Magnetism for Chemists

I. Introduction to Magnetism

II. Survey of Magnetic Behavior

III. Van Vleck's Equation

III. Applications
   A. Complexed ions and SOC
   B. Inter-Atomic Magnetic "Exchange" Interactions

Magnetism Intro

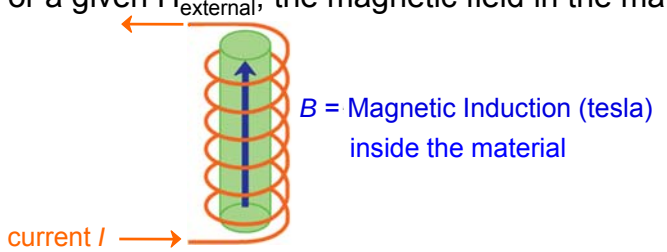
1. Magnetic properties depend on # of unpaired e- and how they interact with one another.
2. Magnetic susceptibility measures ease of alignment of electron spins in an external magnetic field .
3. Magnetic response of e- to an external magnetic field ~ 1000 times that of even the most magnetic nuclei.
4. Best definition of a magnet: a solid in which more electrons point in one direction than in any other direction

Uses of Magnetic Susceptibility

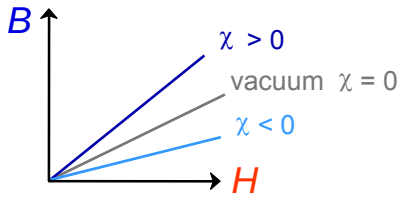
1. **Determine # of unpaired e-**
2. **Magnitude of Spin-Orbit Coupling.**
3. **Thermal populations of low lying excited states (e.g., spin-crossover complexes).**
4. **Intra- and Inter- Molecular magnetic exchange interactions.**

Response to a Magnetic Field

- For a given $H_{external}$, the magnetic field in the material is B



- Magnetic susceptibility, χ (dimensionless)



χ measures the material response relative to a vacuum.

Magnetic field definitions

B – magnetic induction
H – magnetic intensity

Two quantities describing a magnetic field

In vacuum: $\mathbf{B} = \mu_0 \mathbf{H}$ *(Système Internationale, SI)*

$\mu_0 = 4\pi \cdot 10^{-7}\ N A^{-2}$ - the permeability of free space (the permeability constant)

$\mathbf{B} = \mathbf{H}$ *(cgs: centimeter, gram, second)*

Magnetism: Definitions

The magnetic field inside a substance <u>differs</u> from the free-space value of the <u>applied</u> field:

$$\vec{H} = \vec{H}_0 + \Delta\vec{H}$$

inside sample — applied field — shielding/deshielding due to induced internal field

Usually, this equation is rewritten as (physicists use B for H):

$$\vec{B} = \vec{H}_0 + 4\pi\vec{M}$$

magnetic induction — magnetization (mag. moment per unit volume)

or $\vec{B} / \vec{H}_0 = 1 + 4\pi\chi_V$ = magnetic permeability

where χ_V = volume susceptibility (also called κ),

and B/H_0 = permeability = mag. equiv. of dielectric constant

~ ratio of magnetism arising from sample vs applied magnetic field

Magnetism: Definitions

"chi" = $\chi_g = \chi_v / \rho$ = gram or mass magnetic susceptibility

$\chi_m = \chi_g / MW$ = molar magnetic susceptibility

$\mu_{eff} = (3\ k / N\ \mu_B^2)^{1/2} (\chi_m T)^{1/2}$ = effective magnetic moment

$= 2.828\ (\chi_m T)^{1/2}$ in units of Bohr magnetons

$\mu_B = \beta = eh/4\pi m_e c$ = Bohr magneton = 0.93×10^{-20} erg/Gauss

= magnitude of single electron's spin mag moment = 9.27×10^{-24} J/T

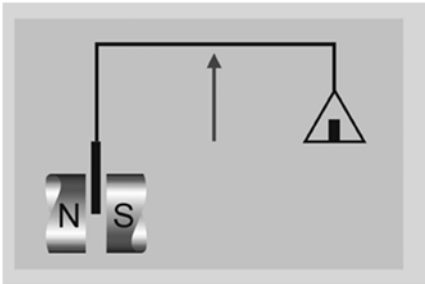
ICBST χ is proportional to $-(\partial E/\partial H_0) / H_0$

Magnetic Units And Conversions

Magnetic Term	Symbol	SI unit	CGS unit	conversion factor
magnetic induction	B	Tesla (T)	Gauss (G)	1 T = 10^4G
magnetic field	H	A/m	Oersted (Oe)	1 A/m =$4\pi/10^3$ Oe
magnetization	M	A/m	emu/cm^3	1 A/m = 10^{-3} emu /cm^3
mass magnetization	σ	Am^2/kg	emu/g	1 Am^2/kg = 1 emu/g
magnetic moment	m	Am^2	emu	1 Am^2 = 10^3 emu
volume susceptibility	κ	dimensionless	dimensionless	4π(SI) = 1 (cgs)
mass susceptibility	χ	m^3/kg	emu/Oe· g	1 m^3 /kg = $10^3/4\pi$ emu /Oe· g
permeability of free space	μ_0	H/m	dimensionless	$4\pi \times 10^{-7}$ H/m = 1 (cgs)

Magnetism: Measurement

Gouy Balance



Homogeneous magnetic field

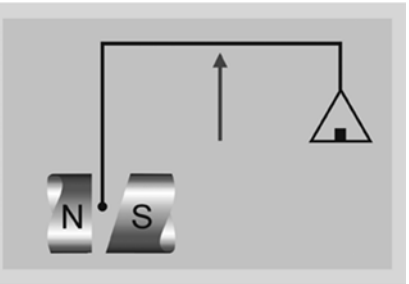
Magnetic force on sample = $\chi_v H^2$

Use calibration standard to find H^2

Weigh sample with and without field

Need large samples, >100 mg

Faraday Balance



Inhomogeneous magnetic field

Magnetic force = $\chi_v V H \partial H/\partial x$

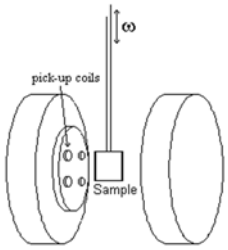
Calibrate to find $H \partial H/\partial x$

Weigh sample with and without field

Small samples, ~10 mg

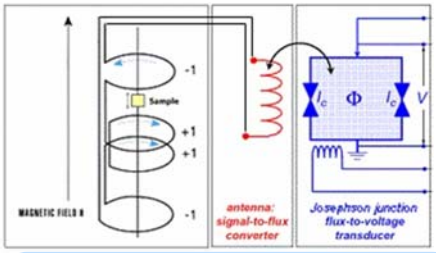
Magnetism: Measurement

Vibrating Sample Magnetometer



1. Sample size ~ 10 mg
2. Sample vibrates at ~50 Hz
3. Often uses supercon magnets
4. Sensitivity similar to Faraday
5. Easier to do variable temp

SQUID: Superconducting Quantum Interference Device Magnetometer

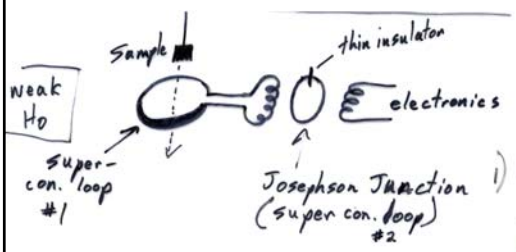


1. Sample size < 1 mg, very sensitive
2. Key component is two supercon half-loops linked by an insulating barrier (Josephson junctions). The loop converts flux into a voltage

For both techniques, oscillation of sample induces a current in the pick-up coils. This current is either detected directly (VSM) or indirectly (SQUID).

