

Continuance from 1.2

Heisenberg Hamiltonian

Spin-dependent energy arising from the Pauli exclusion principle is modeled as a spin - spin interaction in a vector model :

$$H = - \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad J: \text{Exchange integral}$$

This expression is universally known as the Heisenberg Hamiltonian.

Parallel spin orientation for $J > 0$

Antiparallel spin orientation for $J < 0$

Molecular field approximation

Because of the small spatial extent of atomic wave functions, especially in insulators, it is sufficient only nearest-neighbor interactions in the above expression

$$E_{exch} = -J \sum_{i < j}^{nn} \mathbf{S}_i \cdot \mathbf{S}_j \quad E_{exch}^i = -J S_i \sum_j^{nn} S_j \quad E_{exch} = \frac{1}{2} \sum_i E_{exch}^i$$

$$E_{exch}^i = -J S_i \sum_j^{nn} S_j = -g \mu_B H_{eff} \langle S_i \rangle$$

$$H_{eff} = J \sum_j^{nn} S_j / g \mu_B \approx J z \langle S_j \rangle / g \mu_B = [J z / N (g \mu_B)^2] I \quad (I = N g \mu_B \langle S_j \rangle)$$

$$= w I$$

z : number of nearest neighbor atoms

N : Number of atoms per unit volume

$w = Jz/N(g\mu_B)^2$: Molecular field of Weiss

Curie temperature

According to Molecular field theory, Curie temperature is given by

$$T_c = \Theta = Cw,$$

where, $C = N\mu_{\text{eff}}^2/3k_B$ and $\mu_{\text{eff}}^2 = g^2\mu_B^2S(S+1)$

By using $w = Jz/N(g\mu_B)^2$ we obtain

$$T_c = J z S (S + 1) / 3 k_B$$

T_c is proportional to J .

Spinel Ferrites

The electrons in oxides are localized around atoms, and the electronic states in oxides are more atomic like than metals. Thus, the electrons in oxides can be described by the same quantum numbers that apply to isolated atoms. **Spinel ferrites are the typical oxide ferromagnets.**

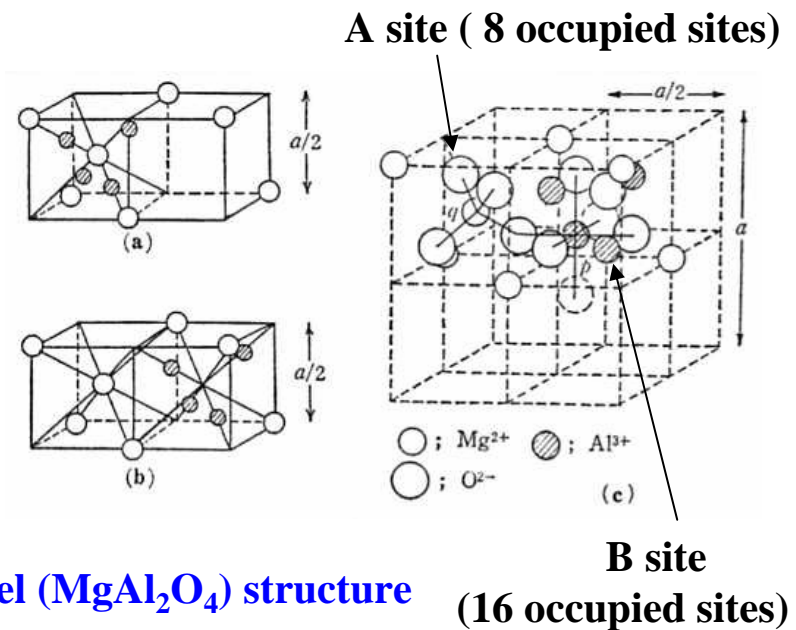
Spinel ferrites: MFe_2O_4 , $M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$

There are two distinct types of sites for transition metal ions occupancy, **tetrahedral (A) sites** and **octahedral (B) sites**.

	A site (Tetrahedral)	B site (Octahedral)
Normal spinel	M^{2+}	$Fe^{3+} \quad Fe^{3+}$
Inverse spinel	Fe^{3+}	$M^{2+} \quad Fe^{3+}$

Normal spinel: $M = Zn$

Inverse spinel: $M = Mn, Fe, Co, Ni, Cu$



Magnetic moment of spinel ferrites

Exchange interactions is superexchange interaction through an oxide atom;
A-O-B and B-O-B




A-B coupling : negative

B-B coupling : negative

$$| \text{A-B coupling} | > | \text{B-B coupling} |$$



Magnetic moments of spinel ferrites

Ex.1) $\text{Fe}_3\text{O}_4 = \text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$: **Inverse**

A site	B site	
Fe^{3+}	Fe^{3+}	Fe^{2+}
		
$3d^5$	$3d^5$	$3d^6$
$S = 5/2$	$S = 5/2$	$S = 2$
$\mu = 5\mu_B$	$\mu = 5\mu_B$	$\mu = 4\mu_B$

Magnetic moment $\mu (\text{Fe}_3\text{O}_4) = 4\mu_B$

Ex.2) $\text{ZnFe}_2\text{O}_4 = \text{Zn}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ **Normal**

