

Chapter 1

Magnetic Materials

1.1 Preliminaries

1.1.1 Required Knowledge

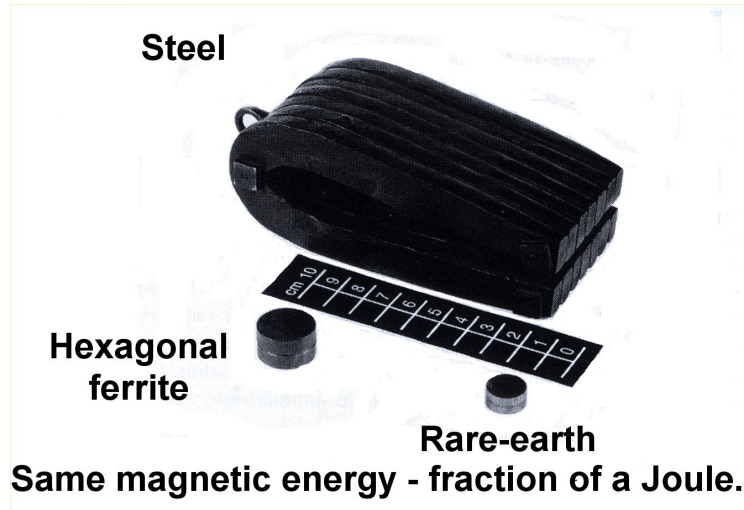
- Magnetism
- Electron spin
- Atom
- Angular momentum (quantum)
- Statistical mechanics

1.1.2 Reading

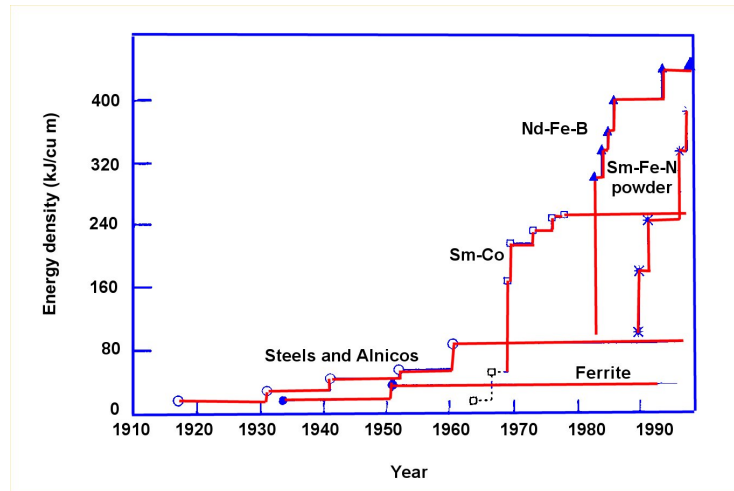
- Hook and Hall 7.1-7.3, 8.1-8.7

1.2 Introduction

- Magnet technology has made enormous advances in recent years – without the reductions in size that have come with these advances many modern devices would be impracticable.



- The important quantity for many purposes is the energy density of the magnet.



1.3 Magnetic properties - reminder

- There are two fields to consider:
 - The magnetic field \mathcal{H} which is generated by currents according to Ampère's law. \mathcal{H} is measured in A m^{-1} (Oersteds in old units)
 - The magnetic induction, or magnetic flux density, \mathcal{B} , which gives the energy of a dipole in a field, $E = -\mathbf{m} \cdot \mathcal{B}$ and the torque experienced by a dipole moment \mathbf{m} as $\mathbf{G} = \mathbf{m} \times \mathcal{B}$. \mathcal{B} is measured in Wb m^{-2} or T (Gauss in old units).

- In free space, $\mathcal{B} = \mu_0 \mathcal{H}$.
- In a material

$$\begin{aligned}\mathcal{B} &= \mu_0(\mathcal{H} + \mathcal{M}) \\ &= \mu_0 \mu_r \mathcal{H}\end{aligned}$$

where μ_r is the relative permeability, χ is the magnetic susceptibility, which is a dimensionless quantity.

- Note, though, that χ is sometimes tabulated as the *molar susceptibility*

$$\chi_m = V_m \chi,$$

where V_m is the volume occupied by one mole, or as the *mass susceptibility*

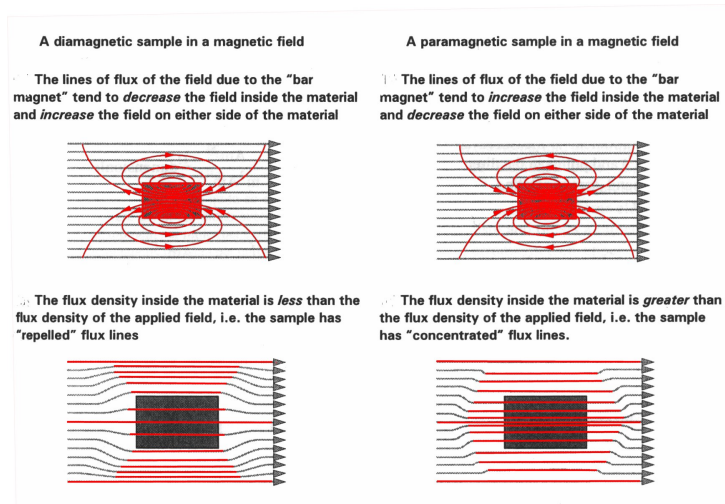
$$\chi_g = \frac{\chi}{\rho},$$

where ρ is the density.

- \mathcal{M} , the magnetisation, is the dipole moment per unit volume.

$$\mathcal{M} = \chi \mathcal{H}.$$

- In general, μ_r (and hence χ) will depend on position and will be tensors (so that \mathcal{B} is not necessarily parallel to \mathcal{H}).
- Even worse, some materials are non-linear, so that μ_r and χ are field-dependent.



- The effects are *highly exaggerated* in these diagrams.

1.4 Measuring magnetic properties

1.4.1 Force method

- Uses energy of induced dipole

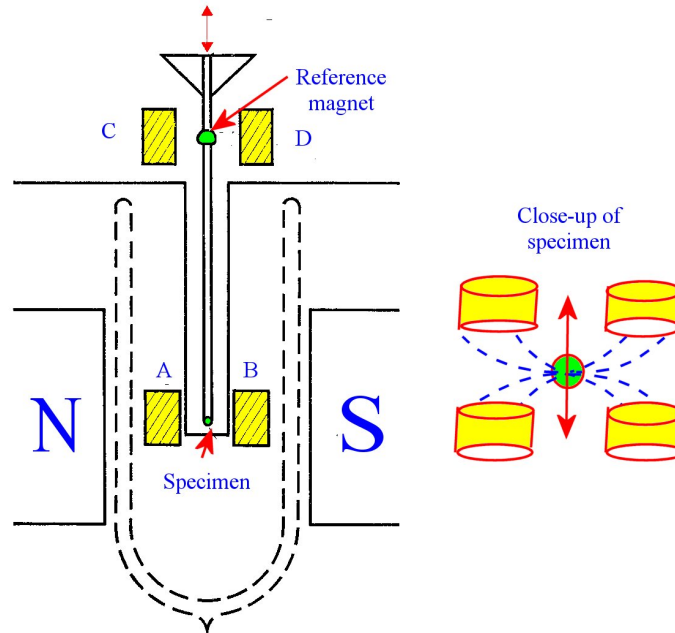
$$E = -\frac{1}{2}m\mathcal{B} = -\frac{1}{2}\mu_0\chi V\mathcal{H}^2,$$

so in an inhomogeneous field

$$F = -\frac{dE}{dx} = \frac{1}{2}\mu_0V\chi\frac{d\mathcal{H}^2}{dx} = \mu_0V\chi\mathcal{H}\frac{d\mathcal{H}}{dx}.$$

