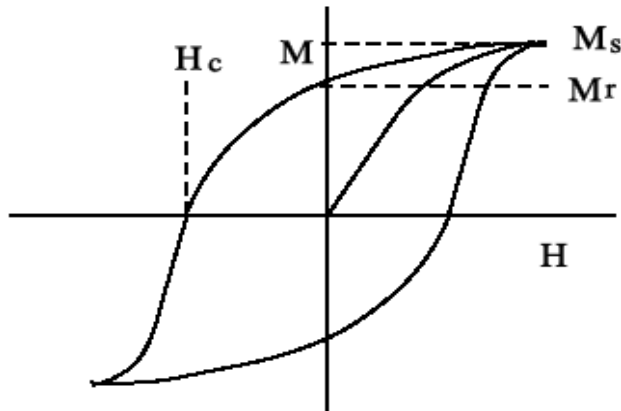# **Lecture contents**

- Ferromagnetism
  - Molecular field theory
  - Exchange interaction

Ferromagnetism – Molecular field theory

- Spontaneous magnetization occurs in some (Ferromagnetic) materials composed of atoms with unfilled shells

- For some reason magnetic moments are aligned even at relatively high temperature

- <u>Hypothesis:</u> magnetic order is due to strong local magnetic field (Weiss effective field) at the site of each dipole

$$B_{loc} = B_a + \mu_0 \gamma M$$

    with a constant γ

- Consider a collection of N identical atoms per unit volume, with total angular momentum J, and use QM treatment of atomic paramagnetism

$$\boxed{M = M_{sat} B_J (y)} \qquad M_{sat} = N \mu_{eff}$$

with $\quad y = \dfrac{\mu_{eff} B_{loc}}{k_B T} \equiv \dfrac{\mu_{eff} (B_a + \mu_0 \gamma M)}{k_B T} = \dfrac{g_J \mu_B J (B_a + \mu_0 \gamma M)}{k_B T}$

Values of Curie temperatures and spontaneous magnetism (at 0 K in Gauss) for a few ferromagnetic materials

(a)	Mat.	$T_c(°K)$	M_s		Mat.	$T_c(°K)$	M_s
	Fe	1043	1752		$CrBr_3$	37	270
	Co	1388	1446		Au_2MnAl	200	323
	Ni	627	510		Cu_2MnAl	630	726
	Gd	293	1980		Cu_2MnIn	500	613
	Dy	85	3000		MnAs	318	870
	EuO	77	1910		MnBi	670	675
	EuS	16.5	1184		$GdCl_3$	2.2	550

(b)	Mat.	$T_N(°K)$		Mat.	$T_N(°K)$
	MnO	122		$KCoF_3$	125
	FeO	198		MnF_2	67.34
	CoO	291		FeF_2	78.4
	NiO	600		CoF_2	37.7
	$RbMnF_3$	54.5		$MnCl_2$	2
	$KFeF_3$	115		VS	1040
	$KMnF_3$	88.3		Cr	311

(c)	Mat.	$T_c(°K)$	M_s		Mat.	$T_c(°K)$	M_s
	Fe_3O_4	858	510		$CuFe_2O_4$	728	160
	$CoFe_2O_4$	793	475		$MnFe_2O_4$	573	560
	$NiFe_2O_4$	858	300		$Y_3Fe_5O_{12}$	560	195

From Burns, 1990

Ferromagnetism – Molecular field theory

Solution of equation with Brillouin function

- Now let's find the spontaneous magnetization ($B_a = 0$)

$$M = M_{sat} B_J(y) \qquad \text{with} \quad y = \frac{\mu_{eff} \mu_0 \gamma M}{k_B T}$$

