Magnetic Properties of Materials

1. Magnetisation of materials due to a set of isolated atoms (or ions)

a) Diamagnetism - magnetic moment of filled shells of atoms. Induced moment opposes applied field

b) Paramagnetism - unfilled shells have a finite magnetic moment (orbital angular momentum) which aligns along the magnetic field direction.

2. Collective magnetisation - magnetic moments of adjacent atoms interact with each other to create a spontaneous alignment - Ferromagnetism, Ferrimagnetism, Antiferromagnetism

Some useful background

Definition of the fields:

B is the magnetic flux density (units Tesla)

H is the magnetic field strength (units Am^{-1})

M is the magnetisation (the magnetic dipole moment per unit volume, units Am^{-1})

$B = \mu_0 (H + M)$

All materials

$= \mu_0 \mu_r H = \mu_0 H (1 + \chi)$

Relative permeability

susceptibility

linear materials only

when non – linear in field $\chi = \left.\frac{\partial M}{\partial H}\right|_{H \to 0}$

Magnetic Energy

Energy in Magnetic Field = ½**B.H** = ½μ_0 (**H** + **M**).**H**

= ½μ_0 H^2 + ½**M.H**

Energy of a magnetic moment **m** in magnetic flux

energy to align one dipole = **- m.B** = $-m_z B_z$

Energy density due to magnetisation

of a material: E = **M.B**

Magnetic moment from a current loop:

$$m_i = \mathbf{I}\oint \mathbf{dS} = IA$$

dm
= I**dS**

Magnetic Flux density B is:

$$\mathbf{B} = \mu_0\mathbf{H} + \mu_0 \frac{N\mathbf{m_i}}{V} = \mu_0(\mathbf{H} + \mathbf{M})$$

M is magnetic dipole moment/unit volume

Langevin Diamagnetism

Electrons in an atom precess in a magnetic field at the Larmor frequency: $\omega = \frac{eB}{2m}$

Act as a current loop which shields the applied field

I = charge/revolutions per unit time = $(-Ze)\left(\frac{1}{2\pi}\frac{eB}{2m}\right)$

Area of loop = $\pi\langle\rho^2\rangle = \pi(\langle x^2\rangle + \langle y^2\rangle) = {}^2/_3\,\pi\langle r^2\rangle$

Hence magnetic moment induced/atom $m_i = -\frac{Ze^2B}{6m}\langle r^2\rangle$

For N atoms susceptibility (per unit vol or per mole) $\chi = \frac{\mu_0 N m_i}{B} = -\frac{\mu_0 N Z e^2}{6m}\langle r^2\rangle$

Magnetic Levitation - An example of magnetic energy density

Energy due to magnetisation = -m.B

Magnetic moment = $V\chi B/\mu_0$ so

force = $-mdB/dx = -V\chi(B\,{}^{dB}/_{dx})/\mu_0 = -\frac{1}{2}\nabla B^2\,V\chi/\mu_0$

force = gradient of Field energy density $\frac{1}{2}\,B^2\,V\chi$

Levitation occurs when force balances gravitational force = $V\rho g$, therefore:

$-\frac{1}{2}\nabla B^2 = \rho g\,\mu_0/\chi$

Typical values of χ are of order 10^{-5} - 10^{-6}

Paramagnetism

Unfilled shells.

Magnetic moment of an atom or ion is:

$\boldsymbol{\mu} = -g\mu_B\mathbf{J}$, where $\hbar J$ is the total angular momentum

$\mathbf{J} = \mathbf{L} + \mathbf{S}$ and μ_B is the Bohr magneton ($e\hbar/2m$)

A magnetic field along z axis splits energy levels so:

$$U = -\boldsymbol{\mu}.\mathbf{B} = m_J g\mu_B B$$

m_J runs from J to -J

Spin ½ system

N ions with $m_J = \pm ½$, g = 2, then $U = \pm \mu_B B$,

ratio of populations is given by Boltzman factor so we can write:

$$\frac{N_1}{N} = \frac{\exp(\mu_B B/kT)}{\exp(\mu_B B/kT) + \exp(-\mu_B B/kT)}$$

$$\frac{N_2}{N} = \frac{\exp(-\mu_B B/kT)}{\exp(\mu_B B/kT) + \exp(-\mu_B B/kT)}$$