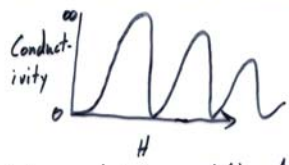
Magnetism: Measurement

Heart of SQID: Josephson Junction



1) As sample passes through loop, current flows through loop inducing mag. field at Josephson Jnct.

2) Josephson Jct. = Superconn loop w/ thin insulator. Has unusual property:



3) electronics detect current flow of 1st loop via J.J.

Magnetism: Measurement

Solution NMR technique – Evans' Method

Dissolution of a paramagnetic substance in a solvent shifts the solvent resonances from the shifts seen for the pure solvent

Experimental technique: a solution containing the paramagnetic substance is placed in NMR tube along with a second tube containing pure solvent. Best to use a solvent with a sharp singlet. The NMR spectrum will contain two peaks, one due to the pure solvent and another peak, shifted from the first, due to the solution.

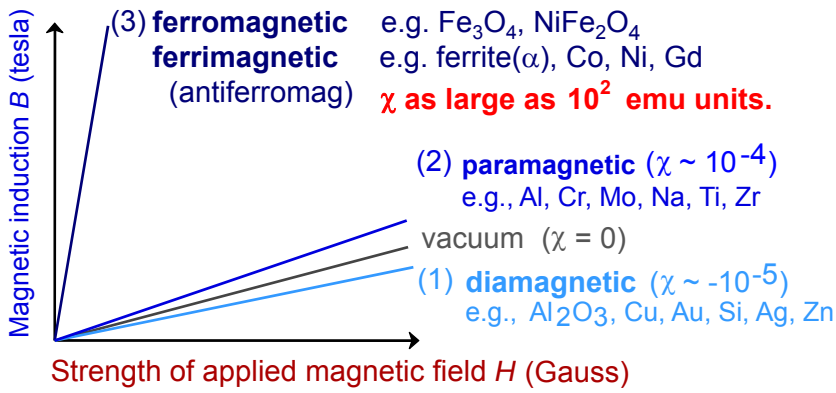
$$\chi_g = 3\Delta v / 2 Q \pi v c + \chi_0 + \chi_0 (d_0 - d_s)/c$$

Δv = frequency shift of solvent resonance
Q = 1 for an electromagnet, = 2 for a superconducting magnet
v = NMR probe frequency
c = concentration of sample (grams per cm^3)
χ_0 = gram susceptibility of solvent
d_0-d_s = change in density of solvent vs solution

4 Types of Magnetism

$$B = (1+\chi)\mu_o H$$

permeability of a vacuum: (1.26×10^{-6} Henries/m)



Types of Magnetic Behavior

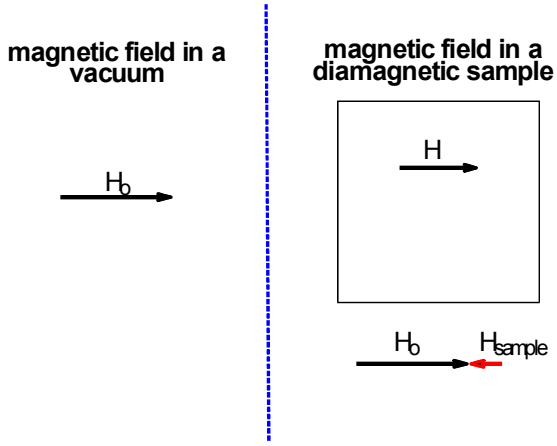
Diamagnetism

i) **Substance repelled by external magnetic field ($\chi < 0$)**

ii) **Due to presence of paired electrons (classically, Lenz's law: in a closed loop carrying current, an applied magnetic field will induce an opposing field in the loop)**

iii) **Very weak magnetic response: ~10^{-4} vs. ferromagnetism**

Diamagnetism



- Magnetic field inside the sample is smaller (slightly) than the applied field by the amount H_{sample}, commonly called ΔH.
- Diamagnetic samples are repelled by a magnetic field (extreme example: mag-lev trains)

Diamagnetism

Diamagnetism of an atom:

sum over all electrons in atom

$$\chi^{dia} = - N_{avo}\, e^2 \sum_i \langle r_i \rangle^2 / 6\, m\, c^2$$

average orbital radius of ith electron

Therefore, bigger atoms have a larger diamagnetism than smaller atoms.

Note, bonding also influences $\langle r_i \rangle$ (bigger box).

Pascal's Approximation

The diamagnetic contribution of the paired electrons in a molecule is equal to the sum of the diamagnetic contributions (DC) from the constituent atoms and bonds

$$\chi_{DC\ molecule} = \sum_i \chi_{atom\ i} + \sum_j \chi_{bond\ j}$$

where $\chi_{atom\ i}$ and $\chi_{bond\ j}$ are empirically derived "Pascal's constants."

Table of Pascal's constants (units of -10^{-6} cm^3)

Ion	DC	Ion	DC
Na^+	6.8	Co^{2+}	12.8
K^+	14.9	Co^{3+}	12.8
NH_4^+	13.3	Ni^{2+}	12.8
Hg^{2+}	40	VO^{2+}	12.5
Fe^{2+}	12.8	Mn^{3+}	12.5
Fe^{3+}	12.8	Cr^{3+}	12.5
Cu^{2+}	12.8	Cl^-	23.4
Br^-	34.6	SO_4^{2-}	40.1
I^-	50.6	OH^-	12
NO_3^-	18.9	$C_2O_4^{2-}$	34
ClO_4^-	32	OAc^-	31.5
IO_4^-	51.9	pyridine	49.2
CN^-	13	Me-pyr	60
NCS^-	26.2	$acac^-$	62.5
H_2O	13	en	46.3
$EDTA^{4-}$	~150	urea	33.4

Examples of diamagnetic minerals

Mineral	κ (SI)
 Quartz (SiO_2)	$-(13\text{-}17) \cdot 10^{-6}$
 Calcite ($CaCO_3$)	$-(8\text{-}39) \cdot 10^{-6}$
 Graphite (C)	$-(80\text{-}200) \cdot 10^{-6}$
 Halite (NaCl)	$-(10\text{-}16) \cdot 10^{-6}$
 Sphalerite (ZnS)	$-(0.77\text{-}19) \cdot 10^{-6}$

Data from Hunt et al (1995)

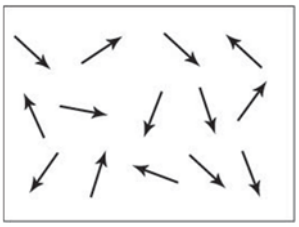
Types of Magnetic Behavior

Paramagnetism: magnetic disorder

i) Substance attracted by external magnetic field ($\chi > 0$)

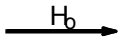
ii) Caused by spin and orbital angular moments of unpaired e-

iii) Temperature dependent magnetic behavior

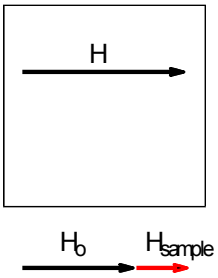


Paramagnetism

magnetic field in a vacuum



magnetic field in a paramagnetic sample



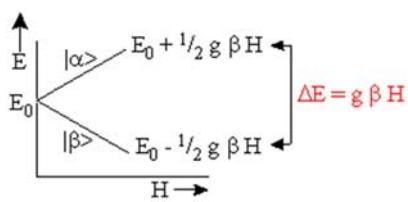
- Paramagnets concentrate magnetic fields inside of themselves, therefore they are attracted to a magnetic field.
- Magnetic field inside the sample is greater than the applied field by the amount H_{sample}, commonly called ΔH.
- There are many complicated kinds of paramagnetism: ferromagnetism, ferrimagnetism, etc.
  These arise from cooperativity leading to very large effects.

