Magnetism, Magnetic Properties, Magnetochemistry
Magnetism

All matter is *electronic*

Positive/negative charges - bound by Coulombic forces
Result of electric field $E$ between charges, electric dipole
Electric and magnetic fields = the electromagnetic interaction
(Oersted, Maxwell)

Electric field = electric $+/−$ charges, electric dipole
Magnetic field ??No source?? No magnetic charges, N-S
No magnetic monopole

Magnetic field = motion of electric charges
(electric current, atomic motions)

Magnetic dipole – magnetic moment $\mu = i \times A \ [A \text{ m}^2]$
Electromagnetic Fields
Magnetism

Magnetic field = motion of electric charges

- Macro - electric current
- Micro - spin + orbital momentum

Ampère 1822

Magnetic dipole – magnetic (dipole) moment $\mu$ [A m$^2$]

$$\mu = i \times A$$
Magnetism

Microscopic explanation of source of magnetism
   = Fundamental quantum magnets
Unpaired electrons = spins (Bohr 1913)
Atomic building blocks (protons, neutrons and electrons = fermions)
   possess an intrinsic magnetic moment

Relativistic quantum theory (P. Dirac 1928) → SPIN
(quantum property ~ rotation of charged particles)
Spin (½ for all fermions) gives rise to a magnetic moment
Atomic Motions of Electric Charges

The origins for the magnetic moment of a free atom

Motions of Electric Charges:

1) The spins of the electrons $S$. Unpaired spins give a paramagnetic contribution. Paired spins give a diamagnetic contribution.

2) The orbital angular momentum $L$ of the electrons about the nucleus, degenerate orbitals, paramagnetic contribution. The change in the orbital moment induced by an applied magnetic field, a diamagnetic contribution.

3) The nuclear spin $I$ – 1000 times smaller than $S$, $L$ nuclear magnetic moment $\mu = \gamma I$

$\gamma = \text{gyromagnetic ratio}$
Magnetic Moment of a Free Electron

\[ \mu_{\text{eff}} = g \sqrt{S(S+1)} \frac{eh}{4\pi m_e} = g \sqrt{S(S+1)} \mu_B \]

the Bohr magneton = the smallest quantity of a magnetic moment

\[ \mu_B = \frac{eh}{4\pi m_e} = 9.2742 \times 10^{-24} \text{ J/T} (= \text{A m}^2) \]
\[ (\mu_B = \frac{eh}{4\pi m_e c} = 9.2742 \times 10^{-21} \text{ erg/Gauss}) \]

S = ½, the spin quantum number

g = 2.0023192778 the Lande constant of a free electron

for a free electron (S = ½)

\[ \mu_{\text{eff}} = 2 \times \sqrt{3}/4 \times \mu_B = 1.73 \mu_B \]
A Free Electron in a Magnetic Field

Magnetic energy

\[ E = -\mu_0 \mu \mathbf{\cdot} \mathbf{H} \]

\[ E = -\mu \mathbf{\cdot} B \]

An electron with spin \( S = \frac{1}{2} \) can have two orientations in a magnetic field

\( m_S = +\frac{1}{2} \) or \( m_S = -\frac{1}{2} \)

Degeneracy of the two states is removed

The state of lowest energy = the moment aligned with the magnetic field
The state of highest energy = aligned against the magnetic field

In SI units

\( \mu_0 = \) permeability of free space

\[ = 4\pi \times 10^{-7} \text{ [N A}^{-2} = \text{ H m}^{-1}] \]
A Free Electron in a Magnetic Field

An electron with spin \( S = \frac{1}{2} \)

The state of lowest energy = the moment aligned with the magnetic field \( m_S = -\frac{1}{2} \)

The state of highest energy = aligned against the magnetic field \( m_S = +\frac{1}{2} \)

The energy of each orientation \( E = \mu H \)
For an electron \( \mu = m_s g \mu_B \),
\( \mu_B = \) the Bohr magneton
\( g = \) the spectroscopic g-factor of the free electron 2.0023192778 \((\approx 2.00)\).
Origin of Magnetism and Interactions

- Spin Momentum
- Zero Field Splitting
- Hyperfine Interaction
- Nuclear Spin
- Spin-Orbit-Coupling
- Nuclear-Zeeman-Effect
- Orbital Momentum
- Zeeman-Effect
- Magnetic Field
Magnetism and Interactions

Magnetic field – splitting + mixing of energy levels

**Zeeman-Effect:** splitting of levels in an applied magnetic field
the simplest case with $S = \frac{1}{2}$:
splitting of the levels with $m_s = + \frac{1}{2}$ and $m_s = - \frac{1}{2}$

$$E = -\mu \cdot B$$
Magnetism and Interactions

Zero Field Splitting (ZFS): The interactions of electrons with each other in a given system (fine interaction), lifting of the degeneracy of spin states for systems with $S > 1/2$ in the absence of an applied magnetic field, a weak interaction of the spins mediated by the spin–orbit coupling. ZFS appears as a small energy gap of a few cm$^{-1}$ between the lowest energy levels.

$S = 3/2$
# Zero Field Splitting in $d^n$ Ions

## Tetrahedral

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>Configuration</th>
<th>Term</th>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^2$</td>
<td>$e^2$</td>
<td>$^3A_2$</td>
<td>$S = 1$</td>
<td>Ti(II), V(III)</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$e^2t_2^3$</td>
<td>$^6A_1$</td>
<td>$S = 5/2$</td>
<td>Mn(II), Fe(III)</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$e^4t_2^3$</td>
<td>$^4A_2$</td>
<td>$S = 3/2$</td>
<td>Co(II)</td>
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</table>

## Octahedral

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>Configuration</th>
<th>Term</th>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^2$</td>
<td>$t_2^3$</td>
<td>$^4A_2g$</td>
<td>$S = 3/2$</td>
<td>Cr(III)</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$t_{2g}^3e_{2g}^1$</td>
<td>$^6A_{1g}$</td>
<td>$S = 5/2$</td>
<td>Mn(II), Fe(III)</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$t_{2g}^5e_{2g}^1$</td>
<td>$^4A_{2g}$</td>
<td>$S = 3/2$</td>
<td>Cr(III)</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$t_{2g}^7e_{2g}^1$</td>
<td>$^3A_{2g}$</td>
<td>$S = 1$</td>
<td>Ni(II)</td>
</tr>
</tbody>
</table>
Magnetism and Interactions

Hyperfine Interactions: The interactions of the nuclear spin I and the electron spin S (only s-electrons).
Magnetism and Interactions

**Spin-Orbit Coupling:** The interaction of the orbital $L$ and spin $S$ part of a given system, more important with increasing atomic mass. $\lambda = L \times S$
Magnetism and Interactions

**Ligand Field:** States with different orbital momentum differ in their spatial orientation, very sensitive to the presence of charges in the nearby environment.

In coordination chemistry these effects and the resulting splitting of levels is described by the ligand field.
<table>
<thead>
<tr>
<th>Effect</th>
<th>System</th>
<th>Energy equivalent [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-electron interaction</td>
<td>$\hat{H}_{ee}$</td>
<td>3d, 4d, 5d 4f, 5f 3d &gt; 4d &gt; 5d $\approx 10^4$ 4f &gt; 5f $\approx 10^4$</td>
</tr>
<tr>
<td>Ligand-field potential</td>
<td>$\hat{H}_{LF}$</td>
<td>3d, 4d, 5d 4f 5f 3d &lt; 4d &lt; 5d $\approx 2 \cdot 10^4$ $\approx 10^2$ $\approx 10^3$</td>
</tr>
<tr>
<td>Spin-orbit coupling</td>
<td>$\hat{H}_{SO}$</td>
<td>3d, 4d, 5d 4f, 5f 3d &lt; 4d &lt; 5d $\approx 10^3$ 4f &lt; 5f $\approx 10^3$</td>
</tr>
<tr>
<td>Exchange interaction</td>
<td>$\hat{H}_{ex}$</td>
<td>nd 4f 4d–4f $\leq 10^2$ $\leq 1$ $\leq 10$</td>
</tr>
</tbody>
</table>
| Magnetic field              | $\hat{H}_{Zeeman}$          | $\approx 0.5$ (1 T) }
Interactions of Spin Centers

\[ \hat{H} = -J \hat{S}_i \hat{S}_j + \tilde{D} \hat{S}_i \hat{S}_j + \tilde{d} \hat{S}_i \times \hat{S}_j \]

**Isotropic interaction**
The parallel alignment of spins favored = ferromagnetic
The antiparallel alignment = antiferromagnetic

**Non-isotropic interactions** (like dipole–dipole interactions)

**Antisymmetric exchange**
Excluded by an inversion center

without orbital contributions (pure spin magnetism) the last two terms are omitted
Lenz's Law

(~1834)

When a substance is placed within a magnetic field, $H$, the field within the substance, $B$, differs from $H$ by the induced field, $M$, which is proportional to the intensity of magnetization, $M$.

