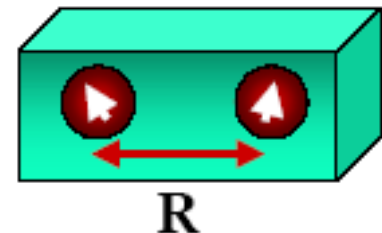
(+ Jahn-Teller effect)

Short range interactions

RKKY interactions (rare earths):

-In rare earth, 4 f states are localized $\Rightarrow$ no overlap with neighboring sites

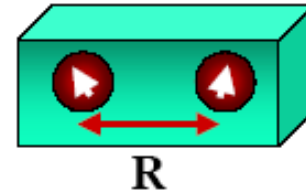-4f states hybridize with conduction band (6s, 5d) $\Rightarrow$ long range interactions

4f

5d 6s itinerant electrons
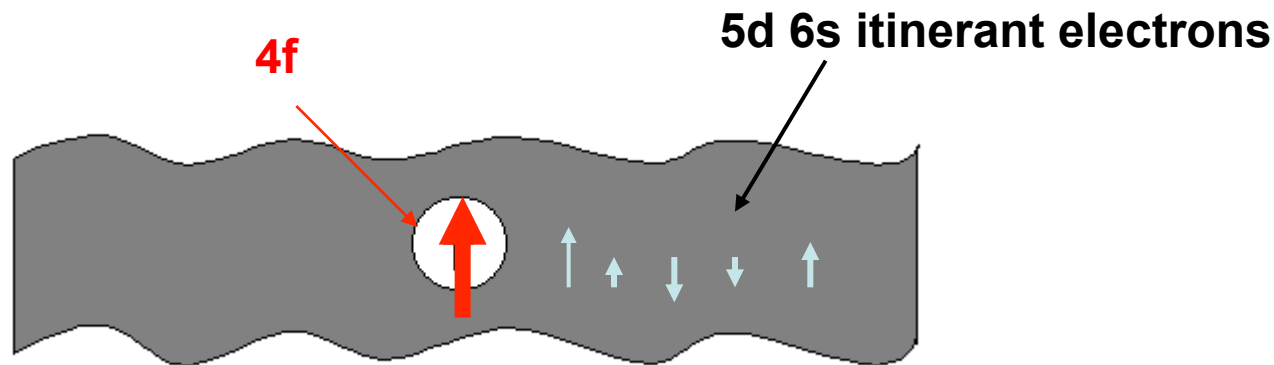
Interaction between 2 RE ions at distance R: transmitted by conduction electrons

R

Microscopic mecanism:

-Local interaction **J** between 4f spin S_i and conduction electron spin density $s(r)$: $- J(R_i-r)S_i.s(r)$
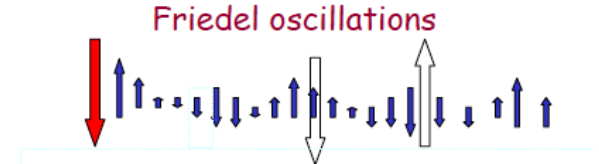
-$J(R_i-r)$ is local: $J\delta(R_i-r)$

R

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

- Induced polarization of conduction
- electrons at all sites: $m_j = \chi_{ij} h_i$

-where χ_{ij} is the generalized (non-local) susceptibility

Friedel oscillations

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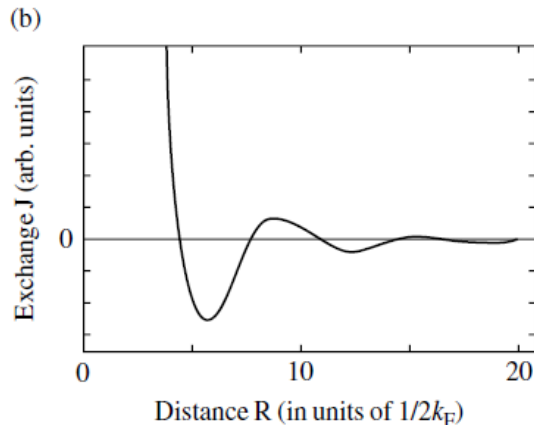$$E_{ij} \propto J^2\chi_{ij}S_i.S_j = J(R_i-R_j)S_i.S_j$$

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

Exchange J (arb. units)

Distance R (in units of $1/2k_F$)

