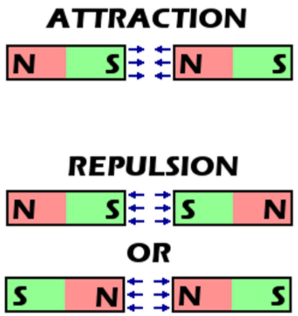
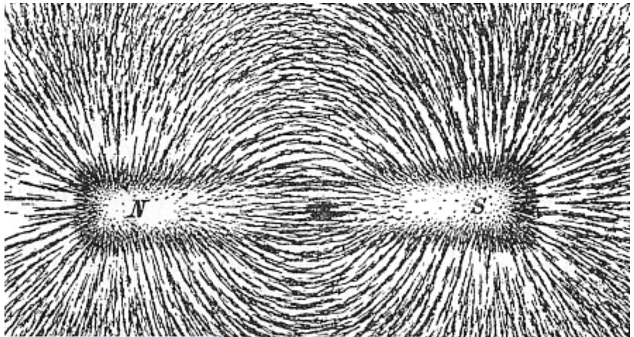
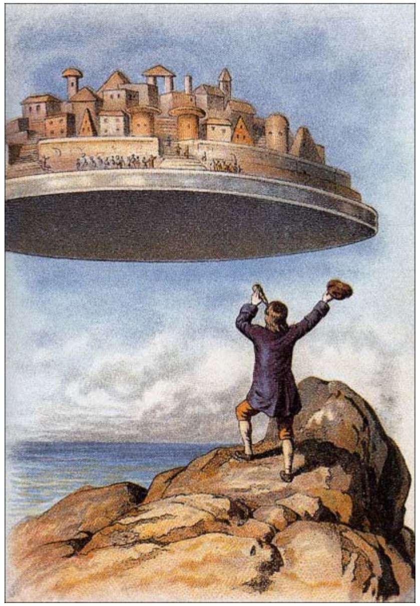
Magnetism, Magnetic Properties, Magnetochemistry







Lecture 1: *Basic notions from atomic and molecular magnetism* (2 h)

Atom in magnetic field
Diamagnetism and paramagnetism
Spin-orbit interaction
Zeeman effect
Van Vleck theory of magnetic susceptibility
Curie law
Magnetization of atoms and molecules

Lecture 2: *Exchange interaction in magnetic molecules* (2 h)
Exchange interaction between electrons
Spin operators
Heisenberg-Dirac-Van Vleck Hamiltonian
Origin of paramagnetism in molecules
Contributions to the exchange interaction in magnetic molecules
Examples: exchange-coupled transition metal complexes

Lecture 3: *Magnetic anisotropy in molecules* (2 h)

Origin of magnetic anisotropy

Ligand field splitting of orbital shells

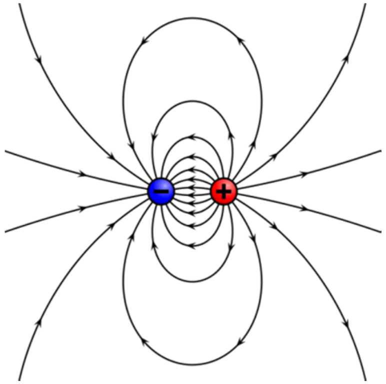
Quenching of orbital and spin momenta in molecules

Magnetic anisotropy in mononuclear complexes:

- zero-field splitting
- *g* tensor
- susceptibility tensor

Example: Ni(II) complexes

Magnetism



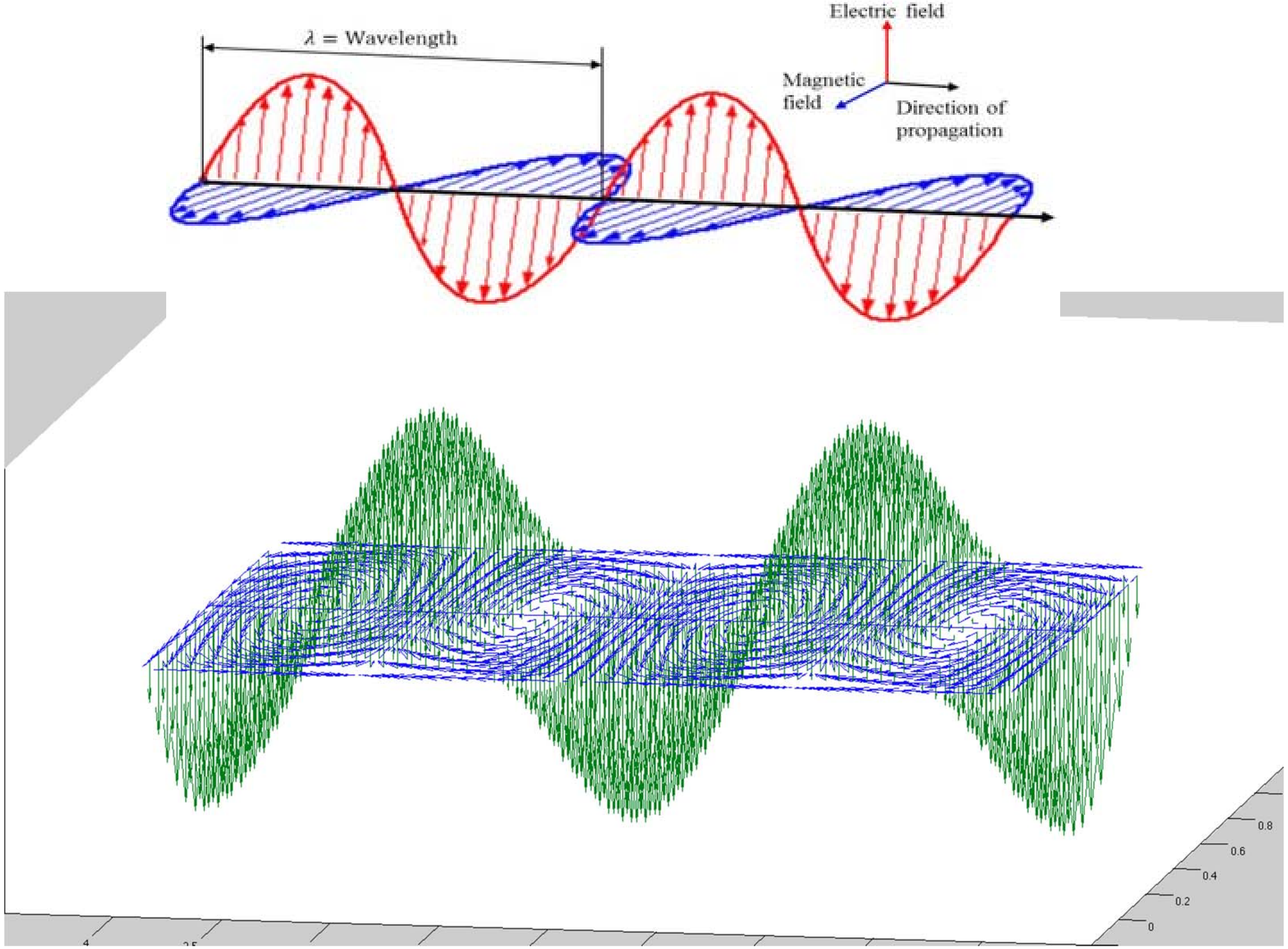
All matter is *electronic*

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 m^2]

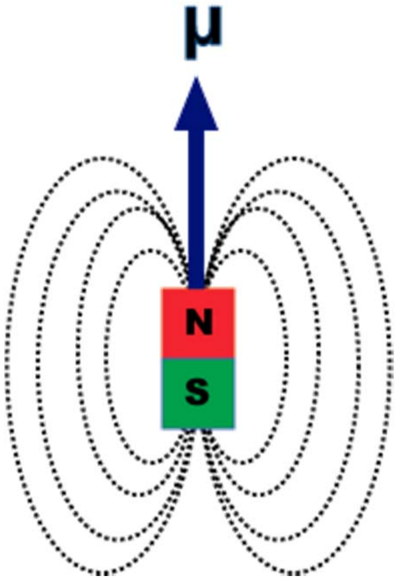
Electromagnetic Fields



Magnetism

Magnetic field = motion of electric charges

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

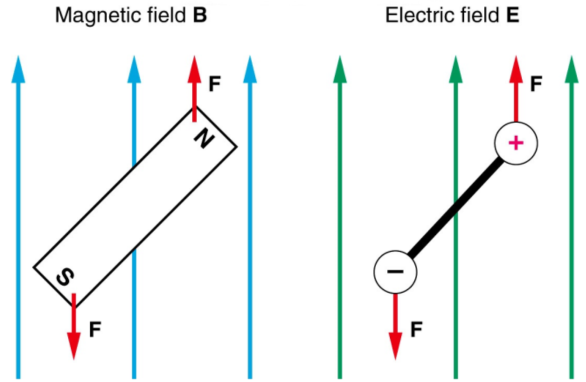


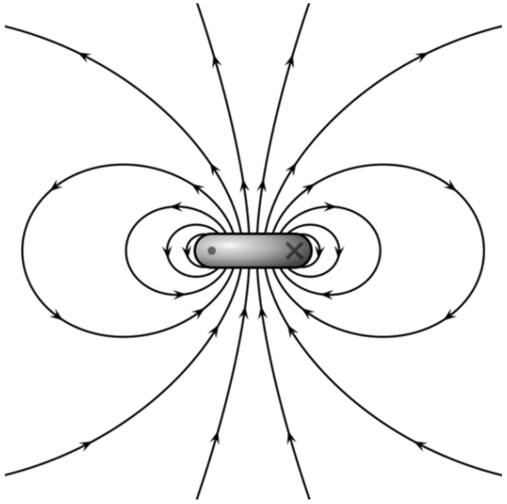
Poisson model

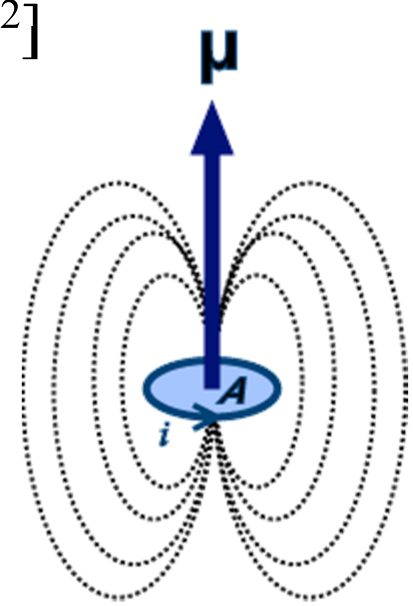
Ampère 1822

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

$$\mu = i \times A$$







Ampere model

Magnetism

Microscopic explanation of source of magnetism
= Fundamental quantum magnets

Unpaired electrons = spins (Bohr 1913)

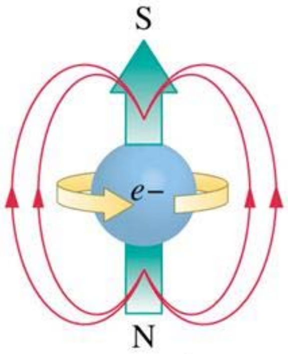
Atomic building blocks (protons, neutrons and electrons = fermions)
possess an intrinsic magnetic moment

Gerlach and Stern 1921

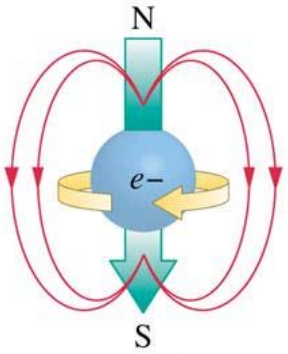
Relativistic quantum theory (P. Dirac 1928) → SPIN

(quantum property ~ rotation of charged particles)

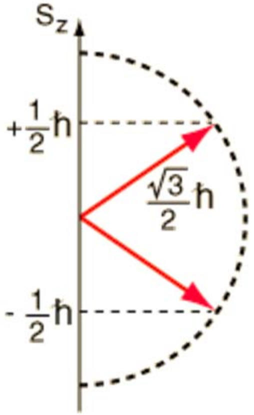
Spin (½ for all fermions) gives rise to a magnetic moment



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



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



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

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 = the smallest quantity of a magnetic moment

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

S = ½, the spin quantum number

g = 2.0023192778 the Lande constant of a free electron

for a free electron (S = ½)

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

A Free Electron in a Magnetic Field

Magnetic energy

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

In SI units

μ_0 = permeability of free space

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

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

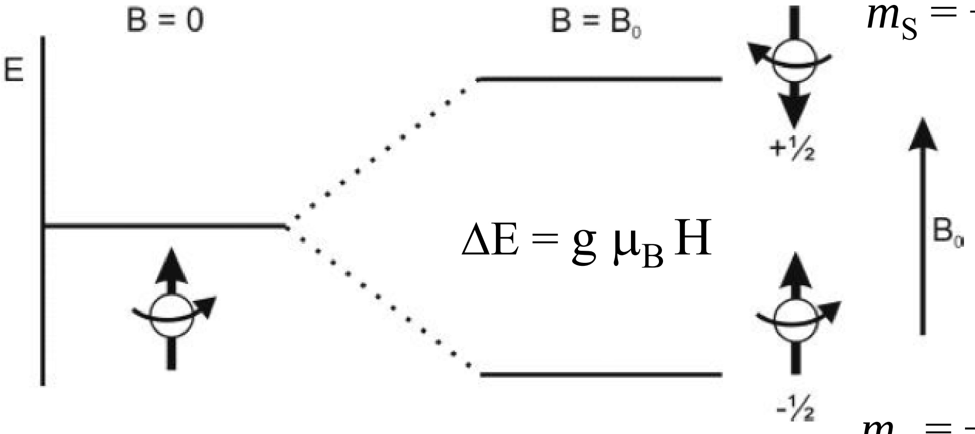
An electron with spin *S* = ½ can have two orientations in a magnetic field

$m_S = +½$ or $m_S = -½$

In a magnetic field

- degeneracy of the two states is removed

A Free Electron in a Magnetic Field



$m_S = +½$

$E = ½\ g\ \mu_B H$

$\Delta E = g\ \mu_B H$

$E = -\ ½\ g\ \mu_B H$

$m_S = -½$

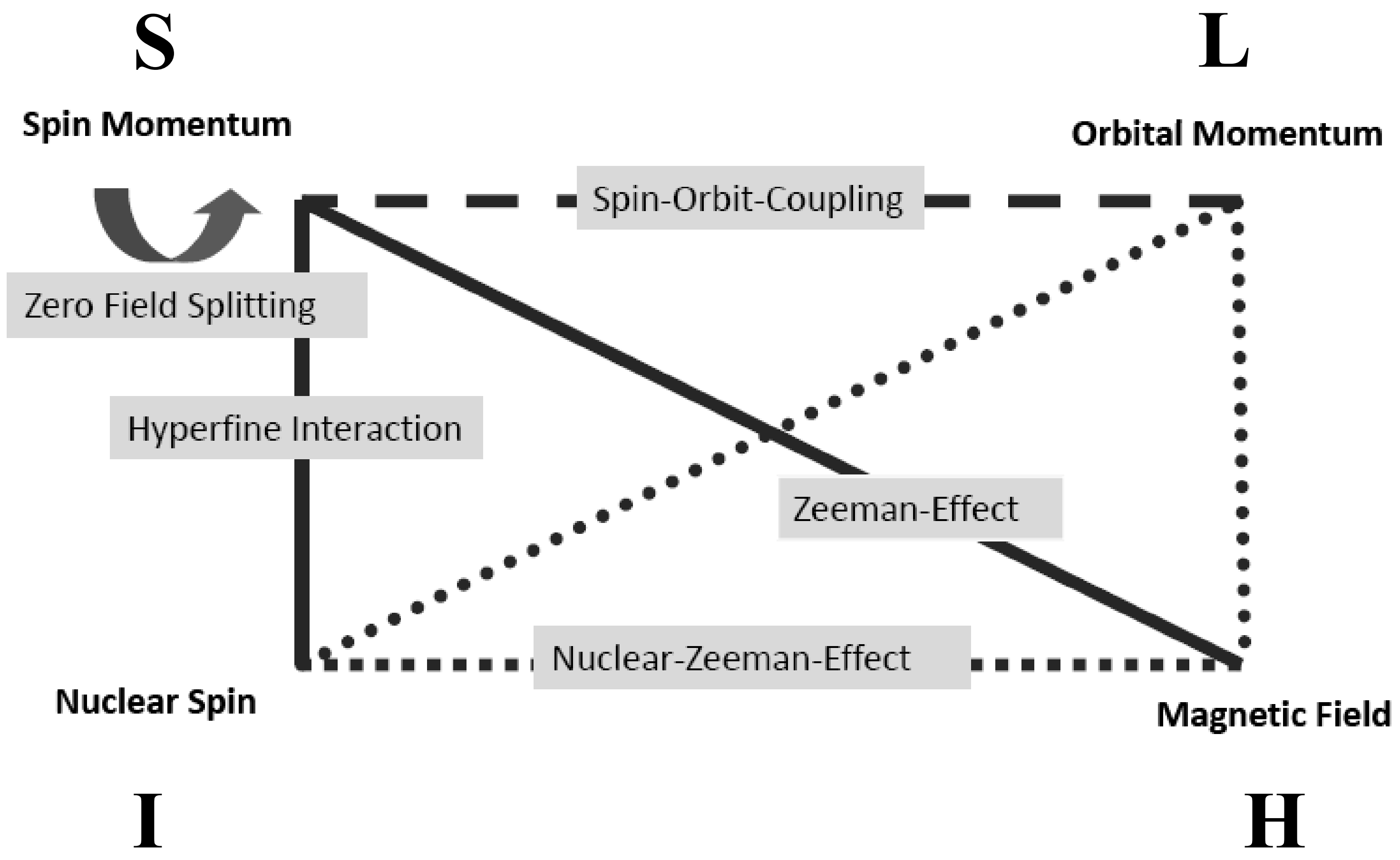
At r.t.
$kT = 205\ cm^{-1}$
$H = 1\ T$
$\Delta E = 28\ GHz$
$= 1\ cm^{-1}$

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

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

The energy of each orientation $E = \mu H$
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).

Origin of Magnetism and Interactions

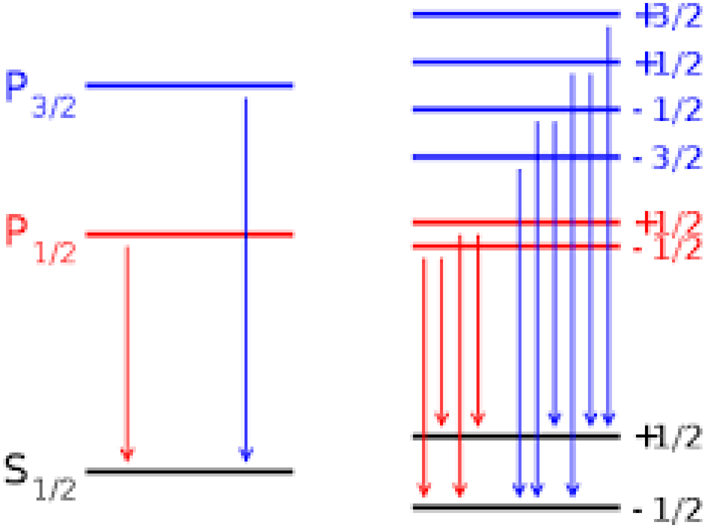


Magnetism and Interactions

Magnetic field – splitting + mixing of energy levels

Zeeman-Effect: splitting of levels in an applied magnetic field
the simplest case with S = ½ :
splitting of the levels with $m_S = +\frac{1}{2}$ and $m_S = -\frac{1}{2}$

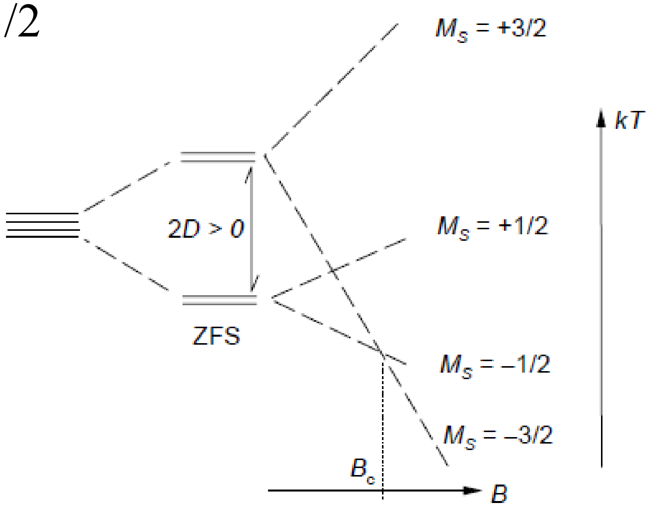
$$E = -\mu \bullet B$$



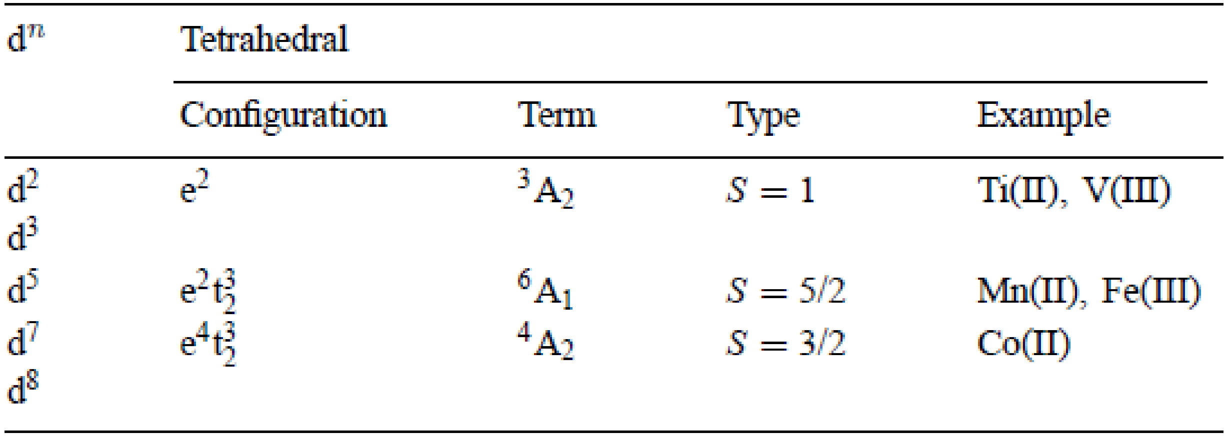
Magnetism and Interactions

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.

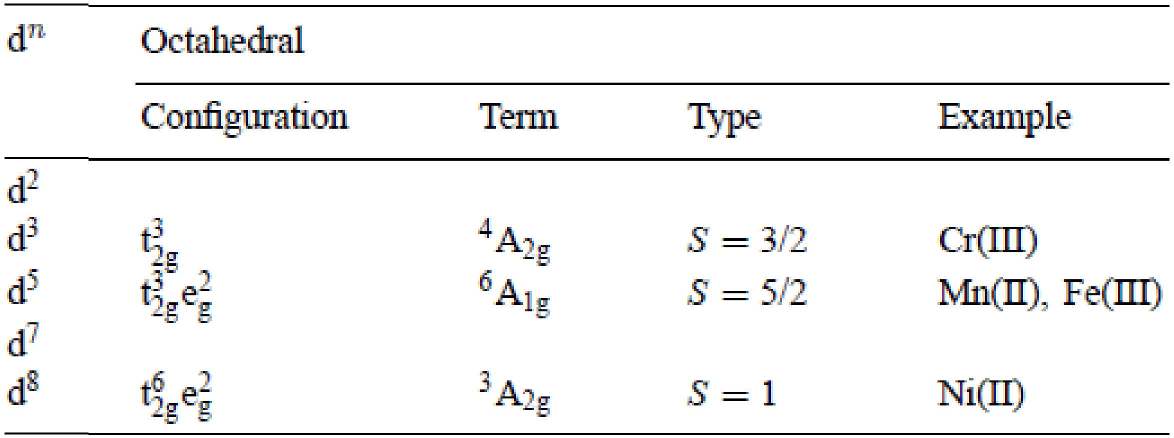
S = 3/2



Zero Field Splitting in d^n Ions



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				

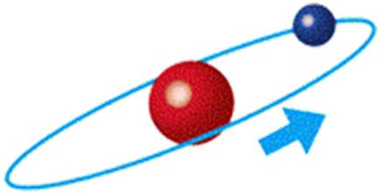


d^n	Octahedral			
	Configuration	Term	Type	Example
d^2				
d^3	t_{2g}^3	$^4A_{2g}$	$S = 3/2$	Cr(III)
d^5	$t_{2g}^3e_g^2$	$^6A_{1g}$	$S = 5/2$	Mn(II), Fe(III)
d^7				
d^8	$t_{2g}^6e_g^2$	$^3A_{2g}$	$S = 1$	Ni(II)

Magnetism and Interactions

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

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.

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)

Interactions of Spin Centers

$$\hat{H} = -J\hat{S}_i\hat{S}_j + \bar{D}\hat{S}_i\hat{S}_j + \bar{d}\hat{S}_i \times \hat{S}_j$$

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

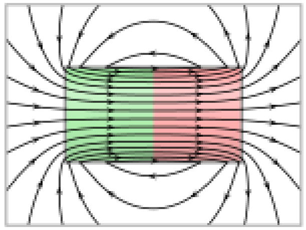
without orbital contributions (pure spin magnetism) the last two terms are omitted

Lenz's Law

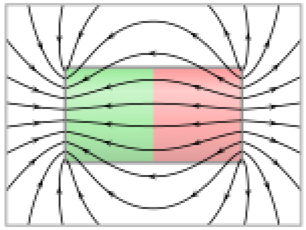
(~1834)

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.

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

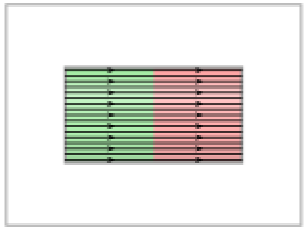


$\vec{B}$



$\vec{H}$

Magnetization does not exists outside of the material.



$\vec{M}$

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)

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

Field equation
(infinite system)

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) 1T = 10^4 G
a field resulting from electric current and spin and orbital motions

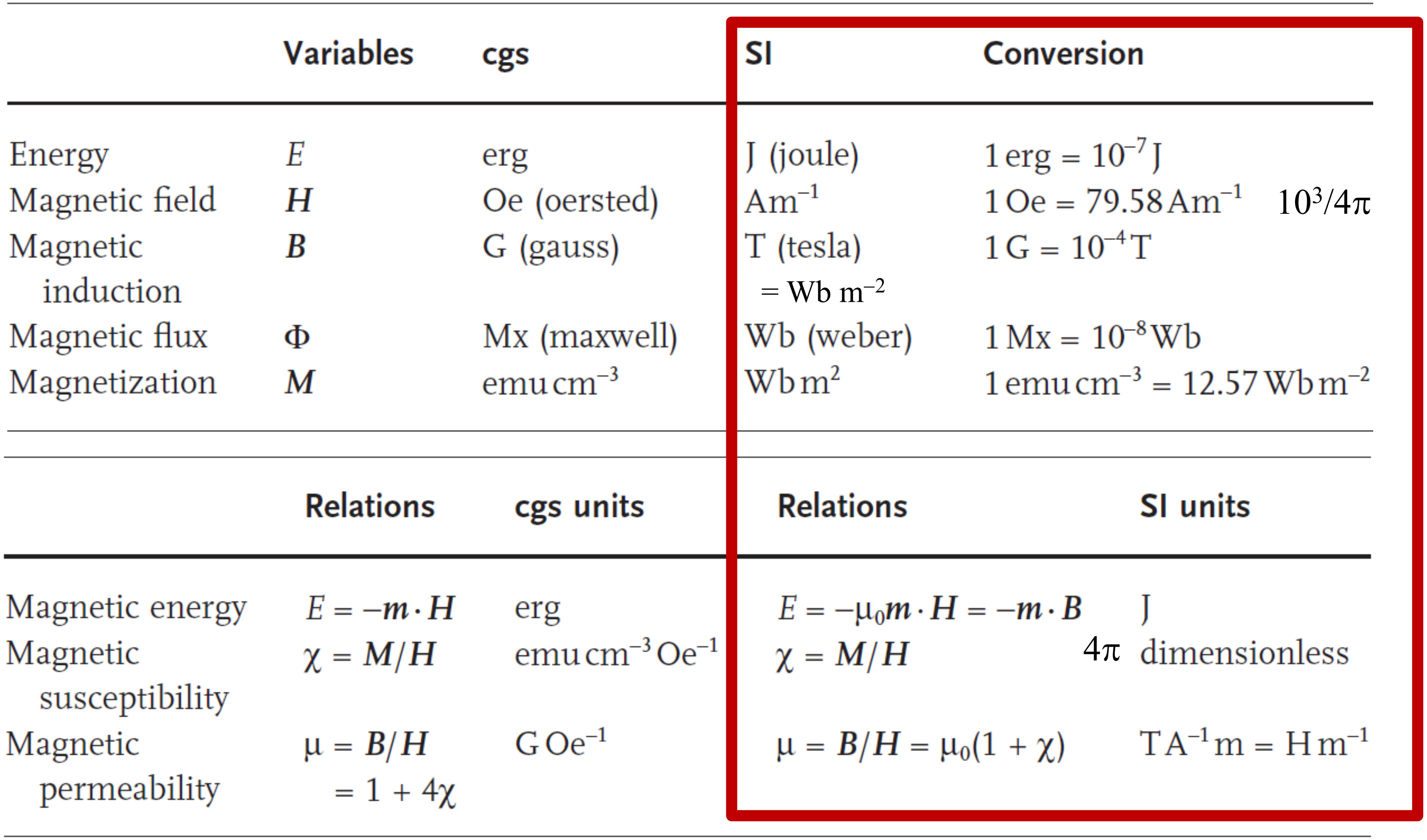
Field equation

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

μ_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)	A m^{-1}	1 Oe = 79.58 A m^{-1} $10^3/4\pi$
Magnetic induction	$\boldsymbol{B}$	G (gauss)	T (tesla) = Wb m^{-2}	1 G = 10^{-4} T
Magnetic flux	Φ	Mx (maxwell)	Wb (weber)	1 Mx = 10^{-8} Wb
Magnetization	$\boldsymbol{M}$	emu cm^{-3}	Wb m^2	1 emu cm^{-3} = 12.57 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	$\chi = \boldsymbol{M}/\boldsymbol{H}$	emu cm^{-3} Oe^{-1}	$\chi = \boldsymbol{M}/\boldsymbol{H}$ 4π	dimensionless
Magnetic permeability	$\mu = \boldsymbol{B}/\boldsymbol{H} = 1 + 4\chi$	G Oe^{-1}	$\mu = \boldsymbol{B}/\boldsymbol{H} = \mu_0(1 + \chi)$	T A^{-1} m = H m^{-1}

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 is weak enough and T not too low, χ is independent of ***H*** and

$$M = \chi \times H$$

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

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.

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)

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

Relative Permeability μ_r

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

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

$$B = \mu \times H$$

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

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

$\mu < 1$ diamagnetic **$\mu > 1$** 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:

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

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

$\chi_{\mathbf{M}}{}^{\mathbf{D}}$ is the sum of contributions from atoms and bonds:

$$\chi_{\mathbf{M}}{}^{\mathbf{D}} = \Sigma\chi_{\mathbf{D\ atom}} + \Sigma\lambda_{\mathbf{bond}}$$

$\chi_{\mathbf{D\ atom}}$ = atom diamagnetic susceptibility increments (Pascal's constants)
$\lambda_{\mathbf{bond}}$ = 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	$\chi_{Di}/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$	Atom	$\chi_{Di}/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$	Atom	$\chi_{Di}/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$	Atom	$\chi_{Di}/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$
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]	$\lambda_i/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$	Bond	$\lambda_i/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$	Bond	$\lambda_i/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$	Bond	$\lambda_i/(1 \text{ x } 10^{-6}\text{ emu mol}^{-1})$
C=C	+5.5	$\mathrm{Cl{-}CR_2CR_2{-}Cl}$	+4.3	Ar–Br	–3.5	Imidazole	+8.0
C≡C	+0.8	$\mathrm{R_2CCl_2}$	+1.44	Ar–Cl	–2.5	Isoxazole	+1.0
C=C–C=C	+10.6	$\mathrm{RCHCl_2}$	+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
$\mathrm{CH_2{=}CH{-}CH_2{-}}$(allyl)	+4.5	$\mathrm{Br{-}CR_2CR_2{-}Br}$	+6.24	$\mathrm{Ar{-}C({=}O)NH_2}$	–1.5	Piperidine	+3.0
C=O	+6.3	C–I	+4.1	$\mathrm{R_2C{=}N{-}N{=}CR_2}$	+10.2	Pyrazine	+9.0
COOH	–5.0	Ar–OH	–1	RC≡C–C(=O)R	+0.8	Pyridine	+0.5
COOR	–5.0	$\mathrm{Ar{-}NR_2}$	+1	Benzene	–1.4[c]	Pyrimidine	+6.5
$\mathrm{C({=}O)NH_2}$	–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
$\mathrm{{-}NO_2}$	–2.0	Ar–Ar	–0.5	Dioxane	+5.5	Triazine	–1.4
C–Cl	+3.1	$\mathrm{Ar{-}NO_2}$	–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)

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

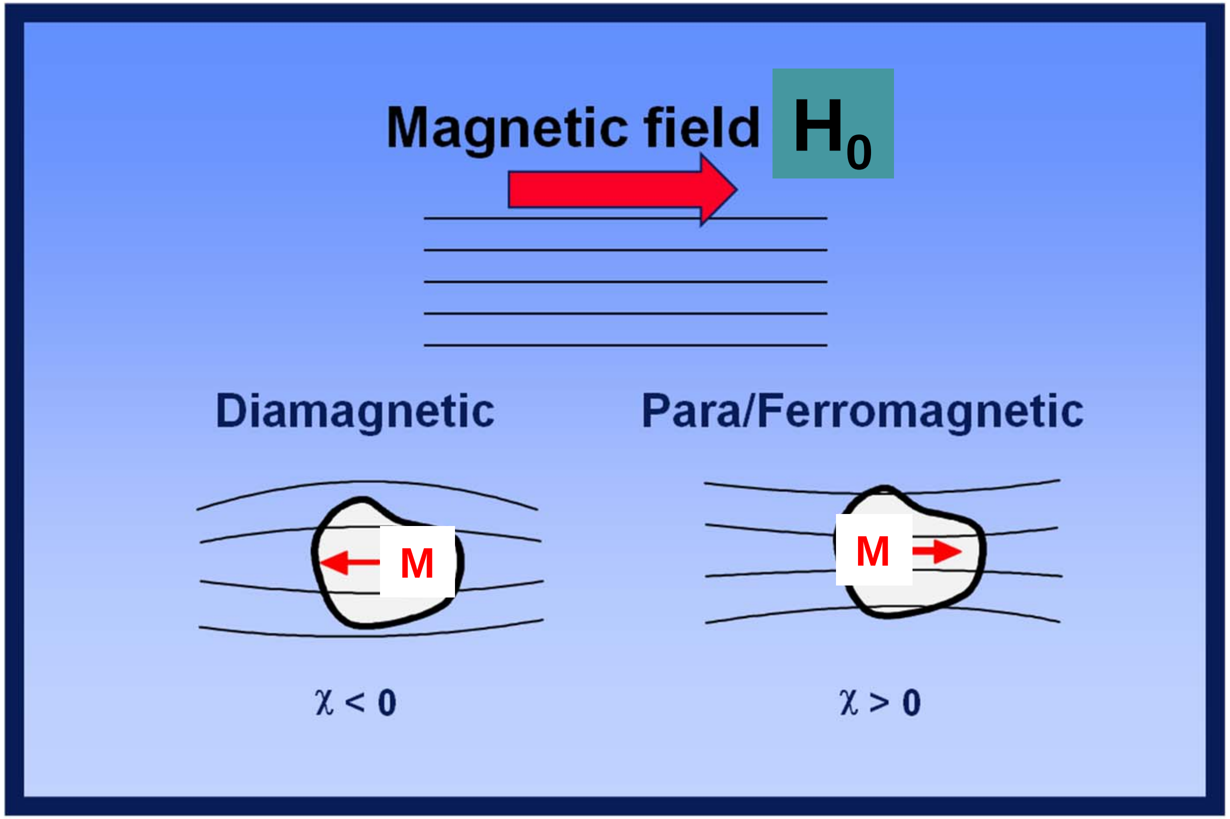
$$\mu_{eff} = \left(\frac{3k_B}{\mu_0 N_A \mu_B^2}\right)^{\frac{1}{2}} \sqrt{\chi_M T}$$

Magnetic Properties

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.