A site	B site	
Zn^{2+}	Fe^{3+}	Fe^{3+}
$3d^{10}$	$3d^5$	$3d^5$
$S = 0$	$S = 5/2$	$S = 5/2$
$\mu = 0$	$\mu = 5\mu_B$	$\mu = 5\mu_B$
		

Magnetic moment $\mu (\text{ZnFe}_2\text{O}_4) = 0$:
Antiferromagnet

Site preference

Consider the composition of $(\text{T}^{2+})_{1-x}(\text{Zn}^{2+})_x(\text{Fe}^{3+})_2\text{O}_4$

Zn^{2+} ions have a stronger normal tendency than any of the ions shown, particularly stronger than Fe^{3+} . Thus, Zn^{2+} preferentially occupies A sites, driving the A site Fe^{3+} ions to B sites. The magnetic moment per formula unit is given by

$$\begin{aligned}\mu &= 5(1+x) + \mu_T(1-x) - 5(1-x) \\ &= 10x + \mu_T(1-x)\end{aligned}$$

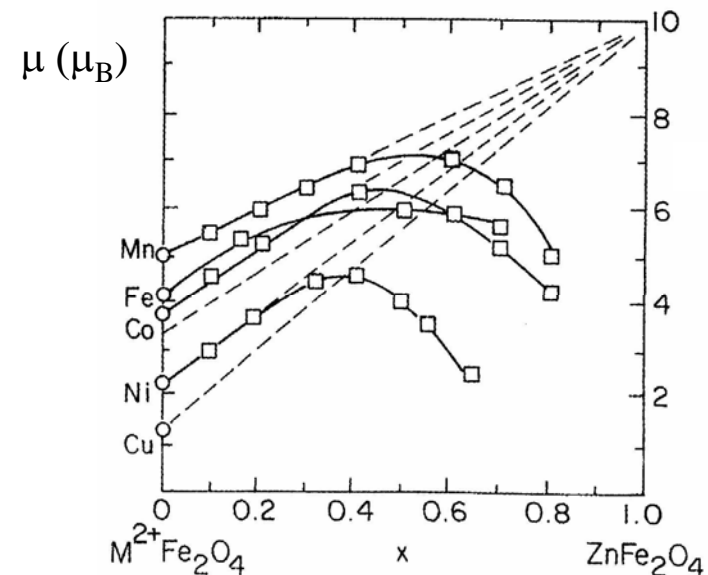
With increasing x , the moment is predicted to increase linearly toward $10 \mu_B$. These lines describe the data fairly well until $x \sim 0.3 - 0.4$.

At large Zn concentrations the A sites have no magnetic moments and the antiferromagnetic B – B interactions start flipping those B site Fe^{3+} moments. Thus, the moment starts to decrease.

Summary

For oxides or ionic solids, the valence electronic configuration is a good measure of the magnetic moment localized on a atomic or ionic sites.

	A site	B site
	$\text{Zn}^{2+}_x \text{Fe}^{3+}_{1-x}$	$\text{T}^{2+}_{1-x} \text{Fe}^{3+}_{1+x}$
moment	$5(1-x)$ ↓	$\mu_T(1-x) + 5(1+x)$ ↑ ↑



