Magnetochemistry – A Brief Introduction:

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Magnetochemistry

- **Magnetochemistry** is concerned with the magnetic properties of chemical compounds.
- Magnetic properties arise from the spin and orbital angular momentum of the electrons contained in a compound.
- Compounds broadly classified into diamagnetic: contain no unpaired electrons.

  or paramagnetic: contain one or more unpaired electrons.

- The magnitude of the paramagnetism is expressed as an effective magnetic moment, μ_{eff}.
- For first-row transition metals the magnitude of μ_{eff} is, to a first approximation, a simple function of the number of unpaired electrons, the spin-only formula. In general, spin-orbit coupling causes μ_{eff} to deviate from the spin-only formula. For the heavier transition metals, lanthanides and actinides, spin-orbit coupling cannot be ignored.
- Exchange interaction can occur in clusters and infinite lattices, resulting in ferromagnetism, antiferromagnetism or ferrimagnetism depending on the relative orientations of the individual spins.

Magnetic susceptibility

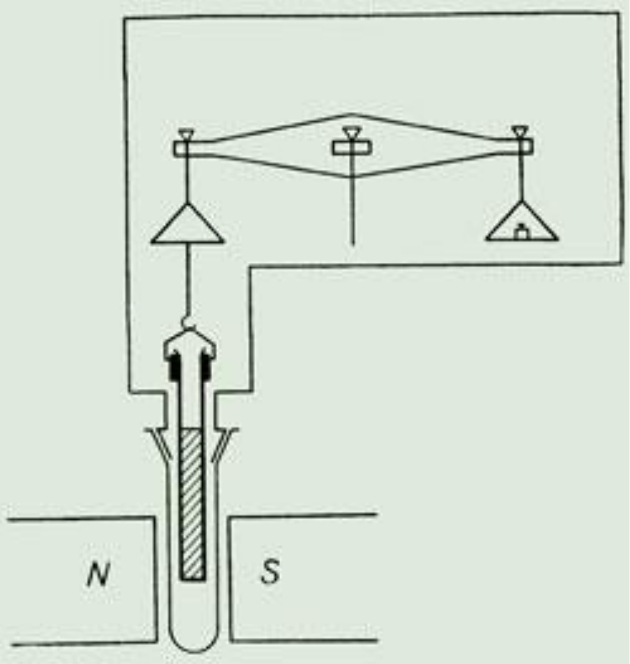
- The primary measurement in magnetochemistry is magnetic susceptibility. This measures the strength of interaction on placing the substance in a magnetic field. The **volume magnetic susceptibility**, represented by the symbol χ_v is defined by the relationship M = H. χ_v

  where, M is the magnetization of the material (the magnetic dipole moment per unit volume), measured in amperes per meter (SI units), and H is the magnetic field strength, also measured in amperes per meter.

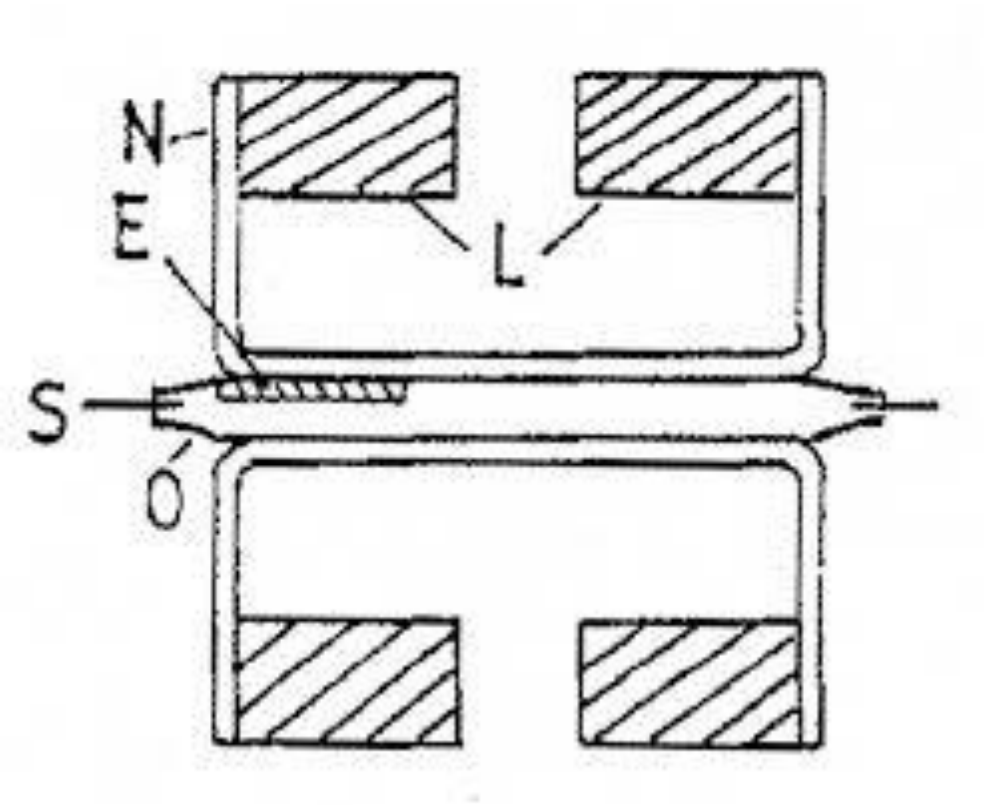
- Susceptibility is a dimensionless quantity.
- For chemical applications the molar magnetic susceptibility (χ_{mol}) is the preferred quantity. It is measured in $m^3 \cdot mol^{-1}$ (SI) or $cm^3 \cdot mol^{-1}$ (CGS) and is defined as $\chi_m = M\,\chi_v/\rho$ where ρ is the density in $kg \cdot m^{-3}$ (SI) or $g \cdot cm^{-3}$ (CGS) and *M* is molar mass in $kg \cdot mol^{-1}$ (SI) or $g \cdot mol^{-1}$ (CGS).