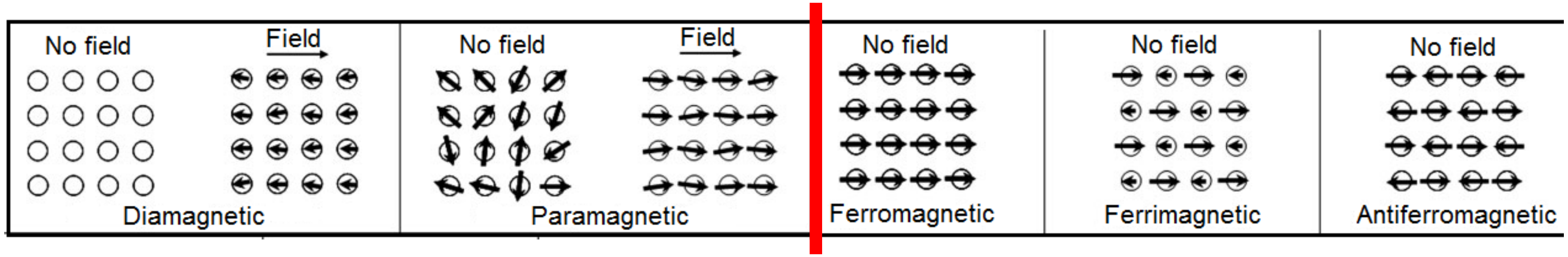
Magnetic Properties

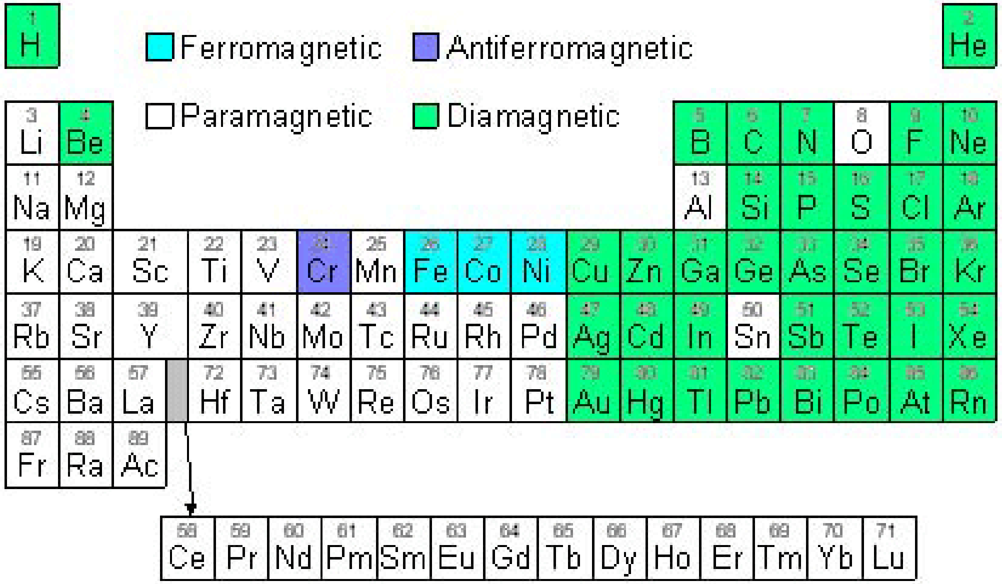
Magnetic behavior of a substance = magnetic polarization in a mg field H_0



Magnetic Properties

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





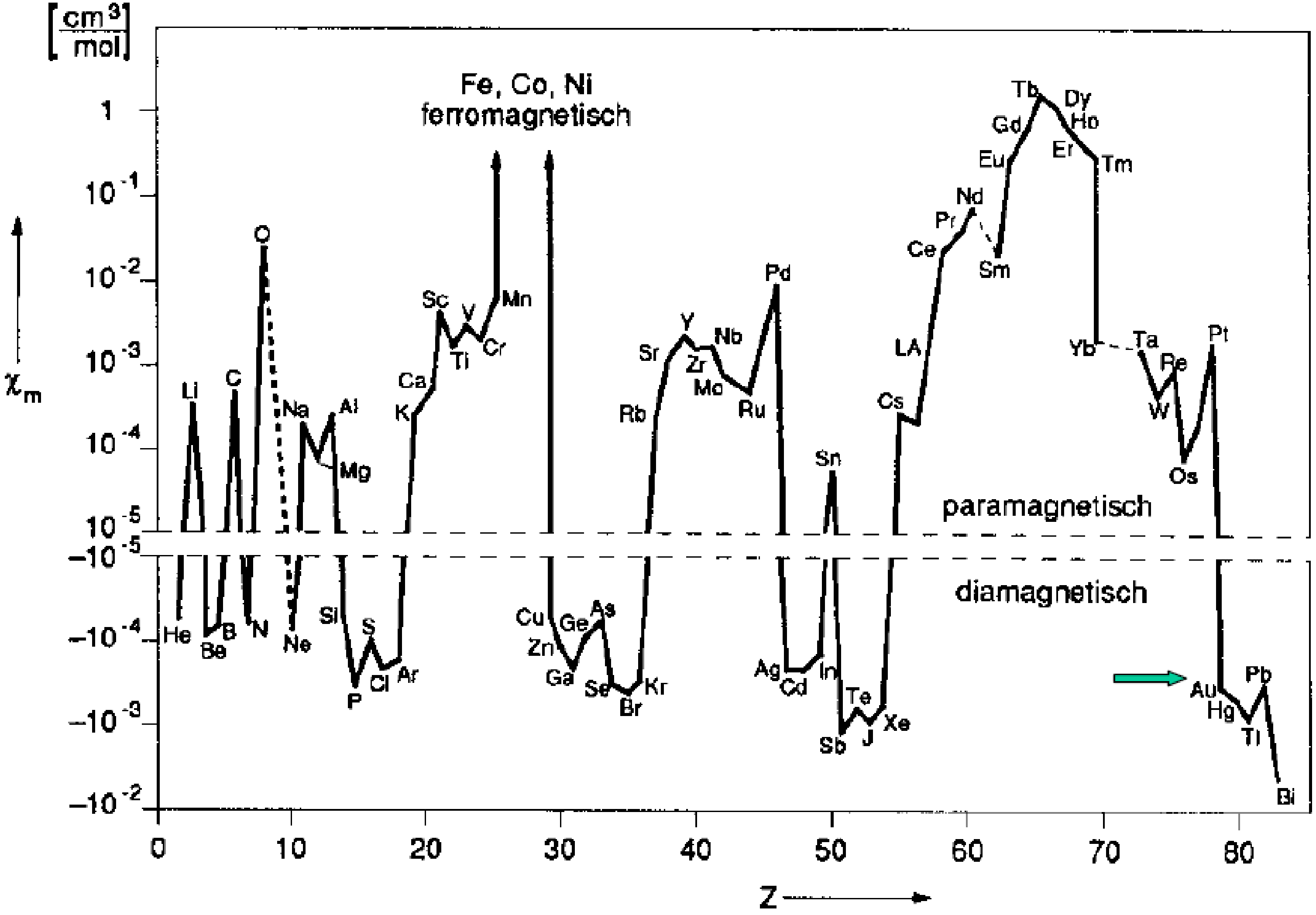
🟦 Ferromagnetic 🟪 Antiferromagnetic

☐ Paramagnetic 🟩 Diamagnetic

🟩 1 H																		🟩 2 He
☐ 3 Li	🟩 4 Be												🟩 5 B	🟩 6 C	🟩 7 N	☐ 8 O	🟩 9 F	🟩 10 Ne
☐ 11 Na	☐ 12 Mg												☐ 13 Al	🟩 14 Si	🟩 15 P	🟩 16 S	🟩 17 Cl	🟩 18 Ar
☐ 19 K	☐ 20 Ca	☐ 21 Sc		☐ 22 Ti	☐ 23 V	🟪 24 Cr	☐ 25 Mn	🟦 26 Fe	🟦 27 Co	🟦 28 Ni	🟩 29 Cu	🟩 30 Zn	🟩 31 Ga	🟩 32 Ge	🟩 33 As	🟩 34 Se	🟩 35 Br	🟩 36 Kr
☐ 37 Rb	☐ 38 Sr	☐ 39 Y		☐ 40 Zr	☐ 41 Nb	☐ 42 Mo	☐ 43 Tc	☐ 44 Ru	☐ 45 Rh	☐ 46 Pd	🟩 47 Ag	🟩 48 Cd	🟩 49 In	☐ 50 Sn	🟩 51 Sb	🟩 52 Te	🟩 53 I	🟩 54 Xe
☐ 55 Cs	☐ 56 Ba	☐ 57 La	▨	☐ 72 Hf	☐ 73 Ta	☐ 74 W	☐ 75 Re	☐ 76 Os	☐ 77 Ir	☐ 78 Pt	🟩 79 Au	🟩 80 Hg	🟩 81 Tl	🟩 82 Pb	🟩 83 Bi	🟩 84 Po	🟩 85 At	🟩 86 Rn
☐ 87 Fr	☐ 88 Ra	☐ 89 Ac																

☐ 58 Ce	☐ 59 Pr	☐ 60 Nd	☐ 61 Pm	☐ 62 Sm	☐ 63 Eu	☐ 64 Gd	☐ 65 Tb	☐ 66 Dy	☐ 67 Ho	☐ 68 Er	☐ 69 Tm	☐ 70 Yb	☐ 71 Lu

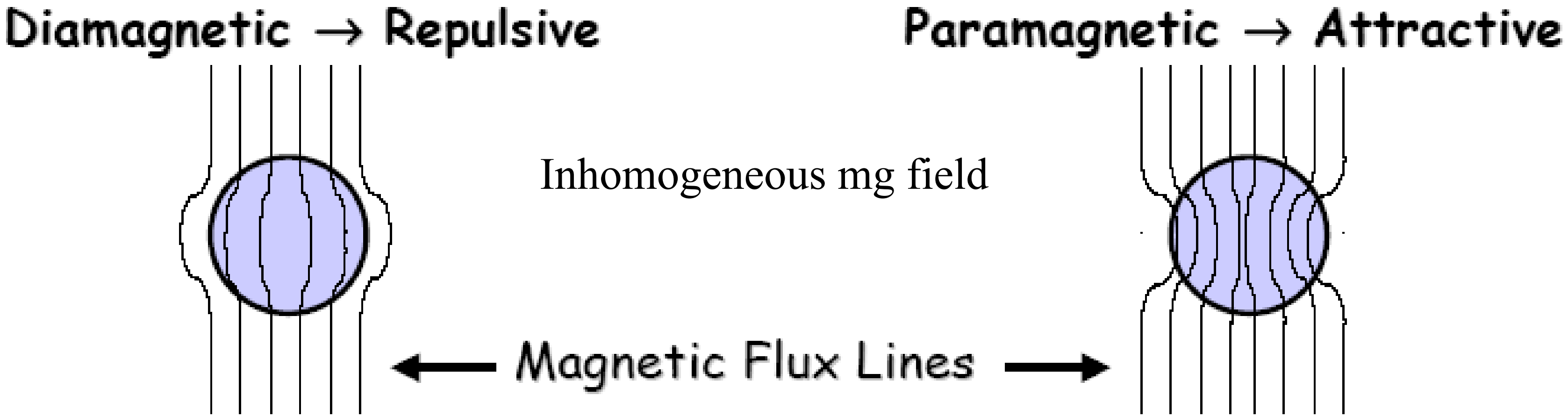
Magnetism of the Elements



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

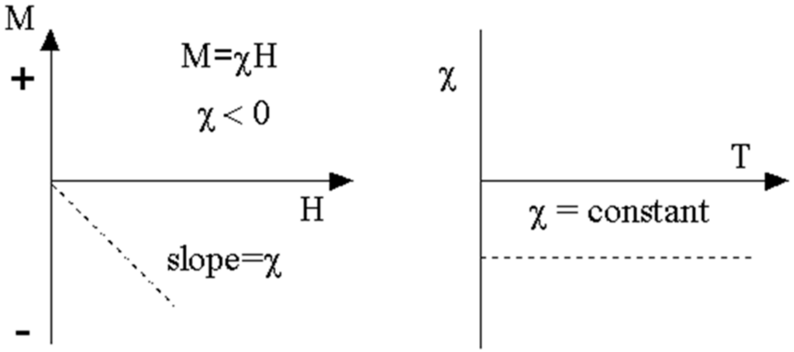
Electrons in closed shells (paired) cause a material to be repelled by H

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

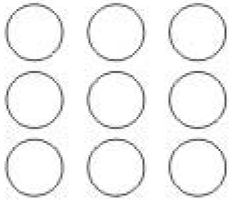
$$M = \chi \times H$$

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

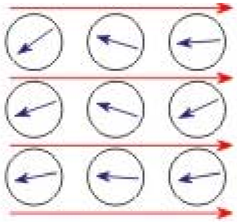
Superconductors $\chi = -1$ perfect diamagnets



Diamagnetism



H=0
Zero moment



H > 0
Opposing Induced moment

Diamagnetism

Large and heavy atoms have large diamagnetic susceptibilities

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

Substance	**Molar Magnetic Susceptibility** χ_M

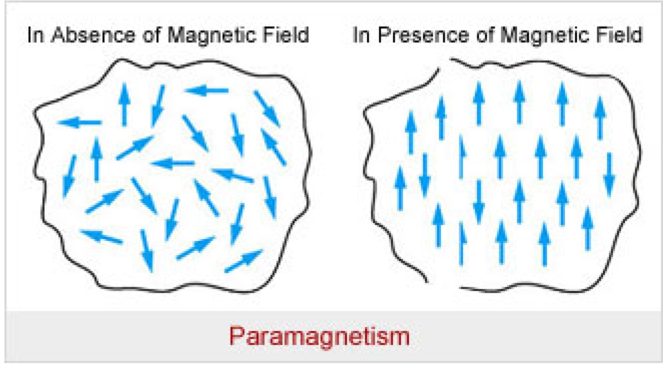
(Curie) Paramagnetism

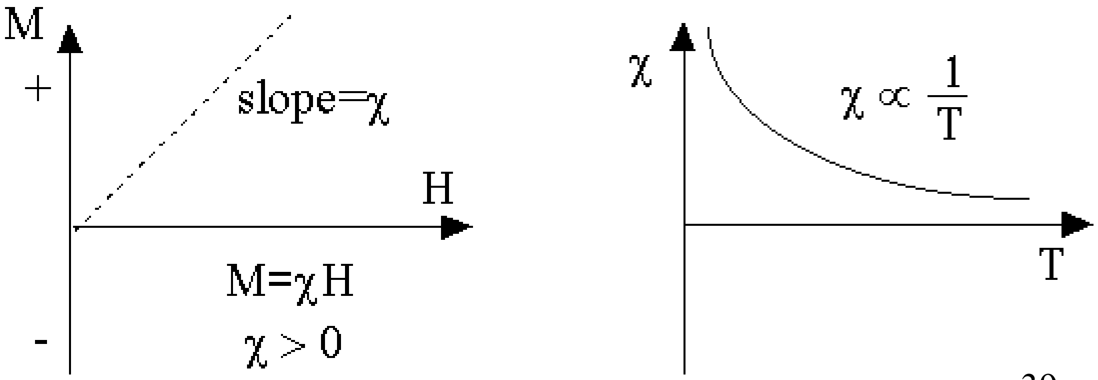
Paramagnetism arises from the interaction of H with the magnetic field of the unpaired electron due to the spin and orbital angular momentum.

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

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

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

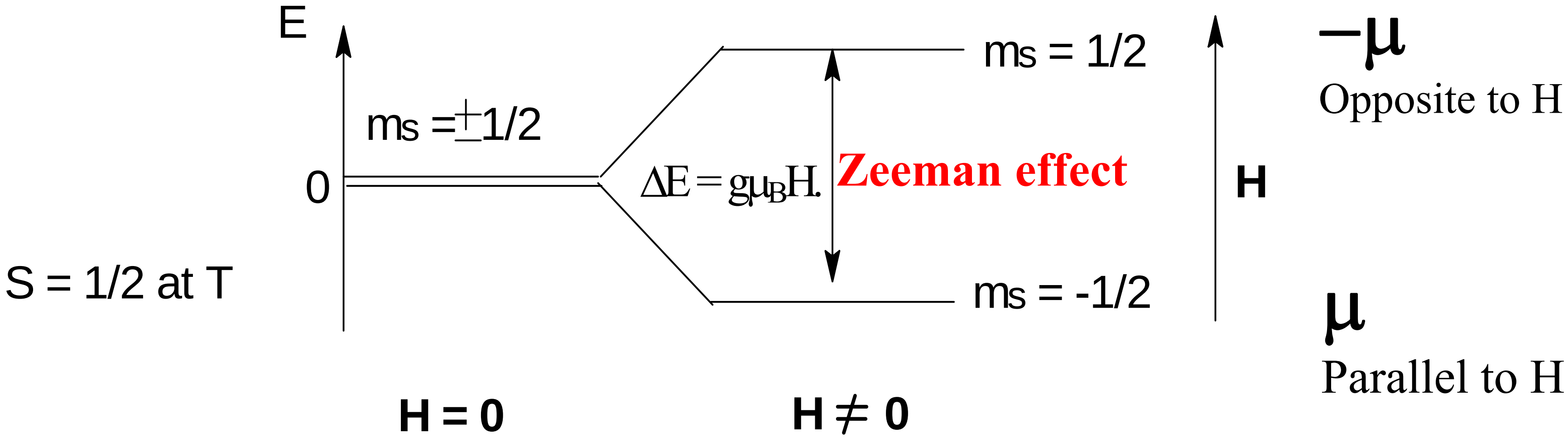




Paramagnetism

(Curie) Paramagnetism for $S = ½$

Energy diagram of ONE $S = 1/2$ spin in an external magnetic field



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

The interaction energy of magnetic moment with the applied magnetic field

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

$\Delta E = g\ \mu_B\,H$ 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 ΔE ~ 2.3 cm^{-1}

At 300 K kT ~ 200 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

$M = N_A \Sigma \mu_n P_n$

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

P_n = probability in state n
N_n = population of state n
N_T = population of all the states

(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

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

For $x << 1$

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

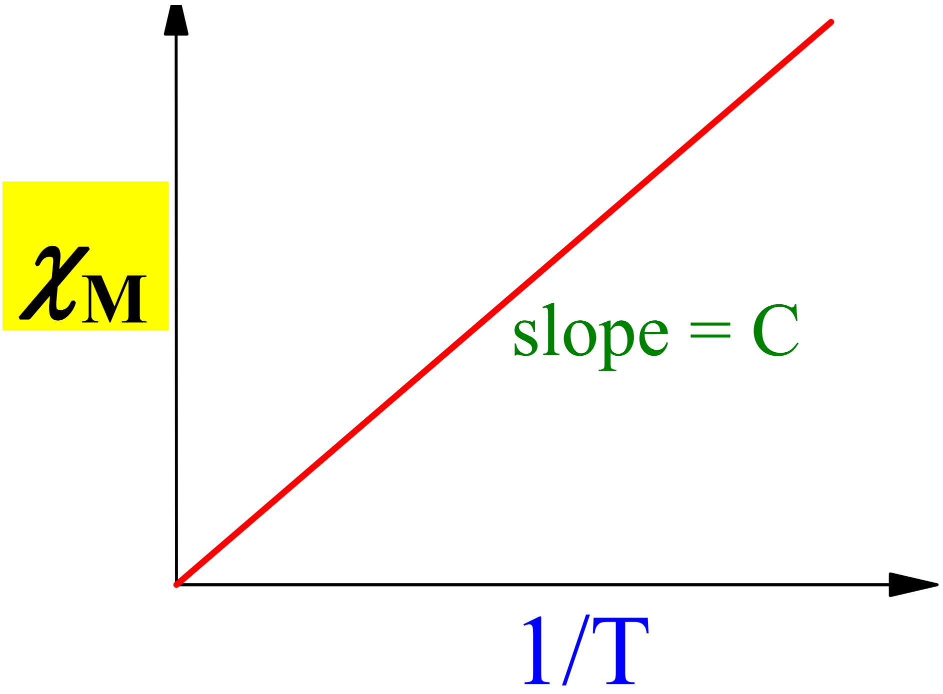
$$= \frac{N g\beta}{2} \left[\frac{1 + g\beta H/2kT - (1 - g\beta H/2kT)}{1 + g\beta H/2kT + (1 - g\beta H/2kT)} \right]$$

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

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

(Curie) Paramagnetism for S = ½

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



Curie Law:

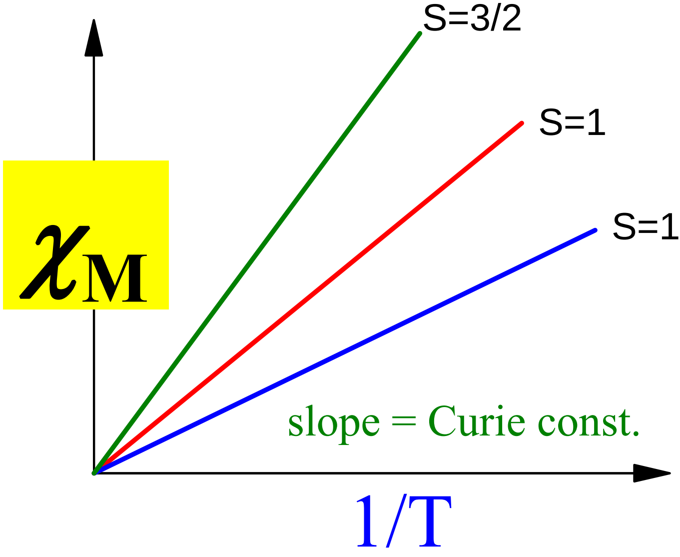
$$\chi_M = \frac{C}{T}$$

(Curie) Paramagnetism for general S

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

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

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



non-interacting, non-cooperative, independent, dilute ions

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 $$\chi_M = \frac{5N_A g^2 \mu_B^2}{4k_B T}$$

(Curie) Paramagnetism

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

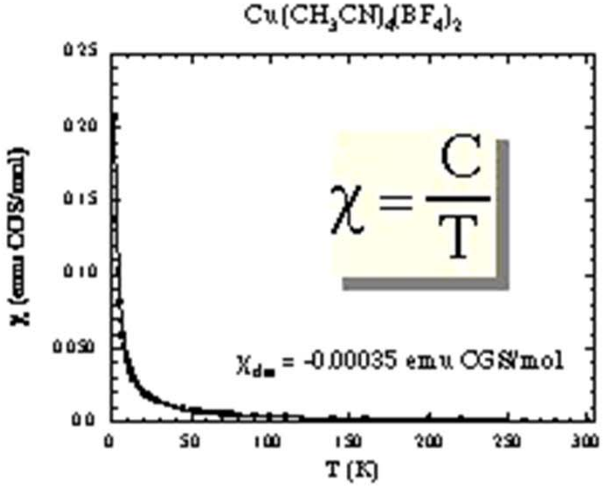
$$\mu_{eff} = g\sqrt{S(S+1)} = \sqrt{n(n+1)}$$

(in BM, Bohr Magnetons)

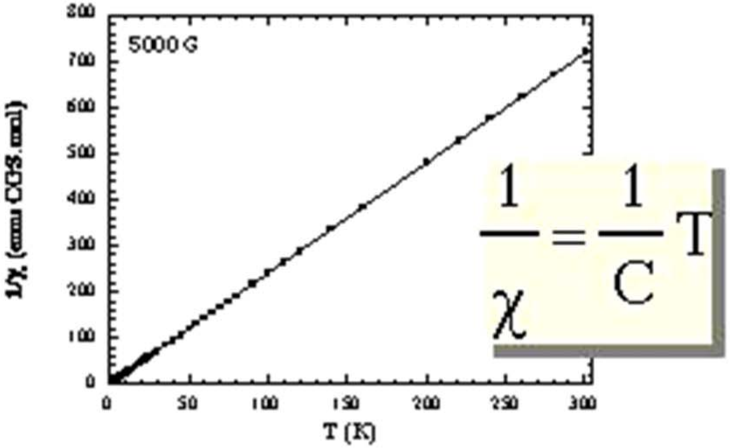
n = number of unpaired electrons
g = 2

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

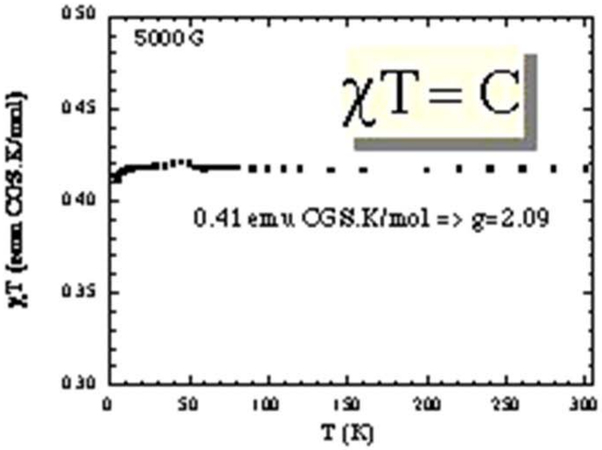
Curie Law



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



$$\frac{1}{\chi} = \frac{1}{C}T$$



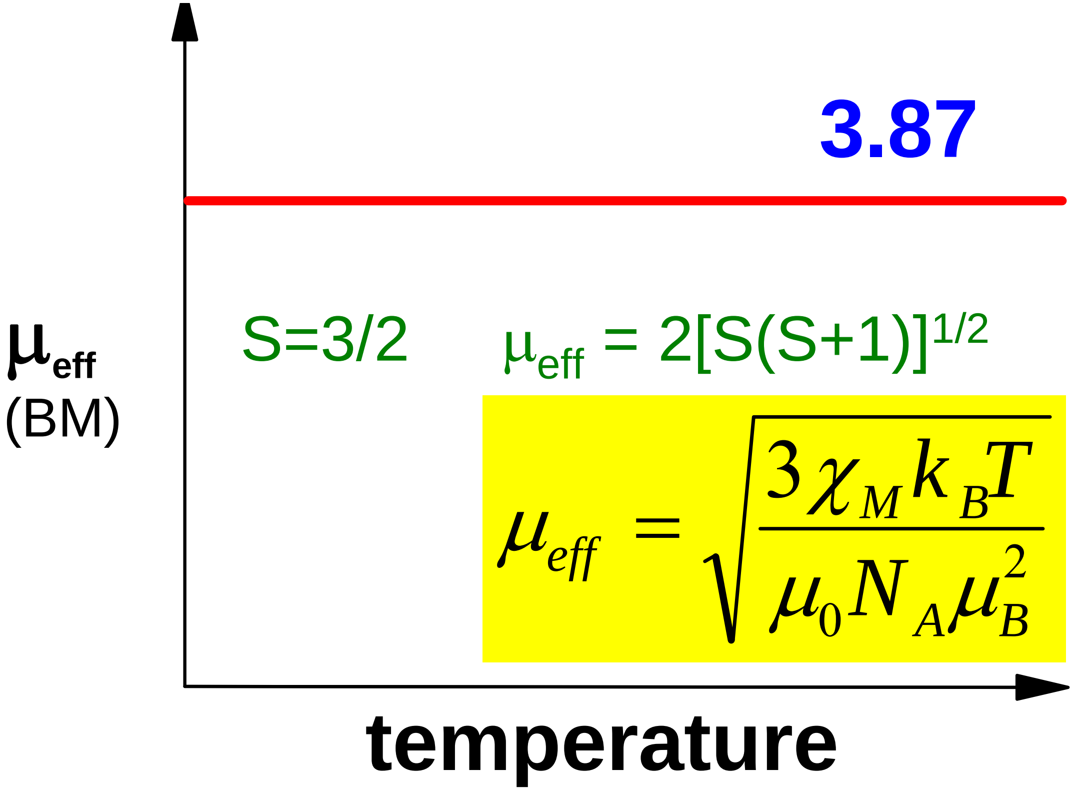
$$\chi T = C$$

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

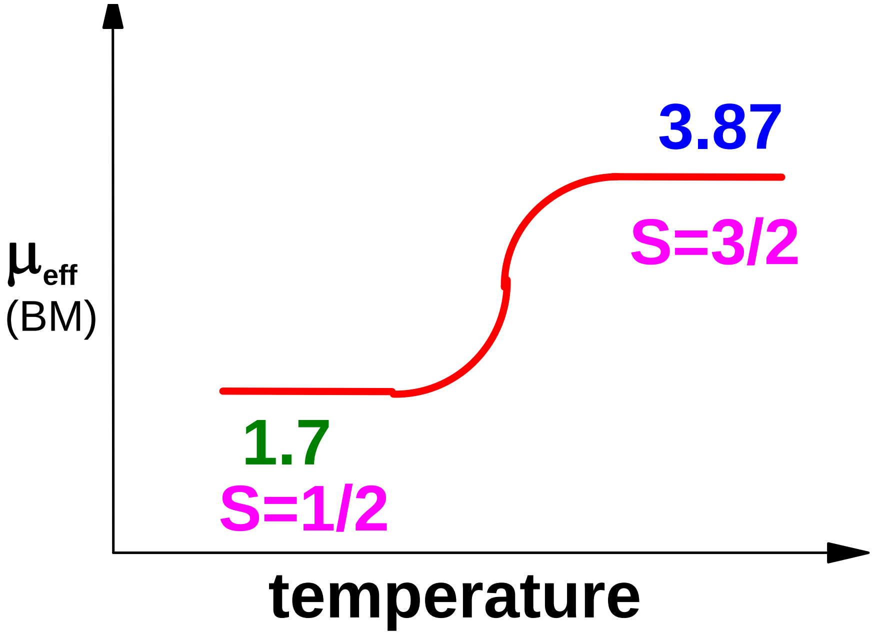


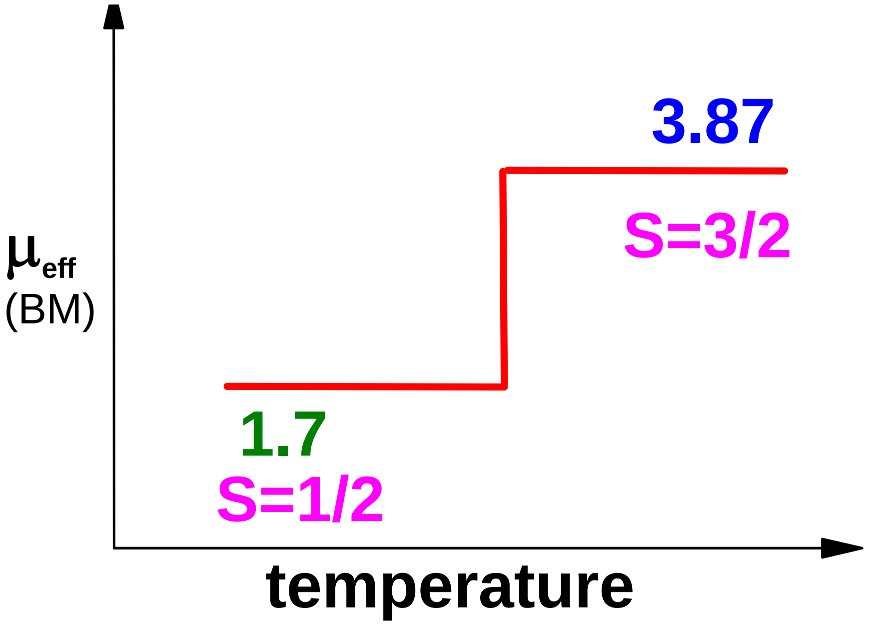
S=3/2

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

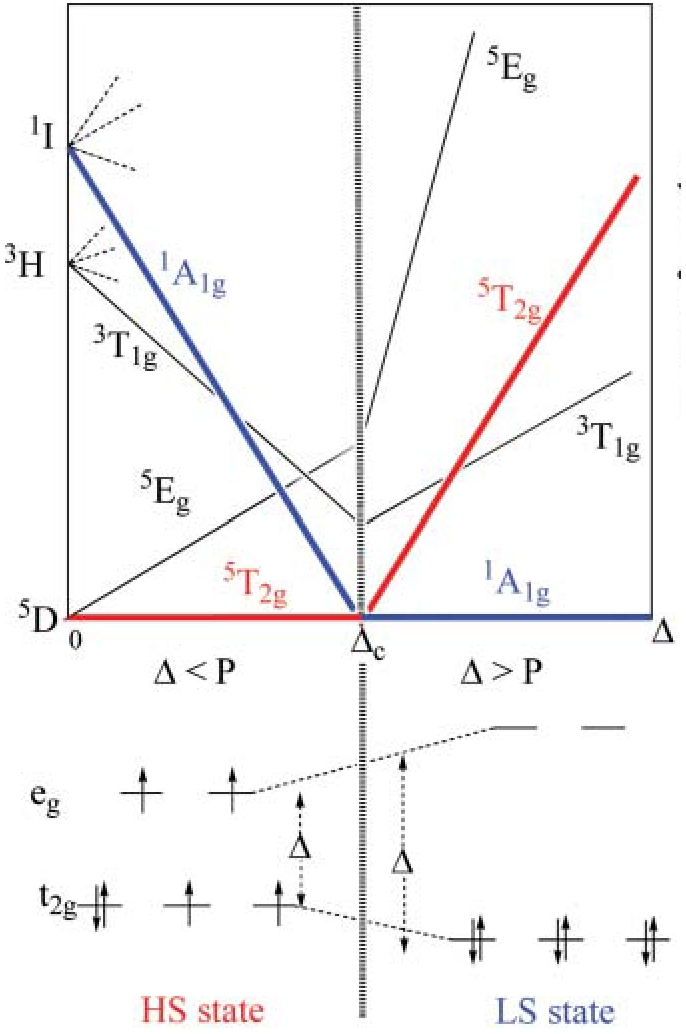
$$\mu_{eff} = \sqrt{\frac{3\chi_M k_B T}{\mu_0 N_A \mu_B^2}}$$