$$B = \mu_0(H + M)$$

Magnetization does not exist outside of the material.
Magnetic Variables SI

Magnetic field strength (intensity) \( H \) [A m\(^{-1}\)]
fields resulting from electric current

Magnetization (polarization) \( M \) [A m\(^{-1}\)]
Vector sum of magnetic moments (\( \mu \)) per unit volume \( \Sigma \mu/V \)
spin and orbital motion of electrons [A m\(^2\)/m\(^3\) = A m\(^{-1}\)]
Additional magnetic field induced internally by \( H \), opposing or supporting \( H \)

Magnetic induction (flux density) \( B \) [T, Tesla = Wb m\(^{-2}\) = J A\(^{-1}\)m\(^{-2}\)]
a field within a body placed in \( H \) resulting from electric current and spin and orbital motions

Field equation
(infinite system)
\( \mu_0 = 4\pi \times 10^{-7} \) [N A\(^{-2}\) = H m\(^{-1}\) = kg m A\(^{-2}\)s\(^{-2}\)] permeability of free space

In vacuum: \( B = \mu_0(H + 0) \)
Magnetic Variable Mess

Magnetic field strength (intensity) \( H \) (Oe, Oersted)
fIELDS RESULTING FROM ELECTRIC CURRENT \( (1 \text{ Oe} = 79.58 \text{ A/m}) \)

Magnetization (polarization) \( M \) (emu/cm\(^3\) )
magnetic moment per unit volume
spin and orbital motion of electrons \( 1 \text{ emu/g} = 1 \text{ Am}^2/\text{kg} \)

Magnetic induction \( B \) (G, Gauss) \( 1 \text{T} = 10^4 \text{ G} \)
a field resulting from electric current and spin and orbital motions

Field equation

\[
B = \mu_0 (H + 4\pi M)
\]

\( \mu_0 = 1 \) permeability of free space, dimensionless

See:
Magnetochemistry in SI Units, Terence I. Quickenden and Robert C. Marshall,
Journal of Chemical Education, 49, 2, 1972, 114-116
## Important Variables, Units, and Relations

<table>
<thead>
<tr>
<th>Variables</th>
<th>cgs units</th>
<th>SI</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>$E$</td>
<td>erg</td>
<td>J (joule)</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>$H$</td>
<td>Oe (oersted)</td>
<td>Am$^{-1}$</td>
</tr>
<tr>
<td>Magnetic induction</td>
<td>$B$</td>
<td>G (gauss)</td>
<td>T (tesla)</td>
</tr>
<tr>
<td>Magnetic flux</td>
<td>$\Phi$</td>
<td>Mx (maxwell)</td>
<td>Wb (weber)</td>
</tr>
<tr>
<td>Magnetization</td>
<td>$M$</td>
<td>emu cm$^{-3}$</td>
<td>Wb m$^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Relations</th>
<th>cgs units</th>
<th>SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic energy</td>
<td>$E = -m \cdot H$</td>
<td>erg</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>$\chi = M/H$</td>
<td>emu cm$^{-3}$ Oe$^{-1}$</td>
</tr>
<tr>
<td>Magnetic permeability</td>
<td>$\mu = B/H$ = $1 + 4\chi$</td>
<td>G Oe$^{-1}$</td>
</tr>
</tbody>
</table>
Magnetic Susceptibility $\chi$

(volume) magnetic susceptibility $\chi$ of a sample [dimensionless]

$\chi = \text{how effectively an applied magnetic field } H \text{ induces magnetization } M \text{ in a sample, how susceptible are dipoles to reorientation measurable, extrinsic property of a material, positive or negative}$

\[ \chi = \frac{\delta M}{\delta H} \]

If the magnetic field is weak enough and $T$ not too low, $\chi$ is independent of $H$ and

\[ M = \chi \times H \]

$M$ is a vector, $H$ is a vector, therefore $\chi$ is a second rank tensor.
If the sample is magnetically isotropic, $\chi$ is a scalar.

$M = \text{the magnetic moment magnetization } [\text{A m}^{-1}]$

$H = \text{the macroscopic magnetic field strength (intensity) } [\text{A m}^{-1}]$
Mass and Molar Magnetic Susceptibility

mass magnetic susceptibility $\chi_m$ of a sample

$$\chi_m = \frac{\chi}{\rho} \left[ \frac{cm^3}{g} \right]$$

$m = \text{density}$

molar magnetic susceptibility $\chi_M$ of a sample (intrinsic property)

$$\chi_M = \chi_m \times M \left[ \frac{cm^3}{mol} = \frac{emu}{mol} \right]$$

Typical molar susceptibilities

- Paramagnetic $\sim +0.01 \ \mu_B$
- Diamagnetic $\sim -1 \times 10^{-6} \ \mu_B$
- Ferromagnetic $\sim +0.01 - 10 \ \mu_B$
- Superconducting $\sim$ Strongly negative, repels fields completely (Meisner effect)
Relative Permeability $\mu$

Magnetic field $H$ generated by a current is enhanced in materials with **permeability $\mu$** to create larger fields $B$

$$\mu = \frac{B}{H}$$

$$B = \mu \times H$$

$$\mu = \frac{B}{H} = \frac{\mu_0(M + H)}{H} = \mu_0(\chi + 1) = \mu_0 \mu_r.$$  

$\mu_0 = 4\pi \times 10^{-7} \text{ [N A}^{-2} = \text{kg m A}^{-2}\text{s}^{-2}]$ permeability of free space

$$B = \mu_0(H + M) = \mu_0(H + \chi H) = \mu_0(1 + \chi)H = \mu H$$

$$\mu = \mu_0(1 + \chi)$$
Magnetic Susceptibility

$\chi_M$ is the algebraic sum of contributions associated with different phenomena, measurable:

$$\chi_M = \chi_M^D + \chi_M^P + \chi_M^{\text{Pauli}}$$

$\chi_M^D =$ diamagnetic susceptibility due to closed-shell (core) electrons. Always present in materials. Can be calculated from atom/group additive increments (Pascal’s constants) or the Curie plot. Temperature and field independent.

$\chi_M^P =$ paramagnetic susceptibility due to unpaired electrons, increases upon decreasing temperature.

$\chi_M^{\text{Pauli}} =$ Pauli, in metals and other conductors - due to mixing excited states that are not thermally populated into the ground (singlet) state - temperature independent.
Dimagnetic Susceptibility

\[ \chi_M^D \] is the sum of contributions from atoms and bond:

\[ \chi_M^D = \Sigma \chi_{D\;\text{atom}} + \Sigma \lambda_{\text{bond}} \]

\( \chi_{D\;\text{atom}} \) = atom diamagnetic susceptibility increments (Pascal’s constants)
\( \lambda_{\text{bond}} \) = bond diamagnetic susceptibility increments (Pascal’s constants)

See: Diamagnetic Corrections and Pascal’s Constants

Gordon A. Bain and John F. Berry: Journal of Chemical Education Vol. 85, No. 4, 2008, 532-536

For a paramagnetic substance, e.g. Cr(acac)_3 it is difficult to measure its diamagnetism directly.
Synthesize Co(acac)_3, Co^{3+}: d^6 low spin.
Use the \( \chi_{\text{dia}} \) value of Co(acac)_3 as that of Cr(acac)_3.
Diamagnetic Susceptibility

Table 1. Values of $\chi_D$, for Atoms in Covalent Species

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\chi_D/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
<th>Atom</th>
<th>$\chi_D/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
<th>Atom</th>
<th>$\chi_D/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
<th>Atom</th>
<th>$\chi_D/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>-31.0</td>
<td>C (ring)</td>
<td>-6.24</td>
<td>Li</td>
<td>-4.2</td>
<td>S</td>
<td>-15.0</td>
</tr>
<tr>
<td>Al</td>
<td>-13.0</td>
<td>Ca</td>
<td>-15.9</td>
<td>Mg</td>
<td>-10.0</td>
<td>Sb(III)</td>
<td>-74.0</td>
</tr>
<tr>
<td>As(III)</td>
<td>-20.9</td>
<td>Cl</td>
<td>-20.1</td>
<td>N (ring)</td>
<td>-4.61</td>
<td>Se</td>
<td>-23.0</td>
</tr>
<tr>
<td>As(V)</td>
<td>-43.0</td>
<td>F</td>
<td>-6.3</td>
<td>N (open chain)</td>
<td>-5.57</td>
<td>Si</td>
<td>-13</td>
</tr>
<tr>
<td>B</td>
<td>-7.0</td>
<td>H</td>
<td>-2.93</td>
<td>Na</td>
<td>-9.2</td>
<td>Sn(IV)</td>
<td>-30</td>
</tr>
<tr>
<td>Bi</td>
<td>-192.0</td>
<td>Hg(II)</td>
<td>-33.0</td>
<td>O</td>
<td>-4.6</td>
<td>Te</td>
<td>-37.3</td>
</tr>
<tr>
<td>Br</td>
<td>-30.6</td>
<td>I</td>
<td>-44.6</td>
<td>P</td>
<td>-26.3</td>
<td>Ti(II)</td>
<td>-40.0</td>
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<tr>
<td>C</td>
<td>-6.00</td>
<td>K</td>
<td>-18.5</td>
<td>Pb(II)</td>
<td>-46.0</td>
<td>Zn</td>
<td>-13.5</td>
</tr>
</tbody>
</table>