1.3 Itinerant electron magnetism

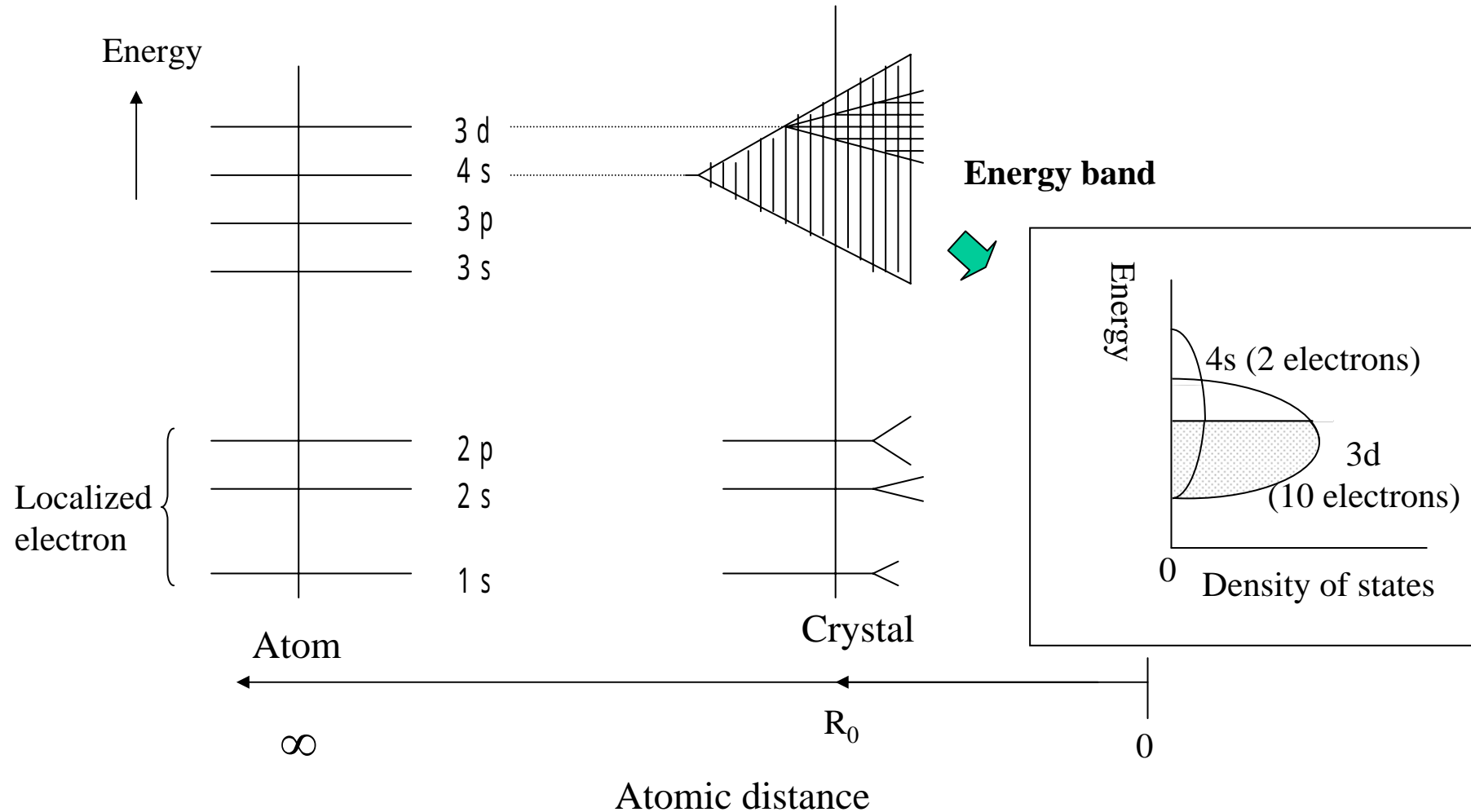
In the last sections 1.1 and 1.2, magnetism in atoms as well as in oxides is considered, where the electrons remain fairly well localized on the atomic or ionic sites;

There is little hopping or itinerant character in the valence electrons.

In this case the electronic states of the ions are atomic like and Hund's rules provide a good starting point for determining ionic moments.

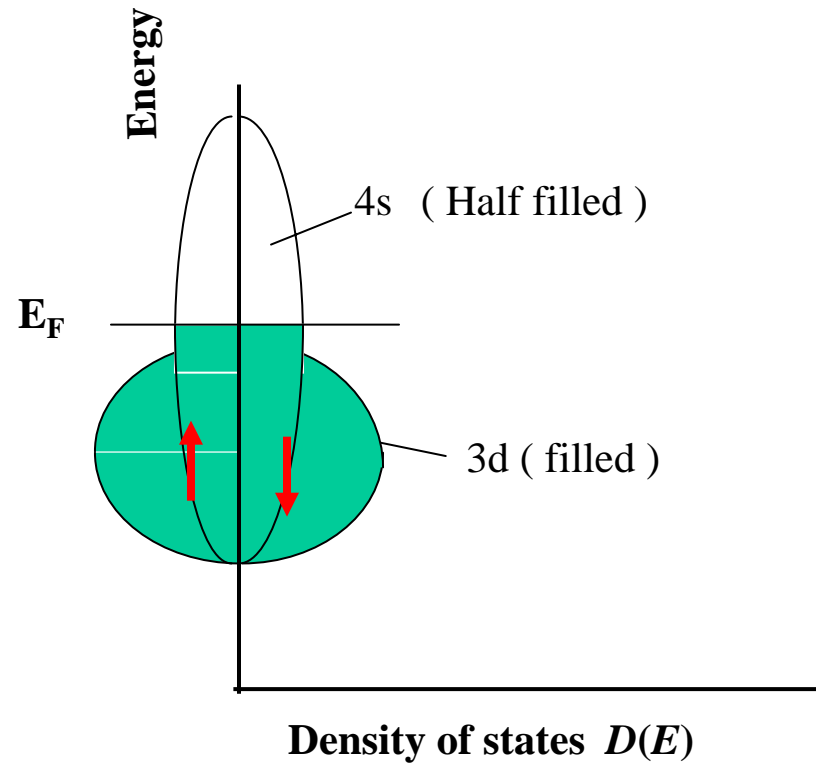
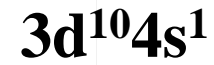
In this section the magnetism in **metals** is considered, in which electrons from two or more sites occupy a common band, covalent or metallic. The difficulty in treating transition metals in terms of their electronic structure comes from the fact that **d electrons in metals are neither free electrons nor atomic-like.**

Energy levels in a free atom and a solid



Bradening of atomic levels into bands when atoms are brought together to form solids.