A variety of methods are available for the measurement of magnetic susceptibility.

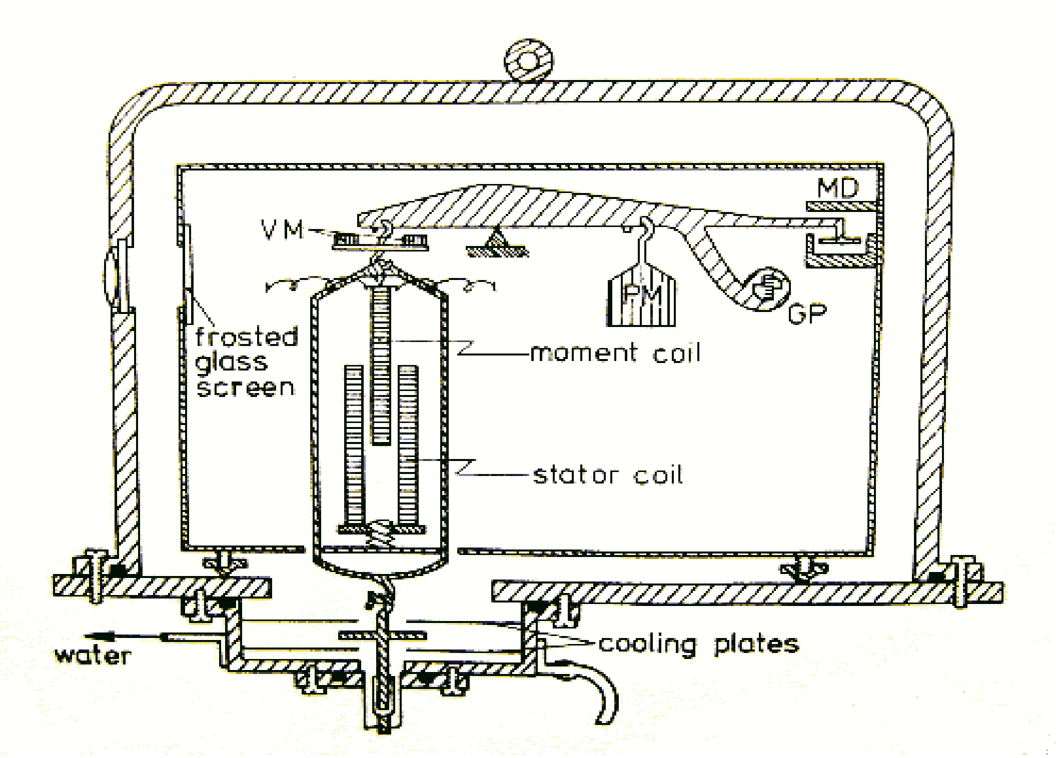
- With the Gouy balance the weight change of the sample is measured with an analytical balance when the sample is placed in a homogeneous magnetic field. The measurements are calibrated against a known standard, such as mercury cobalt thiocyanate, $HgCo(NCS)_4$. Calibration removes the need to know the density of the sample. Variable temperature measurements can be made by placing the sample in a cryostat between the pole pieces of the magnet.



- The Evans balance is a torsion balance which uses a sample in a fixed position and a variable secondary magnet to bring the magnets back to their initial position. It, too, is calibrated against $HgCo(NCS)_4$.



