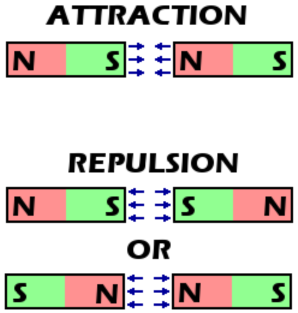
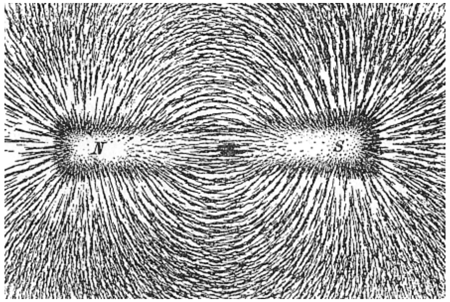
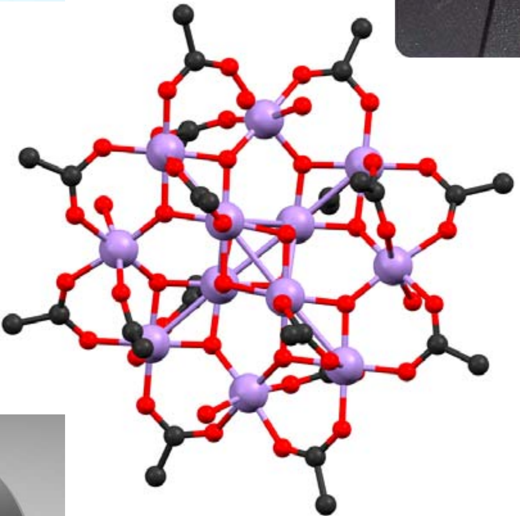
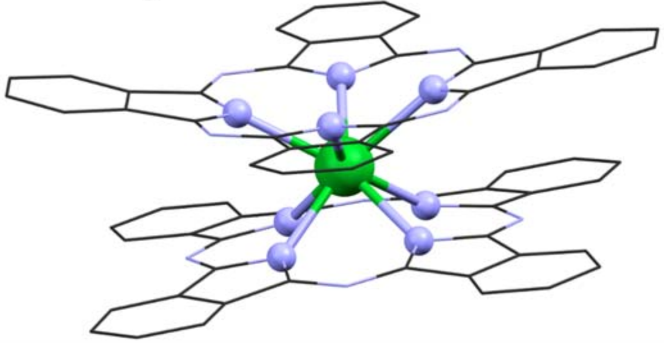
Magnetochemistry

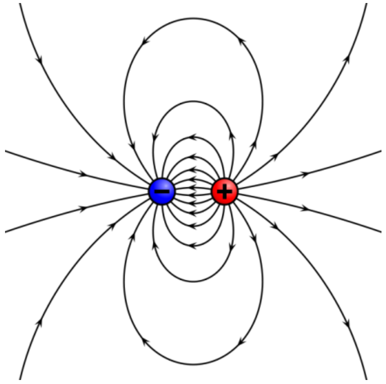








Magnetism



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

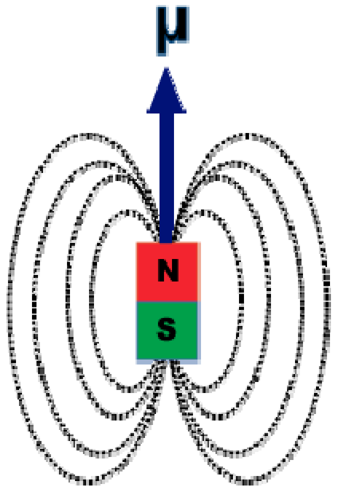
$$\mu = i \times A \qquad [A\,m^2]$$

Magnetism

Magnetic field = motion of electric charges

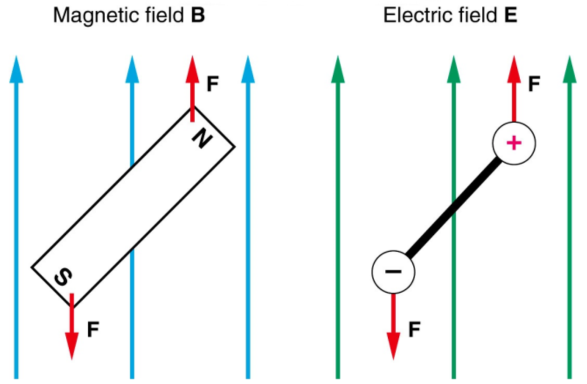
- Macro = electric current
- Micro = spin + orbital momentum

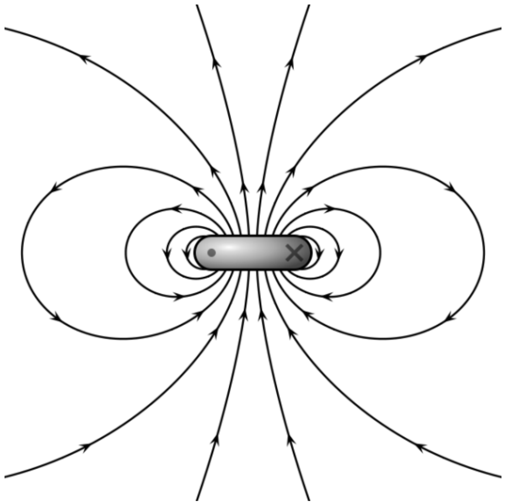
1822 Ampère
Magnetic dipole – magnetic (dipole) moment **μ** [A m^2]

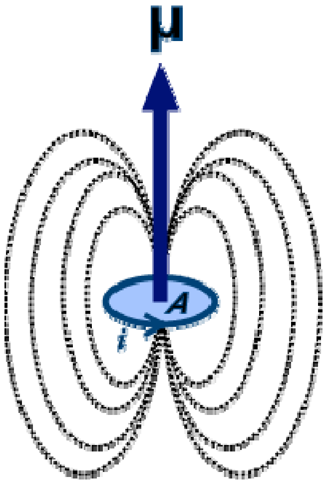


Poisson model

$$\mu = i \times A$$

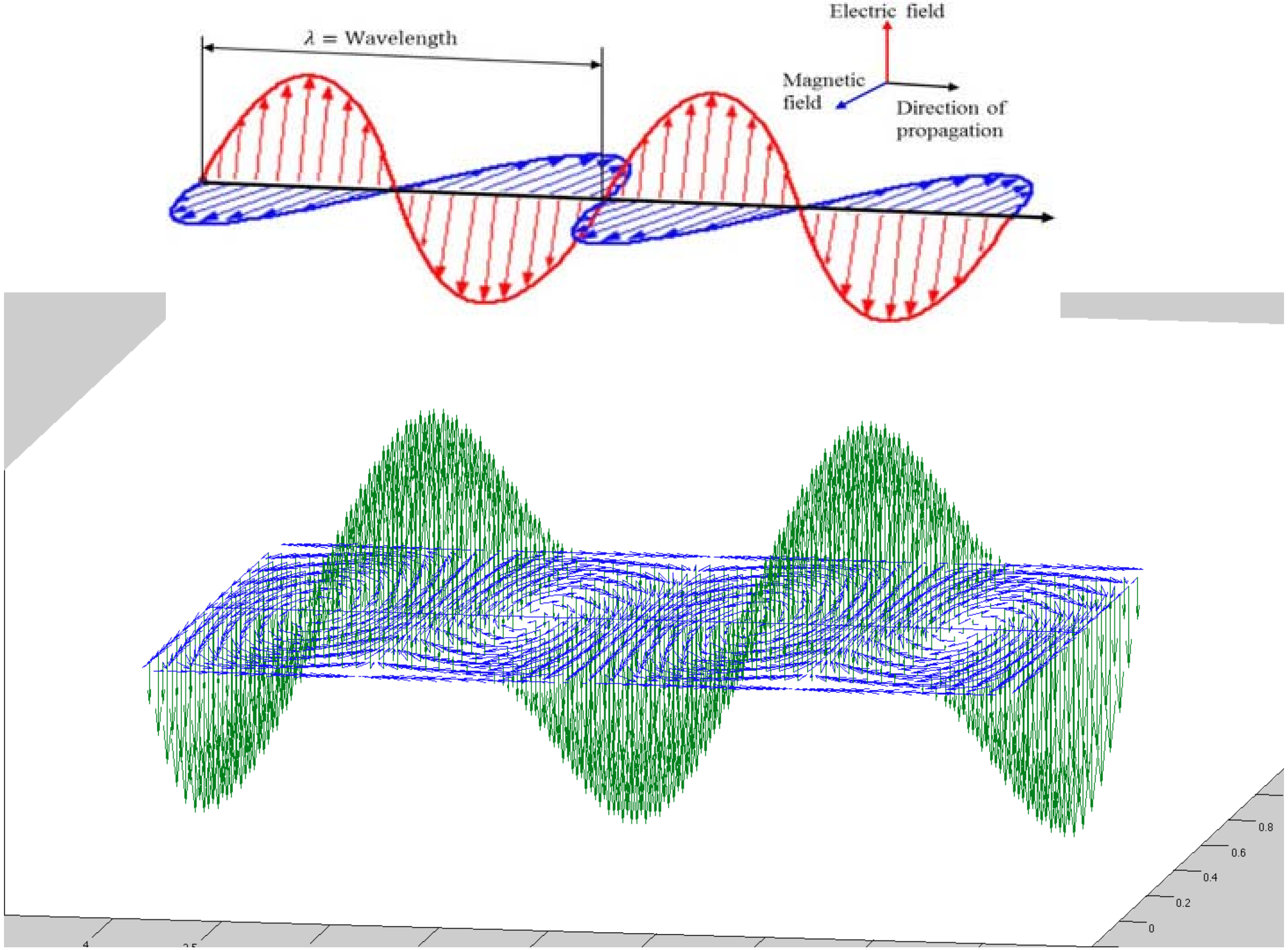






Ampere model

Electromagnetic Fields



Magnetism

Microscopic explanation of source of magnetism
= Fundamental quantum magnets
1913 Bohr - Unpaired electrons
1921 Gerlach and Stern experiment (Ag)
1925 Uhlenbeck and Goudsmit - postulated the existence of a new intrinsic property of particles that behaved like an angular momentum

Pauli later termed it **spin**
Unlike mass and charge, there is **no classical analog to spin**!

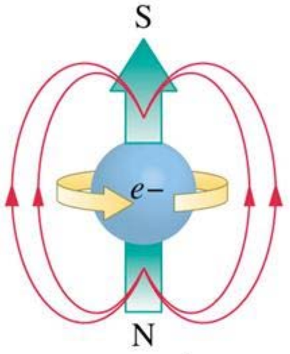
1928 Dirac - Relativistic quantum theory → **spins**
Quantum property, two-state quantum mechanical system
(~ rotation of charged particles?)
Spin arises in a correct relativistic formulation of the quantum theory
the relativistic generalization of the Schrödinger equation = the *Dirac equation*

Magnetism

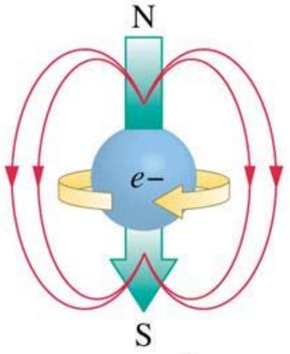
According to the Uhlenbeck and Goudsmit proposal, **the spin** of a particle should behave like an angular momentum and, therefore, should have an associated **magnetic moment**

Atomic building blocks (protons, neutrons, and electrons = fermions) possess **an intrinsic magnetic moment**

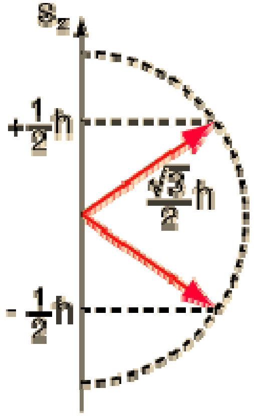
Spin (½ for all fermions) gives rise to a **magnetic moment**



$m_s = +\frac{1}{2}$



$m_s = -\frac{1}{2}$



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

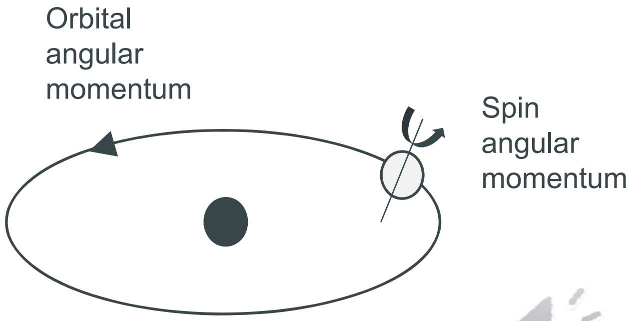
2) The orbital angular momentum L of the electrons about the nucleus, degenerate orbitals, *paramagnetic* contribution

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 $\mu = \gamma I$

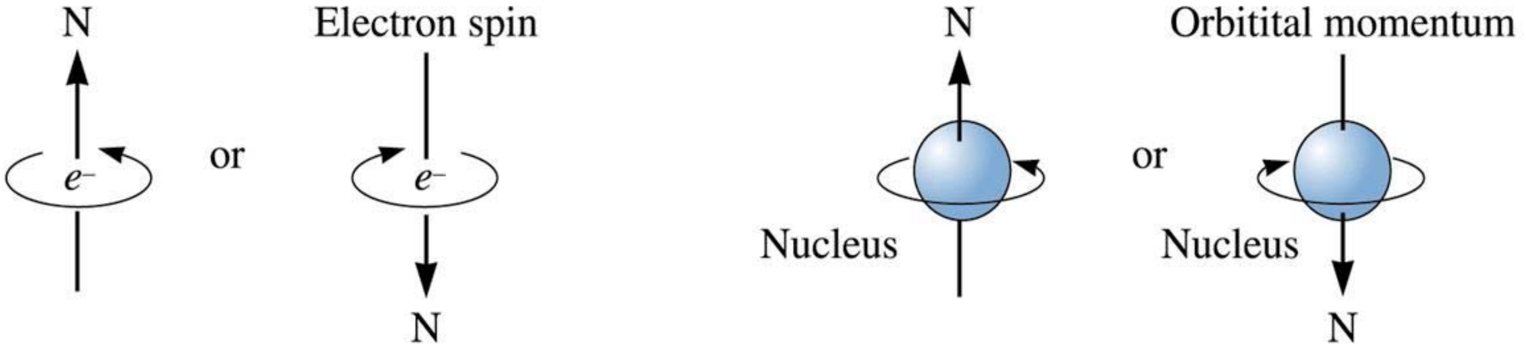
γ = gyromagnetic ratio



Atomic Motions of Electric Charges

The origins for the magnetic moment of **unparied electrons**

1) The spin of the electron S - Spin motion
2) The orbital angular momentum L - Orbital motion



SPIN MAGNETIC MOMENT (μ_s)
ORBITAL MAGNETIC MOMENT (μ_l)

Quantum number ***S***
For more than 1 e
$S = n \times s$, $s = 1/2$ and n is number of unparied electrons
Number of magnetic levels – spin multiplicity $M_S = 2S + 1$

Magnetic Moment of a Free Electron

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

The Bohr magneton μ_B = the smallest quantity of a magnetic moment

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

S = ½, the spin quantum number

g = 2.0023192778 the Lande constant of a free electron (g ≅ 2)

For **a free electron (S = ½)**

$$\mu_{eff} = 2 \times \sqrt{3/4} \times \mu_B = 1.73\ \mu_B$$

A Free Electron in a Magnetic Field

An electron with spin *S* = ½ can have two orientations in a magnetic field

$m_\mathrm{S} = +\tfrac{1}{2}$ or $m_\mathrm{S} = -\tfrac{1}{2}$

In a magnetic field

- degeneracy of the two states is removed

= Zeeman-Effect

Magnetic energy

$$E = -\mu_0 \mu \bullet H$$

In SI units

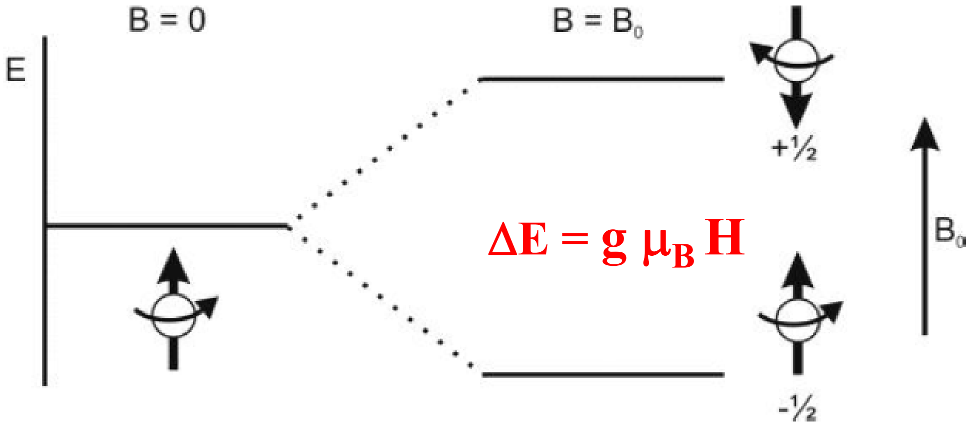
μ_0 = permeability of free space

$= 4\pi\ 10^{-7}\ [\mathrm{N\ A^{-2} = H\ m^{-1}}]$

$$E = -\mu \bullet B$$

A Free Electron in a Magnetic Field

$m_S = +½$



$\Delta E = g\ \mu_B\ H$

$E = ½\ g\ \mu_B\ H$

At r.t.
kT = 205 cm^{-1}

H = 1 T
ΔE = 28 GHz
= 1 cm^{-1}

$E = -½\ g\ \mu_B\ H$

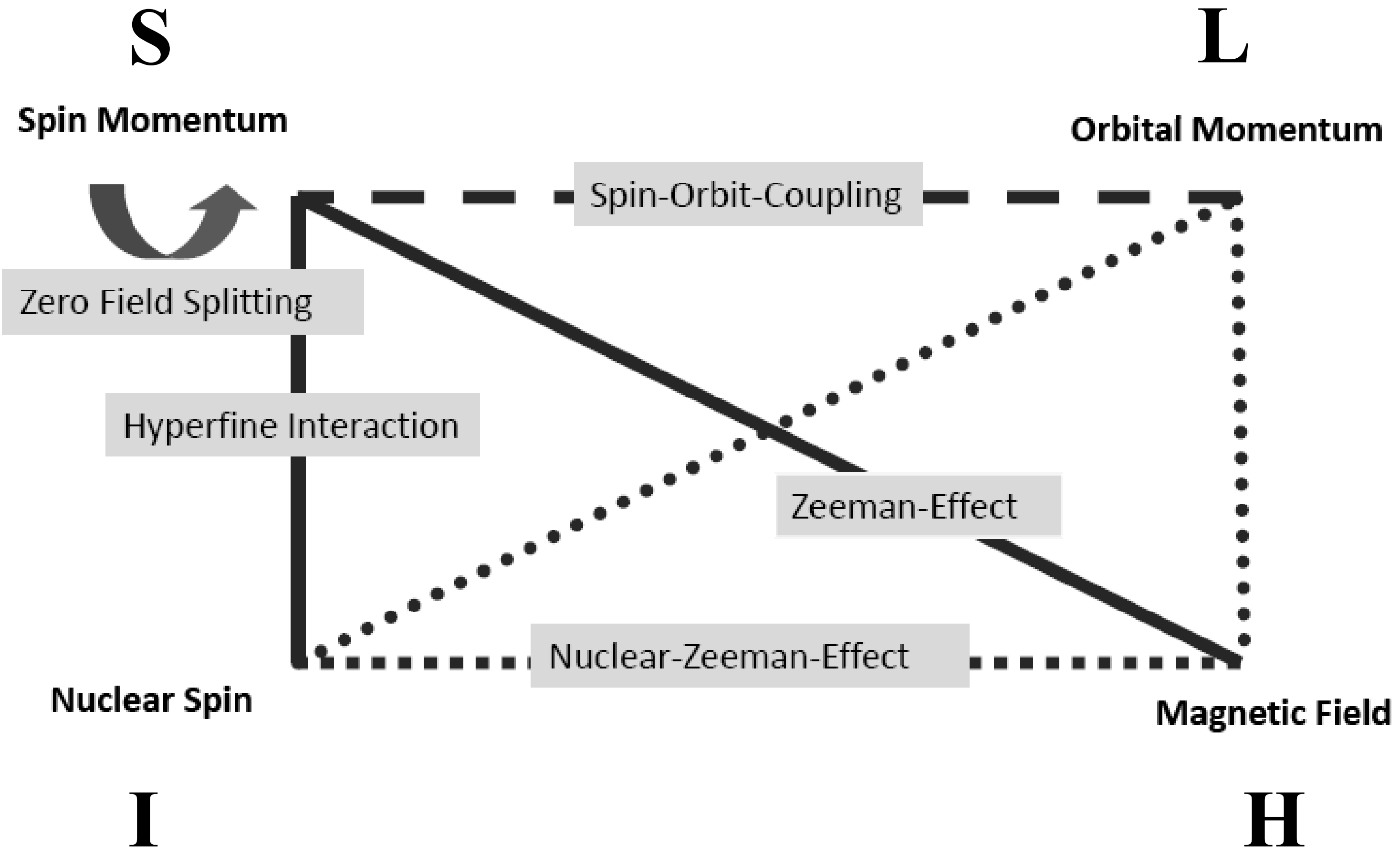
$m_S = -½$

An electron with spin *S* = ½
The state of lowest energy = the moment aligned **along** the magnetic field
$m_S = -½$

The state of highest energy = aligned **against** the magnetic field
$m_S = +½$

The energy of each orientation **E = μ H**
For an electron $\mu = m_s\ g\ \mu_B$,
μ_B = the Bohr magneton
g = the spectroscopic g-factor of the free electron 2.0023192778 (≈ 2.00)

Magnetism and Interactions



S

Spin Momentum

L

Orbital Momentum

Spin-Orbit-Coupling

Zero Field Splitting

Hyperfine Interaction

Zeeman-Effect

Nuclear-Zeeman-Effect

Nuclear Spin

Magnetic Field

I

H

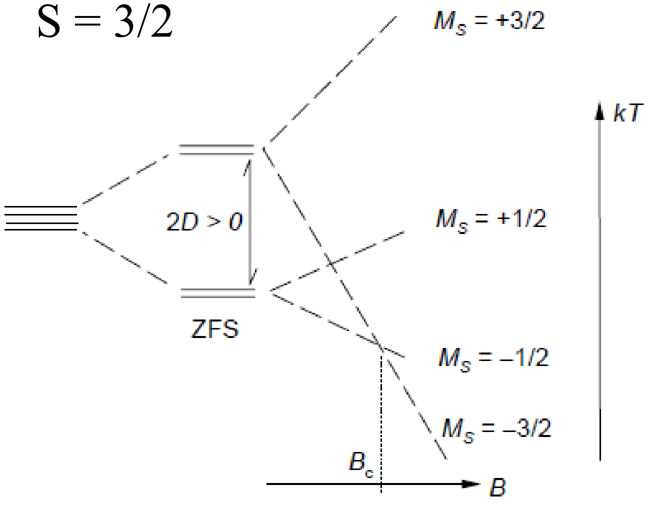
Magnetism and Interactions

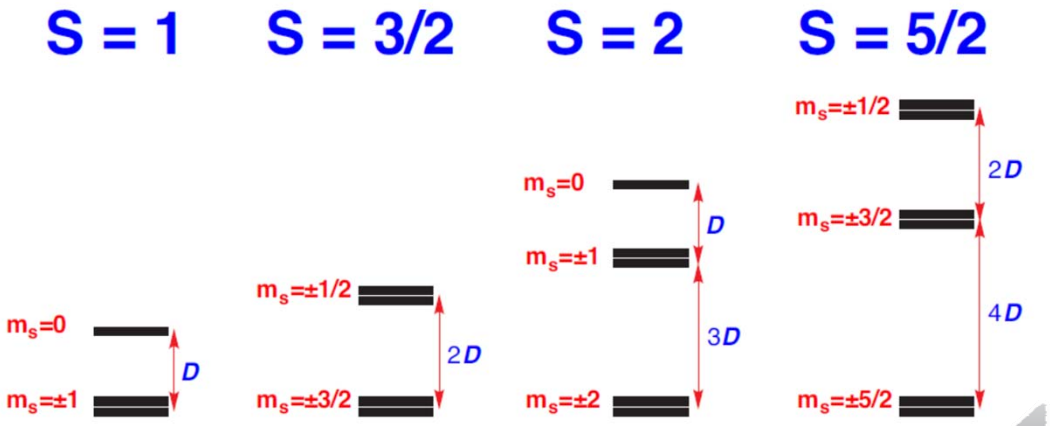
Zero Field Splitting (ZFS): The interactions of electrons with each other, lifting of the degeneracy of spin states for systems with S > ½ in the **absence** of an applied **magnetic field**, interaction of the spins mediated by the spin-orbit coupling and dipole-dipole interactions

ZFS = as a small energy gap of a few cm^{-1} between the lowest energy levels

D = the axial zero-field splitting (ZFS) parameter

S = 3/2





$D < 0$

Zero Field Splitting in d^n Ions

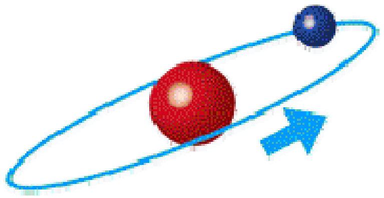
d^n	Tetrahedral			
	Configuration	Term	Type	Example
d^2	e^2	$^3A_2$	$S = 1$	Ti(II), V(III)
d^3				
d^5	$e^2t_2^3$	$^6A_1$	$S = 5/2$	Mn(II), Fe(III)
d^7	$e^4t_2^3$	$^4A_2$	$S = 3/2$	Co(II)
d^8				

d^n	Octahedral			
	Configuration	Term	Type	Example
d^2				
d^3	t_{2g}^3	$^4A_{2g}$	$S = 3/2$	Cr(III)
d^5	$t_{2g}^3e_g^2$	$^6A_{1g}$	$S = 5/2$	Mn(II), Fe(III)
d^7				
d^8	$t_{2g}^6e_g^2$	$^3A_{2g}$	$S = 1$	Ni(II)

Magnetism and Interactions

Hyperfine Interactions: The interactions of the nuclear spin I and the electron spin S (only s-electrons) – NMR spectroscopy

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



Ligand Field: States with different orbital momentum **L** 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**

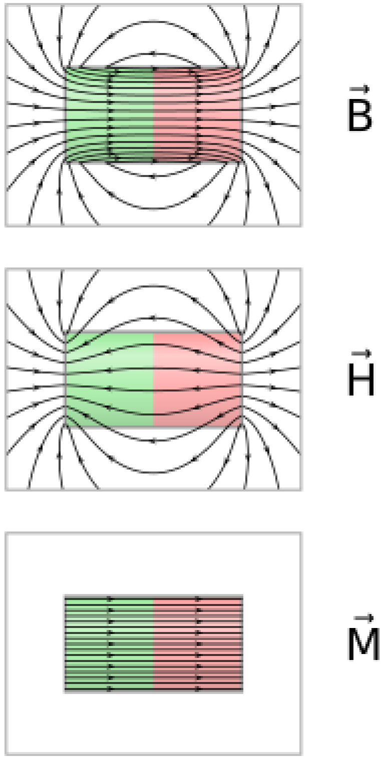
Magnetism and Interactions

Effect		System	Energy equivalent [cm^{-1}]
Electron-electron interaction	$\hat{H}_{ee}$	3d, 4d, 5d 4f, 5f	$3d > 4d > 5d \approx 10^4$ $4f > 5f \approx 10^4$
Ligand-field potential	$\hat{H}_{LF}$	3d, 4d, 5d 4f 5f	$3d < 4d < 5d \approx 2 \cdot 10^4$ $\approx 10^2$ $\approx 10^3$
Spin-orbit coupling	$\hat{H}_{SO}$	3d, 4d, 5d 4f, 5f	$3d < 4d < 5d \approx 10^3$ $4f < 5f \approx 10^3$
Exchange interaction	$\hat{H}_{ex}$	nd 4f nd–4f	$\leq 10^2$ ≤ 1 ≤ 10
Magnetic field	$\hat{H}_{Zeeman}$		≈ 0.5 (1 T)

$1\ \mathrm{eV} = 8065.73\ \mathrm{cm}^{-1} = 1.60210\ 10^{-19}\ \mathrm{J}$

Magnetization

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***



$$B = \boldsymbol{\mu_0}(H + M)$$

$$\mathbf{B} = \mu_0 \left(\mathbf{H} + \mathbf{H}_d + \mathbf{M}\right)$$

H_d = demagnetizing or stray field (ferromagnets)

Magnetization does not exist outside of the material

μ_0 = permeability of vacuum

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 (μ) 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 (Earth's magnetic field = 50 microtesla)

Field equation
(infinite system)

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

μ_0 = 4π 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 (cgs)

Magnetic field strength (intensity) *H* [Oe, Oersted]
Fields resulting from electric current (1 Oe = 79.58 A/m)