- **Interaction is long range (≈ 1/R³)**

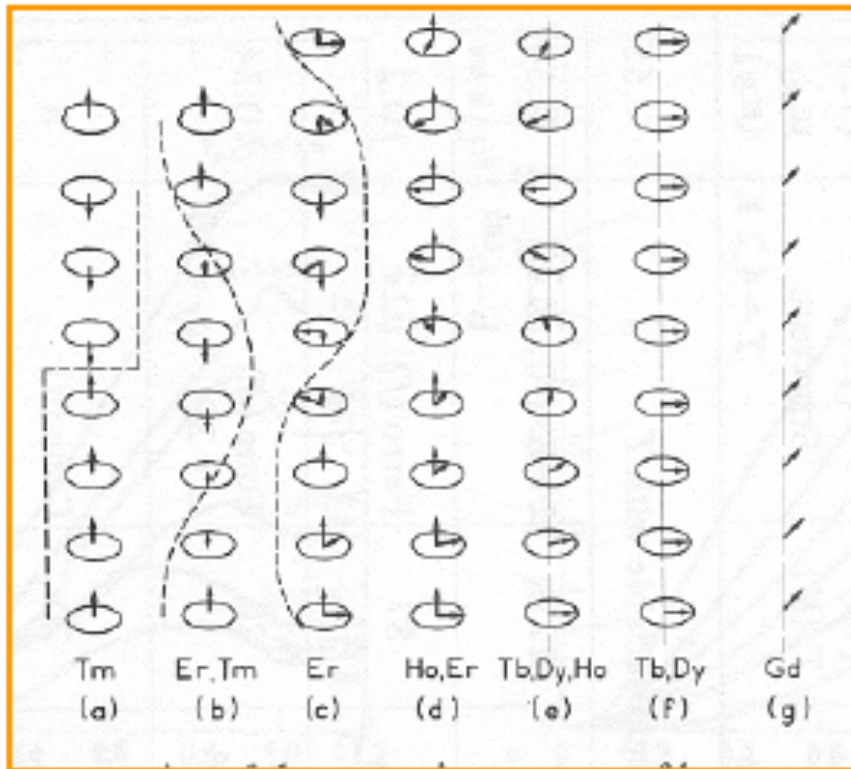- **caracteristic length ≈ 1/2k_F**

- Oscillating interaction

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

26

Magnetic structures of rare-earth metals:

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

Large variety of structures: Ferro, AF, helicoidal….
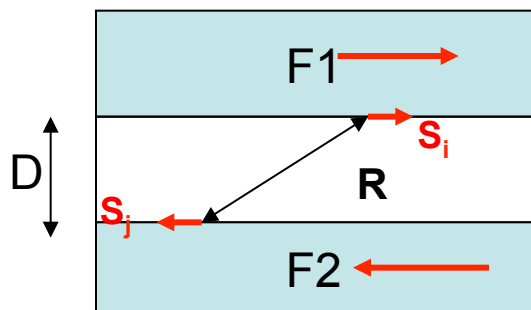
Long range + oscillating

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

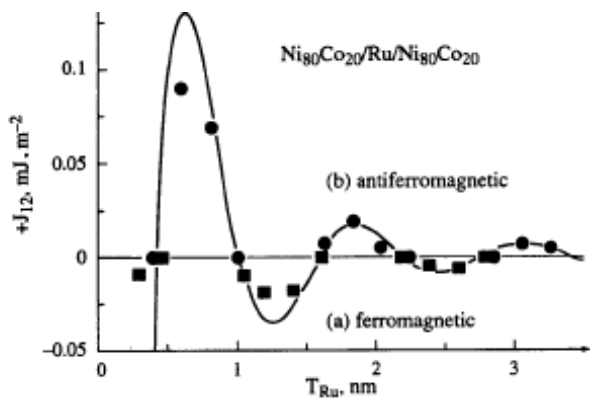in 2D: $\qquad J(r) \propto \dfrac{\sin(2k_F r)}{r^2}$