- Practically:
 - set up large uniform \mathcal{H} ;
 - superpose linear gradient with additional coils
 - vary second field sinusoidally and use lock-in amplifier to measure varying force

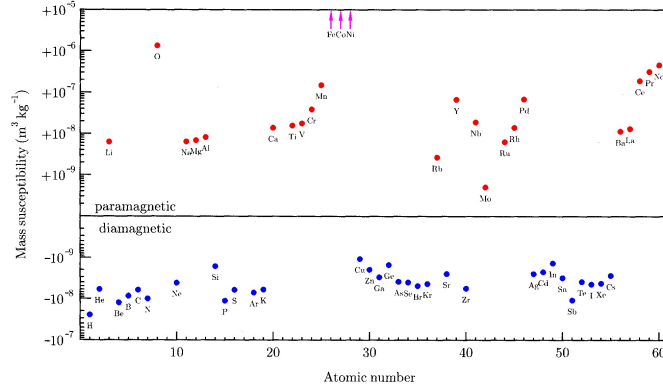
1.4.2 Vibrating Sample magnetometer



- oscillate sample up and down
- measure emf induced in coils A and B

- compare with emf in C and D from known magnetic moment
- hence measured sample magnetic moment

1.5 Experimental data



- In the first 60 elements in the periodic table, the majority have negative susceptibility – they are *diamagnetic*.

1.6 Diamagnetism

- Classically, we have Lenz's law, which states that the action of a magnetic field on the orbital motion of an electron causes a back-emf which opposes the magnetic field which causes it.
- Frankly, this is an unsatisfactory explanation, but we cannot do better until we have studied the inclusion of magnetic fields into quantum mechanics using magnetic vector potentials.
- Imagine an electron in an atom as a charge e moving clockwise in the x-y plane in a circle of radius a , area A , with angular velocity ω .
- This is equivalent to a current

$$I = \text{charge/time} = e\omega/(2\pi),$$

so there is a magnetic moment

$$\mu = IA = e\omega a^2/2.$$

- The electron is kept in this orbit by a central force

$$F = m_e\omega^2 a.$$

- Now if a flux density \mathcal{B} is applied in the z direction there will be a Lorentz force giving an additional force along a radius

$$\Delta F = ev\mathcal{B} = e\omega a\mathcal{B}$$

- If we assume the charge keeps moving in a circle of the same radius it will have a new angular velocity ω' ,

$$m_e\omega'^2 a = F - \Delta F$$

so

$$m_e\omega'^2 a = m_e\omega^2 a - e\omega a\mathcal{B},$$

or

$$\omega'^2 - \omega^2 = -\frac{e\omega\mathcal{B}}{m_e}.$$

- If the change in frequency is small we have

$$\omega'^2 - \omega^2 \approx 2\omega\Delta\omega,$$

where $\Delta\omega = \omega' - \omega$. Thus

$$\Delta\omega = -\frac{e\mathcal{B}}{2m_e}.$$

where $\frac{e\mathcal{B}}{2m_e}$ is called the *Larmor frequency*.

- Substituting back into

$$\mu = IA = e\omega a^2/2,$$

we find a change in magnetic moment

$$\Delta\mu = -\frac{e^2 a^2}{4m_e}\mathcal{B}.$$

- Recall that a was the radius of a ring of current perpendicular to the field: if we average over a spherical atom

$$a^2 = \langle x^2 \rangle + \langle y^2 \rangle = \frac{2}{3} [\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle] = \frac{2}{3} \langle r^2 \rangle,$$

so

$$\Delta\mu = \frac{e^2 \langle r^2 \rangle}{6m_e}\mathcal{B},$$

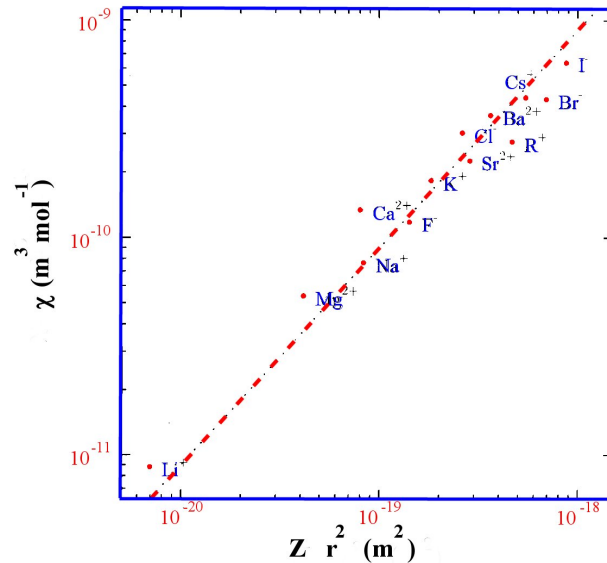
- If we have n atoms per volume, each with p electrons in the outer shells, the magnetisation will be

$$\mathcal{M} = np\Delta\mu,$$

and

$$\chi = \frac{\mathcal{M}}{\mathcal{H}} = \mu_0 \frac{\mathcal{M}}{\mathcal{B}} = -\frac{\mu_0 np e^2 \langle r^2 \rangle}{6m_e}.$$

- Values of atomic radius are easily calculated: we can confirm the $p\langle r^2 \rangle$ dependence.



- *Diamagnetic susceptibility:*
 - Negative
 - Typically -10^{-6} to -10^{-5}
 - Independent of temperature
 - Always present, even when there are no permanent dipole moments on the atoms.

1.7 Paramagnetism

- Paramagnetism occurs when the material contains permanent magnetic moments.
- If the magnetic moments do not interact with each other, they will be randomly arranged in the absence of a magnetic field.
- When a field is applied, there is a balance between the internal energy trying to arrange the moments parallel to the field and entropy trying to randomise them.
- The magnetic moments arise from electrons, but if they are localised at atomic sites we can regard them as distinguishable, and use Boltzmann statistics.

1.7.1 Paramagnetism of spin- $\frac{1}{2}$ ions

- The spin is either up or down relative to the field, and so the magnetic moment is either $+\mu_B$ or $-\mu_B$, where

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24} \text{ Am}^2.$$

- The corresponding energies in a flux density \mathcal{B} are $-\mu_B\mathcal{B}$ and $\mu_B\mathcal{B}$, so the average magnetic moment per atom is

$$\begin{aligned} \langle \mu \rangle &= \frac{\mu_B e^{\mu_B\mathcal{B}/k_B T} - \mu_B e^{-\mu_B\mathcal{B}/k_B T}}{e^{\mu_B\mathcal{B}/k_B T} + e^{-\mu_B\mathcal{B}/k_B T}} \\ &= \mu_B \tanh\left(\frac{\mu_B\mathcal{B}}{k_B T}\right). \end{aligned}$$

