Condensed Matter Option MAGNETISM *Handout 1*

Hilary 2022 **Radu Coldea**

https://canvas.ox.ac.uk/courses/124773

Syllabus

The lecture course on *Magnetism in Condensed Matter Physics* will be given in 8 lectures broken up into three parts as follows:

1. **Isolated Ions**

   Magnetic properties become particularly simple if we are able to ignore the interactions between ions. In this case we are able to treat the ions as effectively "isolated" and can discuss diamagnetism and paramagnetism. For the latter phenomenon we revise the derivation of the Brillouin function outlined in the third-year course. Ions in a solid interact with the crystal field and this strongly affects their properties, which can be probed experimentally using *magnetic resonance* (in particular ESR and NMR).

2. **Interactions**

   Now we turn on the interactions! I will discuss what sort of magnetic interactions there might be, including dipolar interactions and the different types of exchange interaction. The interactions lead to various types of ordered magnetic structures which can be measured using *neutron diffraction*. I will then discuss the mean-field *Weiss model* of ferromagnetism, antiferromagnetism and ferrimagnetism and also consider the magnetism of metals.

3. **Symmetry breaking**

   The concept of broken symmetry is at the heart of condensed matter physics. These lectures aim to explain how the existence of the crystalline order in solids, ferromagnetism and ferroelectricity, are all the result of symmetry breaking. The consequences of breaking symmetry are that systems show some kind of rigidity (in the case of ferromagnetism this is *permanent magnetism*), low temperature elementary excitations (in the case of ferromagnetism these are *spin waves*, also known as *magnons*), and defects (in the case of ferromagnetism these are *domain walls*). I will also discuss experimental measurements of spin waves with *inelastic neutron scattering*.

Reading

• The text designed for this course is '*Magnetism in Condensed Matter*', by S. J. Blundell, OUP 2001. Highly recommended !

• '*Solid State Physics*', by N. W. Ashcroft and N. D. Mermin, chapters 31, 32 and in particular 33 (Magnetic ordering), contain a good overview of some of the material in the course, although written in cgs units. The relevant chapters in the solid state texts by Kittel, Burns and Rosenberg can also be consulted.

Further (somewhat more specialised) material can be found in

• '*Theory of Magnetism*', by K. Yosida (Springer 1996) [much more advanced and uses cgs units]

• An advanced, but informative description of the ideas concerning broken symmetry may be found in the second chapter of '*Basic Notions of Condensed Matter Physics*', P. W. Anderson (Westview Press 1984, 1997). For enthusiasts only!

These handouts contain some background, figures, tables, formulas and other useful material to accompany the lectures. They don't contain any detailed derivations - those will be presented in the lectures.

Some basic definitions.

- A magnetic solid consists of a large number of atoms with magnetic moments. The magnetization $\mathbf{M}$ is defined as the magnetic moment per unit volume. Usually this vector quantity is considered in the 'continuum approximation', i.e. on a lengthscale large enough so that one does not see the graininess due to the individual atomic magnetic moments. Hence $\mathbf{M}$ can be considered to be a smooth vector field, continuous everywhere except at the edges of the magnetic solid.

- In free space (vacuum) there is no magnetization. The magnetic field can be described by the vector fields $\mathbf{B}$ and $\mathbf{H}$ which are linearly related by

$$\mathbf{B} = \mu_0 \mathbf{H}, \tag{1}$$

  where $\mu_0 = 4\pi \times 10^{-7}$ Hm^{-1} is the permeability of free space. The two magnetic fields $\mathbf{B}$ and $\mathbf{H}$ are just scaled versions of each other, the former measured in Tesla (abbreviated to T) and the latter measured in A m^{-1}.

- In a magnetic solid the relation between $\mathbf{B}$ and $\mathbf{H}$ is more complicated and the two vector fields may be very different in magnitude and direction. The general vector relationship is

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}). \tag{2}$$

  In the special case that the magnetization $\mathbf{M}$ is linearly related to the magnetic field $\mathbf{H}$, the solid is called a linear material, and we write

$$\mathbf{M} = \chi \mathbf{H}, \tag{3}$$

  where χ is a dimensionless quantity called the magnetic susceptibility. In this special case there is still a linear relationship between $\mathbf{B}$ and $\mathbf{H}$, namely

$$\mathbf{B} = \mu_0(1 + \chi)\mathbf{H} = \mu_0 \mu_\mathrm{r} \mathbf{H}, \tag{4}$$

  where $\mu_\mathrm{r} = 1 + \chi$ is the relative permeability of the material.

- Consider a region of free space with an applied magnetic field given by fields $\mathbf{B}_\mathrm{a}$ and $\mathbf{H}_\mathrm{a}$, connected by $\mathbf{B}_\mathrm{a} = \mu_0 \mathbf{H}_\mathrm{a}$. So far, everything is simple. Now insert a magnetic solid into that region of free space. The internal fields inside the solid, given by $\mathbf{B}_\mathrm{i}$ and $\mathbf{H}_\mathrm{i}$, can be very different from $\mathbf{B}_\mathrm{a}$ and $\mathbf{H}_\mathrm{a}$ respectively. This difference is because of the magnetic field produced by all magnetic moments in the solid, known as the demagnetization field. In fact $\mathbf{B}_\mathrm{i}$ and $\mathbf{H}_\mathrm{i}$ can both depend on the position inside the magnetic solid at which you measure them.

- A useful simplification occurs when the magnetic susceptibility is very small. For a linear material with $\chi \ll 1$, we have that $M \ll H_\mathrm{a}$, $H_\mathrm{i} \approx H_\mathrm{a}$ and $B_\mathrm{i} \approx \mu_0 H_\mathrm{i}$. We can then get away with imagining that the magnetic field in the material is the same as the magnetic field that we apply. Hence we can drop the subscripts and write the susceptibility as

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B}. \tag{5}$$

- Measurement of magnetization

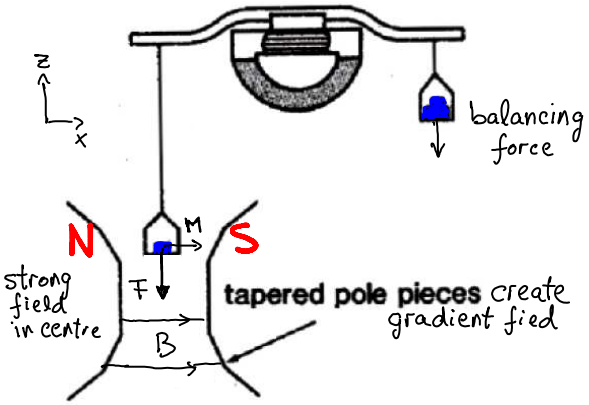
(a) Force in gradient field

In a non-uniform magnetic field sample with a net magnetic moment will be attracted towards regions of stronger field in order to minimise its magnetic energy $E = -\mathbf{M} \cdot \mathbf{B}V$. The sample will experience a force proportional to the magnetization M and the local field gradient

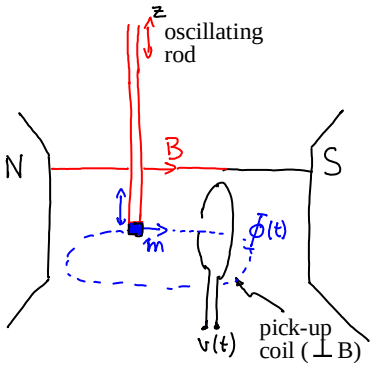
$$F_z = -\frac{dE}{dz} = M\frac{dB}{dz}V \tag{6}$$

(b) Induced magnetic flux

Moving a magnetized sample relative to a pickup coil creates a variable magnetic flux $\Phi(t)$ and this induces an emf in the coil. An oscillating sample motion will induce an oscillating emf with an amplitude proportional to the sample magnetization.



FARADAY BALANCE



VIBRATING SAMPLE MAGNETOMETER

Magnetization measurement via force in gradient field (Faraday balance) and induced flux (vibrating sample magnetometer).

1. Isolated ions

Magnetic properties become particularly simple if we are able to ignore the interactions between ions. In this case we are able to treat the ions as effectively "isolated" and can discuss diamagnetism and paramagnetism. For the latter phenomenon we revise the derivation of the Langevin and Brillouin functions outlined in the third-year course. The ions can interact with the crystal field and this can be probed experimentally using *magnetic resonance* (in particular ESR and NMR).

1.1 Introduction

> In this introductory section we recall some basic facts about magnetism and also prove a theorem (the Bohr-van Leeuwen theorem) which shows that even the existence of a bar magnet is enough to show that quantum mechanics is needed!

The Bohr magneton: Consider an electron (charge $-e$, mass $m_{\rm e}$) performing a circular orbit around the nucleus of a hydrogen atom. The current I around the atom is $I = -e/\tau$ where $\tau = 2\pi r/v$ is the orbital period, $v = |\mathbf{v}|$ is the speed and r is the radius of the circular orbit. The magnitude of the angular momentum of the electron, $m_{\rm e}vr$, must equal $\hbar$ in the ground state so that the magnetic moment of the electron is

$$\mu = \pi r^2 I = -\frac{e\hbar}{2m_{\rm e}} \equiv -\mu_{\rm B} \tag{7}$$

where $\mu_{\rm B}$ is the **Bohr magneton**, defined by

$$\mu_{\rm B} = e\hbar/2m_{\rm e}. \tag{8}$$

This is a convenient unit for describing the size of atomic magnetic moments. The Bohr magneton takes the value 9.274×10^{-24} Am^2. Note that sign of the magnetic moment in equation 7 is negative. Because of the negative charge of the electron, its magnetic moment is antiparallel to its angular momentum.

g-factor: The energy of the electron in a magnetic field B is

$$E = g\mu_{\rm B} m_s B \tag{9}$$

where g is known as the g-factor. The energy levels therefore split by an amount $g\mu_{\rm B}B$. A natural consequence of Dirac's theory of the electron (outside the scope of this book) is that g is precisely equal to two. Actually the g-factor is not quite two but takes the value

$$g = 2(1 + \frac{\alpha}{2\pi} + \cdots) = 2.0023\ldots \tag{10}$$

where α is the **fine structure constant**, a dimensionless quantity given by

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.04}. \tag{11}$$

This theoretical value obtained from quantum electrodynamics (QED) agrees with experiment to an astonishing degree of precision.

Bohr-von Leeuwen theorem: In classical statistical mechanics the partition function for N particles, each with charge q, is proportional to

$$\int\int \exp(-\beta E(\{\mathbf{r}_i, \mathbf{p}_i\})\ d^{3N}r\ d^{3N}p$$

where $i = 1, \ldots, N$. The effect of a magnetic field is to shift the momentum of each particle; we must replace $\mathbf{p}_i$ by $\mathbf{p}_i - q\mathbf{A}$ where $\mathbf{A}$ is the magnetic vector potential. The limits of the momenta integrals run from $-\infty$ to ∞ so this shift can be absorbed by shifting the origin of the momentum integrations. Since the partition function is not a function of magnetic field, neither is the free energy, so the magnetization must be zero.

$\Longrightarrow$ need quantum theory to account for magnetic properties of materials.

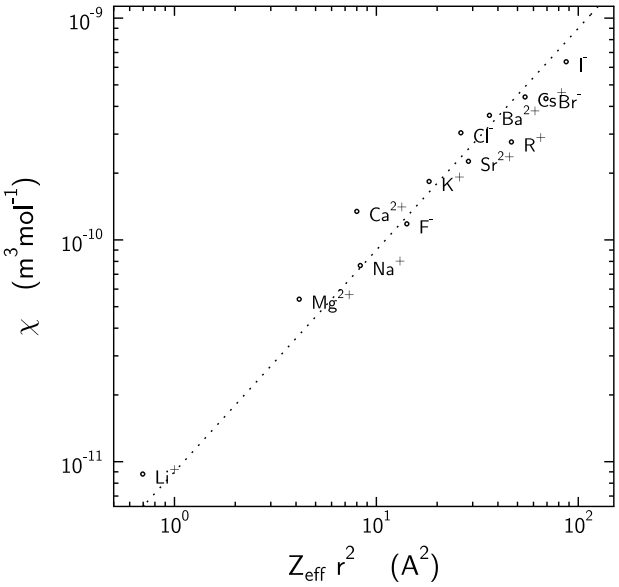
$$\mathcal{H} = \sum_i \frac{\hat{p}_i^2}{2m} + V + \mu_{\rm B}(\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m} \sum_i (\mathbf{B} \times \hat{\mathbf{r}}_i)^2$$

The next two sections explore, respectively, the third and second terms on the right-hand side of this equation.

1.2 Diamagnetism

The diamagnetic susceptibility χ of a solid composed of N ions (each with Z electrons of mass m) in volume V with all shells filled is given by

$$\chi = -\frac{N}{V} \frac{e^2 \mu_0}{6m} \sum_{i=1}^{Z} \langle r_i^2 \rangle$$



The measured diamagnetic susceptibilities of various ions plotted against $Z_{\rm eff} r^2$, where $Z_{\rm eff}$ is the number of electrons in the ion and r is a measured ionic radius.