Upper state N_2 has moment $-\mu_B$, so writing $x = \mu_B B/kT$

$$M = (N_1 - N_2)\mu_B = N\mu_B \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu_B \tanh x$$

Magnetisation

Magnetisation saturates at high fields and low temperatures

$$M = N\mu_B \tanh \frac{\mu_B B}{k_B T}$$

Low field, higher temperature limit tanh x $\rightarrow$ x

Curie's Law: $$\chi = \frac{M}{H} = \frac{N\mu_0 \mu_B^2}{k_B T}$$

Compare with Pauli paramagnetism $$= \frac{3N\mu_0 \mu_B^2}{2k_B T_F}$$

General Result for m_J … J $\rightarrow$ -J

$$M = NgJ\mu_B \left[\left(\frac{2J+1}{2J}\right) \coth\left(\frac{2J+1}{2J}\right)y - \left(1/2J\right) \coth\left(1/2J\right)y \right]$$

Curie's Law

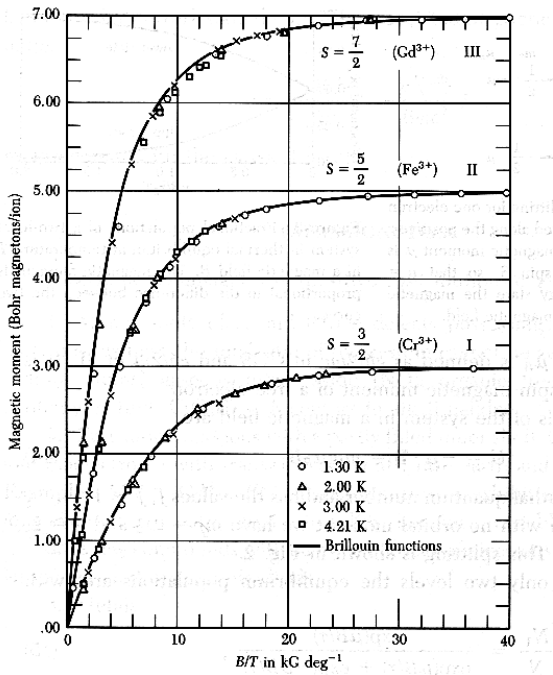
$$as \;\; y \rightarrow 0, \;\; M = NgJ\mu_B \frac{J+1}{3J} \frac{gJ\mu_B B}{kT}$$

$$\chi = \frac{M}{H} = \mu_0 N \frac{J(J+1)\, g^2 \mu_B^{\,2}}{3kT} = \frac{C}{T}$$

as $y \rightarrow \infty$, $M_{sat} = Ng\mu_B J$

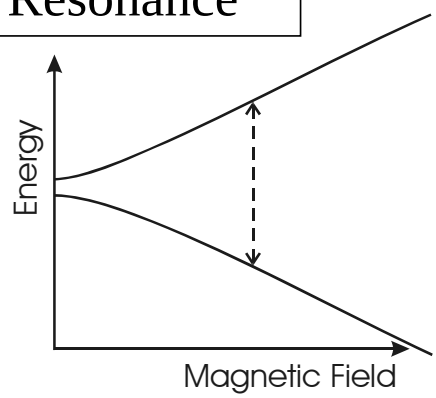
Saturation behaviour

- Curie Law at low field
- Saturation at high field



Magnetic Resonance

Apply a magnetic field to split up energy levels and observe transitions between them