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

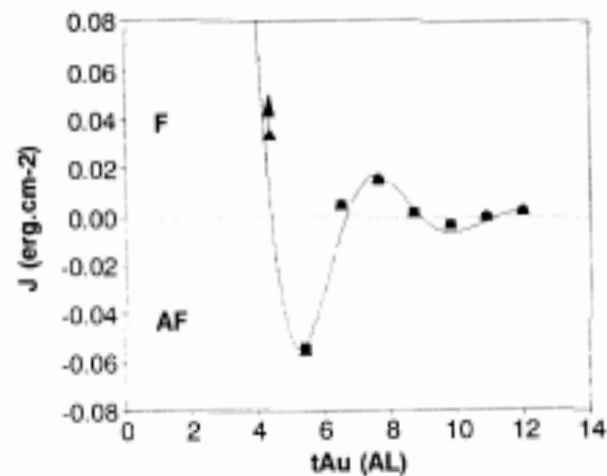# Oscillatory exchange between 2 ferromagnetic layers separated by a non magnetic layer

2 ferromagnetic layers F1 and F2 at distance D
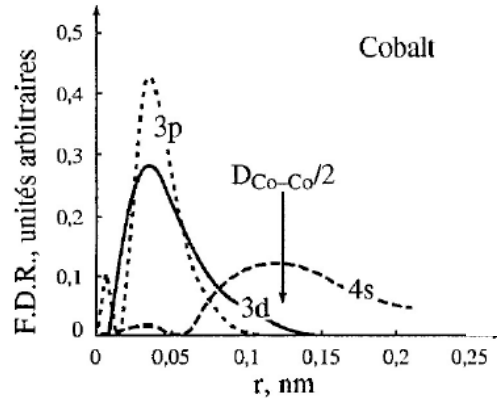
Sign of coupling is an oscillating function of D:

Trilayer Ni$_{80}$Cu$_{20}$/Ru/Ni$_{80}$Cu$_{20}$

Co/Au/Co

# Exchange interaction in 3d itinerant magnetic systems

Cobalt

In 3d: <u>overlap of 3d wave functions </u>of nearest neighbors atoms: metallic systems

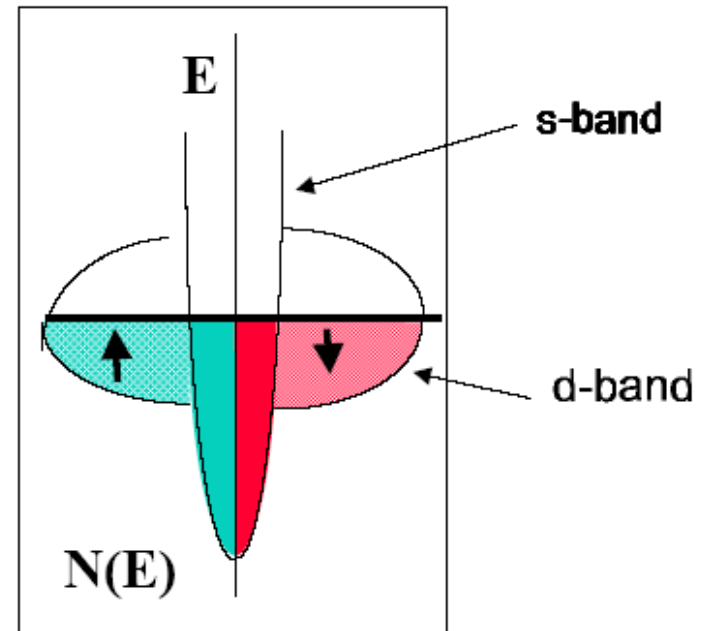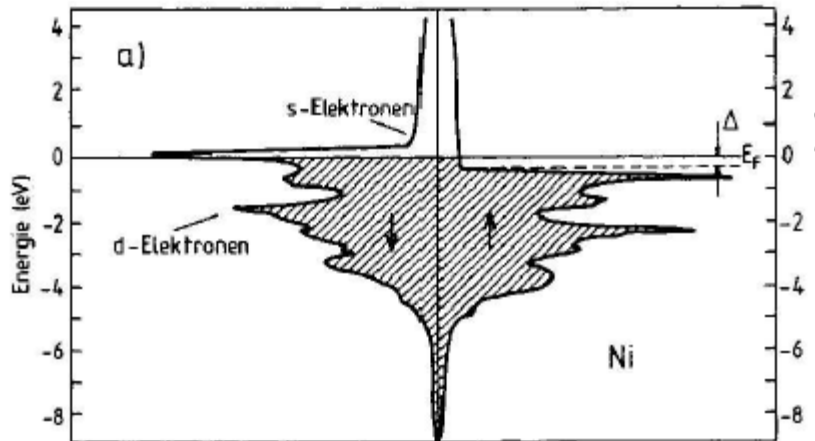⇒ **magnetic and kinetic energy are of the same order**: itinerant magnetism