1.3 Paramagnetism

In general $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$. For a *linear* material $\mathbf{M} = \chi\mathbf{H}$ where $\mathbf{M}$ is the magnetic moment per volume (the magnetization) and χ is the magnetic susceptibility (dimensionless) so that $\mathbf{B} = \mu_0(1 + \chi)\mathbf{H}$. Note that because of the definition of $\mathbf{M}$, χ represents the magnetic moment induced by a field $\mathbf{H}$ *per unit volume*.

Magnetic susceptibilities are often tabulated in terms of the *molar magnetic susceptibility* χ_m where $\chi_m = \chi V_m$ and where V_m is the molar volume (the volume occupied by 1 mole of the substance). The following are measured at 298 K:

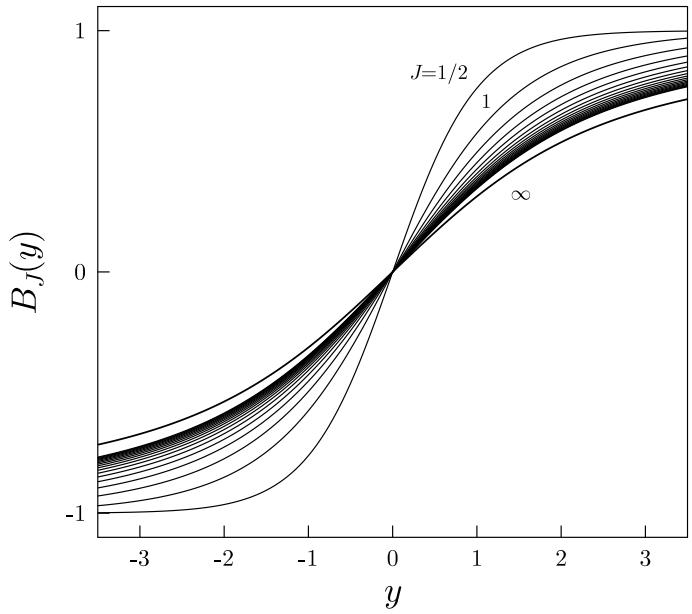
	$\chi/10^{-6}$	$\chi_m/(10^{-10}\ \mathrm{m^3\ mol^{-1}})$
water	-90	-16.0
benzene	-7.2	-6.4
NaCl	-13.9	-3.75
$CuSO_4{\cdot}5H_2O$	176	192
$MnSO_4{\cdot}4H_2O$	2640	2.79×10^3
Al	22	2.2
Na	7.3	1.7

1.4 Langevin and Brillouin functions

For atoms with total angular momentum J a magnetic field will tend to align them while temperature will tend to disorder them. The magnetization (normalized by the saturation magnetization, when they are all aligned) is $M/M_s = B_J(y)$ where $y = g_J\mu_B JB/kT$ and g_J is the appropriate g-factor. $B_J(y)$ is a *Brillouin function* and it, and some limiting cases, will be examined in the lecture.

(a) Langevin function ($J = \infty$): $L(y) = \coth y - \dfrac{1}{y} = B_\infty(y)$

(b) $J = \frac{1}{2} \Longrightarrow B_{1/2}(y) = \tanh(y)$



(c) Brillouin function: This is the general case and is given by

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\frac{y}{2J}$$

1.5 The ground state of an ion and Hund's rules

Hund's Rules:

(1) maximize S;

(2) maximize L;

(3) $J = |L - S|$ if less than half full, $J = |L + S|$ if more than half full.

The ground state can be written using a *term symbol* ${}^{2S+1}L_J$ where L is written using a letter according to

L	0	1	2	3	4	5	6
	S	P	D	F	G	H	I

e.g. For Dy^{3+}, with outer shell $4f^9$: f electrons have $l = 3$, so use $2l + 1 = 7$ of them as spin-up, and have 2 left for spin-down $\implies S = 7 \times \frac{1}{2} - 2 \times \frac{1}{2} = \frac{5}{2}$ ($\implies 2S + 1 = 6$). All the spin-up electrons give no net angular momentum, so only get a contribution from the 2 spin-down electrons which we have to maximize $\implies L = 3 + 2 = 5$. We are more than half full, so $J = |5 + \frac{5}{2}| = \frac{15}{2}$. $\implies$ Term symbol $= {}^6H_{15/2}$.

	↑	↓
$m_l = 3$	•	•
2	•	•
1	•	
0	•	
−1	•	
−2	•	
−3	•	

Theoretical value of effective moment, $\mu_{\text{eff}} = g_J \mu_{\text{B}} \sqrt{J(J+1)}$ where

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

rare-earth (4f) ions:

ion	shell	n	S	L	J	${}^{2S+1}L_J$	g_J	$g_J\sqrt{J(J+1)}$	$\mu_{\text{eff}}/\mu_{\text{B}}$ (exp.)
Gd^{3+}	$4f^7$	7	$\frac{7}{2}$	0	$\frac{7}{2}$	${}^8S_{7/2}$	2	7.94	8.0
Tb^{3+}	$4f^8$	8	3	3	6	${}^7F_6$	$\frac{3}{2}$	9.72	9.5
Dy^{3+}	$4f^9$	9	$\frac{5}{2}$	5	$\frac{15}{2}$	${}^6H_{15/2}$	$\frac{4}{3}$	10.63	10.6
Ho^{3+}	$4f^{10}$	10	2	6	8	${}^5I_8$	$\frac{5}{4}$	10.60	10.4

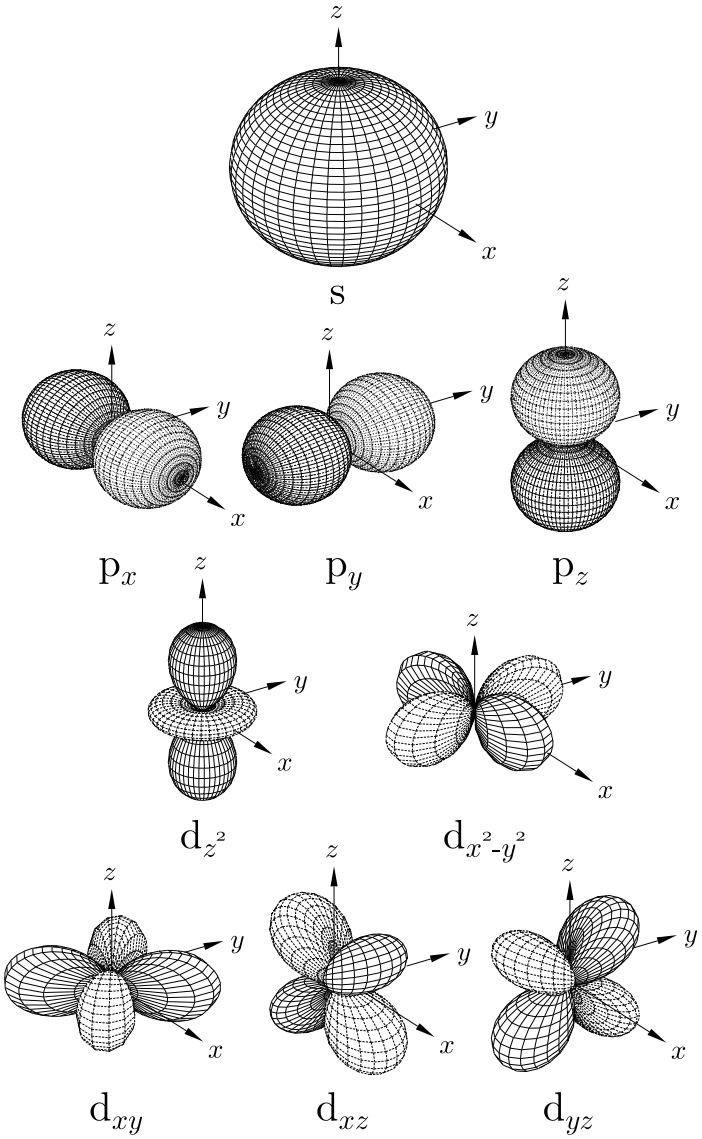
transition metal (3d) ions:

ion	shell	n	S	L	J	${}^{2S+1}L_J$	g_J	$g_J\sqrt{J(J+1)}$	$\mu_{\text{eff}}/\mu_{\text{B}}$ (exp.)	$2\sqrt{S(S+1)}$
Ti^{3+}, V^{4+}	$3d^1$	1	$\frac{1}{2}$	2	$\frac{3}{2}$	${}^2D_{3/2}$	4/5	1.55	1.8	1.73
V^{3+}	$3d^2$	2	1	3	2	${}^3F_2$	2/3	1.63	2.8	2.83
Cr^{3+}, V^{2+}	$3d^3$	3	$\frac{3}{2}$	3	$\frac{3}{2}$	${}^4F_{3/2}$	2/5	0.77	3.8	3.87
Mn^{3+}, Cr^{2+}	$3d^4$	4	2	2	0	${}^5D_0$	-	0.00	4.9	4.90

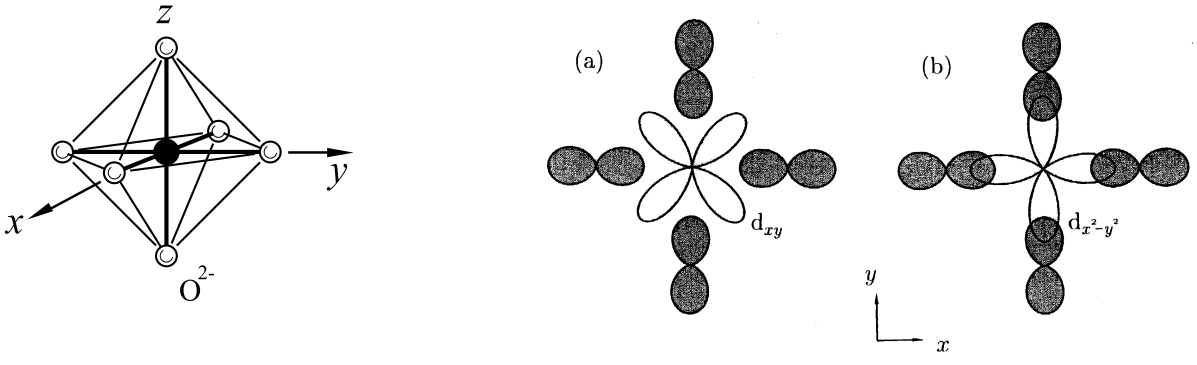
1.6 Crystal field

In a crystal the ion sits in an electric field of the surrounding ions. For transition-metals the magnetic electrons are in the outer shell and they are affected quite strongly by the crystal. This often leads to *orbital quenching* - the orbital part of the wavefunction is frozen - and μ_{eff} is given by $\mu_{\text{eff}} = 2\mu_{\text{B}}\sqrt{S(S+1)}$.

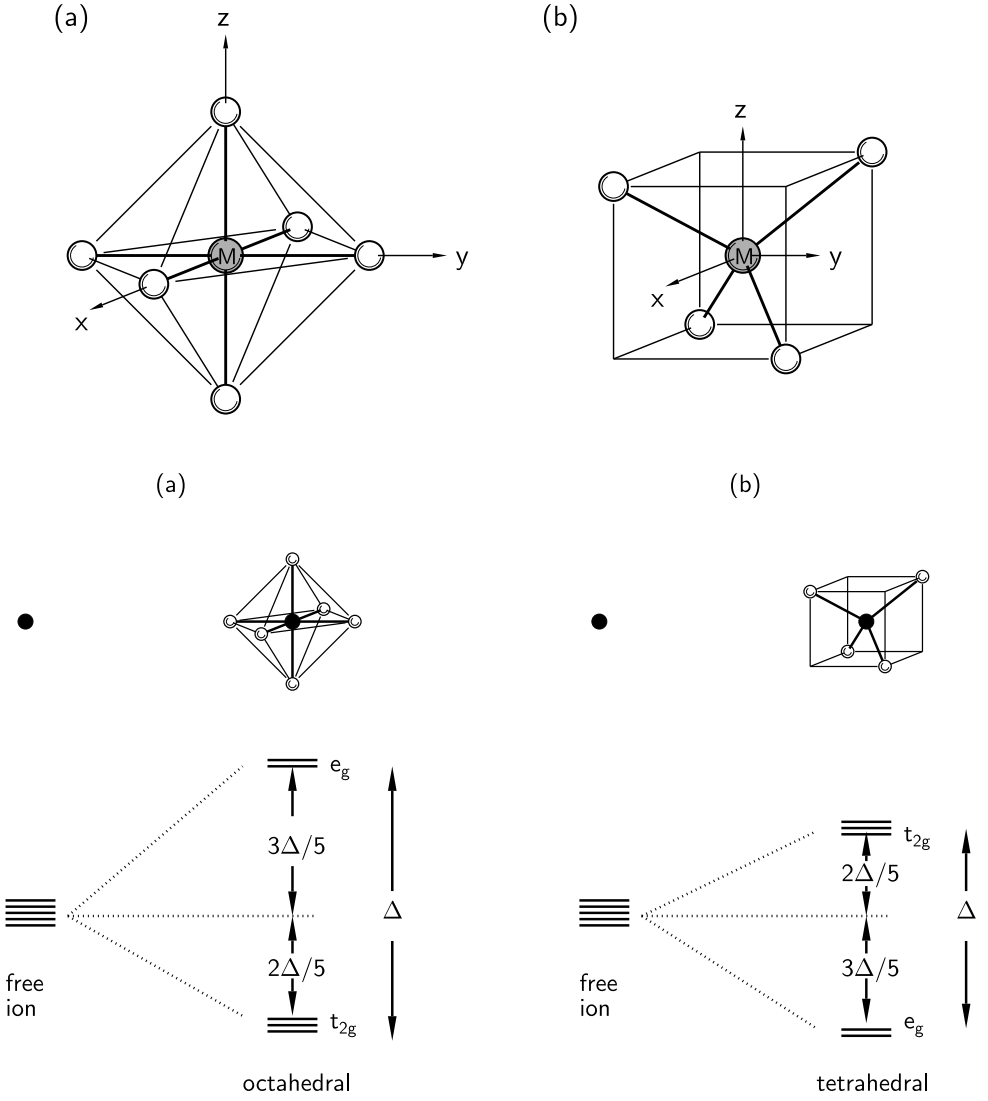
To appreciate crystal field effects consider the shapes of the various d-orbitals, shown below (together with s and p orbitals). The graphs give a visual representation of the distribution of electron density, i.e. $d_{x^2-y^2}$ has large density along the x and y axes whereas d_{xy} has large density *in-between* the x and y axes.