- With a Faraday balance the sample is placed in a magnetic field of constant gradient, and weighed on a torsion balance. This method can yield information on magnetic anisotropy



- SQUID is a very sensitive magnetometer.
- For substances in solution NMR may be used to measure susceptibility.

□ The magnetic moment of an atom has two components:

a spin component(spin moment) and an orbital component (orbital moment).

- Frequently the orbital moment is supressed (spin-only-magnetism, e.g. coordination compounds of 3d elements)

- **Magnetisation M and susceptibility χ:**

$$M = (\Sigma\mu)/V$$

Where $\Sigma\mu$: sum of all magnetic moment spin in a given volume V,

Dimension: $[Am^2/m^3 = A/m]$

The actual magnetization of a given sample is composed of the intrinsic magnetization (susceptibility χ) and an external field H:

$$M = H\chi \quad (\chi\text{: susceptibility})$$

The magnetic moment of a single atom(μ) (μ is a vector):

μ= i F[Am^2], circular current i, area F

μ_B= $eh/4\pi m_e$= 0.9274 $x10^{-23}$ Am^2

(h: Planck constant, m_e: electron mass)

μ_B: Bohr magneton(smallest quantity of a magnetic moment)

→for one unpaired electron in an atom(spin only):

μ_s= 2 $\sqrt{s(s+1)}\ \beta = 1.73\ \beta$

There are three types of susceptibilities:

χ_v = volume susceptibility (dimensionless)

χ_g = gramm susceptibility (cm^3/g)

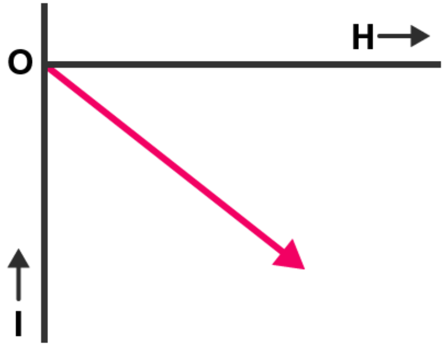
χ_m = molar susceptibility (cm^3/mol)

χ_m is used normally in chemistry!!!!

Classification of Magnetic Bodies

Properties of Diamagnetic Materials:

1. There are no atomic dipoles in diamagnetic materials because the resultant magnetic moment of each atom is zero due to paired electrons.
2. Diamagnetic materials are repelled by a magnet.
3. The substances are weakly repelled by the field so in a nonuniform field, these substances have a tendency to move from a strong to a weak part of the external magnetic field.
4. The intensity of magnetization I is very small, negative and proportional to the magnetizing field.
5. Magnetic susceptibility is small and negative.
6. The relative permeability is slightly less than unity.



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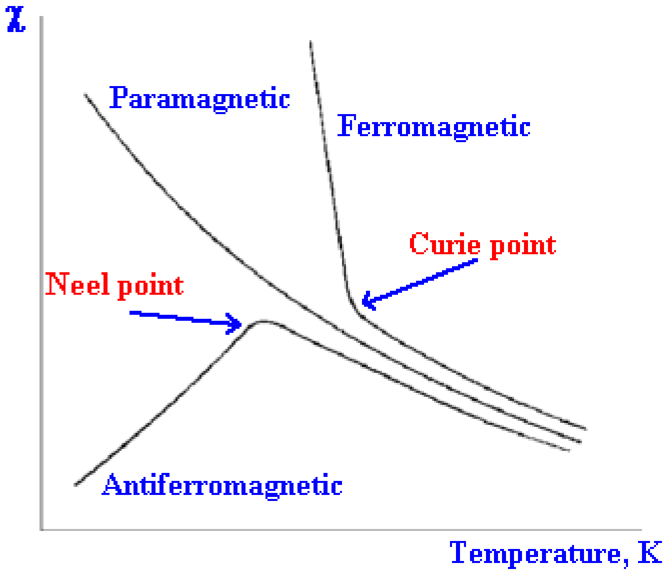
Properties of Paramagnetic substances:

1.**Paramagnetic** materials have a small, positive susceptibility to magnetic fields.

2.These materials are slightly attracted by a magnetic field and the material does not retain the magnetic properties when the external field is removed

3.Paramagnetic properties are due to the presence of some unpaired electrons, and from the realignment of the electron paths caused by the external magnetic field.

4.Paramagnetic materials include magnesium, molybdenum, lithium, and tantalum.



Properties of Ferromagnetic substances

1. The atoms of ferromagnetic substances have permanent dipole moment present in domains.

2. Atomic dipoles in ferromagnetic substances are oriented in the same direction as the external magnetic field.

3. The magnetic dipole moment is large and is in the direction of the magnetizing field.

4. The intensity of magnetization **(M)** is very large and positive and varies linearly with the magnetizing field **(H)**.