Band structure of Cu



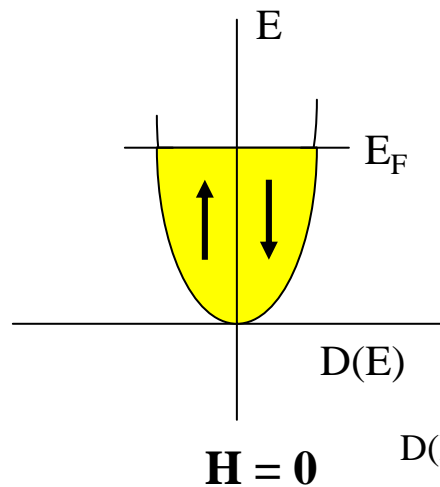
There is no spin polarization: Diamagnetism

Magnetism due to conduction electrons

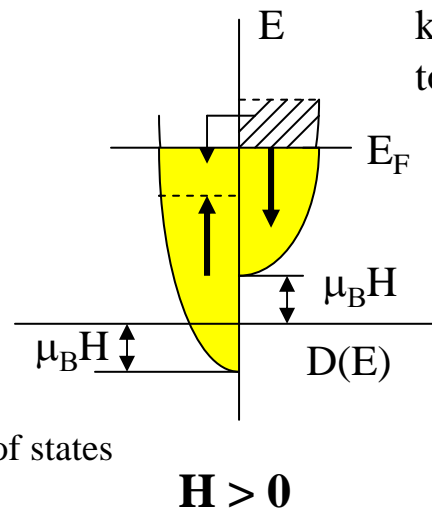
What happens if the magnetic electrons are not localized at the atomic sites ?

Unpaired magnetic electrons except for the lanthanides are usually outer electrons and so are unlikely to be closely bound to the atoms. We therefore need a theoretical description of magnetism due to itinerant electrons. → **Band theory**

Pauli paramagnetism of free electrons



$D(E)$: density of states



Only electrons within an energy $k_B T$ of the Fermi level are able to change orientation.

Only the fraction T/T_F of the total number of electrons can contribute the magnetization, where T_F is the Fermi temperature, defined such that $E_F = k_B T_F$

The number density of electrons parallel to the field is

$$N_+ = \frac{1}{2} \int_{-\mu_B H}^{E_F} f(E) D(E - \mu_B H) dE \approx \frac{1}{2} \int_0^{E_F} f(E) D(E) dE + \frac{1}{2} \mu_B H D(E_F)$$

$$N_- = \frac{1}{2} \int_{+\mu_B H}^{E_F} f(E) D(E + \mu_B H) dE \approx \frac{1}{2} \int_0^{E_F} f(E) D(E) dE - \frac{1}{2} \mu_B H D(E_F)$$

$$\chi_{Pauli} = I / H = (N_+ - N_-) \mu_B / H = \mu_B^2 D(E_F)$$

$$f(E) = \exp[1 - (E - E_F) / kT]^{-1}$$

Fermi-Dirack distribution of electrons

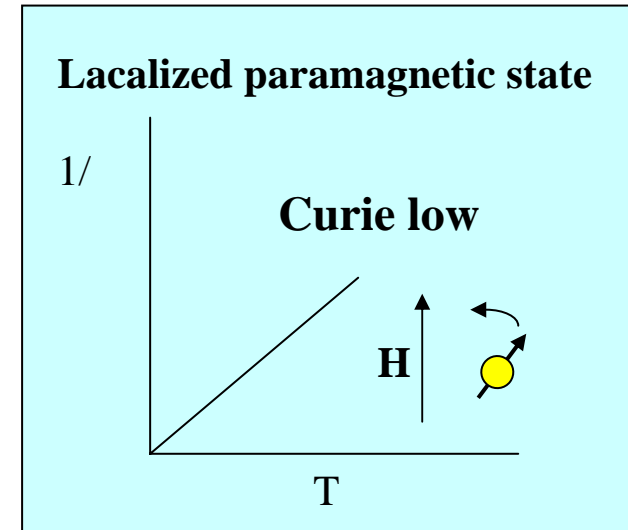
The free electron density of states at E_F is given by

$$D(E_F) = 3N / 2E_F$$

Thus,

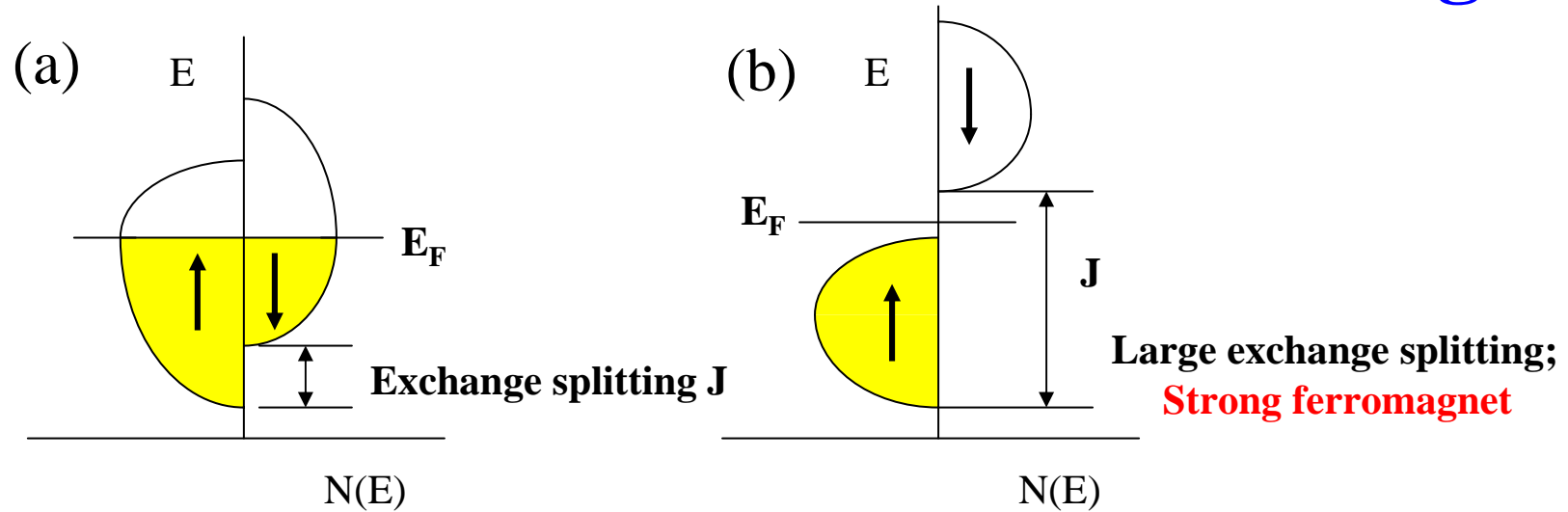
$$\chi_{Pauli} = 3\mu_B^2 N / 2E_F \quad (1.3.1)$$