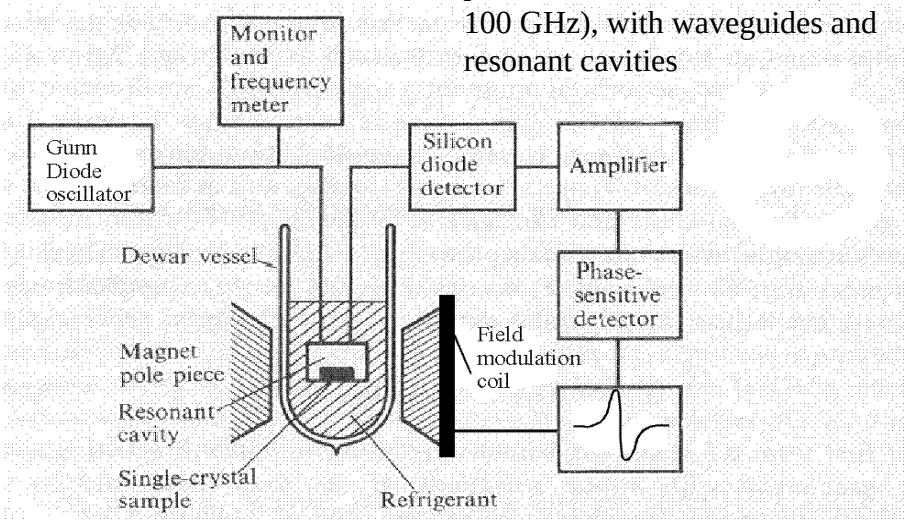


For a simple spin system $\hbar\omega = g\mu_B B$ - selection rule is $\Delta m_J = 1$ (conservation of angular momentum)

When ions interact with the crystal environment or each other then extra splittings can occur.

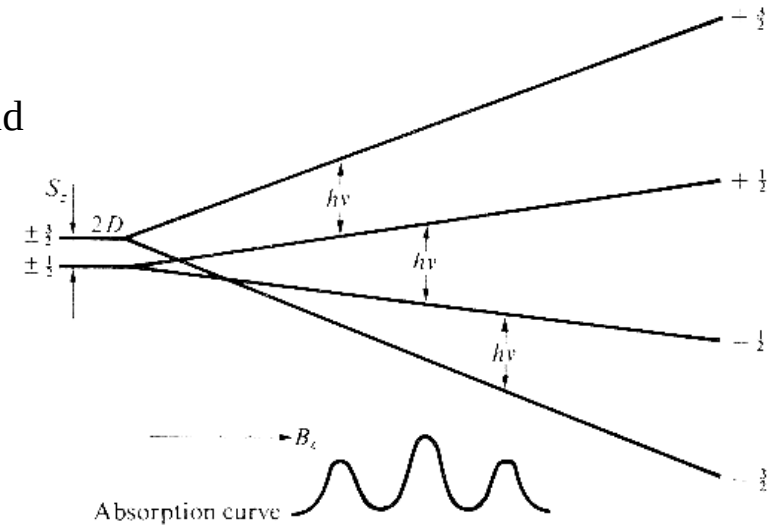
Magnetic Resonance Experiment

Experiment uses microwaves (10 - 100 GHz), with waveguides and resonant cavities



Resonance Spectrum

Relate to Crystal field splittings



Nuclear Magnetic Resonance

Similar to spin resonance of electrons, but from spin of nuclei. Energy is smaller due to the much smaller value of μ_{BN}

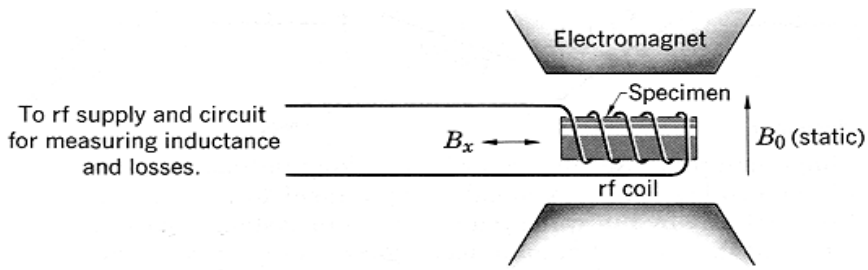
Resonance condition is $\hbar\omega = g\mu_N(B + \Delta B)$

ΔB is the chemical shift due to magnetic flux from orbital motion of electrons in the atom.

$$\Delta B = \frac{\mu_0 m}{r^3} = -\frac{Ze^2 B}{6m}\langle r^2 \rangle . \frac{\mu_0}{r^3}$$

Diamagnetic magnetic moment induced in a single atom

N.M.R. and M.R.I.