- For small z , $\tanh z \approx z$, so for small fields or high temperature

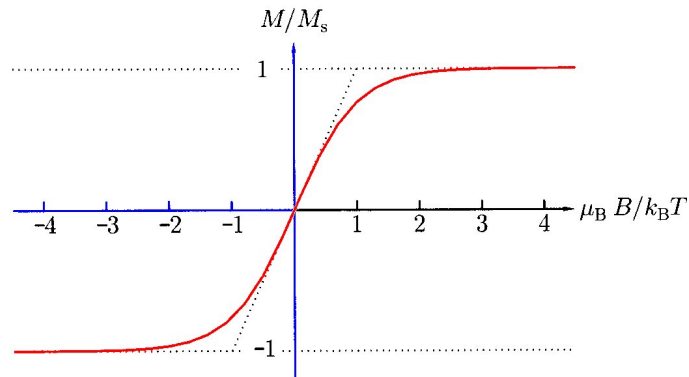
$$\langle \mu \rangle \approx \frac{\mu_B^2 \mathcal{B}}{k_B T}.$$

- If there are n atoms per volume, then,

$$\chi = \frac{n\mu_0\mu_B^2}{k_B T}.$$

- Clearly, though, for low T or large \mathcal{B} the magnetic moment per atom saturates, as it must, as the largest magnetisation possible *saturation magnetisation* has all the spins aligned fully,

$$\mathcal{M}_s = n\mu_B.$$



1.7.2 General J ionic paramagnetism

- An atomic angular momentum J , made of spin S and orbital angular momentum quantum number L , will have a magnetic moment $g_J\mu_B J$, where g_J is the Landé g-factor

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

- If we write $x = g_J\mu_B\mathcal{B}/k_B T$, the average atomic magnetic moment will be

$$\langle\mu\rangle = \frac{\sum_{m=-J}^J m g_J \mu_B e^{mx}}{\sum_{m=-J}^J e^{mx}}.$$

- If we assume that T is large and/or \mathcal{B} is small, we can expand the exponential, giving

$$\langle\mu\rangle \approx g_J \mu_B \frac{\sum_{m=-J}^J m(1+mx)}{\sum_{m=-J}^J (1+mx)}.$$

- We can evaluate this if we note that

$$\begin{aligned} \sum_{m=-J}^J 1 &= 2J+1 \\ \sum_{m=-J}^J m &= 0 \\ \sum_{m=-J}^J m^2 &= \frac{1}{3}J(J+1)(2J+1) \end{aligned}$$

then

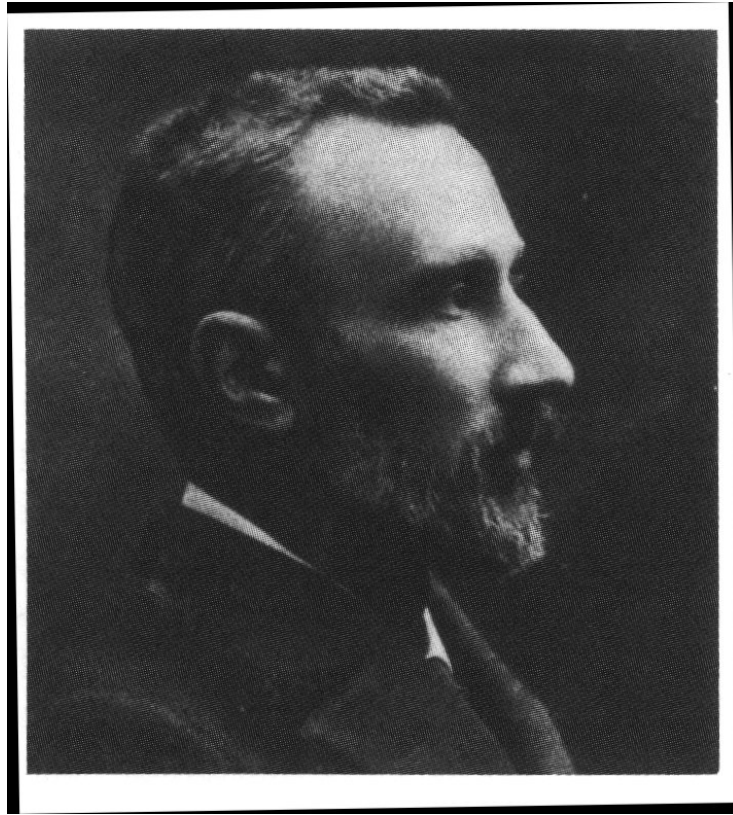
$$\begin{aligned} \langle\mu\rangle &\approx g_J \mu_B \frac{xJ(J+1)(2J+1)}{3(2J+1)} \\ &= \frac{g_J^2 \mu_B^2 \mathcal{B} J(J+1)}{3k_B T}, \end{aligned}$$

- This leads to a susceptibility

$$\chi = \frac{\mu_0 n g_J^2 \mu_B^2 J(J+1)}{3k_B T}.$$

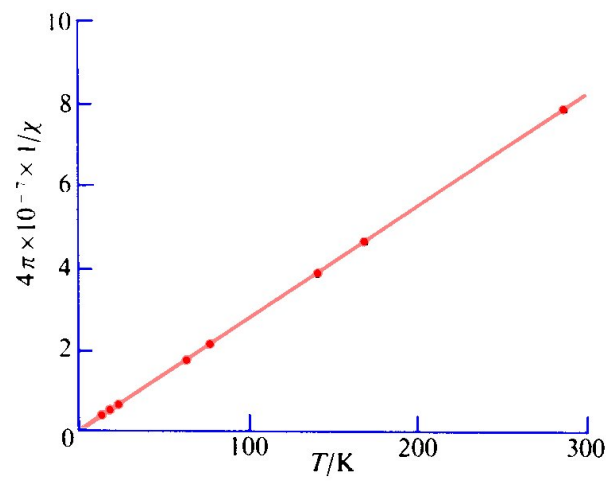
- This is *Curie's Law*, often written

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

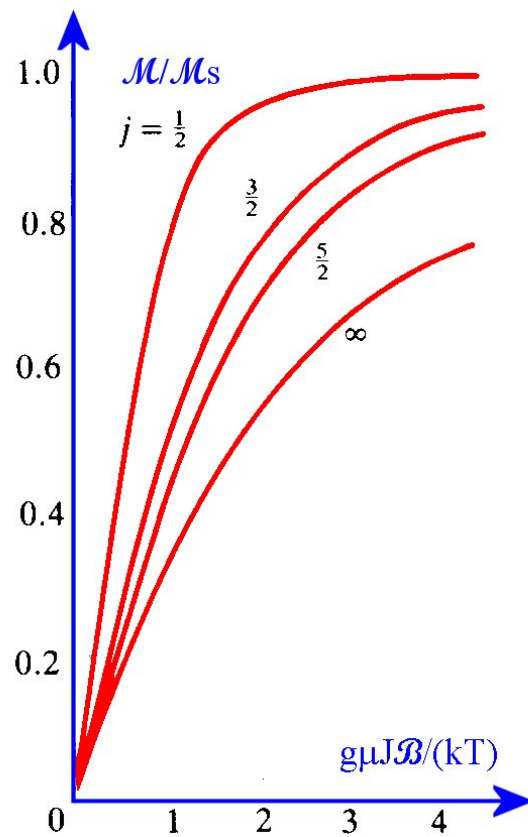


Pierre Curie

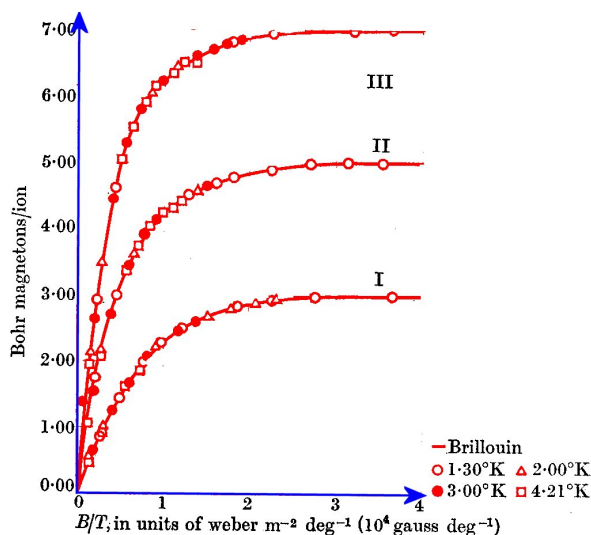
- Chromium potassium alum.