N: Number of electrons per unit volume



Pauli Susceptibility
Temperature independent

Schematic band structure of a ferromagnet

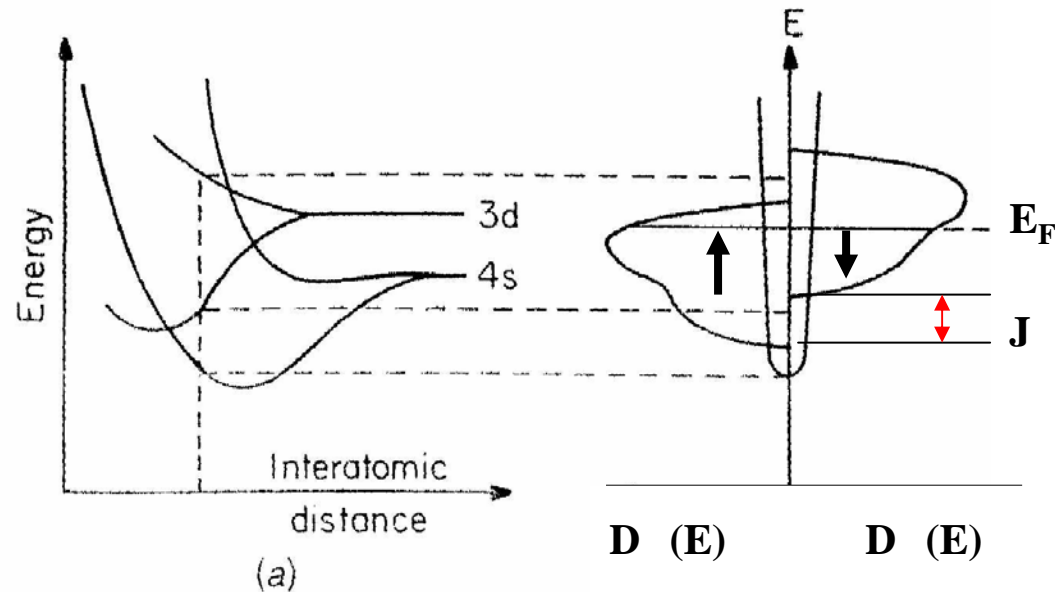


- The interatomic exchange interaction requires a shift in the spin-up and spin-down parts of the d band relative to each other. Electrons fill up the band by occupying the lowest energy levels first.
- Magnetic moments arise from unpaired electrons; $\mu = (n_{\uparrow} - n_{\downarrow})\mu_B$
Non integer magnetic moment per atom is obtained.

The larger the exchange energy the greater the difference in energy between up- and down-spin bands. **A large exchange splitting** can lead to a separation between the up- and down spin bands as shown in (b). This leads to the **integer magnetic moment per atom**.