Magnetization (polarization) *M* [emu/cm^3]
Magnetic moment per unit volume
Spin and orbital motion of electrons 1 emu/g = 1 Am^2/kg

Magnetic induction *B* [G, Gauss] (1 T = 10^4 G)
A field resulting from electric current and spin and orbital motions

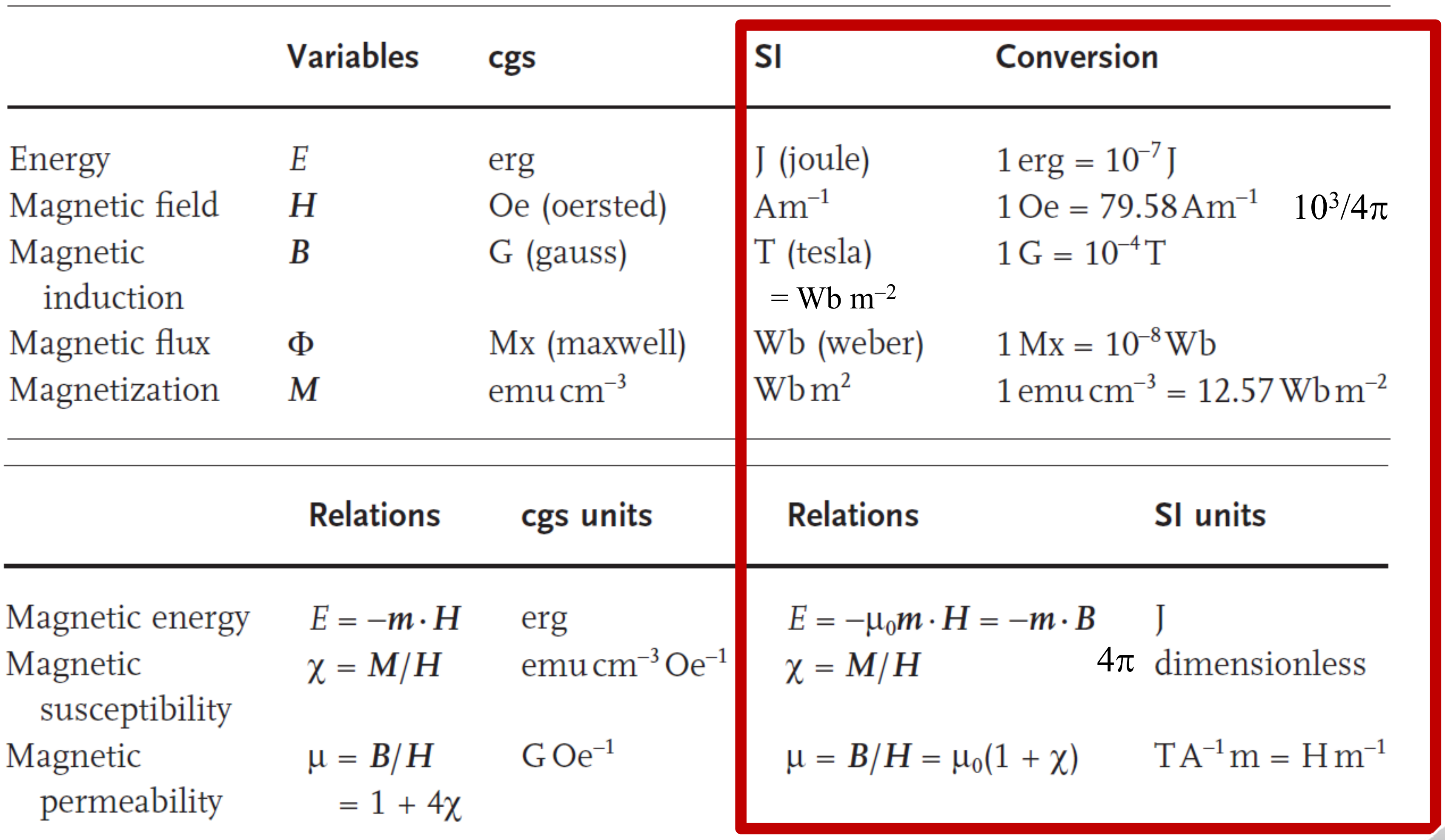
Field equation

$$B = \mu_0 (H + 4\pi M)$$

$\mu_0 = 1$ 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

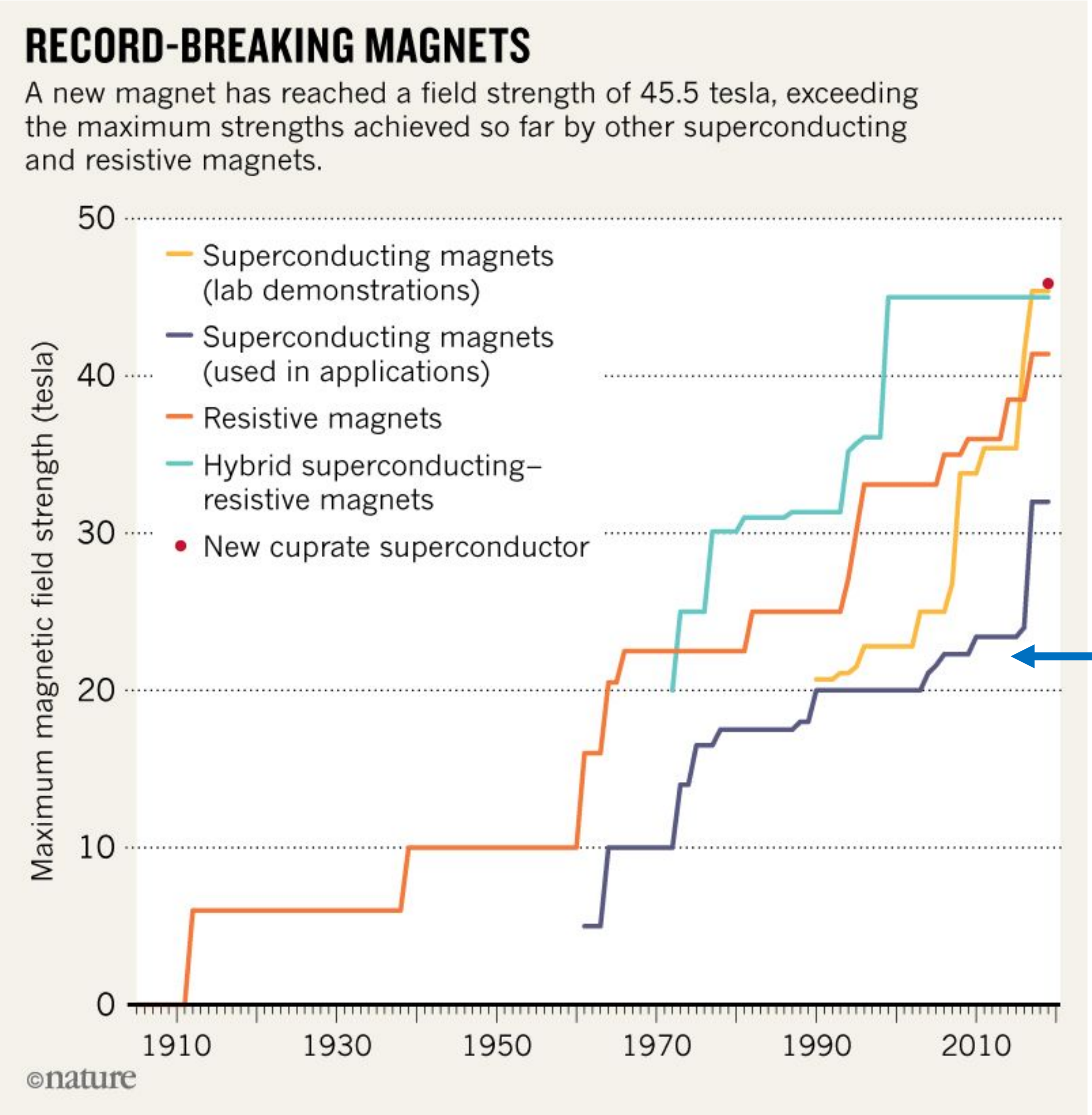
Important Variables, Units, and Relations



	Variables	cgs	SI	Conversion
Energy	E	erg	J (joule)	1 erg = 10^{-7} J
Magnetic field	$\boldsymbol{H}$	Oe (oersted)	$\mathrm{A\,m^{-1}}$	1 Oe = 79.58 $\mathrm{A\,m^{-1}}$ $10^3/4\pi$
Magnetic induction	$\boldsymbol{B}$	G (gauss)	T (tesla) $= \mathrm{Wb\ m^{-2}}$	1 G = 10^{-4} T
Magnetic flux	Φ	Mx (maxwell)	Wb (weber)	1 Mx = 10^{-8} Wb
Magnetization	$\boldsymbol{M}$	$\mathrm{emu\,cm^{-3}}$	$\mathrm{Wb\,m^2}$	1 $\mathrm{emu\,cm^{-3}}$ = 12.57 $\mathrm{Wb\,m^{-2}}$

	Relations	cgs units	Relations	SI units
Magnetic energy	$E = -\boldsymbol{m} \cdot \boldsymbol{H}$	erg	$E = -\mu_0 \boldsymbol{m} \cdot \boldsymbol{H} = -\boldsymbol{m} \cdot \boldsymbol{B}$	J
Magnetic susceptibility	$\chi = \boldsymbol{M}/\boldsymbol{H}$	$\mathrm{emu\,cm^{-3}\,Oe^{-1}}$	$\chi = \boldsymbol{M}/\boldsymbol{H}$ 4π	dimensionless
Magnetic permeability	$\mu = \boldsymbol{B}/\boldsymbol{H}$ $= 1 + 4\chi$	$\mathrm{G\,Oe^{-1}}$	$\mu = \boldsymbol{B}/\boldsymbol{H} = \mu_0(1+\chi)$	$\mathrm{T\,A^{-1}\,m = H\,m^{-1}}$

Magnetic Field



RECORD-BREAKING MAGNETS

A new magnet has reached a field strength of 45.5 tesla, exceeding the maximum strengths achieved so far by other superconducting and resistive magnets.

©nature

950 MHz NMR
B = 22.3 T

Magnetic Susceptibility χ

(Volume) Magnetic susceptibility χ of a sample [dimensionless]

χ = how effectively an applied magnetic field ***H*** induces magnetization ***M*** in a sample, how susceptible (receptive) are dipoles to reorientation

Measurable, extrinsic property of a material, positive or negative

$$\chi = \frac{\delta \vec{M}}{\delta \vec{H}}$$

If the magnetic field ***H*** is weak enough and T not too low, χ is independent of ***H*** and thus:

$$\longrightarrow \quad M = \chi \times H$$

M is a vector, ***H*** is a vector, therefore χ is a second rank tensor
If the sample is magnetically isotropic, χ is a scalar

$$\chi = \frac{M}{H}$$

M = magnetization **[A m^{-1}]**
H = the macroscopic magnetic field strength (intensity) **[A m^{-1}]**

Mass and Molar Magnetic Susceptibility

Mass magnetic susceptibility χ_m of a sample

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

ρ = density

Molar magnetic susceptibility χ_M of a sample

(intrinsic property)

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

Typical molar susceptibilities

Paramagnetic ~ +0.01 μ_B

Diamagnetic ~ -1×10^{-6} μ_B

Ferromagnetic ~ +0.01 - 10 μ_B

Superconducting ~ Strongly negative, repels fields completely (Meisner effect)

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

Relative Permeability μ_r

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

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

$$B = \mu \times H$$

$$M = \chi \times H$$

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

$$\mu_r = \frac{\mu}{\mu_0}$$

$\mu < \mu_0$ diamagnetic **$\mu > \mu_0$** paramagnetic

$\mu_0 = 4\pi\ 10^{-7}$ [N A^{-2} = H m^{-1} = kg m $A^{-2}s^{-2}$] **permeability of free space**

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

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

$$\mu_r = 1 + \chi$$

Magnetic Susceptibility

χ_M is the algebraic sum of contributions associated with different phenomena, measurable:

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

χ_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, small negative values

χ_M **P** = **paramagnetic** susceptibility due to **unpaired electrons**, increases upon decreasing temperature, large positive values

χ_M **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 bonds:

$$\chi_M{}^{D} = \Sigma\chi_{\mathrm{D\ atom}} + \Sigma\lambda_{\mathrm{bond}}$$

$\chi_{\mathrm{D\ atom}}$ = atom diamagnetic susceptibility increments (Pascal’s constants)
λ_{bond} = bond diamagnetic susceptibility increments (Pascal’s constants)

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 χ_{dia} value of $Co(acac)_3$ as that of $Cr(acac)_3$

Pascal’s Constants

Table 1. Values of χ_{Di} for Atoms in Covalent Species

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

Table 2. Values of λ_i for Specific Bond Types

Bond[a]	λ_i/(1 x 10^{-6} emu mol^{-1})	Bond	λ_i/(1 x 10^{-6} emu mol^{-1})	Bond	λ_i/(1 x 10^{-6} emu mol^{-1})	Bond	λ_i/(1 x 10^{-6} emu mol^{-1})
C=C	+5.5	$Cl{-}CR_2CR_2{-}Cl$	+4.3	Ar–Br	–3.5	Imidazole	+8.0
C≡C	+0.8	R_2CCl_2	+1.44	Ar–Cl	–2.5	Isoxazole	+1.0
C=C–C=C	+10.6	$RCHCl_2$	+6.43	Ar–I	–3.5	Morpholine	+5.5
Ar–C≡C–Ar[b]	+3.85	C–Br	+4.1	Ar–COOH	–1.5	Piperazine	+7.0
$CH_2{=}CH{-}CH_2{-}$(allyl)	+4.5	$Br{-}CR_2CR_2{-}Br$	+6.24	$Ar{-}C({=}O)NH_2$	–1.5	Piperidine	+3.0
C=O	+6.3	C–I	+4.1	$R_2C{=}N{-}N{=}CR_2$	+10.2	Pyrazine	+9.0
COOH	–5.0	Ar–OH	–1	RC≡C–C(=O)R	+0.8	Pyridine	+0.5
COOR	–5.0	$Ar{-}NR_2$	+1	Benzene	–1.4[c]	Pyrimidine	+6.5
$C({=}O)NH_2$	–3.5	Ar–C(=O)R	–1.5	Cyclobutane	+7.2	α- or γ-Pyrone	–1.4
N=N	+1.85	Ar–COOR	–1.5	Cyclohexadiene	+10.56	Pyrrole	–3.5
C=N–	+8.15	Ar–C=C	–1.00	Cyclohexane	+3.0	Pyrrolidine	+0.0
–C≡N	+0.8	Ar–C≡C	–1.5	Cyclohexene	+6.9	Tetrahydrofuran	+0.0
–N≡C	+0.0	Ar–OR	–1	Cyclopentane	+0.0	Thiazole	–3.0
N=O	+1.7	Ar–CHO	–1.5	Cyclopropane	+7.2	Thiophene	–7.0
$-NO_2$	–2.0	Ar–Ar	–0.5	Dioxane	+5.5	Triazine	–1.4
C–Cl	+3.1	$Ar{-}NO_2$	–0.5	Furan	–2.5		

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

Magnetic Susceptibility

$\chi_M{}^{P}$ = paramagnetic susceptibility relates to **number of unpaired electrons**

$$\chi_M^P T = \frac{N_A g^2 \mu_B^2}{3k_B}\left[S(S+1)\right]$$

Caclculation of μ_{eff} (microscopic quantity) from χ (macroscopic quantity)

$$\mu_{eff} = \sqrt{\frac{3\chi_M k_B T}{\mu_0 N_A \mu_B^2}} \Rightarrow \mu_{eff} = \left(\frac{3k_B}{\mu_0 N_A \mu_B^2}\right)^{\frac{1}{2}} \sqrt{\chi_M T}$$

$\mu_{eff} = 0.7977 \sqrt{\chi_m T}$ χ_m in $cm^3\ mol^{-1}$

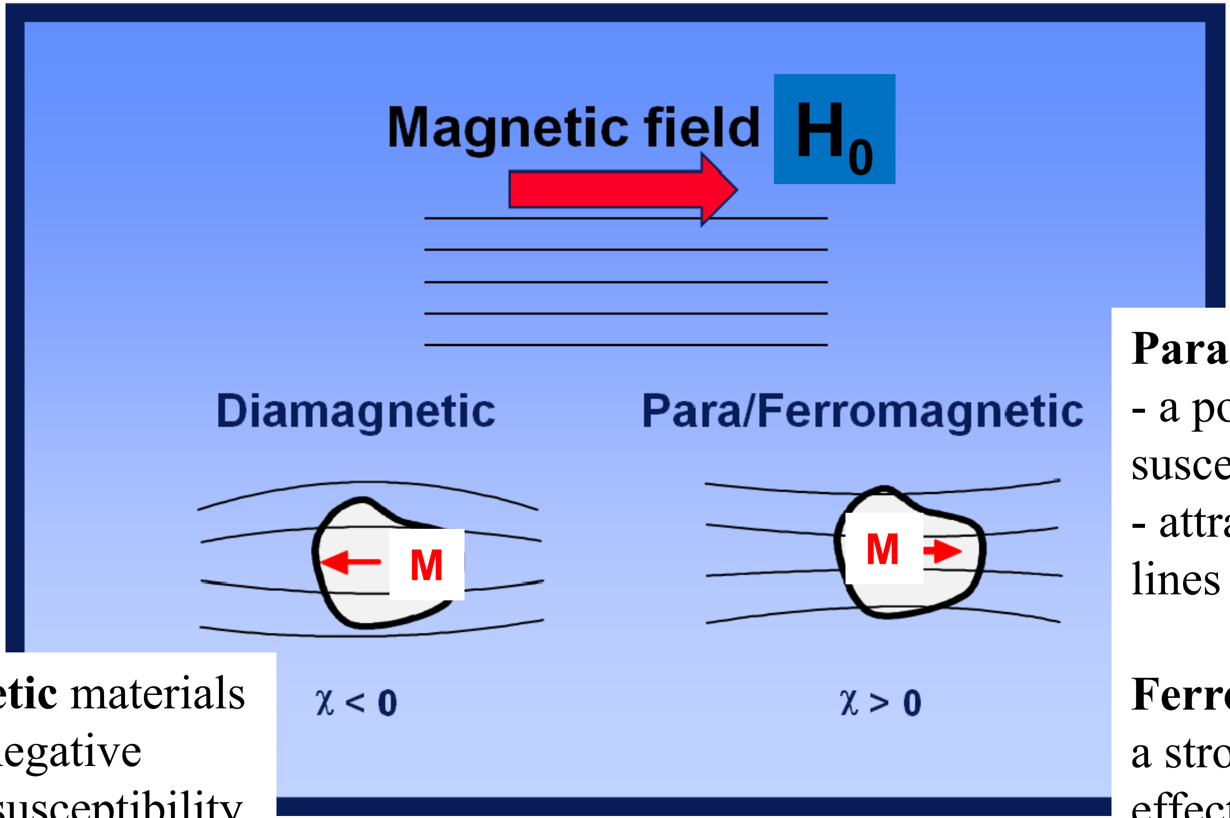
$\mu_{eff} = 2.828 \sqrt{\chi_m T}$ χ_m in emu $Oe^{-1}\ mol^{-1}$

Magnetic Susceptibility

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

Magnetic Properties

Magnetic behavior of a substance = magnetic polarization in a mg field H_0



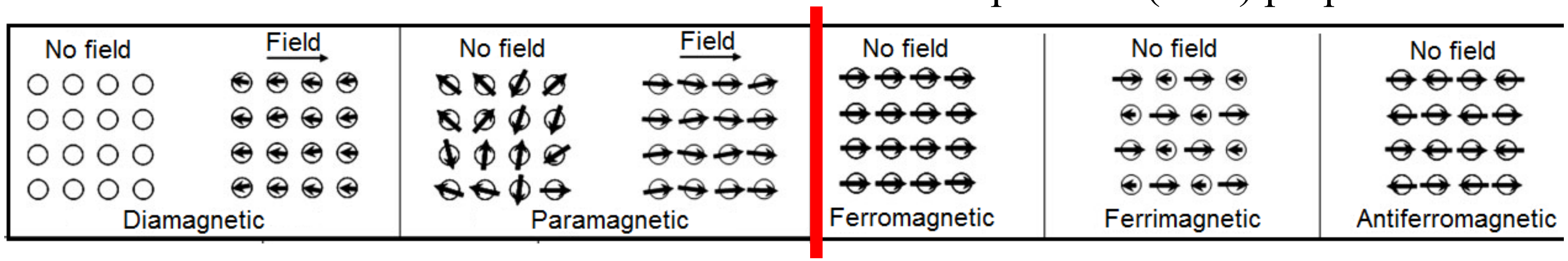
Diamagnetic materials
- a slight negative magnetic susceptibility
- repel the magnetic lines of force

Paramagnetic materials
- a positive magnetic susceptibility
- attract the magnetic lines of force

Ferromagnetic materials
a stronger attractive effect

Magnetic Properties

Magnetic behavior of a substance = orientation of magnetic moments in/outside a magnetic field H_0

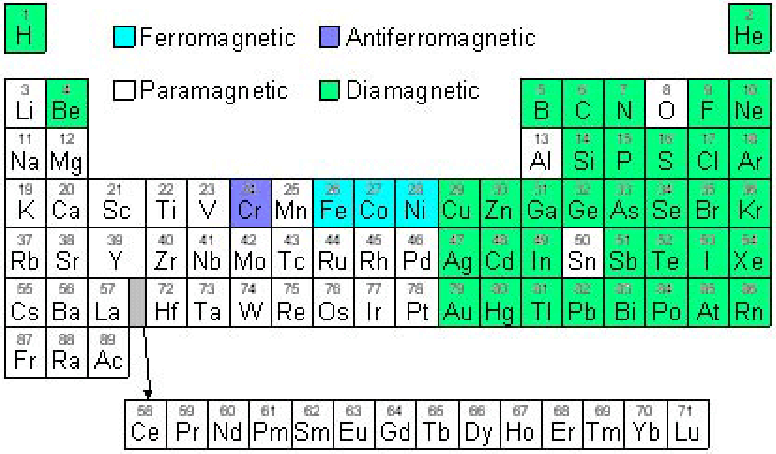


Atomic/ionic properties

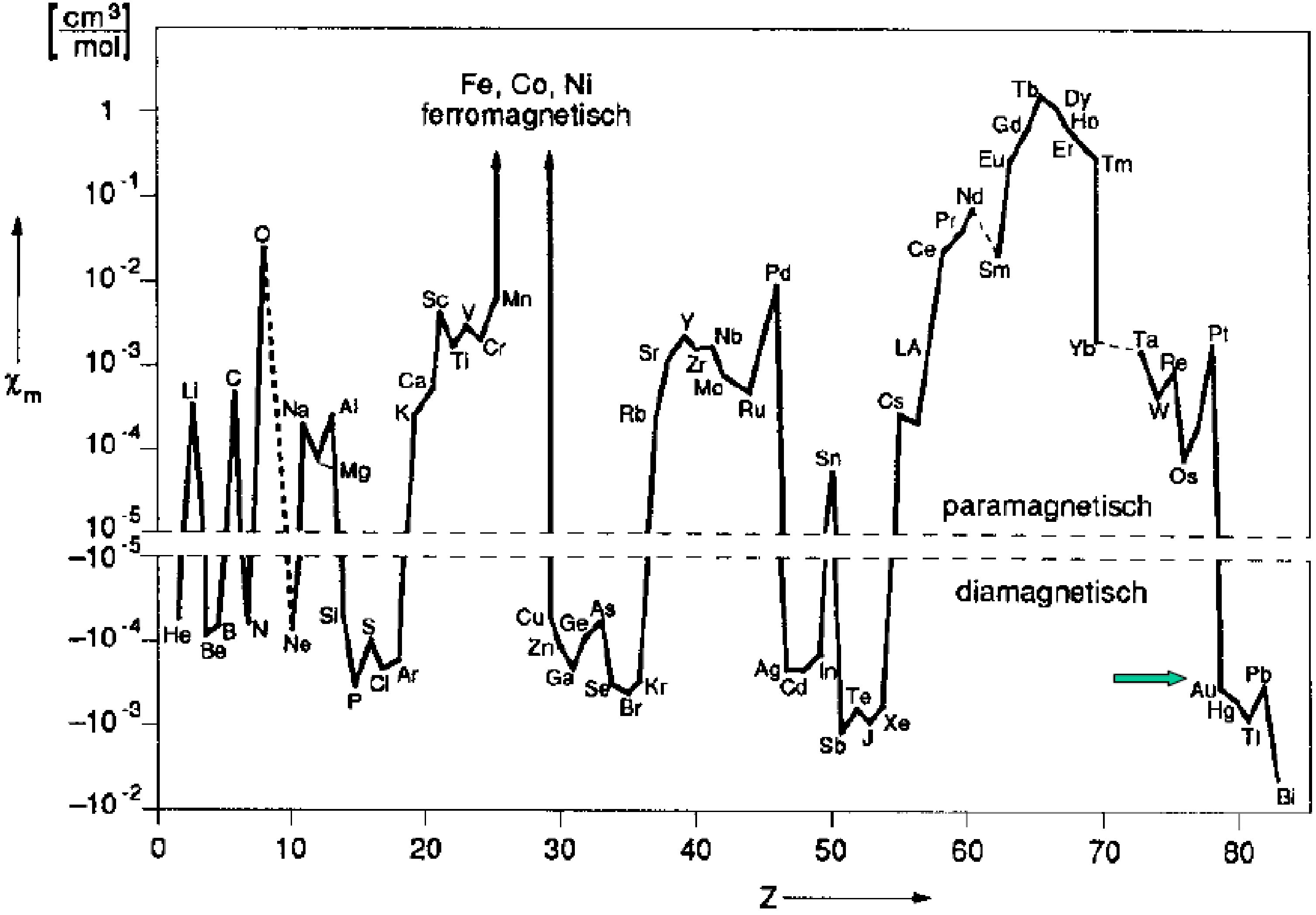
Cooperative (bulk) properties

Magnetically dilute, noninteracting

Magnetically concentrated, interacting



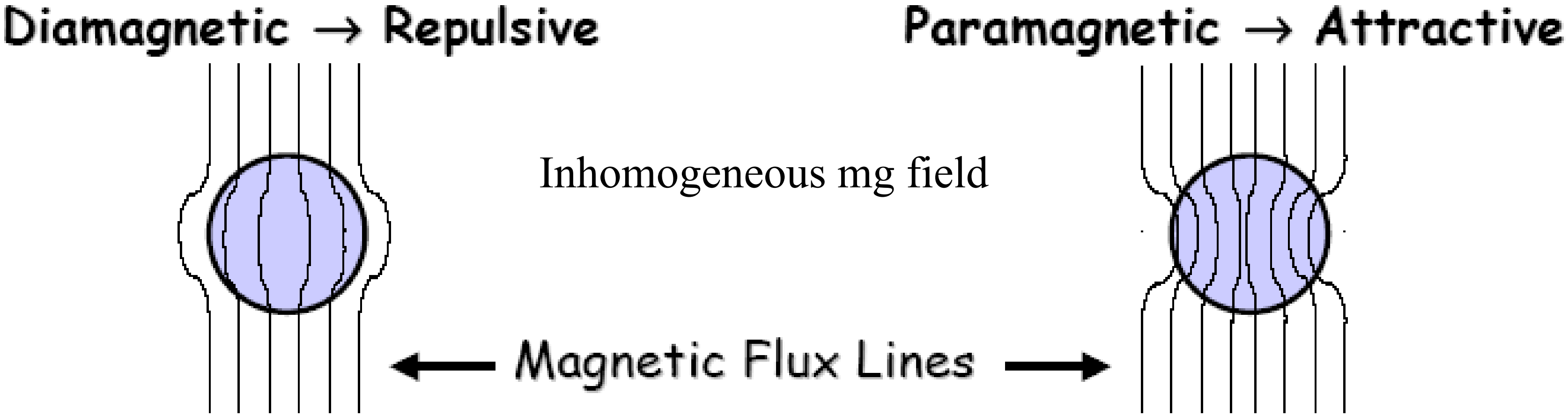
Magnetism of the Elements



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



Inhomogeneous mg field

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

(Langevine) Diamagnetism

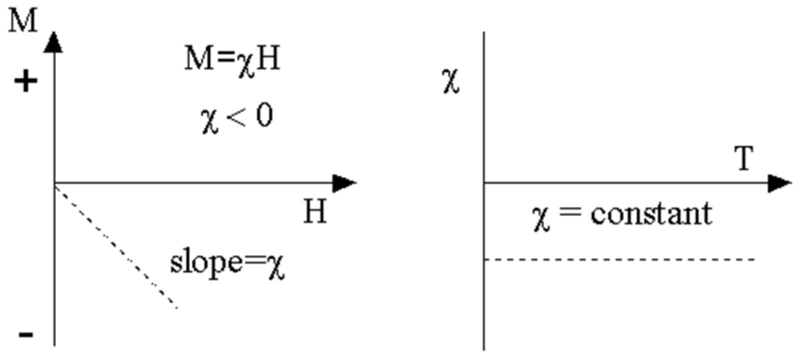
Lenz's Law – when magnetic field acts on a conducting loop, it generates a current that **counteracts** the change in the field