Table 2. Values of $\lambda$, for Specific Bond Types

<table>
<thead>
<tr>
<th>Bond $^a$</th>
<th>$\lambda/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
<th>Bond</th>
<th>$\lambda/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
<th>Bond</th>
<th>$\lambda/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
<th>Bond</th>
<th>$\lambda/(1 \times 10^{-6}$ emu mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>+5.5</td>
<td>Cl-CR$_2$Cr$_2$Cl$_2$</td>
<td>+4.3</td>
<td>Ar-Br</td>
<td>-3.5</td>
<td>Imidazole</td>
<td>+8.0</td>
</tr>
<tr>
<td>C=O</td>
<td>+10.6</td>
<td>R$_2$ClC$_2$</td>
<td>+1.44</td>
<td>Ar-Cl</td>
<td>-2.5</td>
<td>Isoxazole</td>
<td>+1.0</td>
</tr>
<tr>
<td>C=O</td>
<td>+6.3</td>
<td>RCHCl$_2$</td>
<td>+6.43</td>
<td>Ar-I</td>
<td>-3.5</td>
<td>Morpholine</td>
<td>+5.5</td>
</tr>
<tr>
<td>C-Br</td>
<td>+4.1</td>
<td>C-Br</td>
<td>+4.1</td>
<td>Ar-COOH</td>
<td>-1.5</td>
<td>Piperazine</td>
<td>+7.0</td>
</tr>
<tr>
<td>C=O</td>
<td>+6.3</td>
<td>C-I</td>
<td>+4.1</td>
<td>Ar-C=O</td>
<td>+0.8</td>
<td>Piperidine</td>
<td>+3.0</td>
</tr>
<tr>
<td>COOR</td>
<td>-5.0</td>
<td>Ar-OH</td>
<td>-1</td>
<td>Ar-C(=O)NH$_2$</td>
<td>+1.5</td>
<td>Pyrazine</td>
<td>+9.0</td>
</tr>
<tr>
<td>C=O</td>
<td>-5.0</td>
<td>Ar=NR$_2$</td>
<td>+1</td>
<td>Benzene</td>
<td>-1.4$^c$</td>
<td>Pyridine</td>
<td>+0.5</td>
</tr>
<tr>
<td>C(=O)N$^+$H$_2$</td>
<td>-3.5</td>
<td>Ar-C(=O)R</td>
<td>-1.5</td>
<td>Cyclobutane</td>
<td>+7.2</td>
<td>Pyrimidine</td>
<td>+6.5</td>
</tr>
<tr>
<td>N=N</td>
<td>+1.85</td>
<td>Ar-COOH</td>
<td>-1.5</td>
<td>Cyclocarbocyclic</td>
<td>+10.56</td>
<td>ac- or γPyron</td>
<td>-1.4</td>
</tr>
<tr>
<td>C-CN</td>
<td>+8.15</td>
<td>Ar-C=C</td>
<td>-1.00</td>
<td>Cyclhexane</td>
<td>+3.0</td>
<td>Pyrrole</td>
<td>-3.5</td>
</tr>
<tr>
<td>C-CN</td>
<td>+0.8</td>
<td>Ar-C=C</td>
<td>-1.5</td>
<td>Cyclhexano</td>
<td>+6.9</td>
<td>Pyrrolidine</td>
<td>+0.0</td>
</tr>
<tr>
<td>C-CN</td>
<td>+0.0</td>
<td>Ar-OR</td>
<td>-1</td>
<td>Cyclpentane</td>
<td>+0.0</td>
<td>Tetrachlorofuran</td>
<td>+0.0</td>
</tr>
<tr>
<td>C-CN</td>
<td>+1.7</td>
<td>Ar-CHO</td>
<td>-1.5</td>
<td>Cyclopropane</td>
<td>+7.2</td>
<td>Thiazole</td>
<td>-3.0</td>
</tr>
<tr>
<td>C-CN</td>
<td>-2.0</td>
<td>Ar-Ar</td>
<td>-0.5</td>
<td>Dioxane</td>
<td>+5.5</td>
<td>Thiophene</td>
<td>-7.0</td>
</tr>
<tr>
<td>C-CN</td>
<td>-0.5</td>
<td>Ar-N=O</td>
<td>-0.5</td>
<td>Furan</td>
<td>-2.5</td>
<td>Triazine</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

$^a$Ordinary C-H and C-C single bonds are assumed to have a $\lambda$ value of 0.0 emu mol$^{-1}$. $^b$The symbol Ar represents an aryl ring. $^c$Some sources list the $\lambda$ value for a benzene ring as -18.00 to which three times $\lambda$(C=C) must then be added. To minimize the calculations involved, this convention was not followed such that $\lambda$ values given for aromatic rings are assumed to automatically take into account the corresponding double bonds in the ring.
Magnetic Susceptibility

\( \chi^p_M = \text{paramagnetic susceptibility relates to number of unpaired electrons} \)

\[
\chi^p_M T = \frac{N_A g^2 \mu_B^2}{3k_B} [S(S + 1)]
\]

Caclulation of \( \mu \) from \( \chi \)

\[
\mu_{\text{eff}} = \left( \frac{3k_B}{\mu_0 N_A \mu_B^2} \right)^{1/2} \sqrt{\chi_M T}
\]
## Magnetic Properties

<table>
<thead>
<tr>
<th>Type</th>
<th>Sign of $\chi$</th>
<th>Typical $\chi$ (SI units)</th>
<th>Dependence of $\chi$ on H</th>
<th>Change of $\chi$ w/inc. temp.</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>-</td>
<td>$(1-600) \times 10^{-5}$</td>
<td>Independent</td>
<td>None</td>
<td>Electron charge</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>+</td>
<td>0-0.1</td>
<td>Independent</td>
<td>Dec.</td>
<td>Spin and orbital motion of electrons on atoms.</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>+</td>
<td>$0.1-1 \times 10^{-7}$</td>
<td>Dependent</td>
<td>Dec.</td>
<td>Cooperative interaction between magnetic moments of individual atoms.</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>+</td>
<td>0-0.1</td>
<td>May be dependent</td>
<td>Inc.</td>
<td></td>
</tr>
<tr>
<td>Pauli paramagnetism</td>
<td>+</td>
<td>$1 \times 10^{-5}$</td>
<td>Independent</td>
<td>None</td>
<td>Spin and orbital motion of delocalized electrons.</td>
</tr>
</tbody>
</table>
Magnetic Properties

Magnetic behavior of a substance = magnetic polarization in a magnetic field $H_0$
Magnetic Properties

Magnetic behavior of a substance = magnetic polarization in a mg field $H_0$
Magnetism of the Elements
Diamagnetism and Paramagnetism

Diamagnetic Ions
a small magnetic moment associated with electrons traveling in a closed loop around the nucleus.

Paramagnetic Ions
The moment of an atom with unpaired electrons is given by the spin, S, orbital angular momentum, L and total momentum, J, quantum numbers.

Diamagnetic $\rightarrow$ Repulsive

Paramagnetic $\rightarrow$ Attractive

Inhomogeneous $mg$ field

$B = \mu_0 (H + M)$
(Langevine) Diamagnetism

Lenz’s Law – when magnetic field acts on a conducting loop, it generates a current that counteracts the change in the field

Electrons in closed shells (paired) cause a material to be repelled by H

Weakly repulsive interaction with the field H
All the substances are diamagnetic

\[ \chi < 0 = \text{an applied field induces} \]
\[ \chi = \text{a small moment opposite to the field} \]
\[ \chi = -10^{-5} \text{ to } -10^{-6} \]

Superconductors \( \chi = -1 \) perfect diamagnets

\[ M = \chi \times H \]
(Curie) Paramagnetism

Paramagnetism arises from the interaction of $H$ with the magnetic field of the unpaired electron due to the spin and orbital angular momentum.