Condition for ferromagnetism

- Stoner criterion for ferromagnetism -

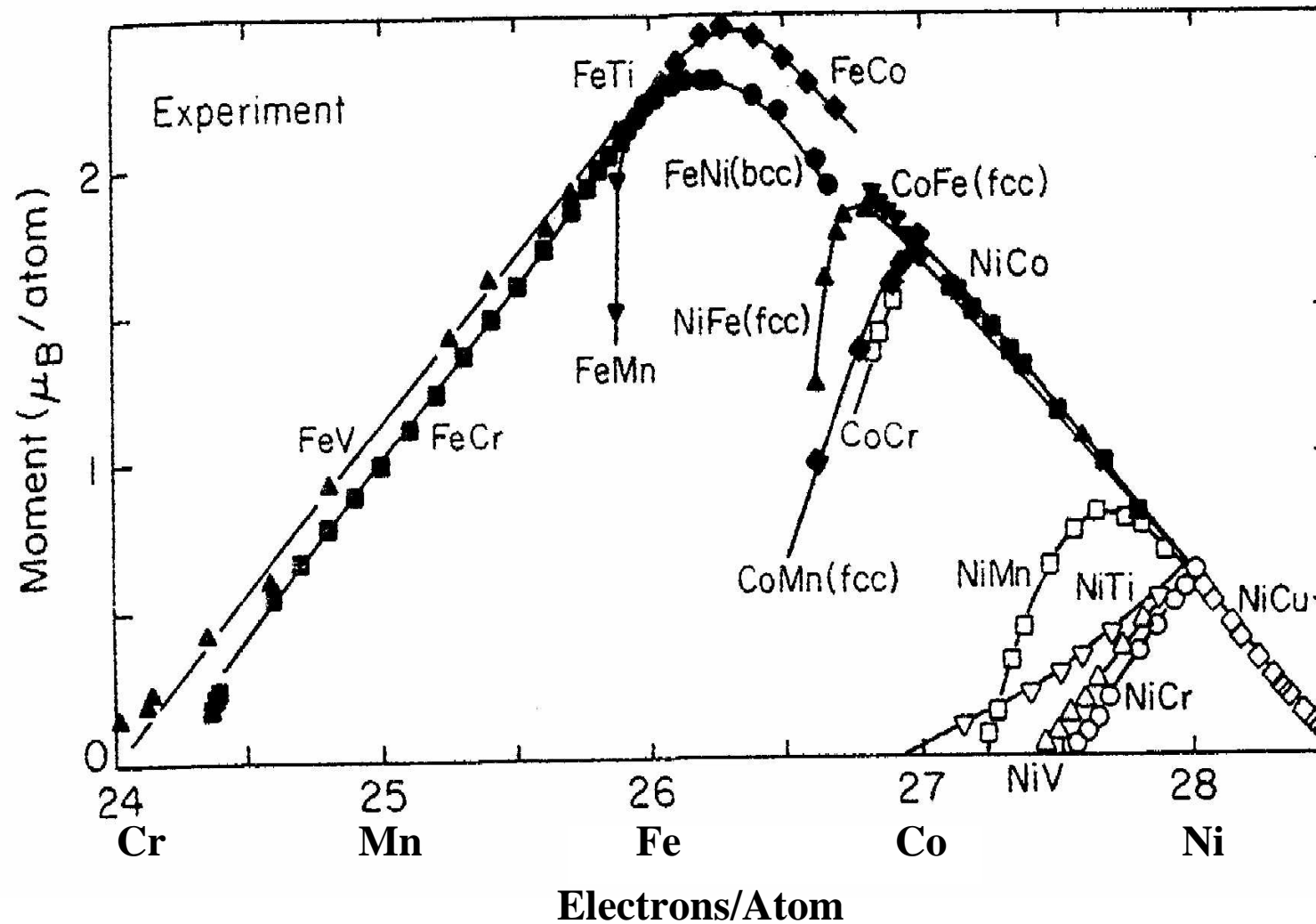


Stoner criterion;

$$J(E_F) D(E_F) > 1 : \text{Ferromagnetism}$$

—→ This suggests that d-electron systems is easy to exhibit ferromagnetism.

Slater - Pauling curve



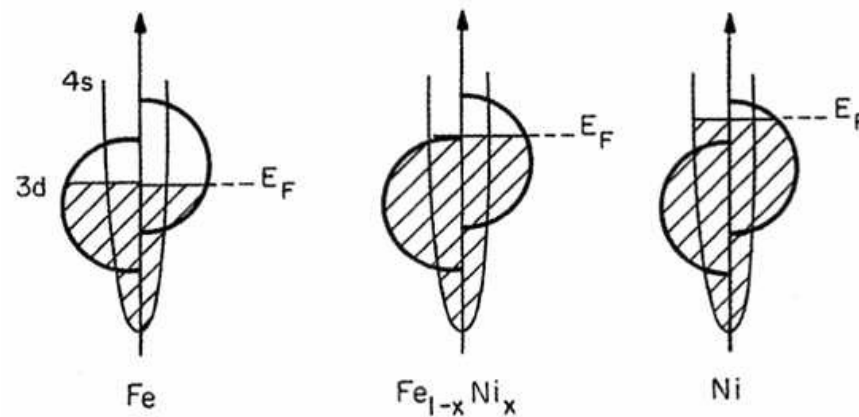
Fe: $2.2 \mu_B$

Co: $1.7 \mu_B$

Ni: $0.6 \mu_B$

Rigid band model

The s and d bands are rigid in shape as atomic number changes. This simplifies modeling the behavior of different alloys by simply moving E_F up or down through the bands according to the number of electrons present.



This premise of the rigid-band model is not correct. Nevertheless, this model can account for some trends in physical properties on alloying, and thus serves as a starting point for qualitative discussion of alloying effects.

Magnetic properties of 3d band electrons

The magnetic moment μ per atom of an alloy is given the spin imbalance $\mu = (n_{\uparrow} - n_{\downarrow})\mu_B$. In transition metal alloys the net spin imbalance is due mostly to the d electrons. Thus

$$\mu \sim (n_{d\uparrow} - n_{d\downarrow})\mu_B.$$

When the Fermi level lies above the top of the up-spin band (strong ferromagnets), the magnetic moment per atom may be simply calculated.