- $1/\chi$ is proportional to T , confirming Curie's law.
- Of course, eventually \mathcal{M} must saturate, as for the spin-1/2 system.
- The larger J the slower the saturation.
- A full treatment results in the *Brillouin function*, $B_J(g_J\mu_B J\mathcal{B}/k_B T)$ giving the variation of $\mathcal{M}/\mathcal{M}_s$.



- Experimental results confirm this.



Plot of average magnetic moment per ion m against B/T for (I) potassium chromium alum ($J = S = \frac{3}{2}$), (II) iron ammonium alum ($J = S = \frac{5}{2}$), and (III) gadolinium sulphate octahydrate ($J = S = \frac{7}{2}$).

- *Ionic paramagnetic susceptibility:*
 - Positive
 - Typically 10^{-5} to 10^{-3}
 - Temperature-dependent
 - Arises from permanent dipole moments on the atoms
 - Saturates for large B or low T

1.7.3 States of ions in solids

- The ions which concern us here are those with part-filled shells, giving a nett angular momentum.

IA																				VIII	
H	IIA																				He
Li	Be																				Ne
Na	Mg	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB	Al	Si	P	S	Cl	Ar						
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac																			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es									

■ Part-filled d shell
■ Part-filled f shell

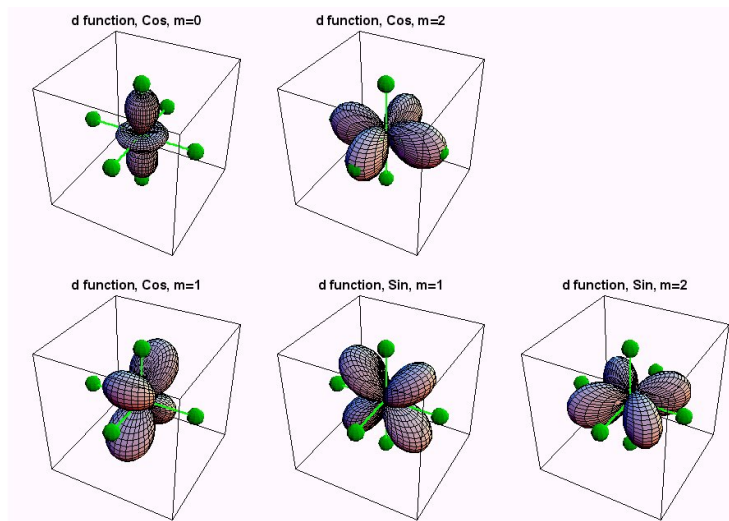
- Best studied are the first and second transition series, (Ti to Cu and Zr to Hg) and the rare earths (La to Lu).
- From atomic physics we know that a free atom or ion is characterised by quantum numbers L , S and J , and for a given L and S may take up J values between $|L - S|$ and $L + S$.
- Hund's rules tell us that the ground state is that for which
 - S is as large as possible
 - L is as large as possible for that S
 - $J = \begin{cases} L - S & \text{if the shell is less than half full} \\ L + S & \text{if the shell is more than half full} \end{cases}$
- These represent the effects of exchange, correlation, and spin-orbit coupling respectively.
- We can deduce the magnetic moment per atom $p\mu_B$ from the susceptibility, and compare with what Hund's rules tell us.

Ion	State	Term	$g\sqrt{J(J+1)}$	Experimental p
Ce ³⁺	4f ¹ 5s ² p ⁶	² F _{5/2}	2.54	2.4
Pr ³⁺	4f ² 5s ² p ⁶	³ H ₄	3.58	3.5
Nd ³⁺	4f ³ 5s ² p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² p ⁶	⁵ I ₄	2.68	-
Sm ³⁺	4f ⁵ 5s ² p ⁶	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	4f ⁶ 5s ² p ⁶	⁷ F ₀	0.00	3.4
Gd ³⁺	4f ⁷ 5s ² p ⁶	⁸ S _{7/2}	7.94	8.0
Tb ³⁺	4f ⁸ 5s ² p ⁶	⁷ F ₆	9.72	9.5
Dy ³⁺	4f ⁹ 5s ² p ⁶	⁶ H _{15/2}	10.63	10.6
Ho ³⁺	4f ¹⁰ 5s ² p ⁶	⁵ I ₈	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² p ⁶	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹² 5s ² p ⁶	³ H ₆	7.57	7.3
Yb ³⁺	4f ¹³ 5s ² p ⁶	² F _{7/2}	4.54	4.5

- All look fine except for Sm and Eu, where higher J levels are very close to the ground state which means they are partly occupied above 0 K.
- Now look at the first transition series.

Ion	State	Term	$g\sqrt{J(J+1)}$	Experimental p
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.8
V ³⁺	3d ²	³ F ₂	1.63	2.8
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	0.77	3.8
Mn ³⁺ , Cr ²⁺	3d ⁵	⁵ D ₀	0.00	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.9
Fe ²⁺	3d ⁶	⁵ D ₄	6.70	5.4
Co ²⁺	3d ⁷	⁴ F _{9/2}	6.63	4.8
Ni ²⁺	3d ⁸	³ F ₄	5.59	3.2
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.9

- The agreement is very poor.
- The problem is *crystal field splitting*. Look at the electronic *d* states in a cubic crystal.



- Two states point directly towards neighbouring ions, three states point between neighbours.
- These states have different electrostatic energies.
- So the *d* states are ‘locked’ to the crystal, and no longer behave like an $l = 2$ state with $2l + 1$ degenerate *m* values.
- This is called *quenching* of the orbital angular momentum.
- In the first transition series, the magnetic moments arise almost entirely from spin.