Paramagnetism, e.g., S = 1/2

1. Magnetic moment $\vec{\mu}_m = - g \beta \vec{S}$

   where g = electron g-factor
   β = Bohr magneton
   S = spin angular momentum

2. In applied field, $\hat{\mathcal{H}} = - \vec{\mu}_m \cdot \vec{H} = g \beta \vec{S} \cdot H$



3. There is a slight excess of spins aligned with H:

   $N_\alpha / N_\beta = e^{-g\beta H/kT}$ (Boltzmann)

Paramagnetism

For general case of spin-only magnetism, not just S = ½, we have:

$$\chi = N g^2 \beta^2 S (S + 1) / 3kT$$

Plugging this into the definition of eff. mag. moment:

$$\mu_{eff} = (3\, k / N\, \beta^2)^{1/2} (\chi_{eff}\, T)^{1/2} \quad \text{or} \quad \mu_{eff} = g\, [\, S\, (S + 1)]^{1/2}$$

where $\chi_{eff} = \chi_{measured} - \chi_{diamag\ contribution}$

$\equiv \chi_{paramag}$

Magnetic Moments vs. Number of Electron Spins

- The energy of a highly magnetic species changes significantly in a high magnetic field.
- Inorganic chemists evaluate magnetism of coordination compounds by their magnetic moment, μ_m
- For a free ion: $\mu_{S+L} = g\,[S(S+1) + L(L+1)]^{1/2}$

  which reduces to g ~ 2 if L=0 (i.e., no orbital contribution).

  i.e., magnetic moment is directly related to the angular momentum of the e-

Lande constant g = 2.0023192778 for a free electron

$$\underbrace{\mu_n}_{\text{Magnetic moment of an electron in quantum state } n} = -m_S \overbrace{g}^{\text{Lande constant}} \beta \quad \text{in BM}$$

μ_{S+L} = magnetic moment, units of energy/magnetic field

g = μ_B = Bohr Magneton = magnitude of single electron's spin mag moment = 9.27×10^{-24} J/T

S = spin angular momentum = ½ number of unpaired electrons

L = orbital angular momentum, usually smaller correction to spin mom.

Simplified Magnetic Moments vs. Electron Count

Inorganic chemists evaluate magnetism of coordination compounds by their magnetic moment, μ_m

$$\mu_m = [n(n+2)]^{1/2} \quad \text{(in units of "Bohr Magnetons")}$$

n = sum of unpaired e^-'s

"Spin-only" magnetic moments (μ_{SO}):

n = 1, μ = 1.73 BM (Bohr magnetons)
n = 2, μ = 2.83
n = 3, μ = 3.87
n = 4, μ = 4.9
n = 5, μ = 5.92

So which metal ions *might* have 1, 2, 3, 4, 5 unpaired electrons?

Simplified Magnetic Moments vs. Electron Count

# unpaired e-	S	d^n	$\mu_{S.O.} = \sqrt{n(n+2)}$	ion	μ_{obs}
1	½	1	1.73	Ti^{3+}	1.85-2.08
1	½	9	1.73	Cu^{2+}	1.96-2.5
2	1	2	2.83	V^{3+}	2-2.2
2	1	8	2.83	Ni^{2+}	2.1-2.4
3	3/2	3	3.87		
3	3/2	7 HS	3.87	Co^{2+}	>2.7
1	½	7 LS	1.73	Co^{2+}	2.0
4	2	4	4.90	Mn^{3+}	4.8-4.9
5	5/2	5	5.92	Fe^{3+}	5.3

The μ_{obs} can be either less than or greater than the μ_{SO}.

Why?

Orbital Contributions (i.e., SOC).

Mixing from XSs.

Simplified Magnetic Moments vs. Electron Count

Ion	config	O_h	Free Ion	μ_{eff}^{obs}	w/ orbital contribution $g(J^*(J+1))^{1/2}$	Spin-only $g(S^*(S+1))^{1/2}$
Ti^{3+}	$3d^1$	$^2T_{2g}$	$^2D_{3/2}$	1.7 μ_{eff}^{obs}	1.55	1.73
V^{3+}	$3d^2$	$^2T_{1g}$	$^3F_2$	2.6-2.8	1.63	2.83
Cr^{3+}	$3d^3$	$^2A_{2g}$	$^4F_{3/2}$	3.8	0.77	3.87
Fe^{2+}	$3d^6$	$^5T_{2g}$	$^5D_4$	5.5	6.70	4.90
Co^{2+}	$3d^7$	$^4T_{1g}$	$^4F_{9/2}$	4.1-5.2	6.63	3.87
Cu^{2+}	$3d^9$	^2E_g	$^2D_{5/2}$	1.7-2.2	3.55	1.73

Simplified Magnetic Moments vs. Electron Count

Ion	e⁻ Config.	S	Spin-only $g\,(S*(S+1))^{1/2}$ $\mu_S(\mu_B)$	w/ orbital contribution $g\,(J*(J+1))^{1/2}$ $\mu_{S+L}(\mu_B)$	μ_{obs} (μ_B)
Ti^{3+}	d^1	1/2	1.73	3.01	1.7-1.8
V^{2+}	d^2	1	2.83	4.49	2.8-3.1
Cr^{3+}	d^3	3/2	3.87	5.21	3.7-3.9
Fe^{3+}	d^5 (HS)	5/2	5.92	5.92	5.7-6.0
Ni^{2+}	d^8 (HS)	1	2.83	4.49	2.9-3.9
Cu^{2+}	d^9	1/2	1.73	3.01	1.9-2.1

Deviations from the spin-only value can occur for the following reasons:

Orbital (L) Contribution

- Can arise for partially filled (not ½ full) t_{2g} orbitals

Spin-orbit Coupling

- Increases the moment for d^6, d^7, d^8, d^9
- Decreases the moment for d^1, d^2, d^3, d^4

"Quenching" of Orbital Contribution

Depends on extent of S.O.C.

$\therefore$ ^{2S+1}A gnd. state $\Rightarrow$ $\mu_{eff}^{spin\ only}$

^{2S+1}E $\Rightarrow$ $\mu_{eff}^{S.O.}$ + small diff.

^{2S+1}T $\Rightarrow$ $\mu_{eff}^{S.O.}$ + larger diff.

As predicted from $\underbrace{\Gamma_{2S+1}}_{\text{spin state}} \otimes \underbrace{\Gamma_{2L+1}}_{\text{orbital symm}}$

Paramagnetism

Alternatively:

Orbital Momentum will contribute iff an e^- occupies a degenerate set of d-orbitals that permits "circulation" of e^- about an axis.

i.e. a rotation must convert d orbital into another one of the degenerate set.

Paramagnetism, e.g., S = 1/2

From earlier: $N_\alpha/N_\beta = e^{-g\beta H / kT}$

$g\beta H << kT$ (even if T is small). (recall: $e^x \sim (1 + x)$ if $x \sim 0$)

$$N_\alpha/N_\beta = 1 - g\beta H / kT$$

If we define $N = N_\alpha + N_\beta$, then ICBST

$$N_\alpha = N(1 - g\beta H / 2kT)/2$$

$$N_\beta = N(1 + g\beta H / 2kT)/2$$

Now, net magnetization is:

$$M = \tfrac{1}{2}\, g\, \beta\, (N_\beta - N_\alpha) = Ng^2\beta^2 H / 4kT$$

Paramagnetism, e.g., S = 1/2

From last slide: $M = Ng^2\beta^2H / 4kT$

Remember that $\chi = M/H$, therefore $\chi = Ng^2\beta^2 / 4kT$, or

$\chi = C / T$ where $C = Ng^2\beta^2 / 4k$

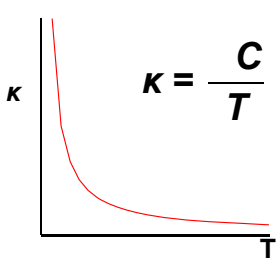
This is the (Pierre) Curie law; indicates spin centers are acting independently.