For $n_{d\downarrow} = 5$

$$\mu \sim [5 - (n_{d\downarrow} - 5)]\mu_B = (10 - n_{d\downarrow})\mu_B$$

$$n_{d\downarrow} = n_{d\uparrow} + n_{d\downarrow}$$

For strong ferromagnets this equation is a straight line with slope -1 , as in the Slater - Pauling curve.

For the alloy $A_{1-x}B_x$ $n_d^{\text{alloy}} = (1-x)n_d^A + x n_d^B$

If the atomic number of species B differs from that of A by ΔZ , then $n_d^B = n_d^A + \Delta Z$. Thus,

$$n_d^{\text{alloy}} = (1-x)n_d^A + x(n_d^A + \Delta Z) = n_d^A + x\Delta Z$$

$$\mu^{\text{alloy}} = (10 - n_d^A - x\Delta Z)\mu_B$$

$$= (\mu_{\text{host}} - x\Delta Z)\mu_B \quad \text{for strong ferromagnets}$$

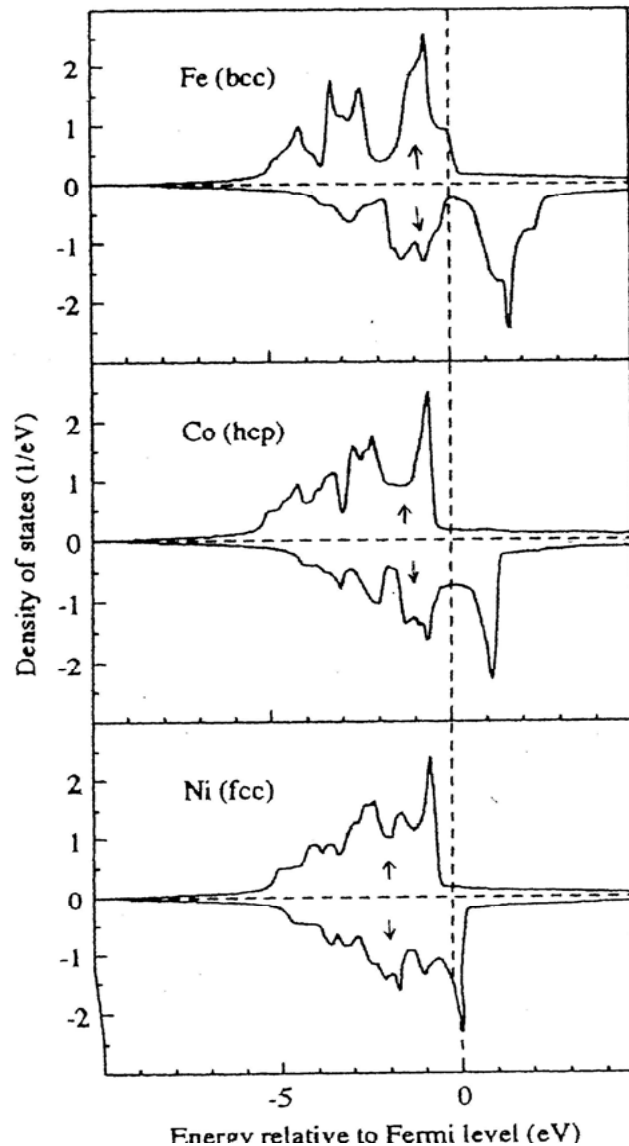
The rigid band model affords a simple explanation for the compositional dependence of μ in strong ferromagnetic alloys over broad concentration ranges such as in Ni-Fe and Ni-Co alloys ($\Delta Z = -1$).

The rigid band model fails for $|\Delta Z| \geq 2$ as in the case for Mn, Cr, V in Co or in Ni (see Slater - Pauling curve).

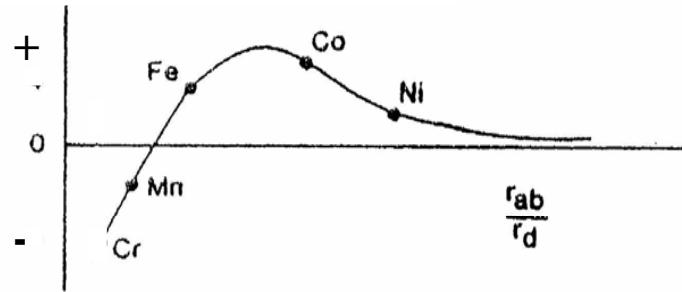
Density of states in ferromagnets

First principle
calculation

The rigid band model
is not correct in fact.