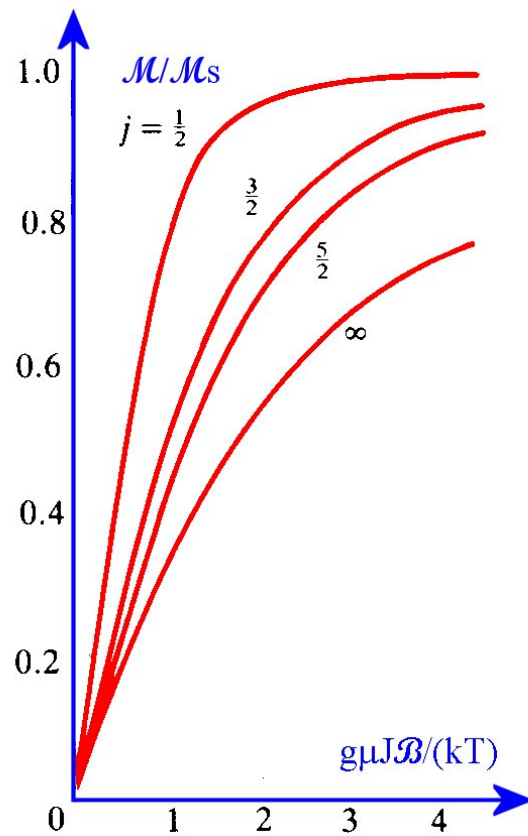
Ion	State	Term	$g\sqrt{S(S+1)}$	Experimental <i>p</i>
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.73	1.8
V ³⁺	3d ²	³ F ₂	2.83	2.8
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	3.87	3.8
Mn ³⁺ , Cr ²⁺	3d ⁵	⁵ D ₀	4.90	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.9
Fe ²⁺	3d ⁶	⁵ D ₄	4.90	5.4
Co ²⁺	3d ⁷	⁴ F _{9/2}	3.87	4.8
Ni ²⁺	3d ⁸	³ F ₄	2.83	3.2
Cu ²⁺	3d ⁹	² D _{5/2}	1.73	1.9

- Magnetism in transition metal ions arises almost entirely from *spin*.

- The rare earths behave differently because the 4f electrons are in smaller orbits than the 3d ones, and because spin-orbit coupling is larger in the 4f ions.

1.8 Interacting magnetic moments

- So far we have no explanation for the existence of ferromagnetism.
- By measuring the magnetic moment of a specimen of a ferromagnet, we can see that the magnetisation must be near saturation.
- A quick look at the Brillouin function



- shows that at room temperature this needs

$$\frac{g_J \mu_B \mathcal{B}}{k_B T} \approx 1,$$

- At room temperature, taking $g_J \approx 2$, $\mathcal{B} \approx 200$ T.

1.8.1 Direct magnetic interaction

- Where can such a large field come from?
- Can it be direct interactions between spins a lattice spacing (say 0.25 nm) apart?
- The field from one Bohr magneton at a distance r is of order

$$\mathcal{B} = \frac{\mu_0 \mu_B}{4\pi r^3} \approx 0.06 \text{ T},$$

- So direct magnetic interactions are irrelevant (though they are significant in, for example, limiting the temperatures that can be reached by adiabatic demagnetisation).

1.8.2 Exchange interaction

- The interaction is *quantum mechanical*, a form of *exchange interaction*.
- Recall Hund's rules: there exchange favoured parallel spins.
- We write the Hamiltonian for the interaction between two spins on different sites i and j as

$$\mathcal{H}_{ij}^{\text{spin}} = -2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

where J_{ij} , the exchange integral, depends on the overlap between wavefunctions on different sites.

- Positive J favours parallel spins, negative J favours antiparallel spins.
- For the whole crystal,

$$\mathcal{H}^{\text{spin}} = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

or

$$\mathcal{H}^{\text{spin}} = -2 \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j.$$

1.8.3 Effective field model

- For a particular spin, i , we can write the interaction term as

$$\begin{aligned}\mathcal{H}_i^{\text{spin}} &= -2 \sum_{j \neq i} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \\ &= - \left(2 \sum_{j \neq i} J_{ij} \mathbf{S}_j \right) \cdot \mathbf{S}_i.\end{aligned}$$

- Now note two points:

1. The form of the interaction, $-(\dots) \cdot \mathbf{S}$, looks like the interaction of a spin with a magnetic field. Write

$$\begin{aligned}\mathcal{H}_i^{\text{spin}} &= - \left(2 \sum_{j \neq i} (J_{ij} / (g_S \mu_B)) \mathbf{S}_j \right) \cdot (g_S \mu_B \mathbf{S}_i) \\ &= -\mathcal{B}_{\text{eff}} \cdot \mathbf{m}_i,\end{aligned}$$

where m_i is the magnetic moment on atom i .

2. The summation suggests that we should be able to do some averaging over the spins.

1.8.4 The mean field approximation

- Assume that each spin interacts only with its z nearest neighbours. Then

$$\begin{aligned}\mathcal{B}_{\text{eff}} &= \left(2 \sum_{j=1}^z \frac{J}{g_S \mu_B} \mathbf{S}_j \right) \\ &= 2 \sum_{j=1}^z \frac{J}{g_S \mu_B} \frac{\mathbf{m}_j}{g_S \mu_B} \\ &= 2 \frac{J}{g_S \mu_B} \frac{z \langle \mathbf{m}_j \rangle}{g_S \mu_B}.\end{aligned}$$

- Now identify the average magnetic moment per volume with the magnetisation:

-

$$n \langle \mathbf{m}_j \rangle = \mathcal{M},$$

for n spins per unit volume, giving

$$\begin{aligned}\mathcal{B}_{\text{eff}} &= 2 \frac{J}{g_S \mu_B} \frac{z \mathcal{M}}{n g_S \mu_B} \\ &= \frac{2zJ}{n g_S^2 \mu_B^2} \mathcal{M}.\end{aligned}$$

- This gives the *Weiss internal field model* or *molecular field model* (not originally derived in this way)
- The energy of a dipole in the ferromagnet is equivalent to an effective field

$$\mathcal{B}_{\text{eff}} = \lambda\mathcal{M}.$$

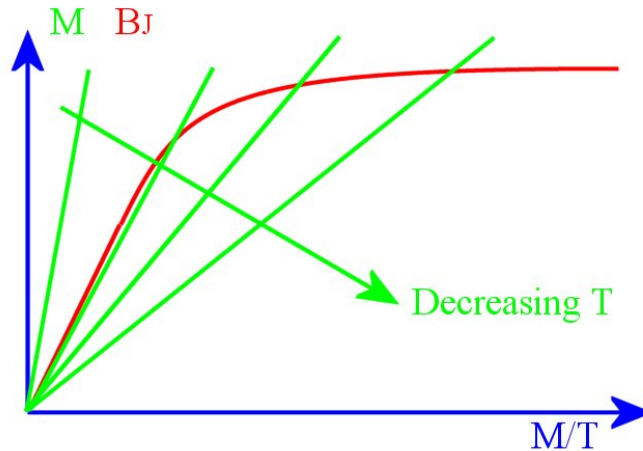
- Note that this is *NOT* a real magnetic field. The origin is quantum-mechanical exchange, not magnetism, and as the interaction that underlies exchange is the Coulomb interaction it can be much stronger.

1.8.5 Mean field theory of ferromagnetism

- Armed with the mean field picture, and a picture of the way \mathcal{M} depends on \mathcal{B} through the Brillouin function, we have

$$\frac{\mathcal{M}}{\mathcal{M}_s} = B_J \left(\frac{g_J \mu_B J (\mathcal{B} + \lambda\mathcal{M})}{k_B T} \right). \quad (1.1)$$

- Assume for the moment that $\mathcal{B} = 0$. Then we can plot the two sides of equation as functions of \mathcal{M}/T :



- As T decreases the straight line \mathcal{M} gets less steep. Thus for lower T there is a solution to

$$\frac{\mathcal{M}}{\mathcal{M}_s} = B_J \left(\frac{g_J \mu_B J \lambda \mathcal{M}}{k_B T} \right)$$

for finite \mathcal{M} .

- Furthermore the shape of B_J , a convex curve, shows that there is a critical temperature T_C above which the \mathcal{M} line is too steep to intersect the B_J curve except at $\mathcal{M} = 0$.