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

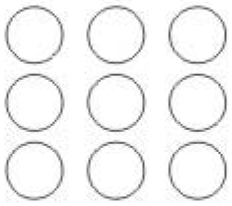
$$M = \chi \times H$$

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

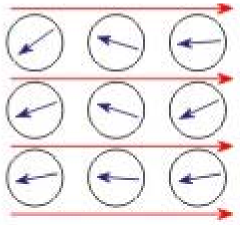


Diamagnetism

Superconductors $\chi = -1$ perfect diamagnets



H=0
Zero moment

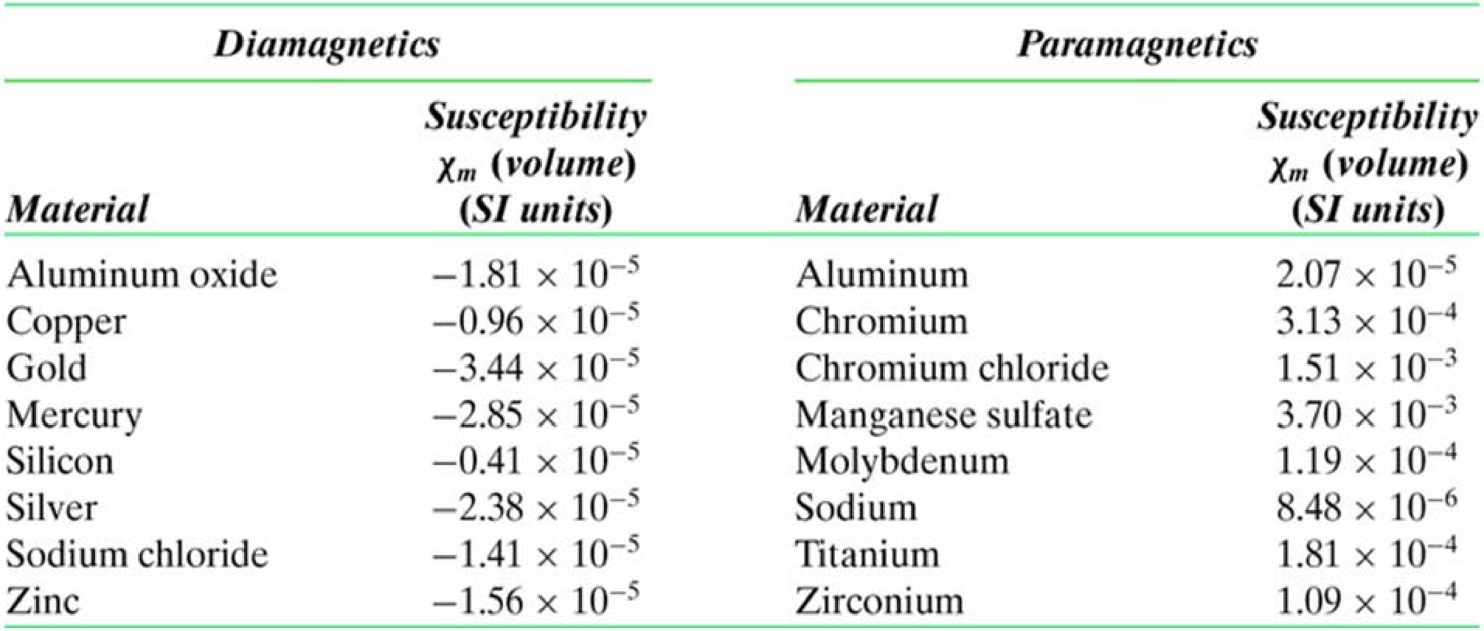


H > 0
Opposing Induced moment

Diamagnetism

Large and heavy atoms have large diamagnetic susceptibilities

$$\chi = \frac{NZe^2}{mc^2}\left\langle r^2 \right\rangle$$



Diamagnetics		*Paramagnetics*	
Material	*Susceptibility* χ_m *(volume) (SI units)*	*Material*	*Susceptibility* χ_m *(volume) (SI units)*
Aluminum oxide	-1.81×10^{-5}	Aluminum	2.07×10^{-5}
Copper	-0.96×10^{-5}	Chromium	3.13×10^{-4}
Gold	-3.44×10^{-5}	Chromium chloride	1.51×10^{-3}
Mercury	-2.85×10^{-5}	Manganese sulfate	3.70×10^{-3}
Silicon	-0.41×10^{-5}	Molybdenum	1.19×10^{-4}
Silver	-2.38×10^{-5}	Sodium	8.48×10^{-6}
Sodium chloride	-1.41×10^{-5}	Titanium	1.81×10^{-4}
Zinc	-1.56×10^{-5}	Zirconium	1.09×10^{-4}

(Curie) Paramagnetism

Paramagnetism arises from the interaction of H with the magnetic field of **the unpaired electron** due to the spin (S) and orbital angular (L) momentum

Randomly oriented, rapidly reorienting magnetic moments

No permanent spontaneous magnetic moment

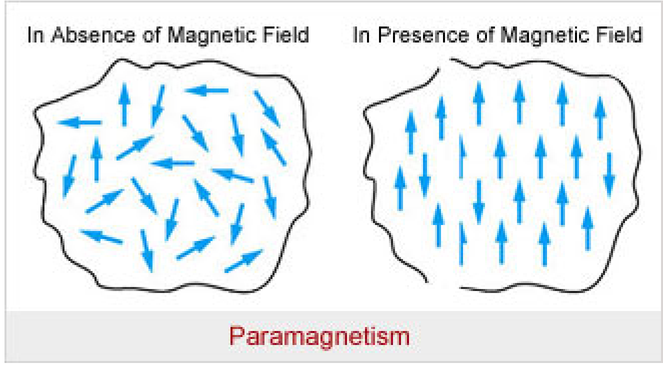
M = 0 at H = 0

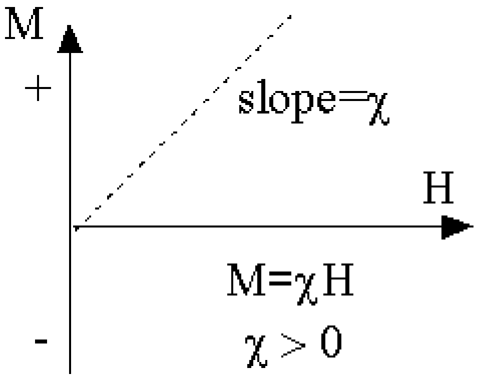
Spins are non-interacting, non-cooperative, independent, dilute system

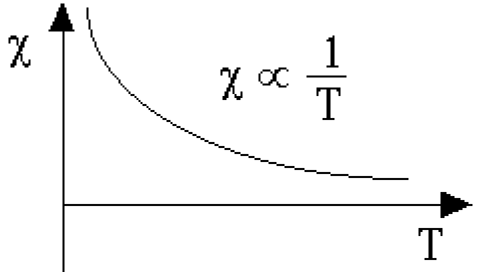
Weakly attractive interaction with the field

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

$\chi = 10^{-3}$ to -10^{-5}



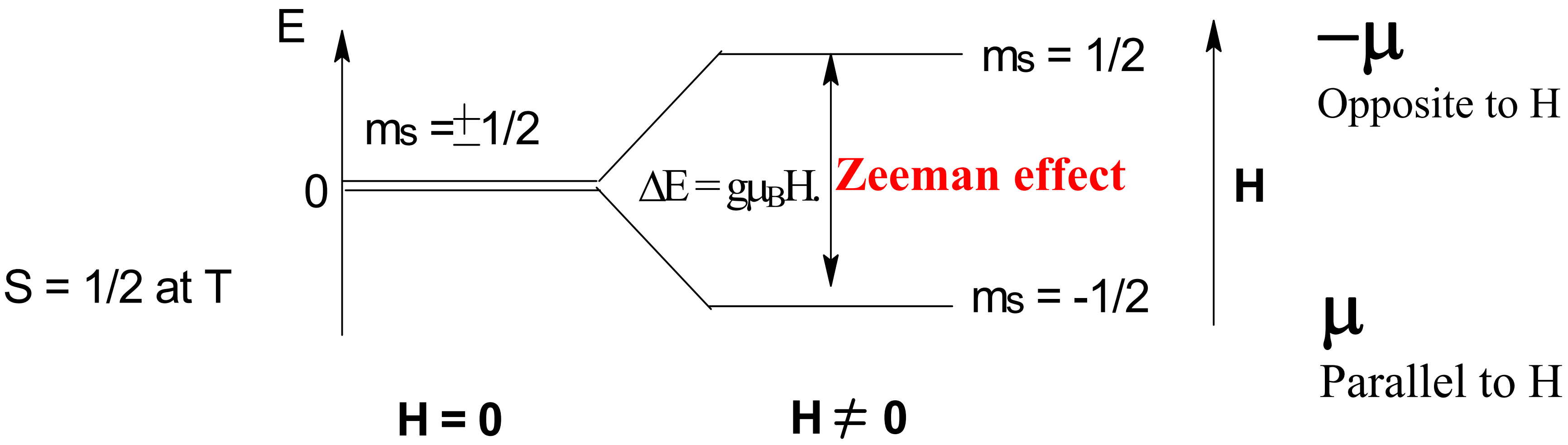




Paramagnetism

(Curie) Paramagnetism for S = ½

Energy diagram of **ONE** S = ½ spin in an external magnetic field H



E

$m_s = \pm 1/2$

0

$m_s = 1/2$

$\Delta E = g\mu_B H$

Zeeman effect

$m_s = -1/2$

H

$-\mu$

Opposite to H

μ

Parallel to H

S = 1/2 at T

H = 0

$H \neq 0$

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

The interaction energy of magnetic moment with the applied magnetic field

$\mathbf{E} = -\mu\ \mathbf{H} = g\,\mu_B\,S\,H = m_s\,g\,\mu_B\,H$

$\Delta E = g\,\mu_B\,H$ about 1 cm^{-1} at 1 T (10 000 G)

μ_B = Bohr magneton (= $9.27\ 10^{-24}$ J/T)

g = the Lande constant (= 2.0023192778)

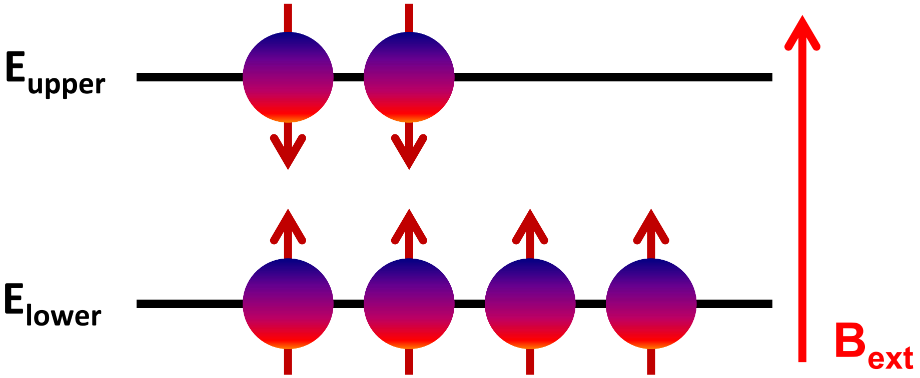
(Curie) Paramagnetism for S = ½

MANY SPINS

Relative populations P of ½ and –½ states
For H = 25 kG = 2.5 T $\Delta E \sim 2.3\ \mathrm{cm}^{-1}$
At 300 K $kT \sim 200\ \mathrm{cm}^{-1}$

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 = ½

To obtain **magnetization M** (or χ_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, μ_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

$$\mathbf{M = N_A\,\Sigma\,\mu_n P_n}$$

P_n = probability in state n
N_n = population of state n
N_{Tot} = population of all the states

$$P_n = \frac{N_n}{N_{Tot}} = \frac{e^{-\frac{E_n}{k_B T}}}{\Sigma e^{-\frac{E_n}{k_B T}}}$$

(Curie) Paramagnetism for S = ½

$$M = \frac{N \sum_{m_s} \mu_n e^{-E_n/kT}}{\sum_{m_s} e^{-E_n/kT}}$$

$g \mu_B H << kT$ when $H \sim 5$ kG

$$= \frac{N\left[\frac{g\beta}{2} e^{g\beta H/2kT} - \frac{g\beta}{2} e^{-g\beta H/2kT}\right]}{\left[e^{g\beta H/2kT} + e^{-g\beta H/2kT}\right]}$$

For $x << 1$

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

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

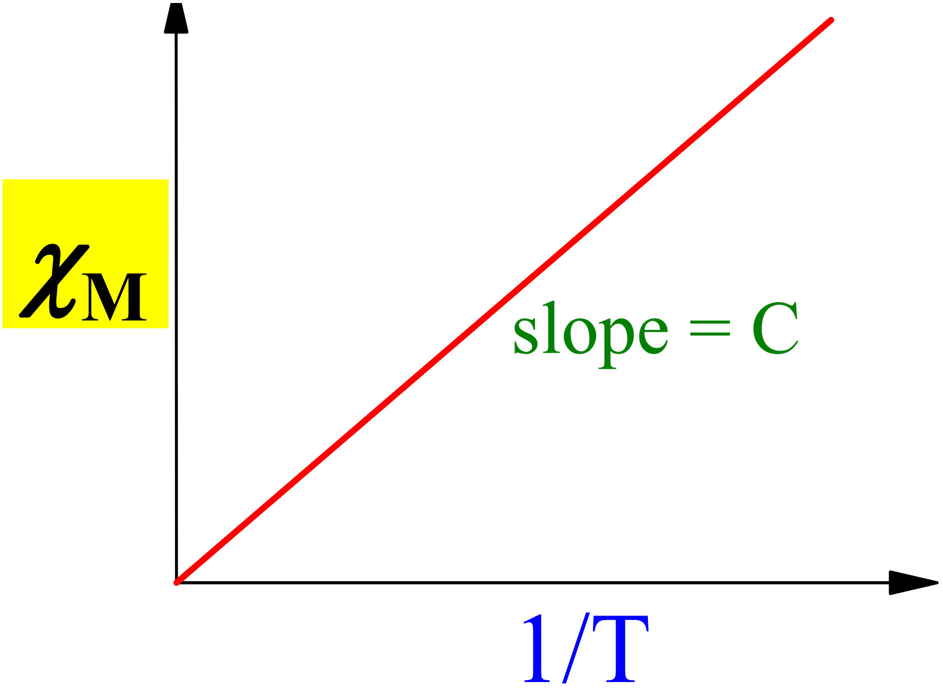
$$= \frac{N g^2 \beta^2 H}{4kT}$$

$$M_M = \frac{N_A g^2 \mu_B^2}{4 k_B T} H$$

Curie Law for S = ½

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

Pierre Curie
(1859 – 1906)
NP in physics 1903



1895 Curie Law:

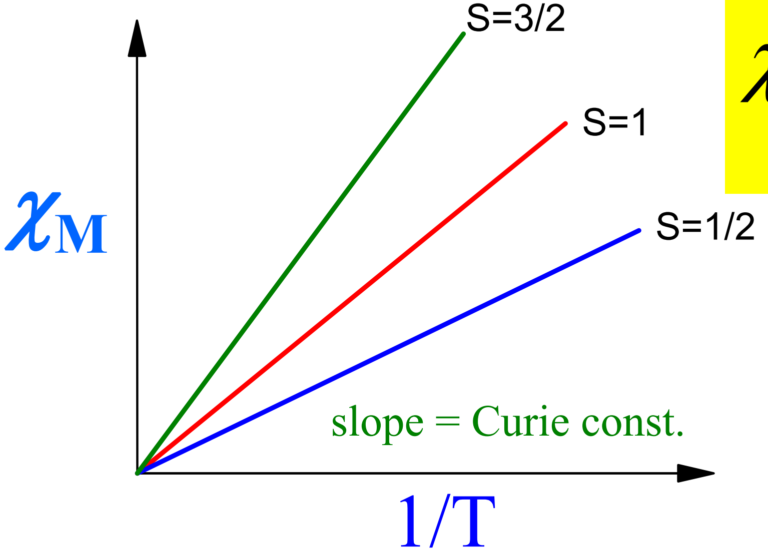
$$\chi_M = \frac{C}{T}$$

(Curie) Paramagnetism for general S

$E_n = m_s \, g \, \mu_B \, H \qquad m_s = -S, -S+1, \ldots, S-1, S$

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

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



Non-interacting, non-cooperative,
independent, dilute ions (spins)

For S = 1/2 $\quad \chi_M = \frac{N_A g^2 \mu_B^2}{4k_B T}$

For S = 1 $\quad \chi_M = \frac{2N_A g^2 \mu_B^2}{3k_B T}$

For S = 3/2 $\quad \chi_M = \frac{5N_A g^2 \mu_B^2}{4k_B T}$

(Curie) Paramagnetism

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

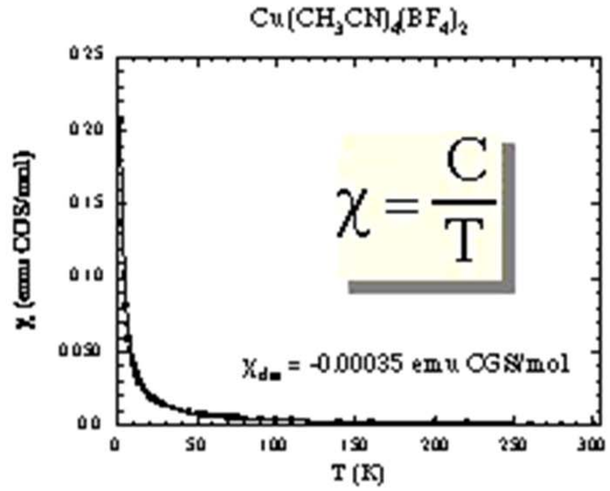
$$\mu_{eff} = \sqrt{\frac{3\chi_M k_B T}{\mu_0 N_A \mu_B^2}}$$

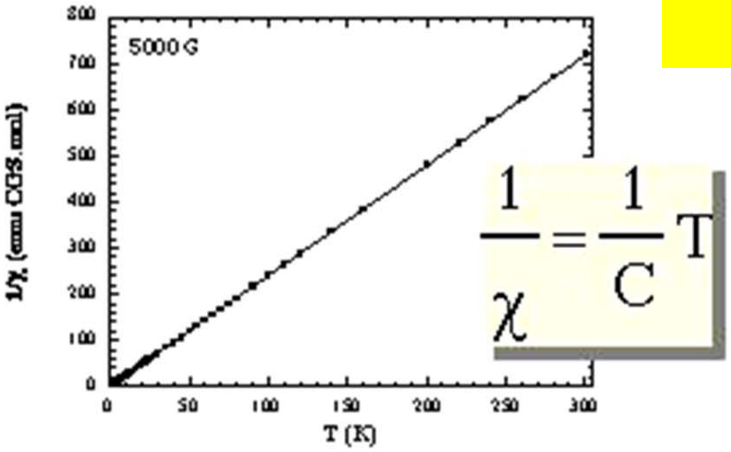
$$\mu_{eff} = g\sqrt{S(S+1)} = \sqrt{n(n+1)}$$ **(in BM, Bohr Magnetons)**

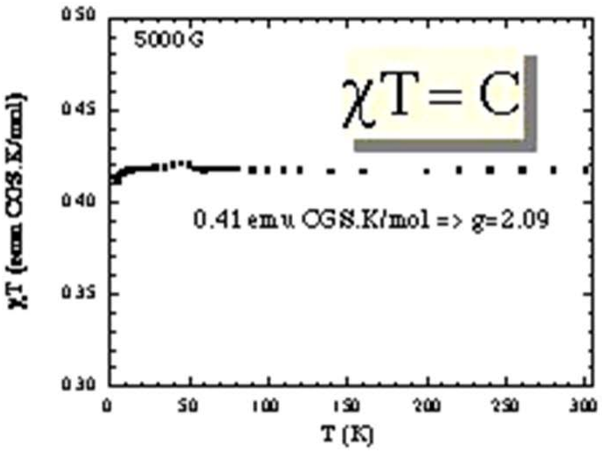
n = number of unpaired electrons
g = 2

Curie Law

$$\chi_M = \frac{C}{T}$$





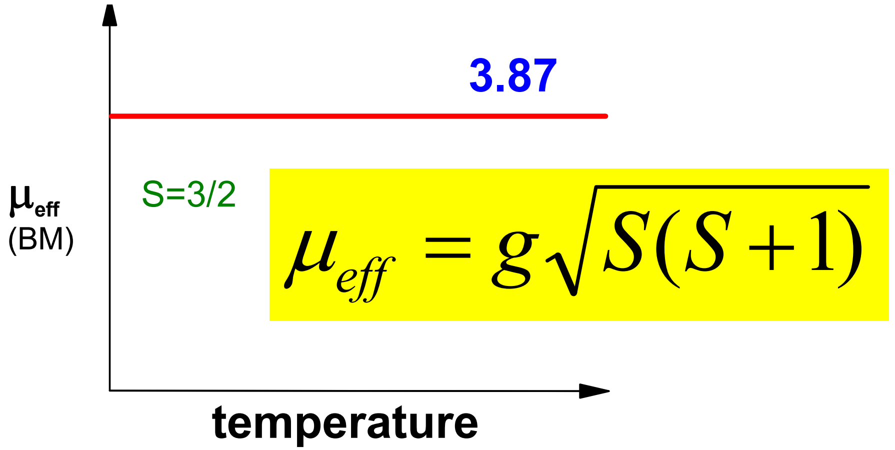


χ *vs*. T plot

$1/\chi = T/C$ plot - a straight line of gradient C^{-1} and intercept zero

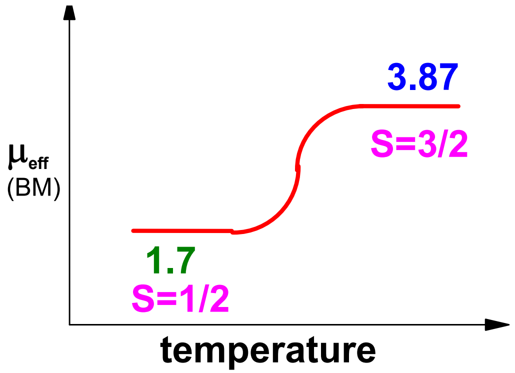
$\chi T = C$ - a straight line parallel to the x-axis at a constant value of χT
showing the temperature independence of the magnetic moment

Plot of μ_{eff} vs Temperature



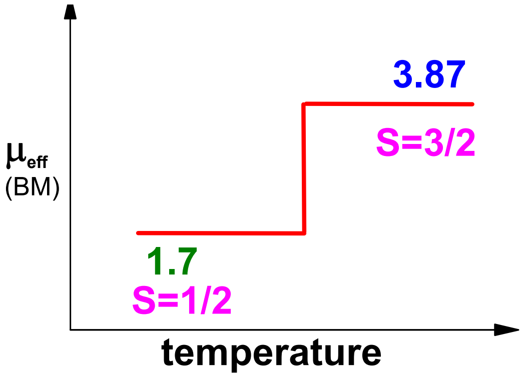
$$\mu_{eff} = g\sqrt{S(S+1)}$$

Spin Equilibrium



The individual spins in the solid material switch independently

Spin Crossover

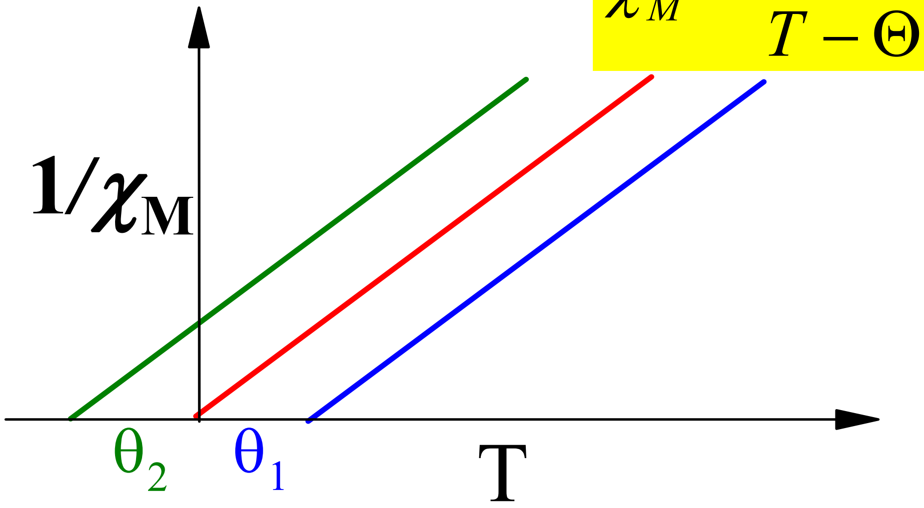


The individual spins in the solid material switch cooperatively, rather than independently of each other

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)

$$\chi_M = \frac{C}{T-\Theta}$$



$$\frac{1}{\chi_M} = \frac{1}{C}T - \frac{\Theta}{C}$$

Θ = the Weiss constant
(the x-intercept!)
$T - \Theta$ continental convention
$T + \Theta$ anglo-american convention

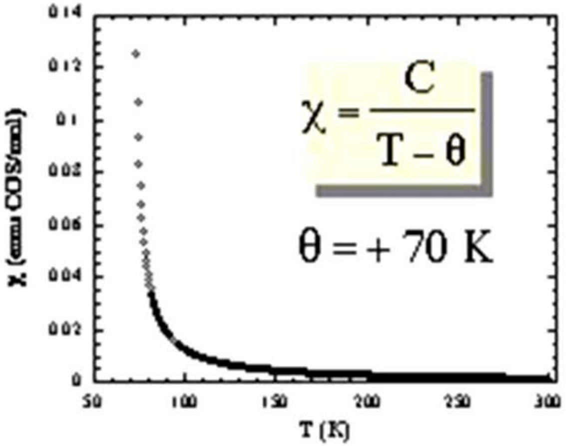
$\Theta = 0$ paramagnetic
spins independent of each other

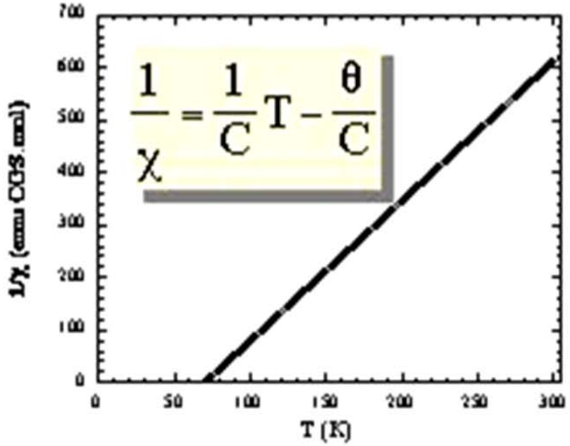
Θ is positive, spins align parallell

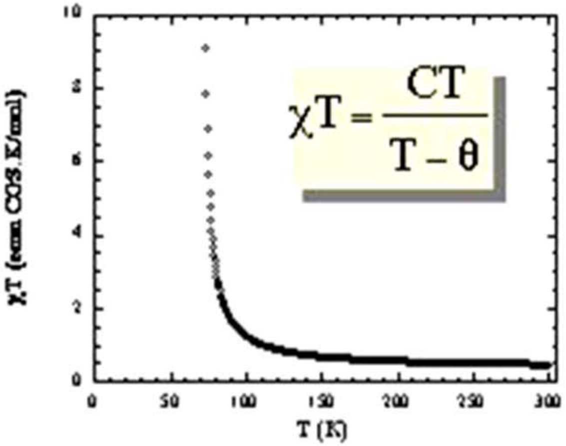
Θ is negative, spins align antiparallell

Curie-Weiss Paramagnetism

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







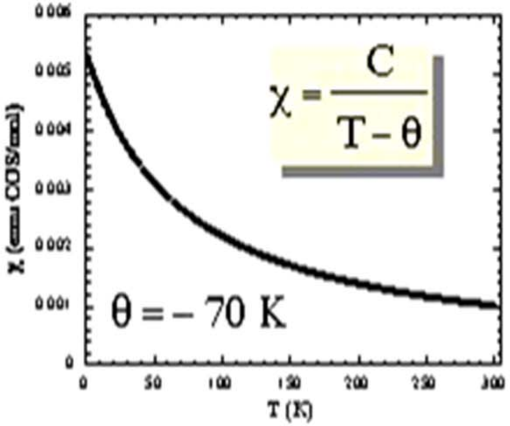
θ = intermolecular interactions among the moments

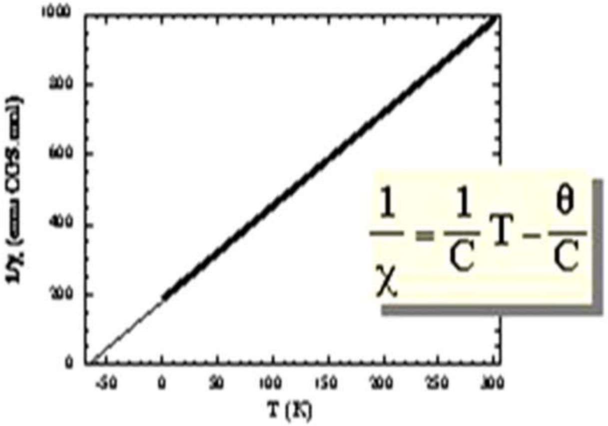
$\theta > 0$ - **ferromagnetic** interactions = **spins align parallell**