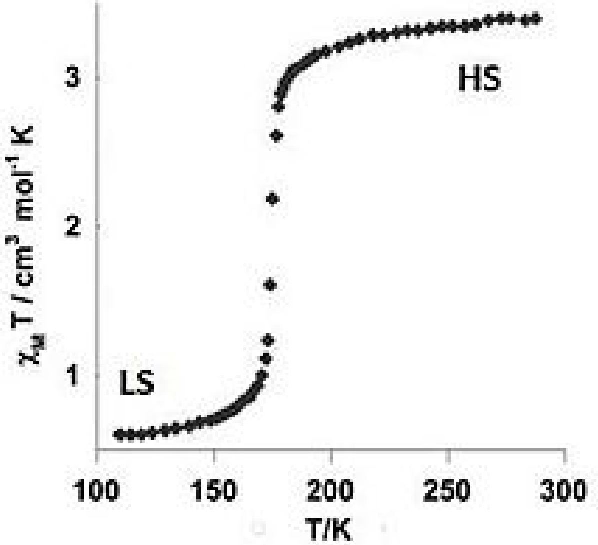
Spin Equilibrium and Spin Crossover

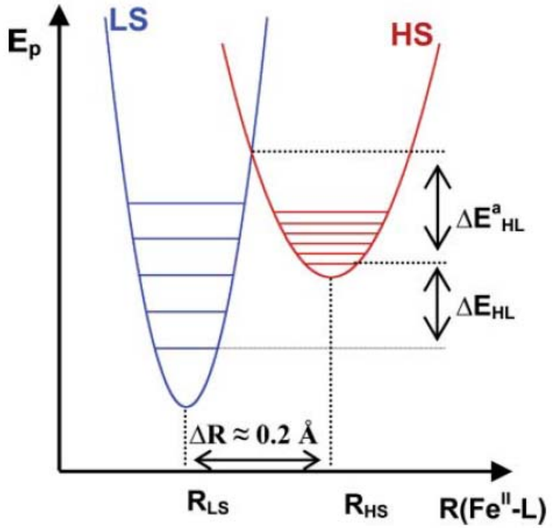




Spin Crossover







See C4010 Bonding – Bond stretch isomers

Curie Plot

$$\chi_{\exp} = \frac{C}{T-\theta} + \chi_T$$

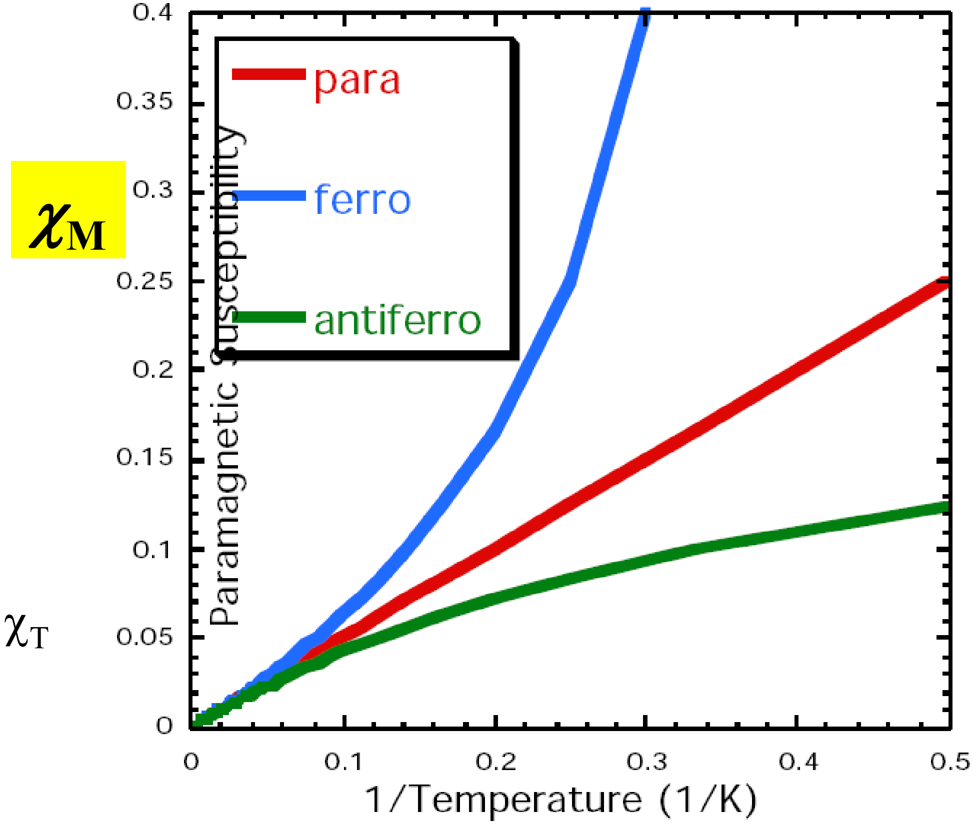
$\chi_T = \chi_{\mathrm{dia}} + \chi_{\mathrm{Pauli}}$ = temperature independent contributions

$$\chi_{\exp} = \frac{C}{T} + \chi_T$$

at high temperature if θ is small

Plot χ_{exp} vs 1/T

slope = C; intercept = χ_T



1/273 K = 0.00366

1/1.8 K = 0.556

Curie Plot

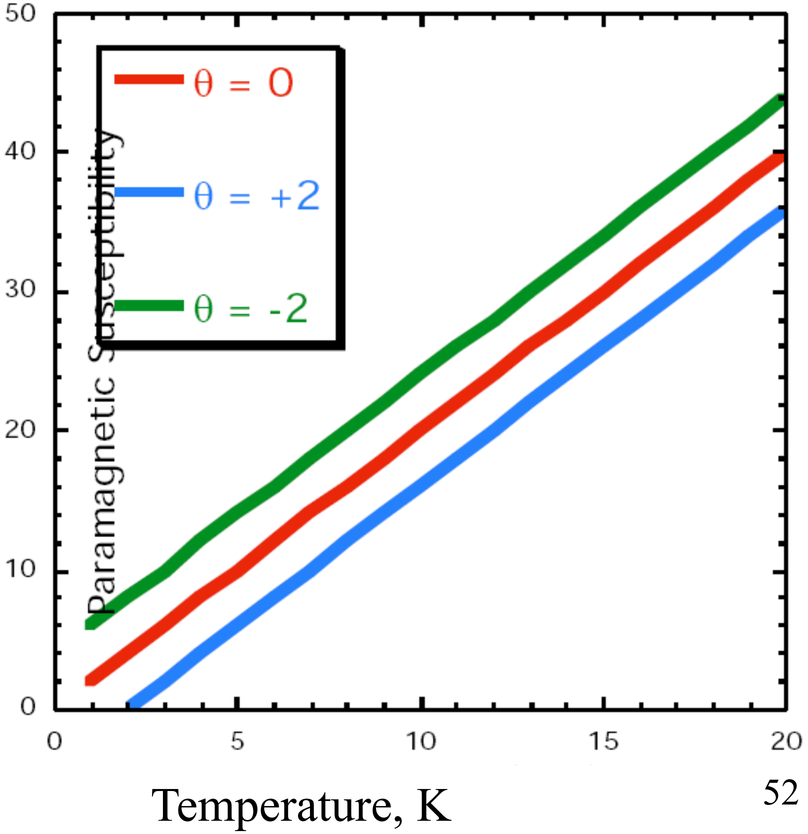
$$\chi_{\exp} = \frac{C}{T-\theta} + \chi_T$$

$\chi_T = \chi_{\mathrm{dia}} + \chi_{\mathrm{Pauli}}$ = temperature independent contributions

$$\chi_{\exp} = \frac{C}{T} + \chi_T$$

at high temperature if θ is small

$1/\chi_{\mathrm{M}}$



Plot $1/\chi_{\exp}$ vs T

slope = 1/C; intercept = θ/C

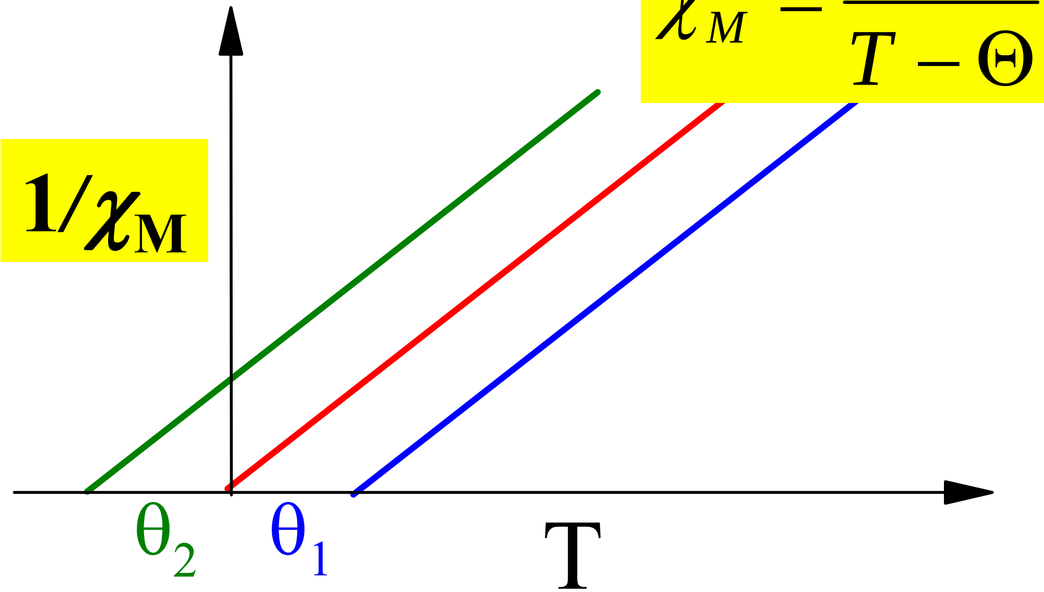
Curie-Weiss Law

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)

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



Θ = the Weiss constant
(the x-intercept)

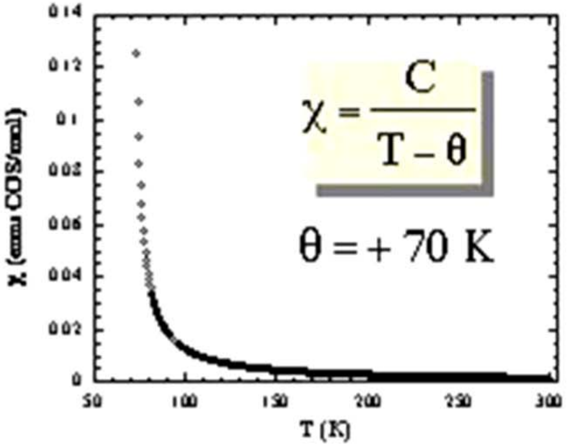
$\Theta = 0$ paramagnetic spins independent of each other

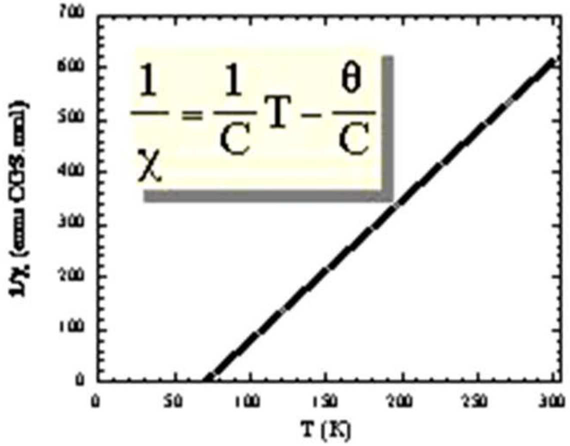
Θ is positive, spins align parallell

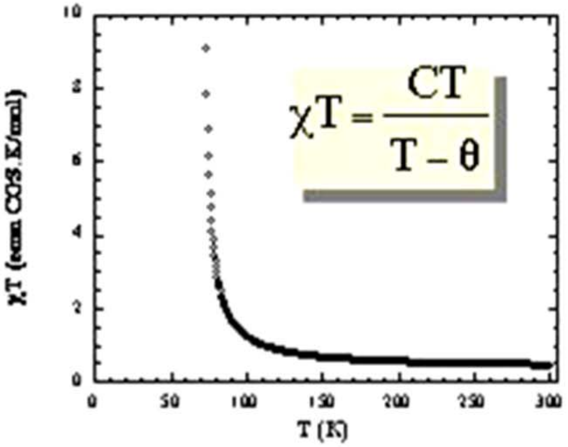
Θ is negative, spins align antiparallell

Curie-Weiss Paramagnetism

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







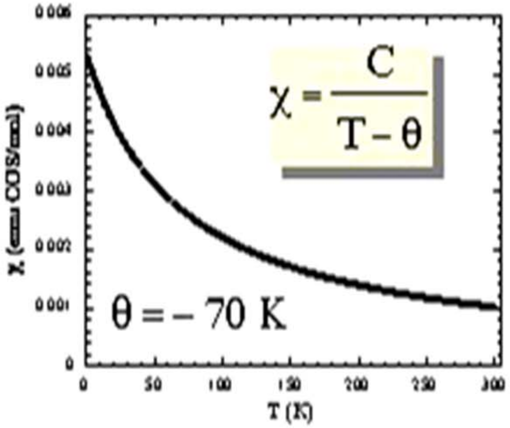
θ = intermolecular interactions among the moments

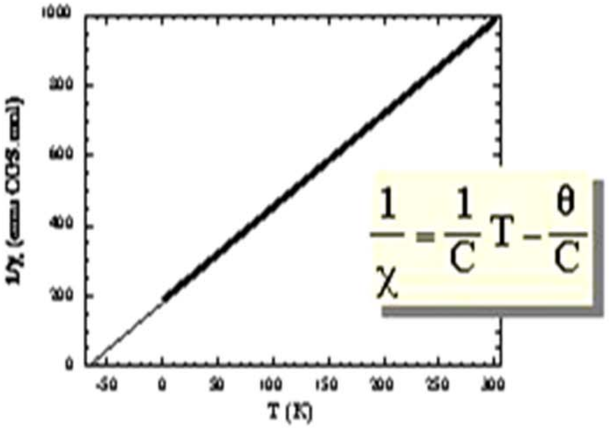
$\theta > 0$ - **ferromagnetic** interactions = **spins align parallell**

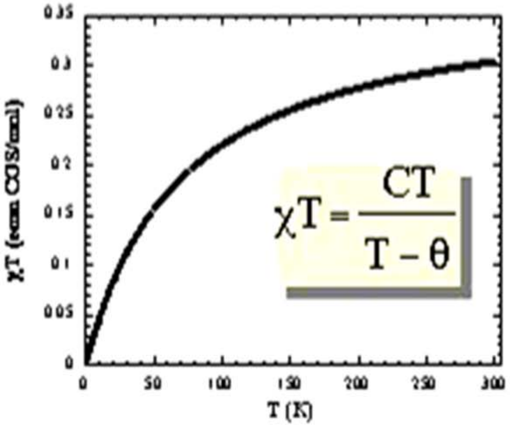
(NOT ferromagnetism)

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**

θ (NOT antiferromagnetism)

Temperature-independent Paramagnetism

Induced in mg. field

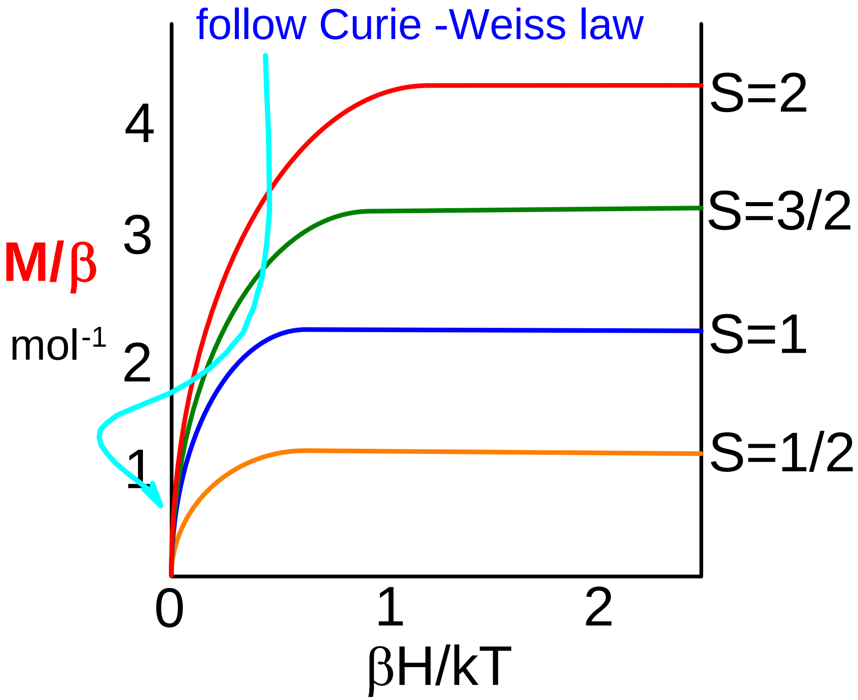
Saturation of Magnetization

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

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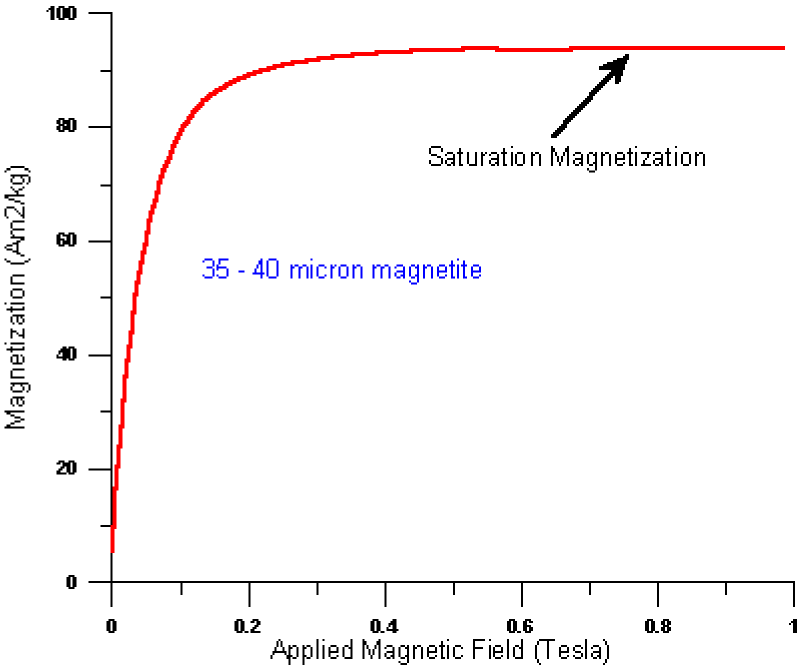
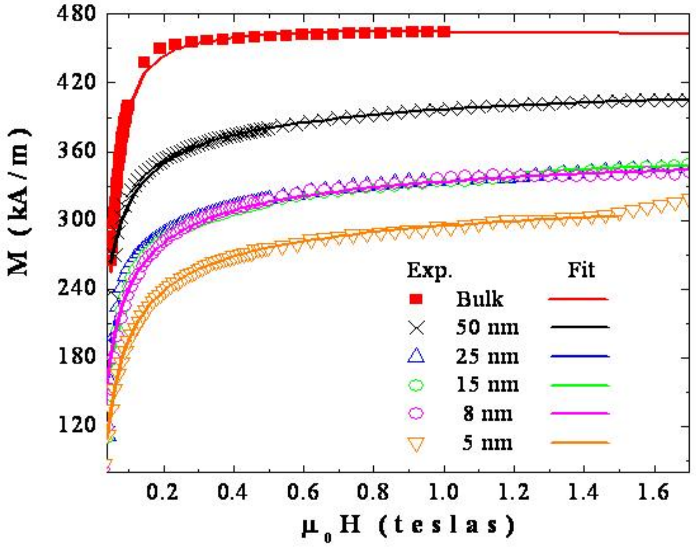


Fe_3O_4 films



Saturation of Magnetization

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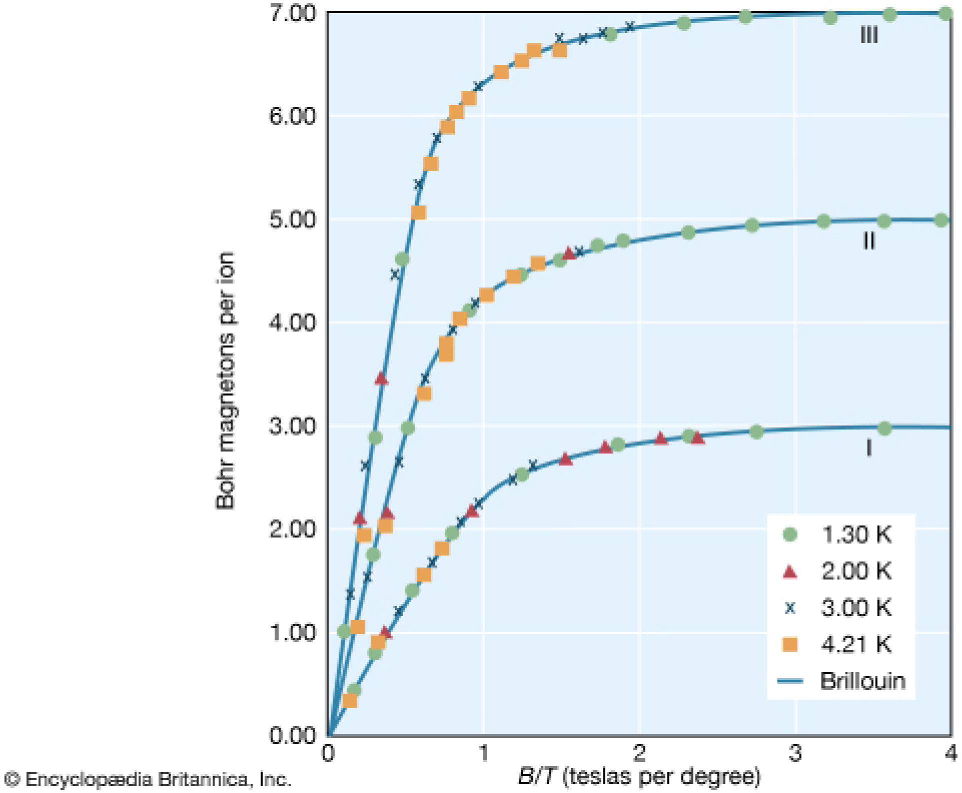


Curves I, II, and III refer to ions of chromium potassium alum, iron ammonium alum, and gadolinium sulfate octahydrate for which *g* = 2 and *j* = 3/2, 5/2, and 7/2, respectively.

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 (μ_l)

Spin motion of the electron generates

SPIN MAGNETIC MOMENT (μ_s)

l = orbital angular momentum
s = spin angular momentum

For multi-electron systems
$L = l_1 + l_2 + l_3 + \ldots\ldots\ldots\ldots\ldots$

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

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

Paramagnetism in Transition Metal Complexes

The magnetic properties arise mainly from the 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

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

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

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 ions with partially filled d-shells (l = 2)

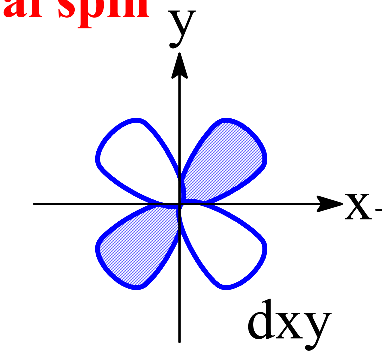
$el.$	$m_l =$	2	1	0	-1	-2	S	$L = \lvert \sum m_l \rvert$	J	Symbol
1		$\downarrow$					$1/2$	2	$3/2$	${}^2D_{3/2}$
2		$\downarrow$	$\downarrow$				1	3	2	${}^3F_2$
3		$\downarrow$	$\downarrow$	$\downarrow$			$3/2$	3	$3/2$	${}^4F_{3/2}$
4		$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$		2	2	0	${}^5D_0$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

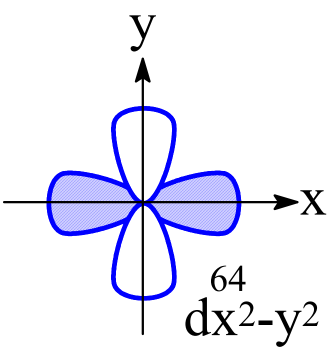
Orbital Angular Momentum Contribution

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 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_x2-_y2 by a rotation of 45° about the z-axis.)
3. Orbitals must **not** contain electrons of **identical spin**





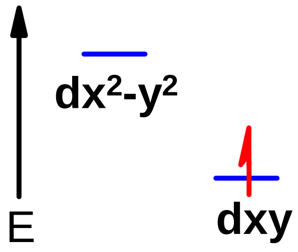
Orbital Contribution in Octahedral Complexes

Condition	**t_{2g} set**	**e_g set** $d_{x^2-y^2} + d_{z^2}$
1	Obeyed	Obeyed
2	Obeyed	Not obeyed
3	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

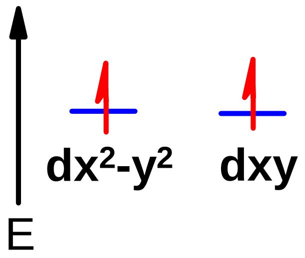
These conditions are fulfilled whenever one or two of the three t_{2g} orbitals contain an odd no. of electrons.

Spin-Orbit Coupling

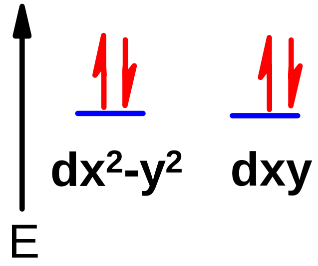
Little contribution from orbital angular momentum



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

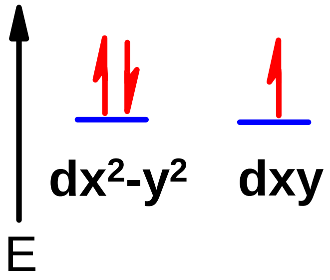


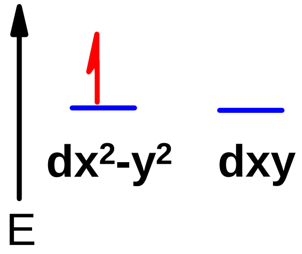
Electrons have to change directions of spins to circulate



Orbitals are filled

Spin-orbit couplings are significant



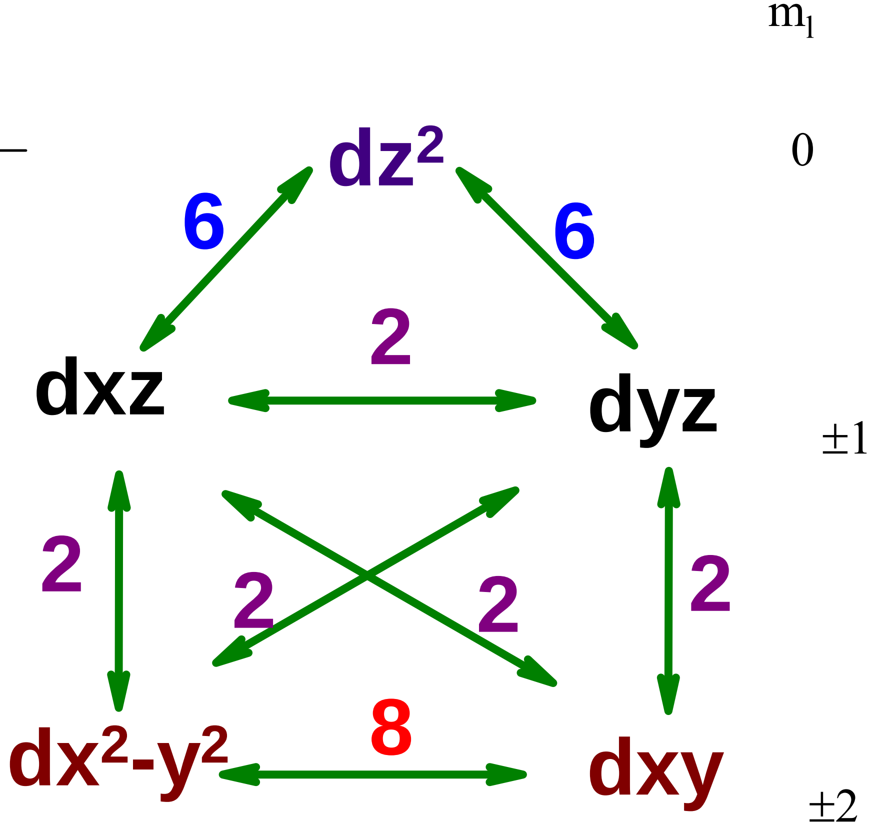


Magic Pentagon

Spin-orbit coupling influences g-value

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

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



m_l

dz^2 0

6 6

dxz 2 dyz ±1

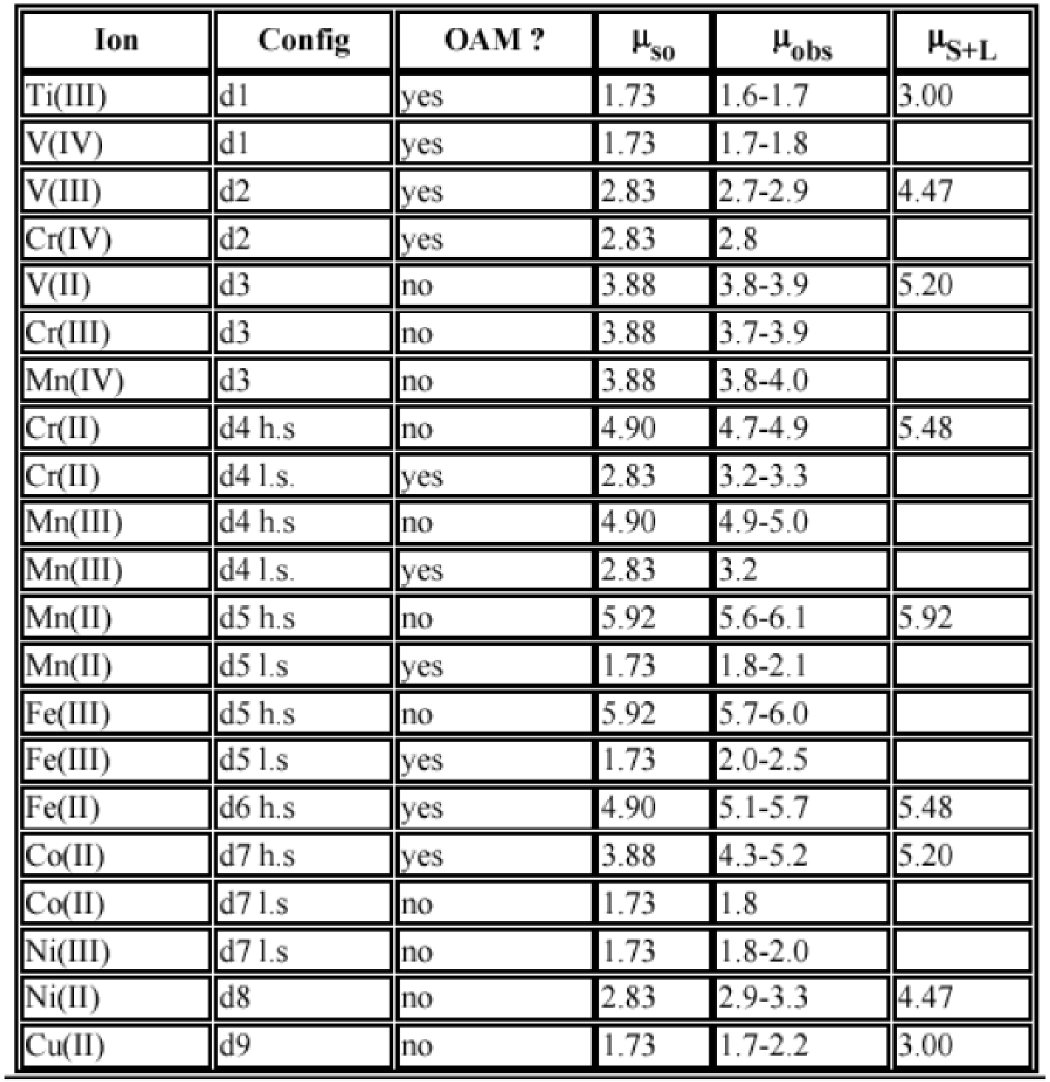
2 2 2 2

dx^2-y^2 8 dxy ±2

orbital sets that may give spin-orbit coupling

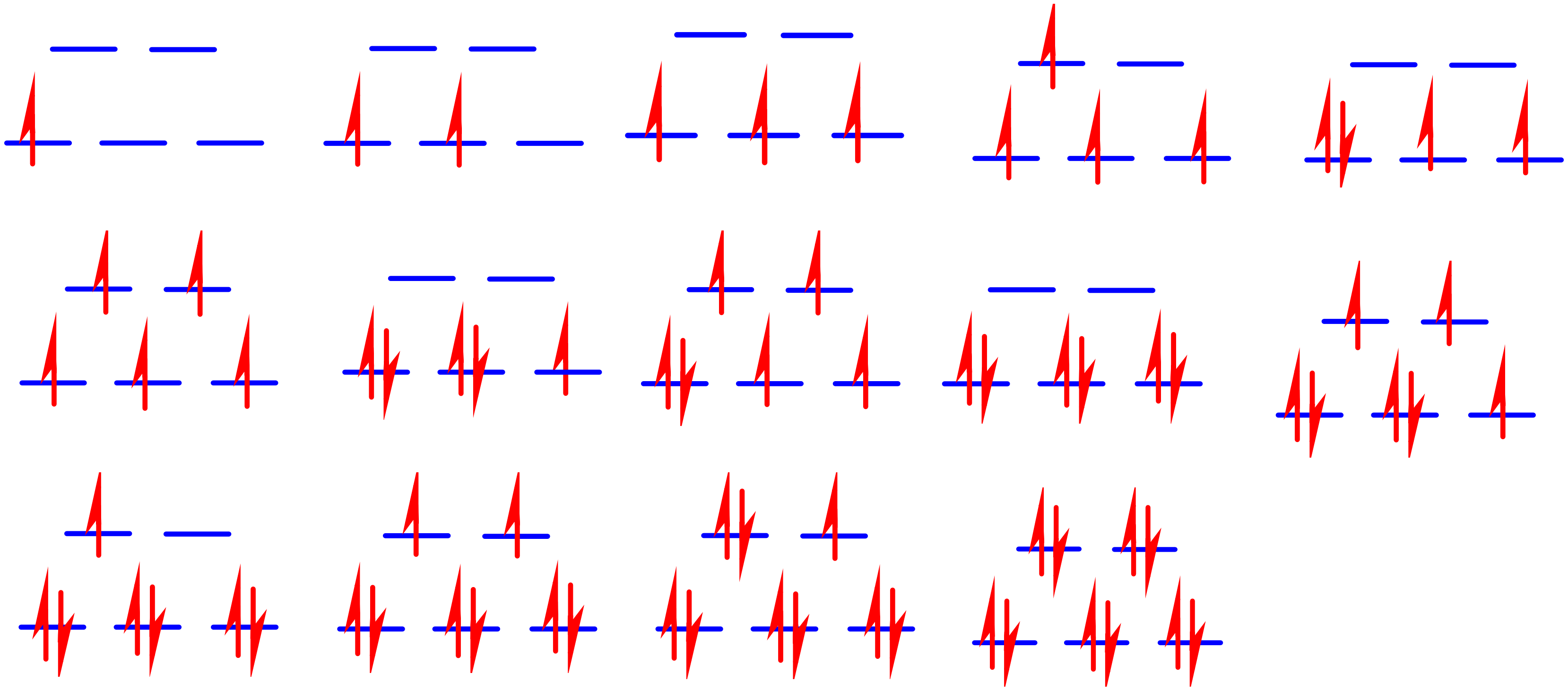
no spin-orbit coupling contribution for **dz^2/dx^2-y^2** and **dz^2/dxy**