5. The magnetic flux density of the material will be very large and positive. Magnetic field lines become very dense inside ferromagnetic materials. Magnetic flux density **B =** $_0$ **(H + M),** where $_0$ is the magnetic permittivity of free space, **H** is the strength of the applied magnetic field and **M** is the intensity of magnetization.

6. The relative permeability is also very large and varies linearly with the magnetizing field the field inside the material is much stronger than the magnetizing field. They have a tendency of pulling in a large number of lines of force by the material. Relative permeability of material $_r$ **= 1 +** $_m$

7. Ferromagnetic substances are strongly attracted by the field. So in a nonuniform field, they have a tendency to stick at the poles where the field is strongest.

8. If a ferromagnetic powder is placed in a watch glass placed on two poles pieces which are sufficient apart then powder accumulates at sides and shows depression in the middle because the field is strongest at poles.

9. When a ferromagnetic substance is liquefied, it loses ferromagnetic properties due to higher temperature.

Antiferromagnetic Material – Antiferromagnetism:

In an antiferromagnet, unlike a ferromagnet, there is a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in opposite directions. When all atoms are arranged in a substance so that each neighbor is anti-parallel, the substance is antiferromagnetic. Antiferromagnets have a zero net magnetic moment, meaning that no field is produced by them. **Manganese oxide** (MnO) is one material that displays this behavior. Generally, antiferromagnetic order may exist at sufficiently low temperatures, but vanishes at and above the **Néel temperature**. Above the Néel temperature, the material is typically paramagnetic, that is, the thermal energy becomes large enough to destroy the microscopic magnetic ordering within the material. The Néel temperature of MnO is about 116K.

Electron Orbit Magnetic Moment

From the classical expression for magnetic moment, μ = IA, an expression for the magnetic moment from an electron in a circular orbit around a nucleus can be deduced. It is proportional to the angular momentum of the electron. The effective current is:

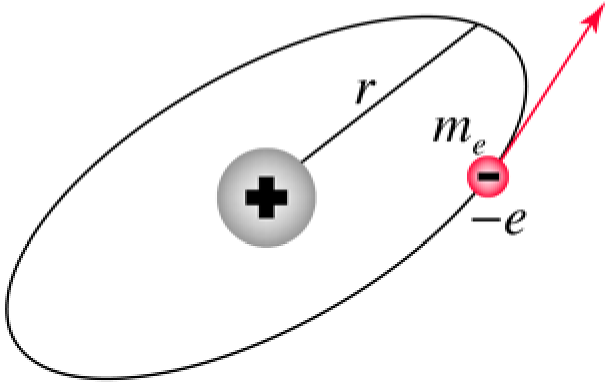
$$I = \frac{-e}{T} = \frac{ev}{2\pi r}$$

which can be rewritten as

$$I = \frac{-em_e vr}{2\pi m_e r^2}$$

so that the magnetic moment is

$$\mu = IA = \frac{-e}{2m_e} L$$



T = period of orbit

L = orbital angular momentum

Orbital Magnetic Moment

The magnetic moment associated with an electron orbit is given by: $\mu = IA = \frac{-e}{2m_e}L$

Taking into account the quantization of angular momentum for such orbits, the magnitude of the magnetic moment can be written

$$\mu = \frac{-e}{2m_e}L = \frac{-e}{2m_e}\sqrt{\ell(\ell+1)}\hbar = \sqrt{\ell(\ell+1)}\,\mu_B$$

A unit of magnetic moment called the "Bohr magneton" is introduced here.

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27\,x\,10^{-24}\,J/T = 5.79\,x\,10^{-5}\,eV/T$$

The z-component of the magnetic moment is given by

$$\mu_z = -m_\ell \mu_B$$

Spin Magnetic Moment

The ratio of orbital magnetic moment to the orbital angular momentum is e/2mc. The ratio of the spin magnetic moment to the spin angular momentum is, due to the anomalous behaviour of spin , e/mc.

Now spin angular momentum of an electron is: $\sqrt{s(s+1)} \cdot h/2\pi$, we have,

Spin magnetic moment = (e/mc) x spin angular momentum

$\mu_s = \sqrt{s(s+1)} \cdot eh/2\pi mc = 2\sqrt{s(s+1)} \cdot eh/4\pi mc = 2\sqrt{s(s+1)} \cdot \mu_B$

Thus we can write:

$\mu_l = g\sqrt{l(l+1)} \cdot \mu_B$ and $\mu_s = g\sqrt{s(s+1)} \cdot \mu_B$

Where g = 1 for orbital moment and g = 2 spin moment.