Empirically, many substances obey modified version, i.e., the Curie-Weiss equation:

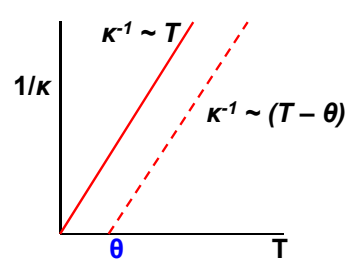
$$\chi = C / (T - \theta)$$

Weiss constant, $\theta \neq 0$ when weak interactions between adjacent spin centers (but also sometimes without interactions).

Paramagnetism: Temperature dependence



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



$$\kappa = \frac{C}{T - \theta}$$

The Curie-Weiss law

θ = paramagnetic Curie temperature (near 0 K for most paramagnetic solids)

The constant C is material-specific

Examples of paramagnetic minerals

	Mineral	κ (SI)
	Olivine $(Fe,Mg)_2SiO_4$	$1.6 \cdot 10^{-3}$
	Montmorillonite (clay)	$0.34 \cdot 10^{-3}$
	Siderite $(FeCO_3)$	$1.3\text{-}11.0 \cdot 10^{-3}$
	Serpentinite $(Mg_3Si_2O_5(OH)_4)$	$3.1\text{-}75.0 \cdot 10^{-3}$
	Chromite $(FeCr_2O_4)$	$3\text{-}120 \cdot 10^{-3}$

Data from Hunt et al (1995)

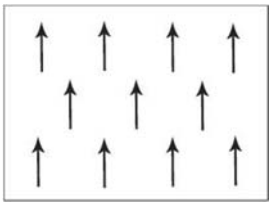
Ferromagnetism

i) Adjacent magnetic moments adopt a common (parallel) alignment

ii) Moments remain aligned even in absence of external magnetic field

iii) Macroscopic magnitude is immense

iv) Field-dependent and temperature dependent magnetic behavior



This is a magnetically ordered state, cooperative behavior in solid.

Ferromagnets become paramagnetic when heated in a cooperative, coordinated phase transition.

The transition temperature is called the Curie point.

Ferromagnetism

Ferromagnetism:

i) Dipole-Dipole interaction between adjacent Magnetic Moments w/ Common Alignment

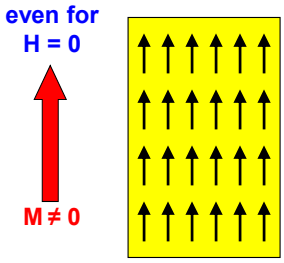
ii) Microscopic Magnitude of Coupling $\sim 10^{-2}$ size of Paramagnetism

iii) Macroscopic Magnitude immense

iv) Field Dependent, Temp dependent

Ferromagnetism

Atomic magnetic moments are always aligned (even for H = 0) due to exchange interaction (quantum-mechanical effect)



Spontaneous magnetization

Conditions for ferromagnetism:

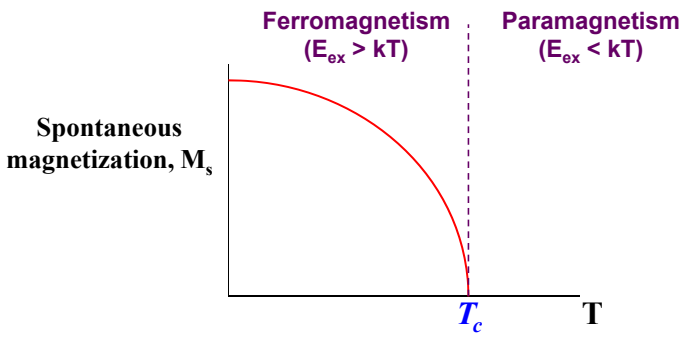
1) Non-compensated spin moments

2) Positive exchange interaction (i.e. co-directed spins)

Ferromagnetic elements:

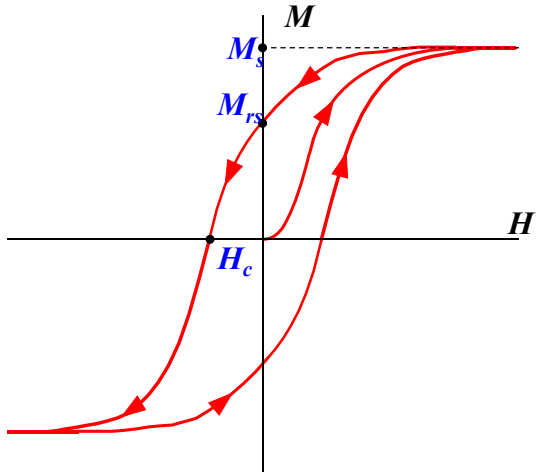
- Iron (Fe) (κ = 3,900,000)
- Nickel (Ni)
- Cobalt (Co)
- Gadolinium (Gd)

Ferromagnetism



T_c = ferromagnetic Curie temperature (material-specific)

Ferromagnetism: Magnetic hysteresis vs H

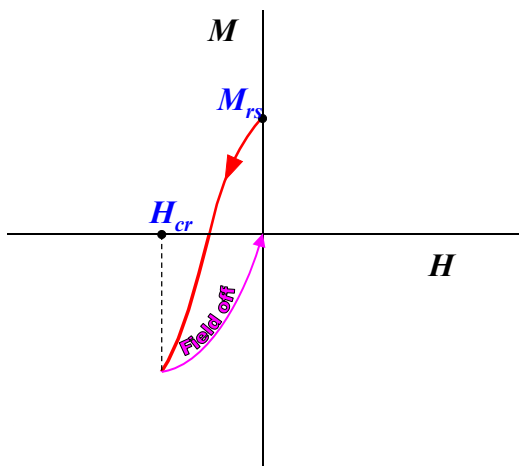


M_s – Saturation magnetization

M_{rs} – Saturation remanent magnetization

H_c – Coercive force *(the field needed to bring the magnetization back to zero)*

Ferromagnetism: Magnetic hysteresis vs H



M_s – Saturation magnetization

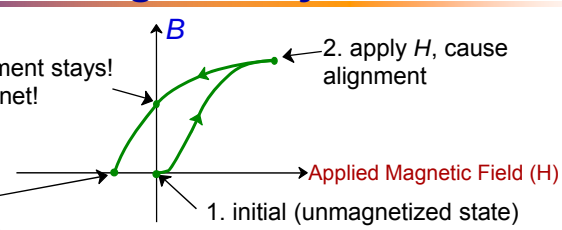
M_{rs} – Saturation remanent magnetization

H_c – Coercive force *(the field needed to bring the magnetization M_s back to zero)*

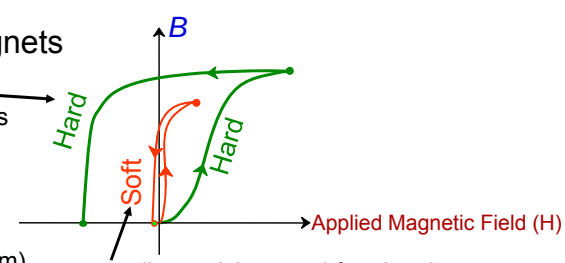
H_{cr} – Coercivity of remanence *(the field needed to bring M_{rs} to zero)*

Permanent Magnets: Hysteresis

- Process:

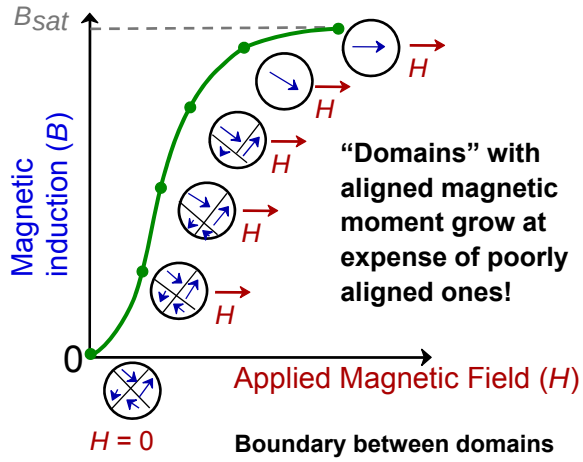


- Hard vs Soft Magnets



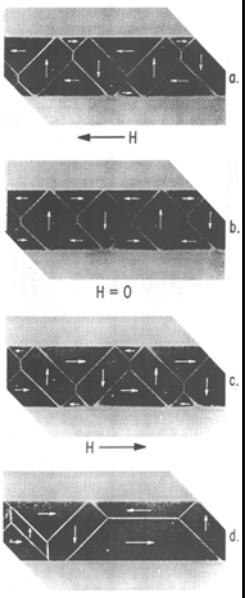
Magnetizing Ferro- and Ferri-Magnetic Materials

- As the applied field (*H*) increases...
  --the magnetic moment aligns with *H*.



"Domains" with aligned magnetic moment grow at expense of poorly aligned ones!

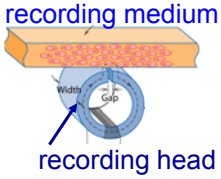
Boundary between domains = "Bloch wall"



Magnetic Storage

- Information is stored by magnetizing material.
- Head can...
  apply magnetic field H & align domains (i.e., magnetize the medium).
  detect a change in the magnetization of the medium.

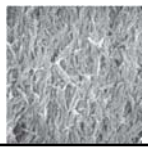
fig 1.1



A - Platter/s
B - Read/Write Head/s (and slider)
C - Actuator Arm/s
D - Actuator
E - Spindle

- Two media types:

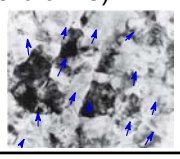
Particulate: needle-shaped γ-Fe_2O_3. +/- mag. moment along axis. (tape, floppy)



~2.5 μm

Thin film: CoPtCr or CoCrTa alloy. Domains are ~ 10 - 30 nm! (hard drive)

~120 nm



Antiferromagnetism & Ferrimagnetism

i) Anti-alignment of adjacent magnetic moments

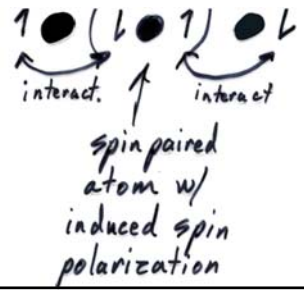
ii) Magnitude of coupling ~ that of paramagnetism

iii) Field and T dependent

Causes:

a) Direct interaction (spin-pairing, i.e., bonding!)\

b) Super-Exchange (thru-bond interaction)



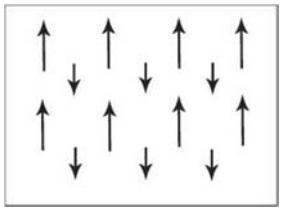
Ferrimagnetism: A magnetically ordered state

i) Anti-alignment of adjacent magnetic moments

ii) Spin cancellation is not complete, however, owing to different numbers of up and down spins

iii) Alignment persists even in absence of external field

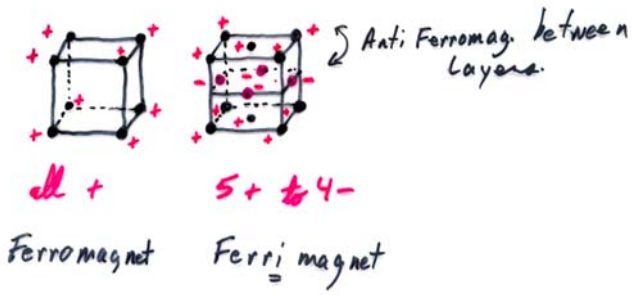
iv) Very strong magnetic response to external magnetic field

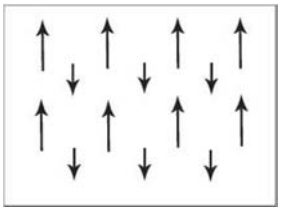


Ferrimagnets become paramagnetic when heated. The change from a ferrimagnetic state at low temperature to a paramagnetic state at higher temperature is a phase transition.

The transition temperature is called the Neél point.

Ferrimagnetism: A magnetically ordered state





Ferrimagnets become paramagnetic when heated. The change from a ferrimagnetic state at low temperature to a paramagnetic state at higher temperature is a phase transition.

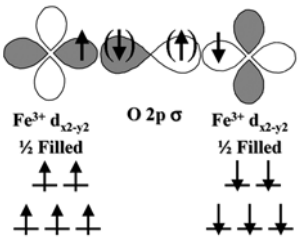
The transition temperature is called the Neél point.

Causes of ferrimagnetism

Causes of ferrimagnetism:

a) Direct interaction (spin pairing, i.e., bonding)

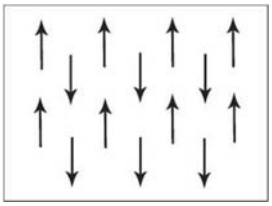
b) Superexchange (through-bond interaction) – diamagnetic bridging ligand is polarized by spins on magnetic neighbors



Antiferromagnetism: a special case of ferrimagnetism

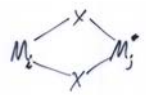
i) In magnetically ordered state, there are equal number of spin up and spin down electrons

ii) Diamagnetic below a certain temperature; paramagnetic above



Super-Exchange = Antiferromagnetic Coupling

e.g.



Both Metals Paramagnetic

Interaction between M_i and M_j represented by a Spin Hamiltonian:

$$\hat{H} = -2J\,\hat{S}_i \cdot \hat{S}_j \qquad J \equiv \text{"Exchange Coefficient"}$$

if $J < 0$ ⇒ Antiferromag. Interaction

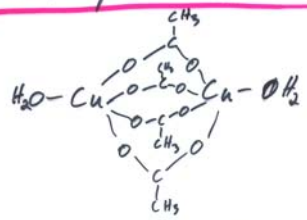
if $J > 0$ ⇒ Ferromag. " "

e.g.