Orbital Contribution in Octahedral Complexes

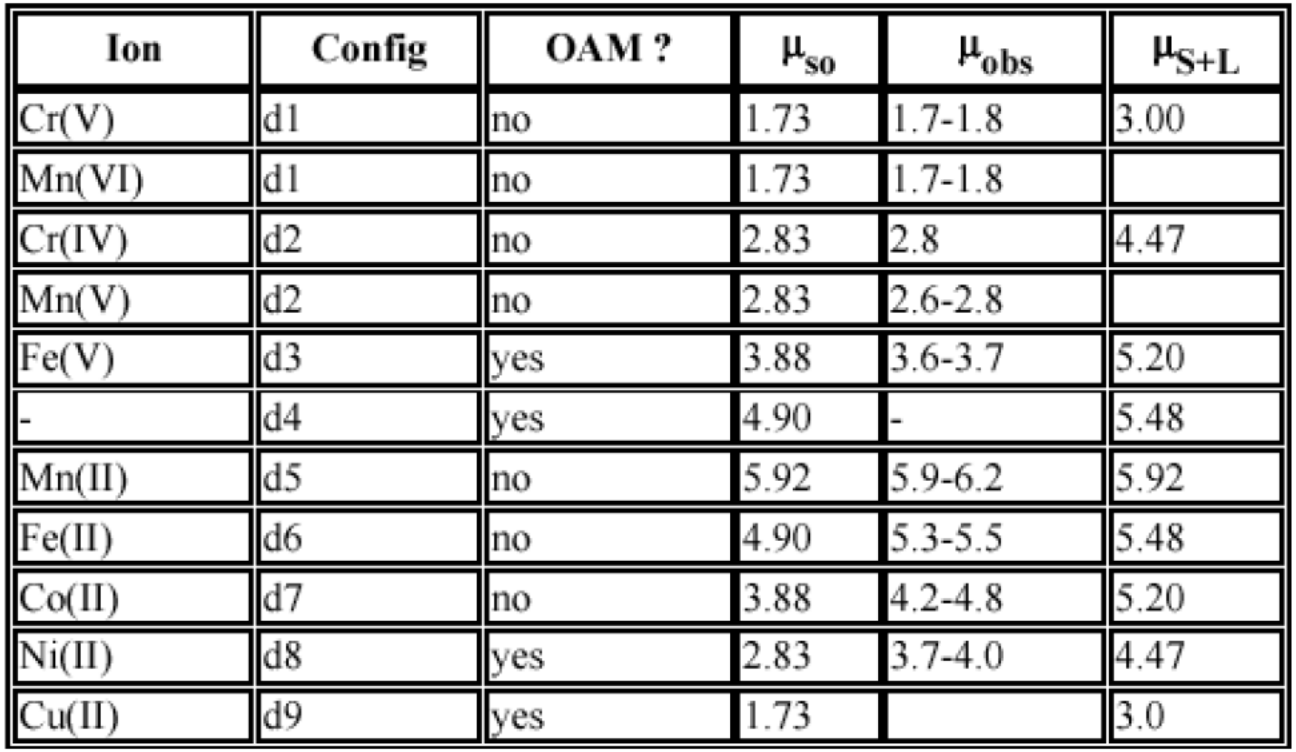


Ion	Config	OAM ?	μ_{so}	μ_{obs}	μ_{S+L}
Ti(III)	d1	yes	1.73	1.6-1.7	3.00
V(IV)	d1	yes	1.73	1.7-1.8	
V(III)	d2	yes	2.83	2.7-2.9	4.47
Cr(IV)	d2	yes	2.83	2.8	
V(II)	d3	no	3.88	3.8-3.9	5.20
Cr(III)	d3	no	3.88	3.7-3.9	
Mn(IV)	d3	no	3.88	3.8-4.0	
Cr(II)	d4 h.s	no	4.90	4.7-4.9	5.48
Cr(II)	d4 l.s.	yes	2.83	3.2-3.3	
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

Orbital Contribution
in Octahedral Complexes



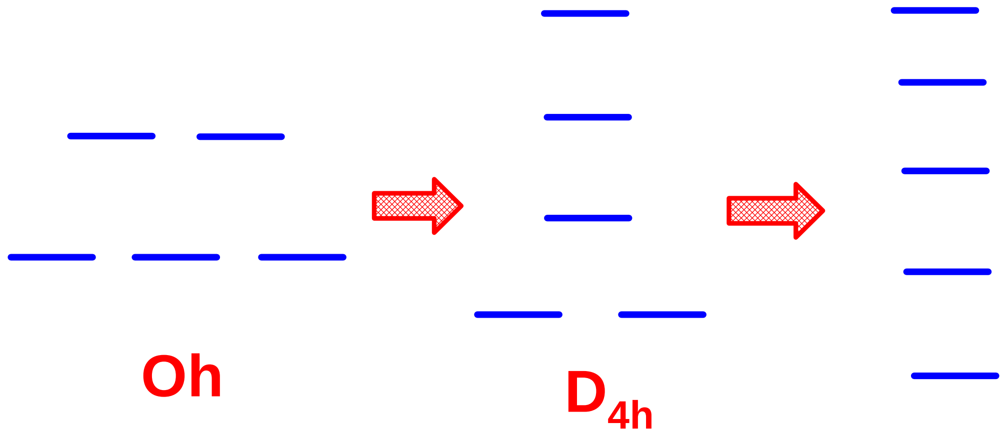
Orbital Contribution in Tetrahedral Complexes



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

Orbital Contribution
in Low-symmetry Ligand Field

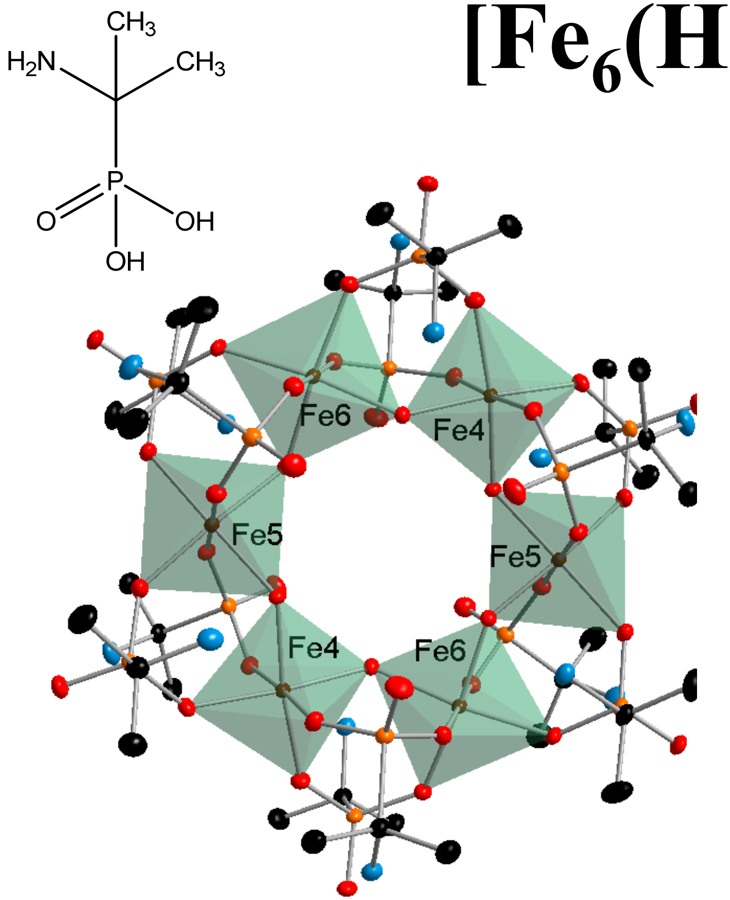
If the symmetry is lowered, degeneracy will be destroyed and the orbital contribution will be quenched.

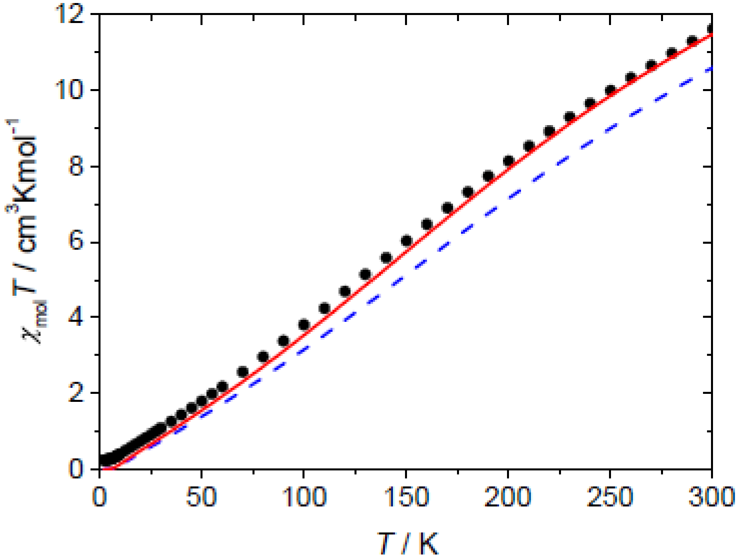


D_{4h}: all are quenched except d^1 and d^3

$\mu_{eff} = g[S(S+1)]^{1/2}$ (**spin-only**) is valid

$[Fe_6(HAIPA)_{12}(OH)_6]$





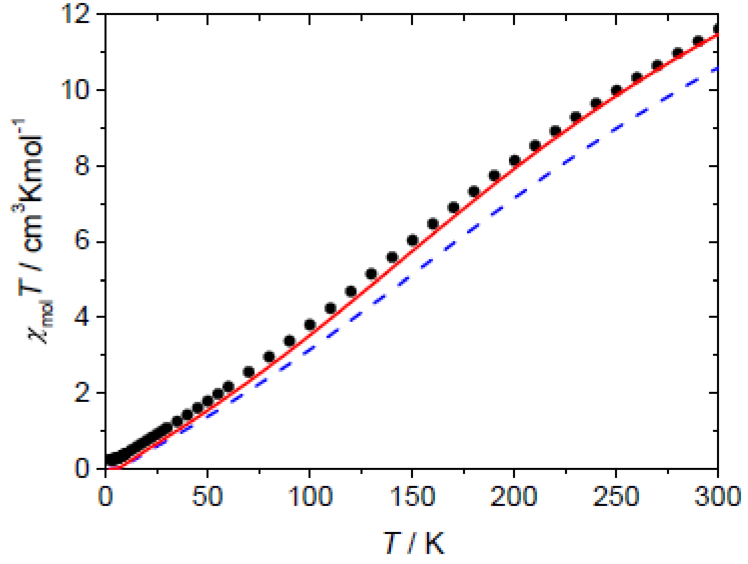
$11.6\ cm^3\ K\ mol^{-1}$

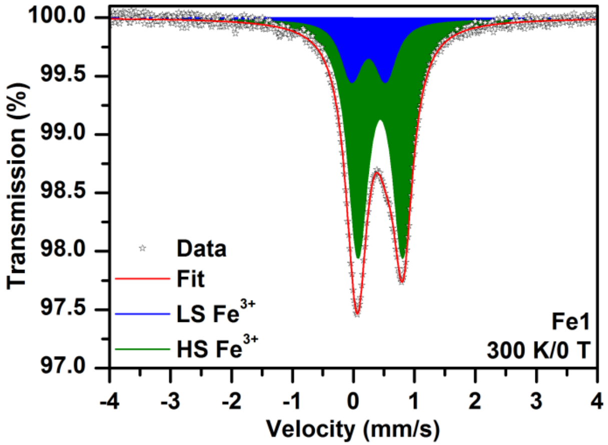
300 K, spin-only (g = 2), six independent (N = 6) ions:

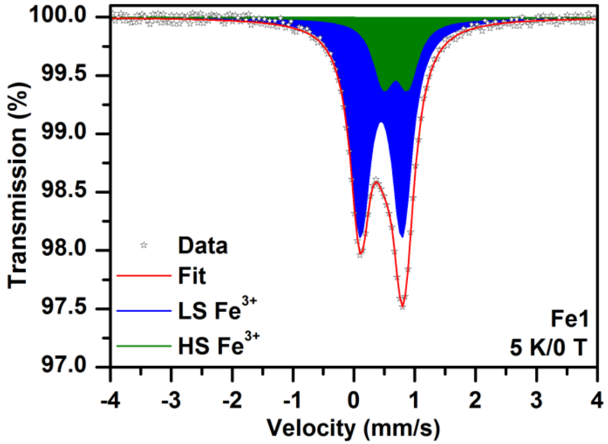
$$\chi T = \frac{1}{2} S(S+1)N$$

HS Fe(III) S = 5/2 $\chi T = 26.25\ cm^3\ K\ mol^{-1}$
LS Fe(III) S = 1/2 $\chi T = 2.25\ cm^3\ K\ mol^{-1}$

$[Fe_6(HAIPA)_{12}(OH)_6]$







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

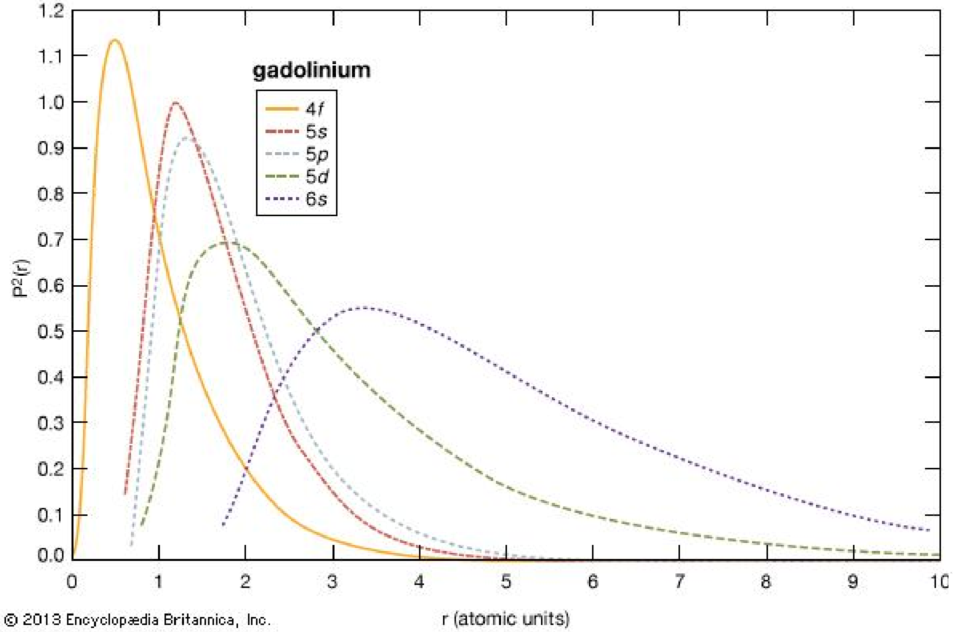
Thus 4f normally **unaffected** by surrounding ligands

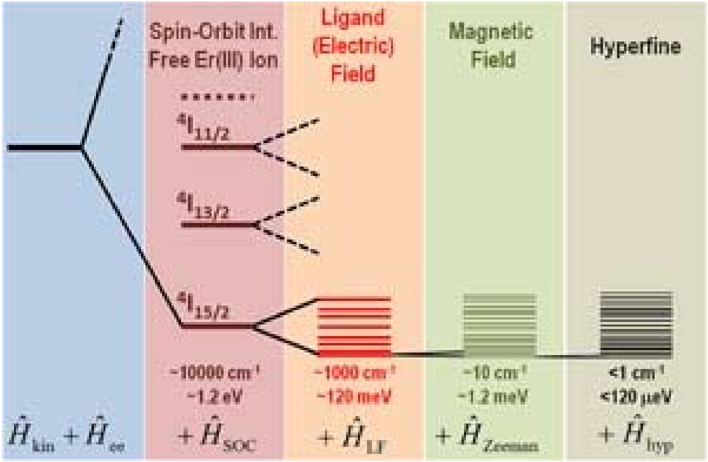
The magnetic moments of Ln^{3+} ions are generally well-described from **the coupling of spin and orbital angular momenta** to give J vector

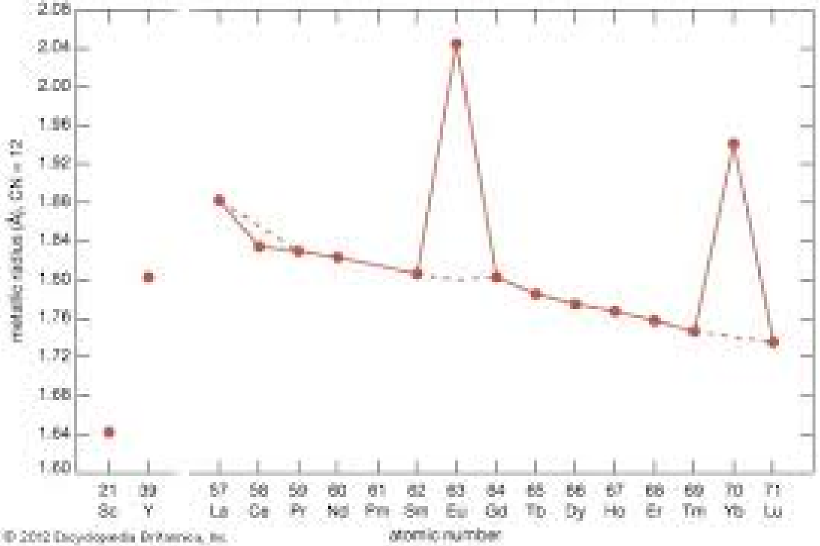
Russell-Saunders Coupling (J = L + S)
- spin-orbit coupling constants are large (ca. 1000 cm^{-1})
- ligand field effects are very small (ca. 100 cm^{-1})

– 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,……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

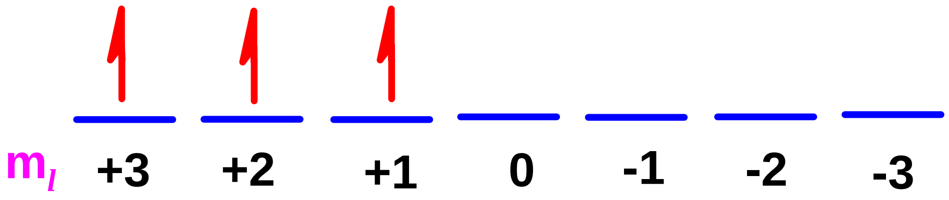
For the calculation of g value, use
minimum value of J for the configurations up to half-filled;
i.e. J = L − S for f^0 - f^7 configurations
maximum value of J for configurations more than half-filled;
i.e. J = L + S for f^8 - f^{14} configurations

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

Magnetic Properties of Lanthanides Ln^{3+}

					μ_{eff}	
	config	g.s.	No. e-	color	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

μ_{eff} of Nd^{3+} ($4f^3$)



$^{M}L_{J}$

Term symbol of electronic state

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

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

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

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

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

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

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

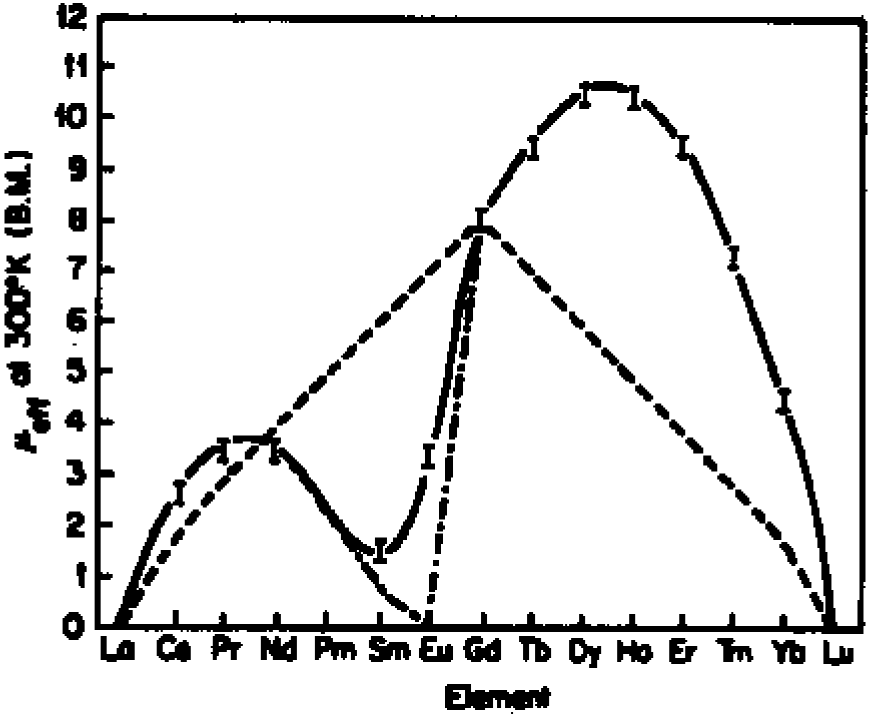
Total Angular Momentum **J** = (L + S), (L + S) - 1, …L - S = 6 , 5, 4
f^2 = less than half-filled sub-shell **-** choose minimum J → **J = 4**

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

μ_J = 3.577 B.M. Experiment = 3.4 - 3.6 B.M.

Magnetic Properties of Lanthanides Ln^{3+}

μ_{eff} at 300 K (B.M.)



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)

Van Vleck Equation

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

$M = N_A \Sigma \mu_n P_n$

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

P_n = probability in state n
N_n = population of state n
N_T = population of all the states

Van Vleck Equation

$$\boxed{M = N_A \frac{\sum_n \left(\frac{-\partial E_n}{\partial H}\right)\exp\left(-E_n/kT\right)}{\sum_n \exp\left(-E_n/kT\right)}}$$

Brillouin Function

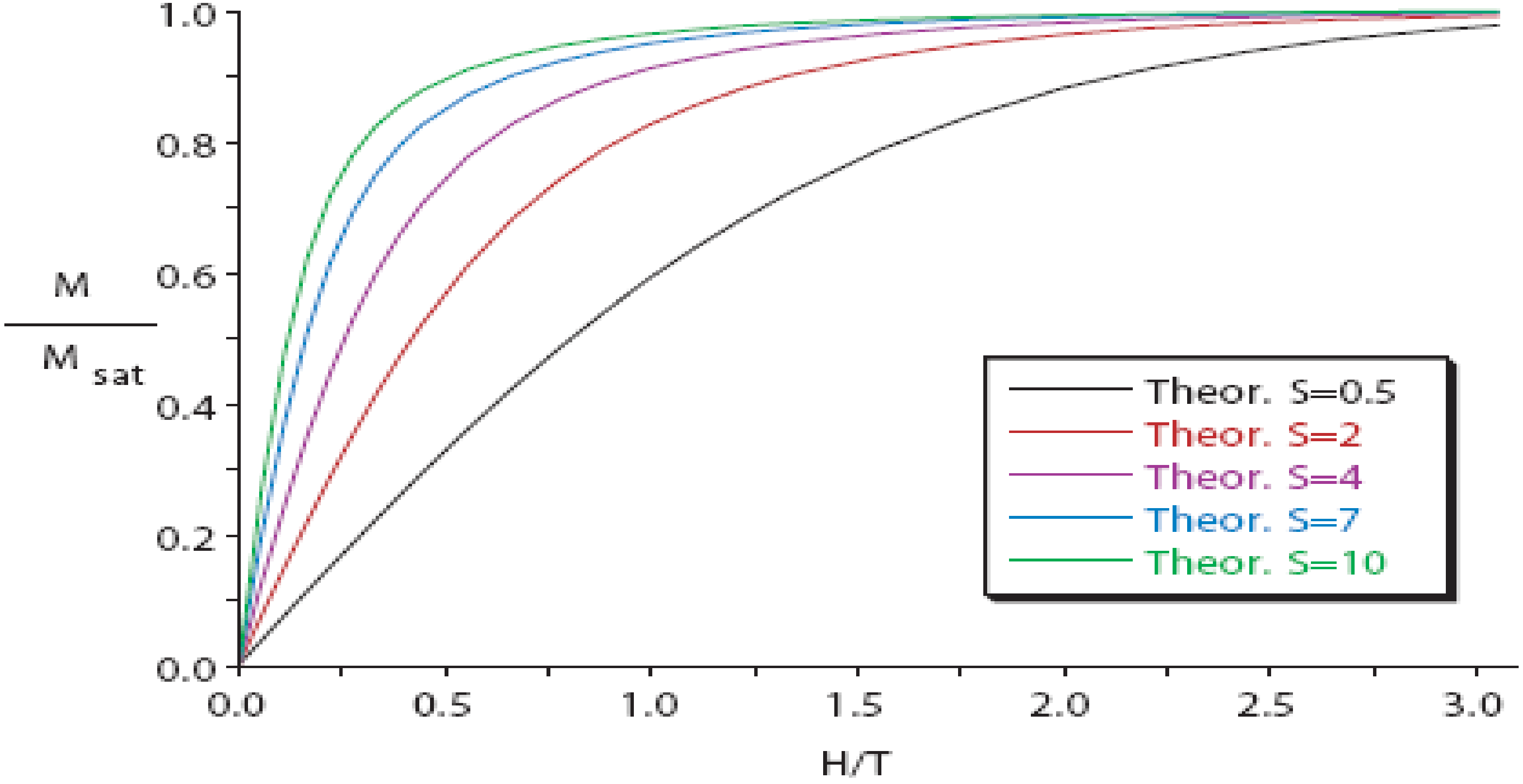
Many-electron systems 2J + 1 states, small energy gaps between states, populates according to Boltzman distribution

N_1 = Population of the lower level
N_2 = Population of the upper level

$$\frac{N_1}{N} = \frac{e^{\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} \qquad \frac{N_2}{N} = \frac{e^{-\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}}$$

$$M = (N_1 - N_2)\mu = N\mu \frac{e^{\mu B/kt} - e^{-\mu B/kT}}{e^{\mu B/kt} + e^{-\mu B/kT}} = N\mu \tanh(\mu B/kT)$$

Brillouin Functions for different S



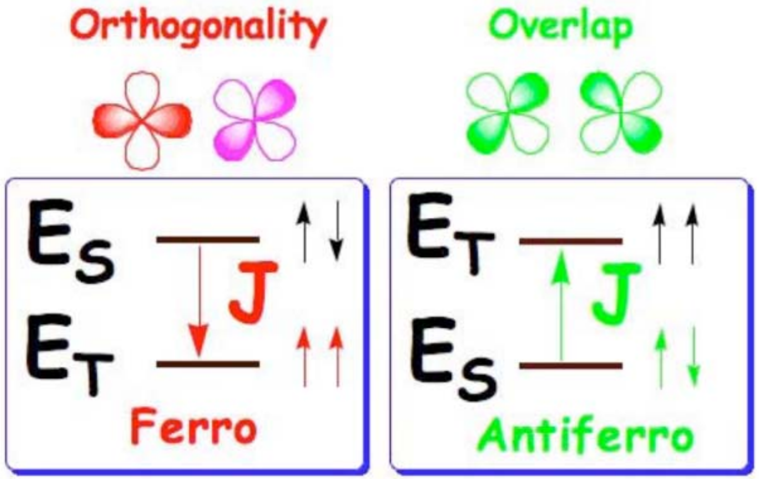
Spin Hamiltonian in Cooperative Systems

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

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

J = the magnitude of the coupling

J > 0

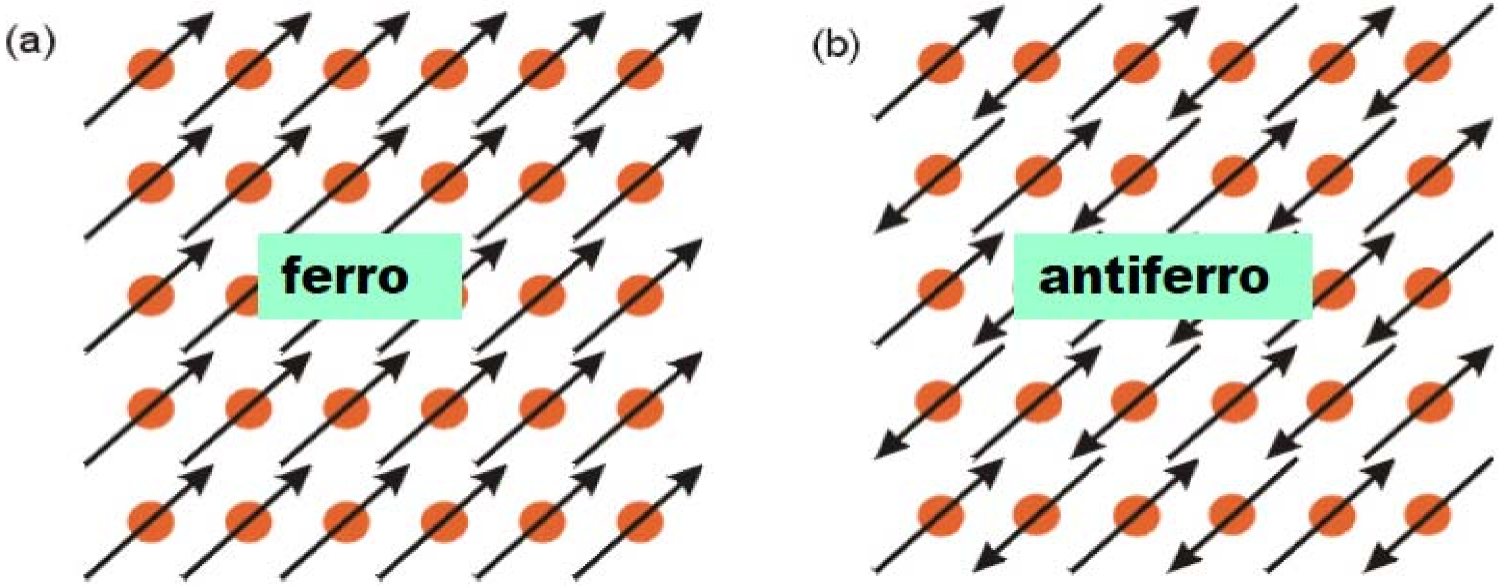


J < 0

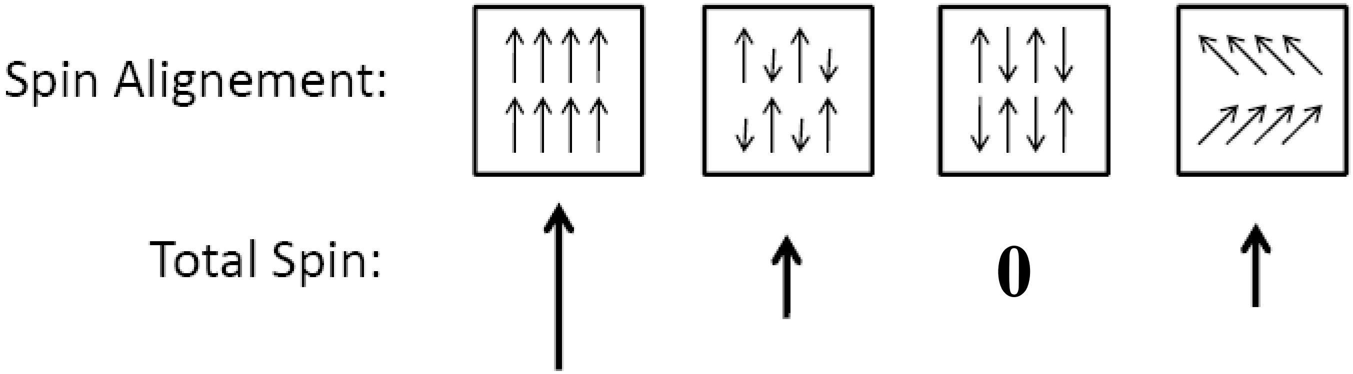
Magnetism in Solids
Cooperative Magnetism

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.