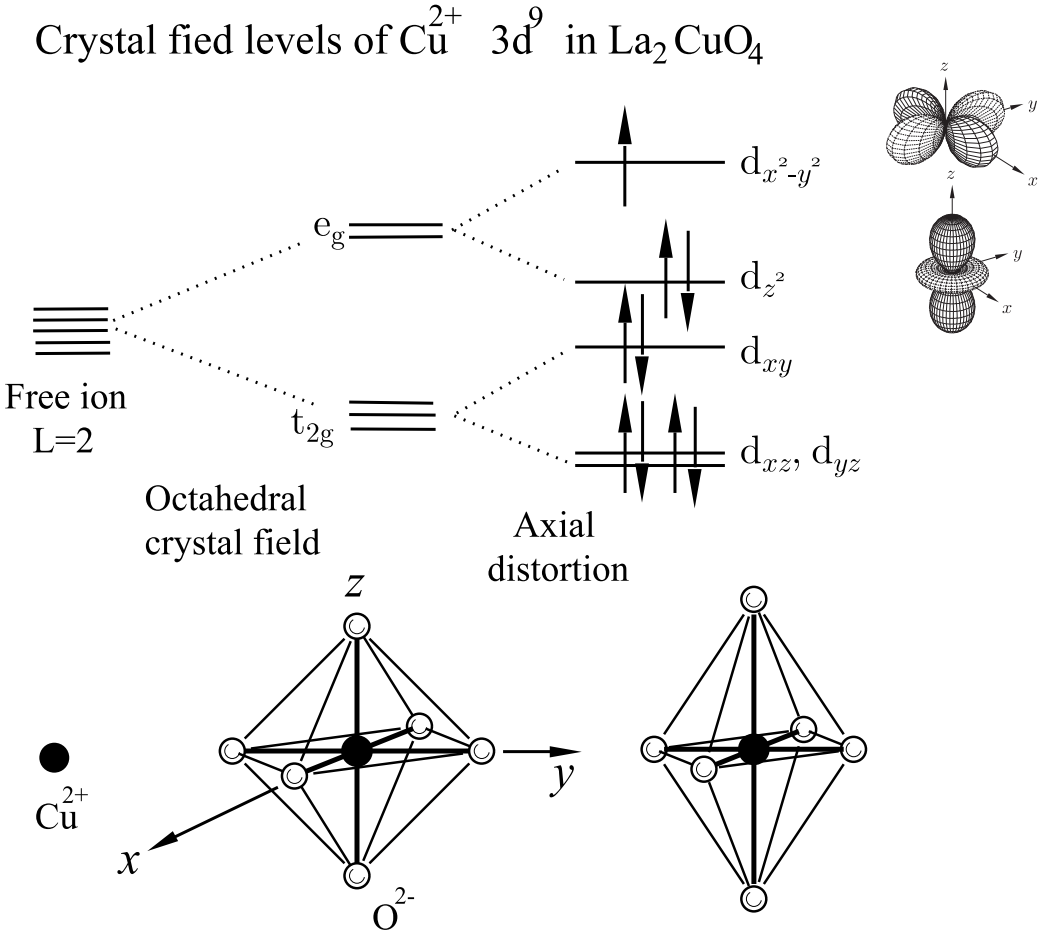
Consider now the 3d ion in the centre of an octahedron of oxygen ions, as is usually the case in transition-metal oxides. Examine the projection of orbitals in the xy plane. The $d_{x^2-y^2}$ orbital has higher energy than the d_{xy} orbital due to the electrostatic Coulomb interaction with the Oxygen orbitals.



The d-orbitals can be classified into 2 classes, e_g orbitals which point along the x, y and z axes (d_{z^2},$d_{x^2-y^2}$) and the t_{2g} (d_{xy}, d_{yz}, d_{zx}), which point between these axes. The following figures show the crystal-field splitting for a 3d element in an octahedral and a tetrahedral environment.

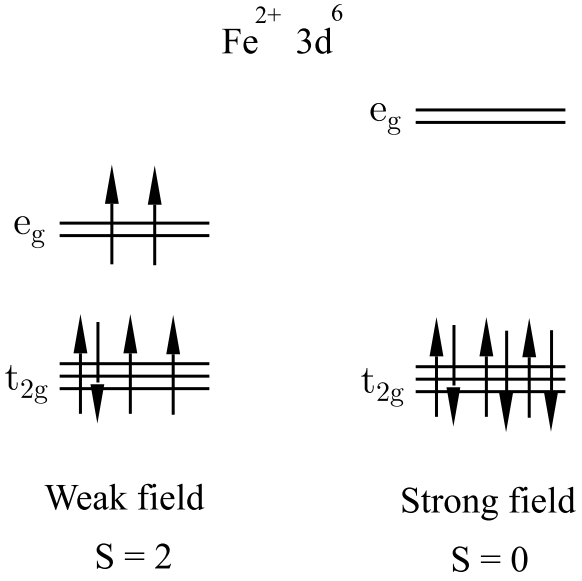


Simple example of orbital quenching In La_2CuO_4 Cu^{2+} ions sit in the centre of an oxygen octahedron with a small elongation along the c-axis. The highest single-electron orbital level is $d_{x^2-y^2}$ as this has the largest overlap with the four close-by Oxygens in the basal plane. Cu^{2+} has 9 electrons in the $3d$ shell, which occupy the levels in increasing energy, this leaves an unpaired electron in the $d_{x^2-y^2}$ orbital.

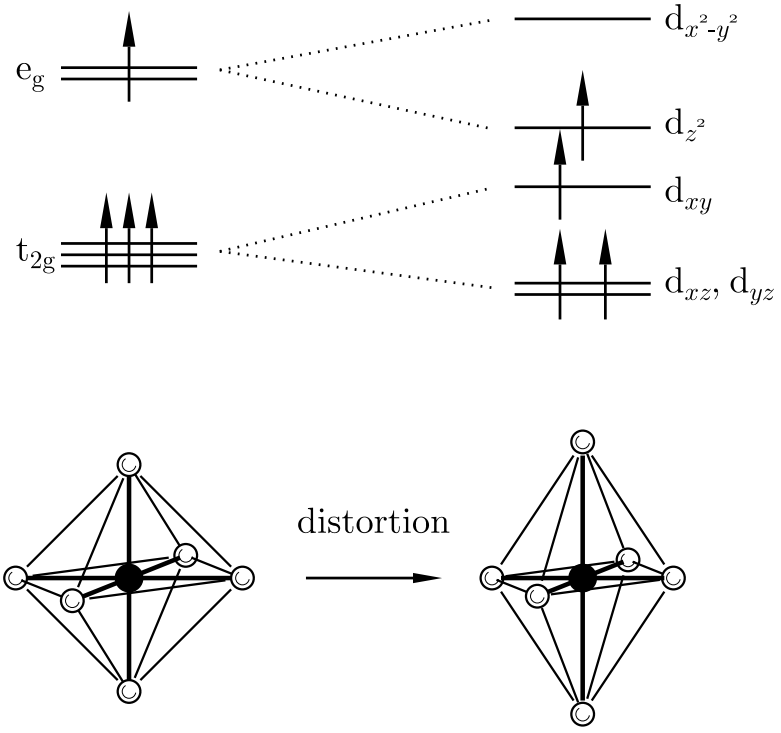


Hund's rules for the *free* ion give $L = 2, S = 1/2, J = 5/2$, however the strong crystal-field splitting lead to an orbital singlet ground state. The strong crystal field environment has essentially *quenched* the orbital part of the angular momentum, so the magnetic moment is given by spin alone, $L = 0$ and $J = S$, $g = 2$.

Strong- and weak-field cases Consider Fe^{2+} $3d^6$ ions in an octahedral crystal field. Two possible ground states can occur depending on the strength of the crystal field splitting Δ compared to the Coulomb energy cost U for putting two electrons in the same orbital. The (a) **weak-field** $\Delta < U$ and (b) **strong field** $\Delta > U$ cases are illustrated below. In some materials case (a) high-spin is realized, other materials case (b) low-spin.



Jahn-Teller Effect We have assumed so far that all we need to do is to work out what kind of symmetry the local environment has and then deduce the electronic structure and hence figure out the magnetic properties based on how many electrons there are to fill up the energy levels. Sometimes the magnetic properties themselves can influence the symmetry of the local environment! This comes about because it can sometimes be energetically favourable for, say, an octahedron to spontaneously distort as shown below. The energy cost of increased elastic energy is balanced by a resultant electrostatic energy saving due to the distortion. This phenomenon is known as the *Jahn-Teller effect*. For example, Mn^{3+} ions ($3d^4$) in an octahedral environment show this kind of behaviour, but Mn^{4+} ($3d^3$) do not.



1.7 Magnetic resonance techniques

Principle: use static field B to induce splitting of levels and a much smaller transverse oscillating field $B_x(t) = B_x \cos(2\pi\nu t)$ to induce transitions between levels. The system can absorb energy from the oscillating field when the frequency matches that of an allowed transition $h\nu = \Delta E$.

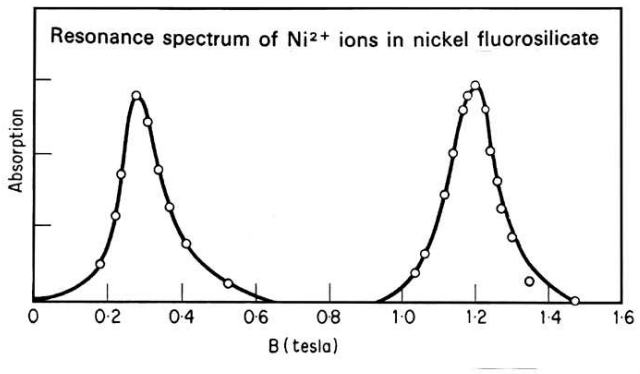
Semiclassically one can think that the magnetic moments precess around the field at a frequency given by γB where γ is the gyromagnetic ratio. A system of magnetic moments in a magnetic field can absorb energy at this frequency and thus one may observe a resonant absorption of energy from an electromagnetic wave tuned to the correct frequency. This is magnetic resonance and it can take a number of different experimental forms, depending on what type of magnetic moment is resonating.

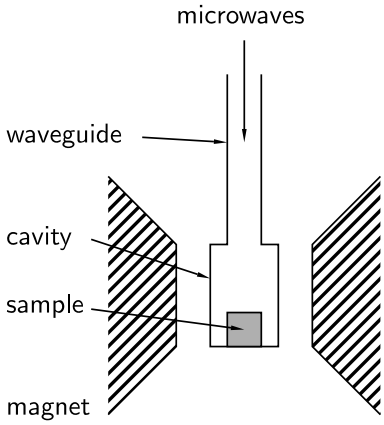
Electron spin resonance

Zeeman splitting of the electron spin in magnetic field of 1 Tesla is $2\mu_B \times 1$ T =0.1 meV, which corresponds to electromagnetic radiation with frequency $\nu \sim 25$ GHz in the microwave range, so with frequencies of this magnitude one probes Electron Spin Resonances.

Example ESR in Mn^{2+}
S=5/2, L=0, $J = 5/2$, $g_J = 2$.
Hamitonian is $\hat{\mathcal{H}} = g_J \mu_B B J$ and the selection rule for ESR transitions is $\Delta m_J = \pm 1$. Hyperfine interaction with the nuclear moment $I = 5/2$ is $A\mathbf{J} \cdot \mathbf{I}$, and this is usually much smaller than the Zeeman splitting $g_J \mu_B B$. To first order split each Zeeman m_J level into $2I + 1$ levels. The selection rule for transitions is $\Delta m_I = 0$ and $\Delta m_J = \pm 1$ as the high frequency of EM radiation does not couple directly to the nuclear moment (need MHz frequencies see below). Leads to splitting of ESR spectrum in $2I + 1$ lines.