Randomly oriented, rapidly reorienting magnetic moments
no permanent spontaneous magnetic moment
$M = 0$ at $H = 0$
Spins are non-interacting, non-cooperative, independent, dilute system
Weakly attractive interaction with the field

$\chi > 0 = \text{an applied field induces a small moment in the same direction as the field}$

$\chi = 10^{-3} \text{ to } -10^{-5}$
(Curie) Paramagnetism for $S = \frac{1}{2}$

Energy diagram of an $S = 1/2$ spin in an external magnetic field along the z-axis

Energy levels:
- $m_s = \pm 1/2$
- $m_s = 1/2$
- $m_s = -1/2$

Zeeman effect:
- $\Delta E = g \mu_B H$

Magnetic moment:
- $\mu = -g \mu_B S$

The interaction energy of magnetic moment with the applied magnetic field:
- $E = -\mu \cdot H = g \mu_B S \cdot H = m_s \cdot g \mu_B \cdot H$

$\Delta E = g \mu_B H$

Energy shift about 1 cm$^{-1}$ at 1 T (10 000 G)

$\mu_B =$ Bohr magneton ($= 9.27 \times 10^{-24}$ J/T)
$g =$ the Lande constant ($= 2.0023192778$)
(Curie) Paramagnetism for $S = \frac{1}{2}$

Relative populations $P$ of $\frac{1}{2}$ and $-\frac{1}{2}$ states

For $H = 25$ kG = 2.5 T \hspace{1cm} \Delta E \sim 2.3 \text{ cm}^{-1}$

At 300 K \hspace{1cm} kT \sim 200 \text{ cm}^{-1}$

Boltzmann distribution

\[
\frac{P_{1/2}}{P_{-1/2}} = e^{-\frac{\Delta E}{k_B T}} \approx 1
\]

The populations of $m_s = 1/2$ and $-1/2$ states are almost equal with only a very slight excess in the $m_s = -1/2$ state.

Even under very large applied field $H$, the net magnetic moment is very small.
(Curie) Paramagnetism for S = \(\frac{1}{2}\)

To obtain magnetization M (or \(\chi_M\)), need to consider all the energy states that are populated

\[
E = -\mu H = g \mu_B S H = m_s g \mu_B H
\]

The magnetic moment, \(\mu_n\) (the direction // H) of an electron in a quantum state n

\[
\mu_n = -\frac{\partial E_n}{\partial H} = -m_s g \mu_B
\]

\(\mu = -m_s g \mu_B\)
\(E = m_s g \mu_B H\)

Consider:
- The magnetic moment of each energy state
- The population of each energy state

\[
M = N_A \sum \mu_n P_n
\]

\[
P_n = \frac{N_n}{N_{Tot}} = \frac{e^{-\frac{E_n}{k_B T}}}{\sum e^{-\frac{E_n}{k_B T}}}
\]

\(P_n\) = probability in state n
\(N_n\) = population of state n
\(N_{Tot}\) = population of all the states
(Curie) Paramagnetism for $S = \frac{1}{2}$

\[
M = N \sum_{m_s} \mu_n e^{-E_n/kT} \left( \sum_{m_s} e^{-E_n/kT} \right) \approx g \mu_B H \ll kT \quad \text{when } H \sim 5 \text{ kG}
\]

\[
M = N \left[ \frac{g\beta/2 e^{g\beta H/2kT} - g\beta/2 e^{-g\beta H/2kT}}{e^{g\beta H/2kT} + e^{-g\beta H/2kT}} \right] = \frac{N g\beta}{2} \left[ \frac{1 + g\beta H/2kT - (1 - g\beta H/2kT)}{1 + g\beta H/2kT + (1 - g\beta H/2kT)} \right] = \frac{N g^2 \beta^2 H}{4kT}
\]

For $x \ll 1$

\[
e^{\pm x} \sim 1 \pm x
\]

\[
M_M = \frac{N_A g^2 \mu_B^2}{4k_B T} H
\]
(Curie) Paramagnetism for $S = \frac{1}{2}$

\[ \chi_M = \frac{M}{H} = \frac{N_A g^2 \mu_B^2}{4k_B T} = \frac{C}{T} \]

Curie Law:

\[ \chi_M = \frac{C}{T} \]
(Curie) Paramagnetism for general S

\[ E_n = m_s g \mu_B H \quad m_s = -S, -S + 1, \ldots, S - 1, S \]

\[
M = \frac{N \sum_{m_s=-S}^S (-m_s g \beta) e^{-m_s g \beta H/kT}}{\sum_{m_s} e^{-m_s g \beta H/kT}} = \frac{N g^2 \beta^2 H}{3kT} S(S+1)
\]

\[
\chi_M = \frac{M}{H} = \frac{N_A g^2 \mu_B^2}{3k_B T} S(S + 1)
\]

For \( S = 1/2 \)
\[
\chi_M = \frac{N_A g^2 \mu_B^2}{4k_B T}
\]

For \( S = 1 \)
\[
\chi_M = \frac{2N_A g^2 \mu_B^2}{3k_B T}
\]

For \( S = 3/2 \)
\[
\chi_M = \frac{5N_A g^2 \mu_B^2}{4k_B T}
\]

non-interacting, non-cooperative, independent, dilute
(Curie) Paramagnetism

\[ \chi_M = \frac{M}{H} = \frac{N_A g^2 \mu_B^2}{3k_B T} S(S+1) \]

\[ \mu_{\text{eff}} = g \sqrt{S(S+1)} = \sqrt{n(n+1)} \]  
(in BM, Bohr Magnetons)

\[ \mu_{\text{eff}} = \sqrt{\frac{3 \chi_M k_B T}{\mu_0 N_A \mu_B^2}} \]

n = number of unpaired e-
g = 2
**Curie Law**

\[ \chi = \frac{C}{T} \]

\[ \frac{1}{\chi} = \frac{1}{C} T \]

\( \chi \) vs. \( T \) plot

\( \frac{1}{\chi} = \frac{T}{C} \) plot - a straight line of gradient \( C^{-1} \) and intercept zero

\( \chi T = C \) - a straight line parallel to the x-axis at a constant value of \( \chi T \) showing the temperature independence of the magnetic moment.
Plot of $\mu_{eff}$ vs Temperature

- $S=3/2$
- $\mu_{eff} = 2[S(S+1)]^{1/2}$

$$\mu_{eff} = \sqrt{\frac{3 \chi_M k_B T}{\mu_0 N_A \mu_B^2}}$$
Spin Equilibrium and Spin Crossover

\[ \mu_{\text{eff}} \] (BM)

- Temperature
- \( S = \frac{3}{2} \):
  - 3.87
- \( S = \frac{1}{2} \):
  - 1.7

- Temperature
- \( S = \frac{3}{2} \):
  - 3.87
- \( S = \frac{1}{2} \):
  - 1.7
Curie Plot

\[ \chi_{\text{exp}} = \frac{C}{T - \theta} + \chi_T \]

\[ \chi_T = \chi_{\text{dia}} + \chi_{\text{Pauli}} = \text{temperature independent contributions} \]

at high temperature if \( \theta \) is small

Plot \( \chi_{\text{exp}} \) vs \( 1/T \)

slope = \( C \); intercept = \( \chi_T \)

\[ \frac{1}{273} \text{ K} = 0.00366 \quad \frac{1}{1.8} \text{ K} = 0.556 \]
Curie Plot

\[ \chi_{\text{exp}} = \frac{C}{T - \theta} + \chi_T \]

at high temperature if \( \theta \) is small

\[ \chi_T = \chi_{\text{dia}} + \chi_{\text{Pauli}} = \text{temperature independent contributions} \]

Plot \( 1/\chi_{\text{exp}} \) vs \( T \)

slope = \( 1/C \); intercept = \( \theta/C \)
Curie-Weiss Law

Deviations from paramagnetic behavior
The system is not magnetically dilute (pure paramagnetic) or at low temperatures
The neighboring magnetic moments may align parallel or antiparallel (still considered as paramagnetic, not ferromagnetic or antiferromagnetic)

\[ \Theta = \text{the Weiss constant} \]
\[ (\text{the x-intercept}) \]
\[ \Theta = 0 \] paramagnetic spins independent of each other
\[ \Theta \text{ is positive, spins align parallel} \]
\[ \Theta \text{ is negative, spins align antiparallel} \]
Curie-Weiss Paramagnetism

Plots obeying the Curie-Weiss law with a negative Weiss constant

\[ \chi = \frac{C}{T - \theta} \]

\( \theta = -70 \text{ K} \)

\[ \frac{1}{\chi} = \frac{1}{C} \frac{T - \theta}{T} \]

\( \theta > 0 \) - ferromagnetic interactions

(NOT ferromagnetism)

\( \theta < 0 \) - antiferromagnetic interactions

\( \theta \) (NOT antiferromagnetism)
Curie-Weiss Paramagnetism

Plots obeying the Curie-Weiss law with a positive Weiss constant

\[ \chi = \frac{C}{T - \theta} \]

\[ \theta = +70 \text{ K} \]

\[ \frac{1}{\chi} = \frac{1}{C} \frac{T - \theta}{C} \]

\[ \chi T = \frac{C T}{T - \theta} \]

\[ \theta = \text{intermolecular interactions among the moments} \]

\[ \theta > 0 \ - \text{ferromagnetic interactions} \]

(NOT ferromagnetism)

\[ \theta < 0 \ - \text{antiferromagnetic interactions} \]

\theta (NOT antiferromagnetism)
Saturation of Magnetization

The Curie-Wiess law does not hold where the system is approaching saturation at high $H$ – $M$ is not proportional to $H$

Approximation for $g \mu_B H \ll kT$ not valid

$e^{\pm x} \sim 1 \pm x$

$S=1/2$

$S=1$

$S=3/2$

$S=2$

$\chi_M \neq \frac{M}{H} \neq \frac{N_A g^2 \mu_B^2}{3k_B T} S(S + 1)$

$M_{sat} = N_A g \mu_B S$
Saturation of Magnetization

The Curie-Wiess law does not hold where the system is approaching saturation at high $H$ – $M$ is not proportional to $H$.