Solving equation against y:

$$y \frac{k_B T}{\mu_{eff} \mu_0 \gamma M_{sat}} = B_J(y)$$

- Depending on temperature spontaneous magnetization can be either M=0 or finite
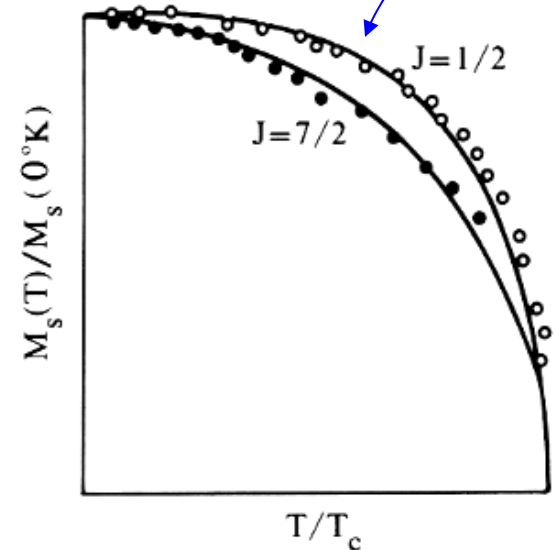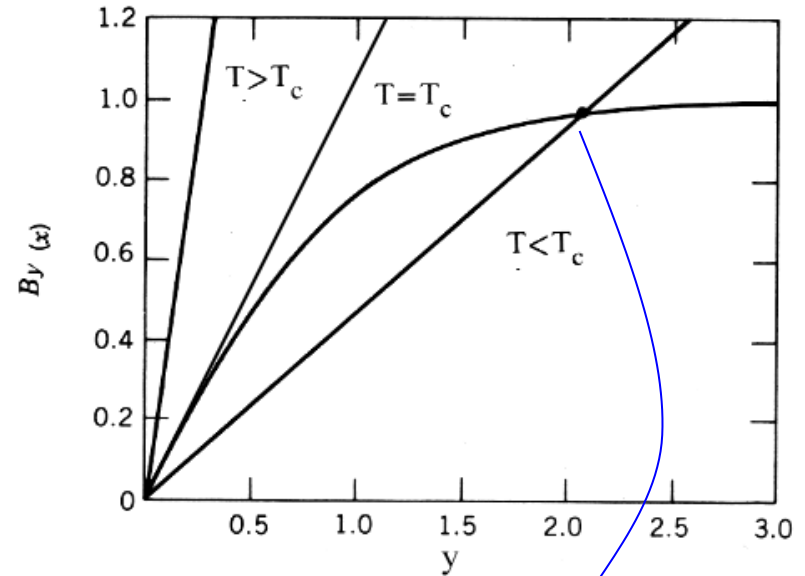- At low y

$$B_J(y << 1) \approx y \frac{J+1}{3J}$$

We can find critical Curie temperature:

μ_{eff}^2

$$\frac{k_B T_C}{\mu_{eff} \mu_0 \gamma M_{sat}} = \frac{J+1}{3J} \qquad \boxed{T_C = \frac{N \mu_0 \gamma}{3 k_B} (g_J \mu_B)^2 J(J+1)}$$

From Burns, 1990

Ferromagnetism – Molecular field theory

- At temperatures T > T_c , there is no spontaneous magnetization, and we can find temperature dependence of magnetization (*B_a > 0*)

$$M = M_{sat} B_J(y)$$

with $y = \dfrac{g_J \mu_B J (B_a + \mu_0 \gamma M)}{k_B T}$

$$M = M_{sat}\, y\, \frac{J+1}{3J} = \frac{N \mu_{eff}^2}{3 k_B T}(B_a + \mu_0 \gamma M)$$

- Solving for *M*:

$$M = \frac{C}{\mu_0 (T - C\gamma)} B_a$$

with Curie constant

$$C = \frac{N \mu_0 \mu_{eff}^2}{3 k_B} = \frac{T_C}{\gamma}$$

- Then susceptibility of ferromagnet in paramagnetic region
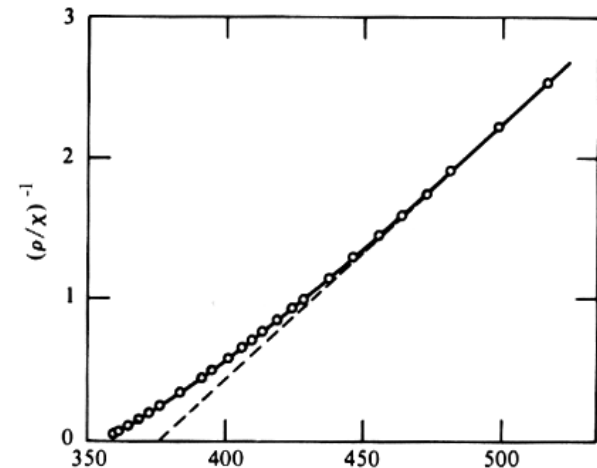
$$\chi = \frac{C}{T - T_C}$$