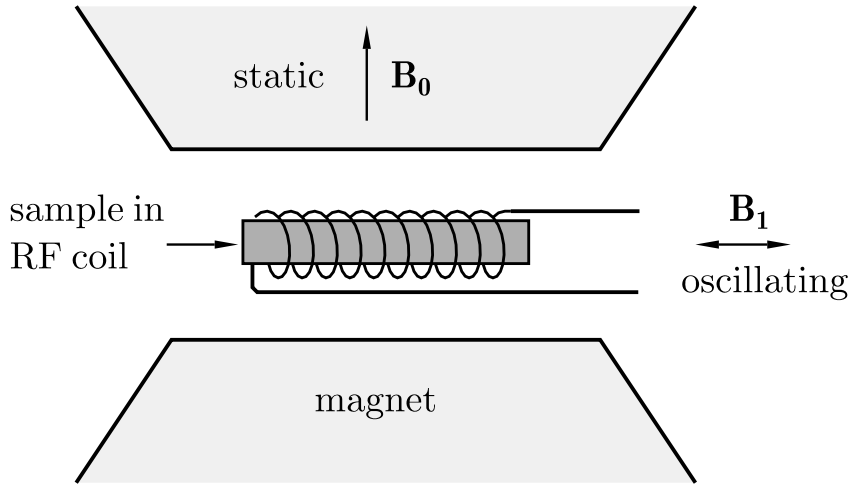
Example ESR for Ni^{2+} $S = 1$ Figure below shows splitting of lines due to easy-axis crystal field anisotropy $\hat{\mathcal{H}} = g\mu_B B S_z - D S_z^2$.





NMR = Nuclear Magnetic Resonance

NMR uses much lower, RF frequency $\nu \sim 10$ MHz because the nuclear magnetic moments are much smaller, $\mu_N = e\hbar/2m_N \sim 10^{-3}\mu_B$. See directly transitions of the nuclear moments with selection rule $\Delta m_I = \pm 1$. Used in chemistry, biology and medicine.



Schematic diagram of an NMR experiment. The sample sits inside a radio frequency (RF) coil which produces an oscillating field at RF frequency. A static magnetic field is provided by a magnet. The static field $\mathbf{B}_0$ and the oscillating field $\mathbf{B}_1$ are perpendicular.

Applications of Magnetic Resonance
- understand hyperfine effects
- determine g-factors and anisotropy effects, hence understand local symmetry of ions/dopants in crystals
- detect structural phase transitions via local symmetry changes

Appendix: Some remarks about spin

Magnetism in solids depends crucially on the properties of electronic spin. Here are some brief notes which remind you of some of the basic quantum mechanics that describes the spin of an electron, a spin-$\frac{1}{2}$ particle.

The behaviour of the electron's spin is connected with a rather strange algebra, based on the three *Pauli spin matrices* which are defined as

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{\sigma}_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{12}$$

It will be convenient to think of these as a vector of matrices,

$$\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z). \tag{13}$$

We now define the spin angular momentum operator by

$$\hat{\mathbf{S}} = \frac{1}{2}\hat{\boldsymbol{\sigma}} \tag{14}$$

so that

$$\hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{S}_y = \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{15}$$

Notice that we are using the convention that angular momentum is measured in units of $\hbar$, so that the angular momentum associated with an electron is actually $\hbar\mathbf{S}$. A general wave function can then be written

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix} = a|\uparrow_z\rangle + b|\downarrow_z\rangle \tag{16}$$

where a and b are complex numbers and it is conventional to normalize this state so that

$$|a|^2 + |b|^2 = 1. \tag{17}$$

The wave function $|\psi\rangle$ is known as a spinor.

The total spin angular momentum operator $\hat{\mathbf{S}}$ is defined by

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{18}$$

and since the eigenvalues of $\hat{S}_x^2$, $\hat{S}_y^2$ or $\hat{S}_z^2$ are always $\frac{1}{4} = (\pm\frac{1}{2})^2$, we have the result that for any spin-state $|\psi\rangle$

$$\hat{\mathbf{S}}^2|\psi\rangle = (\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2)|\psi\rangle = \left(\frac{1}{4} + \frac{1}{4} + \frac{1}{4}\right)|\psi\rangle = \frac{3}{4}|\psi\rangle. \tag{19}$$

Many of these results can be generalised to the case of particles with spin quantum number $s > \frac{1}{2}$. The most important result is that the eigenvalue of $\hat{\mathbf{S}}^2$ becomes $s(s+1)$. In the case of $s = \frac{1}{2}$ which we are considering in this appendix, $s(s+1) = \frac{3}{4}$, in agreement with equation 19. The commutation relation between the spin operators is

$$[\hat{S}_x, \hat{S}_y] = \mathrm{i}\hat{S}_z \tag{20}$$

and cyclic permutations thereof. Each of these operators commutes with $\hat{\mathbf{S}}^2$ so that

$$[\hat{\mathbf{S}}^2, \hat{S}_z] = 0. \tag{21}$$

Thus it is possible to simultaneously know the total spin and one of its components, but not possible to know more than one of the components simultaneously.

The *raising and lowering operators* $\hat{S}_+$ and $\hat{S}_-$ are defined by

$$\begin{aligned} \hat{S}_+ &= \hat{S}_x + \mathrm{i}\hat{S}_y \\ \hat{S}_- &= \hat{S}_x - \mathrm{i}\hat{S}_y. \end{aligned} \tag{22}$$

For an operator $\hat{A}$ to be Hermitian, one must have that $\hat{A}^\dagger = \hat{A}$ where † implies an adjoint operation (for matrices this means "take the transpose and then complex conjugate each element"). The raising and lowering operators are not Hermitian (because $\hat{S}_+^\dagger = \hat{S}_-$ and $\hat{S}_-^\dagger = \hat{S}_+$) and therefore they do not correspond to observable quantities. They are nevertheless very useful. Straightforward application of equations 20 and 22 yields the following commutation relations

$$[\hat{S}_+, \hat{S}_-] = 2\hat{S}_z, \tag{23}$$

$$[\hat{S}_z, \hat{S}_\pm] = \pm\hat{S}_\pm, \tag{24}$$

and

$$[\hat{\mathbf{S}}^2, \hat{S}_\pm] = 0. \tag{25}$$

Another useful relation, proven by direct substitution is

$$\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+ = 2(\hat{S}_x^2 + \hat{S}_y^2) \tag{26}$$

and this provides a convenient representation for $\hat{\mathbf{S}}^2$, namely

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{27}$$

$$= \frac{1}{2}\left(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+\right) + \hat{S}_z^2. \tag{28}$$

---

2. Interactions

Now we turn on the interactions! I will discuss what sort of interactions there might be, including dipolar interactions and the different types of exchange interaction. The interactions lead to various types of ordered magnetic structures which can be measured using *neutron diffraction*. I will then discuss the *Weiss model* of ferromagnetism, antiferromagnetism and ferrimagnetism and also consider the magnetism of metals.

2.1 Magnetic dipolar interaction

Two magnetic dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ separated by $\mathbf{r}$ have an energy

$$\frac{\mu_0}{4\pi r^3}\left[\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2-\frac{3}{r^2}(\boldsymbol{\mu}_1\cdot\mathbf{r})(\boldsymbol{\mu}_2\cdot\mathbf{r})\right]$$

2.2 Exchange interaction

(a) Origin of exchange

Consider a simple model with just 2 electrons which have spatial coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. The wave function for the joint state can be written as a product of single-electron states, so that if the first electron is in state $\psi_a(\mathbf{r}_1)$ and the second electron is in state $\psi_b(\mathbf{r}_2)$, then the joint wave function is $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$. However this product state does not obey exchange symmetry, since if we exchange the two electrons we get $\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$ which is not a multiple of what we started with. Therefore, the only states which we are allowed to make are symmetrised or antisymmetrised product states which behave properly under the operation of particle exchange.

For electrons the overall wave function must be antisymmetric so the spin part of the wave function must either be an antisymmetric singlet state $\chi_{\rm S}$ ($S=0$) in the case of symmetric spatial state or a symmetric triplet state $\chi_{\rm T}$ ($S=1$) in the case of an antisymmetric spatial state. Therefore we can write the wave function for the singlet case $\Psi_{\rm S}$ and the triplet case $\Psi_{\rm T}$ as

$$\begin{aligned}\Psi_{\rm S} &= \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\,\chi_{\rm S}\\ \Psi_{\rm T} &= \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)-\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\,\chi_{\rm T}\end{aligned}\qquad(29)$$

where both the spatial and spin parts of the wave function are included. The energies of the two possible states are

$$\begin{aligned}E_{\rm S} &= \int \Psi_{\rm S}^*\hat{\mathcal{H}}\Psi_{\rm S}\,{\rm d}\mathbf{r}_1\,{\rm d}\mathbf{r}_2\\ E_{\rm T} &= \int \Psi_{\rm T}^*\hat{\mathcal{H}}\Psi_{\rm T}\,{\rm d}\mathbf{r}_1\,{\rm d}\mathbf{r}_2\end{aligned}$$

so that the difference between the two energies is

$$E_{\rm S}-E_{\rm T}=2\int \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\hat{\mathcal{H}}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\,{\rm d}\mathbf{r}_1\,{\rm d}\mathbf{r}_2.\qquad(30)$$

Now $\mathbf{S_1} \cdot \mathbf{S_2}$ is equal to $-3/4$ if $S = 0$ and $1/4$ if $S = 1$. Hence, the Hamiltonian can be written in the form

$$\hat{\mathcal{H}} = \frac{1}{4}(E_\mathrm{S} + 3E_\mathrm{T}) - (E_\mathrm{S} - E_\mathrm{T})\mathbf{S_1} \cdot \mathbf{S_2}. \tag{31}$$

This is the sum of a constant term and a term which depends on spin. The constant can be absorbed into other constant energy terms, but the second term is more interesting. The exchange constant (or exchange integral), J is defined by

$$\mathsf{J} = E_\mathrm{S} - E_\mathrm{T} = 2\int \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\hat{\mathcal{H}}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2. \tag{32}$$

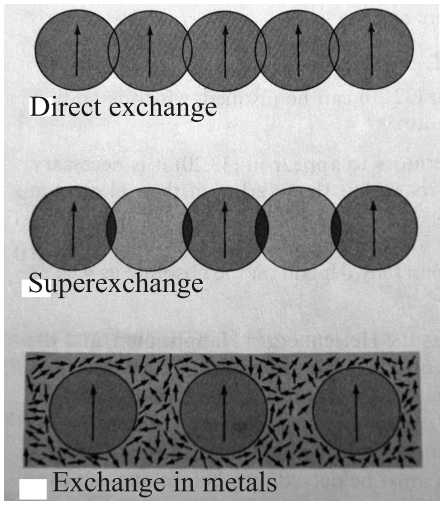
and hence the spin-dependent term in the Hamiltonian can be written

$$\hat{\mathcal{H}}^\mathrm{spin} = -\mathsf{J}\mathbf{S_1} \cdot \mathbf{S_2}. \tag{33}$$

If $\mathsf{J} > 0$, $E_\mathrm{S} > E_\mathrm{T}$ and the triplet state $S = 1$ is favoured. If $\mathsf{J} < 0$, $E_\mathrm{S} < E_\mathrm{T}$ and the singlet state $S = 0$ is favoured. This equation is relatively simple to derive for 2 electrons, but generalising to a many body system is far from trivial. Nevertheless, it was recognised in the early days of quantum mechanics that interactions such as that in equation 33 probably apply between all neighbouring atoms. This motivates the Hamiltonian of the Heisenberg model:

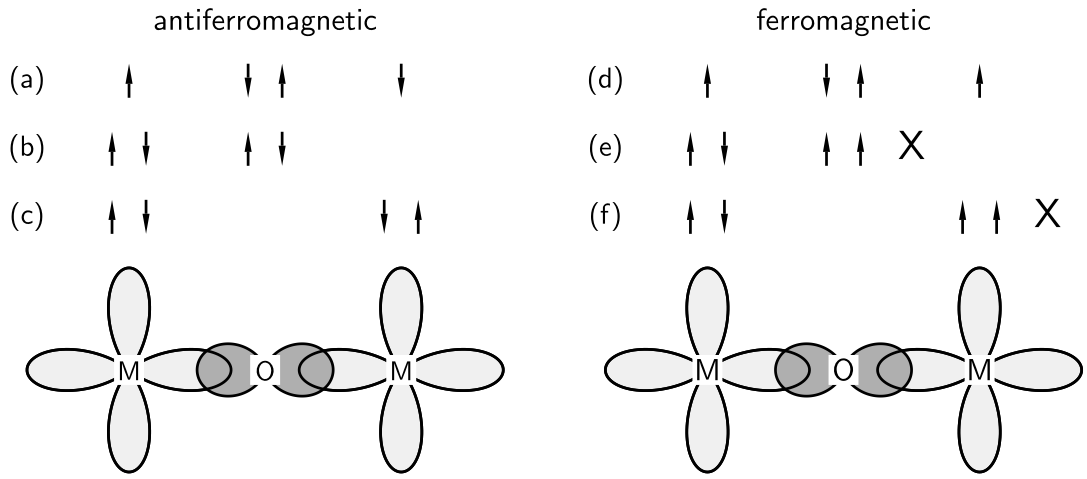
$$\hat{\mathcal{H}} = -\sum_{\langle ij \rangle} \mathsf{J}_{ij}\mathbf{S_i} \cdot \mathbf{S_j} \tag{34}$$

where J_{ij} is the exchange constant between the i^th and j^th spins. $\langle ij \rangle$ means that each interacting pair of spins ij is counted only once in the summation. Usually J_{ij} is equal to a constant J for nearest neighbour spins and is 0 otherwise.