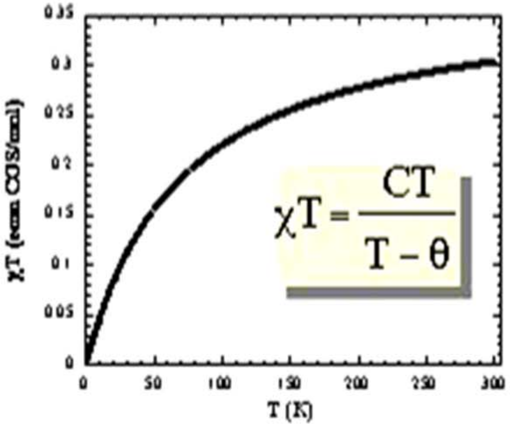
(NOT ferromagnetism)

Curie-Weiss Paramagnetism

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







θ = intermolecular interactions among the moments

θ < 0 - **antiferromagnetic** interactions
= **spins align antiparallell**

(NOT antiferromagnetism)

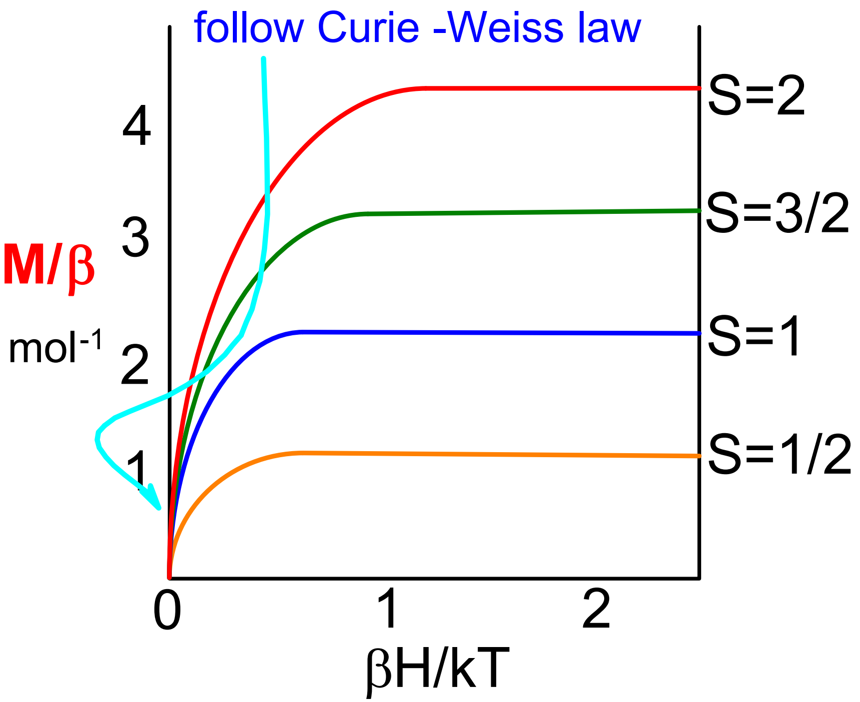
Saturation of Magnetization

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 μ_B H << kT not valid

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

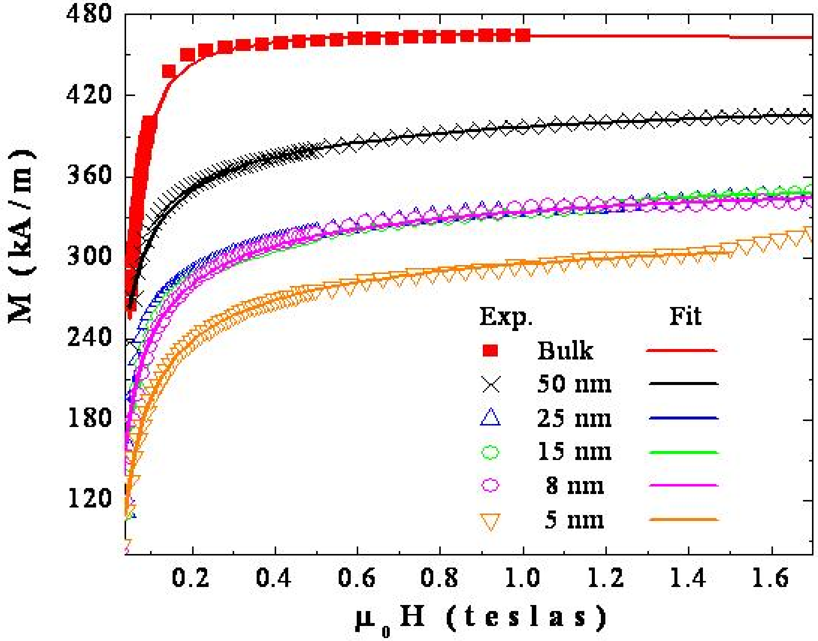
$$\chi_M \neq \frac{M}{H} \neq \frac{N_A g^2 \mu_B^2}{3k_B T} S(S+1)$$

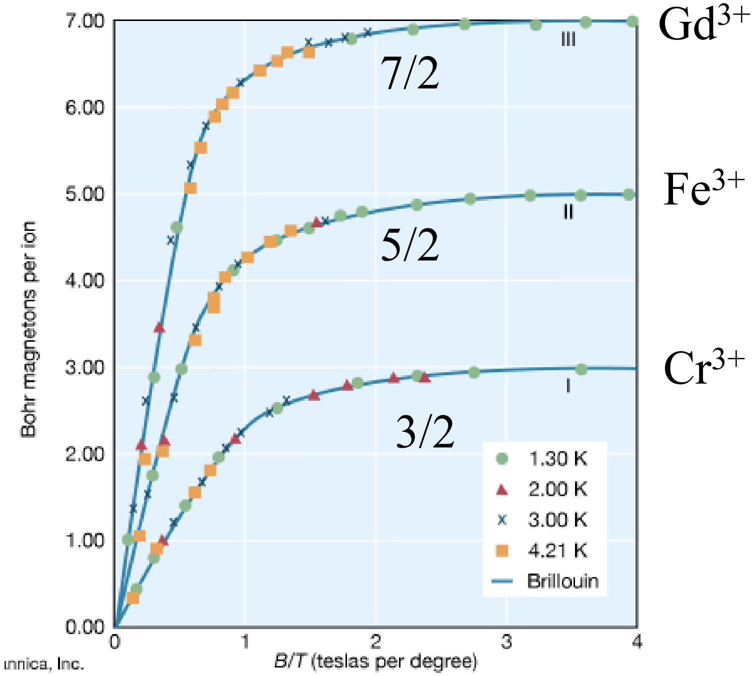


$$M_{sat} = N_A g \mu_B S$$

Saturation of Magnetization

$$M_{sat} = N_A g \mu_B S$$


Fe$_3$O$_4$ films



Curves I, II, and III refer to chromium potassium alum, iron ammonium alum, and gadolinium sulfate octahydrate

$g = 2$

Lande g-factor

A dimensionless proportionality constant of the total magnetic moment μ of a particle and the total angular momentum J

$$\left|\mu_J\right| = g_J \frac{\mu_B}{\hbar}\left|J\right|$$

$\mu_{\mathbf{B}} = eh/(4\pi m_e)$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

J = the total electronic angular momentum

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

L = the orbital angular momentum

S = the spin angular momentum

a) For a single s electron:

L= 0, S = ½, J = L + S = 0 + ½ = ½

g = 2

b) For a single p electron:

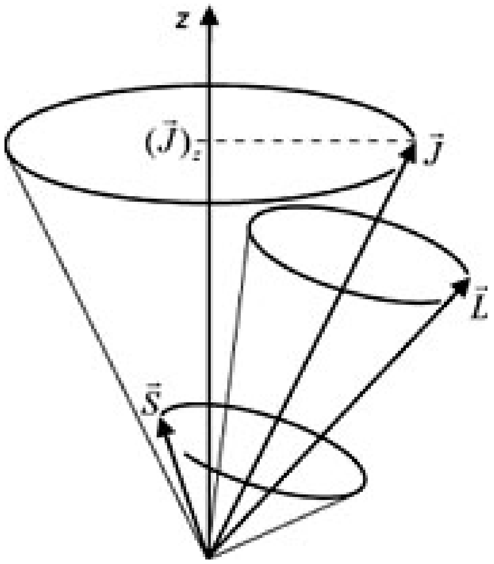
L = 1, S = ½, J = L + S = 1 + ½ = 3/2

g = 4/3

c) For a single d electron:

L = 2, S = ½, J = L + S = 2 + ½ = 5/2

g = 6/5

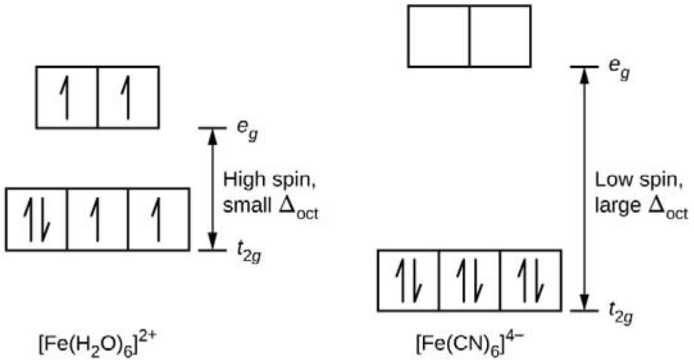


Magnetism in Transition Metal Complexes

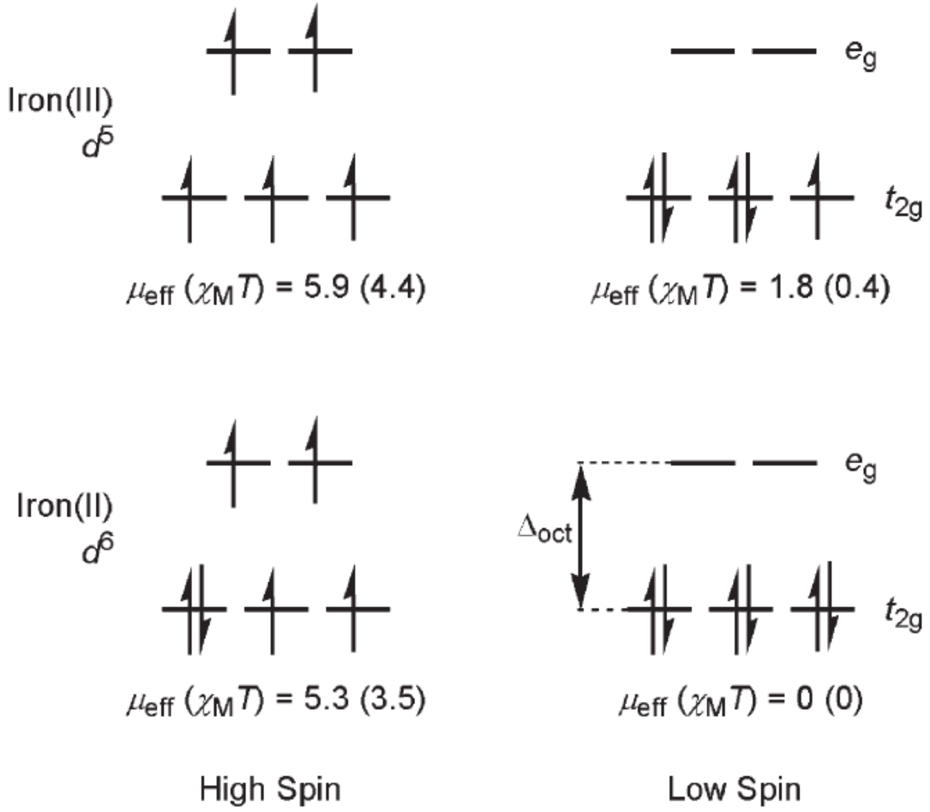
Many transition metal salts and complexes are paramagnetic due to **partially filled d-orbitals**

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

- Number of unpaired electrons present
- Oxidation state
- Distinction between HS and LS octahedral complexes
- Spectral behavior
- Structure of the complexes (tetrahedral vs octahedral vs tetragonal)



Magnetism in Transition Metal Complexes



μ_{eff} in Bohr magnetons, $\chi_M T$ in $cm^3\ mol^{-1}\ K$

Paramagnetism in Transition Metal Complexes

$$\mu_{l+s} = \mu_l + \mu_s$$

Orbital motion of the electron generates

ORBITAL MAGNETIC MOMENT (μ_l)

Spin motion of the electron generates

SPIN MAGNETIC MOMENT (μ_s)

L-S coupling (Russel- Saunders - assumes strong interaction between total orbital and total spin angular momenta)

l = orbital angular momentum
s = spin angular momentum

For multi-electron systems
L $= l_1 + l_2 + l_3 + \ldots$ total orbital angular momentum
S $= s_1 + s_2 + s_3 + \ldots$ total spin angular momentum

Paramagnetism in Transition Metal Complexes

The magnetic properties arise mainly from the d-orbitals

For the first Transition Metal series, spin-orbital interaction is **small**

Orbital angular momentum and spin angular momentum act independently – no spin-orbit coupling

Free ions:

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

Paramagnetism in Transition Metal Complexes

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**

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

$$\mu_s = g\sqrt{S(S+1)}\frac{eh}{4\pi m_e} = \sqrt{4S(S+1)}\mu_B$$

$S = \frac{1}{2} n$

Spin-Only Formula

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

μ_s = 1.73, 2.83, 3.88, 4.90, 5.92, 6.93 BM for n = 1 to 6, respectively
Mn^{2+}, Fe^{3+}, Gd^{3+}

Ground States of Free Ions with Partially Filled d-shells (*l* = 2)

$^{2S+1}L_J$

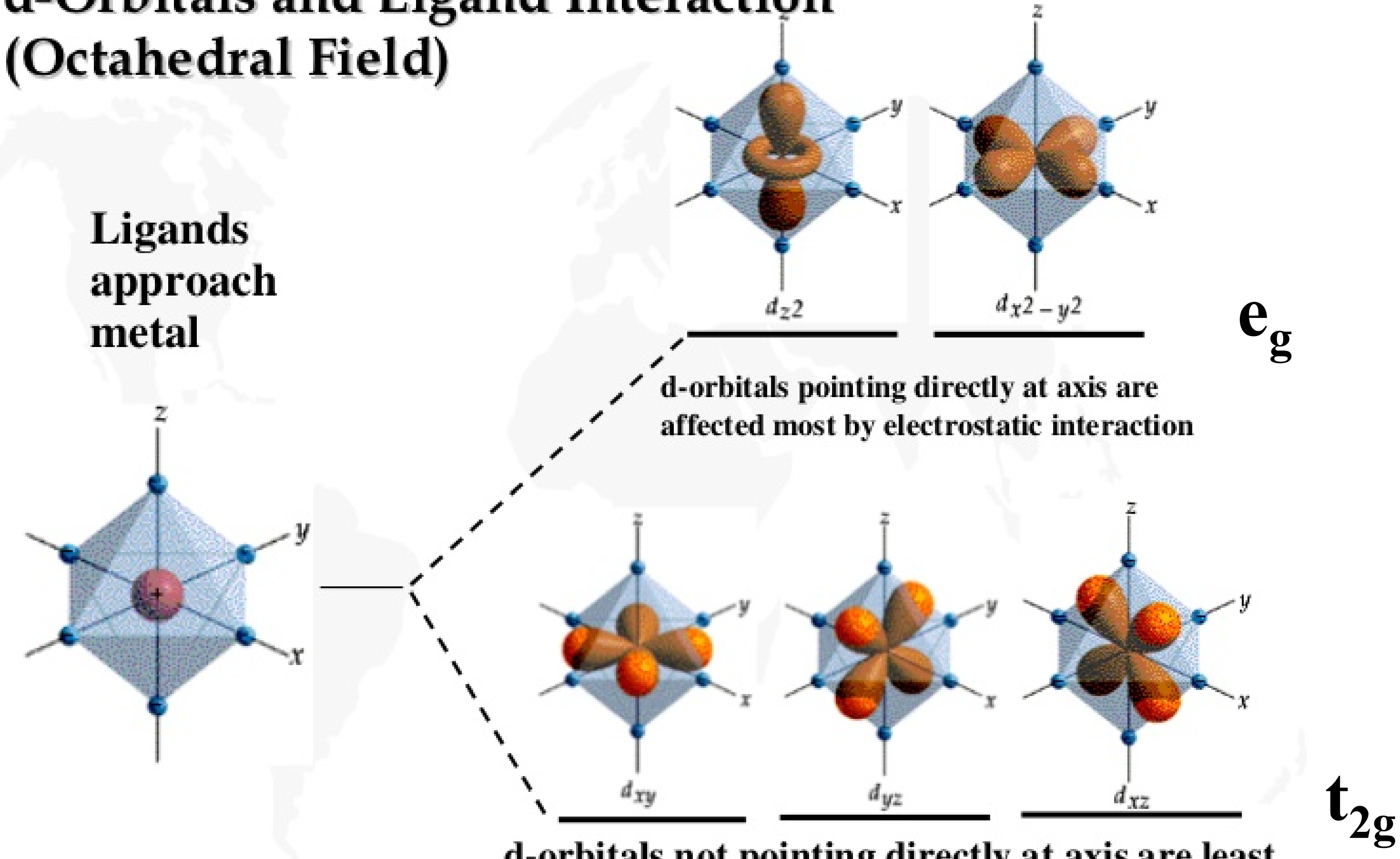
See Hunds Rules

$el.$	$m_l =$	2	1	0	-1	-2	S	$L = \lvert\sum m_l\rvert$	J	Symbol
1		↓					1/2	2	3/2	$^2D_{3/2}$
2		↓	↓				1	3	2	$^3F_2$
3		↓	↓	↓			3/2	3	3/2	$^4F_{3/2}$
4		↓	↓	↓	↓		2	2	0	$^5D_0$
5		↓	↓	↓	↓	↓	5/2	0	5/2	$^6S_{5/2}$
6		↓↑	↓	↓	↓	↓	2	2	4	$^5D_4$
7		↓↑	↓↑	↓	↓	↓	3/2	3	9/2	$^4F_{9/2}$
8		↓↑	↓↑	↓↑	↓	↓	1	3	4	$^3F_4$
9		↓↑	↓↑	↓↑	↓↑	↓	1/2	2	5/2	$^2D_{5/2}$
10		↓↑	↓↑	↓↑	↓↑	↓↑	0	0	0	$^1S_0$

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

Orbital Contribution in Octahedral Complexes

d-Orbitals and Ligand Interaction (Octahedral Field)



d-orbitals pointing directly at axis are affected most by electrostatic interaction

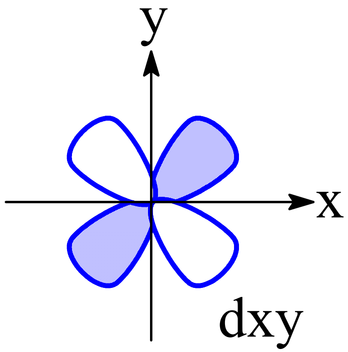
d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

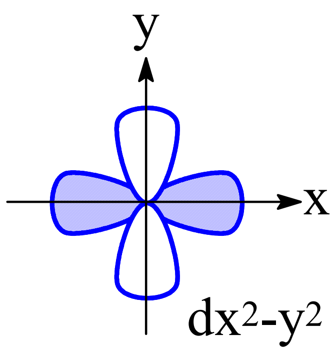
Orbital Angular Momentum Contribution

There must be an unfilled / half-filled orbital similar in energy to that of the orbital occupied by the unpaired electrons
The electrons can make use of the available orbitals to circulate or move around the center of the complexes and hence generate **L** and μ_L

Conditions for orbital angular momentum contribution:

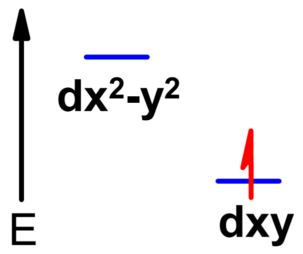
1. The orbitals should be **degenerate** (t_{2g} or e_g)
2. The orbitals should be similar in shape and size, so that they are **transferable** into one another **by rotation** about the same axis (e.g., d_{xy} is related to $d_{x}2\text{-}_{y}2$ by a rotation of 45° about the z-axis)
3. Orbitals must **not contain** electrons of **identical spin**



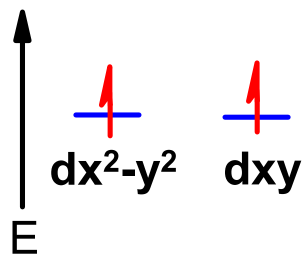


Spin-Orbit Coupling

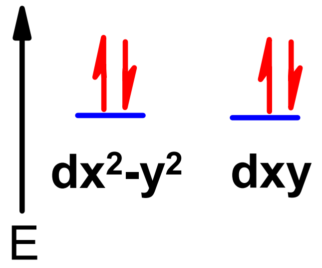
Little contribution from orbital angular momentum



dx^2-y^2 and dxy orbitals have different energies in a certain electron configuration, electrons cannot go back and forth between them

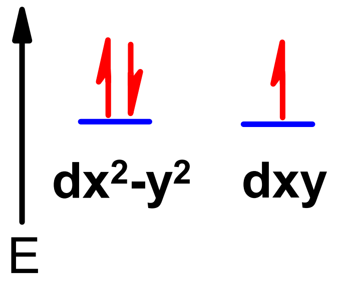


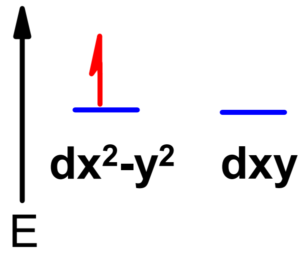
Electrons have to change directions of spins to circulate

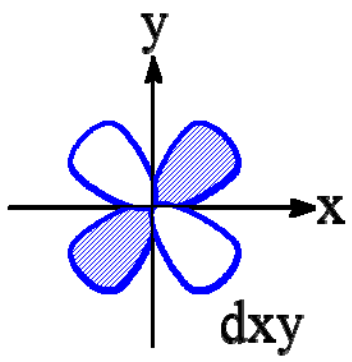


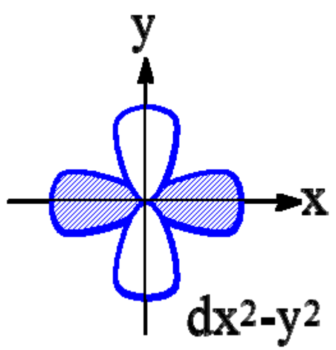
Orbitals are filled

Spin-orbit couplings are significant









Magic Pentagon

Spin-orbit coupling influences g-value

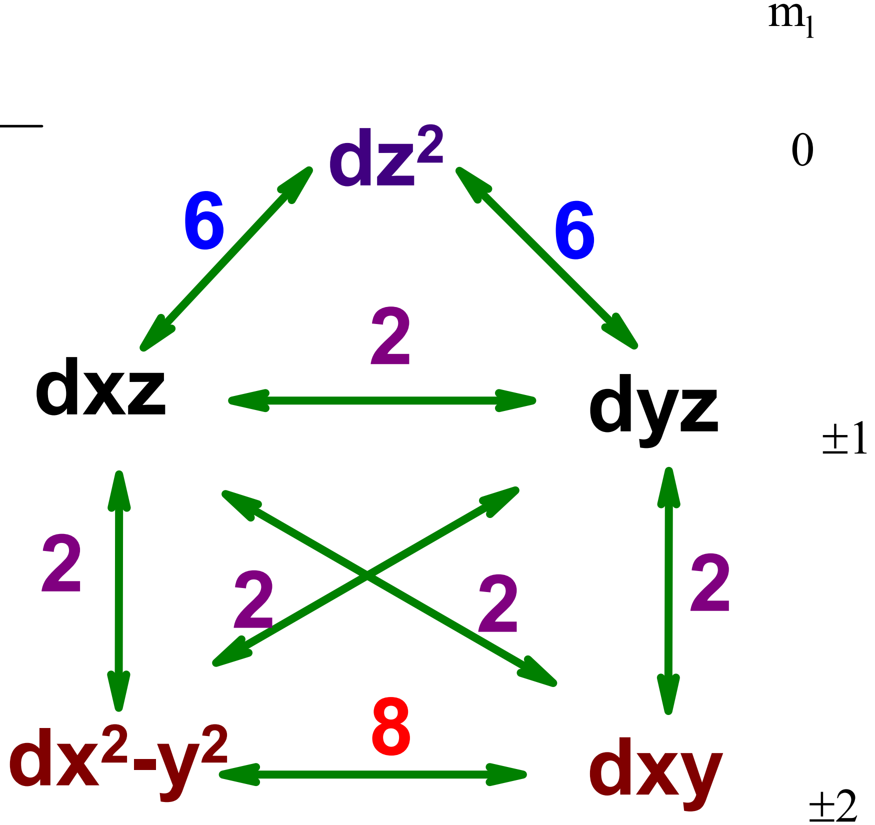
$$g = 2.0023 \pm \frac{n\lambda}{E_1 - E_2}$$

2.0023: g-value for **free** ion

+ sign for <1/2 filled subshell
– sign for >1/2 filled subshell

n: number of magic pentagon

λ: 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**

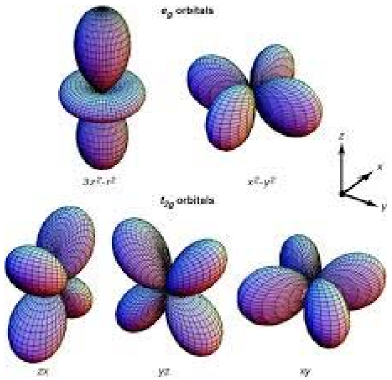
Orbital Contribution in Octahedral Complexes

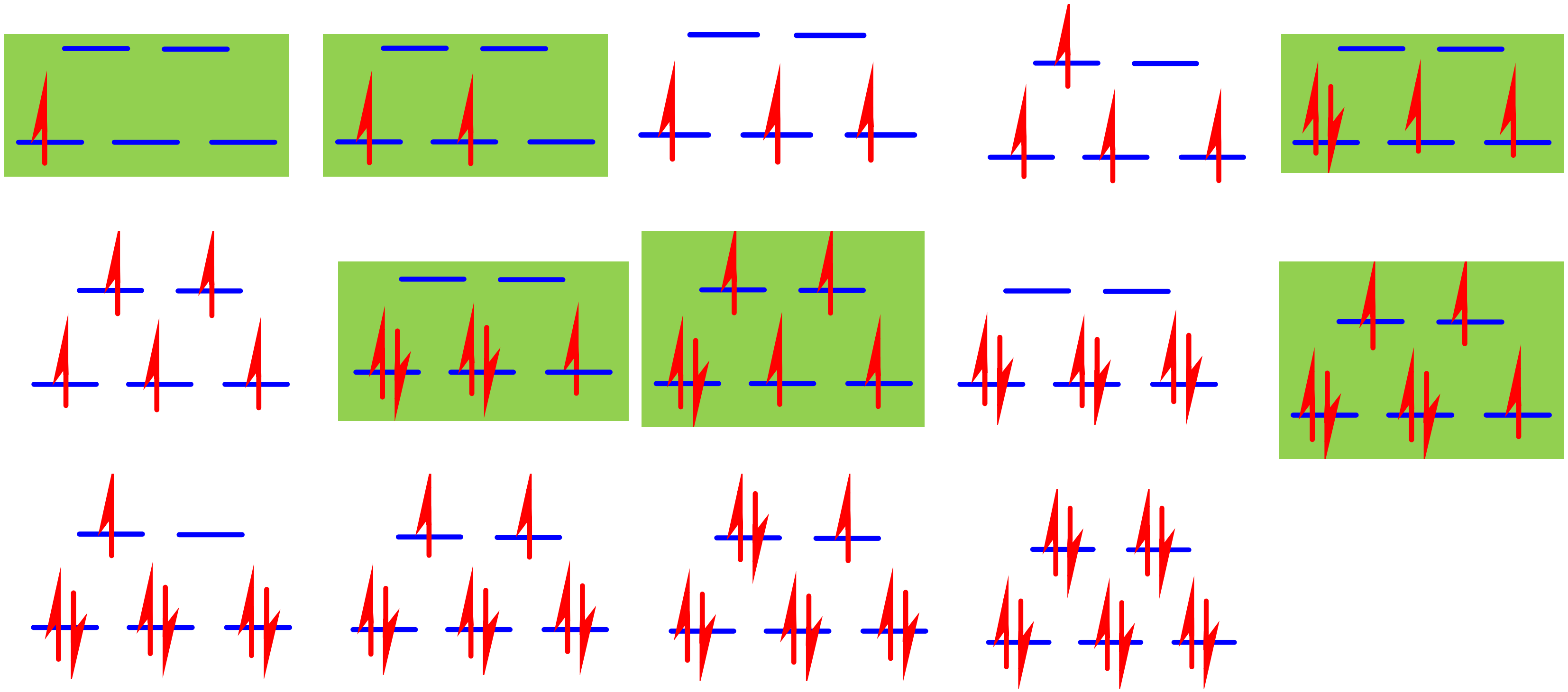
Condition	t_{2g} set	e_g set $d_{x^2-y^2} + d_{z^2}$
1 degenerate	Obeyed	Obeyed
2 rotation	Obeyed	Not obeyed
3 spin	Since 1 and 2 are satisfied condition 3 dictates whether t_{2g} will generate μ_l or not	Does not matter since condition 2 is already not obeyed