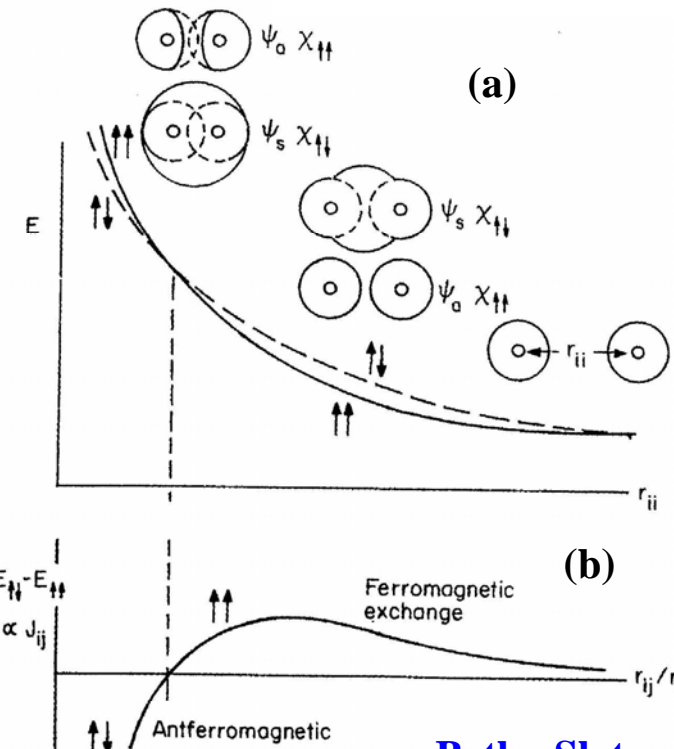
Exchange Integral



$$J_{ij} = \int \phi_i^*(1) \phi_j^*(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \phi_i(2) \phi_j(1)$$

ϕ_i is a atomic wave function
1 and 2 are electrons.

The **Bethe-Slater curve** represents the variations of the exchange integral with interatomic spacing r_{ab} and radius of unfilled d shell r_d .



Bethe-Slater curve

(a) Dependence of energy for spatially symmetric and antisymmetric wave functions versus atomic separation r_{ij} .

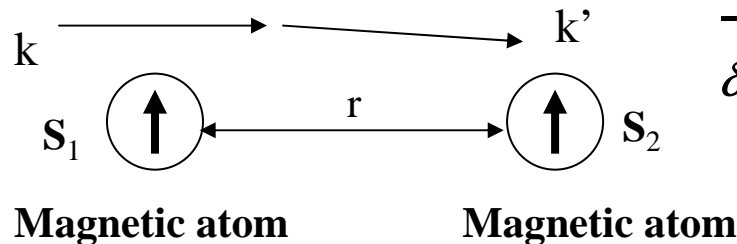
(b) Energy difference versus r_{ij} normalized to d-electron radius (r_d).

Indirect exchange interaction

In rare-earth metals and alloys, the magnetic moments are determined by the partial filling of the highly localized 4f states. The valence states are $5d^1 6s^2$. Many rare - earth metals and alloys order magnetically . **How is the magnetic moment on rare-earth metal site couple to that on another site ?** Heisenberg exchange interaction is small due to the localized 4f electrons. For the magnetically ordered states some electron hopping, or exchange from site to site are required.

Conduction electrons mediate the exchange interaction.

Conduction electron
with spin s and wave
vector k



$$-J_{kk'} S_1 \cdot S_2 \sim -J \delta(r) S_1 \cdot S_2, \\ \delta(r) \neq 0 \text{ for } r = 0$$

RKKY interaction

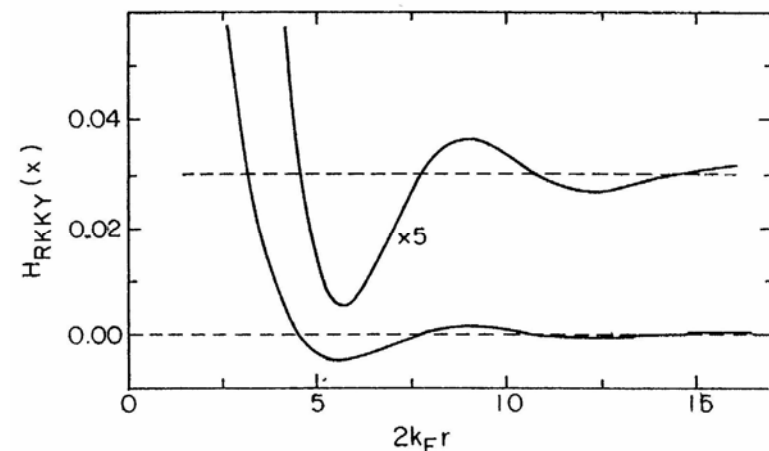
The exchange Hamiltonian is

$$H_{\text{RKKY}}(r) = [(3N/16\pi^2) J^2/E_F] F(r) (S_1 \cdot S_2)$$

$$F(r) = -16\pi k_F^3 [2k_F r \cos(2k_F r) - \sin(2k_F r)] / (2k_F r)^4$$

Attenuation with a oscillation period of $1/2k_F$

→ Ferromagnetic, antiferromagnetic, sinusoidal and helical arrangements of the localized magnetic moments under different conditions.



Hubbard model

The local moment and the itinerant electron models have limitations. However, ferromagnetic metals, particular the 3d transition metals, have features that are characteristic of both types of model.

Temperature dependent susceptibility : indicative of a local moment model

Nonintegral magnetic moment: characteristic of itinerant electron model

These apparent contradictions have been resolved by the **Hubbard model**.

$$H = H_0 + H' = \sum_{(i,j)\sigma} (t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + h.c) + U \sum_j n_{j\uparrow} n_{j\downarrow}$$

Electron hopping

On site correlation

U: Coulomb energy

The detail for this is out of scope of the lecture.