(b) Direct exchange — the exchange interaction arising from the Coulomb interaction between electrons on neighbouring magnetic ions due to *direct* overlap.

(c) Superexchange — the exchange interaction between non-neighbouring magnetic ions which is mediated by a non-magnetic atom (i.e. *no* direct overlap).



Superexchange in a magnetic oxide. If the moments on the transition metal (M) atoms are aligned antiferromagnetically, the ground state (a) can mix with excited configurations like (b) and (c). The magnetic electrons can thus be delocalized over the M–O–M unit, thus lowering the kinetic energy. If the moments on the metal (M) atoms are aligned ferromagnetically, the ground state (d) cannot mix with excited configurations like (e) or (f) because these configurations are prevented by the exclusion principle. The ferromagnetic configuration therefore costs more energy.

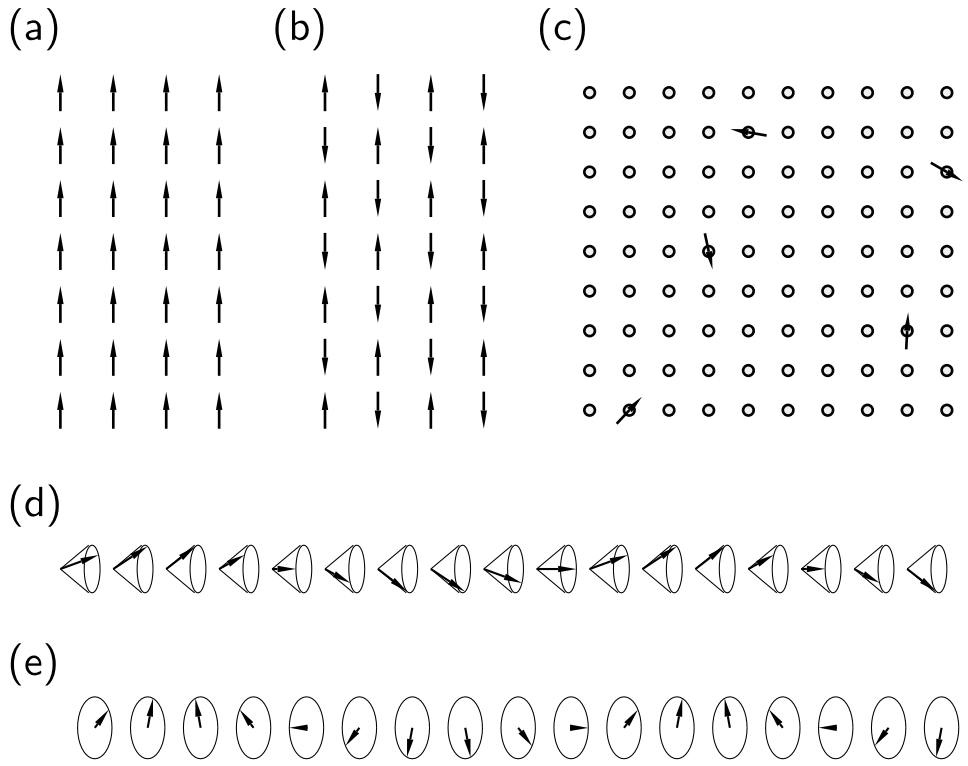
Superexchange is the most common magnetic interaction in insulators, e.g. La_2CuO_4, MnO, MnF_2, NiO.

(d) Exchange in metals — the exchange interaction between magnetic ions mediated by the spin-polarization of the conduction electrons.

RKKY interaction (RKKY=Ruderman, Kittel, Kasuya and Yosida) $\Longrightarrow \mathsf{J}_{RKKY}(r) \propto \dfrac{\cos(2k_{\mathrm{F}}r)}{r^3}$. The interaction is long range and has an oscillatory dependence on the distance between the magnetic moments. Hence depending on the separation it may be either ferromagnetic or antiferromagnetic. The coupling is oscillatory with wavelength π/k_{F} because of the sharpness of the Fermi surface.

Example: metallic Dy, Ho and dilute magnetic alloys, i.e. Mn^{2+} ($S = 5/2$) doped into metallic Cu.

2.3 Magnetic structures



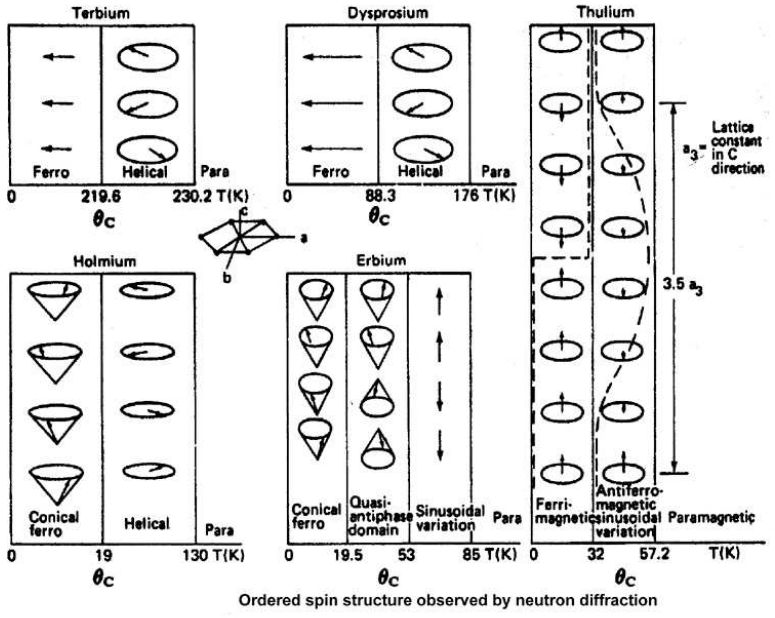
Many different magnetic ground states result from the different interactions which may occur in different crystals. These include (a) ferromagnets, (b) antiferromagnets, (c) spin glasses and (d) cone and (e) helical structures.

In ferromagnets, the magnetic moments are in parallel alignment. In antiferromagnets, adjacent magnetic moments lie in antiparallel alignment. In cone and helical structures, the direction of the magnetic moment precesses around a cone or a circle as one moves from one site to the next. In spin glasses, the magnetic moments lie in frozen random arrangements.

A rich variety of magnetic ground states are found in the rare earth metals. Many of these have hexagonally close packed crystal structures and a few show helimagnetism with the axis of the helix being perpendicular to the hexagonally close packed planes, (i.e. along the c-axis). The plane in which the spins rotate in Tb, Dy and Ho is the hexagonally close packed plane, but in Er and Tm the easy axis for spins is the c-axis so that the c component of the spins is modulated sinusoidally over certain temperature regions. The exchange interaction in rare earth metals is an indirect RKKY interaction via the conduction electrons.

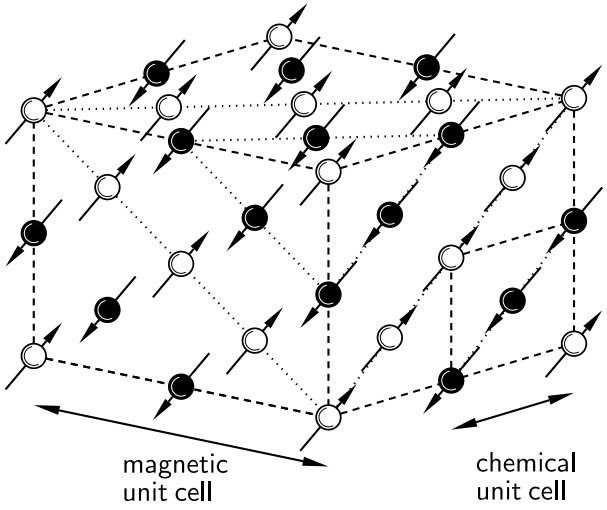
Measurement of magnetic structures with neutron scattering

Neutrons have spin and are scattered by the periodic arrangement of magnetic moments in a crystal. Bragg scattering occurs when the scattering wavevector $\mathbf{Q}$ coincides with a reciprocal lattice vector of the magnetic unit cell. An example for the antiferromagnet MnO is shown on the next page.

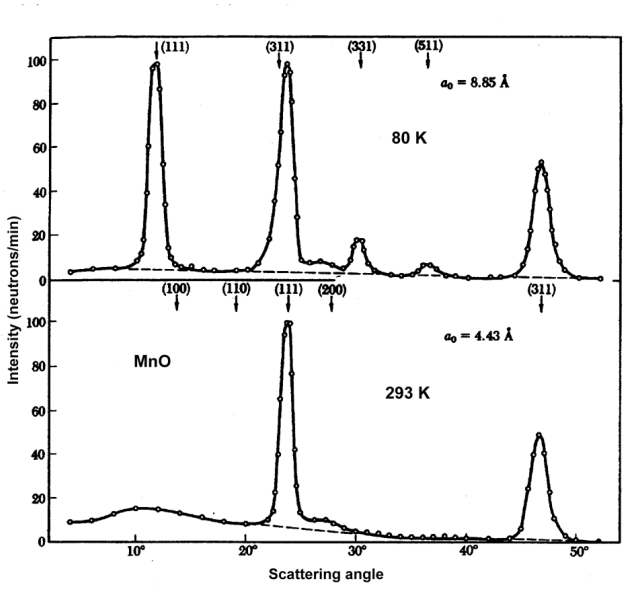


Ordered spin structure observed by neutron diffraction

Magnetic structure of MnO:

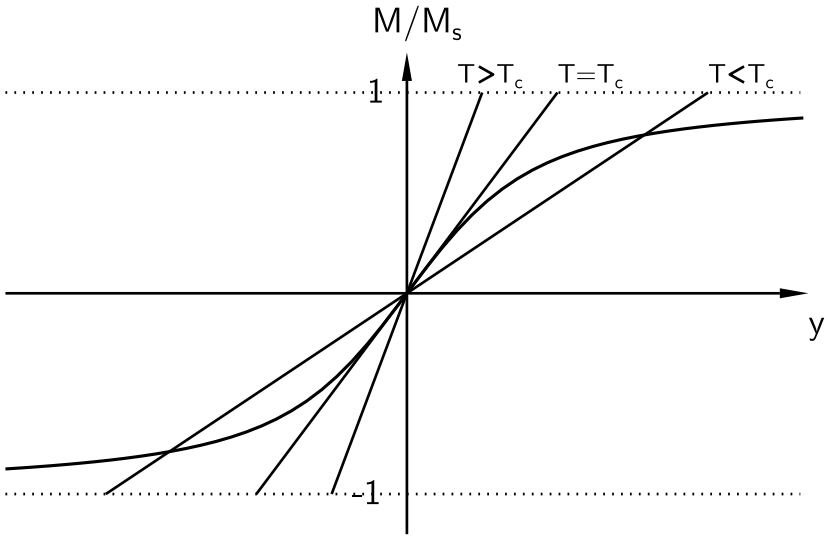


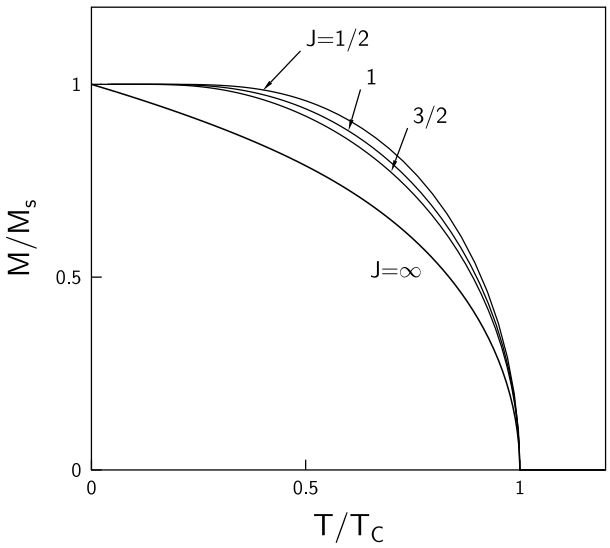
Neutron scattering data from MnO:



2.4 Weiss theory of ferromagnetism, antiferromagnetism and ferrimagnetism

The Weiss model is a particular type of molecular field or *mean-field theory* which means that it assumes that all spins "feel" an identical average internal field produced by all their neighbours. This field is proportional to the magnetization. We will develop this model in detail in the lectures and show how it applies to a ferromagnet. The case of an antiferromagnet and a ferrimagnet is a simple extension of this. The predictions of this model do not work well near T_{C} where the fluctuations play a dominant rôle. The graphical solution of the Weiss model for $B = 0$ is shown below.