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

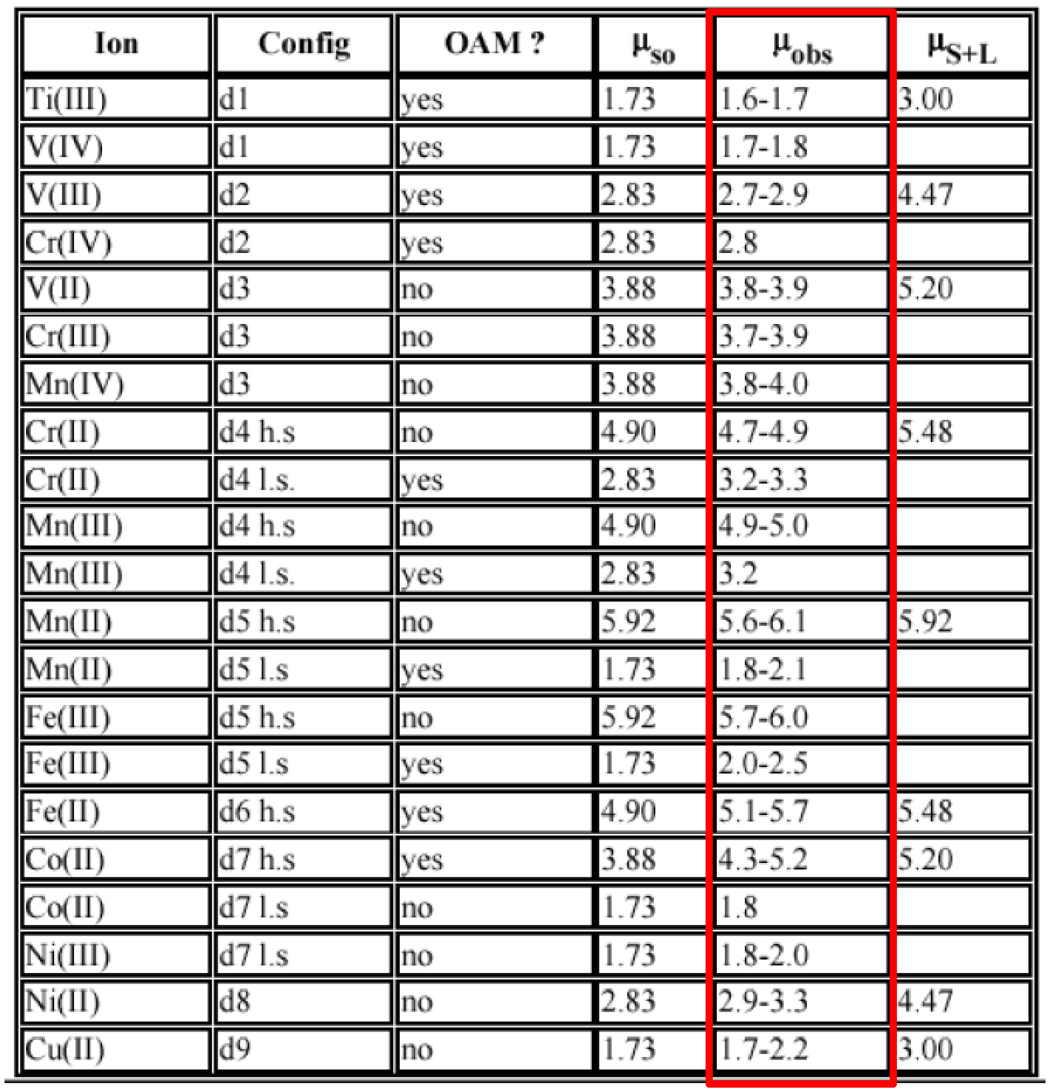
d_{xz} to d_{yz}　　**d_{xy} to d_{yz}**　　**d_{xz} to d_{xy}**

Orbital Contribution in Octahedral Complexes





Orbital Contribution in Octahedral Complexes



Ion	Config	OAM ?	μ_{so}	μ_{obs}	μ_{S+L}
Ti(III)	d1	yes	1.73	1.6-1.7	3.00
V(IV)	d1	yes	1.73	1.7-1.8	
V(III)	d2	yes	2.83	2.7-2.9	4.47
Cr(IV)	d2	yes	2.83	2.8	
V(II)	d3	no	3.88	3.8-3.9	5.20
Cr(III)	d3	no	3.88	3.7-3.9	
Mn(IV)	d3	no	3.88	3.8-4.0	
Cr(II)	d4 h.s	no	4.90	4.7-4.9	5.48
Cr(II)	d4 l.s.	yes	2.83	3.2-3.3	
Mn(III)	d4 h.s	no	4.90	4.9-5.0	
Mn(III)	d4 l.s.	yes	2.83	3.2	
Mn(II)	d5 h.s	no	5.92	5.6-6.1	5.92
Mn(II)	d5 l.s	yes	1.73	1.8-2.1	
Fe(III)	d5 h.s	no	5.92	5.7-6.0	
Fe(III)	d5 l.s	yes	1.73	2.0-2.5	
Fe(II)	d6 h.s	yes	4.90	5.1-5.7	5.48
Co(II)	d7 h.s	yes	3.88	4.3-5.2	5.20
Co(II)	d7 l.s	no	1.73	1.8	
Ni(III)	d7 l.s	no	1.73	1.8-2.0	
Ni(II)	d8	no	2.83	2.9-3.3	4.47
Cu(II)	d9	no	1.73	1.7-2.2	3.00

OAM = orbital angular momentum contribution

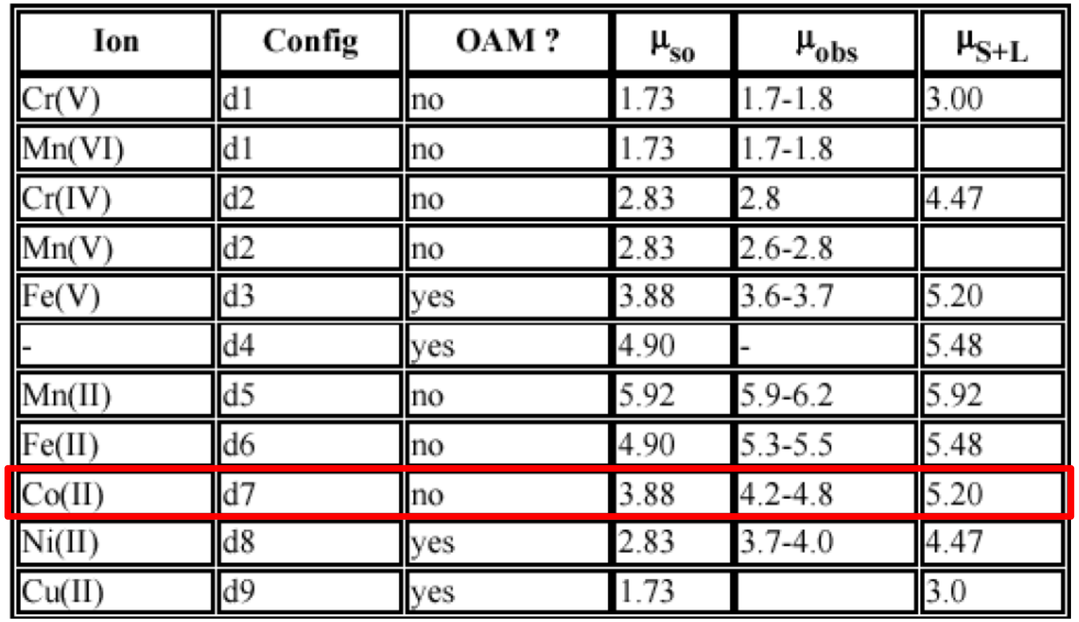
SO = Spin-Only Formula

$$\mu_{SO} = \sqrt{4S(S+1)}$$

S+L = Spin-Orbit Coupling

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$$

Orbital Contribution in Tetrahedral Complexes

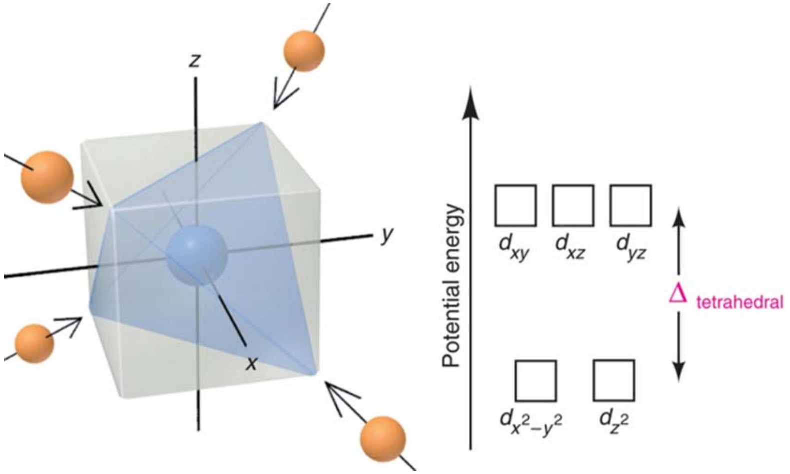


Ion	Config	OAM ?	μ_{so}	μ_{obs}	μ_{S+L}
Cr(V)	d1	no	1.73	1.7-1.8	3.00
Mn(VI)	d1	no	1.73	1.7-1.8	
Cr(IV)	d2	no	2.83	2.8	4.47
Mn(V)	d2	no	2.83	2.6-2.8	
Fe(V)	d3	yes	3.88	3.6-3.7	5.20
-	d4	yes	4.90	-	5.48
Mn(II)	d5	no	5.92	5.9-6.2	5.92
Fe(II)	d6	no	4.90	5.3-5.5	5.48
Co(II)	d7	no	3.88	4.2-4.8	5.20
Ni(II)	d8	yes	2.83	3.7-4.0	4.47
Cu(II)	d9	yes	1.73		3.0

If $\mu_{obs} > \mu_{so}$

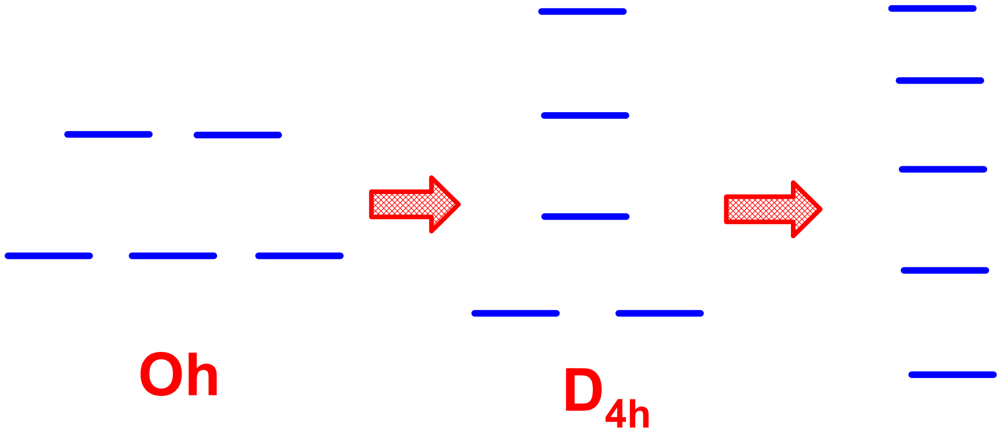
Contribution from **excited** states to the magnetic moment

Co(II) d^7
ground: $e^4\ t_2^3$ no OAM
excited: $e^3\ t_2^4$ yes OAM



Orbital Contribution
in Low-symmetry Ligand Field

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



D_{4h}: all are quenched except d^1 and d^3

$\mu_{eff} = g[S(S+1)]^{1/2}$ (**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 are 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 (J = L + S)

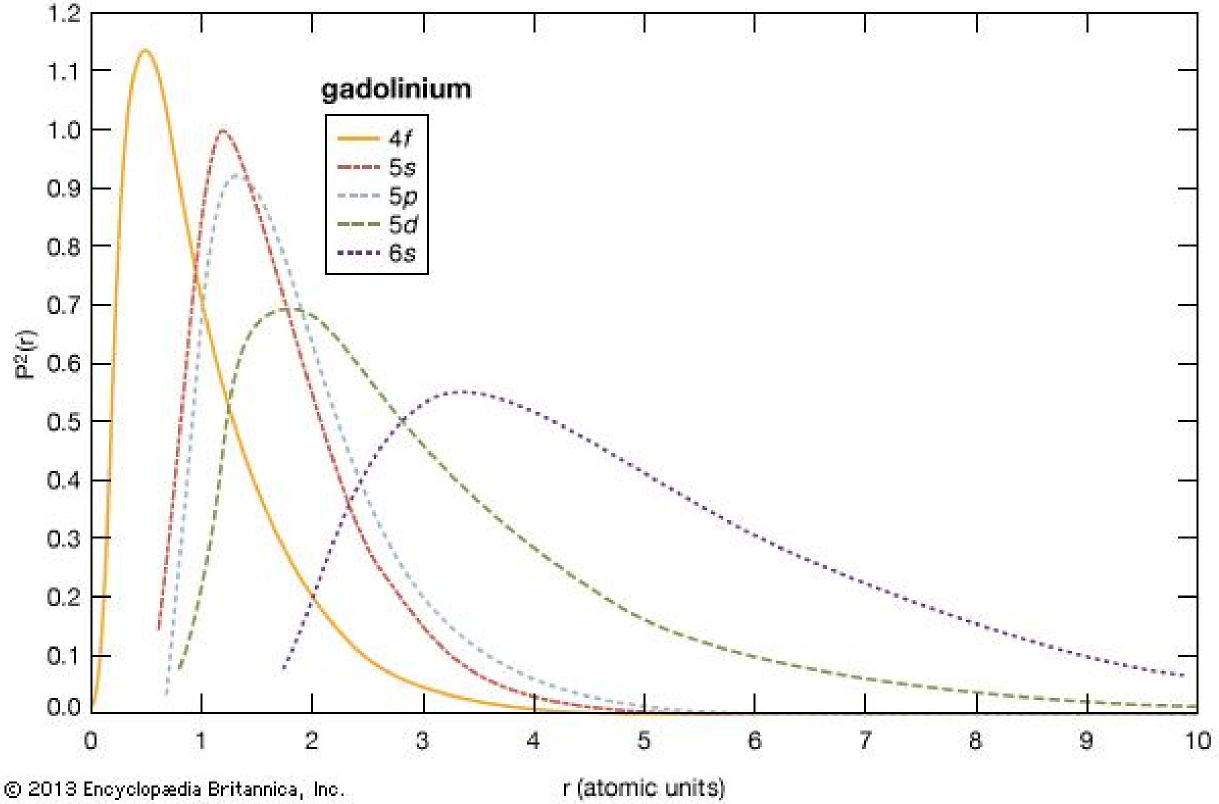
- spin-orbit coupling constants are large (ca. 1000 cm^{-1})
- ligand field effects are very small (ca. 100 cm^{-1})
- spin-orbit coupling >> ligand field splitting
- only ground J-state is populated
- magnetism is essentially independent of coordination environment (ligand field)

Valence Shell of Lanthanides

Xe	[Kr]	$4d^{10}\ 5s^2\ 5p^6$	E(4f) > E(6s)
Cs	[Xe]	$6s^1\ 4f^0\ 5d^0$	
Ba	[Xe]	$6s^2\ 4f^0\ 5d^0$	
La	[Xe]	$\mathbf{5d^1}\ 6s^2\ 4f^0$	transition metal
Ce	[Xe]	$4f^1\ 5d^1\ 6s^2$	E(4f) < E(6s), E(5d)
Pr	[Xe]	$4f^3\ 5d^0\ 6s^2$	
Nd	[Xe]	$4f^4\ 5d^0\ 6s^2$	
Pm	[Xe]	$4f^5\ 5d^0\ 6s^2$	
Sm	[Xe]	$4f^6\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Eu	[Xe]	$4f^7\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Gd	[Xe]	$\mathbf{4f^7}\ 5s^2\ 5p^6\ \mathbf{5d^1}\ 6s^2$	4f half-filled
Tb	[Xe]	$4f^9\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Dy	[Xe]	$4f^{10}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Ho	[Xe]	$4f^{11}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Er	[Xe]	$4f^{12}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Tm	[Xe]	$4f^{13}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Yb	[Xe]	$4f^{14}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$	
Lu	[Xe]	$4f^{14}\ 5s^2\ 5p^6\ \mathbf{5d^1}\ 6s^2$	4f completely filled

Magnetic Properties of Lanthanides

Gd [Xe] $4f^7$ $5s^2$ $5p^6$ $5d^1$ $6s^2$



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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,……L – S

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

g = ?
For singlet
For spin-only

g-value for free ions

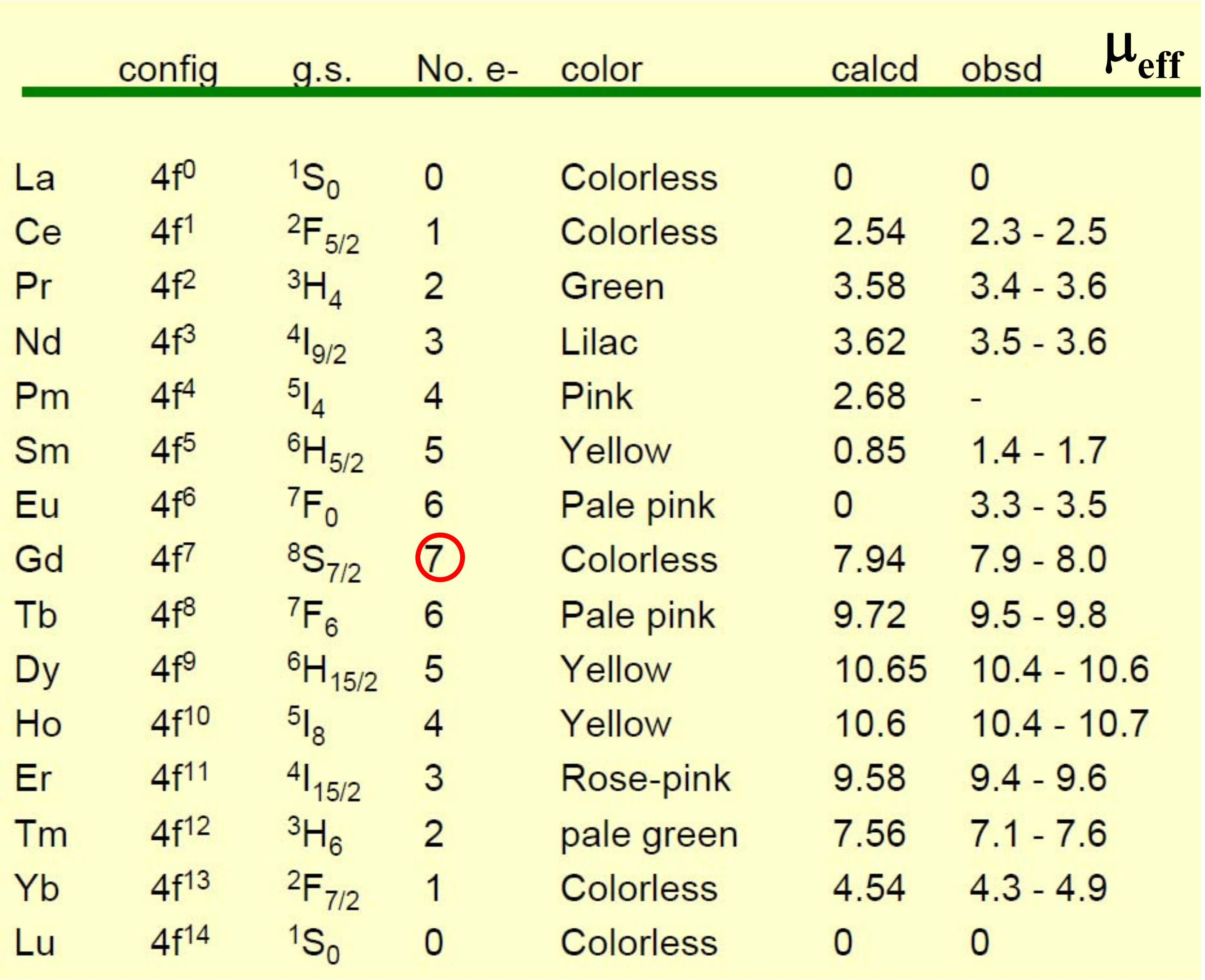
For the calculation of g value, use
minimum value of J for the configurations up to half-filled;
i.e., J = L – S for f^0 - f^7 configurations
maximum value of J for configurations more than half-filled;
i.e., J = L + S for f^8 - f^{14} configurations

For f^0, f^7, and f^{14}, L = 0, hence μ_J becomes μ_S

Magnetic Properties of Lanthanides Ln^{3+}

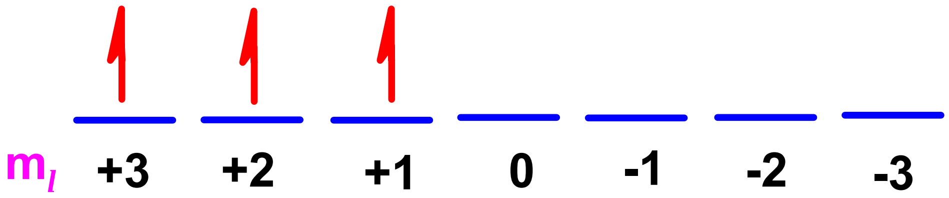
Russell-Saunders Coupling (J = L + S), only ground J-state is populated

$^{M}L_{J}$



	config	g.s.	No. e-	color	μ_{eff}	
					calcd	obsd
La	$4f^0$	$^1S_0$	0	Colorless	0	0
Ce	$4f^1$	$^2F_{5/2}$	1	Colorless	2.54	2.3 - 2.5
Pr	$4f^2$	$^3H_4$	2	Green	3.58	3.4 - 3.6
Nd	$4f^3$	$^4I_{9/2}$	3	Lilac	3.62	3.5 - 3.6
Pm	$4f^4$	$^5I_4$	4	Pink	2.68	-
Sm	$4f^5$	$^6H_{5/2}$	5	Yellow	0.85	1.4 - 1.7
Eu	$4f^6$	$^7F_0$	6	Pale pink	0	3.3 - 3.5
Gd	$4f^7$	$^8S_{7/2}$	7	Colorless	7.94	7.9 - 8.0
Tb	$4f^8$	$^7F_6$	6	Pale pink	9.72	9.5 - 9.8
Dy	$4f^9$	$^6H_{15/2}$	5	Yellow	10.65	10.4 - 10.6
Ho	$4f^{10}$	$^5I_8$	4	Yellow	10.6	10.4 - 10.7
Er	$4f^{11}$	$^4I_{15/2}$	3	Rose-pink	9.58	9.4 - 9.6
Tm	$4f^{12}$	$^3H_6$	2	pale green	7.56	7.1 - 7.6
Yb	$4f^{13}$	$^2F_{7/2}$	1	Colorless	4.54	4.3 - 4.9
Lu	$4f^{14}$	$^1S_0$	0	Colorless	0	0

Magnetic Properties of Nd^{3+} ($4f^3$)



$^{M}L_{J}$

Term symbol of electronic state

$L_{max} = 3 + 2 + 1 = 6$

$S_{max} = 3 \times 1/2 = 3/2$ $M = 2S + 1 = 2 \times 3/2 + 1 = 4$

Ground state $J = L - S = 6 - 3/2 = 9/2$

Ground state term symbol: $^{4}I_{9/2}$

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

$$\mu_{eff} = g[J(J+1)]^{1/2} = 0.727[(9/2)(9/2 + 1)] = 3.62 \text{ BM}$$

Magnetic Properties of Pr^{3+}(4f^2)

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

Find Ground State from Hund's Rules
Maximum Multiplicity **S** = $^1/_2 + ^1/_2 = 1$ **M = 2S + 1 = 3**

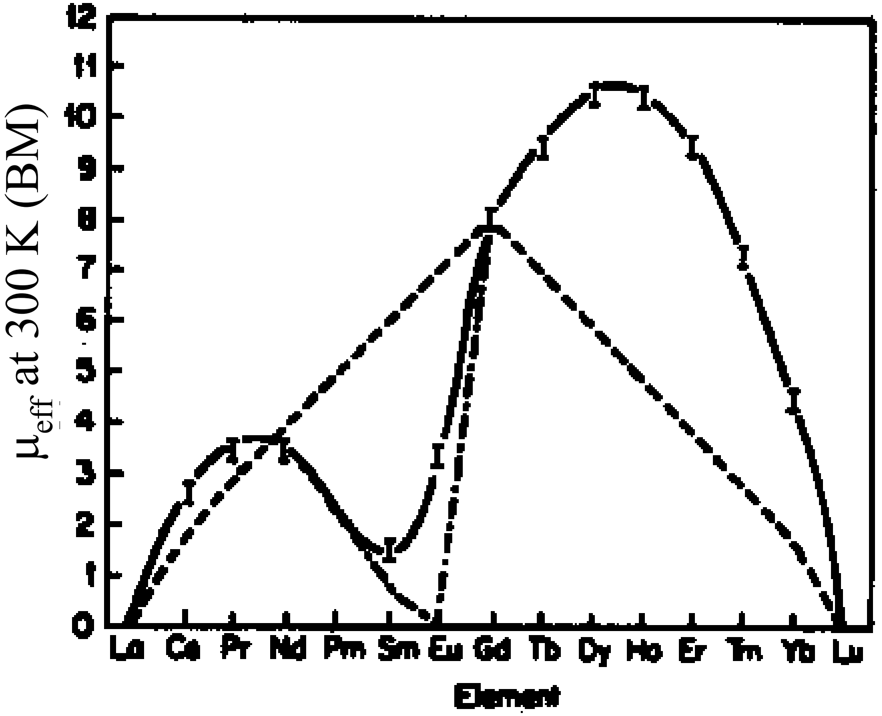
Maximum Orbital Angular Momentum **L** = 3 + 2 = 5

Total Angular Momentum **J** = (L + S), (L + S) - 1, …L - S = 6 , 5, 4
f^2 = less than half-filled sub-shell **-** choose minimum J = L – S → **J = 4**

g = (3/2) + [1(1+1)-5(5+1)/2(4)(4+1)] = 0.8

μ_J = 3.577 BM Experiment = 3.4 - 3.6 BM

Magnetic Properties of Lanthanides Ln^{3+}



Experimental ——Landé Formula -•-•-Spin-Only Formula - - -

Landé formula fits well with observed magnetic moments for all but Sm(III) and 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

Magnetic order is due to the coupling between discrete microscopic magnetic moments

Two **exchange-coupled** unpaired electrons

The Heisenberg-Dirac-Van Vleck Hamiltonian

- an empirical operator that models interaction (coupling) of unpaired electrons

$$H = -2J\sum_{ij}\vec{S}_i.\vec{S}_j$$

The coupling between pairs of individual spins, ***S***, on atom *i* and atom *j*