Approximation for $g\mu_B H \ll kT$ not valid

$$e^{\pm x} \approx 1 \pm x$$

$$\chi_M \neq \frac{M}{H} \neq \frac{N_A g^2 \mu_B^2}{3k_B T} S(S + 1)$$
Saturation of Magnetization

The Curie-Wiess law does not hold where the system is approaching saturation at high $H$ – $M$ is not proportional to $H$

Approximation for $g \mu_B H << kT$ not valid

\[ e^{\pm x} \sim 1 \pm x \]

\[ \chi_M \neq \frac{M}{H} \neq \frac{N_A g^2 \mu_B^2}{3k_B T} S(S+1) \]

Curves I, II, and III refer to ions of chromium potassium alum, iron ammonium alum, and gadolinium sulfate octahydrate for which $g = 2$ and $j = 3/2$, 5/2, and 7/2, respectively.
Magnetism in Transition Metal Complexes

Many transition metal salts and complexes are paramagnetic due to partially filled d-orbitals.

The experimentally measured magnetic moment (μ) can provide important information about the compounds:

- Number of unpaired electrons present
- Distinction between HS and LS octahedral complexes
- Spectral behavior
- Structure of the complexes (tetrahedral vs octahedral)
Paramagnetism in Metal Complexes

Orbital motion of the electron generates

ORBITAL MAGNETIC MOMENT ($\mu_l$)

Spin motion of the electron generates

SPIN MAGNETIC MOMENT ($\mu_s$)

$l = \text{orbital angular momentum}$
$s = \text{spin angular momentum}$

For multi-electron systems

$L = l_1 + l_2 + l_3 + \ldots$

$S = s_1 + s_2 + s_3 + \ldots$

\[ \mu_{l+s} = [4S(S+1) + L(L+1)]^{1/2} \text{ B.M.} \]
Paramagnetism in Transition Metal Complexes

The magnetic properties arise mainly from the exposed d-orbitals. The energy levels of d-orbitals are perturbed by ligands – ligand field spin-orbit coupling is less important, the orbital angular momentum is often “quenched” by special electronic configuration, especially when the symmetry is low, the rotation of electrons about the nucleus is restricted which leads to \( L = 0 \)

\[
\mu_{l+S} = [4S(S+1) + \ell(\ell+1)]^{1/2} \text{ B.M.}
\]

\[
\mu_s = g \sqrt{S(S+1)} \frac{e\hbar}{4\pi m_e} = \sqrt{4S(S+1)} \mu_B
\]

Spin-Only Formula

\[
\mu_s = \sqrt{n(n+2)} \mu_B
\]

\( \mu_s = 1.73, 2.83, 3.88, 4.90, 5.92 \) BM for \( n = 1 \) to 5, respectively
Orbital Angular Momentum Contribution

There must be an unfilled / half-filled orbital similar in energy to that of the orbital occupied by the unpaired electrons. If this is so, the electrons can make use of the available orbitals to circulate or move around the center of the complexes and hence generate $L$ and $\mu_L$.

Conditions for orbital angular momentum contribution:

• The orbitals should be degenerate ($t_{2g}$ or $e_g$)

• The orbitals should be similar in shape and size, so that they are transferable into one another by rotation about the same axis (e.g. $d_{xy}$ is related to $d_{x^2-y^2}$ by a rotation of 45° about the z-axis.)

• Orbitals must not contain electrons of identical spin
Orbital Contribution in Octahedral Complexes

<table>
<thead>
<tr>
<th>Condition</th>
<th>$t_{2g}$ set</th>
<th>$e_g$ set</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Obeyed</td>
<td>Obeyed</td>
</tr>
<tr>
<td>2</td>
<td>Obeyed</td>
<td>Not obeyed</td>
</tr>
<tr>
<td>3</td>
<td>Since 1 and 2 are satisfied condition 3 dictates whether $t_{2g}$ will generate $\mu_1$ or not</td>
<td>Does not matter since condition 2 is already not obeyed</td>
</tr>
</tbody>
</table>

These conditions are fulfilled whenever one or two of the three $t_{2g}$ orbitals contain an odd no. of electrons.
Spin-Orbit Coupling

Little contribution from orbital angular momentum

dx²-y² and dxy orbitals have different energies in a certain electron configuration, electrons cannot go back and forth between them.

Electrons have to change directions of spins to circulate.

Orbitals are filled.

Spin-orbit couplings are significant.
Spin-orbit coupling influences g-value

\[ g = 2.0023 \pm \frac{n\lambda}{E_1-E_2} \]

2.0023: g-value for free ion
+ sign for \(<1/2\) filled subshell
– sign for \(>1/2\) filled subshell
\(n\): number of magic pentagon
\(\lambda\): free ion spin-orbit coupling constant

orbital sets that may give spin-orbit coupling
no spin-orbit coupling contribution for \(dz^2/dx^2-y^2\) and \(dz^2/dxy\)
# Orbital Contribution in Octahedral Complexes

<table>
<thead>
<tr>
<th>Ion</th>
<th>Config</th>
<th>OAM?</th>
<th>$\mu_{s0}$</th>
<th>$\mu_{obs}$</th>
<th>$\mu_{S+L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(III)</td>
<td>d1</td>
<td>yes</td>
<td>1.73</td>
<td>1.6-1.7</td>
<td>3.00</td>
</tr>
<tr>
<td>V(IV)</td>
<td>d1</td>
<td>yes</td>
<td>1.73</td>
<td>1.7-1.8</td>
<td></td>
</tr>
<tr>
<td>V(III)</td>
<td>d2</td>
<td>yes</td>
<td>2.83</td>
<td>2.7-2.9</td>
<td>4.47</td>
</tr>
<tr>
<td>Cr(IV)</td>
<td>d2</td>
<td>yes</td>
<td>2.83</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>V(II)</td>
<td>d3</td>
<td>no</td>
<td>3.88</td>
<td>3.8-3.9</td>
<td>5.20</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>d3</td>
<td>no</td>
<td>3.88</td>
<td>3.7-3.9</td>
<td></td>
</tr>
<tr>
<td>Mn(IV)</td>
<td>d3</td>
<td>no</td>
<td>3.88</td>
<td>3.8-4.0</td>
<td></td>
</tr>
<tr>
<td>Cr(II)</td>
<td>d4 h.s.</td>
<td>no</td>
<td>4.90</td>
<td>4.7-4.9</td>
<td>5.48</td>
</tr>
<tr>
<td>Cr(II)</td>
<td>d4 l.s.</td>
<td>yes</td>
<td>2.83</td>
<td>3.2-3.3</td>
<td></td>
</tr>
<tr>
<td>Mn(III)</td>
<td>d4 h.s.</td>
<td>no</td>
<td>4.90</td>
<td>4.9-5.0</td>
<td></td>
</tr>
<tr>
<td>Mn(III)</td>
<td>d4 l.s.</td>
<td>yes</td>
<td>2.83</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>d5 h.s.</td>
<td>no</td>
<td>5.92</td>
<td>5.6-6.1</td>
<td>5.92</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>d5 l.s.</td>
<td>yes</td>
<td>1.73</td>
<td>1.8-2.1</td>
<td></td>
</tr>
<tr>
<td>Fe(III)</td>
<td>d5 h.s.</td>
<td>no</td>
<td>5.92</td>
<td>5.7-6.0</td>
<td></td>
</tr>
<tr>
<td>Fe(III)</td>
<td>d5 l.s.</td>
<td>yes</td>
<td>1.73</td>
<td>2.0-2.5</td>
<td></td>
</tr>
<tr>
<td>Fe(II)</td>
<td>d6 h.s.</td>
<td>yes</td>
<td>4.90</td>
<td>5.1-5.7</td>
<td>5.48</td>
</tr>
<tr>
<td>Co(II)</td>
<td>d7 h.s.</td>
<td>yes</td>
<td>3.88</td>
<td>4.3-5.2</td>
<td>5.20</td>
</tr>
<tr>
<td>Co(II)</td>
<td>d7 l.s.</td>
<td>no</td>
<td>1.73</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Ni(III)</td>
<td>d7 l.s.</td>
<td>no</td>
<td>1.73</td>
<td>1.8-2.0</td>
<td></td>
</tr>
<tr>
<td>Ni(II)</td>
<td>d8</td>
<td>no</td>
<td>2.83</td>
<td>2.9-3.3</td>
<td>4.47</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>d9</td>
<td>no</td>
<td>1.73</td>
<td>1.7-2.2</td>
<td>3.00</td>
</tr>
</tbody>
</table>
Orbital Contribution in Octahedral Complexes
Orbital Contribution in Tetrahedral Complexes