- Some estimation for iron:

$$g_J = 2; \quad J = 1; \quad N = 8.5 \cdot 10^{28}\, m^{-3} \quad \Rightarrow \quad C = 1.77\ K$$

$$T_C = 1043\ K; \quad \Rightarrow \quad \gamma = 588$$

$$M \approx 1700\ \text{Gauss}; \quad \Rightarrow \quad B \sim 10^6\, \text{Gauss} = 100\ T$$

Huge !

Reciprocal susceptibility vs. temperature for nickel

From Burns, 1990

Ferromagnetism – Heisenberg exchange interaction

- What is the reason for so high local magnetic field ? – Exchange interaction

- Consider two electrons on two atoms. We need to find the energy difference = exchange integral J_{ex}) :

- Their wavefunction is antisymmetric due to Pauli exclusion principle

- Usually the interaction between the space and spin parts is small, and the variables can be separated :

- Antiparallel spins give antisymmetric spin wavefunction, etc.

- We can construct wavefunctions for singlet and triplet states with correct symmetry:
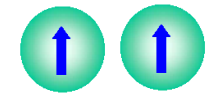
$$H_{ex} = -J_{ex}\left(s_1 \cdot s_2\right)$$

Singlet   Triplet
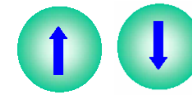
$$\left(s_1 \cdot s_2\right) = -\frac{3}{4} \qquad \left(s_1 \cdot s_2\right) = +\frac{1}{4}$$

$$\Psi\left(r_1, s_1, r_2, s_2\right) = -\Psi\left(r_2, s_2, r_1, s_1\right)$$

space   spin

$$\Psi\left(r_1, s_1, r_2, s_2\right) = \varphi\left(r_1, r_2\right) g\left(s_1, s_2\right)$$

Wavefunction	Singlet	Triplet
Total	Antisym.	Antisym.
Spin part	Antisym.	Symmetric
Space part	Symmetric	Antisym.

$\Psi_1(\mathbf{r}_1, \mathbf{r}_2) = \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)$ $\Psi_2(\mathbf{r}_1, \mathbf{r}_2) = \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)$

r_2 r_1 $\Longleftrightarrow$ r_1 r_2

a b a b
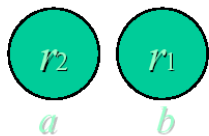
$$\varphi_S\left(x_1, x_2\right) = \phi_a\left(r_1\right)\phi_b\left(r_2\right) + \phi_a\left(r_2\right)\phi_b\left(r_1\right) = \Psi_1 + \Psi_2$$
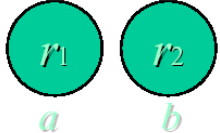
$$\varphi_T\left(x_1, x_2\right) = \phi_a\left(r_1\right)\phi_b\left(r_2\right) - \phi_a\left(r_2\right)\phi_b\left(r_1\right) = \Psi_1 - \Psi_2$$

Ferromagnetism – Heisenberg exchange interaction-contd

- The energy shift of singlet and triplet states can be calculated from perturbation theory:

$$E_S = \langle \phi_S | V | \phi_S \rangle = \langle \Psi_1 | V | \Psi_1 \rangle + \langle \Psi_2 | V | \Psi_2 \rangle + \langle \Psi_1 | V | \Psi_2 \rangle + \langle \Psi_2 | V | \Psi_1 \rangle$$

$$E_T = \langle \phi_T | V | \phi_T \rangle = \langle \Psi_1 | V | \Psi_1 \rangle + \langle \Psi_2 | V | \Psi_2 \rangle - \langle \Psi_1 | V | \Psi_2 \rangle - \langle \Psi_2 | V | \Psi_1 \rangle$$