- For small values of \mathcal{M}/T we can use Curie's law,

$$\chi = \frac{\mu_0 n g_J^2 \mu_B^2 J(J+1)}{3k_B T}$$

and

$$\chi = \frac{\mathcal{M}}{\mathcal{H}} = \frac{n g_J J \mu_B B_J}{\mathcal{H}}$$

to deduce

$$B_J \left(\frac{g_J \mu_B J \mathcal{B}}{k_B T} \right) \approx \frac{g_J \mu_B (J+1) \mathcal{B}}{3k_B T}.$$

- In terms of $x = \mathcal{M}/T$, the straight line is

$$\frac{\mathcal{M}}{\mathcal{M}_s} = \frac{T x}{\mathcal{M}_s}$$

and the approximation to the Brillouin function is (putting $\lambda \mathcal{M}$ for \mathcal{B})

$$B_J \approx \lambda \mathcal{M} \frac{g_J \mu_B (J+1)}{3k_B T} = \lambda \frac{g_J \mu_B (J+1)}{3k_B} x.$$

- Equating the gradients with respect to x ,

$$\frac{T_C}{\mathcal{M}_s} = \lambda \frac{g_J \mu_B (J+1)}{3k_B},$$

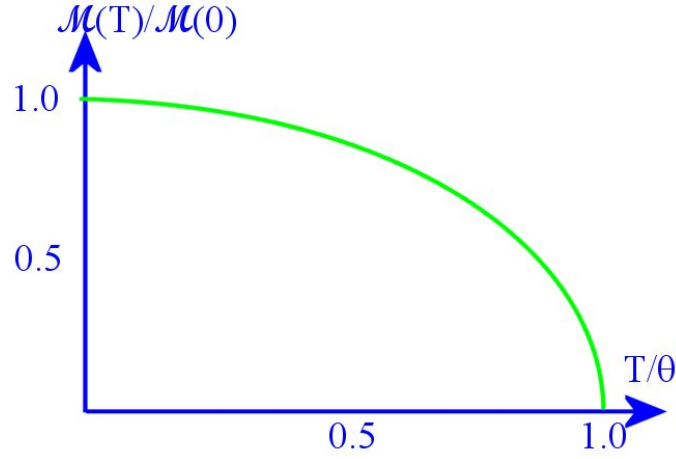
or

$$\begin{aligned} T_C &= \lambda \frac{g_J \mu_B (J+1) \mathcal{M}_s}{3k_B} \\ &= \frac{\lambda n g_J^2 \mu_B^2 J(J+1)}{3k_B}. \end{aligned}$$

- The critical temperature T_C is the *Curie temperature* – often denoted by θ .
- Some ferromagnetic materials

Material	T_C (K)	μ_B per formula unit
Fe	1043	2.22
Co	1394	1.715
Ni	631	0.605
Gd	289	7.5
MnSb	587	3.5
EuO	70	6.9
EuS	16.6	6.9

- Below T_C the spontaneous magnetisation varies with temperature.



1.8.6 Paramagnetic regime

- Above the Curie temperature, if we apply a magnetic field, we have

$$B_J = \frac{\mathcal{M}}{\mathcal{M}_s} \approx (\mathcal{B} + \lambda\mathcal{M}) \frac{g_J \mu_B (J+1)}{3k_B T}$$

- This can be rearranged to give

$$\mathcal{M} = \frac{\frac{\mathcal{M}_s \mathcal{B} g_J (J+1) \mu_B}{3k_B}}{T - \frac{\lambda \mathcal{M}_s g_J (J+1) \mu_B}{3k_B}},$$

- With $\mathcal{M}_s = n g_J J \mu_B$

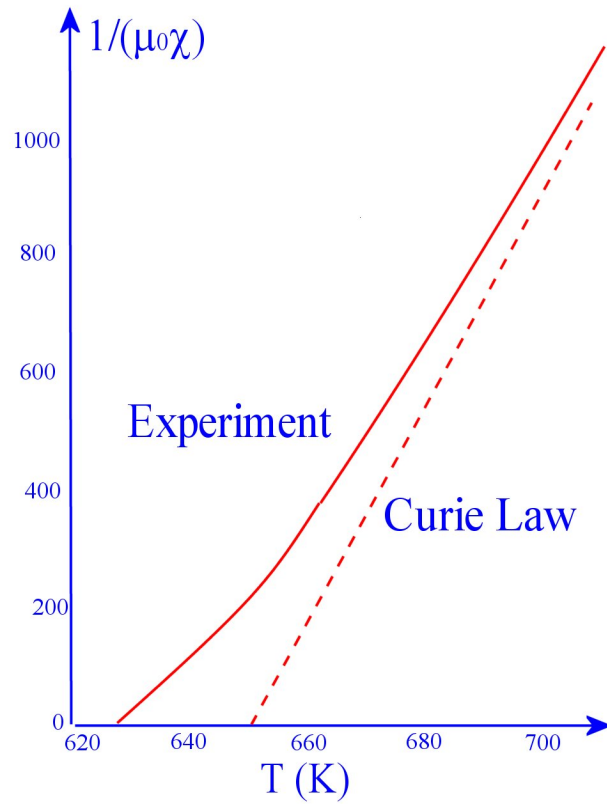
$$\begin{aligned} \mathcal{M} &= \frac{\frac{n \mathcal{B} g_J^2 J (J+1) \mu_B^2}{3k_B}}{T - \frac{\lambda n g_J^2 J (J+1) \mu_B^2}{3k_B}} \\ &= \frac{\frac{n \mathcal{B} g_J^2 J (J+1) \mu_B^2}{3k_B}}{T - T_C} \end{aligned}$$

- This gives a susceptibility

$$\chi \propto \frac{1}{T - T_C},$$

which is the *Curie-Weiss law*.

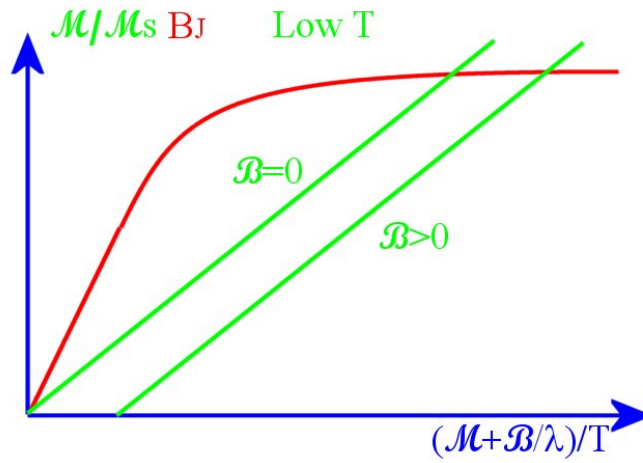
- The Curie-Weiss law works quite well at high T



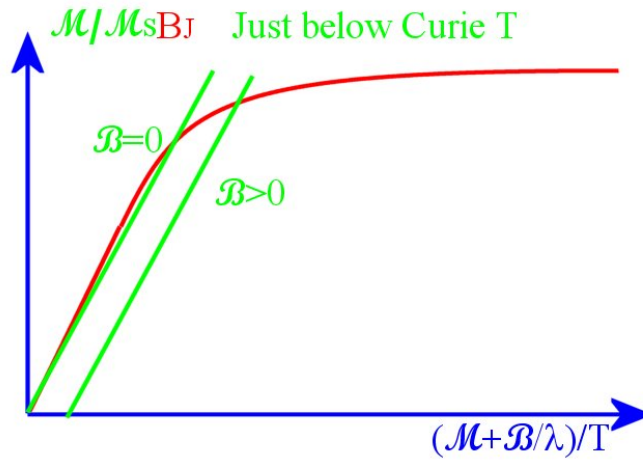
- It breaks down near the Curie temperature T_C or θ , where the mean field approximation fails.