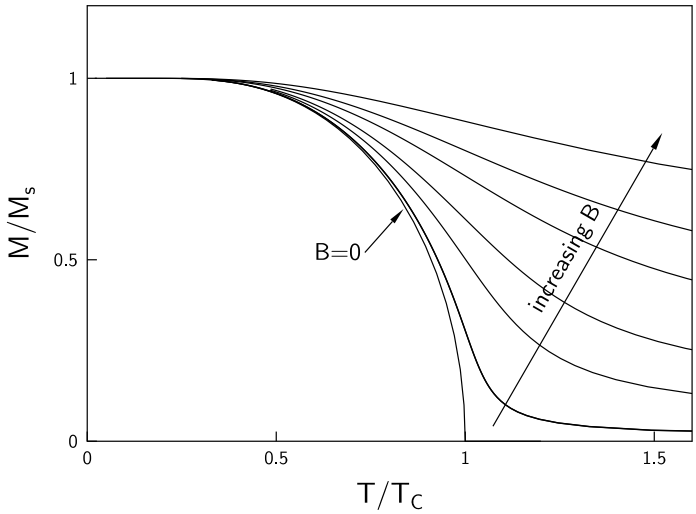




Above: The magnetisation as a function of temperature, deduced for different values of J.

Material	T_{C} (K)	magnetic moment (μ_{B}/formula unit)
Fe	1043	2.2
Co	1395	1.7
Ni	631	0.6
Gd	289	7.5
MnSb	587	3.5
EuO	70	6.9
EuS	16.5	6.9

Properties of some common ferromagnets.



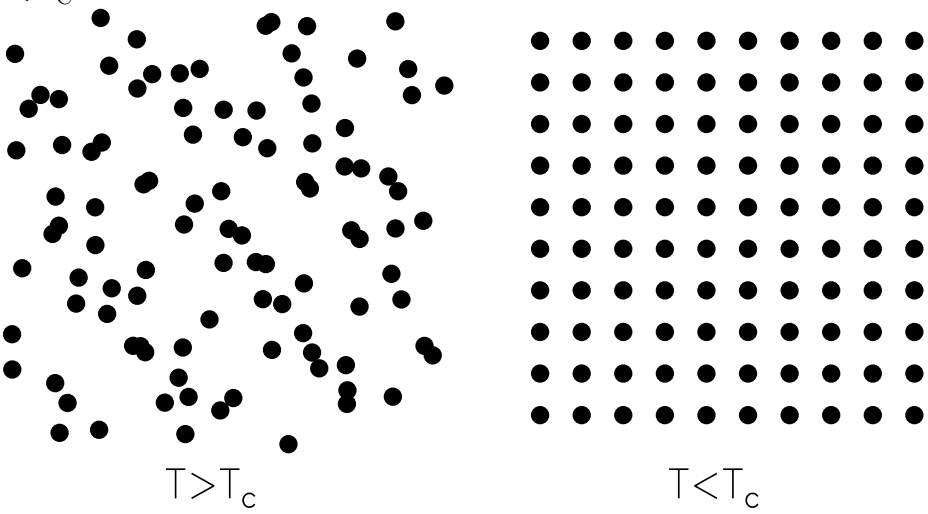
The magnetisation as a function of temperature for $J = \frac{1}{2}$, calculated for different values of the applied field B. The phase transition is only present when $B = 0$.

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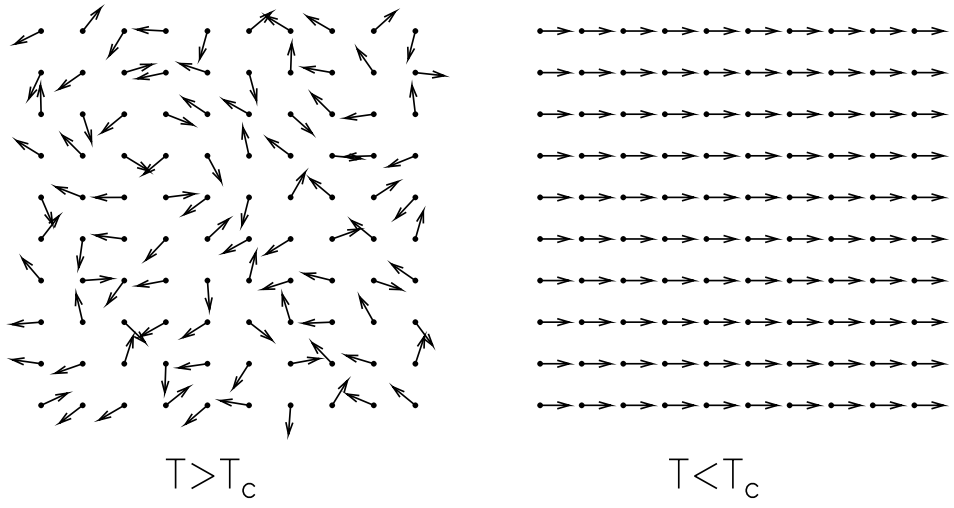
3. Symmetry breaking

3.1 Introduction

Lots of ordered phases in condensed matter physics (e.g. ferromagnets and antiferromagnets, even solids themselves) are characterised by a temperature dependence in which physical properties show a marked difference above and below some *critical temperature* T_C. Such phases are characterised by an *order parameter*, which in the case of ferromagnetism is just the magnetization, and is zero for $T > T_C$ and non-zero for $T < T_C$.



Liquid–solid phase transition. The high temperature state has translational symmetry. This symmetry is broken as the system becomes a solid.



Paramagnet–Ferromagnet phase transition. The high temperature state has rotational symmetry. This symmetry is broken as the system becomes a ferromagnet.

It is found to be a general principle that symmetry is broken at the critical point. As illustrated above, in a ferromagnet above T_C all directions are equivalent, whereas below T_C the system "chooses" a unique direction for all the spins to point. The higher rotational symmetry is broken. In a liquid there is perfect translational invariance, but in a solid this symmetry is broken. All points are no longer equivalent (although there is still the lower periodic symmetry that every point is equivalent to any point located an integer combination of lattice basis vectors away).

An important point to notice is that it is impossible to change symmetry *gradually*. Either a particular symmetry is present or it is not. Hence, phase transitions are sharp.

3.2 Landau's Theory of Phase Transitions

Mean field theories are the simplest type of theory that can be constructed to describe many different types of phase transition and give similar results in each case. (They go under different names in different cases: e.g. Bragg-Williams theory for order-disorder transitions in alloys, Weiss theory in ferromagnetism, and the general idea is contained in Landau's theory of phase transitions). A *mean-field theory* means that it assumes that all spins "feel" an identical average exchange field produced by all their neighbours. This field is proportional to the magnetization.

In Landau's theory, we write down the free energy for a ferromagnet with magnetization M as a power series in M. Because there is no energetic difference between 'up' or 'down', this power series cannot contain any odd power of M. There we can write for the free energy $F(M)$ the expression

$$F(M) = F_0 + a(T)M^2 + bM^4 \tag{35}$$

where F_0 and b are constants (we assume $b > 0$) and $a(T)$ is temperature dependent. We can show that this system yields an appropriate phase transition if we allow $a(T)$ to change sign at the transition temperature T_C. Thus in the region of interest, near the transition, we write $a(T) = a_0(T - T_\mathrm{C})$ where a_0 is a positive constant. To find the ground state of the system, it is necessary to minimize the free energy so we look for solutions of $\partial F/\partial M = 0$. This condition implies

$$2M[a_0(T - T_\mathrm{C}) + 2bM^2] = 0. \tag{36}$$

The left-hand side of this equation is a product of two terms, so either of them could be zero. This means

$$M = 0 \quad \text{or} \quad M = \pm\left[\frac{a_0(T_\mathrm{C} - T)}{2b}\right]^{1/2}. \tag{37}$$

The second condition is only valid when $T < T_\mathrm{C}$, otherwise one is trying to take the square root of a negative number. The first condition applies above or below T_C but below T_C it only produces a position of unstable equilibrium (which can be deduced by evaluating $\partial^2 F/\partial M^2$). Thus the magnetization is zero for temperatures $T \geq T_\mathrm{C}$ and is non-zero and proportional to $(T_\mathrm{C} - T)^{1/2}$ for T just below T_C.

3.3 Models

In order to discuss some of the consequences of symmetry breaking it is convenient to think about some simple *models*. At this stage we won't worry about what the microscopic basis of these models are.

The nearest neighbour *Heisenberg model* has a Hamiltonian

$$H = -\sum_{\langle ij \rangle} J\mathbf{S}_i \cdot \mathbf{S}_j$$

where the constant J is the *exchange integral* and $\sum_{\langle ij \rangle}$ denotes a sum over nearest neighbours. The spins $\mathbf{S}_i$ are treated as three-dimensional vectors because we allow them to point in any direction in three-dimensional space. However the sum can taken be over a lattice of 1, 2 or 3 dimensions. We must distinguish between the dimensionality of the lattice on which the spins sit, d, and the dimensionality of the spins themselves (in general this is known as the dimensionality of the *order parameter*), D. For the Heisenberg model $D = 3$ (because the spins are three dimensional vectors). However we could be considering a lattice of spins in 1, 2 or 3 dimensions (or 4 dimensions if we wanted to!) so d can be 1, 2, 3, ...

The Hamiltonian of the *Ising model* involves only the z-component of the spin:

$$H = -\sum_{\langle ij \rangle} JS_i^z S_j^z.$$

Here the dimensionality of the order parameter $D = 1$ (the spins are only allowed to point along $\pm\mathbf{z}$).

The one-dimensional Ising model ($D = 1$, $d = 1$).

If the Ising spins are placed on a one-dimensional lattice, we will show that there is no phase transition.

The two-dimensional Ising model ($D = 1$, $d = 2$).

If the Ising spins are placed on a 2D lattice, a phase transition will result. The proof of this was one of the outstanding achievements of twentieth century statistical physics (Lars Onsager solved it in 1944) and his solution is beyond the scope of the course. This illustrates that even problems which are simple to state are by no means easy to solve.

3.4 Continuous Phase transitions and critical exponents

Near the phase transition temperature T_C, the dimensionless *reduced temperature* t defined by $t = (T - T_C)/T_C$ is small. In this regime

$$\begin{array}{rcll} \chi & \propto & t^{-\gamma} & T > T_C \\ M & \propto & (-t)^{\beta} & T < T_C \\ M & \propto & H^{\frac{1}{\delta}} & T = T_C \end{array}$$

where α, β, and γ are *critical exponents*.

Model	**Mean-field**	**Ising**	**Ising**	**Heisenberg**
D	any	1	1	3
d	any	2	3	3
β	$\frac{1}{2}$	$\frac{1}{8}$	0.326	0.367
γ	1	$\frac{7}{4}$	1.2378(6)	1.388(3)
δ	3	15	4.78	4.78

Critical exponents for various models.

Mean-field methods ignore *correlations* and *fluctuations* which become very important near T_C.

Despite the failure of mean-field theory to successfully account for critical behaviour in systems with dimensionality below four, it is only necessary to consider a small representative set of ideal statistical models to calculate critical exponents of any physical system if the hypothesis of *universality* is accepted. This hypothesis is based on the observation that critical exponents do seem to be surprisingly independent of the type of phase transition, whether liquid—gas, ferromagnetic—paramagnetic, superconducting—non-superconducting, or any other. It is supposed that for a continuous phase transition, the (static) critical exponents depend only on

1. The dimensionality of the *system*, d.
2. The dimensionality of the *order parameter*, D. (Actually the symmetry of the order parameter).
3. Whether the forces are *short* or *long* range.

There are a number of exactly solved models:

1. Most cases for $d = 1$. Unfortunately, such systems do not exhibit continuous phase transitions.
2. All cases for $d \geq 4$, which give mean-field solutions.
3. Most cases for long range interactions, which give mean-field solutions.
4. $d = 2$, $D = 1$. This is the 2D Ising model (Onsager 1944).

Unfortunately, most real situations correspond to $d = 3$ and short-range interactions, which have not been solved exactly.

3.5 Consequences of broken symmetry

When you break symmetry there are various consequences:

- **Phase transitions**: The system will have a sharp change of behaviour at a temperature T_c. We describe this by saying the system has changed *phase* (e.g. liquid → solid, paramagnet → ferromagnet, etc). The region near the phase transition is called the *critical region*. (see section 3.4)
- **Rigidity**: Having broken the symmetry, the system will have a strong energetic preference for staying in that broken-symmetry state and attempts to change the way the system has broken the symmetry meet with resistance. Thus crystals don't bend easily and ferromagnets show permanent magnetism. (see section 3.5)
- **Excitations**: At $T = 0$ the system is perfectly ordered. At finite temperature this order is weakened by excitations in the order parameter. In crystals these excitations are called lattice waves (quantized into phonons), in ferromagnets the analogous modes are called spin waves (quantized into magnons). (see section 3.6)
- **Defects**: If you break the symmetry differently in two adjacent parts of a macroscopic sample, the boundary will contain a defect: e.g. a dislocation in a crystal or a domain wall in a ferromagnet. (see section 3.7)

A summary of the properties of different broken symmetry phases is contained in the following table.