Magnetic Ordering



Spin Alignement:

Total Spin:

0

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

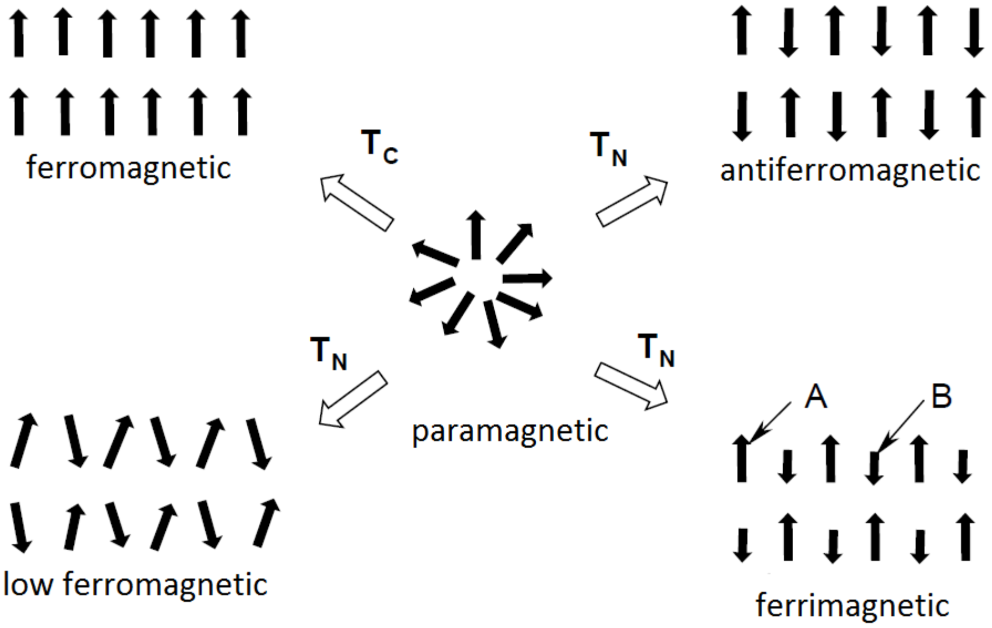
Spin glasses – spins are correlated but not long-range ordered

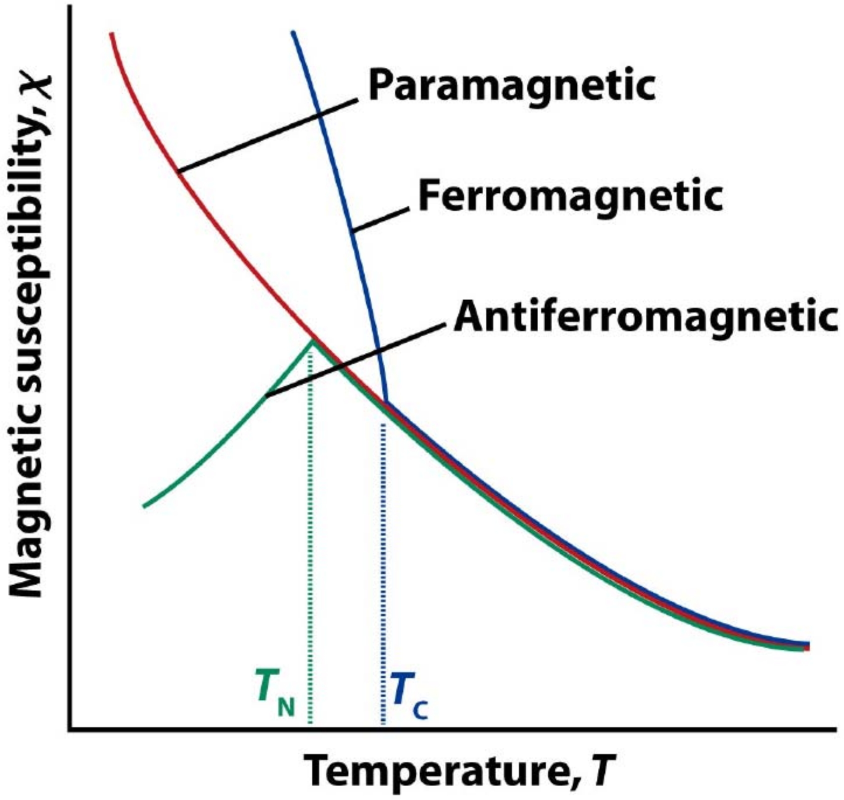
Metamagnets

Magnetic Ordering

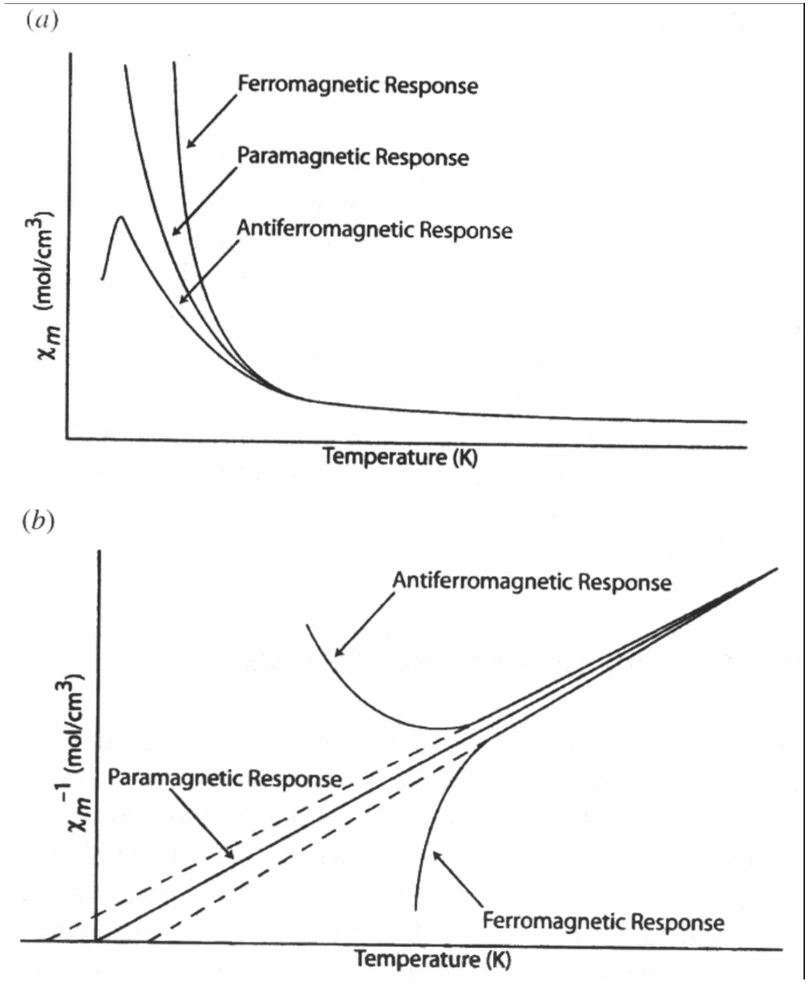
Critical temperature – **under** T_{crit} the magnetic coupling energy between spins is bigger than thermal energy resulting in spin ordering

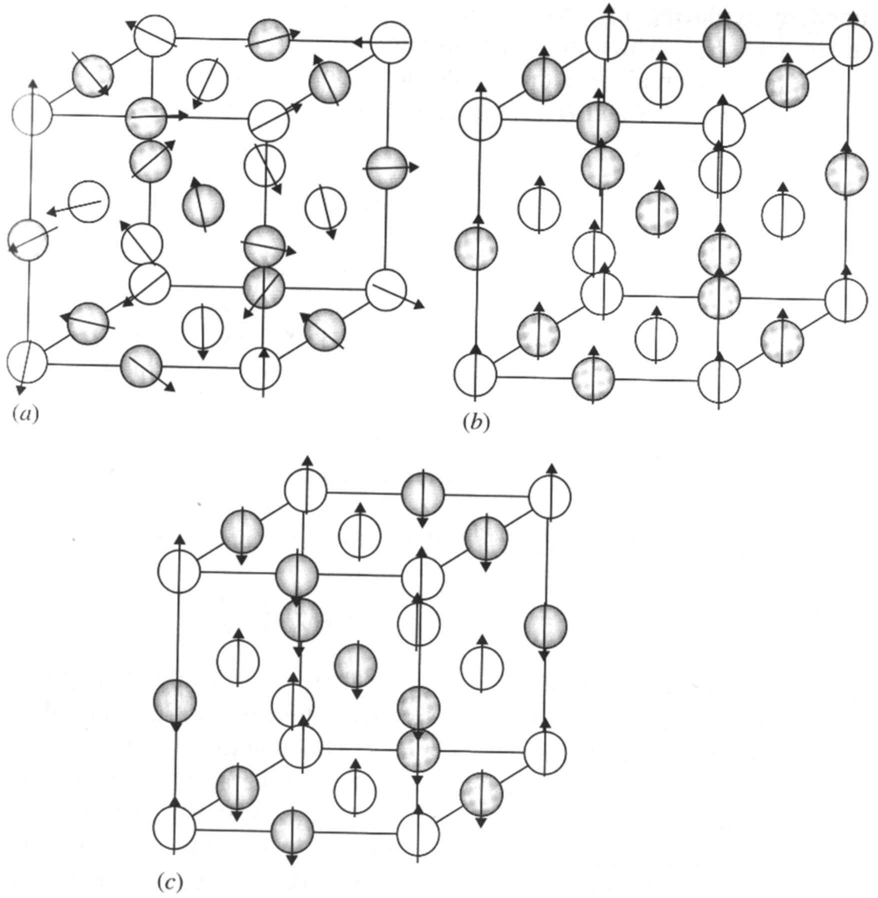
T_C = Curie temperature
T_N = Neel temperature





Para-, Ferro-, Antiferromagnetic





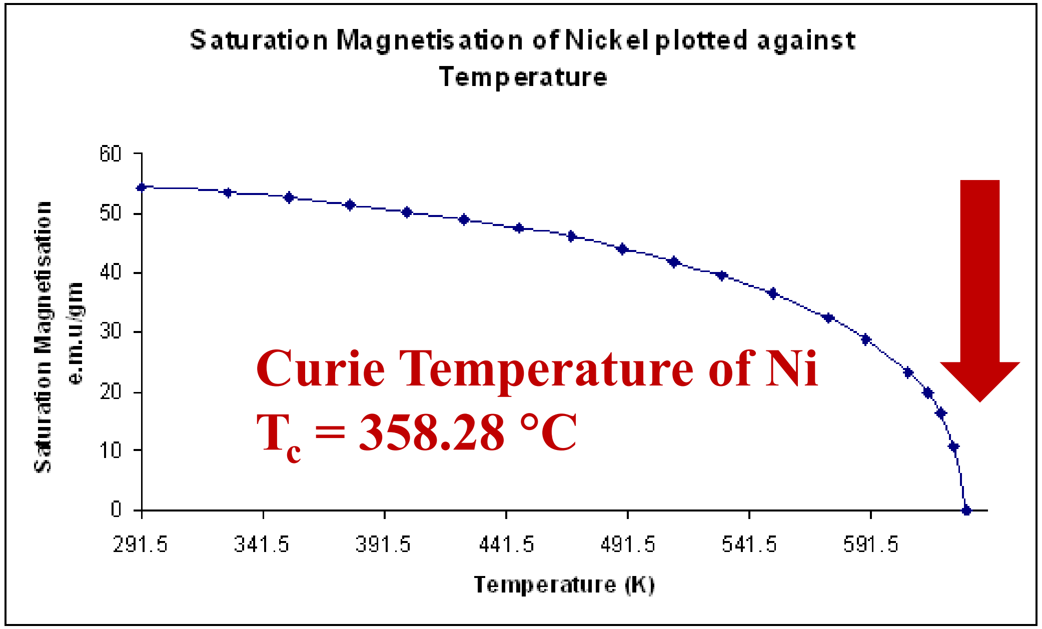
Curie Temperature

1832, Pouillet
nickel, iron and cobalt
Observed a limit for the
temperature of magnetism

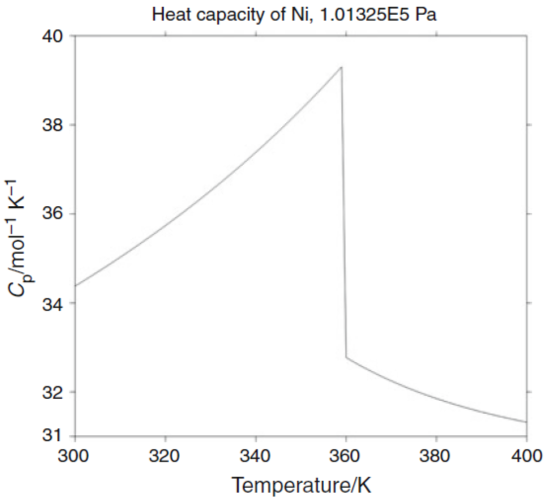
1895 Curie
a transition from
ferromagnetic to
paramagnetic

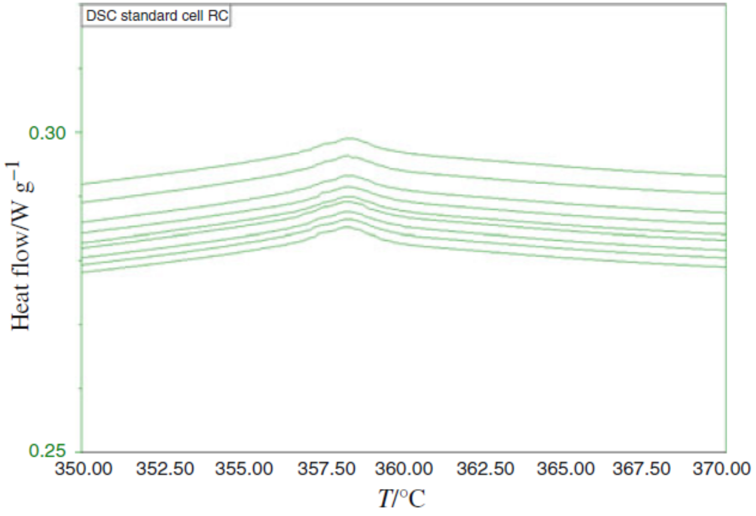
A second order transition
Lambda shape of the C_p
versus T
a maximum
= the Curie point

not associated with an
enthalpy change



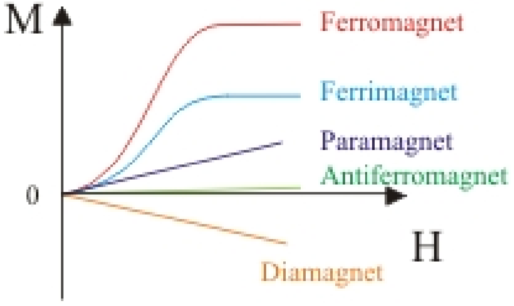
Curie Temperature of Ni
T_c = 358.28 °C



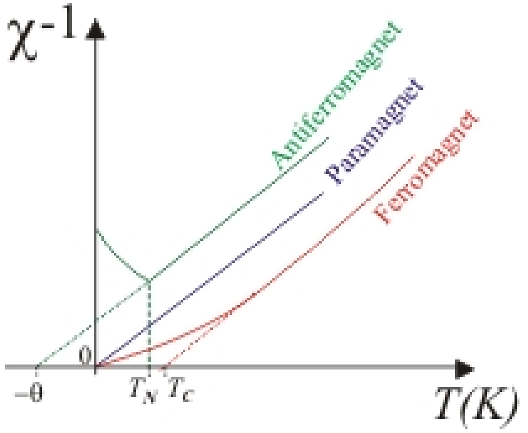


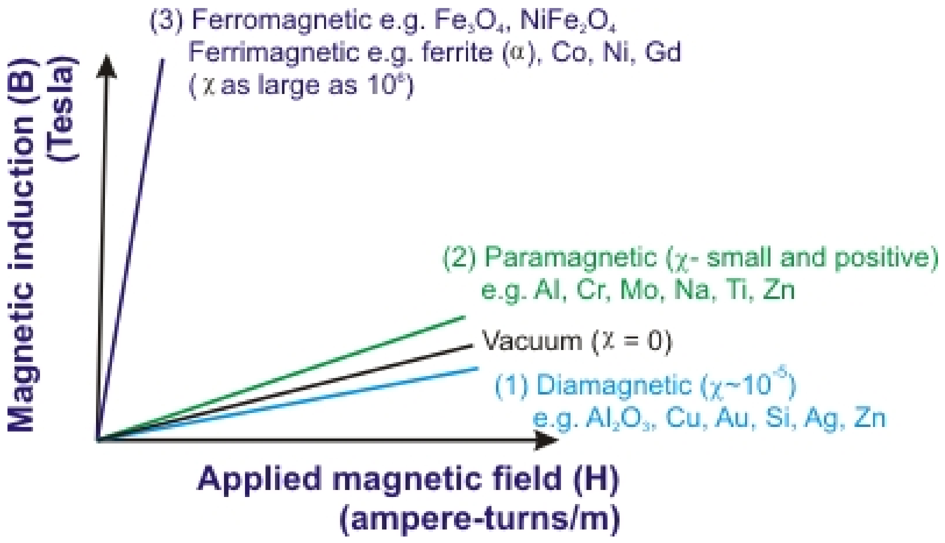
Magnetic Ordering

Comparison of M-H Behaviour

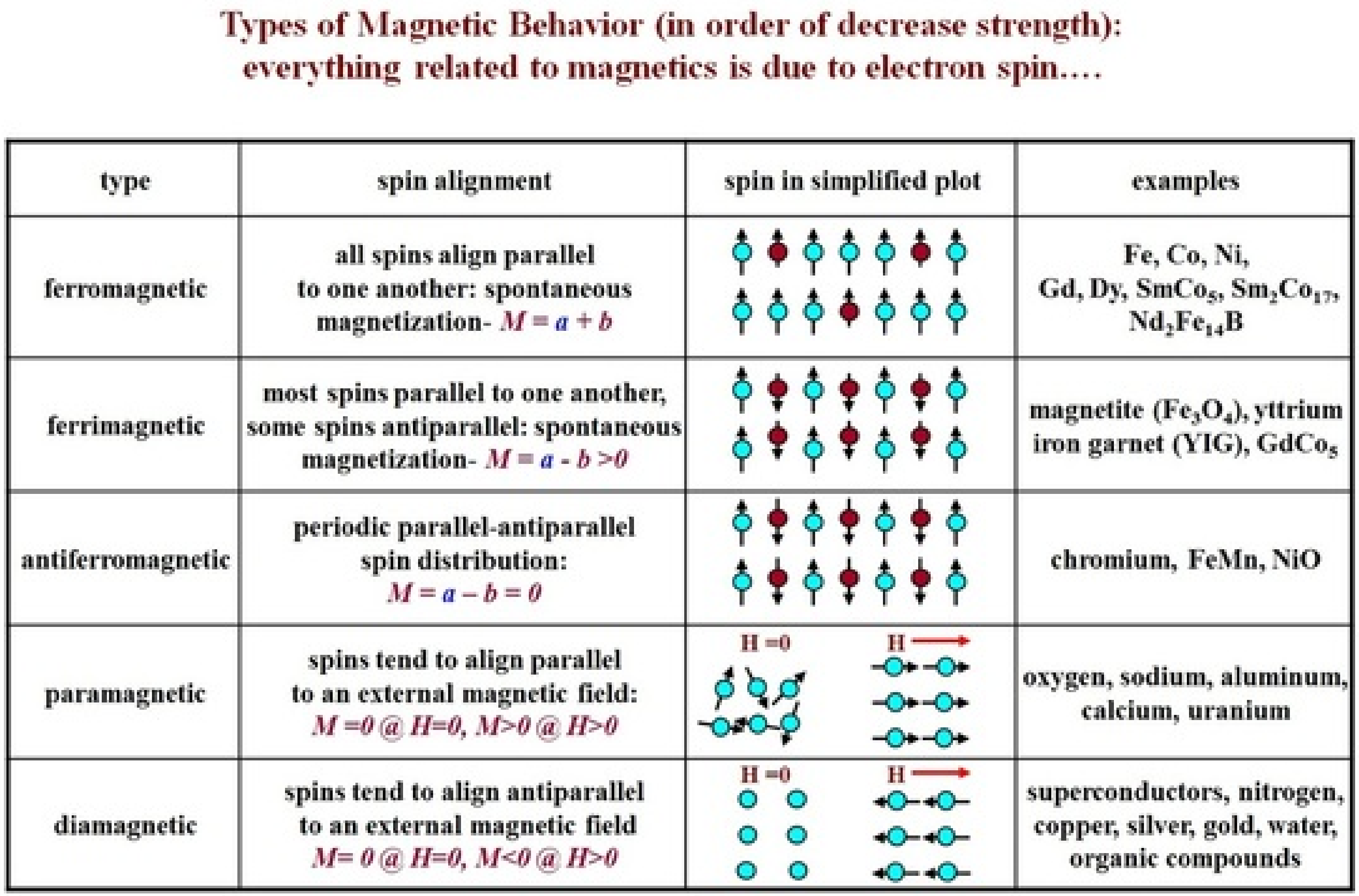


Comparison of Susceptibility vs Temperature Behaviour





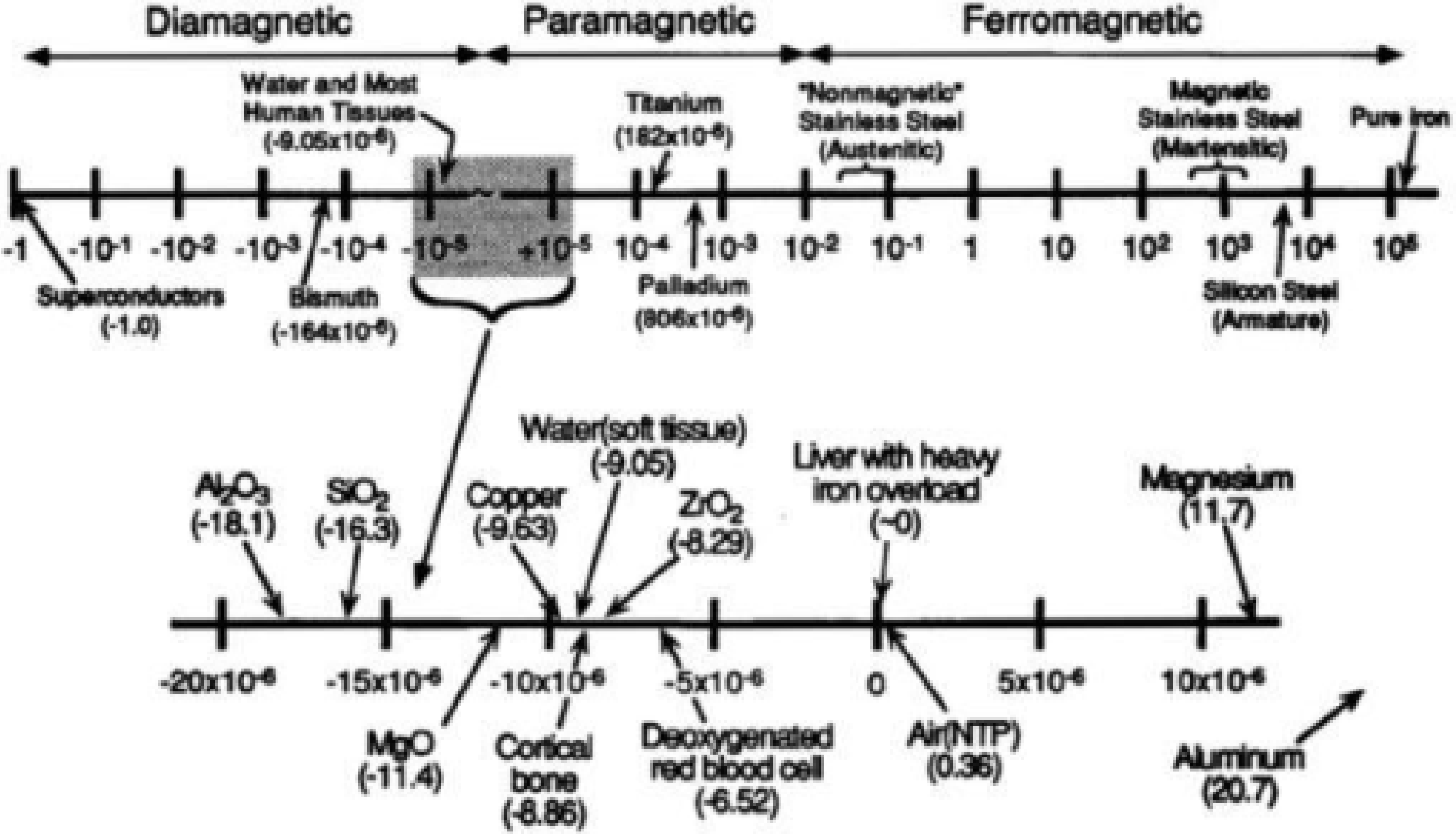
Magnetic Ordering



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$_2$Co$_{17}$, Nd$_2$Fe$_{14}$B
ferrimagnetic	most spins parallel to one another, some spins antiparallel: spontaneous magnetization- $M = a - b > 0$		magnetite (Fe$_3$O$_4$), 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

Para-, Ferro-, Antiferromagnetic Ordering

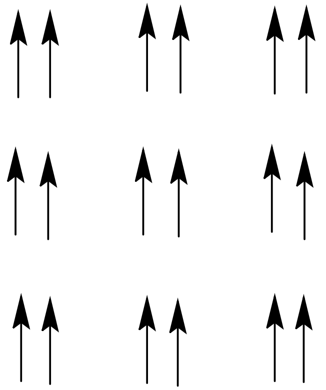


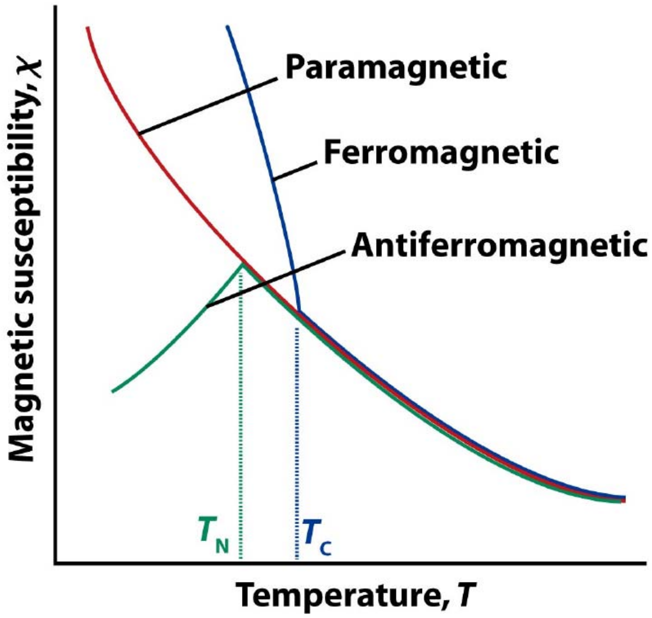
Ferromagnetism

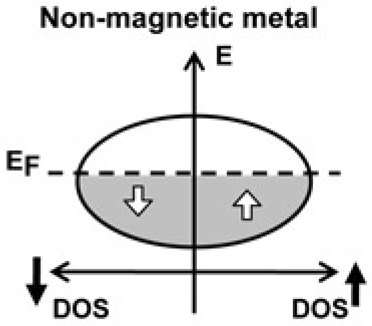
J positive with spins parallel below T_c

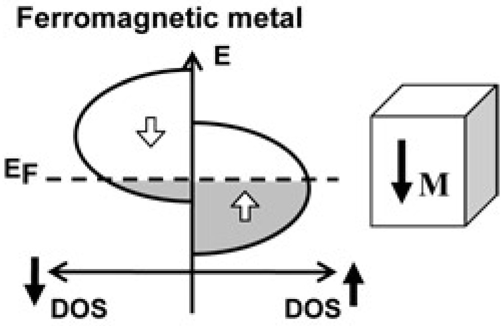
a spontaneous permanent M (in absence of H)

T_c = Curie Temperature, above T_c = paramagnet



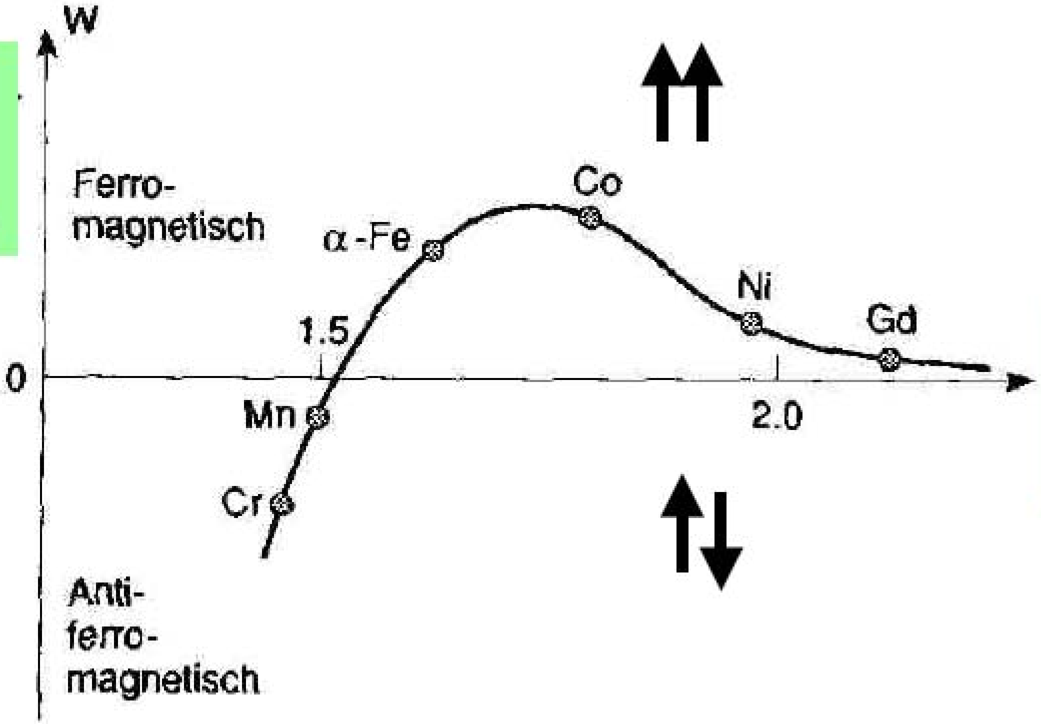






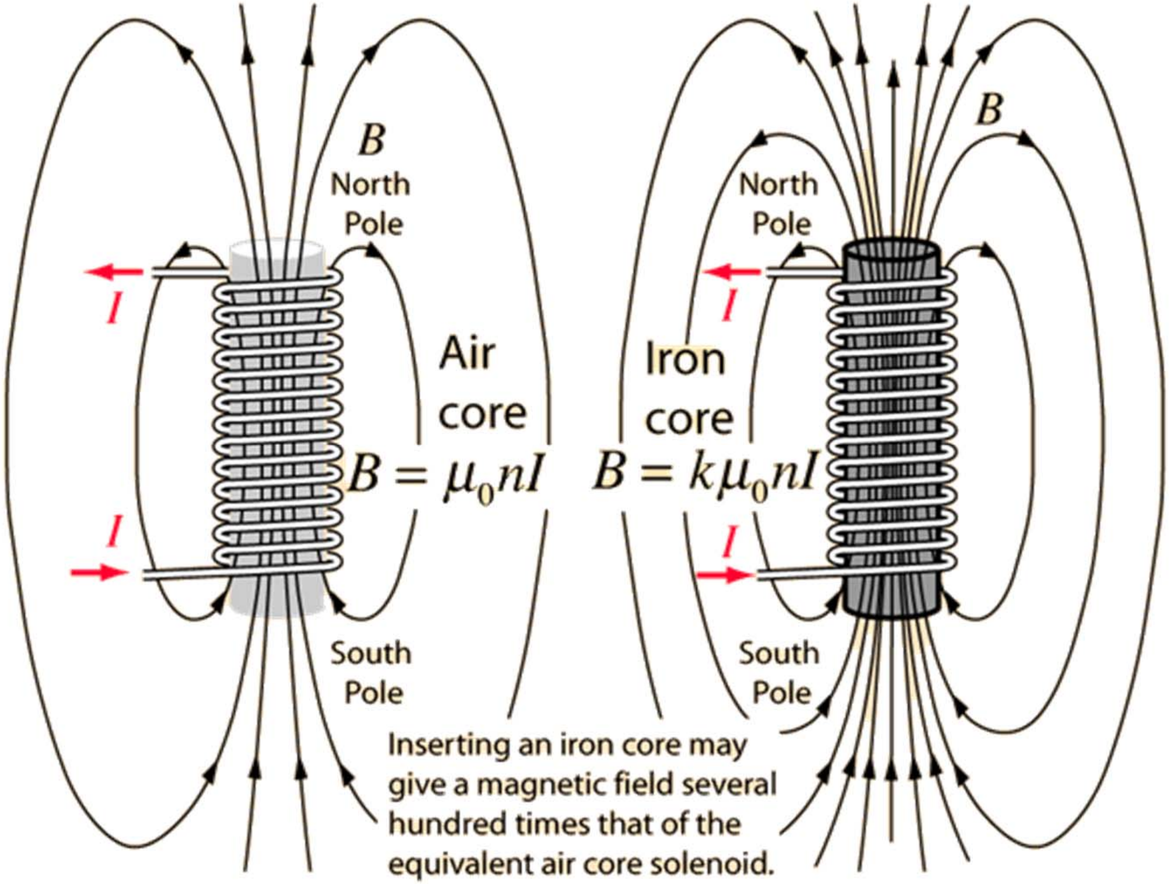
Ferromagnetism

calculated exchange interaction



interatomic distances/radius of 3d orbitals

Ferromagnetism

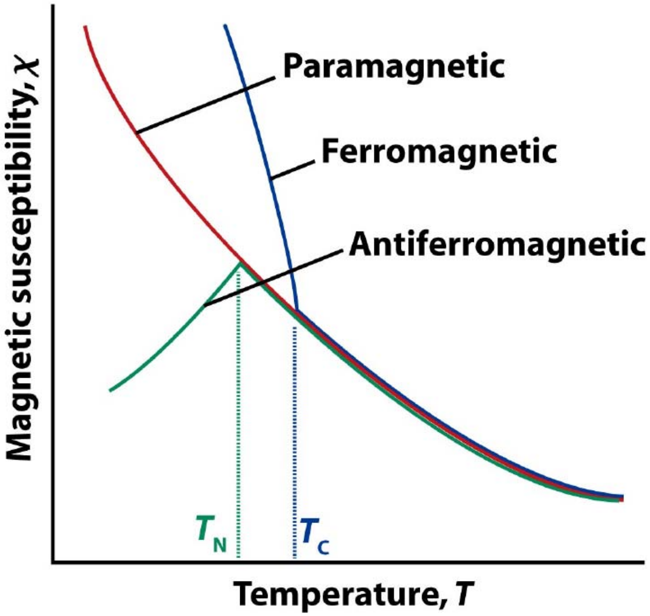


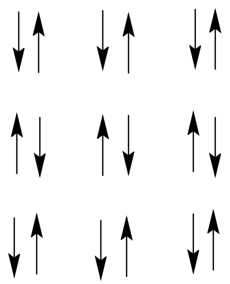
Antiferromagnetism

J negative with spins antiparallel below T_N

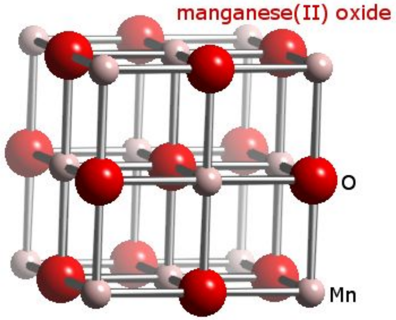
no spontaneous M, no permanent M

critical temperature: T_N (Neel Temperature), above T_N = paramagnet





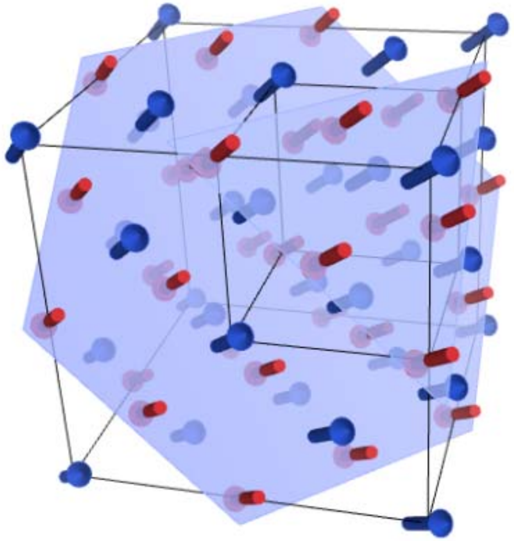
Neutron Diffraction

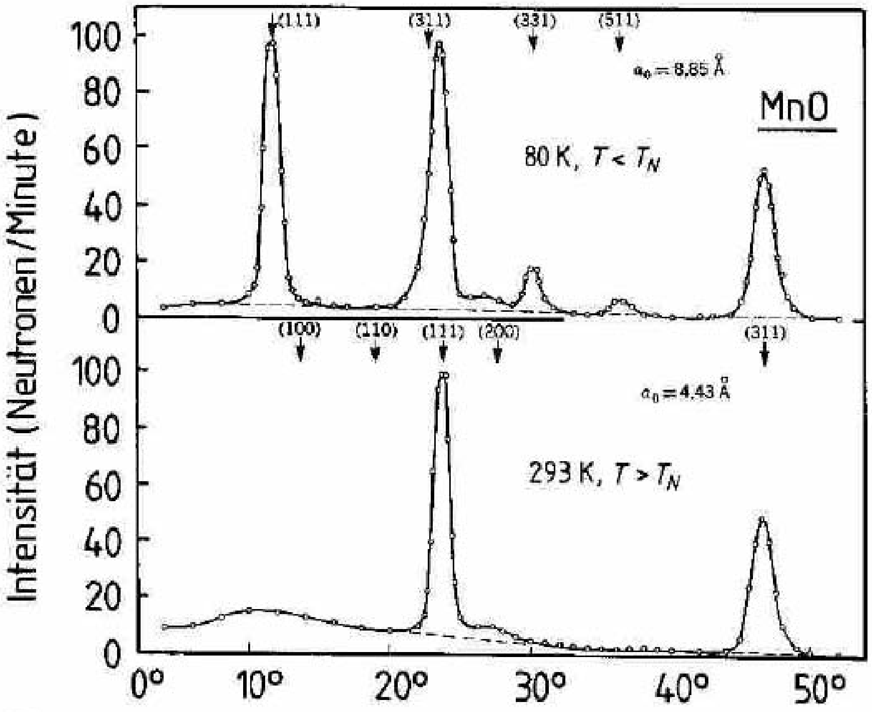


Single crystal may be anisotropic

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: $\lambda = h/m_n v_n$ (requires neutron radiation of a nuclear reactor)