'g' is called gyromagnetic ratio and is the ratio of the appropriate magnetic moment to the appropriate angular momentum.

Spin magnetic moment of a single unpaired electron system is given by:

$\mu_s = 2\sqrt{½ (½ +1)} \cdot \mu_B = 2\sqrt{½ (½ +1)} \cdot \beta = 1.73\ \beta$ (or B.M.)

Spin only (S.O.) moments of d^n ions:

- The formula used to calculate the spin-only magnetic moment can be written in two forms:
- 1. The first based on the number of **unpaired** electrons, n,

$$\mu_{so} = \sqrt{n(n+2)}\ \text{B.M.}$$

- 2. The second based on the **total** electron spin quantum number, S. Since for each unpaired electron, n=1 and S=1/2 then the two formulae are clearly related and the answer obtained must be identical.

$$\mu_{so} = \sqrt{4S(S+1)}\ \text{B.M.}$$

- $\mu_{S+L} = \sqrt{\{4S(S+1) + L(L+1)\}}$ B.M.

Comparison of calculated spin-only magnetic moments with experimentally observed data for some octahedral complexes:

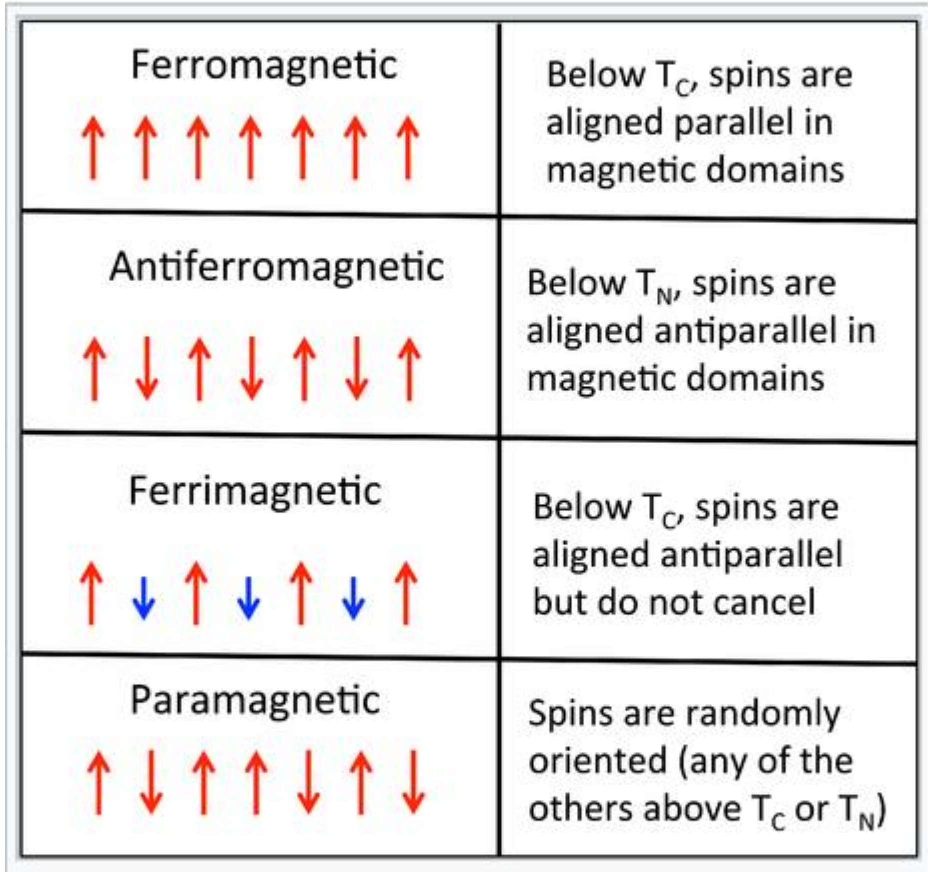
Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d^1 (t_{2g}^1)	√3 = 1.73	1.6-1.7
V(III)	d^2 (t_{2g}^2)	√8 = 2.83	2.7-2.9
Cr(III)	d^3 (t_{2g}^3)	√15 = 3.88	3.7-3.9
Cr(II)	d^4 high spin (t_{2g}^3 e_g^1)	√24 = 4.90	4.7-4.9
Cr(II)	d^4 low spin (t_{2g}^4)	√8 = 2.83	3.2-3.3
Mn(II)/ Fe(III)	d^5 high spin (t_{2g}^3 e_g^2)	√35 = 5.92	5.6-6.1
Mn(II)/ Fe(III)	d^5 low spin (t_{2g}^5)	√3 = 1.73	1.8-2.1
Fe(II)	d^6 high spin (t_{2g}^4 e_g^2)	√24 = 4.90	5.1-5.7
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin (t_{2g}^5 e_g^2)	√15 = 3.88	4.3-5.2
Co(II)	d^7 low spin (t_{2g}^6 e_g^1)	√3 = 1.73	1.8
Ni(II)	d^8 (t_{2g}^6 e_g^2)	√8 = 2.83	2.9-3.3
Cu(II)	d^9 (t_{2g}^6 e_g^3)	√3 = 1.73	1.7-2.2