Itinerant spin systems: magnetic moment is due to electrons in <u>partially filled bands </u>(3d band of transition metals)

metal	order	$m(\mu_B)$
Cr	af	0.6
Mn	af	1.0
Fe	ferro	2.2
Co	ferro	1.7
Ni	ferri	0.6
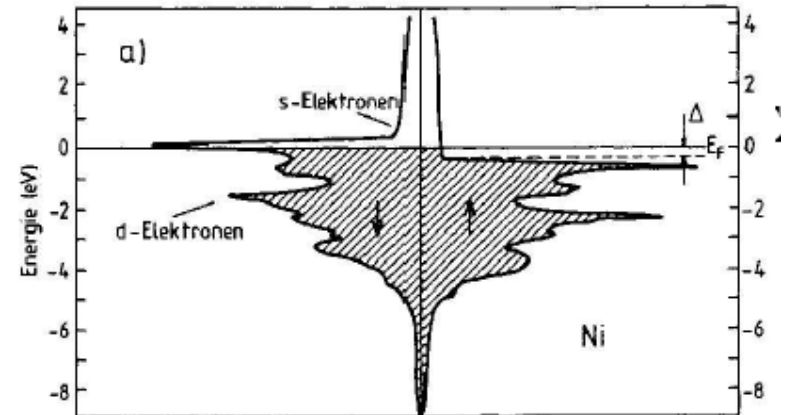
Magnetism of 3d metals: due to itinerant caracter of 3 d electrons

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≈W (few eV)

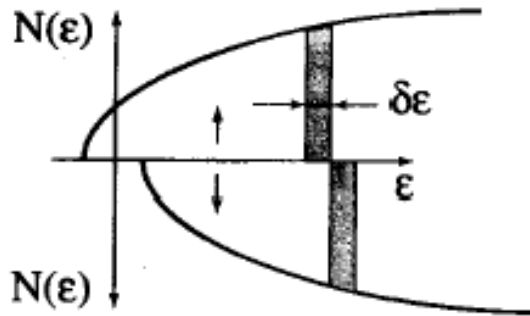$$\sum_{k\sigma} \varepsilon_k n_{k\sigma} \quad + \quad U n_{i\downarrow} n_{i\downarrow}$$

2 energies of the same order

Susceptibility of band electrons:

Magnetic field B splits the ↓ and ↑ spin bands: $\quad H_Z = -\vec{M}.\vec{B}$

$$\longrightarrow \quad \delta\varepsilon = \mu_B B$$

Induced magnetization: $\quad M = \mu_B(N_\uparrow - N_\downarrow) = 2\mu_B\rho(E_F)\,\delta\varepsilon$

Decrease of magnetic energy: $E_M = U n_\uparrow n_\downarrow = U\dfrac{N^2}{4} - U\rho(E_F)^2(\delta\varepsilon)^2$

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

Zeeman energy: $E_Z = -\vec{M}.\vec{B} = -2\mu_B\rho(E_F)B\,\delta\varepsilon$

$$\Delta E_{total} = \left(\frac{M}{2\mu_B}\right)^2 \rho(E_F)\big(1 - U\rho(E_F)\big) - MB$$

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

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

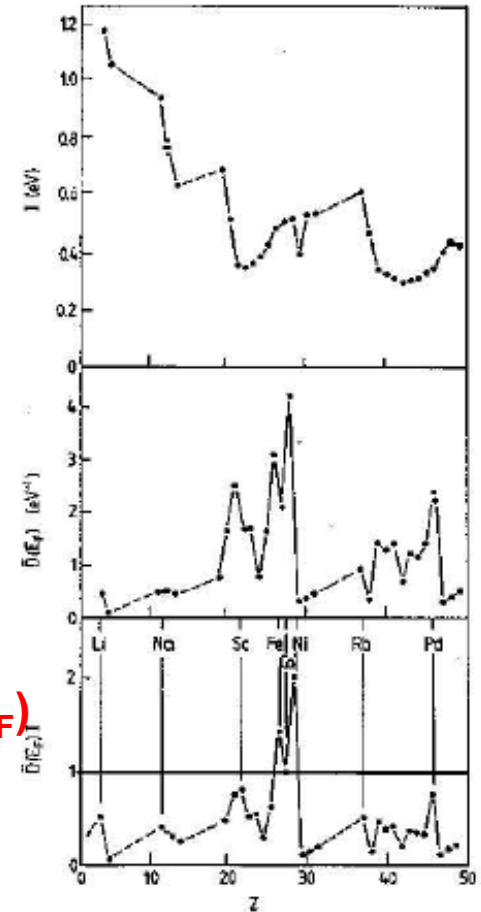Susceptibility is enhanced by the Stoner factor $S = 1 - U\rho(E_F)$