$$V(r_1, r_2) = \frac{e^2}{\varepsilon_0} \left[\frac{1}{r_{ab}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} \right]$$

r_1 r_2

a b

- The energy difference between the singlet and triplet states

$$E_S - E_T = J_{exc} = 4 \langle \Psi_1 | V | \Psi_2 \rangle = 4 \langle \phi_a(r_1) \phi_b(r_2) | V | \phi_a(r_2) \phi_b(r_1) \rangle$$

$$= \frac{e^2}{\varepsilon_0} \left[-8 \left\langle \phi_a(r_1) \phi_b(r_2) \left| \frac{1}{r_{a2}} \right| \phi_a(r_2) \phi_b(r_1) \right\rangle + 4 \left\langle \phi_a(r_1) \phi_b(r_2) \left| \frac{1}{r_{ab}} \right| \phi_a(r_2) \phi_b(r_1) \right\rangle + 4 \left\langle \phi_a(r_1) \phi_b(r_2) \left| \frac{1}{r_{12}} \right| \phi_a(r_2) \phi_b(r_1) \right\rangle \right]$$

- At small *a-b* distance $J_{exc} < 0$ and singlet state is favorable
- At large *a-b* distance $J_{exc} > 0$ and triplet state is favorable
- BTW if the electrons are on the same atom, the ion interaction change is zero, $J_{exc} > 0$ and antiparallel spins are favorable = Hund's rule

Ferromagnetism – Heisenberg exchange interaction contd.

Exchange integral vs. interatomic distance

r_d – average radius of 4d electron

- Exchange interaction can be ferromagnetic or antiferromagnetic depending on interatomic distance

- Exchange interaction is electrostatic (strong) in nature

- To correlate it with molecular field theory, we can write:

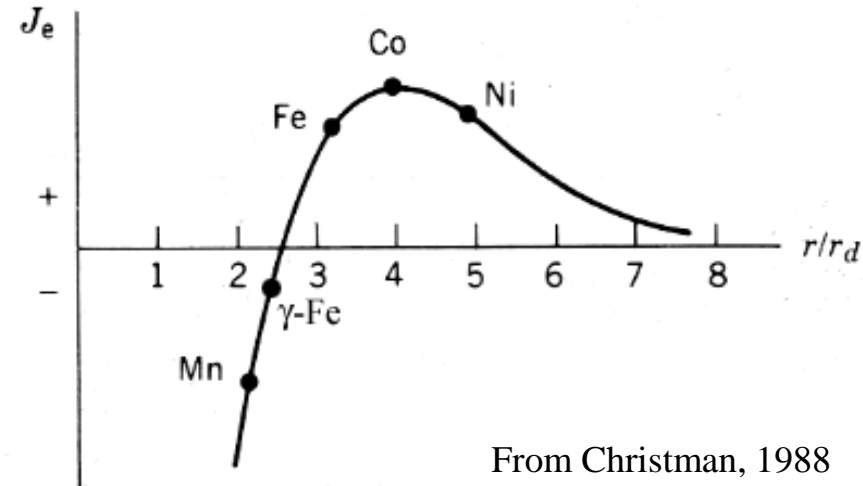$$H_{ex} = -\sum_{i,j} J_{ex}\left(s_i \cdot s_j\right) \equiv \sum_i g_J \mu_B s_i B_{loc}$$

$$z J_{ex} s = g_J \mu_B B_{loc}$$

Number of nearest neighbors

From Christman, 1988

- For Fe: $J_{ex} = \dfrac{g_J \mu_B \mu_0 \gamma M}{zs} = \dfrac{\left(g_J \mu_B\right)^2 \mu_0 \gamma n}{z} \approx 11 meV$