Chemical sensitivity is used in monitoring many biochemical and biological processes

NMR

Scan magnetic field with a field gradient in order to achieve chemically sensitive imaging

MRI

Magnetic Cooling (adiabatic demagnetisation)

Cool a solid containing alot of magnetic ions in a magnetic field. Energy levels are split by $U = \pm \mu_B B_i$

Population ratio is

$$\frac{N_+}{N_-} = \exp\left(-\frac{2\mu_B B_i}{kT_i}\right)$$

Remove magnetic field quickly while keeping population of spins the same - **Adiabatically**

$$\frac{kT_f}{\mu_B B_f} = \frac{kT_i}{\mu_B B_i}$$

T_f is limited by small interactions between ions which split energy levels at B = 0

Interactions between magnetic ions

Dipole - dipole interactions

Neighbouring atoms exert a force on each other which tries to align dipoles **m**. Interaction energy is U = -**m**.**B**.

Magnetic flux B is $\mu_0(\mathbf{m}/4\pi r^3 - 3(\mathbf{m}.\mathbf{r})\mathbf{r}/4\pi r^5)$ so

$$U = -\mathbf{m}.\mathbf{B} \sim -\mu_0 \mathbf{m}_1.\mathbf{m}_2/4\pi r^3 = -\mu_0 \mu_B{}^2/4\pi r^3$$

r is separation of atoms (approx. 0.3nm) giving

$$U = 4 \times 10^{-25} \text{ J} = 0.025 \text{ K}$$

If all atomic dipoles are aligned the magnetisation is:
$M = N\mu_B$ giving a total magnetic flux $B = \mu_0 N\mu_B \sim 1T$
so: $U = 0.9 \times 10^{-23}$ J ~ 0.7 K

Collective Magnetism - Ferro-, Antiferro- and Ferrimagnetism

Oldest piece of Condensed Matter physics known about and exploited is ferromagnetism.

Why do spins align at temperatures as high as 1000 K ??

It is definitely not due to magnetic dipole-dipole interactions.

The strong interaction is due to the action of the Pauli exclusion principle which produces:

Exchange Interactions

Exchange Interaction

Consider two adjacent atoms and two electrons with a total wavefunction $\psi(r_1,r_2;s_1,s_2)$

Pauli exclusion principle: $\psi(r_1,r_2;s_1,s_2) = -\psi(r_2,r_1;s_2,s_1)$

If $r_1 = r_2$ and $s_1 = s_2$ then $\psi = 0$

Electrons with same spin 'repel' each other and form symmetric and antisymmetric wavefunctions $[\phi_a(r_1) = \phi_{3d}(r_1-r_a)]$

$$\psi_s(1,2) = [\phi_a(r_1)\,\phi_b(r_2) + \phi_a(r_2)\,\phi_b(r_1)]\chi_s(\uparrow\downarrow)$$

$$\psi_t(1,2) = [\phi_a(r_1)\,\phi_b(r_2) - \phi_a(r_2)\,\phi_b(r_1)]\chi_t(\uparrow\uparrow)$$

Energy difference between singlet and triplet is dependent on alignment of the spins $U = -2J\mathbf{s_1}.\mathbf{s_2}$

energy difference given by the ‘exchange integral’

$$J = 2\int \phi^*_a(1)\phi_b(1)\left[\frac{e^2}{4\pi\varepsilon_0 r_{12}} - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right]\phi^*_a(2)\phi_b(2)d^3r_1 d^3r_2$$

Positive term electron-electron coupling	Negative term electron-ion coupling

Comes from electrostatic (Coulomb) interactions

J > 0	J < 0
Electron spins align	Electron spins antiparallel
Ferromagnetic coupling	Anti-ferromagnets
	Covalent bonding

Molecular Field Model

Energy of one spin in an external magnetic flux B_0

$$U = -\mathbf{S_i}.\sum J_{ij}\mathbf{S_j} + g\mu_B\mathbf{B_0}.\mathbf{S_i}$$

$$= -J_{ij}\,\mathbf{S_i}.\langle\mathbf{S_j}\rangle + g\mu_B\mathbf{B_0}.\mathbf{S_i}$$

which can be considered as due to an effective flux B_{eff}

$$B_{eff} = B_0 + \mu_0\lambda M,$$

where $M = -Ng\mu_B\langle S\rangle$ *and* $\lambda = \dfrac{2\sum_{j\neq i} J_{ij}}{N\mu_0 g^2\mu_B^2}$

Spins are aligned by the combination of the external flux B and the internal magnetisation.