Paramagnetic state becomes unstable when $\boxed{U\rho(E_F) > 1}$

    - large U

    - or large density of states at the Fermi level

Stoner criterion is satisfied only for the 3d elements
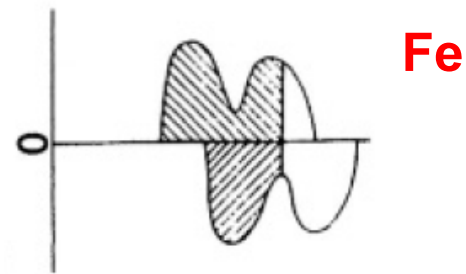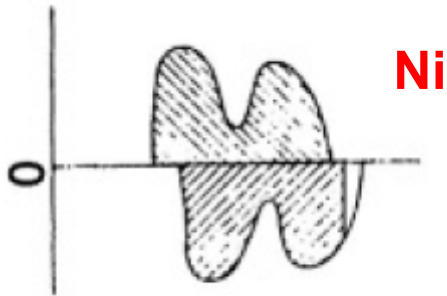

U

$\rho(E_F)$

$U\,\rho(E_F)$

<u>Itinerant ferromagnetism</u>:

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

Origin of magnetism: Coulomb interaction U

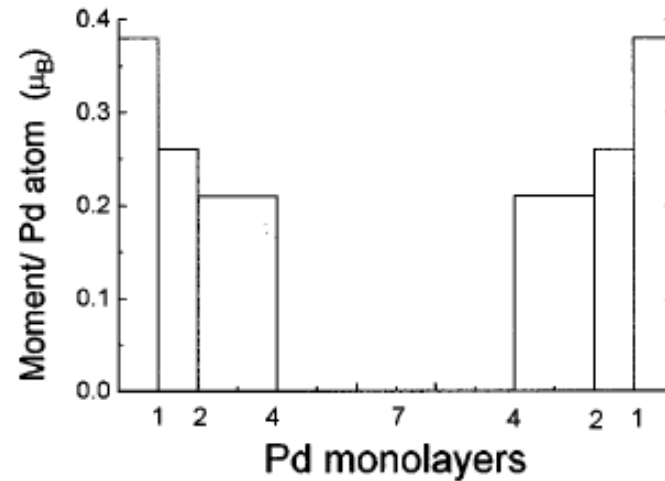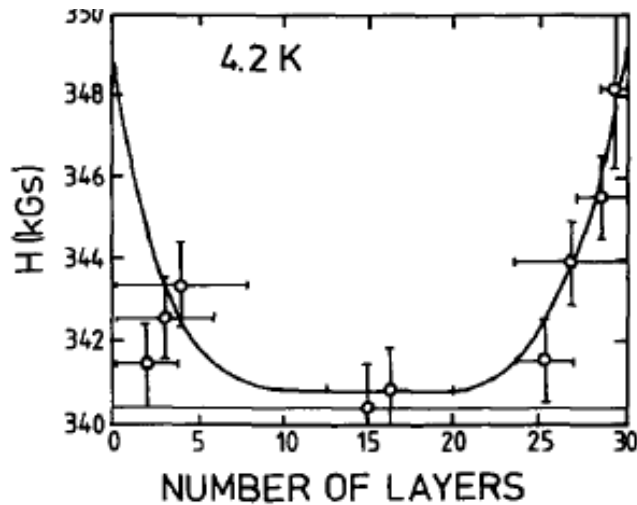Strong / weak ferromagnets

Ni

Fe

<u>Magnetic moments are non-integer</u>
For pure transition metals: Fe $\rightarrow$ $m_0 \approx 2.2$ μ_B / atom
                            Co $\rightarrow$ $m_0 \approx 1.8$ μ_B / atom
                            Ni $\rightarrow$ $m_0 \approx 0.64$ μ_B / atom

Magnetism of impurities in metals: (i.e. Fe, Co, Ni in no-magnetic metals Al, Cu, Ag….)