<table>
<thead>
<tr>
<th>Ion</th>
<th>Config</th>
<th>OAM?</th>
<th>$\mu_{so}$</th>
<th>$\mu_{obs}$</th>
<th>$\mu_{S+L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(V)</td>
<td>d1</td>
<td>no</td>
<td>1.73</td>
<td>1.7-1.8</td>
<td>3.00</td>
</tr>
<tr>
<td>Mn(VI)</td>
<td>d1</td>
<td>no</td>
<td>1.73</td>
<td>1.7-1.8</td>
<td></td>
</tr>
<tr>
<td>Cr(IV)</td>
<td>d2</td>
<td>no</td>
<td>2.83</td>
<td>2.8</td>
<td>4.47</td>
</tr>
<tr>
<td>Mn(V)</td>
<td>d2</td>
<td>no</td>
<td>2.83</td>
<td>2.6-2.8</td>
<td></td>
</tr>
<tr>
<td>Fe(V)</td>
<td>d3</td>
<td>yes</td>
<td>3.88</td>
<td>3.6-3.7</td>
<td>5.20</td>
</tr>
<tr>
<td>-</td>
<td>d4</td>
<td>yes</td>
<td>4.90</td>
<td>-</td>
<td>5.48</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>d5</td>
<td>no</td>
<td>5.92</td>
<td>5.9-6.2</td>
<td>5.92</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>d6</td>
<td>no</td>
<td>4.90</td>
<td>5.3-5.5</td>
<td>5.48</td>
</tr>
<tr>
<td>Co(II)</td>
<td>d7</td>
<td>no</td>
<td>3.88</td>
<td>4.2-4.8</td>
<td>5.20</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>d8</td>
<td>yes</td>
<td>2.83</td>
<td>3.7-4.0</td>
<td>4.47</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>d9</td>
<td>yes</td>
<td>1.73</td>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>
Orbital Contribution in Low-symmetry Ligand Field

If the symmetry is lowered, degeneracy will be destroyed and the orbital contribution will be quenched.

\[ \mu_{\text{eff}} = g[S(S+1)]^{1/2} \text{ (spin-only)} \] is valid
Magnetic Properties of Lanthanides

4f electrons are too far inside $4f^n 5s^2 5p^6$ as compared to the d electrons in transition metals.

Thus 4f normally unaffected by surrounding ligands.

The magnetic moments of Ln$^{3+}$ ions are generally well-described from the coupling of spin and orbital angular momenta to give J vector.

Russell-Saunders Coupling
- spin orbit coupling constants are large (ca. 1000 cm$^{-1}$)
- ligand field effects are very small (ca. 100 cm$^{-1}$)
  - only ground J-state is populated
  - spin-orbit coupling $>>$ ligand field splitting
- magnetism is essentially independent of coordination environment
Magnetic Properties of Lanthanides
Magnetic Properties of Lanthanides

Magnetic moment of a J-state is expressed by the Landé formula:

$$\mu_J = g_J \sqrt{J(J+1)} \mu_B$$

$$J = L+S, L+S-1, \ldots L-S$$

For the calculation of g value, use:
- minimum value of J for the configurations up to half-filled; i.e. $J = L-S$ for $f^0$ - $f^7$ configurations
- maximum value of J for configurations more than half-filled; i.e. $J = L+S$ for $f^8$ - $f^{14}$ configurations

For $f^0$, $f^7$, and $f^{14}$, $L = 0$, hence $\mu_J$ becomes $\mu_S$
# Magnetic Properties of Lanthanides \( \text{Ln}^{3+} \)

<table>
<thead>
<tr>
<th>config</th>
<th>q.s.</th>
<th>No. e-</th>
<th>color</th>
<th>( \mu_{\text{eff}} )</th>
</tr>
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<tbody>
<tr>
<td>La</td>
<td>( 4f^0 )</td>
<td>( ^1S_0 )</td>
<td>0</td>
<td>Colorless</td>
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<tr>
<td>Ce</td>
<td>( 4f^1 )</td>
<td>( ^2F_{5/2} )</td>
<td>1</td>
<td>Colorless</td>
</tr>
<tr>
<td>Pr</td>
<td>( 4f^2 )</td>
<td>( ^3H_4 )</td>
<td>2</td>
<td>Green</td>
</tr>
<tr>
<td>Nd</td>
<td>( 4f^3 )</td>
<td>( ^4I_{9/2} )</td>
<td>3</td>
<td>Lilac</td>
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<tr>
<td>Pm</td>
<td>( 4f^4 )</td>
<td>( ^5I_4 )</td>
<td>4</td>
<td>Pink</td>
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<tr>
<td>Sm</td>
<td>( 4f^5 )</td>
<td>( ^6H_{5/2} )</td>
<td>5</td>
<td>Yellow</td>
</tr>
<tr>
<td>Eu</td>
<td>( 4f^6 )</td>
<td>( ^7F_0 )</td>
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<td>Pale pink</td>
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<tr>
<td>Gd</td>
<td>( 4f^7 )</td>
<td>( ^8S_{7/2} )</td>
<td>7</td>
<td>Colorless</td>
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<tr>
<td>Tb</td>
<td>( 4f^8 )</td>
<td>( ^7F_6 )</td>
<td>6</td>
<td>Pale pink</td>
</tr>
<tr>
<td>Dy</td>
<td>( 4f^9 )</td>
<td>( ^6H_{15/2} )</td>
<td>5</td>
<td>Yellow</td>
</tr>
<tr>
<td>Ho</td>
<td>( 4f^{10} )</td>
<td>( ^5I_8 )</td>
<td>4</td>
<td>Yellow</td>
</tr>
<tr>
<td>Er</td>
<td>( 4f^{11} )</td>
<td>( ^4I_{15/2} )</td>
<td>3</td>
<td>Rose-pink</td>
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<tr>
<td>Tm</td>
<td>( 4f^{12} )</td>
<td>( ^3H_6 )</td>
<td>2</td>
<td>pale green</td>
</tr>
<tr>
<td>Yb</td>
<td>( 4f^{13} )</td>
<td>( ^2F_{7/2} )</td>
<td>1</td>
<td>Colorless</td>
</tr>
<tr>
<td>Lu</td>
<td>( 4f^{14} )</td>
<td>( ^1S_0 )</td>
<td>0</td>
<td>Colorless</td>
</tr>
</tbody>
</table>
\[ \mu_{\text{eff}} \text{ of } \text{Nd}^{3+} (4f^3) \]

\[ L_{\text{max}} = 3 + 2 + 1 = 6 \]
\[ S_{\text{max}} = 3 \times 1/2 = 3/2 \quad M = 2S + 1 = 2 \times 3/2 + 1 = 4 \]
Ground state \( J = L - S = 6 - 3/2 = 9/2 \)
Ground state term symbol: \( 4I_{9/2} \)

\[ g = 1 + \frac{3/2(3/2+1)-6(6+1)+(9/2)(9/2+1)}{2x(9/2)(9/2+1)} = 0.727 \]

\[ \mu_{\text{eff}} = g[J(J+1)]^{1/2} = 0.727[(9/2)(9/2 + 1)] = 3.62 \text{ BM} \]
Magnetic Properties of Pr\(^{3+}\)

Pr\(^{3+}\) [Xe]4f\(^2\)

Find Ground State from Hund's Rules

Maximum Multiplicity  
\[ S = \frac{1}{2} + \frac{1}{2} = 1 \quad M = 2S + 1 = 3 \]

Maximum Orbital Angular Momentum  
\[ L = 3 + 2 = 5 \]

Total Angular Momentum  
\[ J = (L + S), (L + S) - 1, \ldots L - S = 6, 5, 4 \]

\( f^2 \) = less than half-filled sub-shell  
- choose minimum \( J \)  
\[ J = 4 \]

\[ g = \frac{3}{2} + \left[ \frac{1(1+1)-5(5+1)}{2(4)(4+1)} \right] = 0.8 \]

\[ \mu_J = 3.577 \text{ B.M. Experiment} = 3.4 - 3.6 \text{ B.M.} \]
Magnetic Properties of Lanthanides \( \text{Ln}^{3+} \)

Landé formula fits well with observed magnetic moments for all but \( \text{Sm(III)} \) and \( \text{Eu(III)} \) ions. Moments of these ions are altered from the Landé expression by temperature-dependent population of low lying excited J-state(s).
Spin Hamiltonian in Cooperative Systems

\[ H = -2J \sum_{ij} \vec{S}_i \cdot \vec{S}_j \]

The coupling between pairs of individual spins, \( S \), on atom \( i \) and atom \( j \)

\( J \) = the magnitude of the coupling

\( J > 0 \) \quad \text{Ferro} \quad \text{J} < 0 \) \quad \text{Antiferro}
**Magnetism in Solids**

**Cooperative Magnetism**

Diamagnetism and paramagnetism are characteristic of compounds with individual atoms which do not interact magnetically (e.g. classical complex compounds)

Ferromagnetism, antiferromagnetism and other types of cooperative magnetism originate from an intense magnetical interaction between electron spins of many atoms.