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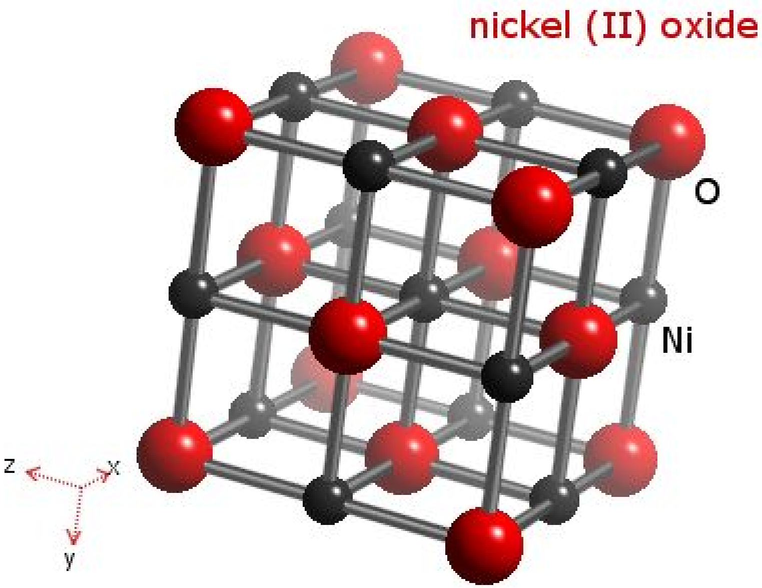
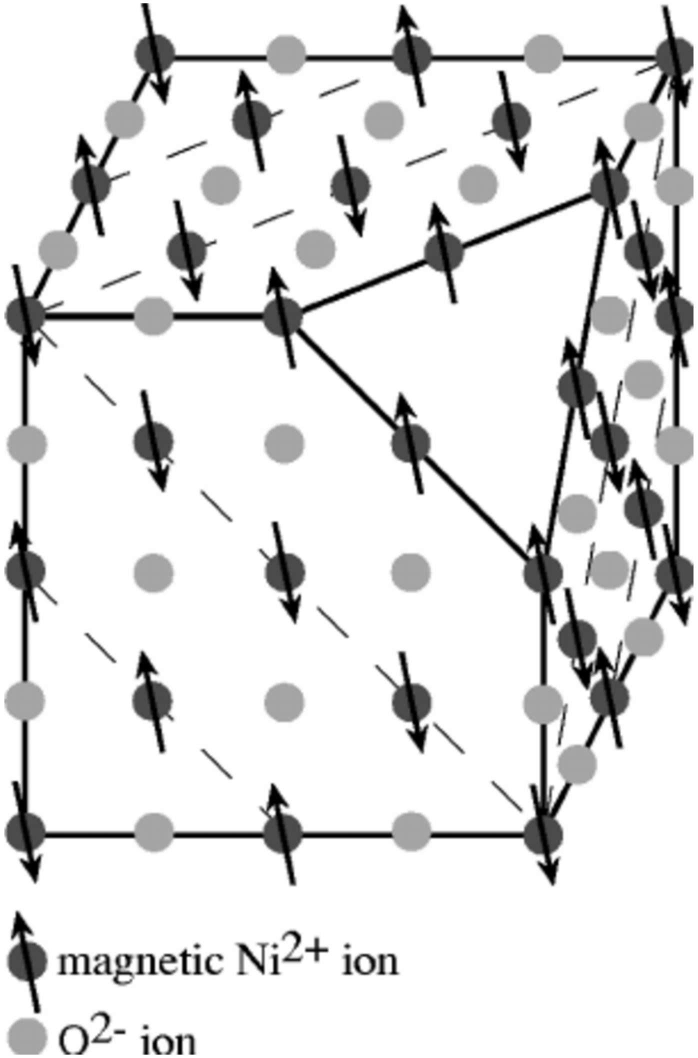




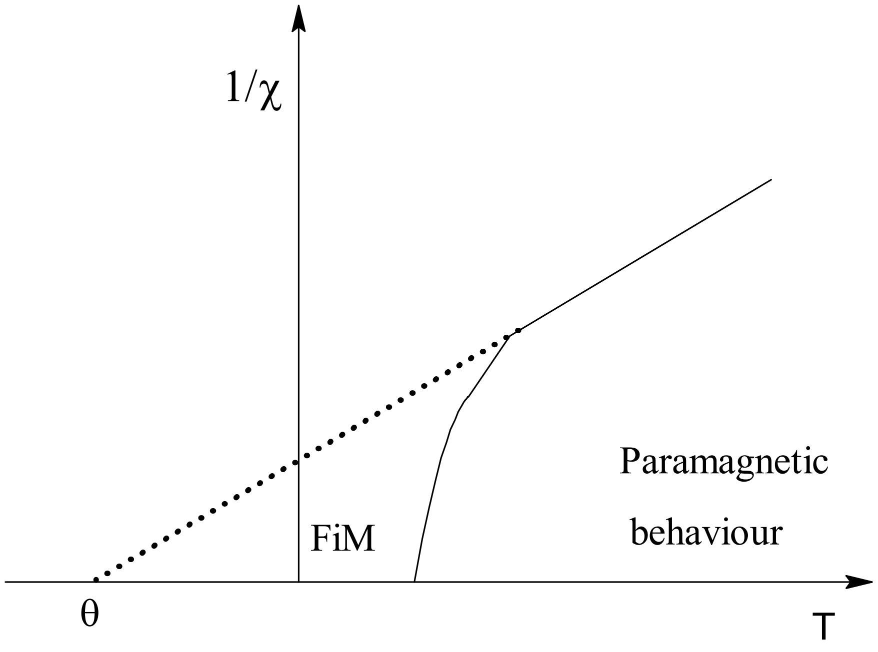
Ferrimagnetism

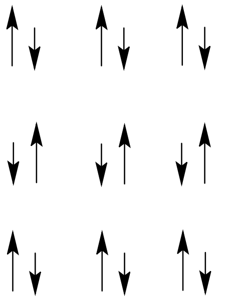
J negative with spins of unequal magnitude antiparallel below critical T

requires two chemically distinct species with different moments coupled antiferomagnetically:

no M; critical T = T_C (Curie Temperature)

bulk behavior very similar to ferromagnetism, Magnetite is a ferrimagnet





Ferromagnetism

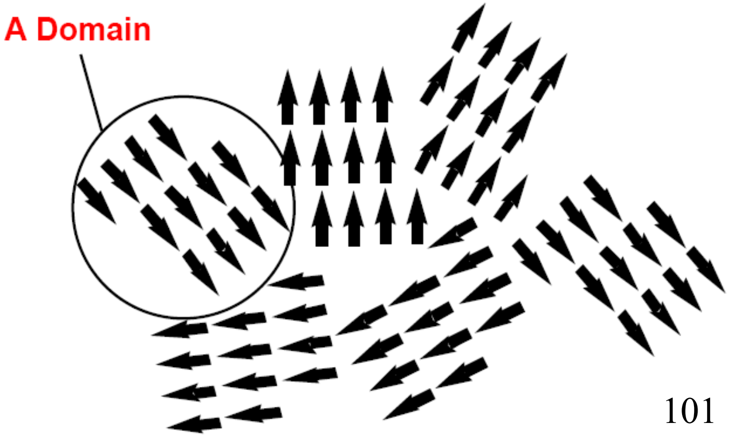
Ferromagnetic elements: Fe, Co, Ni, Gd (below 16 °C), Dy

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

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**

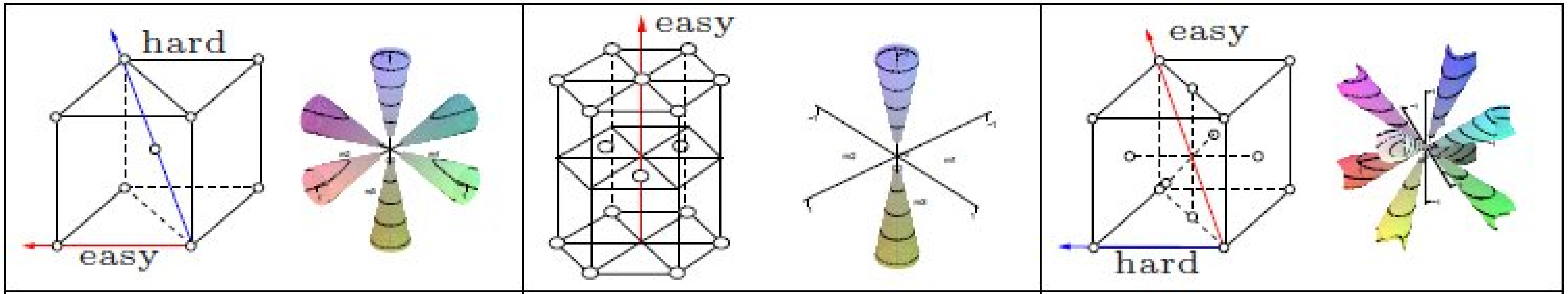


Magnetic Anisotropy

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



6 directions

2 directions

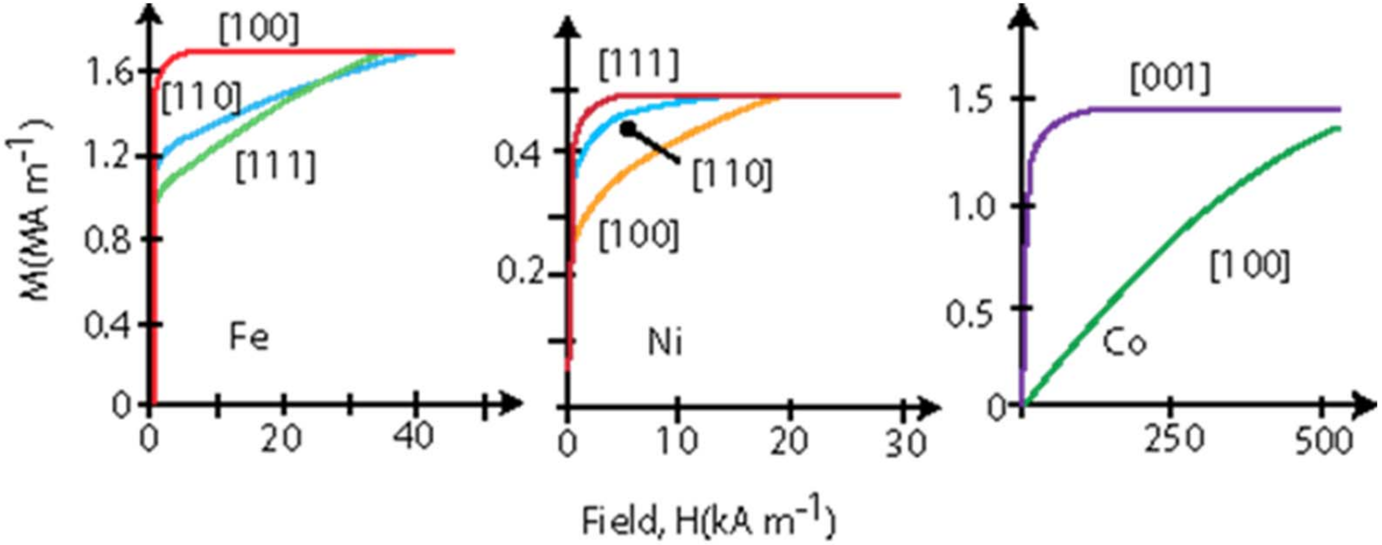
8 directions

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.



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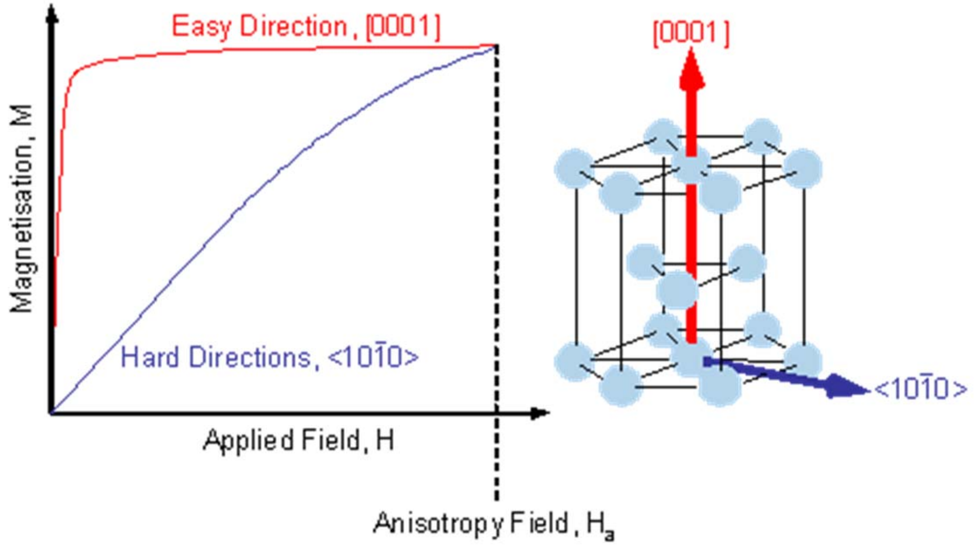
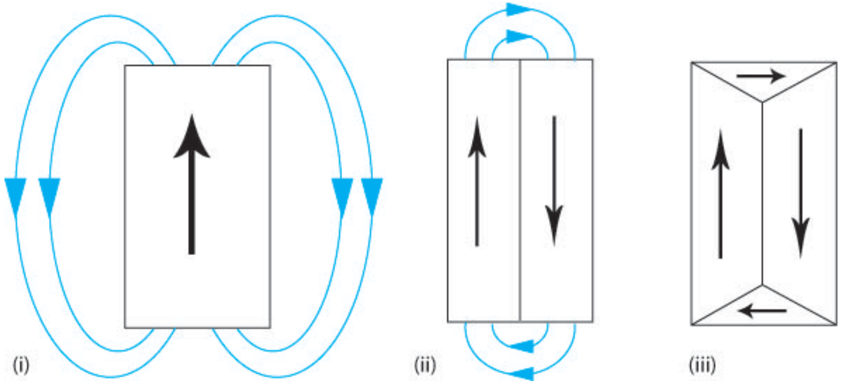


Magnetostatic Energy

A single domain behaves as a block magnet and 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)

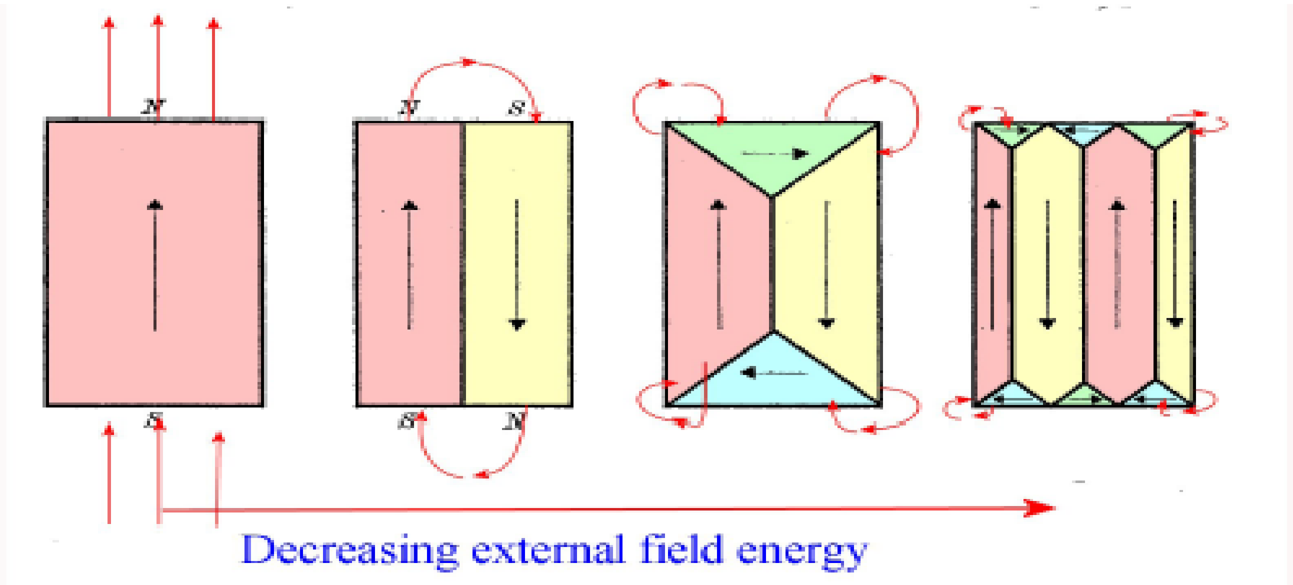
Minimise the total magnetic energy - the magnetostatic energy must be minimised - decreasing the external demagnetising field by dividing the material into domains

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

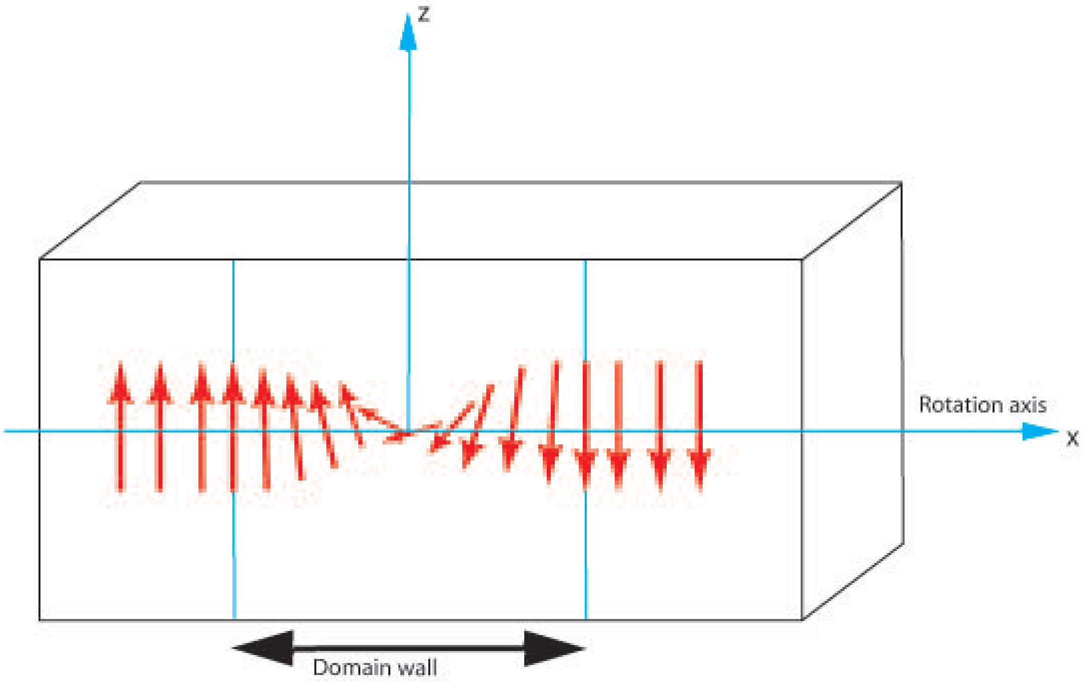
Application of H causes aligned domains to grow at the expense of misaligned

Alignment persists when H is removed

Domain Walls

A domain wall 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

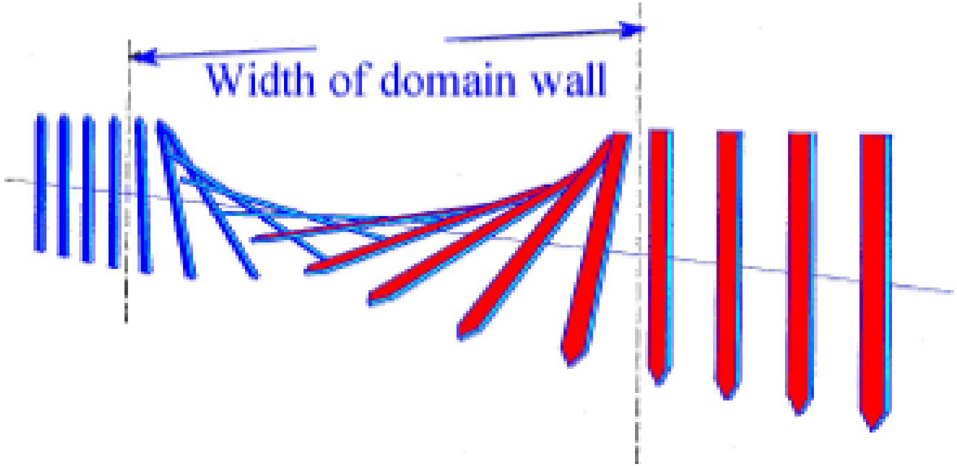


Domain Walls

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 is: $E = K \sin^2\theta$, where 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

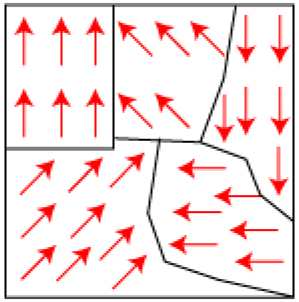
180° domain wall 90° domain wall

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

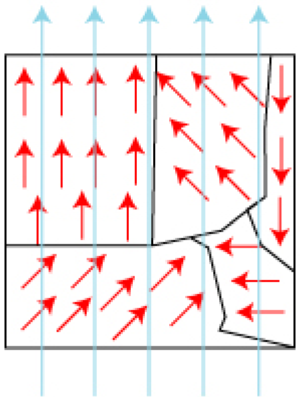
Depends on crystallografic structure of ferromagnet (number of easy axes)

One easy axis = 180° DW (hexagonal Co)
Three easy axes = both180° and 90° DW (bcc-Fe, 100)
Four easy axes = 180°, 109°, and 71° DW (fcc-Ni, 111)

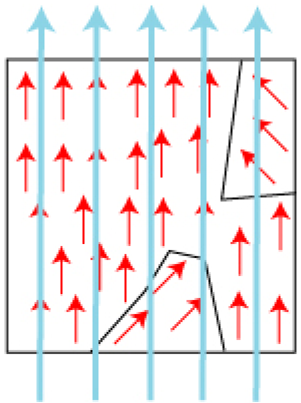
Domain Wall Motion



no field



some field

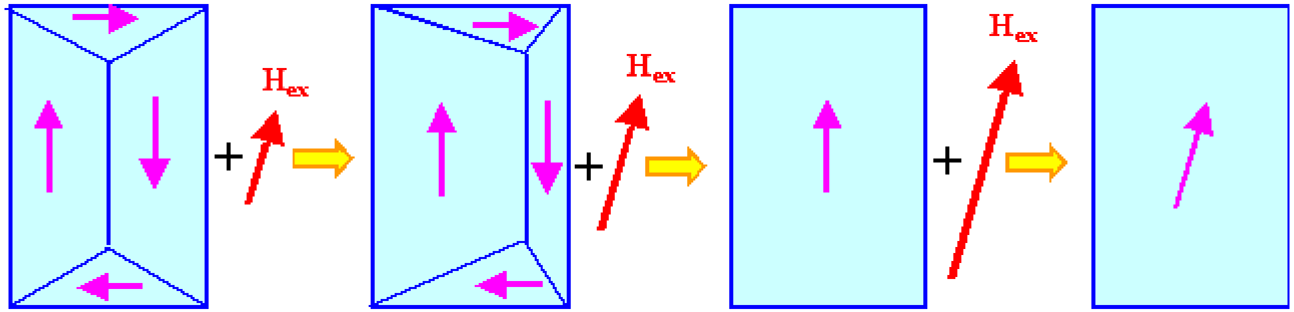


strong field

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

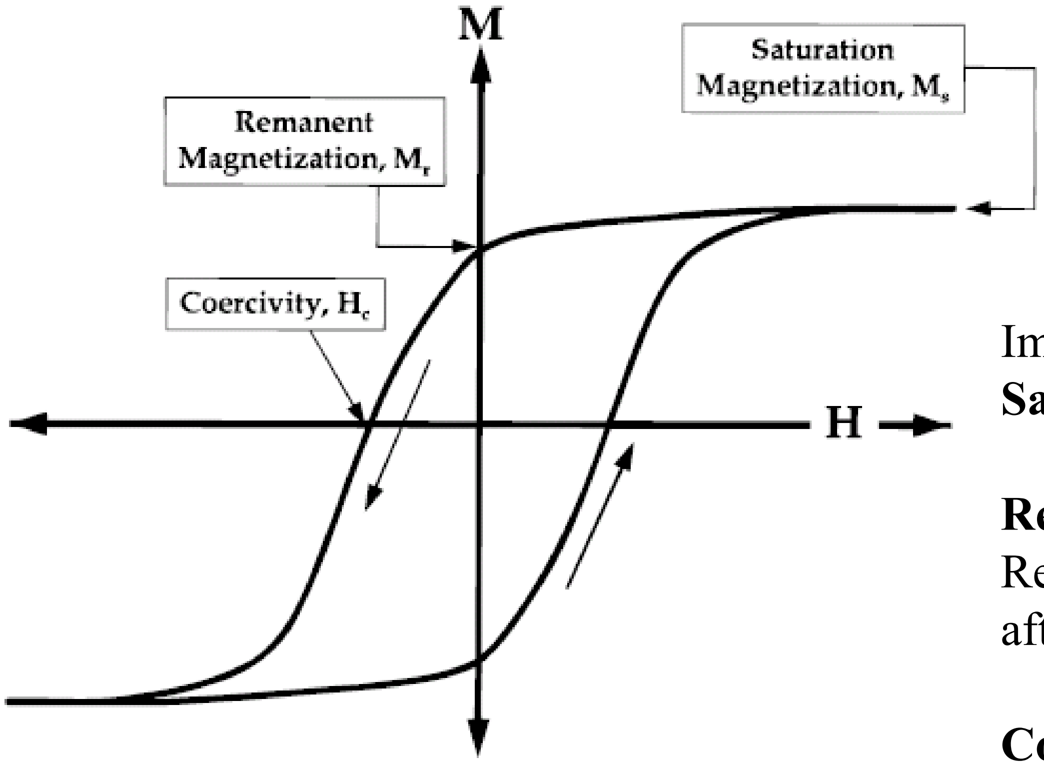
Volume of domains favorably oriented wrt H increases, M increases

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



Magnetic Hysteresis Loop

$$\boxed{\mathbf{M}_{\mathrm{sat}} = \mathrm{N}g\mu_{\mathrm{B}}\mathrm{S}}$$



$$\boxed{\mathbf{M} = \chi\mathbf{H}_{\mathrm{app}}}$$

Important parameters

Saturation magnetization, M_{sat}

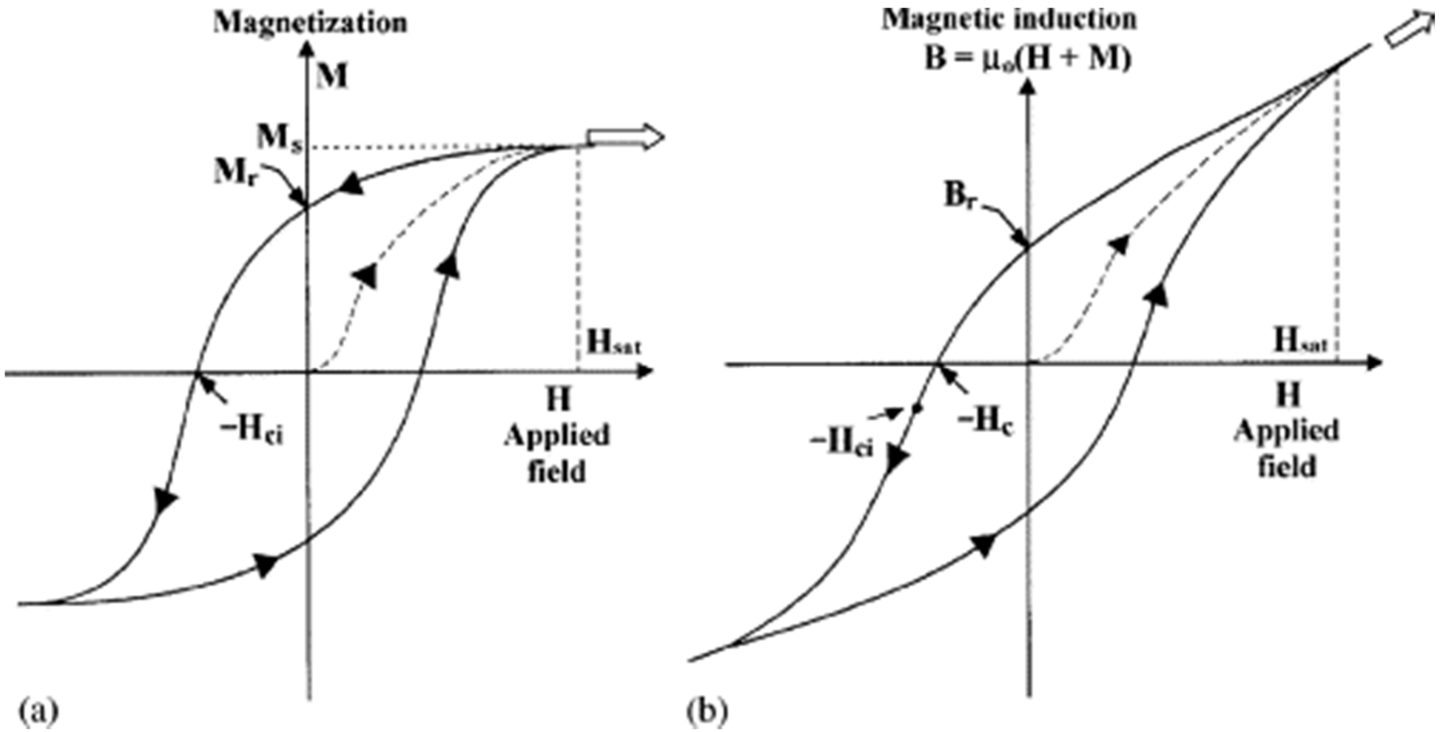
Remanent magnetization, M_r

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



Saturation magnetization, M_{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