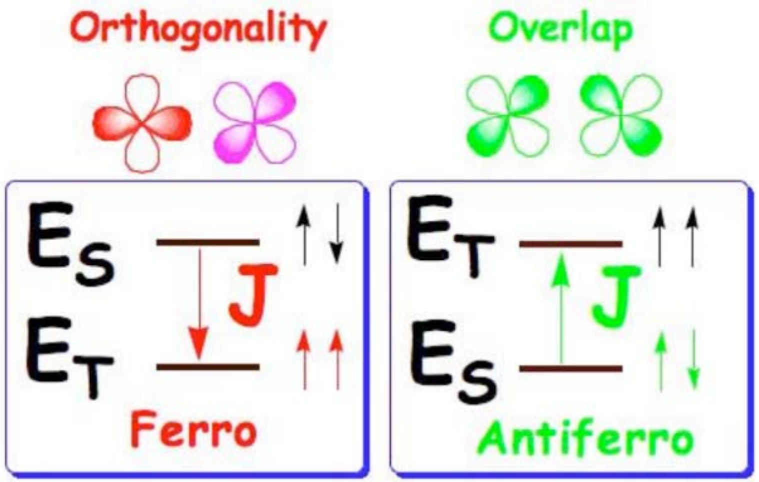
J = the exchange coupling constant

***J* > 0**

parallel

(ferromagnetic)

alignment



***J* < 0**

antiparallel

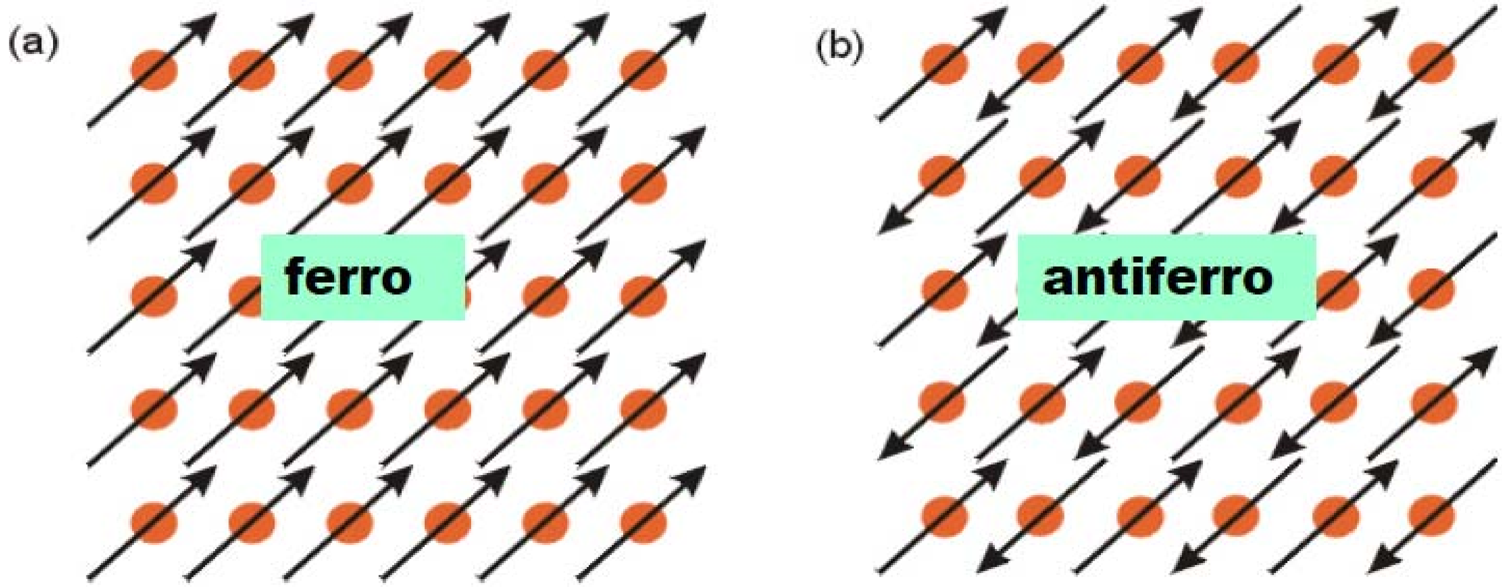
(antiferromagnetic)

alignment

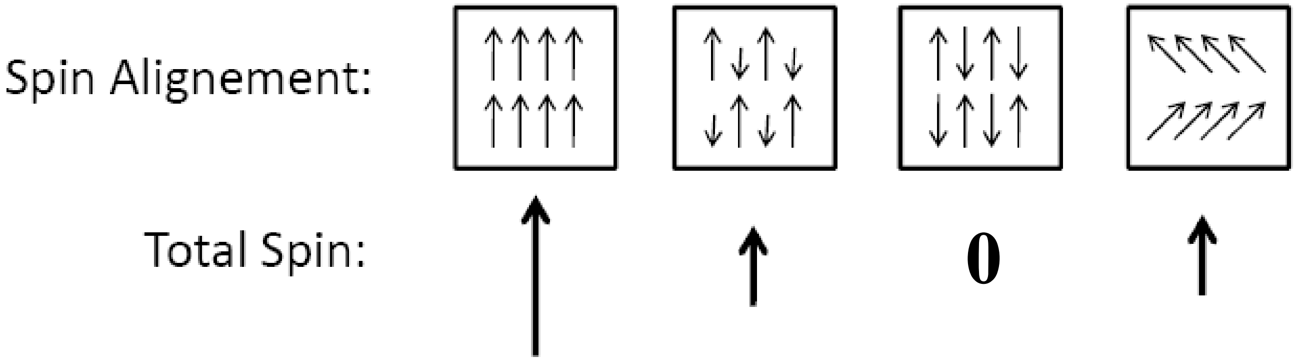
Magnetism in Solids
Cooperative Magnetism

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

Ferromagnetism, antiferromagnetism and other types of cooperative magnetism originate from an intense magnetic interaction between electron spins of many atoms in bulk materials



Magnetic Ordering



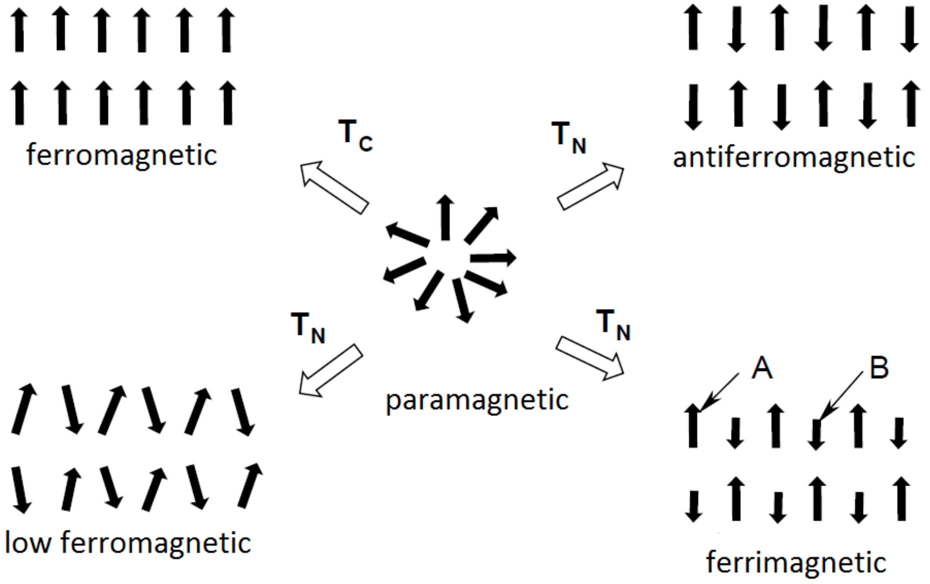
Ferromagnets - all interactions ferromagnetic, a large overall magnetization
Ferrimagnets - the alignment is antiferromagnetic, but due to different magnitudes of the spins, a net magnetic moment is observed
Antiferromagnets - both spins are of same magnitude and are arranged antiparallel

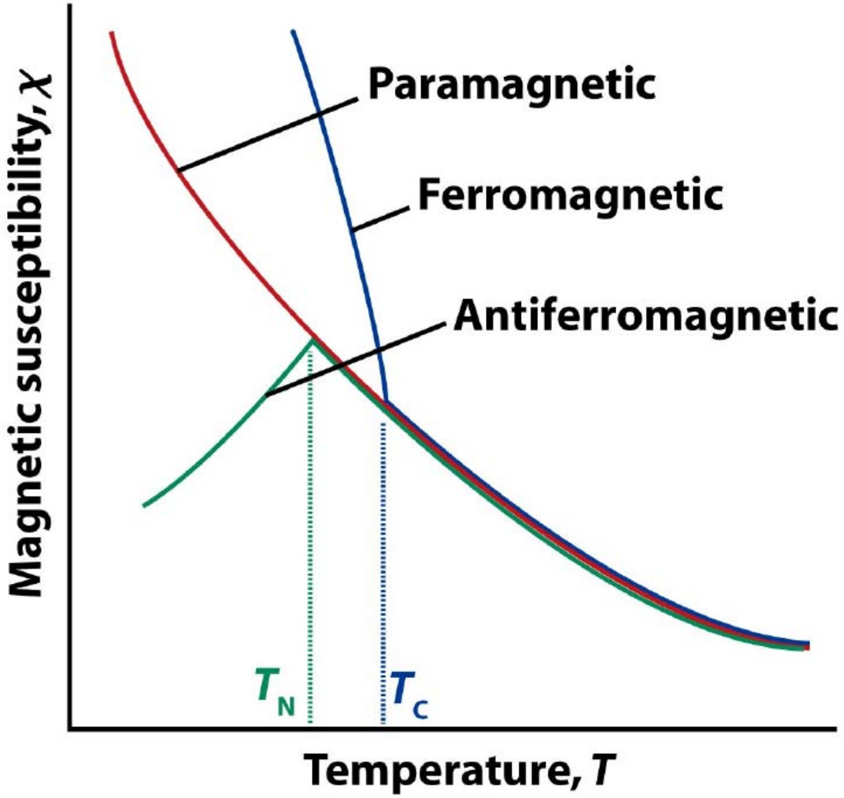
Weak ferromagnets – spins are not aligned anti/parallel but canted
Spin glasses – random orientation of frozen spin orientations, spins are correlated but not long-range ordered, spin coupling mediated through the conduction electrons
Metamagnets - a field-induced magnetic transition from a state of low to high magnetization
Superparamagnets - ferromagnets with particle size too small to sustain the multidomain structure, the particle behaves as one large paramagnetic ion

Magnetic Ordering

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

T_C = Curie temperature
T_N = Neel temperature

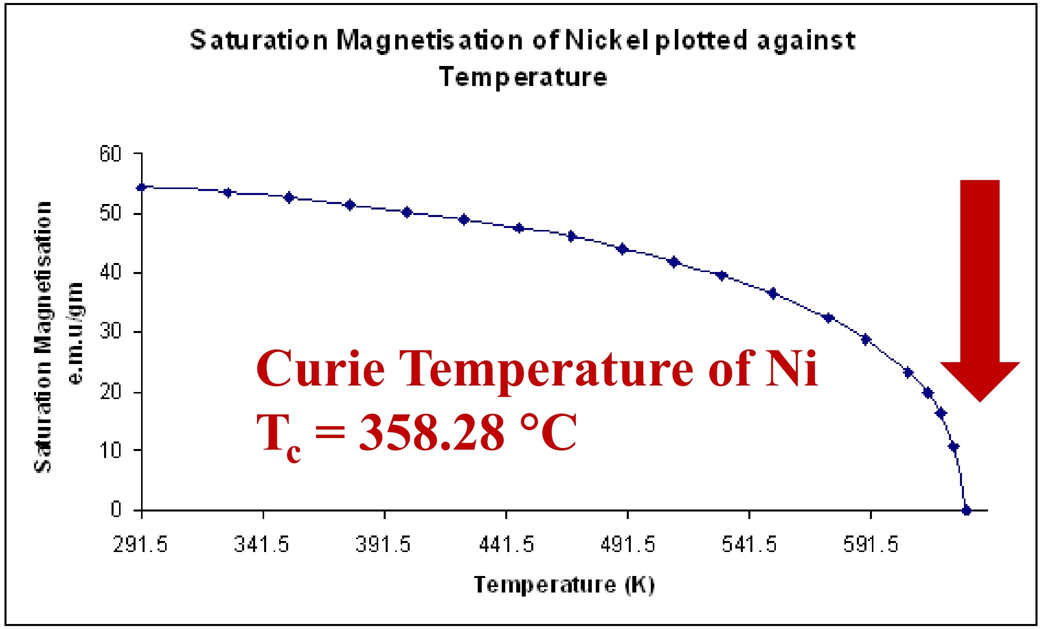




Curie Temperature

1832 Pouillet
Ni, Fe, Co
Observed a limit for the temperature of magnetism

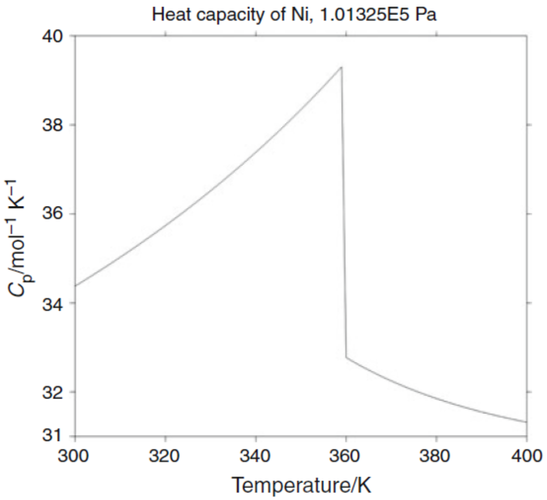
1895 Curie
a transition from ferromagnetic to paramagnetic

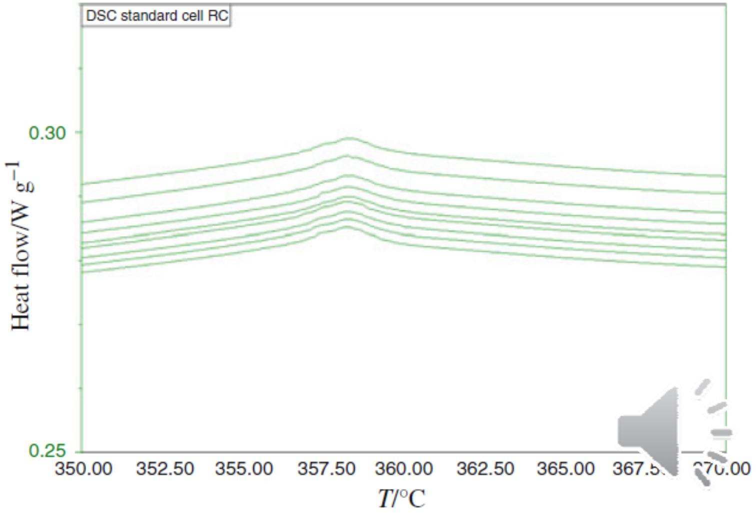


Curie Temperature of Ni
T_c = 358.28 °C

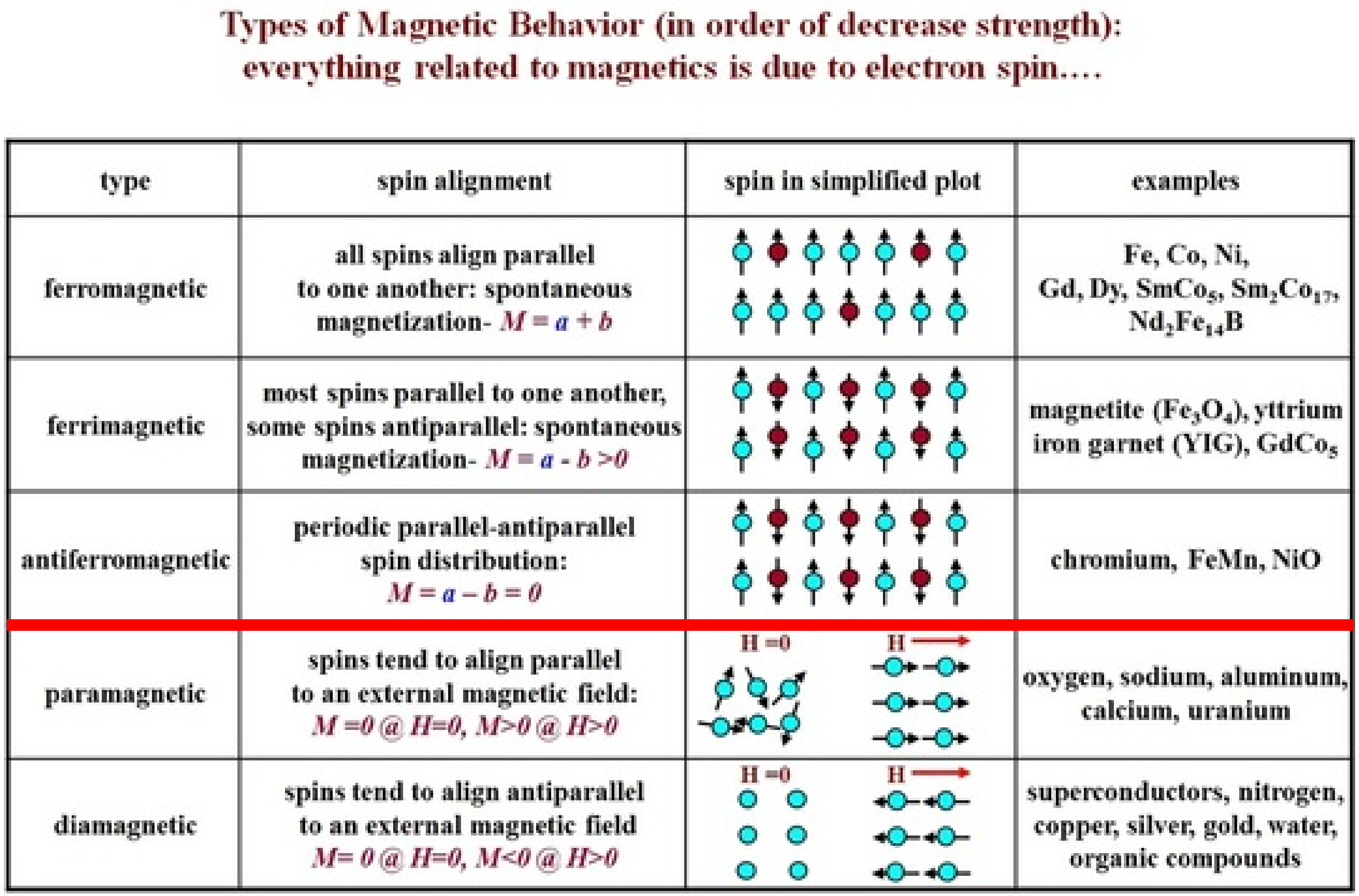
A second order transition
Lambda shape of the C_p versus T
a maximum
= **the Curie point**

Not associated with an enthalpy change





Magnetic Ordering



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

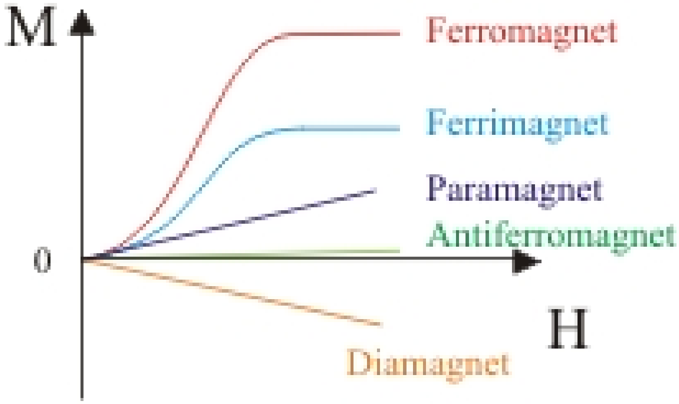
type	spin alignment	spin in simplified plot	examples
ferromagnetic	all spins align parallel to one another: spontaneous magnetization- $M = a + b$		Fe, Co, Ni, Gd, Dy, $SmCo_5$, Sm_2Co_{17}, $Nd_2Fe_{14}B$
ferrimagnetic	most spins parallel to one another, some spins antiparallel: spontaneous magnetization- $M = a - b > 0$		magnetite (Fe_3O_4), yttrium iron garnet (YIG), $GdCo_5$
antiferromagnetic	periodic parallel-antiparallel spin distribution: $M = a - b = 0$		chromium, FeMn, NiO
paramagnetic	spins tend to align parallel to an external magnetic field: $M = 0$ @ $H = 0$, $M > 0$ @ $H > 0$	H =0 H	oxygen, sodium, aluminum, calcium, uranium
diamagnetic	spins tend to align antiparallel to an external magnetic field $M = 0$ @ $H = 0$, $M < 0$ @ $H > 0$	H =0 H	superconductors, nitrogen, copper, silver, gold, water, organic compounds

cooperative

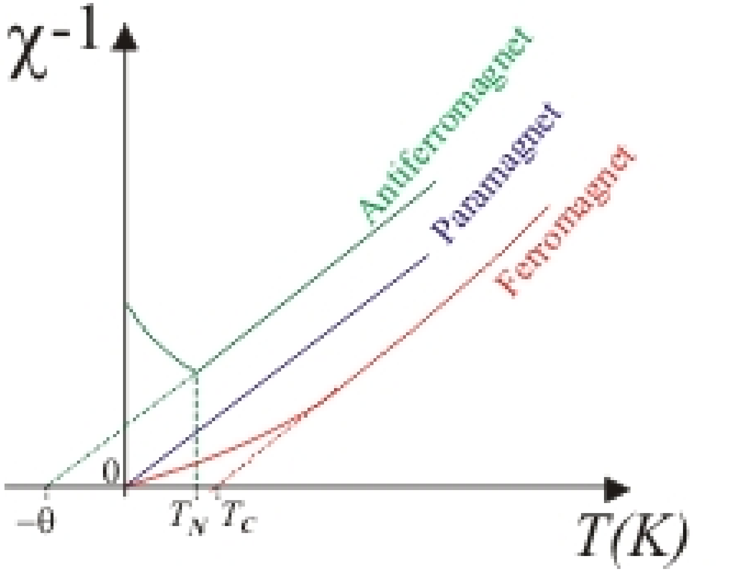
individual

Magnetic Ordering

Comparison of M-H Behaviour



Comparison of
Susceptibility vs Temperature Behaviour



Exchange Interactions

In order for a material to be magnetically ordered, the spins on one atom must couple with the spins on neighboring atoms

Direct Exchange - a direct overlap between the localized orbitals of electrons on adjacent magnetic ion sites

Superexchange - an indirect exchange interaction between the localized electrons on magnetic ions separated by the nonmagnetic ion or ligand

Double Exchange - interactions between localized spin and delocalized spins

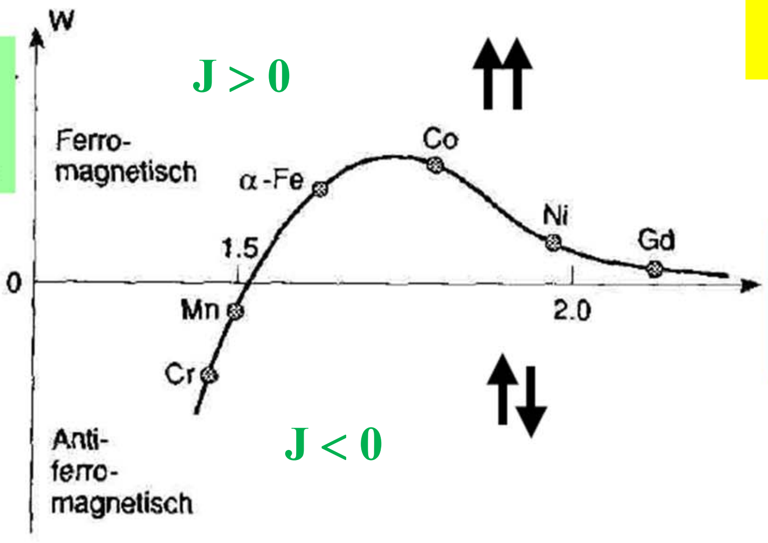
Direct Exchange Interaction

Bethe-Slater curve - J as a function of interatomic distance and radius of partially filled d-shell of an atom

The interatomic distance
- **Small** - the electrons spent most of the time in between the atoms and give rise to the antiferromagnetic order (Pauli's exclusion principle)
- **Large** - the electrons spent most of the time away from each other and give rise to the ferromagnetic order

$$H = -2J \sum_{ij} \vec{S}_i . \vec{S}_j$$

calculated exchange interaction

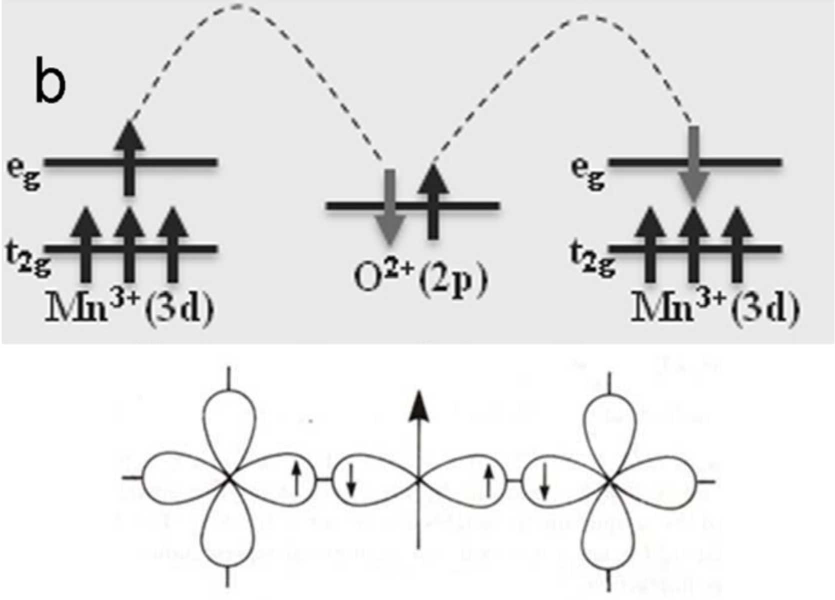


interatomic distances/radius of 3d orbitals

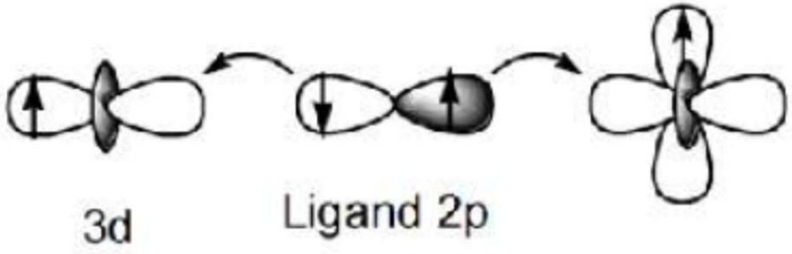
Superexchange Interaction

The most common mechanism for the magnetic coupling (particularly in insulators) - the spin information is transferred through covalent bonds with the intervening ligand (oxygen, halogen)

No movement of electrons from one magnetic site to other magnetic site because the oxidation states of magnetic ions are same or differ by two



antiferromagnetic coupling

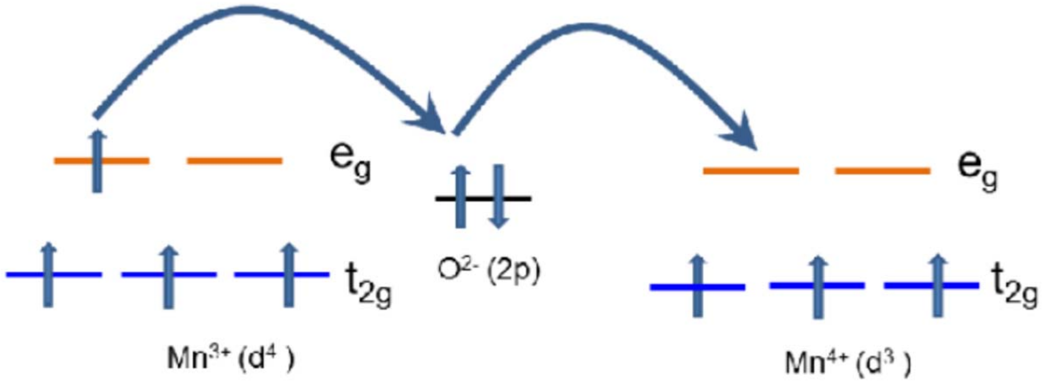


ferromagnetic coupling

Double Exchange Interaction

Movement (hopping) of electrons from one magnetic ion to 2p orbital of oxygen from which one electron simultaneously hops the other magnetic ion because oxidation states of two nearest neighbor ions differs by one This hopping occurs with preservation of the spin sign - **ferromagnetic**

The assumption - intraatomic exchange interactions between localized spin and delocalized (hopping) spins are very strong which aligns the spins of delocalized electrons always parallel to the localized ion spin



ferromagnetic coupling

Antiferromagnetism

1936

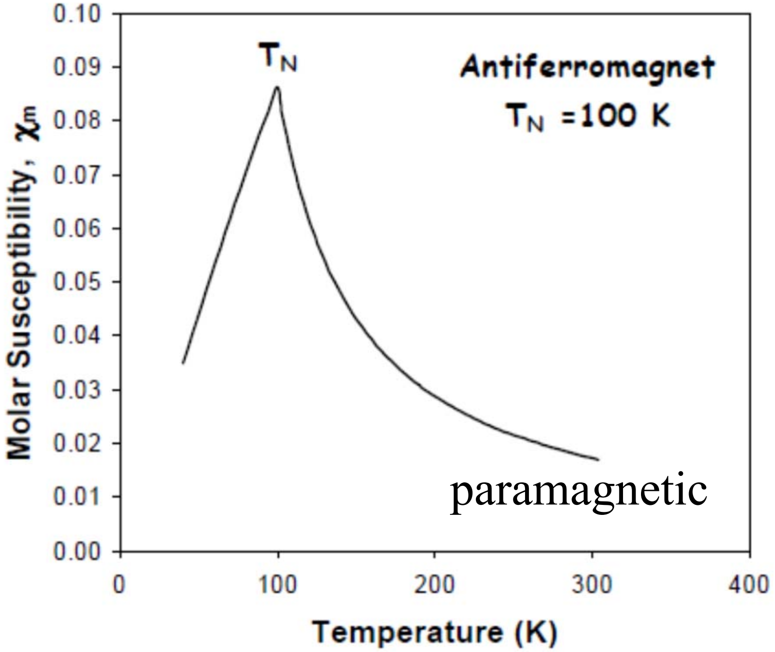
J negative with spins antiparallel below T_N