Comparison of calculated spin-only magnetic moments with experimental data for some tetahedral complexes:

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Cr(V)	d^1 (e^1)	$\sqrt{3} = 1.73$	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	$\sqrt{8} = 2.83$	2.6 - 2.8
Fe(V)	d^3 (e^2 $t_2{}^1$)	$\sqrt{15} = 3.88$	3.6-3.7
-	d^4 (e^2 $t_2{}^2$)	$\sqrt{24} = 4.90$	-
Mn(II)	d^5 (e^2 $t_2{}^3$)	$\sqrt{35} = 5.92$	5.9-6.2
Fe(II)	d^6 (e^3 $t_2{}^3$)	$\sqrt{24} = 4.90$	5.3-5.5
Co(II)	d^7 (e^4 $t_2{}^3$)	$\sqrt{15} = 3.88$	4.2-4.8
Ni(II)	d^8 (e^4 $t_2{}^4$)	$\sqrt{8} = 2.83$	3.7-4.0
Cu(II)	d^9 (e^4 $t_2{}^5$)	$\sqrt{3} = 1.73$	-

Exchange and ordering in magnetic materials:

- **Various types of ordered magnetic structures:**



Ferromagnetic ↑ ↑ ↑ ↑ ↑ ↑ ↑	Below T_C, spins are aligned parallel in magnetic domains
Antiferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_N, spins are aligned antiparallel in magnetic domains
Ferrimagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_C, spins are aligned antiparallel but do not cancel
Paramagnetic ↑ ↓ ↑ ↑ ↓ ↑ ↓	Spins are randomly oriented (any of the others above T_C or T_N)

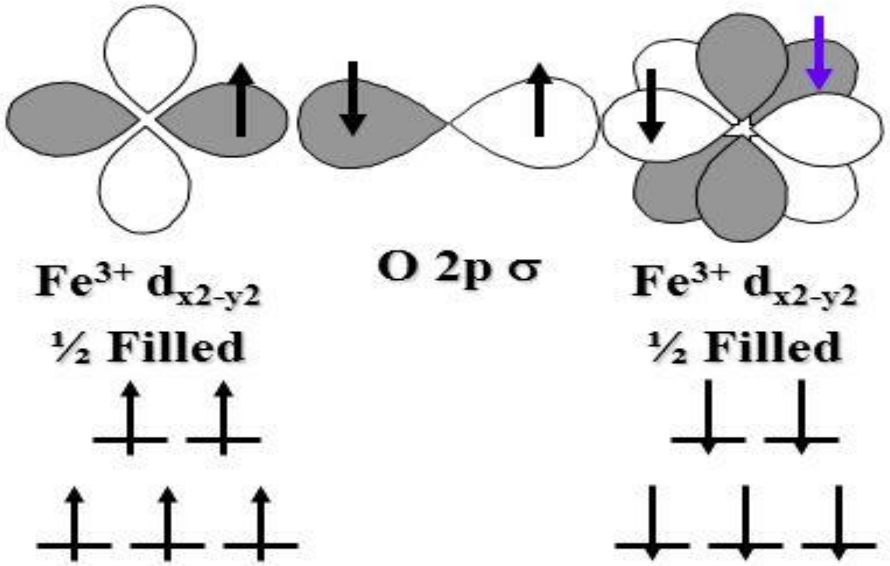
- Type of magnetic order depends on the interactions

Exchange and ordering in magnetic materials:

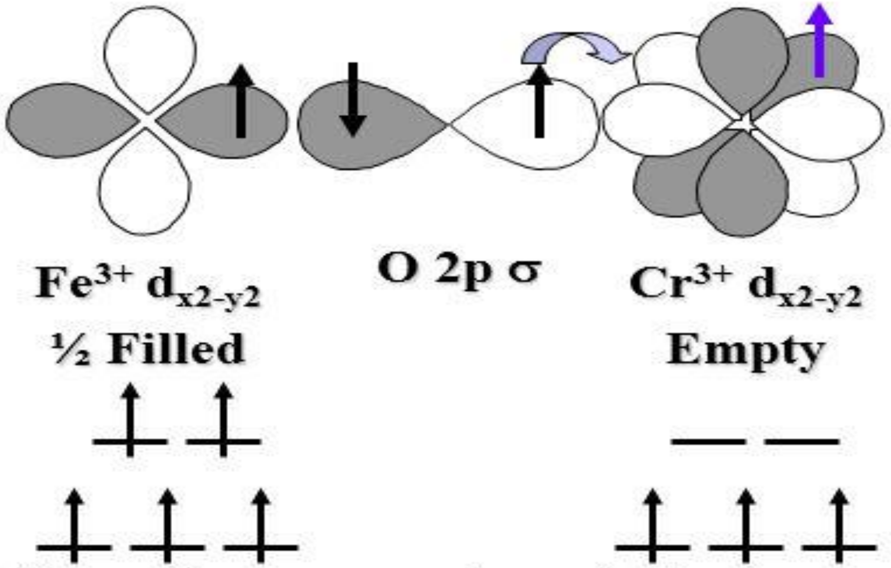
- **1-Origin of exchange**
- **2- Exchange in insulators: superexchange and Goodenough-Kanamori rules**
- **3- Exchange in metals: RKKY, double exchange, band magnetism**
- **4- Magnetic ordering: different types of orderings, role of dimensionality, classical vs quantum spins**

Superexchange

In order for a material to be magnetically ordered, the spins on one atom must couple with the spins on neighboring atoms. The most common mechanism for this coupling (particularly in insulators) is through the semicovalent superexchange interaction. The spin information is transferred through covalent interactions with the intervening ligand (say oxygen).

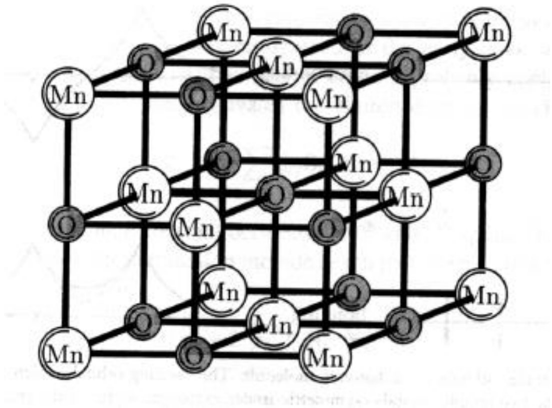


The covalent interaction through the O 2p orbital stabilizes **antiferromagnetic coupling**.



Here the oxygen based electron will spend some time on Cr^{3+} and due to Hund's rule polarize the t_{2g} e^- leading to **ferromagnetic coupling**.

Superexchange:

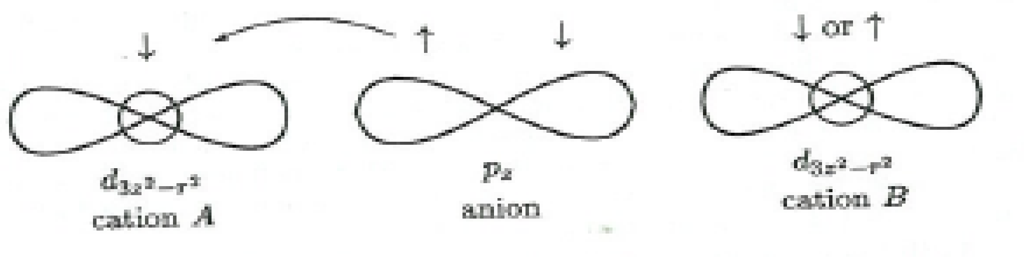
- **In many materials (oxides), magnetic atoms are separated by non-magnetic ions (oxygen)**
- **⇒ Indirect interactions through Oxygen**
- 

MnO:Mn^{2+} are separated by O^{2-}

3d wave functions hybridize with p orbital of O^{2+}

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

Superexchange: due to hybridization:



Hybridization: pz wave function is mixed with dz2 orbitals

- **If A and B antiparallel,**

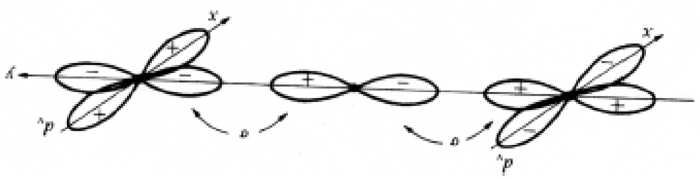
  pz↑ hybridize with A

  pz↓ hybridize with B

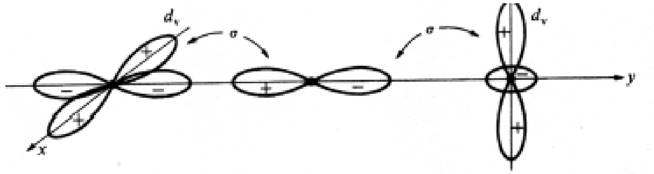
- **If A and B parallel:**
  - **pz↑ hybridize with A and B,**
  - **but no hybridization for pz↓**