- Impurity is magnetic if Stoner criterion is satisfied locally: $U\rho_i(E_F) > 1$
- $\rho_i(E_F)$ depends on surroundings

Magnetic moment of Fe in a 30 layers film

Magnetic moment of Pd in Fe/Pd multilayers

-Magnetism can be enhanced or supressed near a surface or interface (coordination, crystal field, electronic structure….different near surface)

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

Magnetic moment of Fe determined by atomic rules:

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

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

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

<u>Fe-compounds:</u>

- FeO (Fe^{2+}): $m_{eff} = 5.33$ → partial quenching of orbital moment (if total quenching, spin only magnetism → m_{eff} = 4.9) (AF)

- γFe_2O_3 (Fe^{3+}): $m_0 = 5 \mu_B$ (ferrimagnetic)

- α-Fe (metal): m_0=2.2 μ_B (ferromagnet)

- YFe_2 (metal): m_0=1.45 μ_B (ferromagnet)

- YFe_2Si_2 : Fe is non-magnetic (enhanced paramagnet)

- FeS_2 : diamagnetic

- Fe surface: m_0=2.8 μ_B

Rare earth-transition metal compounds

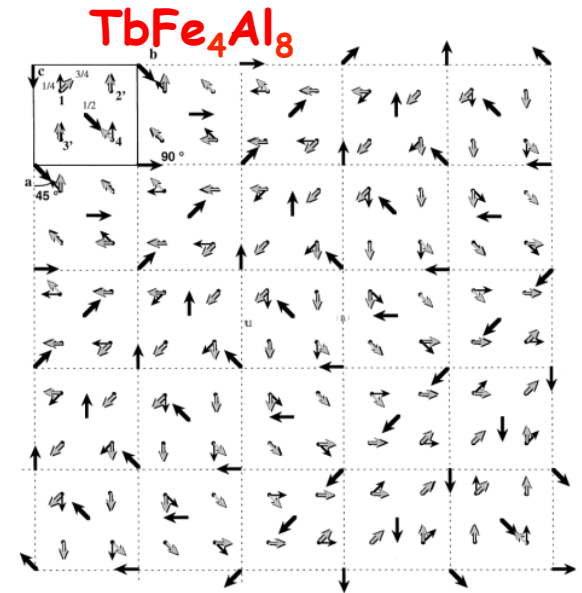2 magnetic sublattices:

M-M interactions: 'band magnetism'

M-R interactions: through d-electrons (3d-5d)

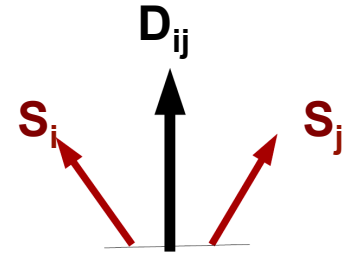R-R interactions: RKKY

⇒ complex magnetic ordering:
- non colinear
- incommensurate
- frustration

⇒ large variety of properties
(possibility of large anisotropy , large
Magnetization, and strong interactions)

$TbFe_4Al_8$

$Nd_{0.5}Tb_{0.5}Co_2$

Other interactions between magnetic moments:

- **Anisotropic exchange** $J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta$ **due to spin-orbit coupling** $(J_{ij}^{\alpha\beta} = J_{ij}^{\beta\alpha})$

- **Dzyaloshinskii-Moriya interacions:** $\overrightarrow{D_{ij}} \cdot (\overrightarrow{S_i} \times \overrightarrow{S_j})$

    - **Due to spin-orbit coupling**
    - **Present when no inversion center**
    - **favors non-colinear structure**

- **Biquadratic exchange** $J_{bq} \overrightarrow{(S_i \cdot S_j)}^2$ **for spins > ½**

The largest interaction is the Heisenberg exchange, other interactions are usually perturbations

$$H = -\sum_{ij} J_{ij} \, \overrightarrow{S_i} \cdot \overrightarrow{S_j}$$