Phenomenon	**High T Phase**	**Low T Phase**	**Order parameter**	**Excitations**	**Rigidity phenomenon**	**Defects**
crystal	liquid	solid	$\rho_{\mathbf{G}}$	phonons	rigidity	dislocations, grain boundaries
ferromagnet	paramagnet	ferromagnet	$\mathbf{M}$	magnons	permanent magnetism	domain walls
antiferromagnet	paramagnet	antiferromagnet	$\mathbf{M}$ (on sublattice)	magnons	(rather subtle)	domain walls
nematic* (liquid crystal)	liquid	oriented liquid	$\langle \frac{1}{2}(3\cos^2\theta - 1)\rangle$	director fluctuations	various	disclinations, point defects
ferroelectric*	non-polar crystal	polar crystal	$\mathbf{P}$	soft modes	ferroelectric hysteresis	domain walls
superconductor*	normal metal	superconductor	$\lvert\psi\rvert e^{i\phi}$	–	superconductivity	flux lines

*liquid crystals and ferroelectrics are outside the scope of this course, superconductivity will be covered in a separate set of lectures

The order parameter for the crystal is $\rho_{\mathbf{G}}$ where $\mathbf{G}$ =reciprocal lattice vector.

3.6. Rigidity

The energy of a broken symmetry system is minimized when the symmetry is broken the same way throughout it. If you try to change the way symmetry is broken in a macroscopic sample, forces will appear reflecting that additional energy cost. This gives rise to a generalized *rigidity*. Three examples:

(1) Crystals do not deform easily (in contrast to liquids) because there is an elastic energy proportional to $(\nabla \mathbf{u})^2$ where $\mathbf{u}$ is the lattice displacement, and the lattice transmits this force to the other end of a macroscopic sample. Solids are therefore rigid.

(2) The spins are aligned in a ferromagnet and it costs energy to turn them with respect to each other. Hence the phenomenon of *permanent magnetism*. (If the magnetization is non-uniform there is an exchange cost proportional to $(\nabla \mathbf{M})^2$.)

3.7. Excitations

A solid is perfectly ordered at $T = 0$ but at non-zero temperature this is disrupted by lattice vibrations, quantized as *phonons*. The crucial feature of these is that it costs a vanishingly small energy to produce a phonon, provided its wavelength is long enough. At low temperature we excite only the long wavelength acoustic phonons; that we can do this expresses the fact that there is no energy gap in the phonon dispersion relation at $q = 0$ (in contrast to the optic phonons). These phonons give rise to the T^3 heat capacity at low temperature.

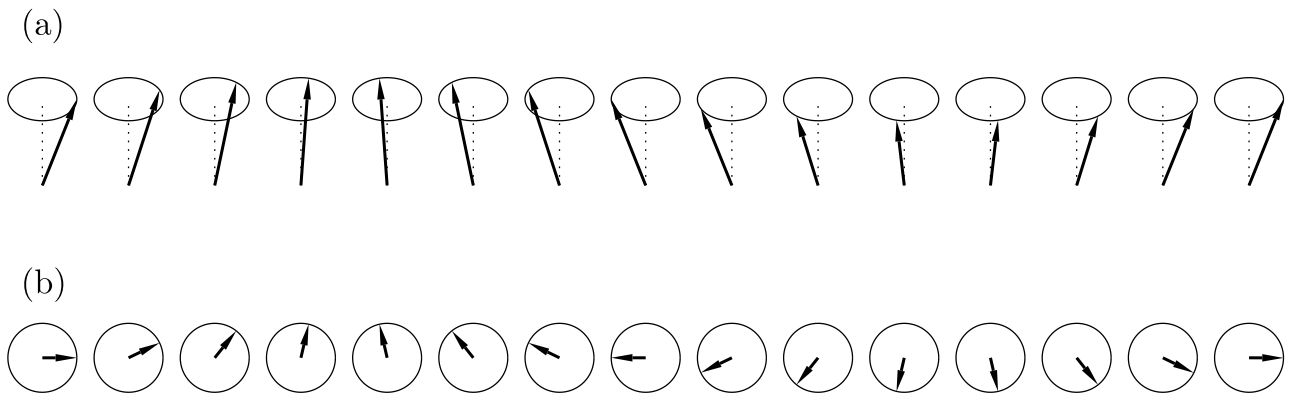
Whenever you have broken a continuous global symmetry (as you do when you make a solid from a liquid or a ferromagnet from a paramagnet) it is possible to produce long-wavelength excitations in the order parameter for vanishingly small energy cost. These excitations are called *Goldstone modes* (or sometimes Goldstone bosons)– because they cost no energy they are "massless".[1]

A ferromagnet is perfectly ordered at $T = 0$ but at non-zero temperature this is disrupted by *spin waves*, quantized as *magnons*. The crucial feature of these is that it costs a vanishingly small energy to produce a magnon, provided its wavelength is long enough. Thus the magnons play the same rôle in ferromagnets as phonons do in solids and are the Goldstone modes of the system. We will show in the lecture that there is no energy gap in the magnon dispersion relation at $q = 0$. These low energy magnons give rise to the so-called *Bloch* $T^{3/2}$ law which describes the low temperature form of the magnetization:

$$M(T) = M(0)[1 - \text{const } \times T^{3/2}].$$

It is also easy to show from this analysis that the heat capacity varies as $T^{3/2}$ at low temperature.

(a) Spin waves



A spin wave on a line of spins. (a) perspective view. (b) view from above.

The spin-wave dispersion and the Bloch-$T^{3/2}$ law will be derived in the lecture. If this derivation is repeated for the one or two dimensional Heisenberg model it is found that the number of spin waves diverges as soon as $T > 0$ so that no long range order is possible.

[1] In particle physics an example of this is the photon which is a Goldstone boson. For a superconductor, the situation is rather different because it turns out that you are breaking a continuous *local* symmetry and you don't get Goldstone modes. The reason for this is rather subtle and is connected with the Higgs mechanism.

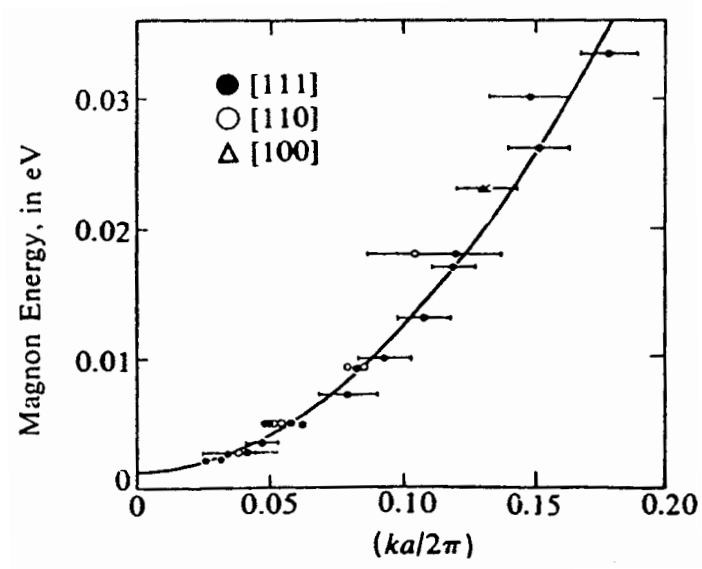
(b) Measurement of spin waves

Spin wave dispersions can be measured using inelastic neutron scattering. In such an experiment the magnitude of the incident neutron wave vector $\mathbf{k}_i$ is not equal to the magnitude of the scattered neutron wave vector $\mathbf{k}_f$. The energy of the neutron also changes from $E_i = \hbar^2 k_i^2/2m_\mathrm{n}$ to $E_f = \hbar^2 k_f^2/2m_\mathrm{n}$ because the neutron produces an excitation in the sample of energy $\hbar\omega$ and wave vector $\mathbf{Q}$. Conservation of energy and momentum implies that

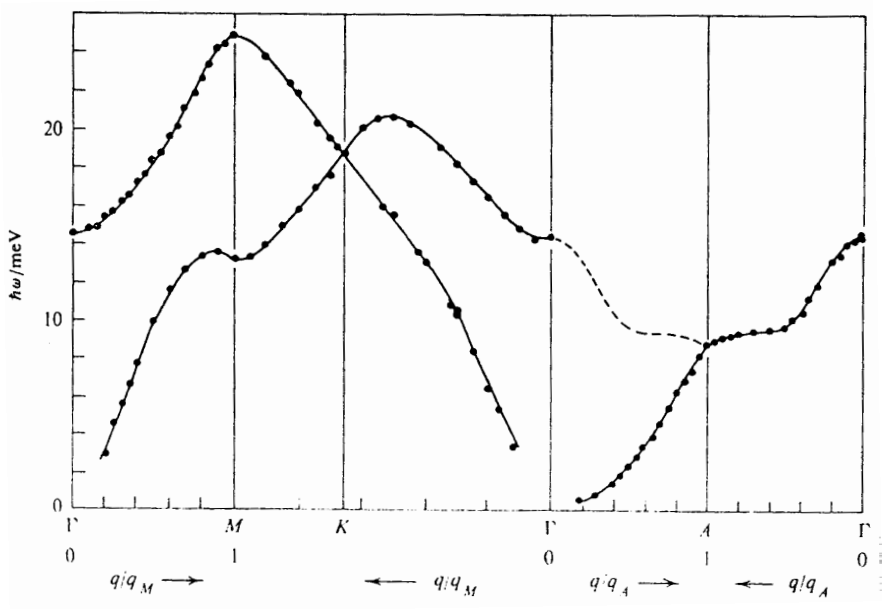
$$E_i - E_f = \hbar\omega \tag{38}$$

$$\mathbf{k}_i - \mathbf{k}_f = \mathbf{Q}, \tag{39}$$

so that a measurement of $\mathbf{k}_i$, $\mathbf{k}_f$, E_i and E_f allows a determination of ω and $\mathbf{Q}$.

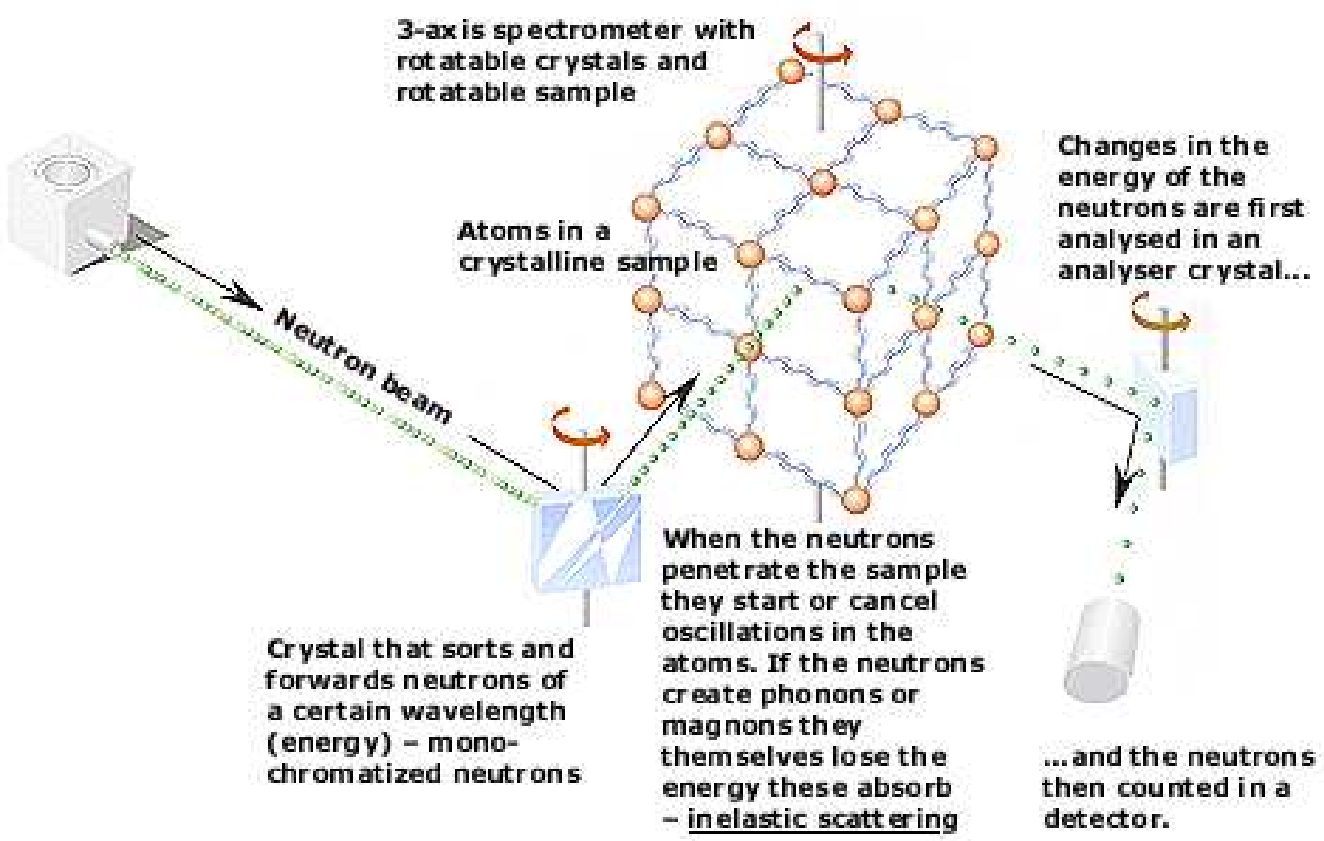


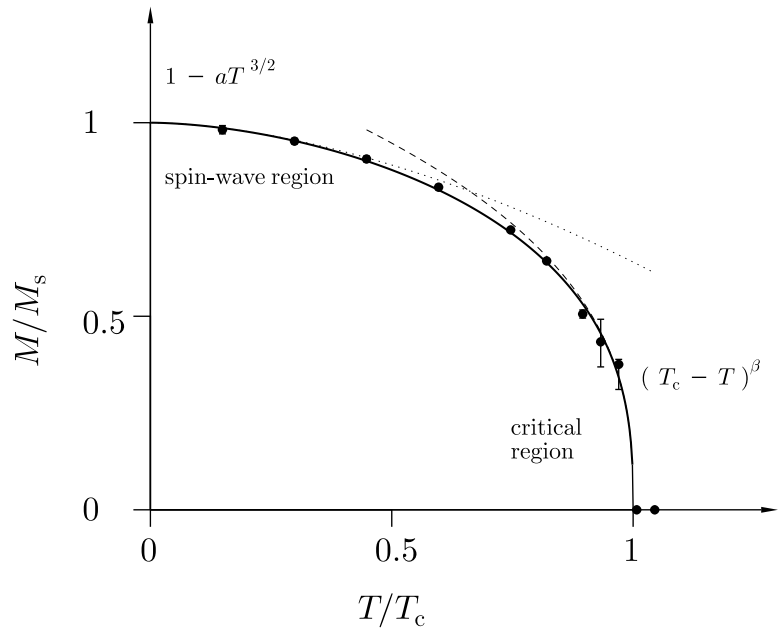
Spin wave evergy vs. momentum in an alloy of $Co_{0.92}Fe_{0.08}$ obtained at room temperature (Sinclair and Brockhouse 1960).