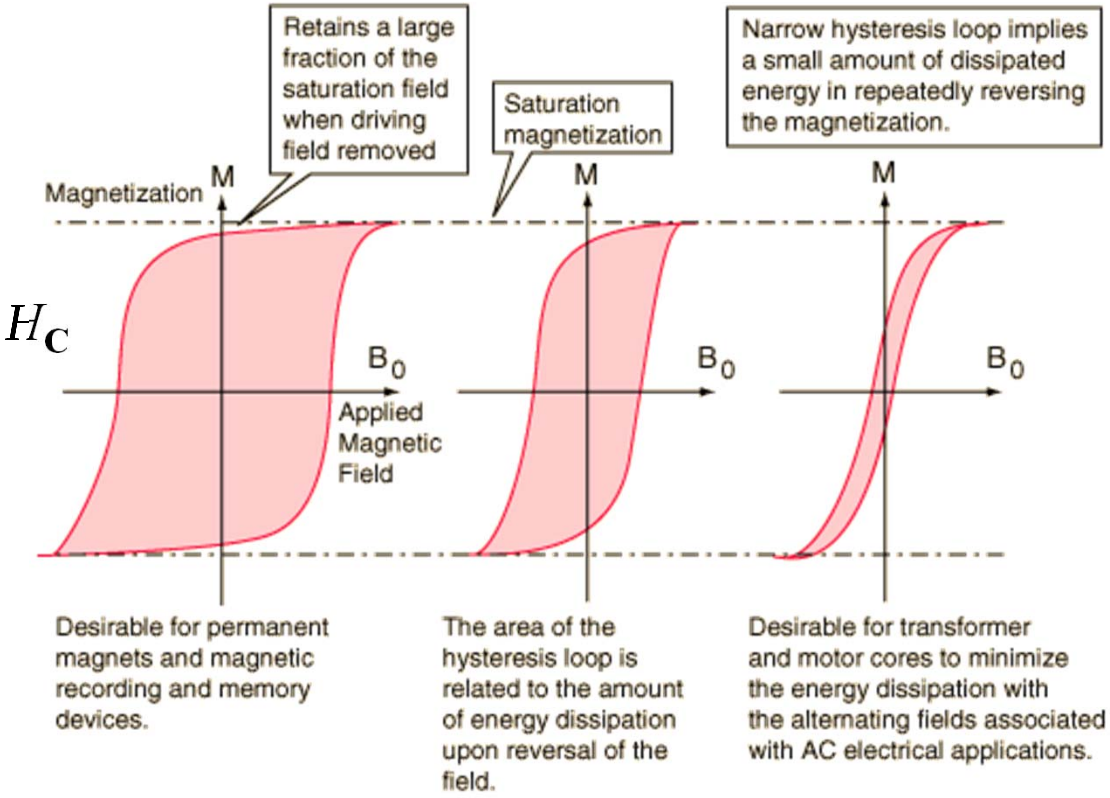
- High M_{sat}, Low M_R, and Low H_C

Magnetic Recording Materials

- High M_r and High H_C

Permanent Magnets

- High M_r and High H_C



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

Saturation magnetization

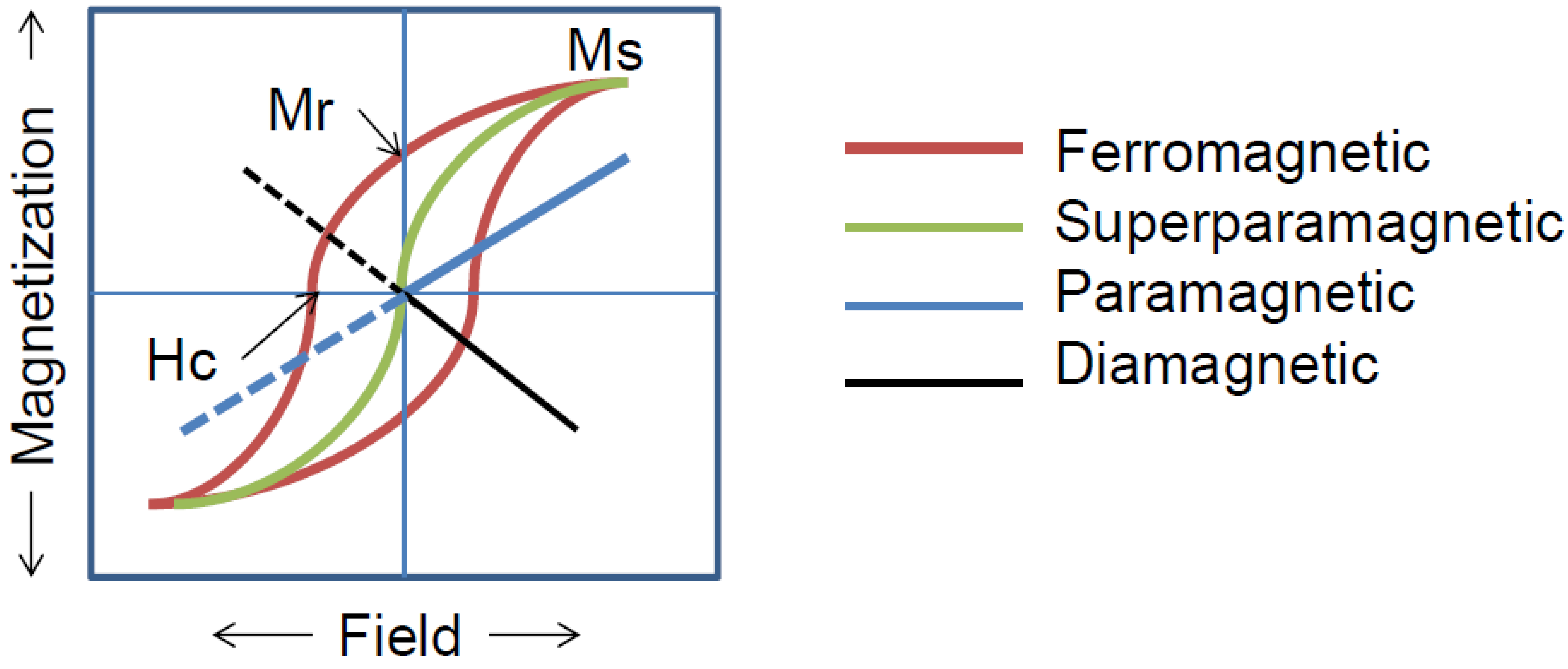
Narrow hysteresis loop implies a small amount of dissipated energy in repeatedly reversing the magnetization.

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



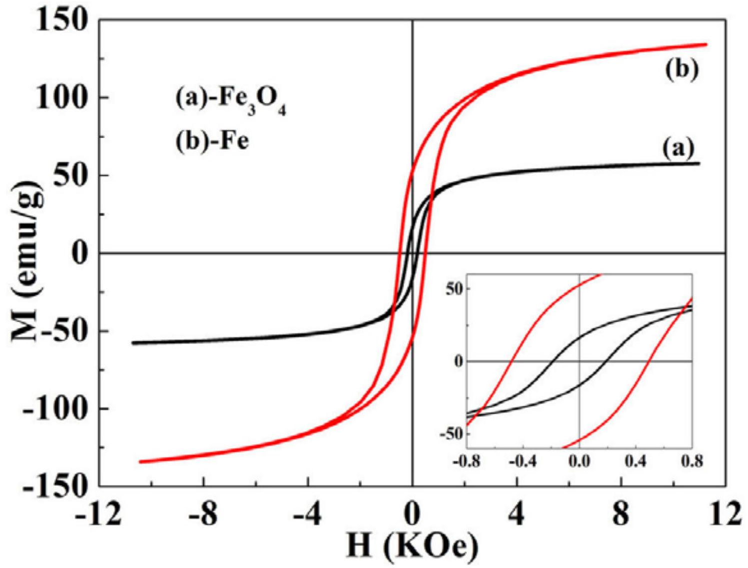
Single-Molecule Magnets (SMM)

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)

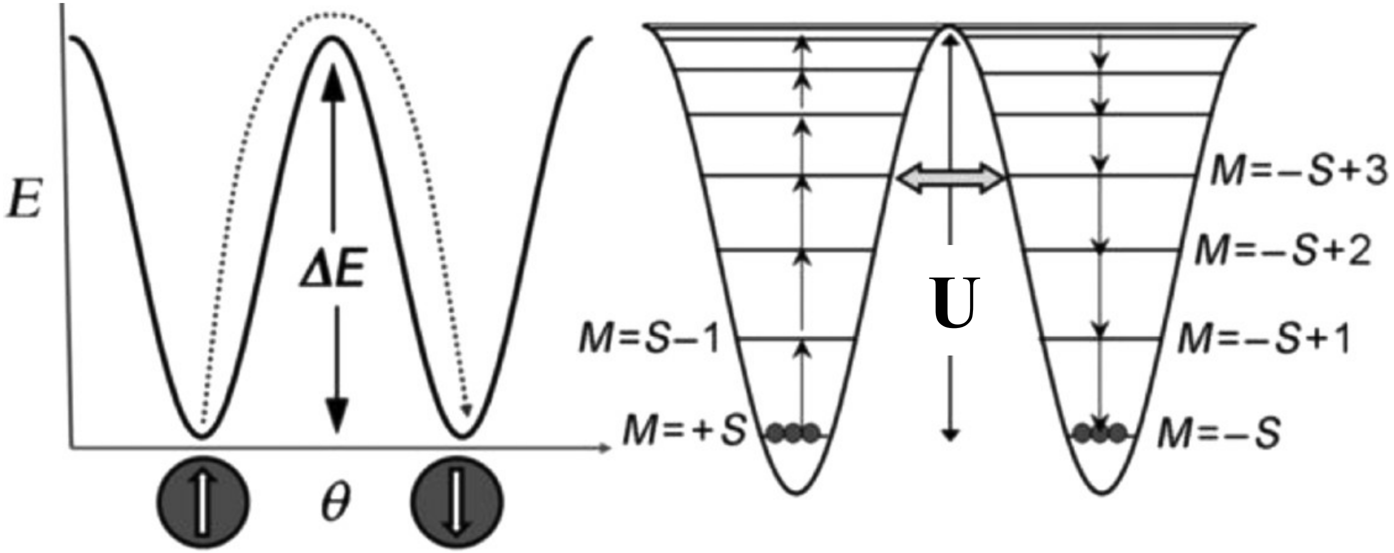
Single-molecule magnet

= individual molecules, magnetically isolated and non-interacting, no domain walls

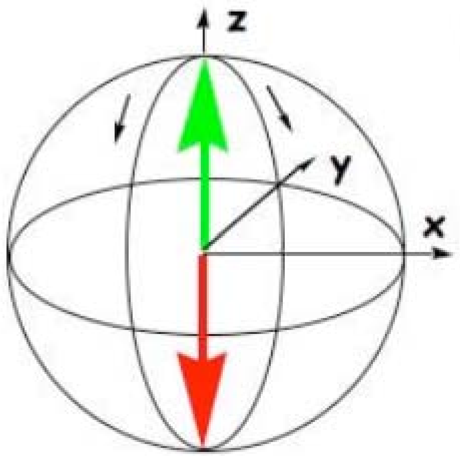
Hysteresis in M vs H plots **at very low temperatures**

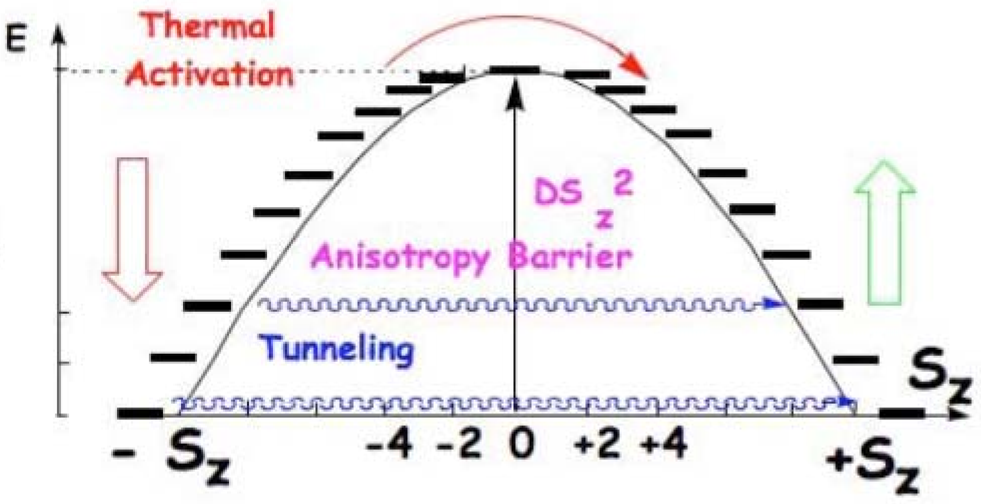
Magnetisation is retained for relatively long periods of time at very low temperatures after removal of the field because there is an energy barrier U to spin reversal (1.44 K = 1 cm^{-1} = 1.986 10^{-23} J)

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)

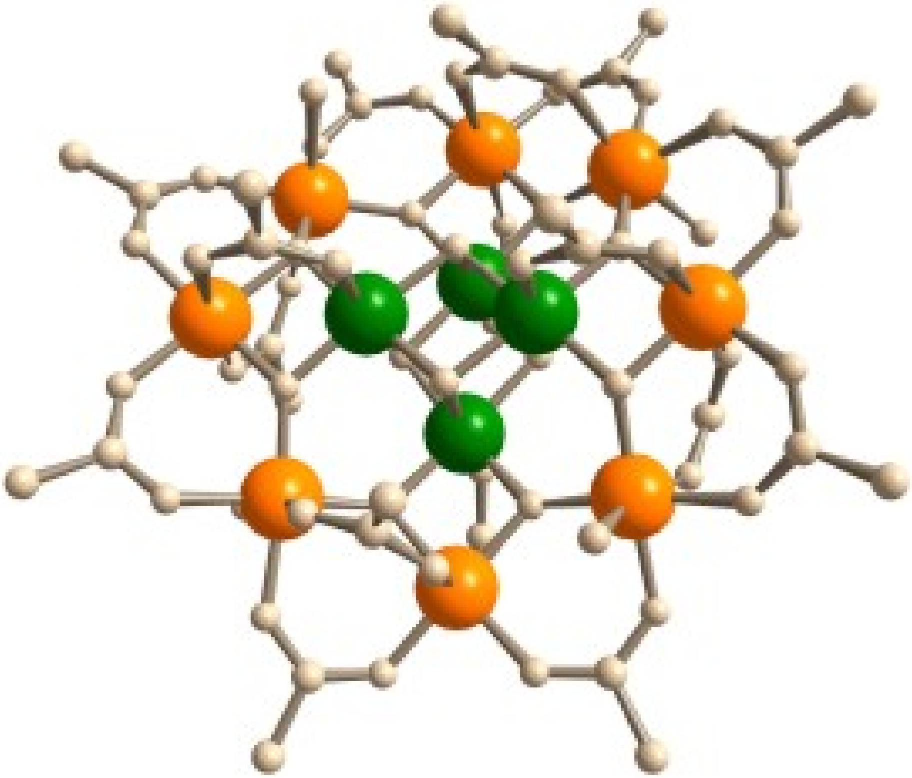




The First SMM: Mn12

Some discrete molecules can behave at low temperature as tiny magnets

$[Mn_{12}O_{16}(CH_3COO)_{16}(H_2O)_4]\mathbf{.}4H_2O\mathbf{.}2CH_3COOH$

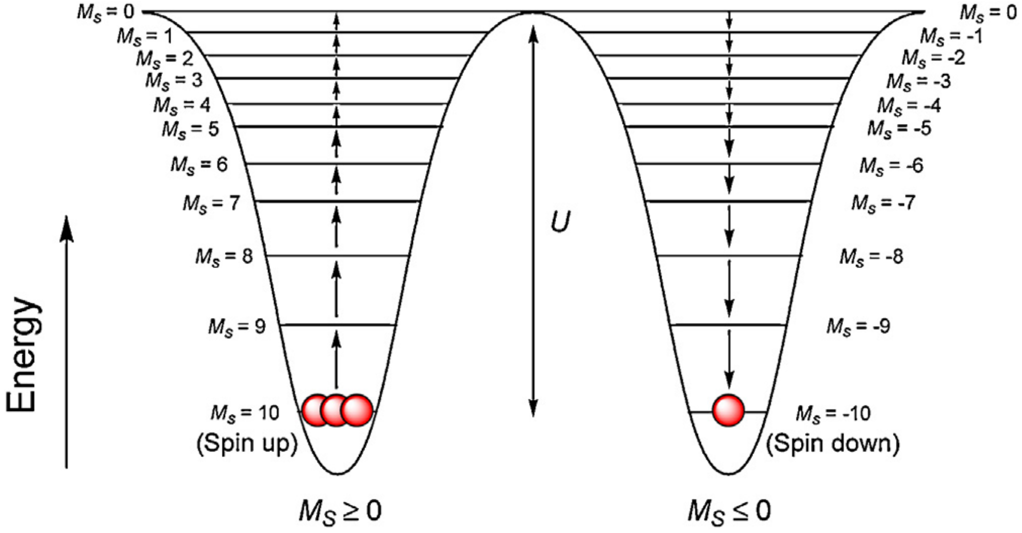


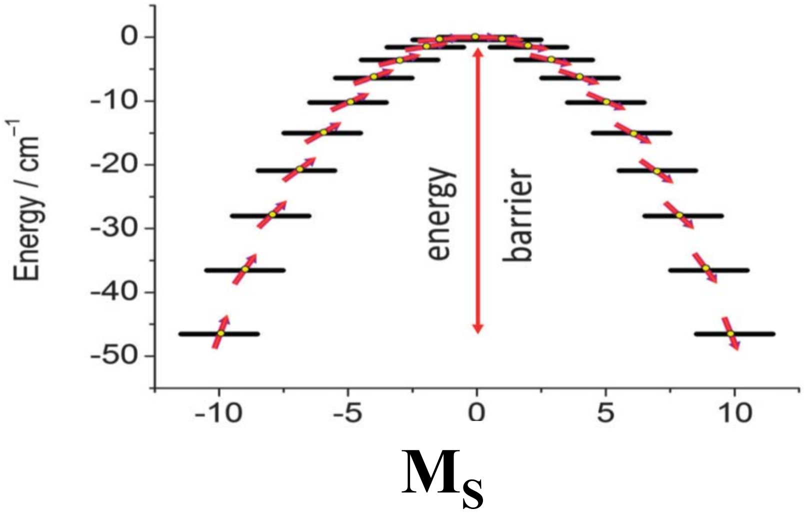
$S = 8 \times 2 - 4 \times 3/2 = 10$

Antiferromagnetic coupling

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

Mn12 Spin Ladder





U = anisotropy energy barrier

$|\mathbf{D}| \times \mathbf{S}^2$ for integer spins

$|\mathbf{D}| \times (\mathbf{S}^2 - 1/4)$ for non-integer spins

D = the axial zero-field splitting (ZFS) parameter
S = the spin ground state of the molecule

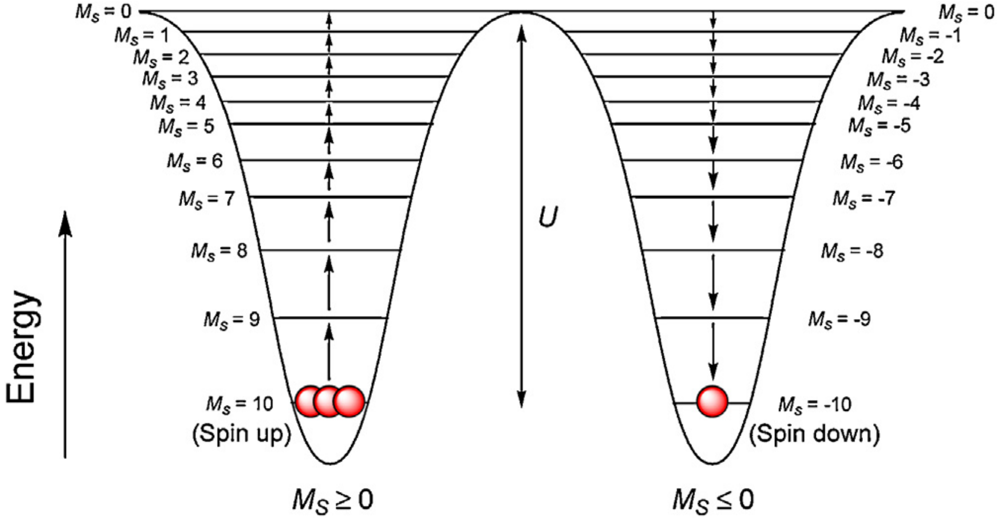
Single-Molecule Magnets (SMM)

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;

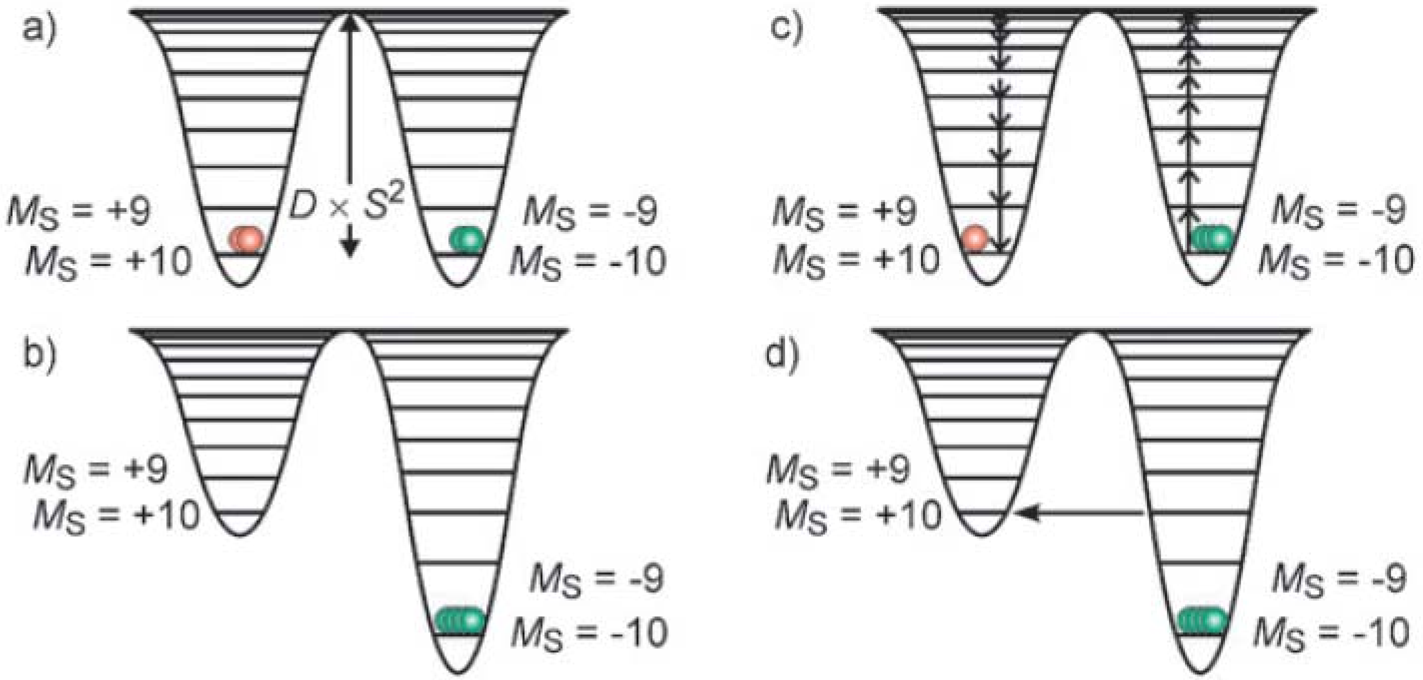
M_S from S to −S
M_S = S 'spin up'
M_S = −S 'spin down'

In the absence of ZFS,
all of the M_S sublevels are degenerate
ZFS lifts degeneracy, doublets $\pm M_S$



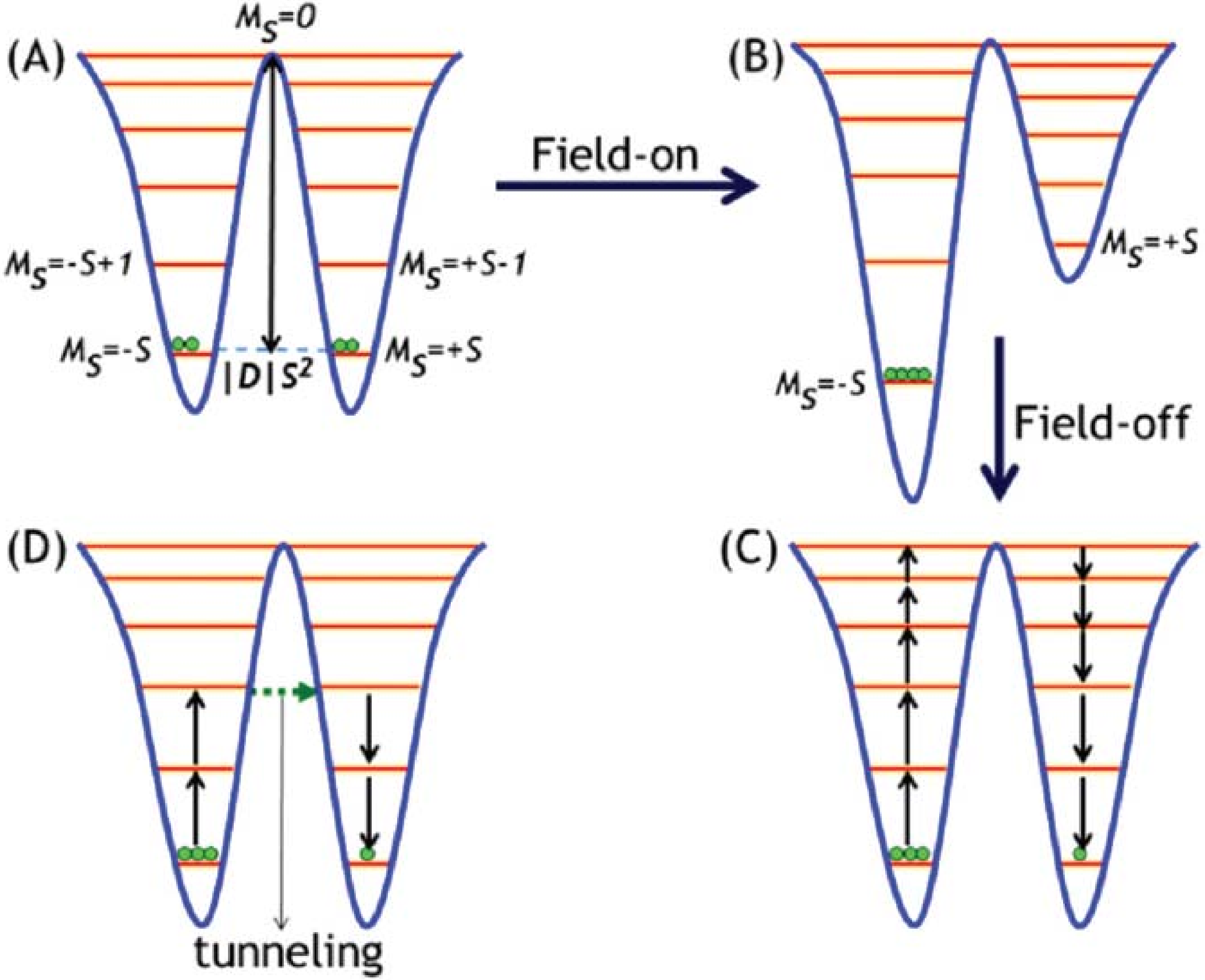
For **D negative**: $M_S = \pm S$ are lower in energy than the intermediary sublevels M_S with $S > M_S > -S$
At low temperatures, the magnetisation remains trapped in one of the two $M_S = \pm S$ because of the energy required to transition through high-energy intermediary states and over the barrier U (its size is related to both D and S) to the other well

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

Anisotropy Barrier in SMMs



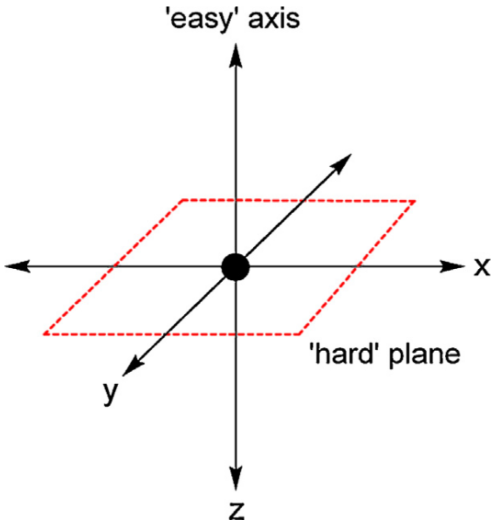
Single-Molecule Magnets (SMM)

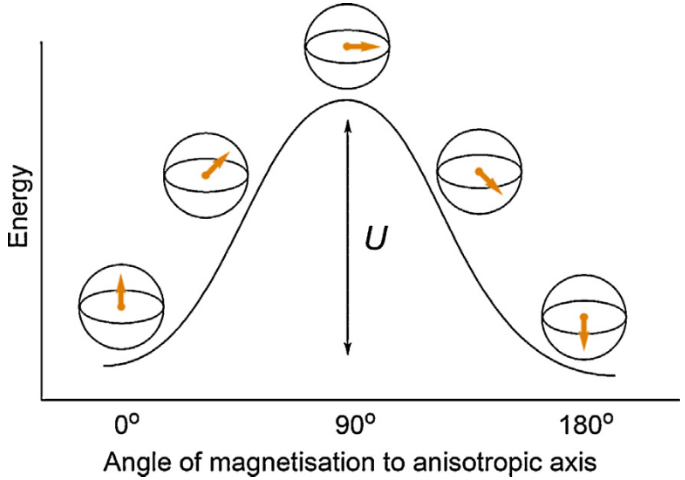
Magnetic anisotropy = a molecule can be more easily magnetized along one direction than along another = the different orientations of the magnetic moment have different energies

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

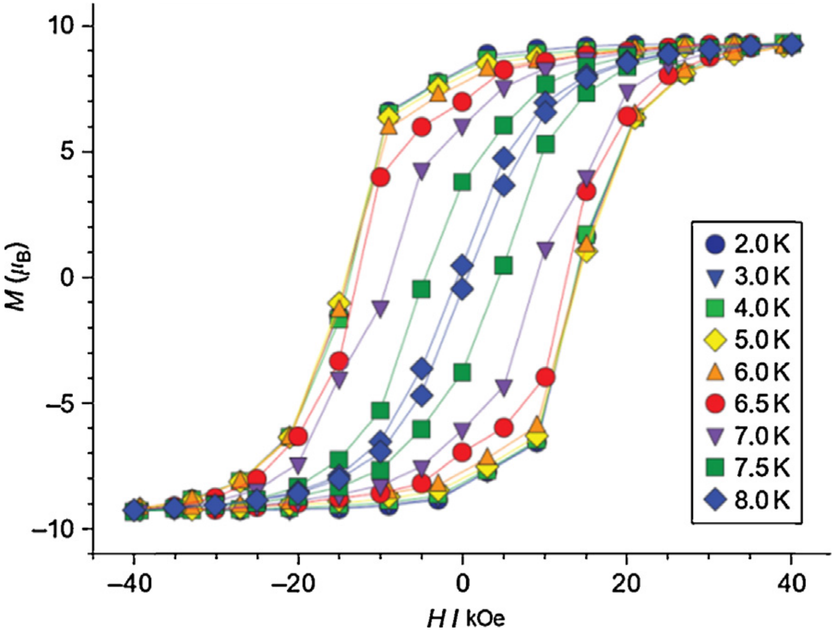




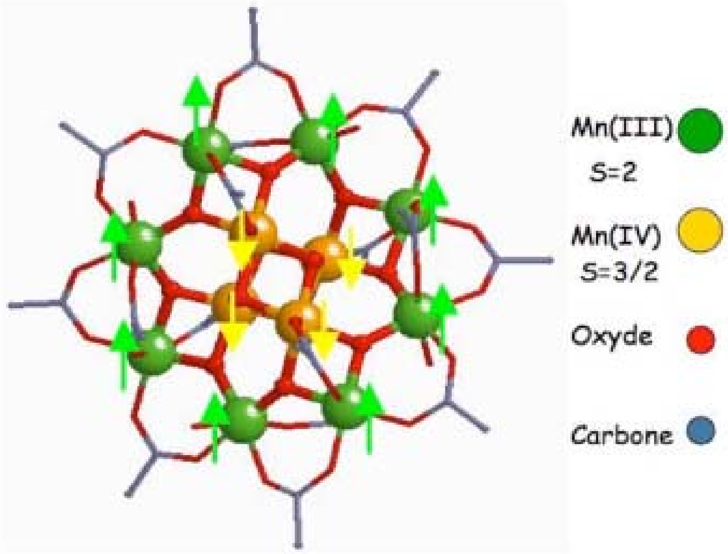
M-H Hysteresis

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

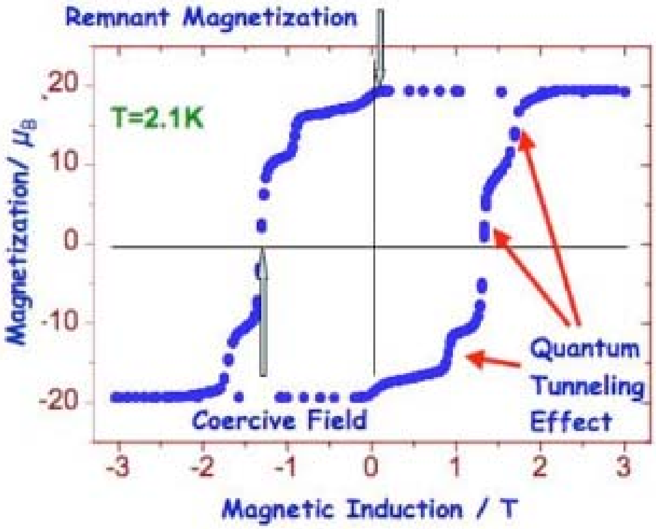
If the magnetisation is retained despite the field being removed ($M \neq 0$ at $H = 0$), the complex has an energy barrier to magnetisation reversal within the temperature and scan rate window of the measurement