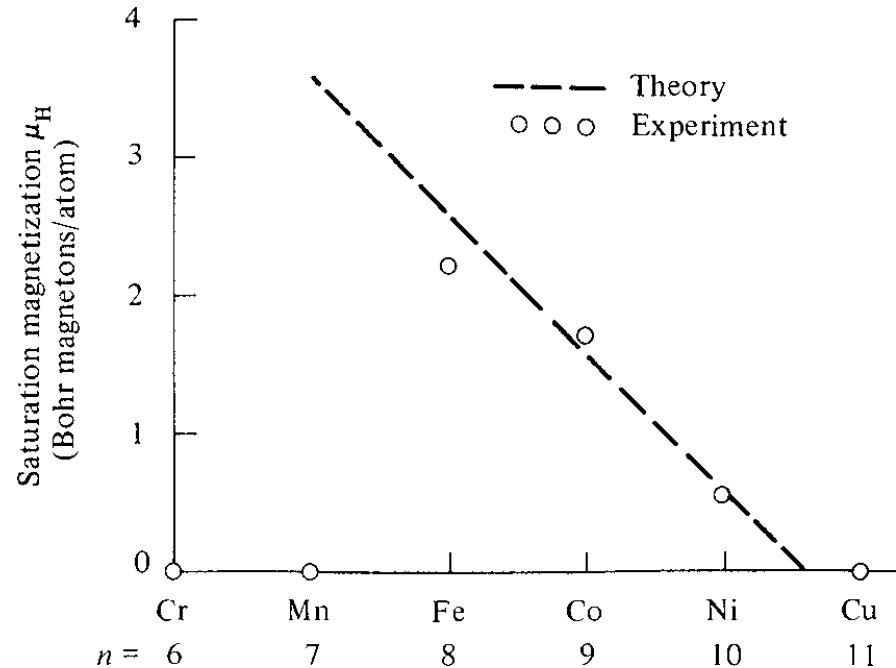- Electrostatic interaction easily accounts for this value

Role of band structure

Density of states in 3d and 4s bands
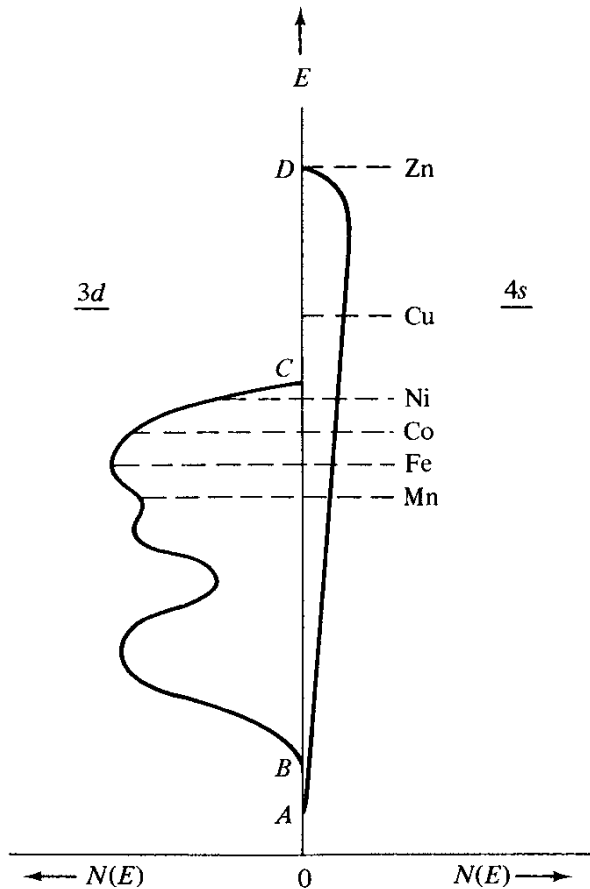
Dependence of the saturation magnetization on the number n of (3d + 4s) electrons per atom