1.8.7 Effect of magnetic field on ferromagnet

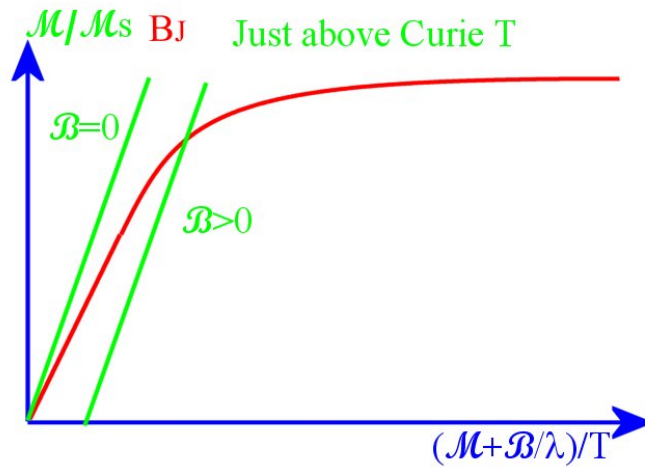
- At low temperatures, the magnetisation is nearly saturated, so a \mathcal{B} field has little effect:



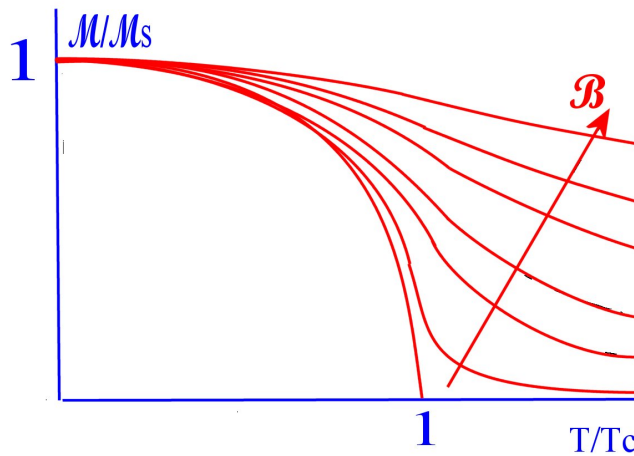
- As we increase the temperature, we reach a regime where the field has a large effect on the magnetisation:



- At high temperature we are in the Curie-Weiss regime than we described above:

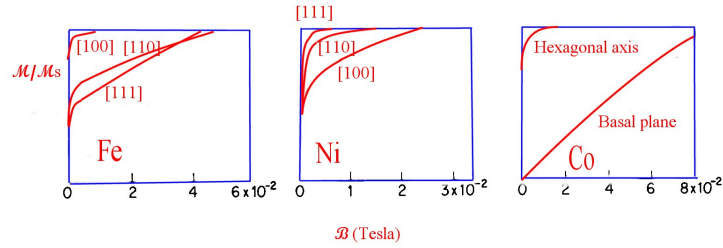


- Overall, then, the effect of a field is:



1.8.8 Anisotropy in magnetic systems

- The quenching of orbital angular momentum in a crystal is one effect of the crystal field (the electrostatic potential variation in the solid).
- But as spin-orbit coupling links the spins to the spatial variation of the wavefunctions, the spins tend to align more readily along certain directions in the crystal: the *easy directions of magnetisation*.

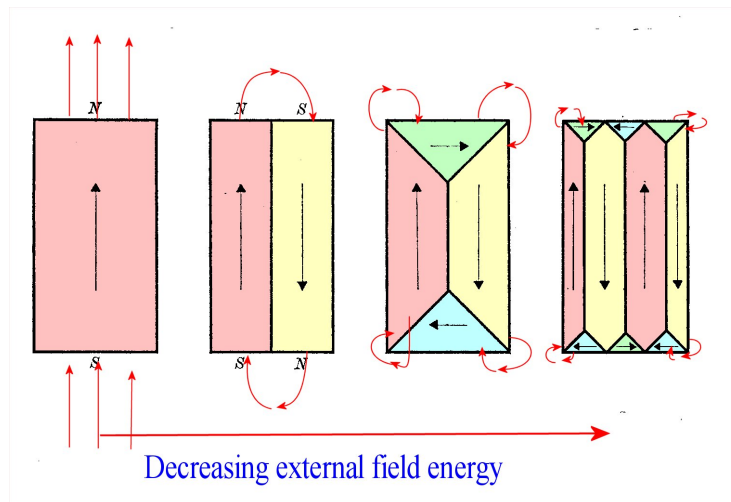


1.9 Magnetic domains

- In general, a lump of ferromagnetic material will not have a net magnetic moment, despite the fact that internally the spins tend to align parallel to one another.

1.9.1 Magnetic field energy

- The total energy of a ferromagnetic material has two components:
 1. The internal energy (including the exchange energy) tending to align spins
 2. The energy $\int \mathcal{B} \cdot \mathcal{H} dV$ in the field outside it.
- The external field energy can be decreased by dividing the material into *domains*.



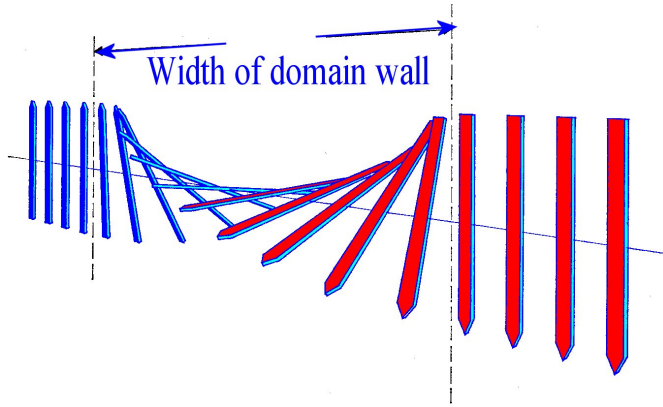
- The internal energy is increased because not all the spins are now aligned parallel to one another.

1.9.2 Domain walls

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

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

where J is the exchange integral.