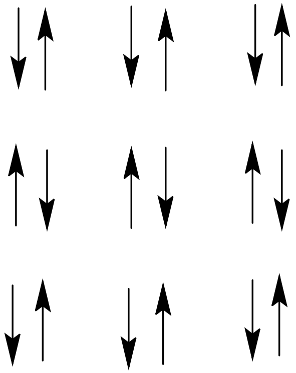
No spontaneous M, no permanent M

Critical temperature: T_N (Neel Temperature)

Above T_N = paramagnet

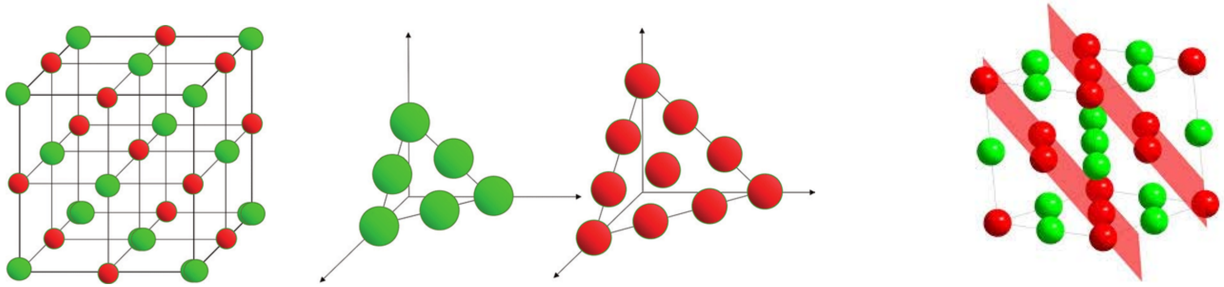
Louis Néel
1904 – 2000
1970 NP in Physics





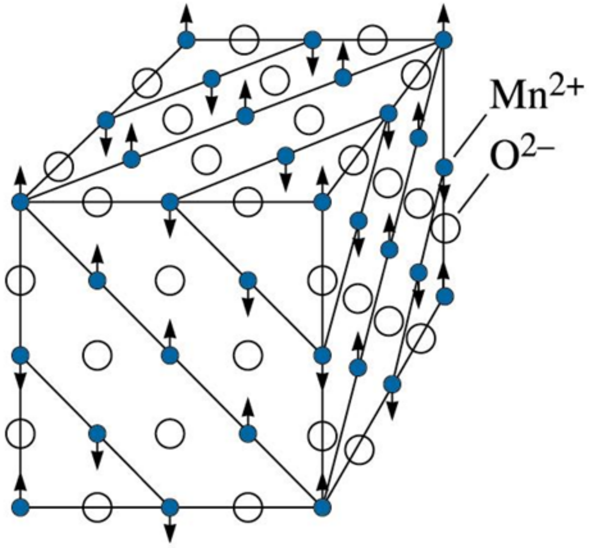
Antiferromagnetism

MnO = NaCl structure type

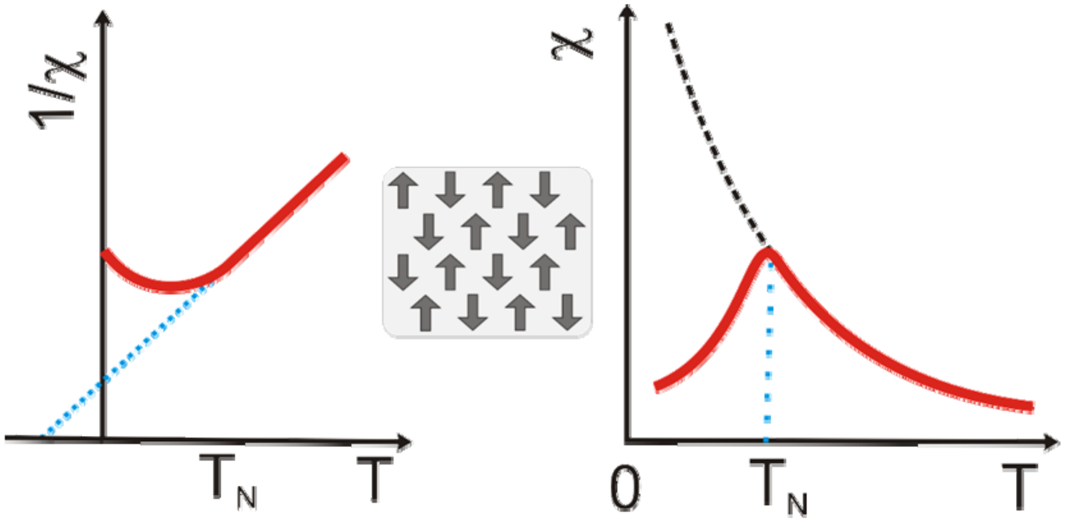


MnO – alternating planes of the O a Mn atoms (111)

Magnetic moments of Mn atoms are in each plane organized in antiparallel manner

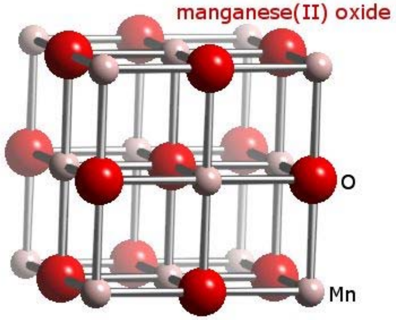


Antiferromagnetism



Material	T_N (K)
NiO	525
Cr	308
Cr_2O_3	307
CoO	291
MnS	160
MnO	116
FeF_2	79
$NiCl_2$	50
$CoCl_2$	25
CoI_2	12

Neutron Diffraction



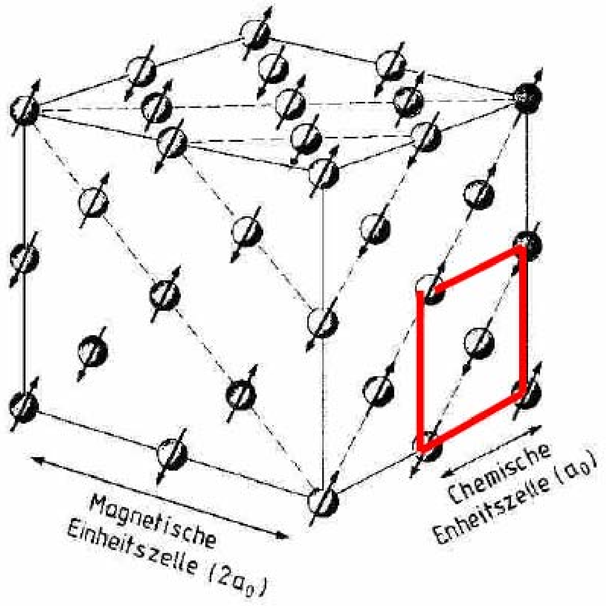
Single crystal may be anisotropic

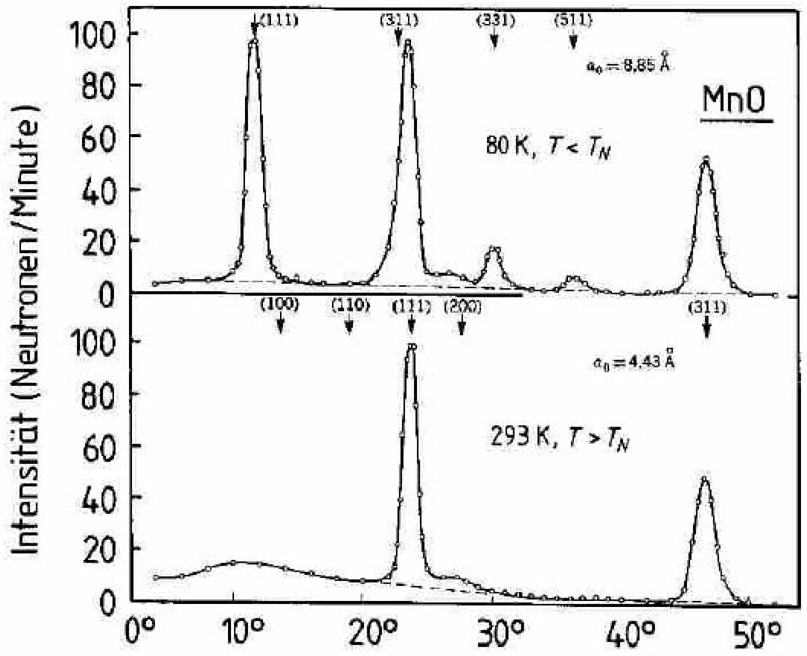
Magnetic and structural unit cell may be different

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

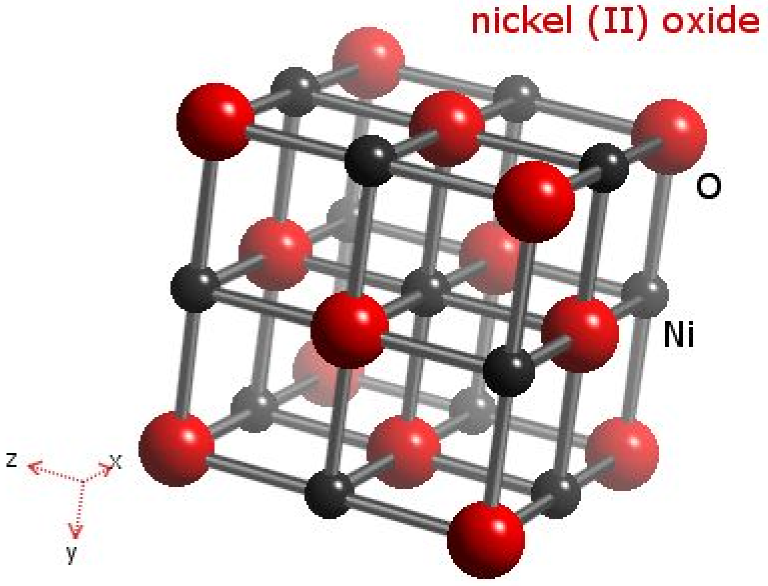
de Broglie equation: $\lambda = h / m_n v_n$

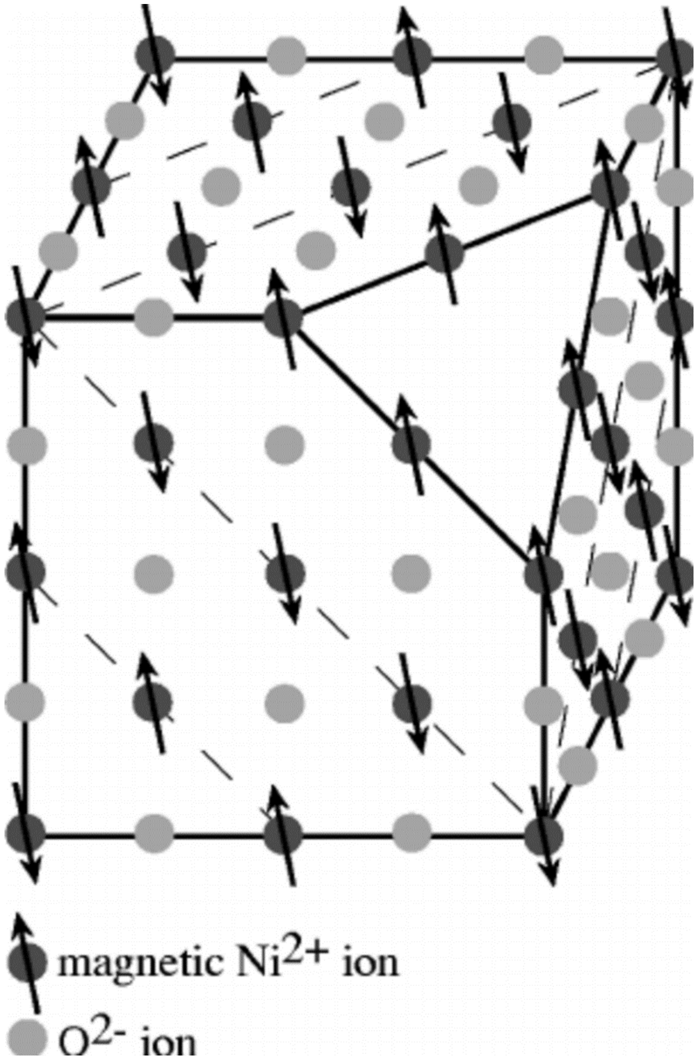
Neutron radiation of a nuclear reactor





Neutron Diffraction





Ferrimagnetism

1948 Néel

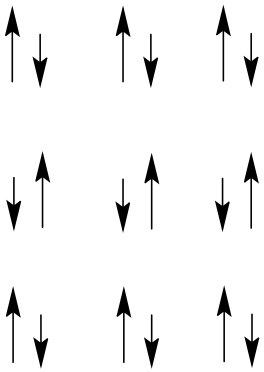
J negative with **spins of unequal magnitude** antiparallel below critical T

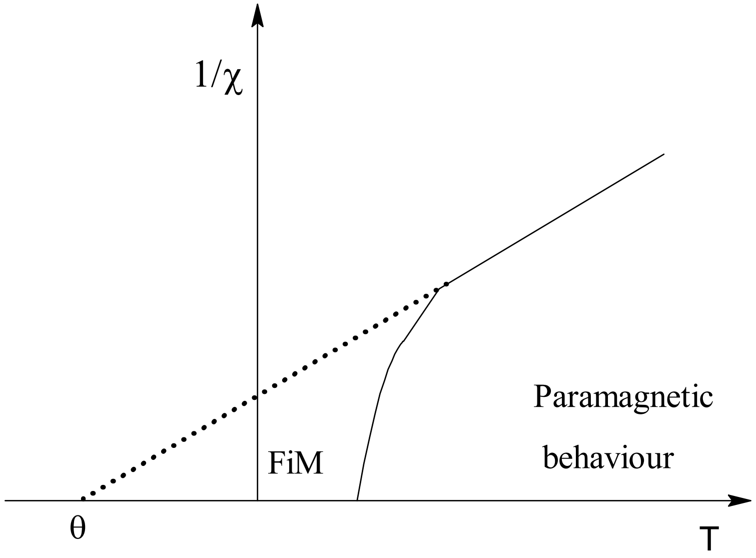
Requires two chemically distinct species with different moments coupled antiferromagnetically

Spontaneous M, Critical T = T_C (Curie Temperature)

Bulk behavior very similar to ferromagnetism

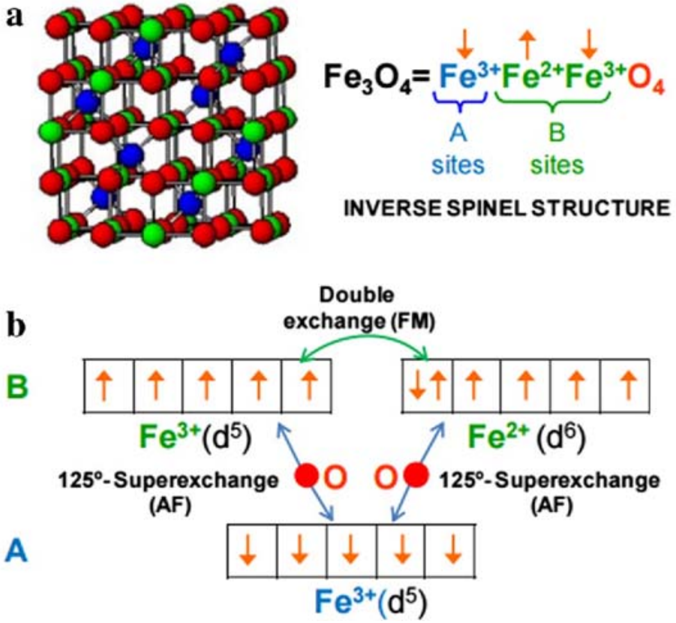
Magnetite Fe_3O_4 is a ferrimagnet

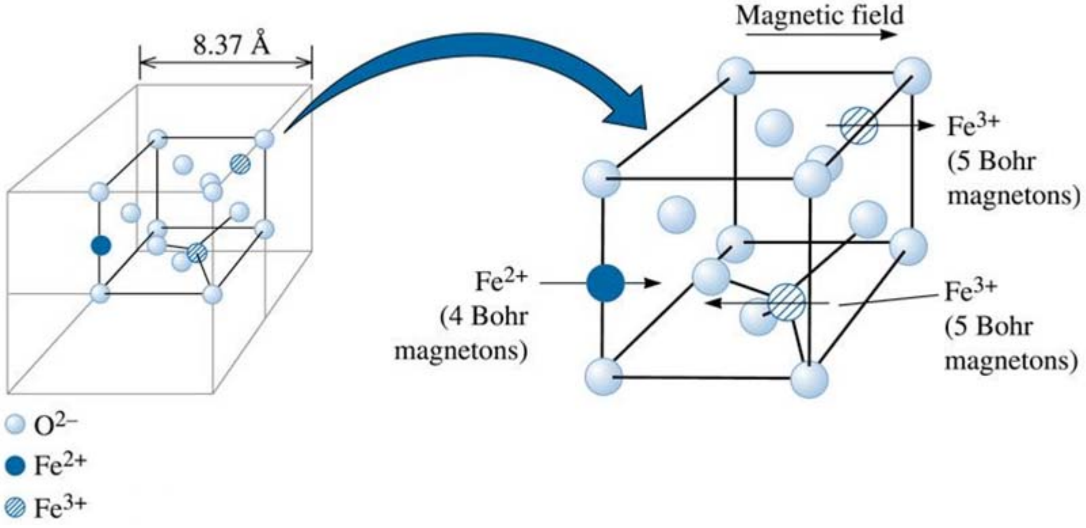




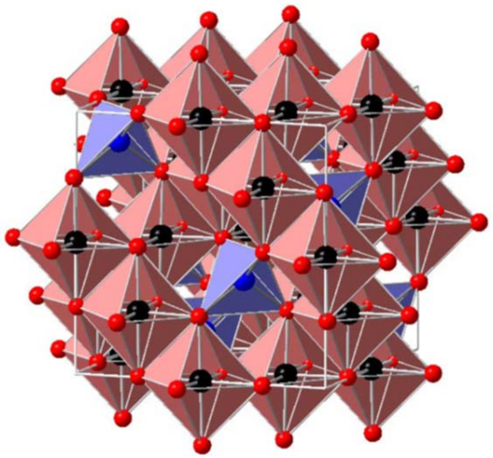
Ferrimagnetism

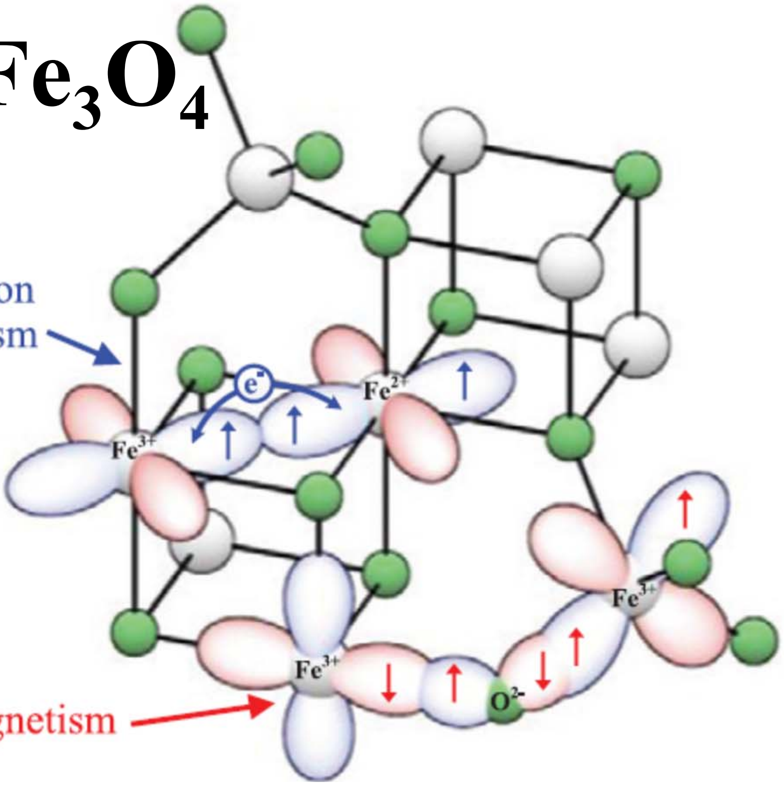
Magnetite Fe_3O_4 = Spinel





Magnetite Fe_3O_4



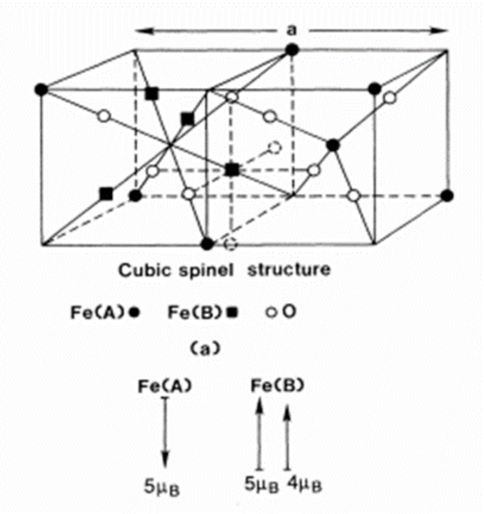


Double-exchange
electron hopping conduction
spin-coupled ferrimagnetism

Super-exchange
spin-coupled anti-ferrimagnetism

An inverse spinel $(Fe^{3+})_8[Fe^{2+}Fe^{3+}]_{16}O_{32}$
$A = (Fe^{3+})$ on the T_d sites ($5\mu_B$)
$B = [Fe^{2+} / Fe^{3+}]$ a 1:1 mixture on the O_h sites
$[Fe^{2+}]$ $3d^6$ ($4\mu_B$)
Fe^{3+} $3d^5$ ($5\mu_B$)

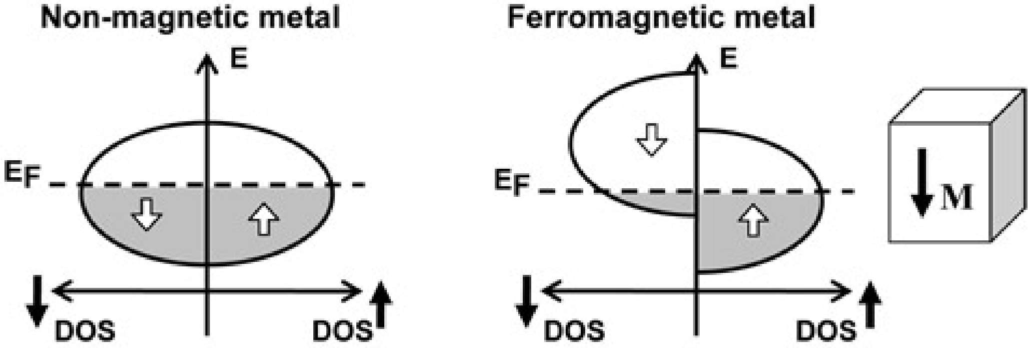
$[Fe^{2+}]$ to $[Fe^{3+}]$ ferrimagnetic double exchange alignment
$[Fe^{3+}]$ to (Fe^{3+}) antiferrimagnetic super-exchange interactions through the O^{2-} anions
These Fe^{3+} moments cancel each other, leaving a net moment of $4\mu_B$ per formula unit from the Fe^{2+} ions



Ferrimagnetic
Curie Temperature = 858 K

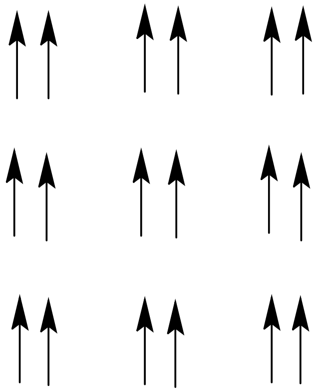
Ferromagnetism

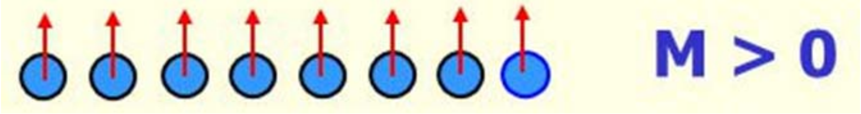
Ferromagnetism is a quantum mechanical effect arising from Coulomb (electric) repulsion – electrons with parallel spins tend to avoid each other spatially due to the Pauli's exclusion principle
This gives rise to the exchange interactions – energy is lowered



The exchange interactions **split** the electronic density of states (DOS) with **spin up** and **spin down** states in a magnetic metal
At Fermi level the DOS are spin polarized which gives rise to the ferromagnetism in a material

Ferromagnetism



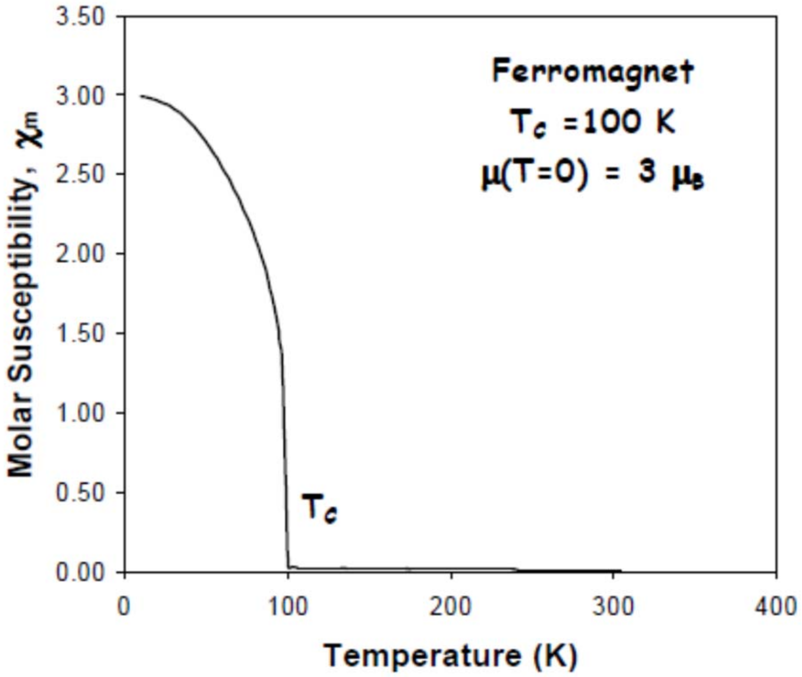


J positive with spins parallel below T_c

A spontaneous permanent M (in absence of H)

T_c = Curie Temperature

Above T_c = paramagnet



Without an external magnetic field the atomic moments are oriented parallel in large areas (Weiss domains)

Material	**T_c, K**
Fe	1063
Co	1404
Ni	631
Gd	293
Dy	88
EuO	77
$GdCl_3$	2.2
$SmCo_5$	1015
$Nd_2Fe_{14}B$	670

Ferromagnetism

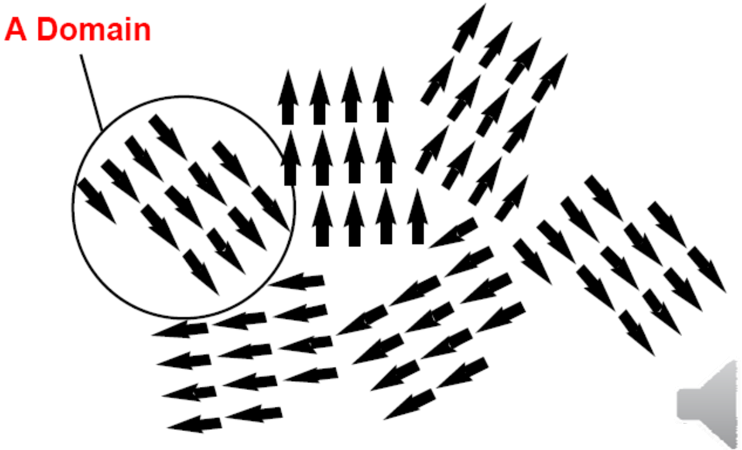
Ferromagnetic elements: Fe, Co, Ni, Gd, Dy