$$\mu_H = \left(10.6 - n\right)\mu_B$$
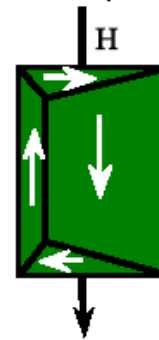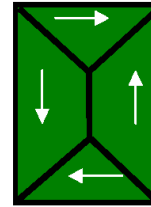
n = number of (3d + 4s) electrons per atom
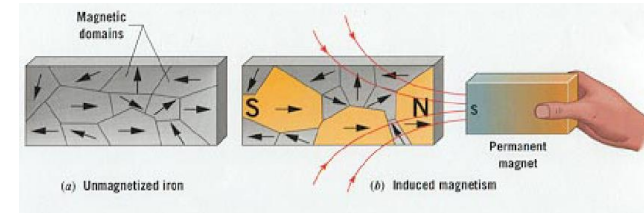
- For Ni (n=10) moment is $0.6\mu_B$
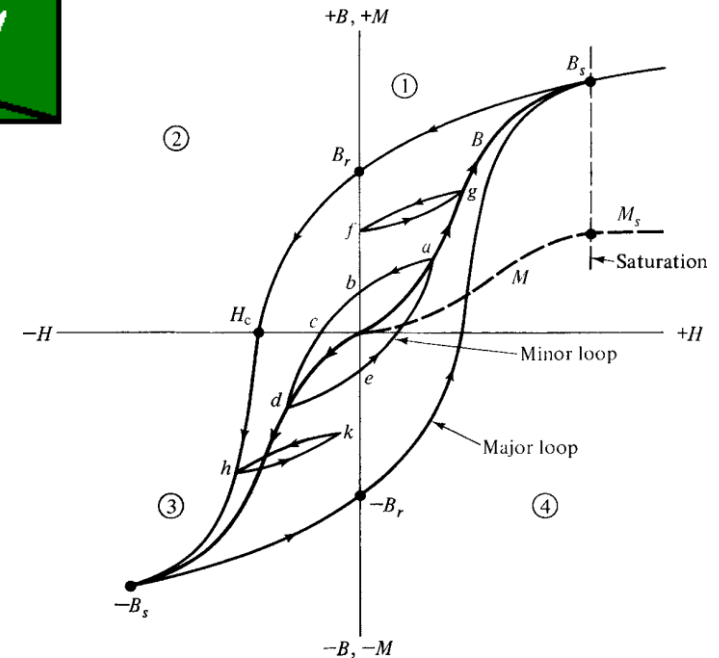
From Cullity, 2008

Ferromagnetic materials

- Energy is minimized by ordering spins into "domains"
  - Net moment, **M**, would cause external field, increase energy
  - Magnetic domains cancel so that **M** = 0
  - Natural ferromagnetism does not produce net magnetic field
- To magnetize a ferromagnet, impose **H**
  - Domain walls move to align **M** and **H**
  - Defects impede domain wall motion
  - Magnetization (M_r) retained when **H** removed

- Magnetic properties

  M_s = saturation magnetization (All spins aligned with field)

  M_r = remanent magnetization (Useful moment of permanent magnet)

  H_c = coercive force (Field required to "erase" moment)

  Area inside curve = magnetic hysteresis (Governs energy lost in magnetic cycle)

Ferromagnetic material is always locally saturated

Magnetic domains

(a) Unmagnetized iron   (b) Induced magnetism

Permanent magnet

Hysteresis loop of a ferromagnetic material

Core magnetism – materials with spontaneously ordered magnetic dipoles

- High temperature:
  - Spins disordered $\Rightarrow$ paramagnetism

- Low Temperature (T < Tc)
  - Spins align = ferromagnetism
    - Elements: Fe, Ni, Co, Gd, Dy
    - Alloys and compounds: AlNiCo, FeCrCo, $SmCo_5$, $Fe_{14}Nd_2B$
  - Like spins alternate = antiferromagnetism ($RbMnF_3$)
  - Unlike spins alternate = ferrimagnetism
    - Compounds: Fe_3O_4 (lodestone, magnetite), CrO_3, $SrFe_2O_3$, other ferrites and garnets

Ferromagnetism

$M = nm$
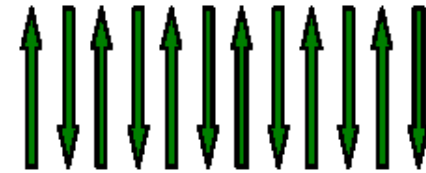
antiferromagnetism

$M = 0$

ferrimagnetism

$M = (n/2)(m_1 - m_2)$

Other types of exchange interaction

- Superexchange (transition metal oxides)