![Diagram](image)

(a) ferro
(b) antiferro
Magnetic Ordering

Critical temperature – under $T_{\text{crit}}$ the magnetic coupling energy between spins is bigger than thermal energy resulting in spin ordering

$T_C = \text{Curie temperature}$
$T_N = \text{Neel temperature}$
Curie Temperature

$T_c = 575^\circ C$
Magnetic Ordering

Spin Alignment:

<p>| | | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>↑↑↑↑</td>
<td>↑↓↑↑</td>
<td>↑↑↓↓</td>
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<td>↑↑↑↑</td>
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<td>↑↑↑↑</td>
<td>↑↓↑↑</td>
<td>↑↑↓↓</td>
<td></td>
</tr>
</tbody>
</table>

Total Spin:

<p>| | |</p>
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<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>↑</td>
<td>0</td>
</tr>
</tbody>
</table>

Ferromagnets - all interactions ferromagnetic, a large overall magnetization

Ferrimagnets - the alignment is antiferromagnetic, but due to different magnitudes of the spins, a net magnetic moment is observed

Antiferromagnets - both spins are of same magnitude and are arranged antiparallel

Weak ferromagnets – spins are not aligned anti/parallel but canted

Spin glasses – spins are correlated but not long-range ordered

Metamagnets
Para-, Ferro-, Antiferromagnetic
Magnetic Ordering

Comparison of M-H Behaviour

- Ferromagnet
- Ferrimagnet
- Paramagnet
- Antiferromagnet
- Diamagnet

Comparison of Susceptibility vs Temperature Behaviour

\[ \chi^{-1} \]

- Antiferromagnet
- Paramagnet
- Ferromagnet

T(K)

(3) Ferromagnetic e.g. Fe₃O₄, NiFe₂O₄
Ferrimagnetic e.g. ferrite (α), Co, Ni, Gd
(\( \chi \) as large as 10³)

(2) Paramagnetic (\( \chi \) small and positive)
e.g. Al, Cr, Mo, Na, Ti, Zn

Vacuum (\( \chi = 0 \))

(1) Diamagnetic (\( \chi \approx 10^{-5} \))
e.g. Al₂O₃, Cu, Au, Si, Ag, Zn

Magnetic induction (B) (Tesla)

Applied magnetic field (H) (ampere-turns/m)

79
Magnetic Ordering

Types of Magnetic Behavior (in order of decrease strength):
everything related to magnetics is due to electron spin.

<table>
<thead>
<tr>
<th>type</th>
<th>spin alignment</th>
<th>spin in simplified plot</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>ferromagnetic</td>
<td>all spins align parallel to one another: spontaneous magnetization: $M = a + b$</td>
<td>![Image of ferromagnetic spin alignment]</td>
<td>Fe, Co, Ni, Gd, Dy, SmCo$_5$, Sm$<em>2$Co$</em>{17}$, Nd$<em>2$Fe$</em>{14}$B</td>
</tr>
<tr>
<td>ferrimagnetic</td>
<td>most spins parallel to one another, some spins antiparallel: spontaneous magnetization: $M = a - b &gt; 0$</td>
<td>![Image of ferrimagnetic spin alignment]</td>
<td>magnetite (Fe$_3$O$_4$), yttrium iron garnet (YIG), GdCo$_5$</td>
</tr>
<tr>
<td>antiferromagnetic</td>
<td>periodic parallel-antiparallel spin distribution: $M = a - b = 0$</td>
<td>![Image of antiferromagnetic spin alignment]</td>
<td>chromium, FeMn, NiO</td>
</tr>
<tr>
<td>paramagnetic</td>
<td>spins tend to align parallel to an external magnetic field: $M = 0$ @ $H = 0$, $M &gt; 0$ @ $H &gt; 0$</td>
<td>![Image of paramagnetic spin alignment]</td>
<td>oxygen, sodium, aluminum, calcium, uranium</td>
</tr>
<tr>
<td>diamagnetic</td>
<td>spins tend to align antiparallel to an external magnetic field: $M = 0$ @ $H = 0$, $M &lt; 0$ @ $H &gt; 0$</td>
<td>![Image of diamagnetic spin alignment]</td>
<td>superconductors, nitrogen, copper, silver, gold, water, organic compounds</td>
</tr>
</tbody>
</table>
Para-, Ferro-, Antiferromagnetic Ordering
Ferromagnetism

J positive with spins parallel below $T_c$
a spontaneous permanent $M$ (in absence of $H$)
$T_c =$ Curie Temperature, above $T_c =$ paramagnet

Ferromagnetic behaviour (FM)
Paramagnetic behaviour (PM)

Curie Point
$T$

χ

Non-magnetic metal
Ferromagnetic metal

E

DOS

DOS

EF

M

82
Ferromagnetism

calculated exchange interaction

interatomic distances/radius of 3d orbitals
Antiferromagnetism

J negative with spins antiparallel below $T_N$
no spontaneous M, no permanent M
critical temperature: $T_N$ (Neel Temperature), above $T_N = \text{paramagnet}$
Neutron Diffraction

Single crystal may be anisotropic
Magnetic and structural unit cell may be different
The magnetic structure of a crystalline sample can be determined with „thermal neutrons“ (neutrons with a wavelength in the order of magnitude of interatomic distances): de Broglie equation: \( \lambda = \frac{h}{m_n v_n} \)
(requires neutron radiation of a nuclear reactor)
Ferrimagnetism

J negative with spins of unequal magnitude antiparallel below critical T requires two chemically distinct species with different moments coupled antiferromagnetically:

no M; critical T = T_C (Curie Temperature)
bulk behavior very similar to ferromagnetism, Magnetite is a ferrimagnet
Ferromagnetism

Ferromagnetic elements: Fe, Co, Ni, Gd (below 16 °C), Dy

Moments throughout a material tend to align parallel
This can lead to a spontaneous permanent $M$ (in absence of $H$)

but, in a macroscopic (bulk) system, it is energetically favorable for spins to segregate into regions called **domains** in order to minimize the magnetostatic energy $E = H \cdot M$

Domains need not be aligned with each other
may or may not have spontaneous $M$

Magnetization inside domains is aligned along the easy axis and is saturated
Magnetic Anisotropy

**Magnetic anisotropy** = the dependence of the magnetic properties on the direction of the applied field with respect to the crystal lattice, result of spin-orbit coupling

 Depending on the orientation of the field with respect to the crystal lattice a lower or higher magnetic field is needed to reach the saturation magnetization

**Easy axis** = the direction inside a crystal, along which small applied magnetic field is sufficient to reach the saturation magnetization

**Hard axis** = the direction inside a crystal, along which large applied magnetic field is needed to reach the saturation magnetization
Magnetic Anisotropy

**bcc Fe** - the highest density of atoms in the $<111>$ direction = the hard axis, the atom density is lowest in $<100>$ directions = the easy axis. Magnetization curves show that the saturation magnetization in $<100>$ direction requires significantly lower field than in the $<111>$ direction.

**fcc Ni** - the $<111>$ is lowest packed direction = the easy axis. $<100>$ is the hard axis.

**hcp Co** the $<0001>$ is the lowest packed direction (perpendicular to the close-packed plane) = the easy axis. The $<1000>$ is the close-packed direction and it corresponds to the hard axis. Hcp structure of Co makes it the one of the most anisotropic materials.
Magnetic Anisotropy

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Magnetic Domains

The external field energy is decreased by dividing into domains.

When $H$ external is applied, saturation magnetization can be achieved through the domain wall motion, which is energetically inexpensive, rather than through magnetization rotation, which carries large anisotropy energy penalty.

Application of $H$ causes aligned domains to grow at the expense of misaligned Alignment persists when $H$ is removed.
Domain Walls

What is the structure of the region between two domains (called a domain wall or a Bloch wall)? The spins do not suddenly flip: a gradual change of orientation costs less energy because if successive spins are misaligned by $\delta \theta$ the change in energy is only

$$\delta E = 2JS^2(1 - \cos(\delta \theta)),$$

where $J$ is the exchange integral.