Sign and value of superexchange depends on:

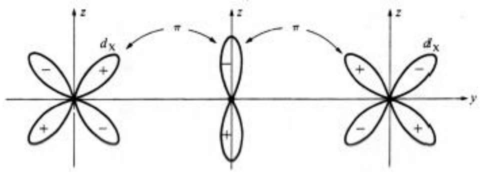
- The angle M - O – M
- The d orbitals involved in the bond
- Some examples (Goodenough-Kanamori rules):
- Antiferromagnetic superexchange
- Strong: weak:

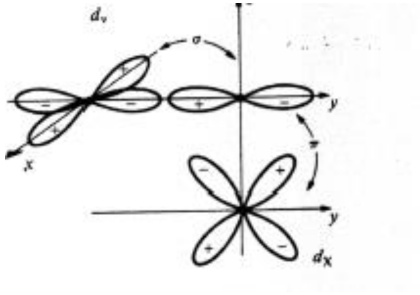


Ferromagnetic



2 diiferent orbitals





90° coupling

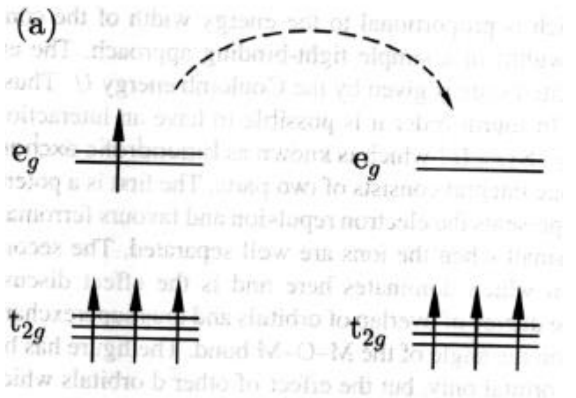
Characteristics of superexchange :

- **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 (no. of 3d-electrons, e_g or t_{2g} character)**
- **A-O-B angle**
- **Very common in oxides or sulfides**

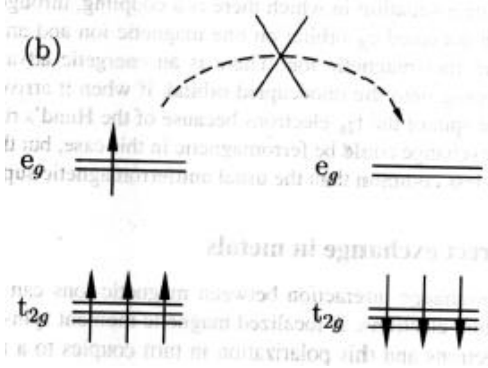
Double exchange in 3d metals:

- **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)

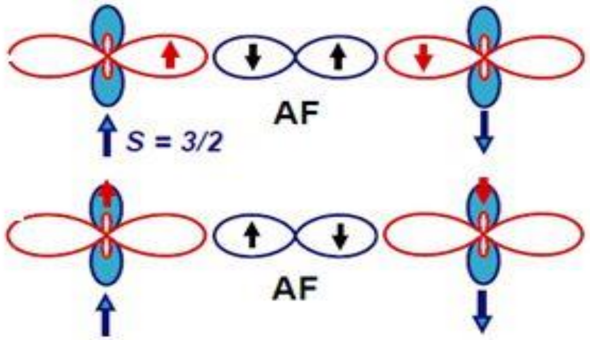
Ferro: possible hopping



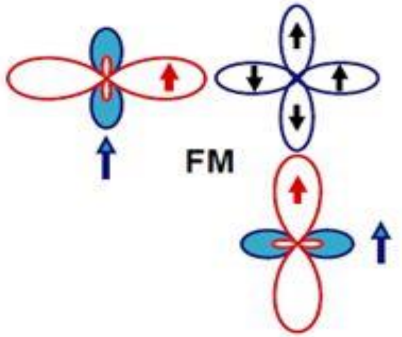
AF: no hopping



Goodenough–Kanamori–Anderson Rules



180° – Exchange between half occupied or empty orbitals is strong and antiferromagnetic



Ferromagnetic superexchange - ferromagnetic when angle 90°