Curie - Weiss Law

Assuming Curie's Law to hold for the total fields

$$\mu_0 M = \frac{CB_{eff}}{T} = \frac{C(B_0 + \lambda\mu_0 M)}{T}$$

$$\mu_0 M = \frac{CB_0}{T - C\lambda}$$

$$\chi = \frac{\mu_0 M}{B_0} = \frac{C}{T - T_c}, \quad T_c = C\lambda$$

Curie - Weiss Law shows that at around T_c there will be a spontaneous magnetisation

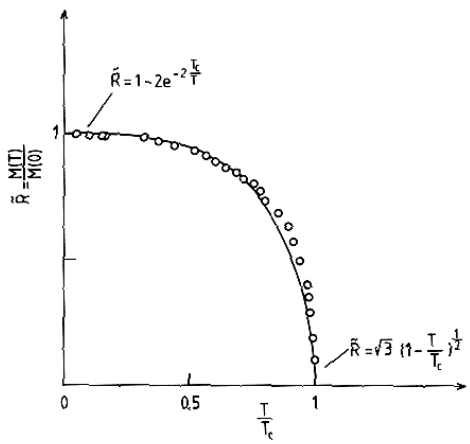
Saturation Magnetisation

Around T_c the spins begin to align.

$$\mu_0 M = \mu_0 NgJ\mu_B B_J(y),$$

For spin 1/2

$$\mu_0 M = N\mu_B \tanh \frac{\mu_B \mu_0 M}{k_B T}$$



No simple analytical solution, but graph shows numerical result is reasonable description of experiment

for spin $\frac{1}{2}$, $C = \frac{N\mu_0\mu_B^2}{k_B}$ and $\lambda = \frac{2\sum_{j\neq i} J_{ij}}{N\mu_0 g^2 \mu_B^2}$

so $T_c = C\lambda = \frac{zJ_{ij}}{2k_B}$, z is No. of nearest neighbours

Typical values of T_c are 1000K, so if z = 8 we find

$$J = \sim 0.02 \text{ eV},$$

At saturation (all spins aligned) $M = N\mu_B$ giving:

$$B_{eff} = \mu_0\lambda M = \mu_0 N\mu_B T_c/C = k_B T_c/\mu_B \sim 1500 \text{ T}$$

This is not a real Magnetic Field

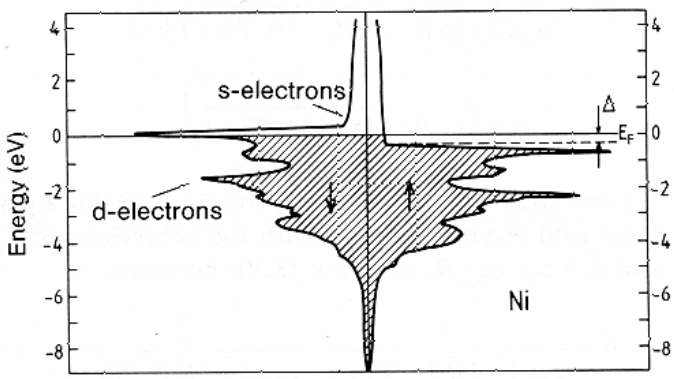
$$B_{ferromagnet} = \mu_0 N\mu_B \sim 1T$$

Result is a non-integer average magnetic moment per electron
e.g.