Antiferromagnetic (Superexchange) Ferromagnetic

Super-Exchange = Antiferromagnetic Coupling

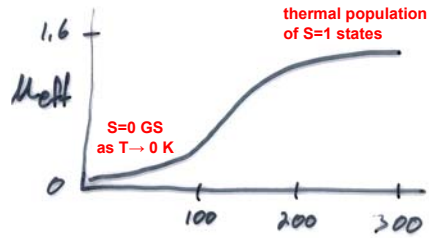
Classic Example: $[Cu(OAc)_2]_2 \cdot 2H_2O$



Cu – Cu = 2.6 Å

$d^9 – d^9$ S = ½ coupled to S = ½ through the bridging carboxylate

Super-Exchange in $Cu(OAc)_2$



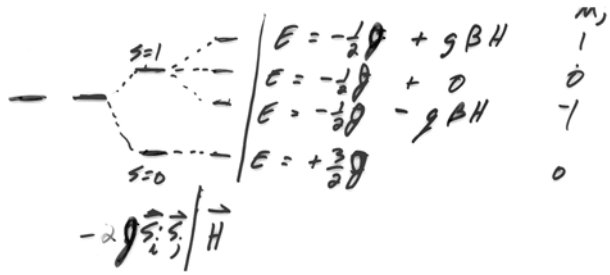
∴ Antiferromag Coupled

$\mathcal{J} = -142\ cm^{-1}$ for $CH_3CO_2^-$

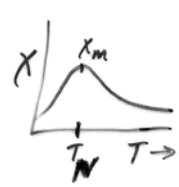
$= -170\ cm^{-1}$ for $C_3H_7CO_2^-$

calculated by Eqn Derived next

Super-Exchange in $Cu(OAc)_2$



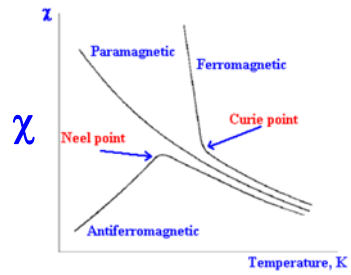
$$\frac{\chi}{N} = \frac{\frac{2(g\beta)^2}{kT}\, e^{\frac{\mathcal{J}}{2kT}}}{3e^{\mathcal{J}/2kT} + e^{-3\mathcal{J}/2kT}}$$

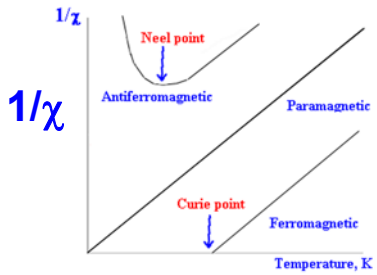


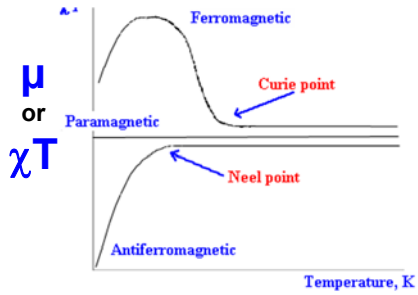
Boltzmann weighting of population of available excited states.

ICBST: $T_N \sim 5/4\ \mathcal{J} / k$

Temperature Effects on Magnetic Behavior







Other Kinds of Magnetism

Spin Glass – A random orientation of frozen spin orientations (in a paramagnet the spin orientations are fluctuating.) Can occur when the concentrations of magnetic ions are dilute or the magnetic exchange interactions are frustrated.

Cluster Glass – The spin orientations lock in with magnetic order in small clusters, but no order between the clusters (similar to a spin glass).

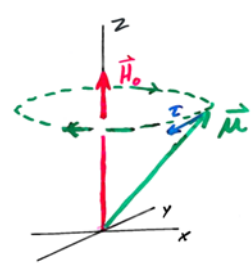
Metamagnet – There is a field-induced magnetic transition from a state of low magnetization to one of relatively high magnetization. Typically the external field causes a transition from an antiferromagnetic state to a different type (such as a ferromagnet).

Superparamagnet – A ferromagnet whose particle size is too small to sustain the multidomain structure. Thus the particle behaves as one large paramagnetic ion.

Mag Moment = Ang. Mom. w/ Charge

Close connection between the magnetic moment and angular momentum: due to the gyromagnetic effect.

- **A magnetic dipole is equivalent to a rotating charged sphere.**
- **When a magnetic moment (μ) is subject to a magnetic field (H), a torque is created that tries to align μ with H, and μ precesses. Precession is a consequence of the conservation of angular momentum associated with μ.**



- **Both the magnetic moment and the angular momentum increase with the rate of rotation of the sphere. The ratio of the two is called the gyromagnetic ratio, usually denoted γ**

Hamiltonian for Magnetic Field Interactions

Hamiltonian for Spin-Orbit Coupling and Magnetic Field:

$$\hat{\mathcal{H}} = \lambda\, \hat{L}\cdot\hat{S} + \beta\left(\hat{L} + g_e \hat{S}\right)\cdot\vec{H}$$

S.O.C.

orbital + spin contributions to e^- mag. moment

i.e., a magnetic field interacts with the angular momentum of electrons (predominantly).

Hamiltonian for Magnetic Field Interactions

Assume that the magnetic field is a perturbation of the full Hamiltonian.

Also assume that $\psi_n = \hat{a}\left(a_1\phi_1^{\alpha} + a_2\phi_2^{\beta} + a_3\phi_3^{\alpha} + \ldots\right)$

$$\therefore\ E_n = \langle \psi_n | \hat{\mathcal{H}} | \psi_n \rangle$$

Energy change from the magnetic perturbation.

$$= \langle \psi_n | \lambda \hat{L}\cdot\hat{S} | \psi_n \rangle + \langle \psi_n | \hat{L} + g_e \hat{S} | \psi_n \rangle \beta \vec{H}$$

1st Order Zeeman — "diagonal"

$$\langle \phi_i | \hat{L} + g_e \hat{S} | \phi_i \rangle$$

2nd Order — "off-diagon

$$\langle \phi_j | \hat{L} + g_e \hat{S} | \phi_i \rangle$$

Van Vleck Approximation (Power Series Expansion)

$$E_n = E_n^{(0)} + \vec{H}\, E_n^{(1)} + \vec{H}^2 E_n^{(2)}$$

S.O.C.

$\langle \psi_n | \lambda \hat{L}\hat{S} | \psi_n \rangle$

Mag Field Independent

1st Order Zeeman

$\beta \vec{H} \langle \phi_i | \hat{L} + g\hat{S} | \phi_i \rangle$

2nd Order Zeeman

$$\beta H \langle \phi_j | \hat{L} + g\hat{S} | \phi_i \rangle \Rightarrow \sum_{l \neq n} \frac{\left[\langle \psi_n | L + g_e S | \psi_l \rangle \beta H \right]^2}{E_l - E_n}$$

mixes XSs with GS

Van Vleck Approximation

$$E_n = E_n^{(0)} + \vec{H}\, E_n^{(1)} + \vec{H}^2 E_n^{(2)} + \ldots$$

magnetic moment = $\boxed{\mu = -\frac{\partial E_n}{\partial H}} = -E_i^{(1)} - 2H E_i^{(2)} + \ldots$ van Vleck Eqn.

$\therefore$ $E_n^{(0)}$ contributes nothing to Mag. Moment

$E_n^{(1)}$ contributes Field Independent Term

$E_n^{(2)}$ contributes Field Dependent Term

$E_n^{(1)}$ leads to Curie Law

$E_n^{(2)}$ is important for Low Lying Excited States

Hamiltonian for Magnetic Field Interactions

- The macroscopic molar magnetization M is then obtained by summing the microscopic magnetizations weighted according to the Boltzmann distribution law:

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

grand molar magnetization eqn.

This expression may be considered as the fundamental expression in molecular magnetism. It does not lean on any approximations!
In fact, it's just the definition of magnetization:
the mag moments of each possible state weighted by their population.

- However, it is difficult to apply this equation because it requires the knowledge of $E_n = f(H)$ variations for all thermally populated states in order to calculate the derivatives $\partial E_n/\partial H$.

Van Vleck Equation

Remember the Van Vleck Eqn. for mag. moment:

$$\mu_n = -\partial E_n/\partial H$$

$$\mu_n = -E_n^{(1)} - 2E_n^{(2)} H + \cdots$$

Now, H/kT << 1,
so the grand molar magnetization eqn. becomes

$$\frac{M}{H} = \chi = \frac{N_A \sum_n \left(\frac{E_n^{(1)2}}{kT} - 2E_n^{(2)}\right) \exp\left(\frac{-E_n^{(0)}}{kT}\right)}{\sum_n \exp\left(\frac{-E_n^{(0)}}{kT}\right)}$$

Van Vleck Equation for Magnetization

Van Vleck Equation

if 2nd order terms are small, then $E_n^{(2)}$ vanishes and

$$\chi = \frac{N_A \sum_n E_n^{(1)^2} \exp\left(-E_n^{(0)}/kT\right)}{kT \sum_n \exp\left(-E_n^{(0)}/kT\right)}$$

simplified Van Vleck Eqn.