  - Can be ferromagnetic or anfiferromagnetic depending upon the energy of delocalization of the p-electrons on M_1 and M_2

  - Ordering temperature up to 900 K in ferrites ($NiFe_2O_4$ - 863 K)

 - Sign mostly negative, though ferromagnetics are known: EuO (T_c=69K) or $CrBr_3$ (T_c=37K)

- RKKY interaction (Ruderman-Kittel-Kasuya-Yosida) - Indirect exchange over relatively large distances trough spin of conduction electrons (4f metals)

  - Interaction oscillates with (k_FR), Fermi wavevector determines the wavelength of oscillations

  - The interaction is of the same order for all rare earths, but ordering temperatures vary due to magnetic moment: 19K for Nd, 289 K for Gd)

Mn – O - Mn

Figure 9.1 - M_1 and M_2: transition metal ions, O: O^{2-}

RKKY interaction

k_FR

NNSE508 / NENG452 Lecture #15
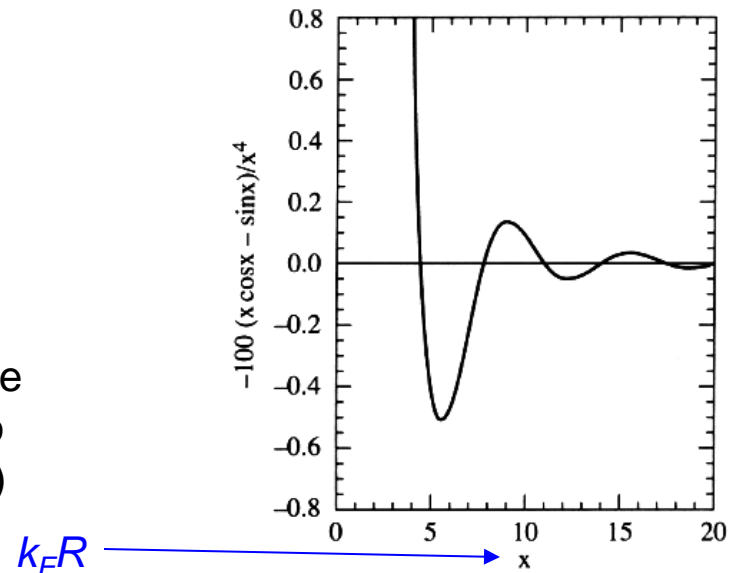
Magnetic materils