Metal	M_s (μ_B / atom)		gJ	
Iron	2.2	Fe^{3+}	5	T_c = 1043
Cobalt	1.7	Co^{2+}	6	T_c = 1388
Nickel	0.6	Ni^{2+}	6	T_c = 627
Gd	6.8	Gd^{3+}	7	T_c = 292
Dy	10.2	Dy^{3+}	10	T_c = 88

Rare-earths have very narrow bands so result is given by free ion result

Band model of Ferromagnetism

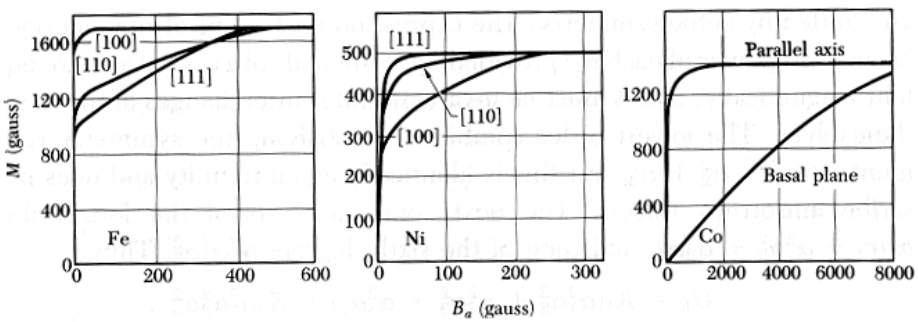


Exchange interaction shifts energy levels of electrons by less than typical band widths in metals, so we have to remember that just as in Pauli paramagnetism not all of the spins can be aligned.

Domains

One thing is missing from our explanation:

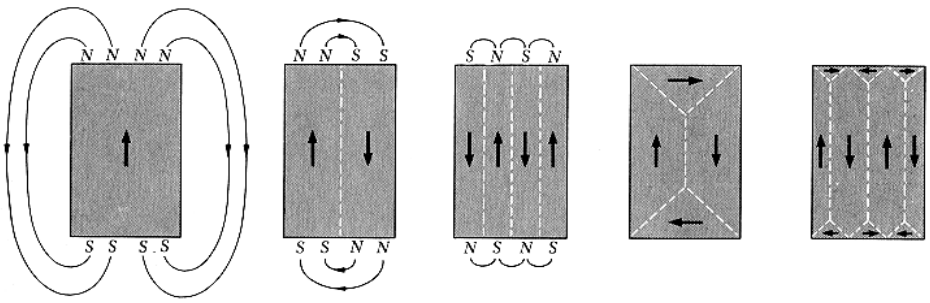
Real magnetic materials need an external magnetic field to be applied in order to produce strong or permanent magnetisation - depends on crystal orientation



Why do Domains form?

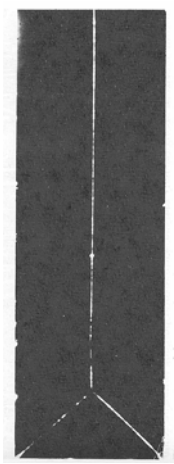
Magnetisation of a single crystal costs a large amount of energy of magnetisation = $\int B_0 . dM$

Balanced by anisotropy energy - spins only like to align along particular crystal directions - energy cost is K per electron spin



Domains in real crystals

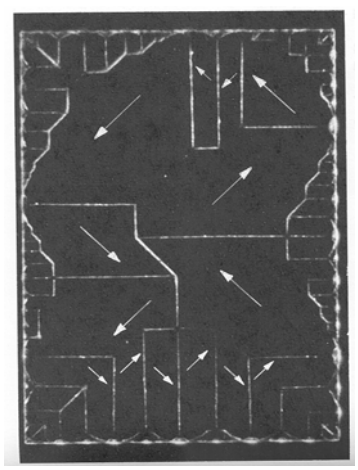
Single ‘whisker’ of iron



Domains can be ‘pinned’ by the presence of impurities, which make it easy for the domain boundary to sit in one place

Causes the difference between ‘soft’ and ‘hard’ magnetic materials

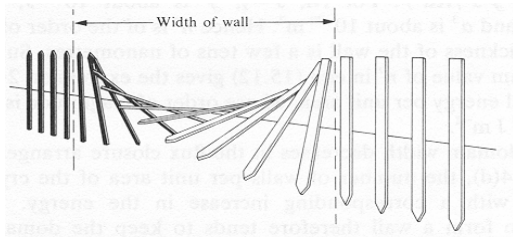
Larger crystal of Nickel



Domain boundaries - Bloch Wall

Energy is minimised by changing the spin slowly in N steps by a small angle $\theta = \pi/N$.