Summary: Types of Magnetic Behavior

Magnetic Ordering in Solids

- **Diamagnetism**: No unpaired e^-
- **Paramagnetism**: Unpaired e^-, disordered and fluctuating
- **Ferromagnetism**: All unpaired e^- spins aligned parallel
- **Antiferromagnetism**: Unpaired e^- aligned antiparallel
- **Ferrimagnetism**: Unpaired e^- aligned antiparallel but don't fully cancel out

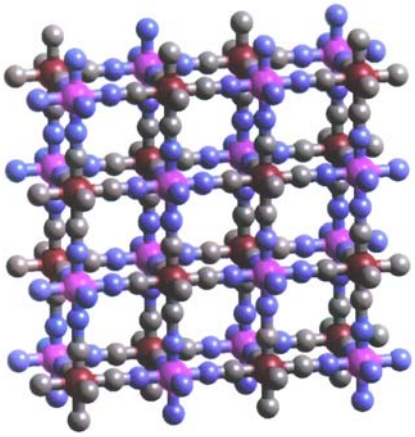
Magnetic Superexchange

- Unpaired electron spins couple through covalent interactions with intervening ligand
- $\frac{1}{2}$ filled metal orbital + $\frac{1}{2}$ filled metal orbital, AFM SE
- $\frac{1}{2}$ filled metal orbital + empty metal orbital, FM SE
- Strength of superexchange interaction increases as covalency increases

Some Examples of Molecule-Based Magnetic Materials

General Structure of Prussian Blue

PB formula: $Fe^{III}[Fe^{II}(CN)_6]_{0.75}\cdot nH_2O$



C = gray spheres

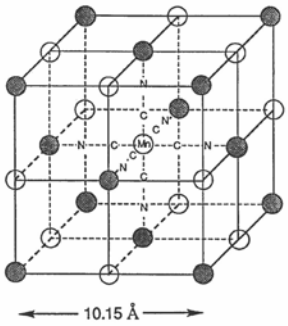
N = blue spheres

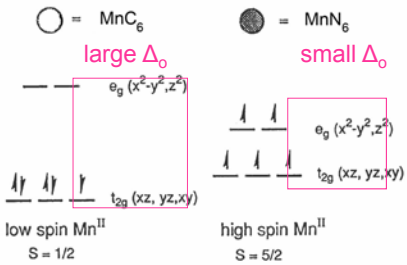
M = red/pink spheres

Structure is similar to perovskite (cubic $CaTiO_3$) except cyanide (CN) replaces oxygen, and there are two different, alternating octahedral metal centers.

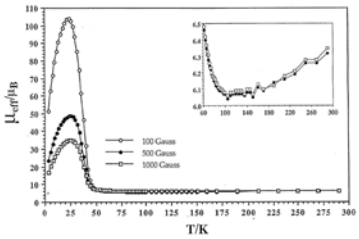
General synthetic route: $M^{m+} + M(CN)_6^{n-} \longrightarrow$ PB Analog

$K_2Mn^{II}[Mn^{II}(CN)_6]$: A Ferrimagnet with T_N = 42 K



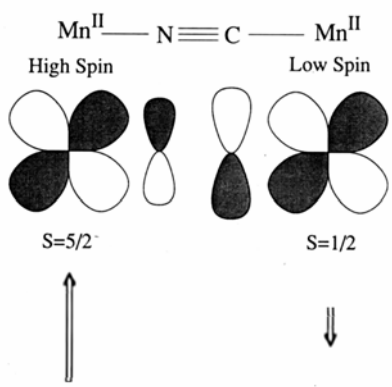


Magnetic moment increases sharply below Neél point of 42 K



The presence of a minimum in χT (or μ_{eff}) vs T curve above T_C is characteristic of a ferrimagnet; when ordering is short-ranged, spins are partially *antiparallel*.

Why is $K_2Mn^{II}[Mn^{II}(CN)_6]$ a Ferrimagnet?



Superexchange pathway provided by π* orbital of bridging CN^-

Coupling is antiparallel because both spin centers possess magnetic orbitals of the same symmetry (here, t_{2g}).

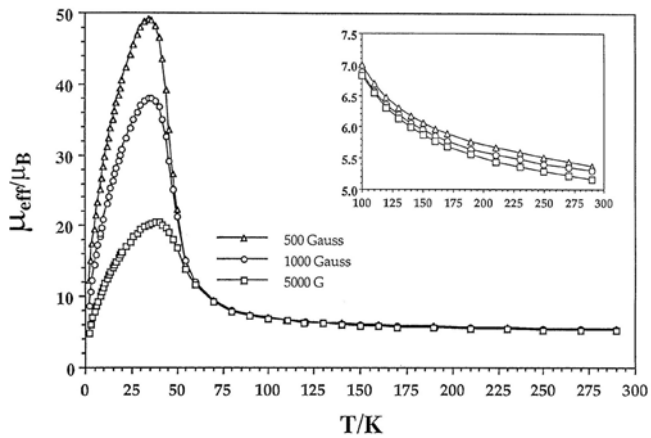
This is an inter-complex analog of Hund's rule.

Net spin: S = 5/2 – 1/2 = 2

Whenever the two metal centers in an PB analog have magnetic orbitals of the same symmetry, the resulting solid is likely to be a ferrimagnet.

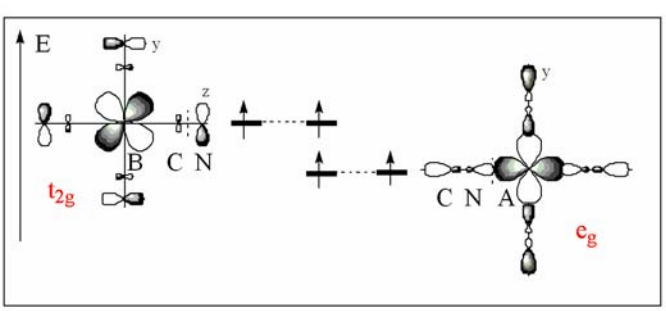
$CsNi^{II}[Mn^{III}(CN)_6]\cdot H_2O$: A *Ferro*magnetic Prussian Blue!

T_C = 42 K



The absence of a minimum in χT (or μ_{eff}) vs T curve above T_C is characteristic of a ferromagnet; when ordering is short-ranged, spins are partially *aligned*.

Orbital Orthogonality Gives Rise to Ferromagnetism



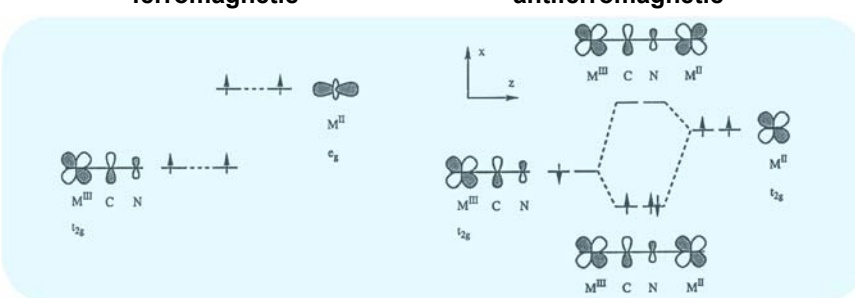
Magnetic Data for Prussian Blue Analogues: What Correlates with T_C?