- For small $\delta\theta$, expanding the cosine,

$$\delta E = 2JS^2(1 - \cos(\delta\theta)) \approx 2JS^2 \frac{1}{2}(\delta\theta)^2$$

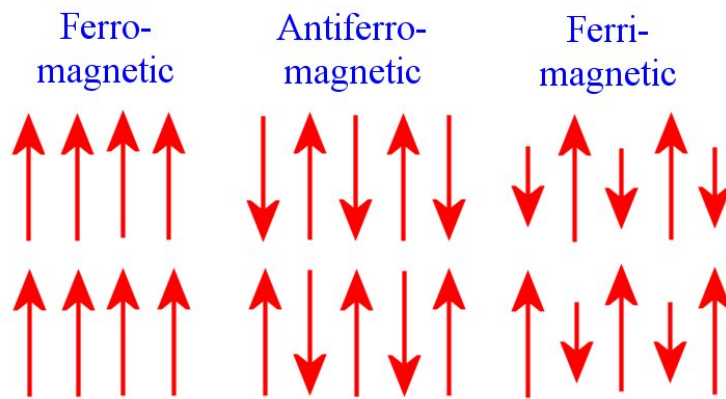
- If we extend the change in spin direction (total angle change of π) over N spins, $\delta\theta = \pi/N$, and there are N such changes of energy δE , the total energy change is

$$\Delta E = JS^2 \frac{\pi^2}{N}.$$

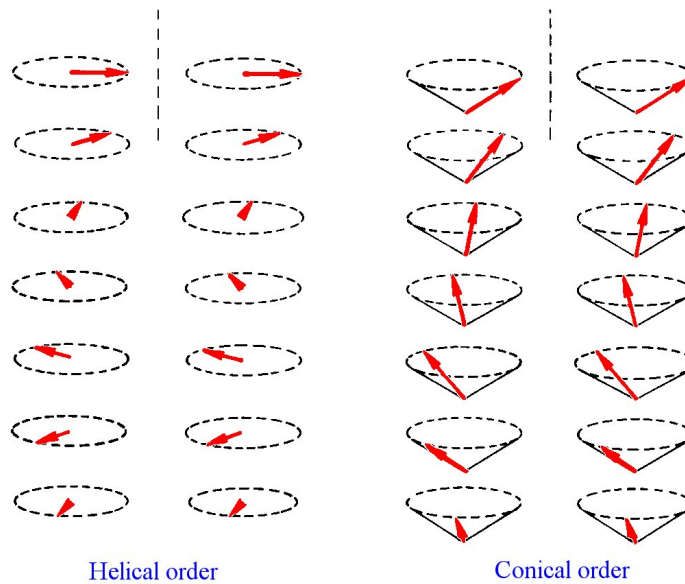
- This favours wide walls, but then there are more spins aligned away from easy directions, providing a balance. Bloch walls are typically about 100 atoms thick.
- In very small particles, the reduction in field energy is too small to balance the domain wall energy. Thus small particles stay as single domains and form *superparamagnets*.
- Small magnetic particles are found in some bacteria (*magnetotactic bacteria*) which use the angle of dip of the Earth's magnetic field to direct them to food.

1.10 Other types of magnetic ordering

- The three easiest types of magnetic ordering to visualise are
 1. ferromagnetic (all spins aligned parallel)
 2. antiferromagnetic (alternating spins of equal size)
 3. ferrimagnetic (alternating spins of different size, leading to nett magnetic moment)



- As the exchange integral J can have complicated dependence on direction, other orderings are possible, for example:

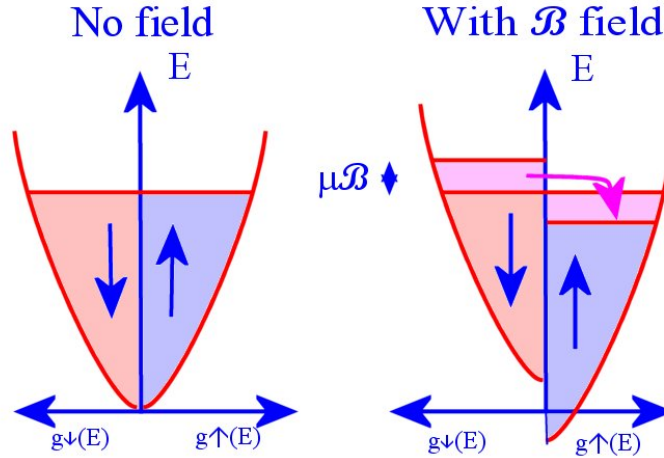


- Helical ordering (spins parallel within planes, but direction changing from plane to plane) – e.g. Dy between 90 and 180 K. Conical ordering – e.g. Eu below 50 K. Polarised neutron scattering reveals these structures.

1.11 Magnetic properties of metals

1.11.1 Free electron paramagnetism

- In a metal, the free electrons have spins, which can align in a field. As the electrons form a degenerate Fermi gas, the Boltzmann statistics we have used so far are inappropriate.



- The field \mathcal{B} will shift the energy levels by $\pm\mu_B\mathcal{B}$.
- Thus the number of *extra* electrons per unit volume with spin up will be

$$\Delta n_{\uparrow} = \frac{1}{2}g(E_F)\mu_B\mathcal{B}$$

and there is a corresponding change in the number with spin down,

$$\Delta n_{\downarrow} = -\frac{1}{2}g(E_F)\mu_B\mathcal{B}.$$

- The magnetisation is therefore

$$\mathcal{M} = \mu_B(n_{\uparrow} - n_{\downarrow}) = g(E_F)\mu_B^2\mathcal{B},$$

- This gives a susceptibility of

$$\chi = \frac{\mathcal{M}}{\mathcal{H}} = \mu_0\mu_B^2g(E_F) = \frac{3n\mu_0\mu_B^2}{2E_F}.$$

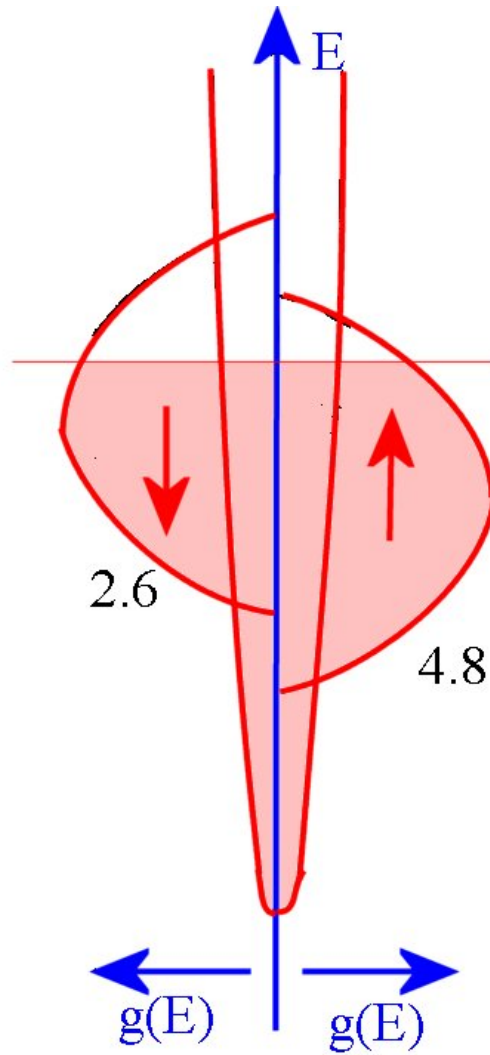
- This is a *temperature-independent* paramagnetism, typically of order 10^{-6} .
- The free electrons also have a diamagnetic susceptibility, about $-\frac{1}{3}$ of the paramagnetic χ .

1.11.2 Ferromagnetic metals

- If we look at the periodic table we find that the ferromagnetic elements are metals.

IA											VIII						
H	IIA											III B	IV B	V B	VI B	VII B	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB	Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es						

- This causes some complication in the magnetic properties.
- They can be treated in a simplified way by *Stoner theory*.
- The exchange interaction splits the narrow d bands: the wide free-electron-like s bands are relatively unaffected.



- The Fermi surface is determined by the total number of electrons: this can lead to apparently non-integer values of the magnetic moment per atom (e.g. 2.2 in Fe, 0.6 in Ni).