Energy cost calculated from exchange energy



$$U = -\sum 2J\mathbf{s_1}.\mathbf{s_2}$$

$\Delta U = 2NJS^2(1-\cos(\theta)) = 2NJS^2(1-(1 - \theta^2/2)) = JS^2\pi^2/N$

Anisotropy energy cost = $KN/2$

Total = $JS^2\pi^2/N + KN/2$,

Minimum when $N = (2JS^2\pi^2/K)^{1/2}$, e.g. 300 in Fe

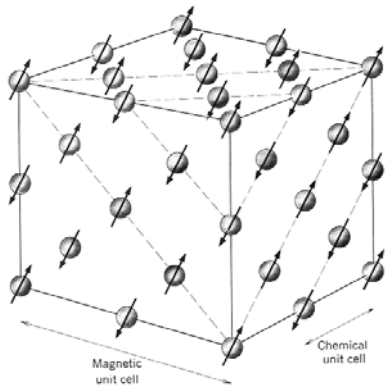
Antiferromagnetism

What if exchange integral $J < 0$?

Adjacent spins line up antiparallel.

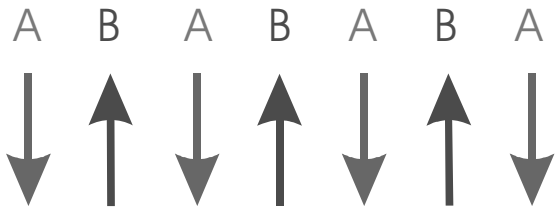
This causes **antiferromagnetism**

An example is MnO



Can model this with a molecular field model with **two** molecular fields corresponding to spin up and spin down

Result gives: $\chi = C/(T + \theta)$



$$B^{A}_{eff} = B_0 - \mu_0 \lambda M_B \ ,$$
$$B^{B}_{eff} = B_0 - \mu_0 \lambda M_A$$

$$\lambda = \frac{4\sum_{j \neq i} J_{ij}}{N \mu_0 g^2 \mu_B^2}$$

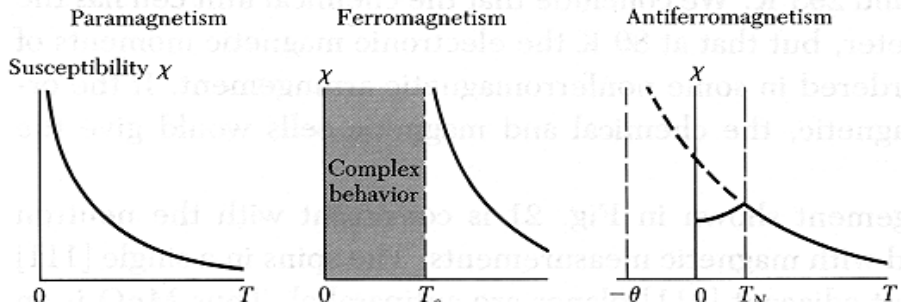
$$\mu_0 M_A = \frac{C}{2T} B^{A}_{eff} \ , \qquad M = M_A + M_B$$

$$\mu_0 M_A = \frac{C}{2T} B - \frac{\lambda C}{2T} \mu_0 M_B$$
$$\mu_0 M_B = \frac{C}{2T} B - \frac{\lambda C}{2T} \mu_0 M_A$$

Sum these two equations

$$\mu_0 M = \frac{C}{T} B - \frac{\lambda C}{2T} \mu_0 M = \frac{C B}{\left(T + \lambda C / 2\right)}$$

Summary of Collective Magnetism



Some crystals can have ions with both J > 0 and J < 0

This causes Ferrimagnetism. Best known example is ferrite Fe_3O_4 ($Fe^{2+}O,Fe^{3+}{}_2O_3$).

Moment = $(2 \times {}^{5}/_{2} - 2)\ \mu_B$ /formula unit