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

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

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**

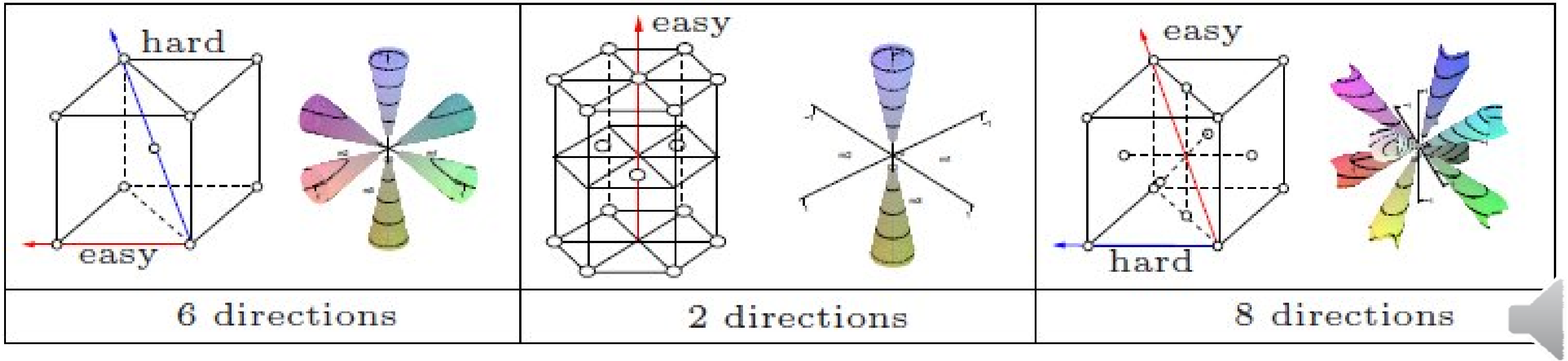


Magnetic Anisotropy

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

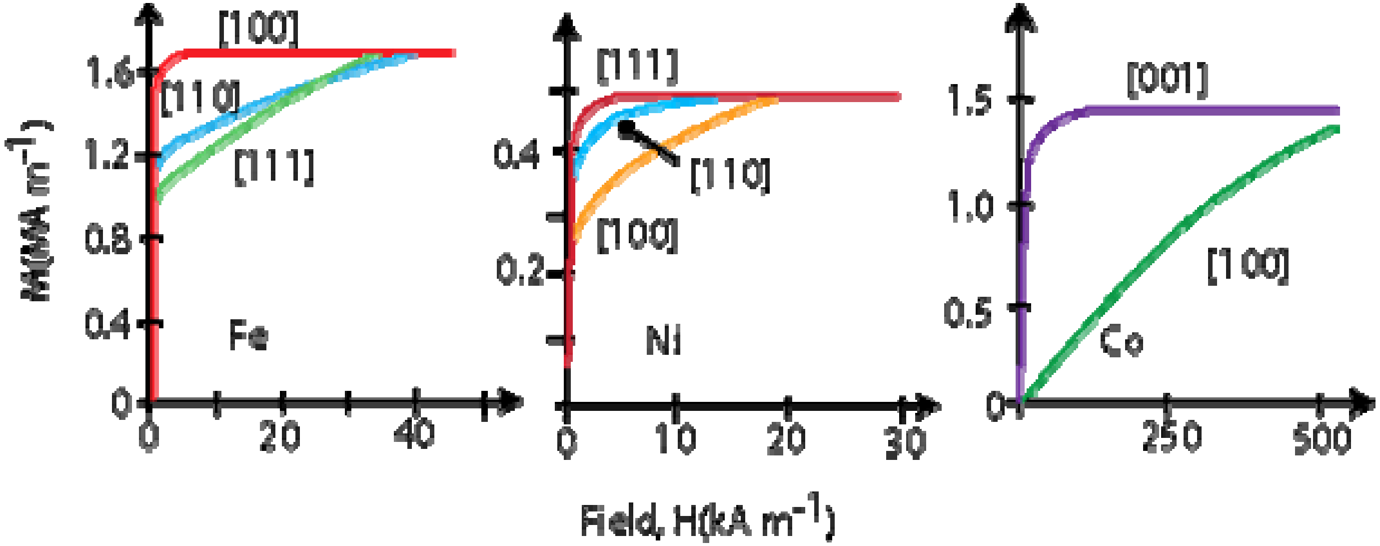


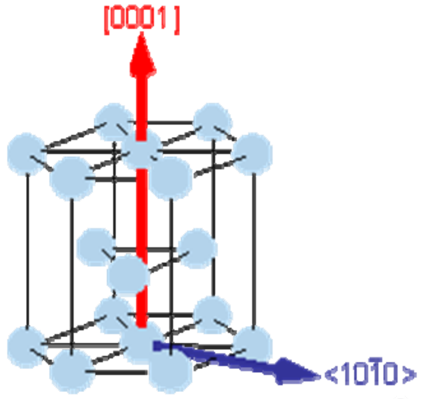
Magnetic Anisotropy

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

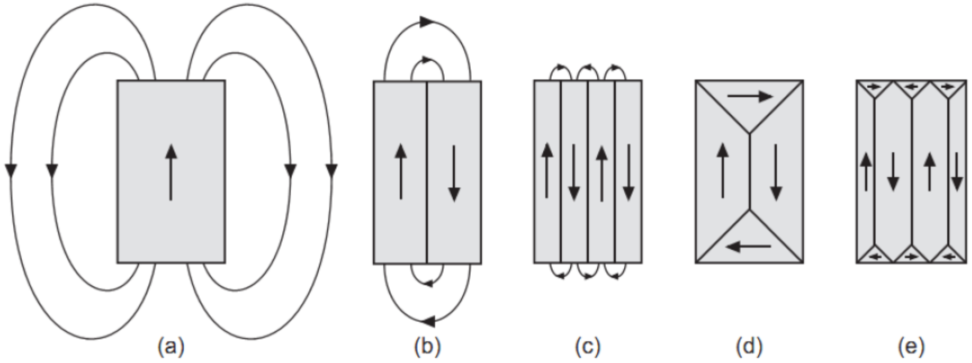




Magnetostatic Energy

A single domain behaves as a block magnet

a demagnetising field is present around the domain



Demagnetising field has a magnetostatic energy that depends on the shape

It is the field that allows work to be done by the magnetised sample (e.g., lifting another ferromagnetic material)

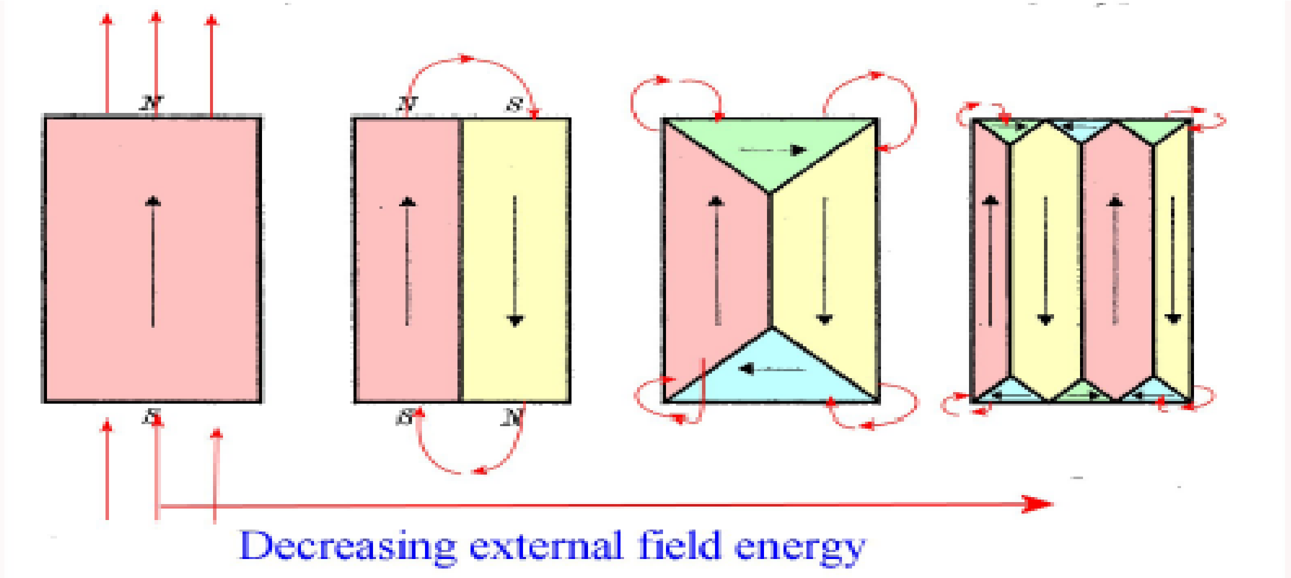
Minimise the total magnetic energy - the magnetostatic energy must be minimised - decreasing the external demagnetising field by dividing the material into **domains**

Adding extra domains increases the exchange energy

The total energy is decreased as the magnetostatic energy is the dominant effect, the magnetostatic energy can be reduced to zero by a domain structure that leaves no external demagnetising field

Magnetic Domains

The external field magnetostatic energy is decreased by dividing into domains



The internal energy is increased because the spins are not parallel

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

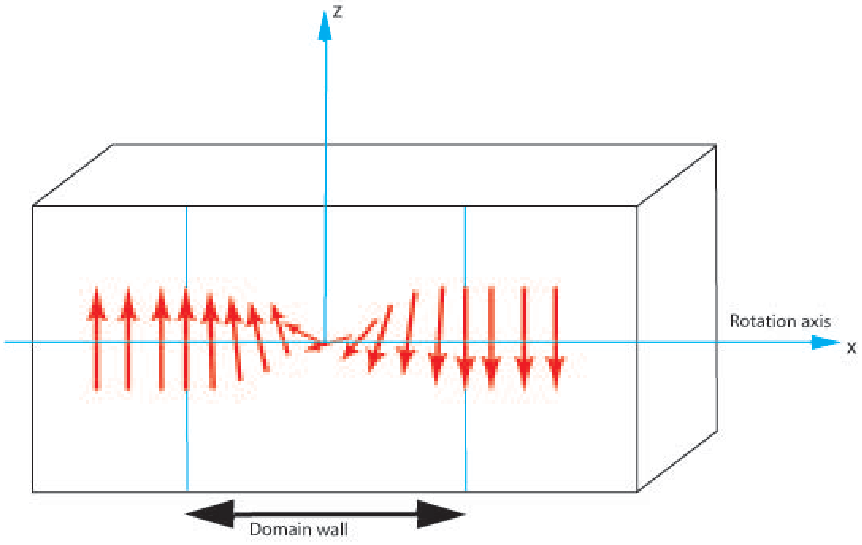
Application of H causes aligned domains to grow at the expense of misaligned, alignment persists when H is removed

Domain Walls

A domain wall (DW) is a transition region between the different magnetic domains of uniform magnetization that develops when a magnetic material forms domains to minimize the magnetostatic energy

Wall energy is the energy required to maintain the wall

When domains form, the magnetostatic energy decreases, and the wall energy and the magnetocrystalline anisotropy energy increase

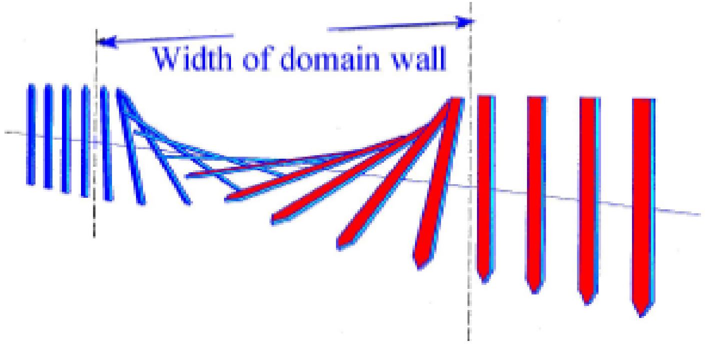


Domain Walls

The domain wall width is determined by the balance between **the exchange energy and the magnetic anisotropy**:
The total exchange energy E is a sum of the penalties between each pair of spins

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

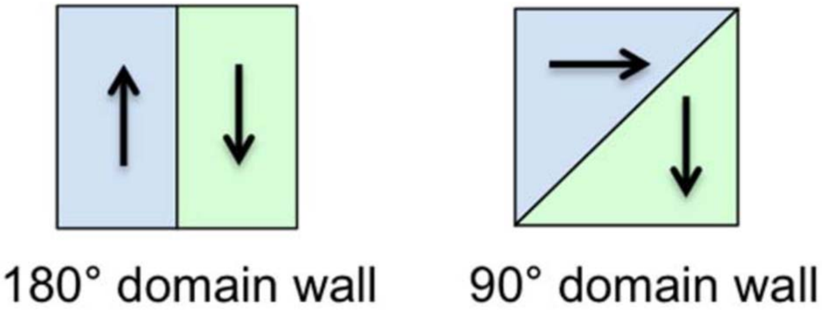
where J is the exchange integral.



The magnetic anisotropy energy: $E = K \sin^2\theta$
θ is the angle between the magnetic dipole and the easy axis

Large exchange integral yields wider walls
High anisotropy yields thinner walls

Domain Walls

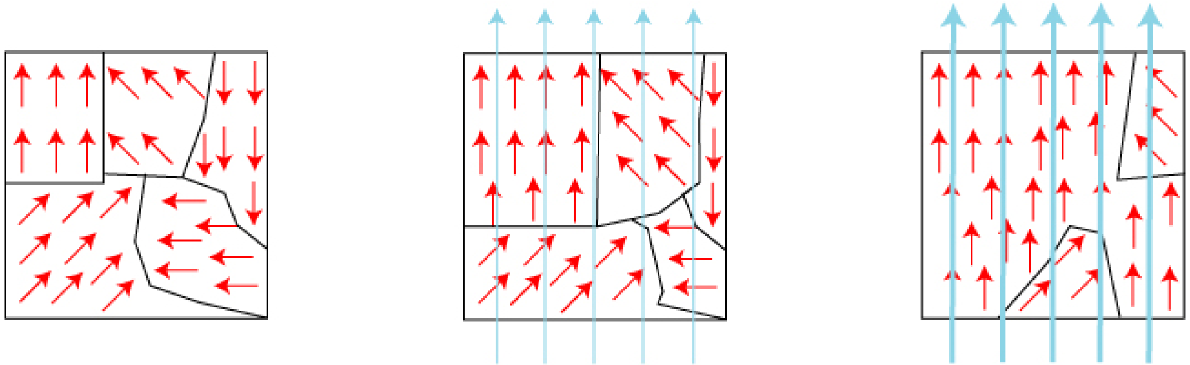


180° domains walls = adjacent domains have opposite vectors of magnetization
90° domains walls = adjacent domains have perpendicular vectors of magnetization

Depends on crystallografic 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)

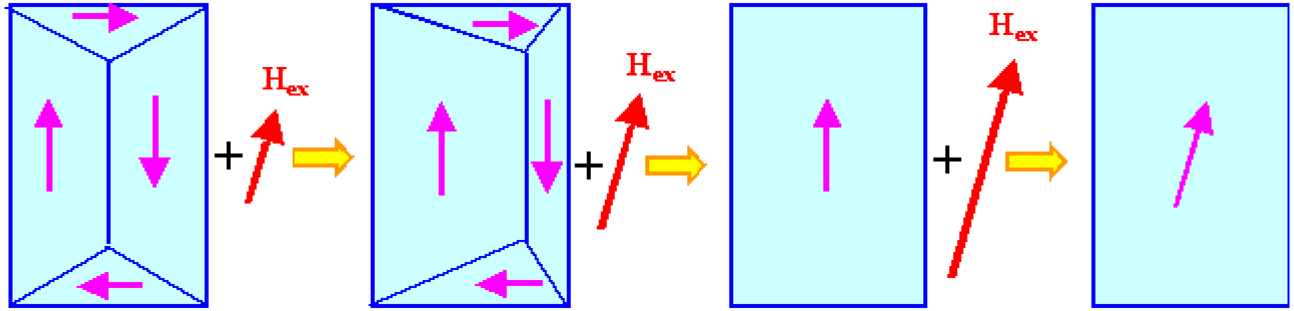
Domain Wall Motion


no field
some field
strong field

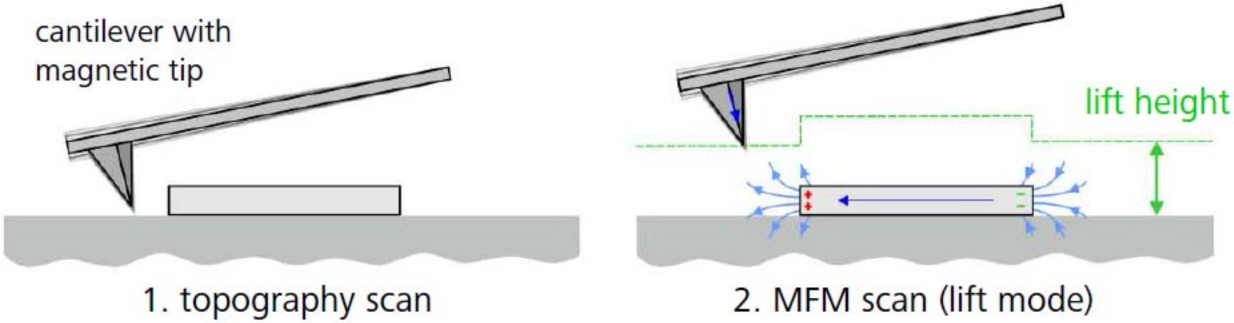
At low H_{ext} = bowing/relaxation of DWs, after removing H_{ext} DWs return back

Volume of domains favorably oriented wrt H increases, M increases

At high H_{ext} = irreversible movements of DW
a) Continues without increasing H_{ext}
b) DW interacts with an obstacle (pinning)

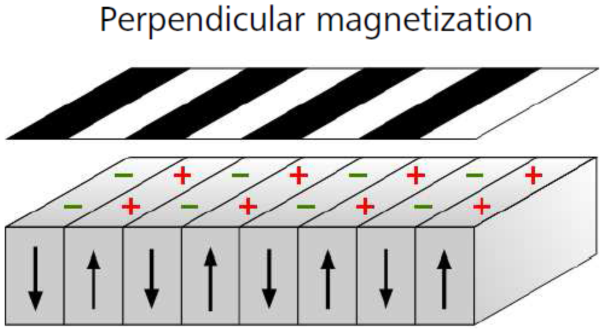


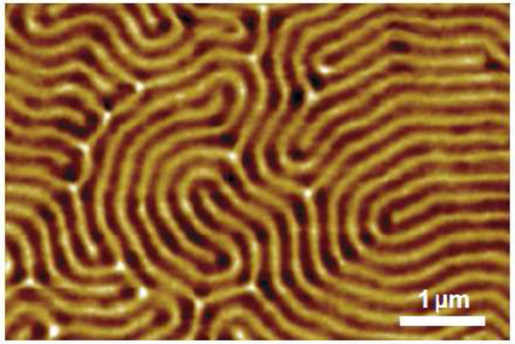
Magnetic Force Microscopy



Magnetized tip scans across a magnetic sample

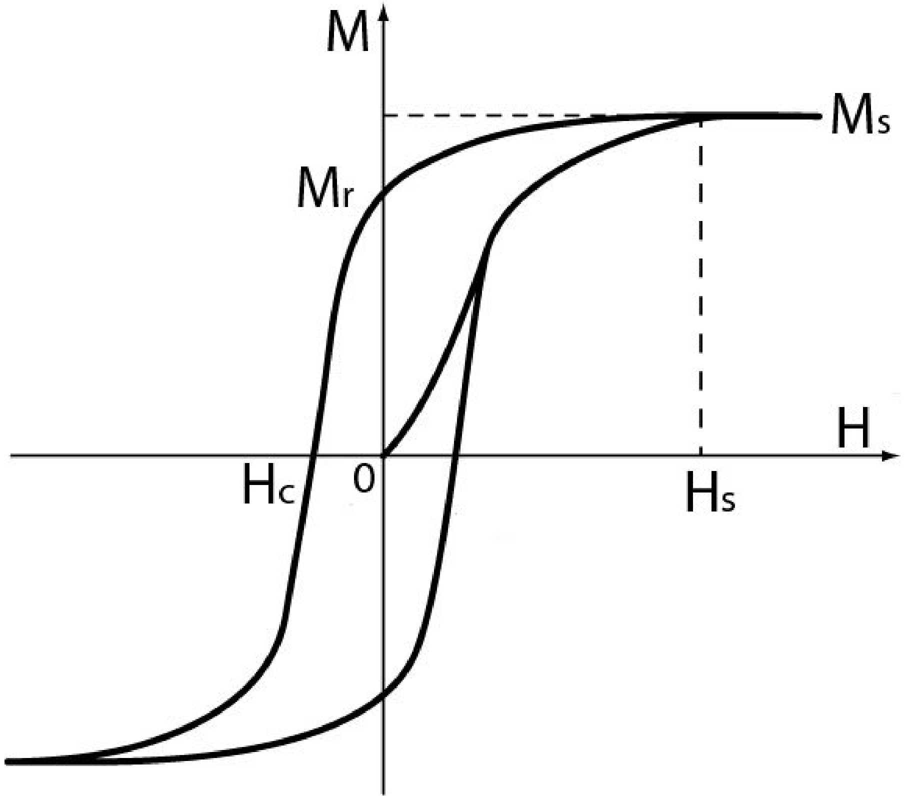
Interaction between the tip and sample are detected and used to reconstruct the magnetic structure of the sample surface





4Å Fe / 4Å Gd (75 layers)

Magnetic Hysteresis Loop



Important parameters
Saturation magnetization, M_s

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

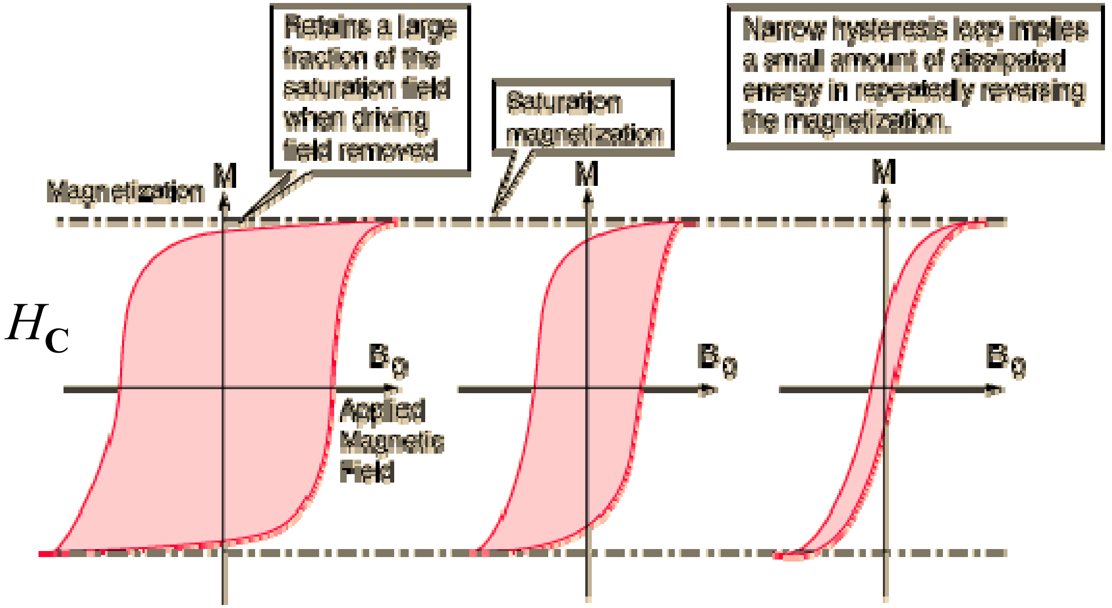
"Hard" magnetic material = high Coercivity
"Soft" magnetic material = low Coercivity

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



Retains a large fraction of the saturation field when driving field removed

Saturation magnetization

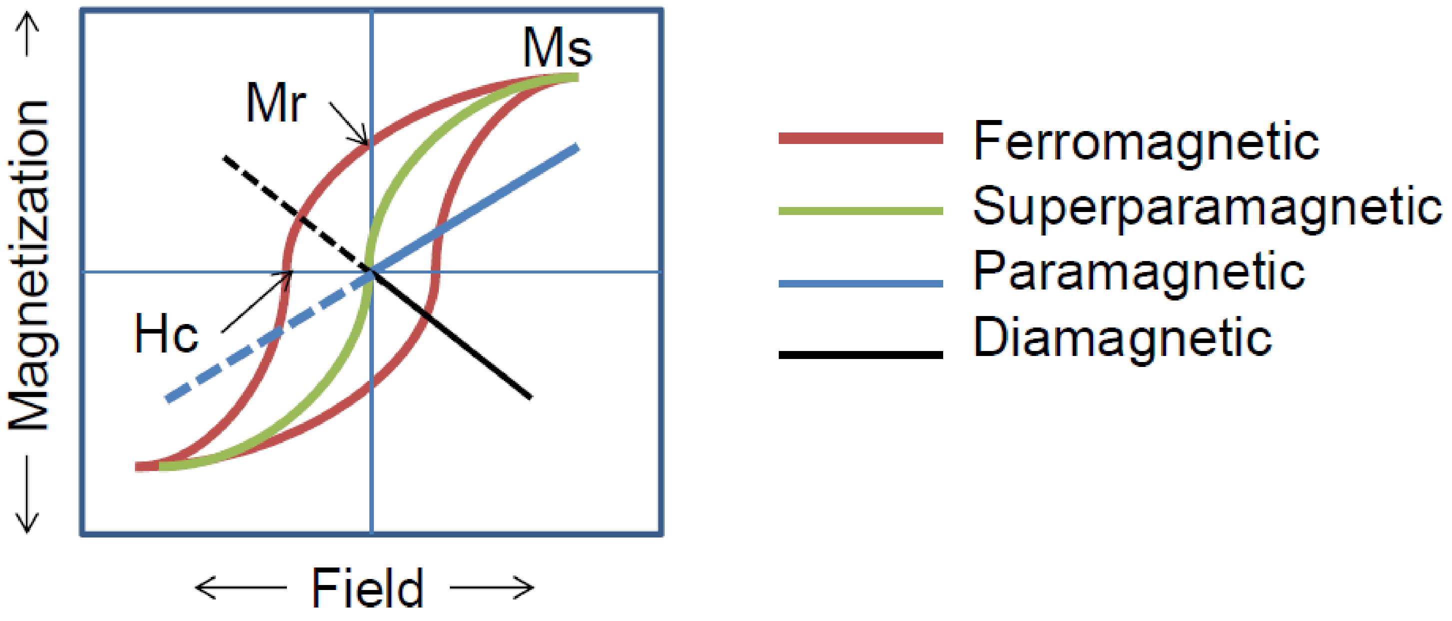
Narrow hysteresis loop implies a small amount of dissipated energy in repeatedly reversing the magnetization.

Desirable for permanent magnets and magnetic recording and memory devices.

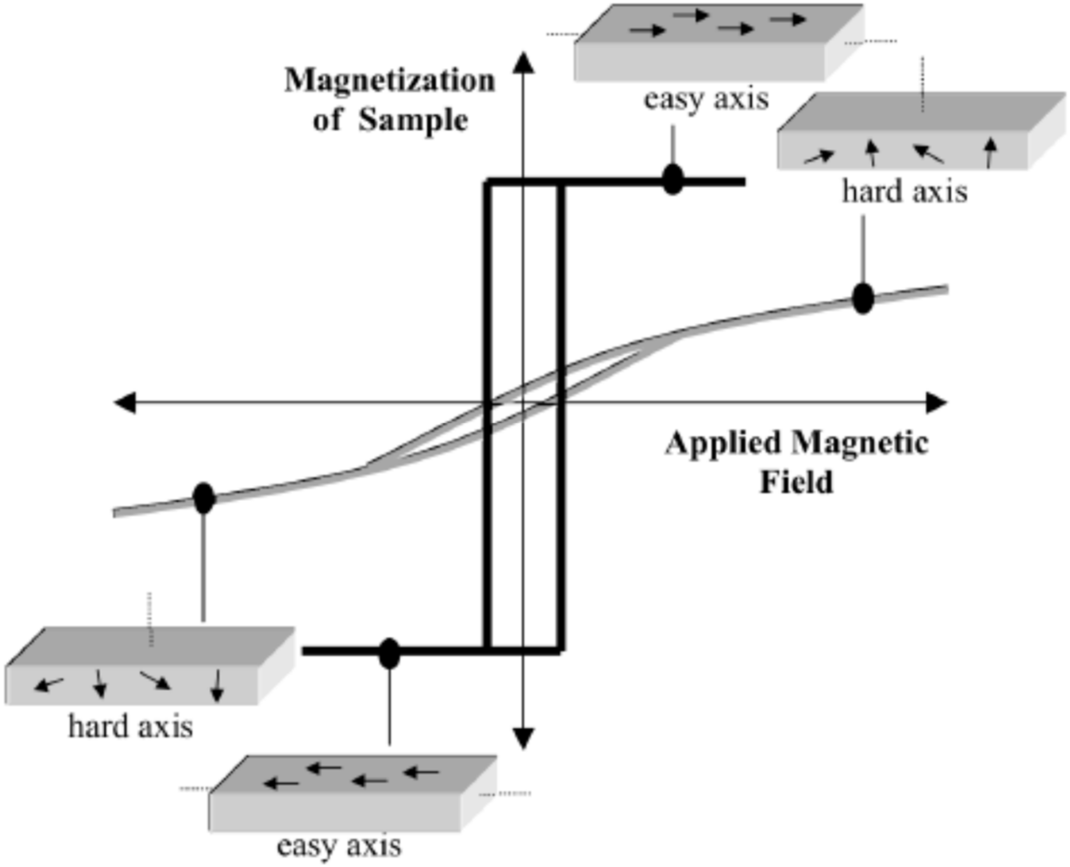
The area of the hysteresis loop is related to the amount of energy dissipation upon reversal of the field.

Desirable for transformer and motor cores to minimize the energy dissipation with the alternating fields associated with AC electrical applications.

Magnetic Hysteresis Loop



Magnetic Hysteresis Loop



Dictionary of Used Terms

Angular momentum – moment hybnosti
Magnetic lines of force – magnetické siločáry
Easy axis – snadná osa
Hard axis - obtížná osa