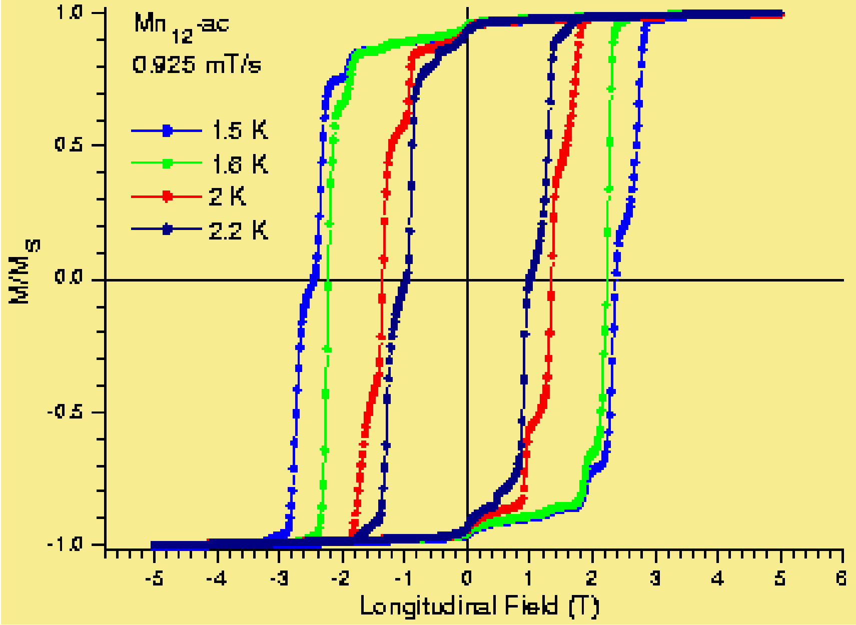
Hysteresis in Mn12



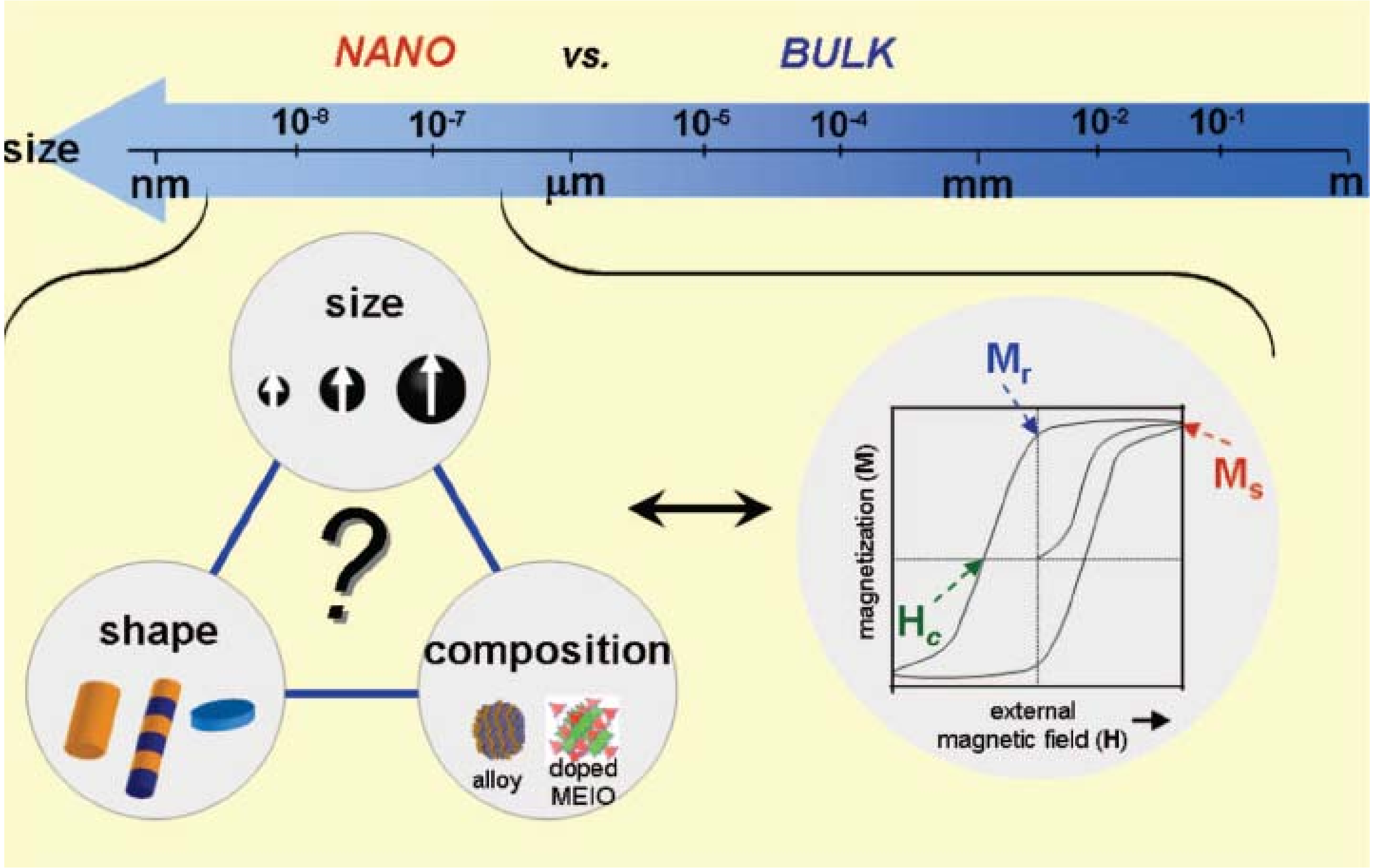
(a)



(b)



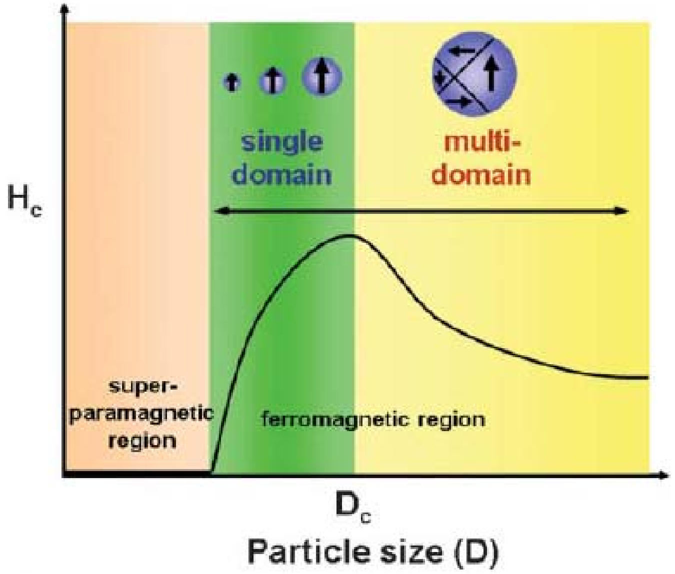
Superparamagnets



Superparamagnets

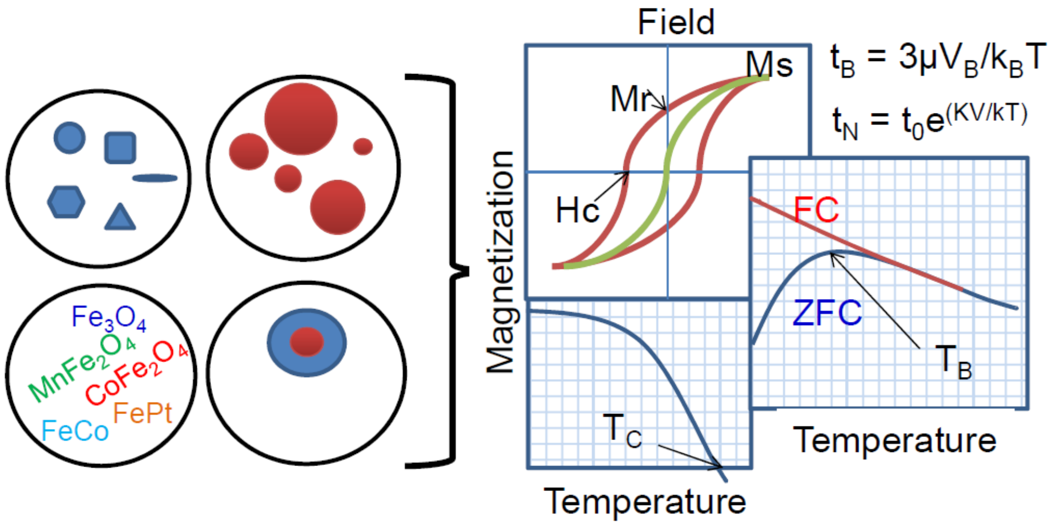
Tunable magnetic properties:

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



Parameters and variables:

- **Shape**
- **Size**
- **Composition**
- **Architecture**



Superparamagnets

Small particles of ferromagnetic and ferrimagnetic materials

Nanoparticles below a critical size (depends on material)

a single magnetic domain

- Nanoparticles (NP) with a size distribution
- Molecular particles which also display hysteresis – effectively behaving as a Single Molecule Magnet (SMM)

Above **blocking** temperature **random spin flipping** = no net magnetization

A zero average magnetic moment in the absence of an external field

All the spins simultaneously flip by **thermal fluctuation**. Each NP behaves as a **paramagnetic** spin with a giant magnetic moment

Magnetic moment strongly increases (as compared to paramagnetic materials) under application of an external field in the direction of the field

Superparamagnets

Above **blocking** temperature **random spin flipping** = no net magnetization

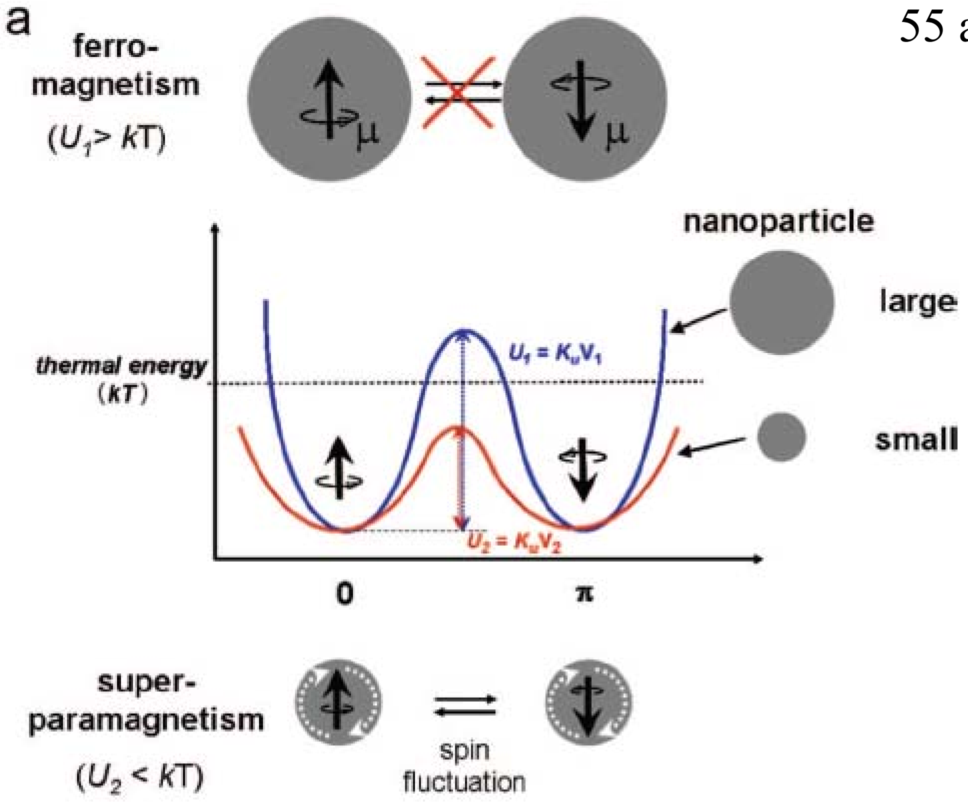
The thermal fluctuations within the nanoparticles are comparable to or greater than the energy barrier for moment reversal = **random spin flipping**

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

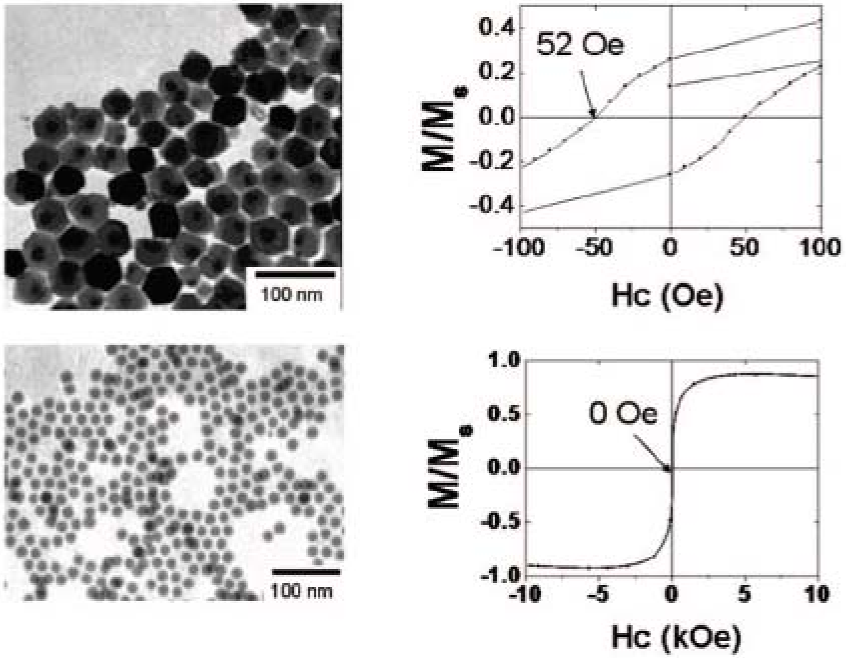
$$\mu = -g\, J\, \mu_B$$

g = the g factor
μ_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

Superparamagnets



55 and 12 nm sized iron oxide nanoparticles



Blocking Temperature

Above the blocking temperature (T_B), ferromagnetic and ferrimagnetic nanoparticles exhibit **superparamagnetic** behavior = rapid random magnetization reversals = a zero time-average magnetic moment

The value of T_B, associated with the energy barrier, depends on the characteristic measuring time (100 to 10^{-8} s)

The magnetic behavior arises from the **relative difference** between the measuring time and the relaxation time

The measuring time > the relaxation time = the **superparagmagnetic** regime

The measuring time < the relaxation time = a “**blocked” (ferromagnetic**) regime

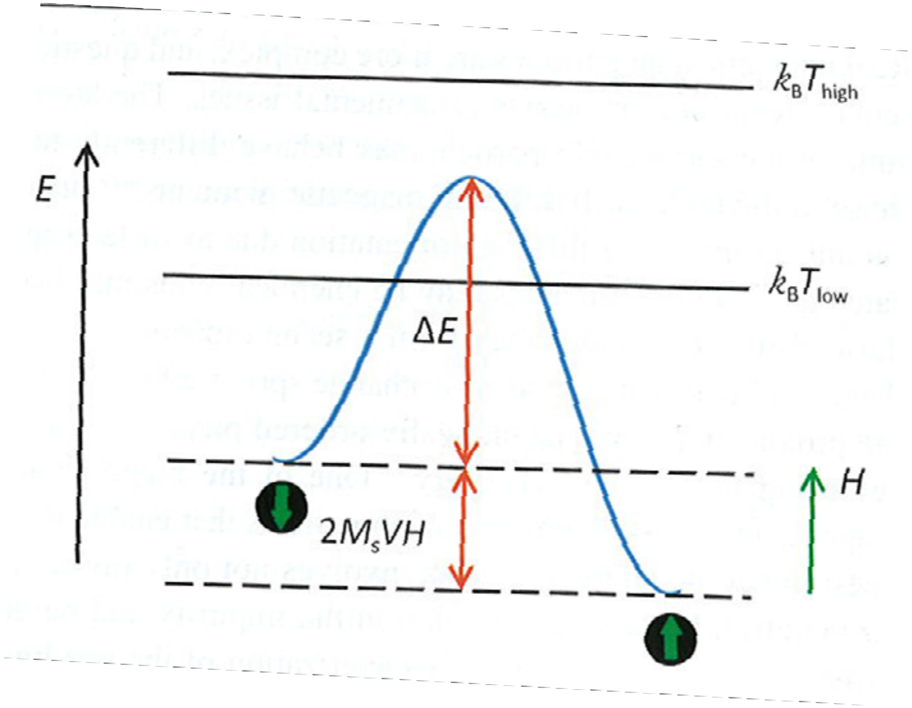
Blocking Temperature

Blocking Temperature $T_B = \dfrac{KV}{25k_B}$

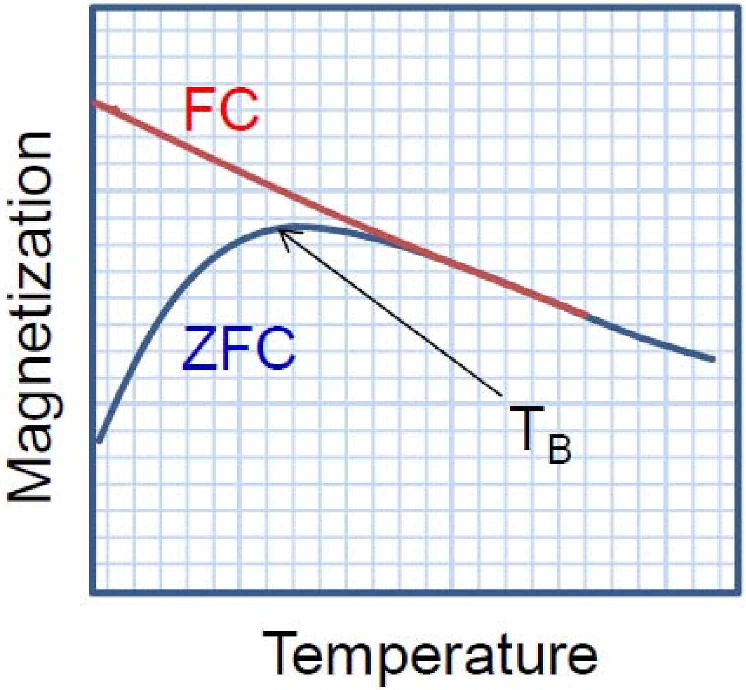
V = particle volume

Particles with volume smaller than V_c will be at $T < T_B$ superparamagnetic

$$V_C = \frac{25k_BT}{K}$$



Blocking Temperature



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

T_B corresponds to the “merging point” of the zero-field cooled (ZFC) and field-cooled (FC) magnetization curves

Blocking temperature by Moessbauer spectroscopy

ZFC and FC Magnetization Curves

ZFC - a sample is first cooled to low temperature (2–10 K) in the absence of an external field (zero-field), at this point, a small external field is applied, and the temperature is gradually increased while measuring the sample magnetization as a function of temperature

the magnetic particles are cooled below their blocking temperature in zero applied filed, the direction of particle's moment will be frozen along the easy direction of magnetization which will be at random orientation,

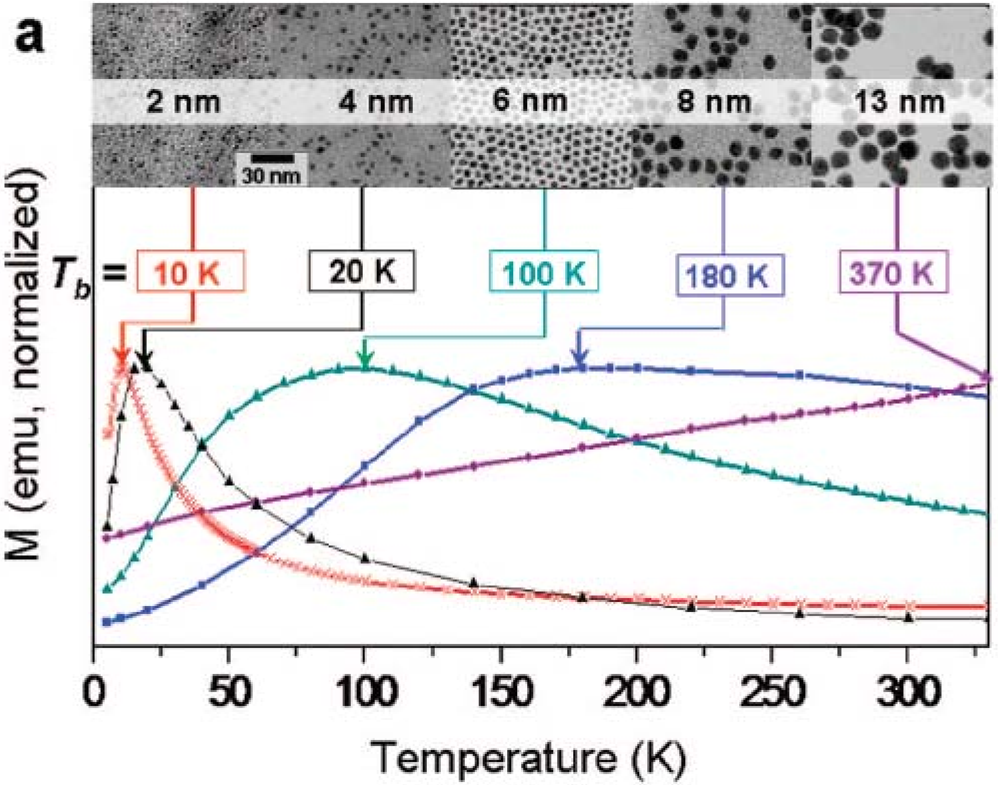
FC - the sample is cooled in the presence of an external field (~50 Oe) and the same external field is applied as the temperature is increased

the point where the two curves merge is the irreversibility temperature, T_{irr},
the maximum on the ZFC curve is the blocking temperature, T_B

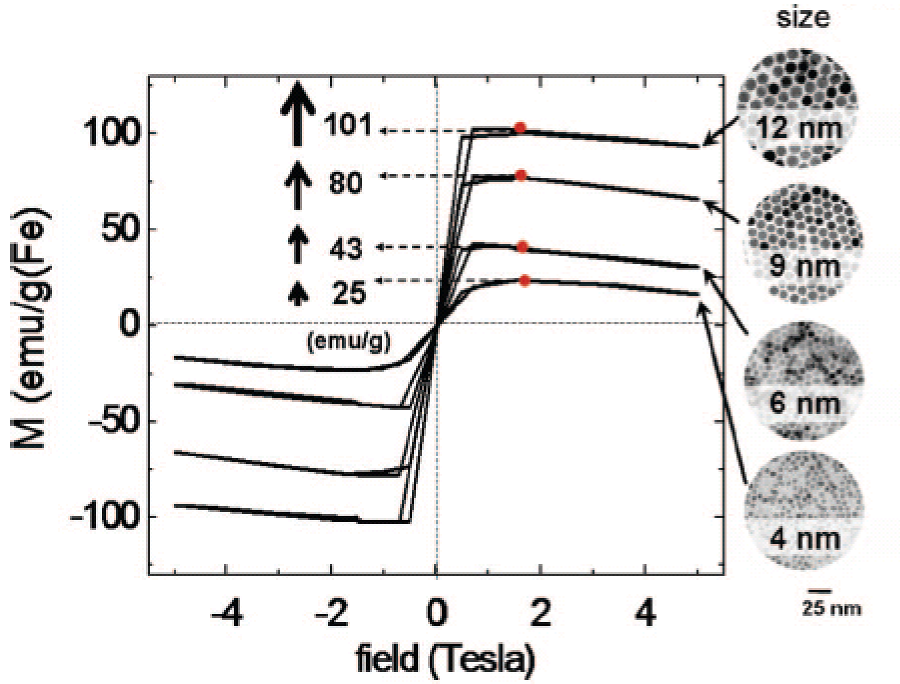
the system of particles is cooled below their blocking temperature in an applied field, the particles direction of magnetization will be frozen in a direction other than the easy axis

Blocking Temperature

Zero-field cooling curves and TEM images of Co nanoparticles



Size Dependent Mass Magnetization



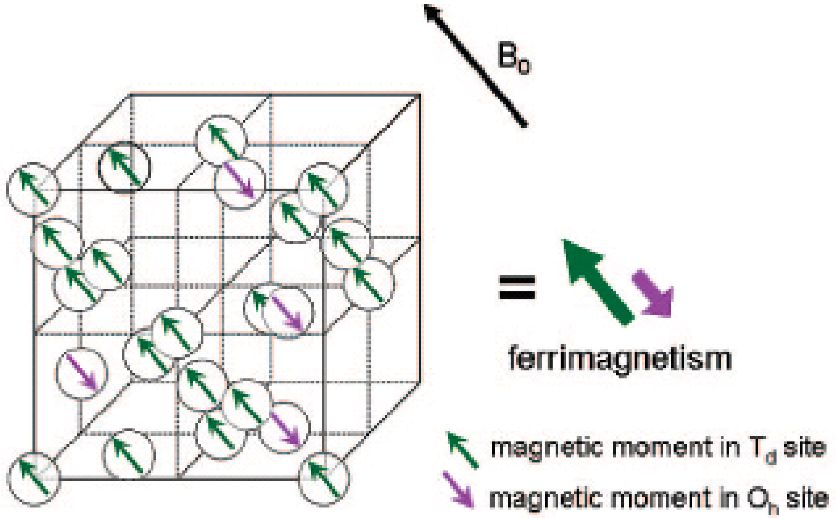
iron oxide Fe_3O_4 nanoparticles hysteresis loops
mass magnetization values at 1.5 T

Compositional Modification of Magnetism of Nanoparticles

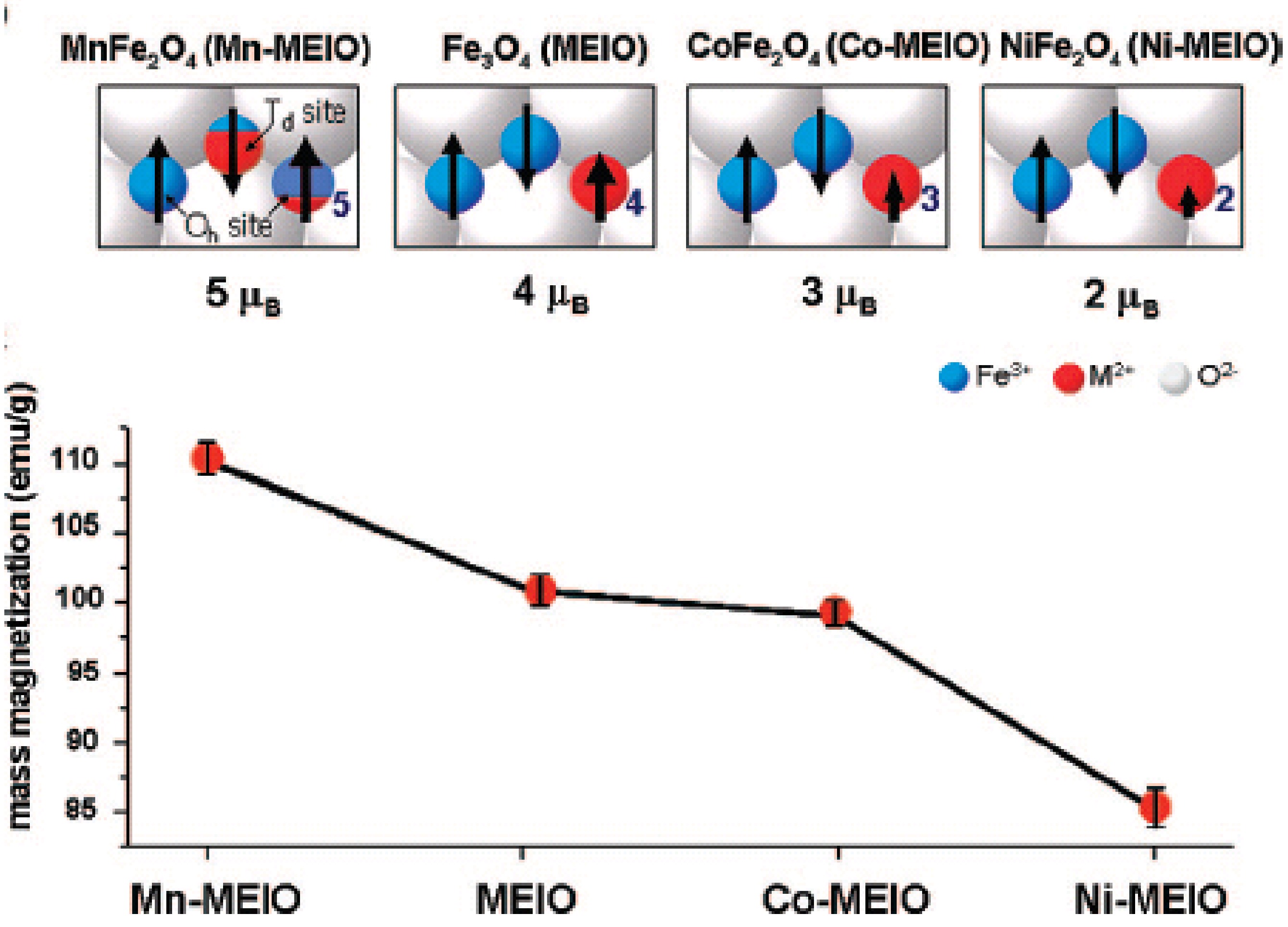
Fe_3O_4 (inverse spinel) nanoparticles - ferrimagnetic spin structure
Fe^{2+} and Fe^{3+} occupying O_h sites align **parallel** to the external magnetic field
Fe^{3+} in the T_d sites of fcc-packed oxygen lattices align **antiparallel** to the field

$Fe^{3+} = d^5$ high spin state = 5 unpaired electrons (upe)
$Fe^{2+} = d^6$ high spin state = 4 upe
the total magnetic moment per unit $(Fe^{3+})_{Td}\ (Fe^{2+}\ Fe^{3+})_{Oh}\ O_4 = 4.9\ \mu_B$

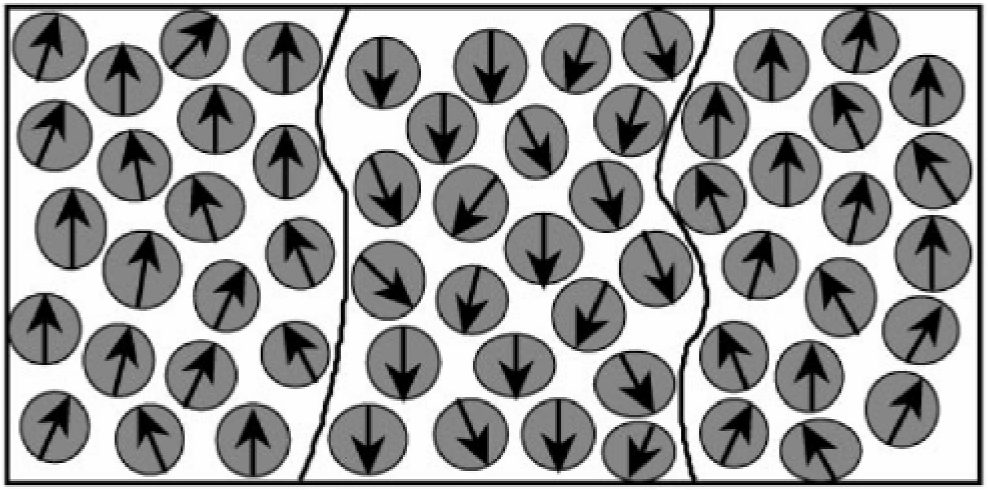
Incorporation of a magnetic dopant M^{2+} (Mn 5 upe, Co 3 upe, Ni 2 upe)
replace O_h Fe^{2+} = change in the net magnetization



Compositional Modification of Magnetism of Nanoparticles



Superferromagnetic, SFM



Spin Frustration

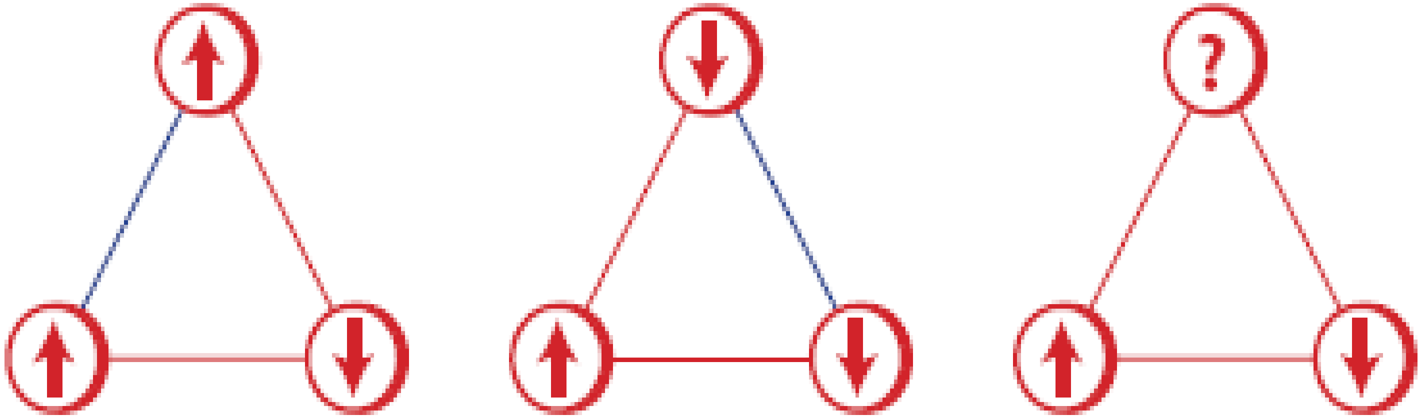
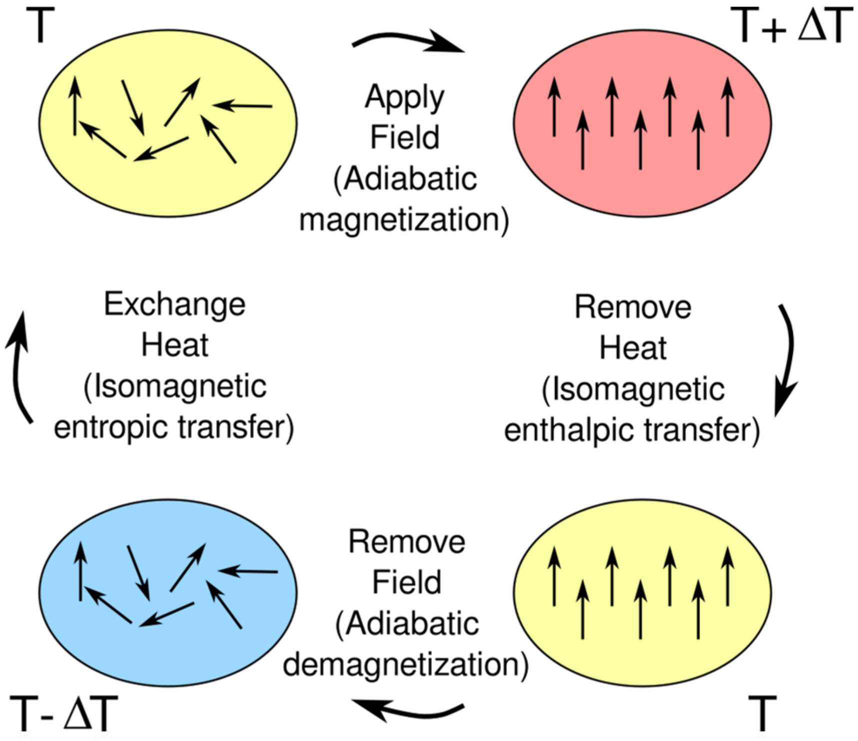


Figure 6.2: Magnetic frustration is illustrated. In the case of magnetically frustrated systems impossible for all spins to be align antiparellel.

Magnetocaloric Effect



T

Apply Field (Adiabatic magnetization)

T+ ΔT

Exchange Heat (Isomagnetic entropic transfer)

Remove Heat (Isomagnetic enthalpic transfer)

Remove Field (Adiabatic demagnetization)

T- ΔT

T