The domain wall width is determined by the balance between the exchange energy and the magnetic anisotropy:
the total exchange energy is a sum of the penalties between each pair of spins
the magnetic anisotropy energy is: $E = K \sin^2 \theta$, where $\theta$ is the angle between the magnetic dipole and the easy axis
Large exchange integral yields wider walls
High anisotropy yields thinner walls
Domain Walls

180° walls = adjacent domains have opposite vectors of magnetization
90° walls = adjacent domains have perpendicular vectors of magnetization

Depends on crystallographic structure of ferromagnet (number of easy axes)

One easy axis = 180° DW (hexagonal Co)
Three easy axes = both 180° and 90° DW (bcc-Fe, 100)
Four easy axes = 180°, 109°, and 71° DW (fcc-Ni, 111)
Domain Wall Motion

At low $H_{\text{ext}}$ = bowing/relaxation of DWs, after removing $H_{\text{ext}}$ DWs return back

Volume of domains favorably oriented wrt H increases, M increases

At high $H_{\text{ext}}$ = irreversible movements of DW
a) Continues without increasing $H_{\text{ext}}$
b) DW interacts with an obstacle (pinning)
Magnetic Hysteresis Loop

\[ M_{\text{sat}} = N g \mu_B S \]

Important parameters:

- **Saturation magnetization**, \( M_{\text{sat}} \)
- **Remanent magnetization**, \( M_r \)
- **Remanence**: Magnetization of sample after \( H \) is removed
- **Coercivity**, \( H_c \)

\( M = \chi H_{\text{app}} \)

Important parameters:

- **Saturation magnetization**, \( M_{\text{sat}} \)
- **Remanent magnetization**, \( M_r \)
  Remanence: Magnetization of sample after \( H \) is removed
- **Coercivity**, \( H_c \)
  Coercive field: Field required to flip \( M \) (from \(+M\) to \( -M\) )
Magnetic Hysteresis Loop

"Hard" magnetic material = high Coercivity
"Soft" magnetic material = low Coercivity

Electromagnets
• High $M_r$ and Low $H_C$

Electromagnetic Relays
• High $M_{sat}$, Low $M_R$, and Low $H_C$

Magnetic Recording Materials
• High $M_r$ and High $H_C$

Permanent Magnets
• High $M_r$ and High $H_C$
Magnetic Hysteresis Loop

- Ms: Saturation Magnetization
- Mr: Remanence
- Hc: Coercivity

- Red: Ferromagnetic
- Green: Superparamagnetic
- Blue: Paramagnetic
- Black: Diamagnetic
Single-Molecule Magnets (SMM)

**Macroscopic magnet**

= magnetic domains (3D regions with aligned spins) + domain walls

Hysteresis in $M$ vs $H$ plots because altering the magnetisation requires the breaking of domain walls with an associated energy-cost

Magnetisation can be retained for a long time after removal of the field because the domains persist
Single-Molecule Magnets (SMM)

Single-molecule magnet
= individual molecules, magnetically isolated and non-interacting, no domain walls
Hysteresis in M vs H plots at very low temperatures
Magnetisation is retained for relatively long periods of time at very low temperatures after removal of the field because there is an energy barrier $U$ to spin reversal ($1.44 \text{ K} = 1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J}$)
The larger the energy barrier to spin reversal ($U$) the longer magnetisation can be retained and the higher the temperature this can be observed at
Single-Molecule Magnets (SMM)

The anisotropy of the magnetisation = the result of zero-field splitting (ZFS)

A metal complex with a total spin S, $2S + 1$ possible spin states, each sublevel with a spin quantum number $M_S$ (the summation of the individual spin quantum numbers ($m_s$) of the unpaired electrons;

$M_S$ from $S$ to $-S$

$M_S = S$ ‘spin up’

$M_S = -S$ ‘spin down’

In the absence of ZFS, all of the $M_S$ sublevels are degenerate

ZFS lifts degeneracy, doublets $\pm M_S$

For D negative: $M_S = \pm S$ are lower in energy than the intermediary sublevels $M_S$ with $S > M_S > -S$

At low temperatures, the magnetisation remains trapped in one of the two $M_S = \pm S$ because of the energy required to transition through high-energy intermediary states and over the barrier $U$ (its size is related to both D and S) to the other well.
Single-Molecule Magnets (SMM)
Anisotropy Barrier in SMMs

(a) effect of a negative zero-field splitting parameter $D$ on a $S = 10$ system
(b) magnetization of the sample by an external magnetic field (Zeeman effect)
(c) frozen magnetized sample showing a slow relaxation of the magnetization over the anisotropy barrier after turning off the external magnetic field
(d) quantum tunneling of the magnetization through the anisotropy barrier for magnetic fields leading to interacting $M_S$ substates at the same energy
Single-Molecule Magnets (SMM)

Magnetic anisotropy = a molecule can be more easily magnetized along one direction than along another = the different orientations of the magnetic moment have different energies

**Easy axis** = an energetically most favorable anisotropic axis in which to orient the magnetisation

**Hard plane** = a plane perpendicular to the easy axis, the least favorable orientation for the magnetisation

The greater the preference for the easy axis over other orientations the longer the magnetisation retained in that direction
Single-Molecule Magnets (SMM)

magnetization
a large value of the molecular spin $S$
for temperature low enough
the only populated state could be that of $M_S = -S$
Mn12

Some discrete molecules can behave at low temperature as tiny magnets

\[ [\text{Mn}_{12}\text{O}_{16}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4].4\text{H}_2\text{O}.2\text{CH}_3\text{COOH} \]

\[
S = 8 \times 2 - 4 \times 3/2 = 10
\]

Antiferromagnetic coupling

Orange atoms are Mn(III) with \( S = 2 \), green are Mn(IV) with \( S = 3/2 \)
Mn12 Spin Ladder

\[ U = \text{anisotropy energy barrier} \]

\[ |D| \times S^2 \quad \text{for integer spins} \]

\[ |D| \times (S^2 - 1/4) \quad \text{for non-integer spins} \]

\( D = \text{the axial zero-field splitting (ZFS) parameter} \)

\( S = \text{the spin ground state of the molecule} \)
Anisotropy Barrier in SMMs

(A) $M_S = 0$

$M_S = -S + 1$

$M_S = -S$

$|D| = S^2$

$M_S = +S - 1$

$M_S = +S$

(B) Field-on

$M_S = +S$

$M_S = -S$

(C) Field-off

(D) tunneling
M-H Hysteresis

Hysteresis: the change in the magnetisation as the field is cycled from $+H$ to $-H$ and back to $+H$, at a range of (very low) temperatures.

If the magnetisation is retained despite the field being removed ($M \neq 0$ at $H = 0$), the complex has an energy barrier to magnetisation reversal within the temperature and scan rate window of the measurement.
Hysteresis in Mn12
Superparamagnets
Superparamagnets

Tunable magnetic properties:
- Saturation magnetization ($M_s$)
- Coercivity ($H_c$)
- Blocking temperature ($T_B$)
- Neel and Brownian relaxation time of nanoparticles ($t_N$ & $t_B$)

Shape, size, composition, architecture
Superparamagnets

Particles which are so small that they define a single magnetic domain
Usually nanoparticles (NP) with a size distribution
Molecular particles which also display hysteresis – effectively behaving as a Single Molecule Magnet (SMM)

When the number of the constitutional atoms is small enough, all the constitutional spins simultaneously flip by thermal fluctuation. Each NP then behaves as a paramagnetic spin with a giant magnetic moment

\[ \mu = -g J \mu_B \]

\( g \) = the \( g \) factor
\( \mu_B \) = the Bohr magneton
\( J \) = the angular momentum quantum number, which is on the order of the number of the constitutional atoms of the NP

Above blocking temperature random spin flipping = no magnetization
Superparamagnets

55 and 12 nm sized iron oxide nanoparticles
Blocking Temperature

\[ T_B = \frac{KV}{25k_B} \]

V = particle volume

Particles with volume smaller than \( V_c \) will be at \( T < T_B \) superparamagnetic

\[ V_C = \frac{25k_B T}{K} \]
Blocking Temperature

Blocking temperature by Moessbauer spectroscopy

FC : Field-cooled
ZFC: Zero field-cooled
$T_B$ : Blocking temperature
Blocking Temperature

Zero-field cooling curves and TEM images of Co nanoparticles
Size Dependent Mass Magnetization

iron oxide Fe₃O₄ nanoparticles hysteresis loops
mass magnetization values at 1.5 T
Compositional Modification of Magnetism of Nanoparticles

$\text{Fe}_3\text{O}_4$ (inverse spinel) nanoparticles - ferrimagnetic spin structure

$\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ occupying $O_h$ sites align **parallel** to the external magnetic field

$\text{Fe}^{3+}$ in the $T_d$ sites of fcc-packed oxygen lattices align **antiparallel** to the field

$\text{Fe}^{3+} = d^5$ high spin state $= 5$ unpaired

$\text{Fe}^{2+} = d^6$ high spin state $= 4$ unpaired

the total magnetic moment per unit $(\text{Fe}^{3+})_{T_d} (\text{Fe}^{2+} \text{Fe}^{3+})_{O_h} \text{O}_4 = 4.9 \ \mu_B$

Incorporation of a magnetic dopant $M^{2+}$ ($\text{Mn}$ 5 upe, $\text{Co}$ 3 upe, $\text{Ni}$ 2 upe)

replace $O_h \text{Fe}^{2+} = \text{change in the net magnetization}$