Compound	T_C/K	Coupling
$CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$	90	AF
$Mn^{II}_3[Cr^{III}(CN)_6]_2\cdot 12H_2O$	66	AF
$Fe^{II}_3[Cr^{III}(CN)_6]_2\cdot 12H_2O$	16	F
$Co^{II}_3[Cr^{III}(CN)_6]_2\cdot 12H_2O$	23	F
$Ni^{II}_3[Cr^{III}(CN)_6]_2\cdot 12H_2O$	53	F
$CsNi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$	89	F
$Cu^{II}_3[Cr^{III}(CN)_6]_2\cdot 12H_2O$	66	F
$K_2Mn^{II}[Mn^{II}(CN)_6]$	41	AF
$CsMn^{II}[Mn^{III}(CN)_6]\cdot H_2O$	31	AF
$Mn^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$	37	AF
$Co^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$	16	F
$CsNi^{II}[Mn^{III}(CN)_6]\cdot H_2O$	42	F
$Ni^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$	30	F
$Mn^{II}[Mn^{IV}(CN)_6]\cdot H_2O$	49	AF
$Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 15H_2O$	5.6	F
$Mn^{II}_3[Fe^{III}(CN)_6]_2\cdot 12H_2O$	9	AF
$Co^{II}_3[Fe^{III}(CN)_6]_2\cdot 12H_2O$	15	AF
$Ni^{II}_3[Fe^{III}(CN)_6]_2\cdot 12H_2O$	23	F
$Cu^{II}_3[Fe^{III}(CN)_6]_2\cdot 12H_2O$	21	F

The Superexchange Mechanism for Prussian Blues

$$J = J_{ferromagnetic} + J_{antiferromagnetic}$$

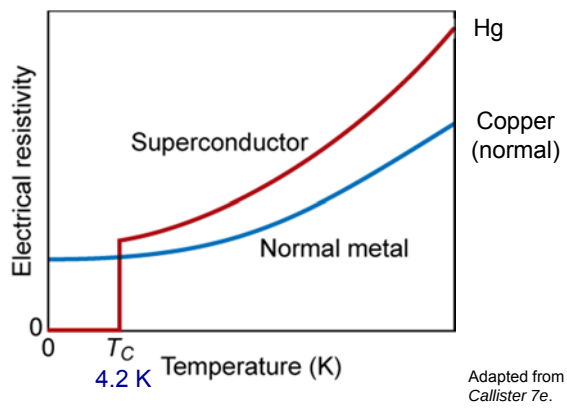
$J_{ferromagnetic} > 0$ $\qquad$ $J_{antiferromagnetic} < 0$



Our key insights: (1) Minimize competition between F and AF terms. Because all $M(CN)_6$ building blocks have spins only in the t_{2g} orbitals, pick a M′ partner that has only t_{2g} (and no e_g) magnetic orbitals also.

(2) Metal centers with high energy d-electrons should delocalize more strongly into the cyanide π* orbital, thus bringing the spin density closer to the other metal center, and giving rise to higher T_C.

Superconductivity



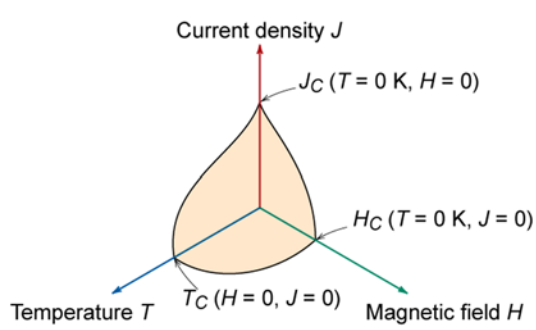
Adapted from Fig. 20.26, *Callister 7e*.

- T_c = temperature below which material is superconductive
  = critical temperature

Limits of Superconductivity

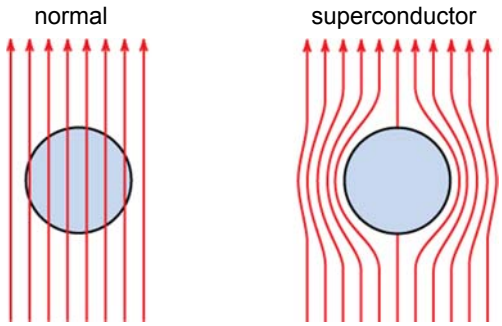
- 26 metals + 100's of alloys & compounds
- Critical Currents and Fields:
  J_c = critical current density if $J > J_c$ not superconducting
  H_c = critical magnetic field if $H > H_c$ not superconducting

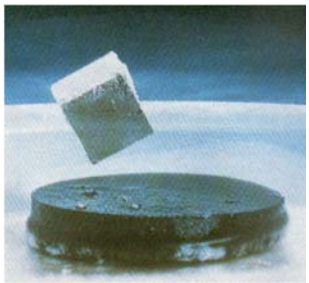
$H_c = H_o\,(1 - (T/T_c)^2)$



Meissner Effect

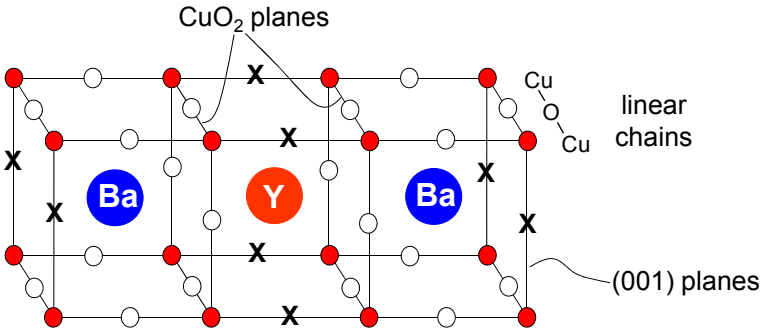
Superconductors expel magnetic fields: perfect diamagnets.





- Expulsion due to electric currents generated near surface that cancel applied mag. field within the bulk of the superconductor. Field expulsion/cancellation does not change with time in a supercon, the currents producing this effect are "persistent currents."
- Near the surface, within a distance called the London penetration depth, the magnetic field is not completely cancelled. Each superconducting material has its own characteristic penetration depth.
- This is why a superconductor will float above a magnet.

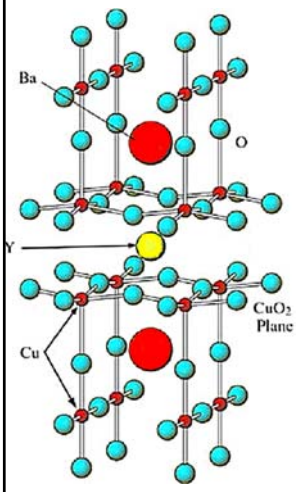
High Tc Superconductors

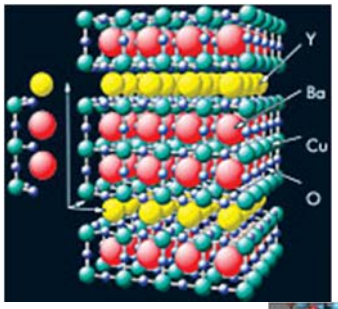


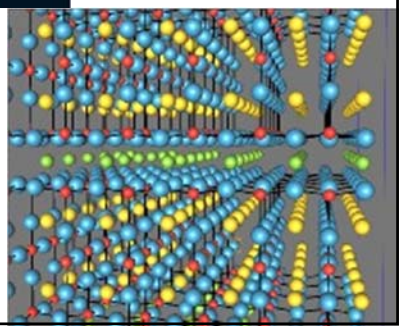
$YBa_2Cu_3O_7$ (aka 123 and YBCO)

Vacancies (X) provide electron coupling between CuO_2 planes.

High Tc Superconductors







$YBa_2Cu_3O_7$ (123, YBCO)