- Magnetic induction field is the same in a

Magnetic Suscpetibility, χ
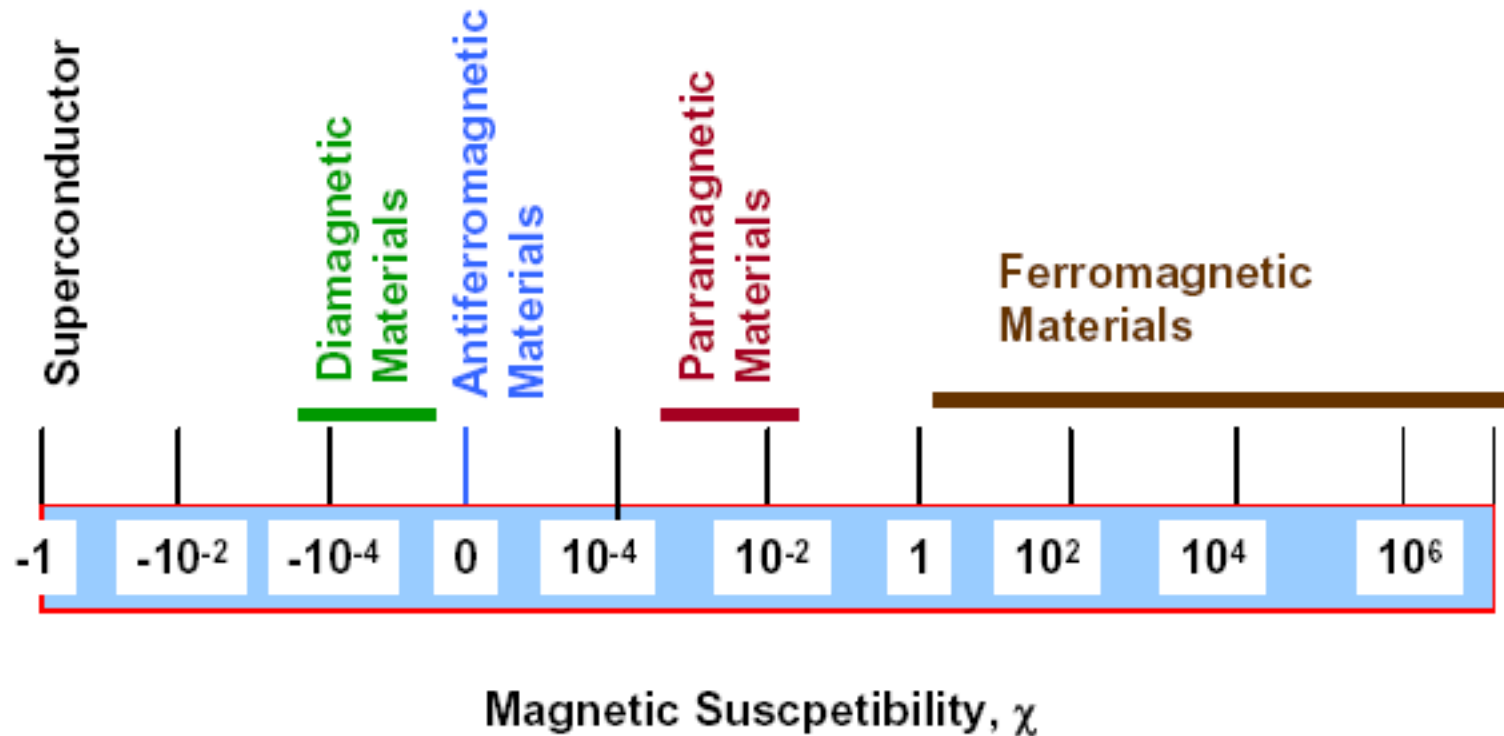
Physical constants

Name and symbol	Numerical value
Speed of light in vacuum, c	2.9979×10^8 m.s^{-1}
Permeability of vacuum, μ_0	$4\pi \times 10^{-7}$ H.m^{-1}
Permittivity of vacuum, $\varepsilon_0 = 1/c^2\mu_0$	8.8542×10^{-12} F.m^{-1}
Planck's constant, h	6.6261×10^{-34} J.s
$\hbar = h/2\pi$	1.0546×10^{-34} J.s
Acceleration of gravity, g	9.8066 m.s^{-2}
Electron rest mass, m	9.1094×10^{-31} kg
Electron charge (absolute value), e	1.6022×10^{-19} C
Bohr magneton, $\mu_B = e\hbar/2m$	9.2742×10^{-24} A.m^2
Flux quantum, $h/2e$	2.0678×10^{-15} Wb
Avogadro's number N	6.0221×10^{23} mol^{-1}
Boltzmann's constant, k_B	1.3807×10^{-23} J.K^{-1}

Length (metre)	: 1 m $= 10^2$ cm $= 39.37$ " (inch) $= 10^{10}$ angström (Å).
Force (newton)	: 1 N $= 10^5$ dyn $= 0.102$ kgf.
Energy (joule)	: 1 J $= 10^7$ erg $= 0.7243 \times 10^{23}$ K $= 0.6241 \times 10^{19}$ eV.
Energy density	: 1 J.m^{-3} $= 10$ erg.cm^{-3}.
Power (watt)	: 1 W $= 10^7$ erg.s^{-1} $= 1.359 \times 10^{-3}$ CV $= 1.340 \times 10^{-3}$ hp.
Pressure (pascal)	: 1 Pa $= 10$ baryes $= 10^{-5}$ bar $= 1.02 \times 10^{-5}$ kgf.cm^{-2} $= 7.49 \times 10^{-3}$ torrs $= 1.45 \times 10^{-4}$ psi.

From Tremolet de Lacheisserie, 2005