Spin wave dispersion relations in ferromagnetic Gadolinium at 78 K ($T_C = 300$ K) along different directions in the Brillouin zone (there are 2 modes as there as 2 atoms in the unit cell). The energy extrapolates to a quadratic form $\sim |\mathbf{q}|^2$ near Γ as expected for a ferromagnet.

Schematic diagram of an inelastic neutron scattering experiment to measure magnons (or phonons).

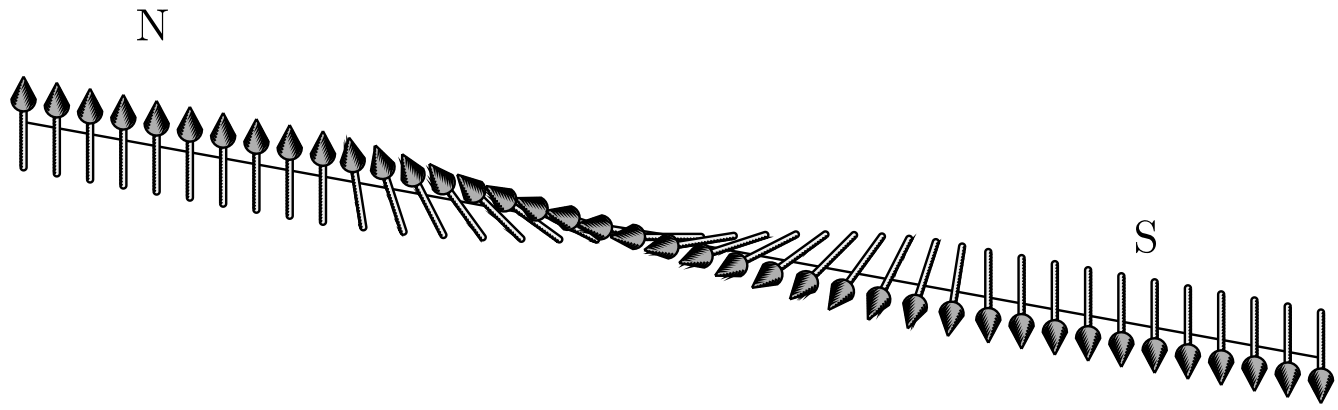




The magnetization in a ferromagnet. At low temperatures this can be fitted using the spin-wave model and follows the Bloch $T^{3/2}$ law. Near the critical temperature, the magnetization is proportional to $(T - T_c)^{\beta}$ where β is a critical exponent. Neither behaviour fits the real data across the whole temperature range. The data are for an organic ferromagnet which has $T_c \approx 0.67$ K for which $\beta \approx 0.36$, appropriate for the three-dimensional Heisenberg model.

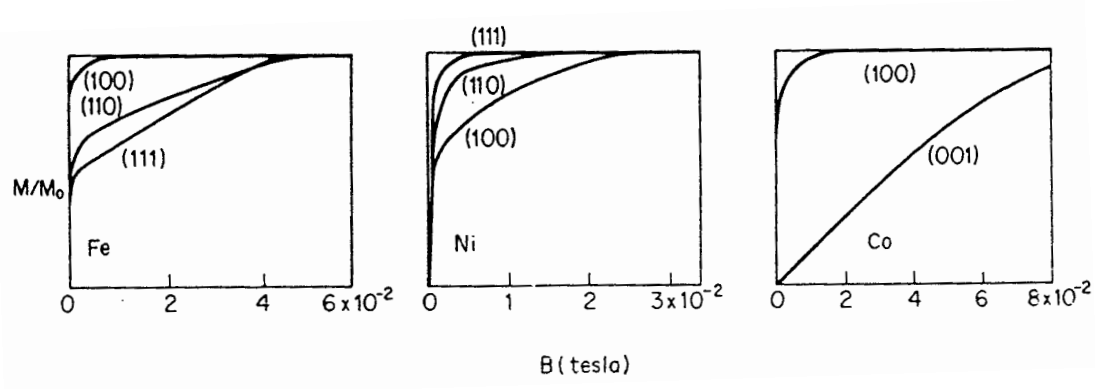
3.7 Domains

If different regions of a macroscopic system break symmetry in different ways, then in the interface between these regions the rigidity can break down. Therefore in general we expect domain walls, defects, vortices, dislocations and other singularities. In ferromagnets the most important singularity is the domain wall.



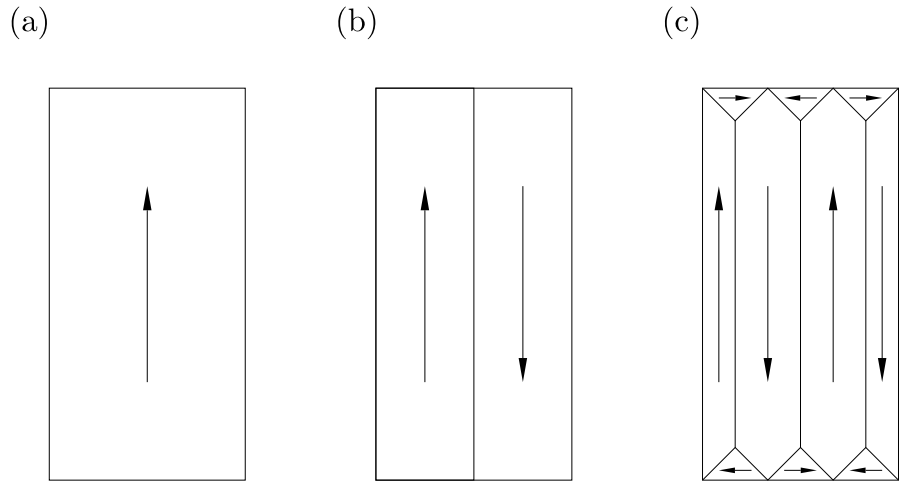
A Bloch wall. The domain wall is about 300 lattice constants thick in iron.

Because it costs energy to have a domain wall (which is because spins have to be twisted with respect to each other), some other interaction must stop the walls untwisting to save energy. This is the magnetocrystalline anisotropy characterised by an energy K. This energy comes about because of the spin-orbit interaction and is responsible for the hard and soft axes of magnetization (see next figure). In the magnetic domains of a ferromagnet the magnetization will prefer to lie along the easy direction but between domains, in the domain wall, it will have to rotate and a component will lie along the hard axis which will cost energy. In the lecture we will show that the width of a Bloch wall is $a\pi\sqrt{J/K}$ where a is the lattice spacing and the energy of the domain wall is proportional to $\sqrt{JK}$.



Magnetization in Fe, Co and Ni for applied fields in different directions showing anisotropy.

A sample which is (a) uniformly magnetized, (b) divided into two domains, and (c) with a simple closure domain structure.

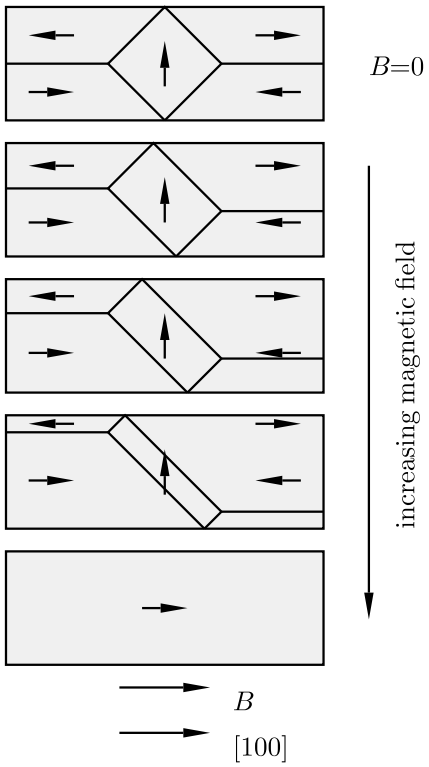


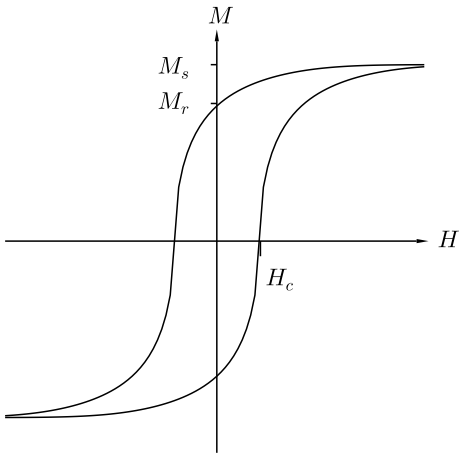
The reason domains often form in ferromagnets (so that symmetry is broken in different ways in different parts of the same sample) is that in this way a ferromagnetic object can save some dipolar energy if the exterior of the object is not filled with magnetic field which costs $B^2/2\mu_0$ energy per cubic metre.

Domains move through a sample as the field is applied (see the following figure). We can distinguish 2 broad classes of ferromagnetic materials based on how easy it is domains to move through a sample.

(1) *Soft magnets* are used in transformer coils, generators and motors. These have broad domain walls (small K) which are thus easy to move. This leads to small coercive fields. An example is permalloy (a commercial Ni/Fe alloy with an additional ingredient) which has a coercive field $B_c \sim 2 \times 10^{-7}$ T.

(2) *Hard* magnets are used as permanent magnets (e.g. in the back of loudspeakers, in motors, on the front of fridges[!]) and in magnetic tape recording (in powder form). These have large hysteresis, narrow domain walls (large K) so that it is easy to have domain wall pinning. Large ion moments and large crystal fields are helpful and suitable materials often involve rare earths, e.g. $Nd_2Fe_{14}B$ which has a $T_C = 585$ K and a coercive field B_c =1.2 T.





Left: Effect of an applied field on the domain pattern on the surface of a single crystal iron whisker showing domain wall displacement. Right: A hysteresis loop showing the saturation magnetization M_{s}, the remanent magnetization M_{r} and the coercive field H_c.

2.5 Magnetism in metals

So far we have only discussed the magnetism of insulators where the magnetic electrons are localized, strongly bound to the parent ions. Metals also show similar magnetic phenomena, like paramagnetism and ferromagnetism, but the fact that electrons are delocalized has important consequences on the magnetic properties.

Pauli paramagnetism

Paramagnetism of the electron gas (*Pauli paramagnetism*): (neglect the orbital contribution and take $g = 2$).

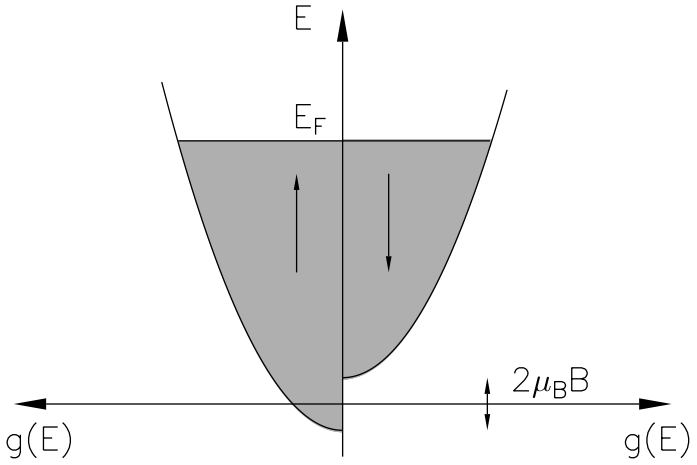
In an applied field B the electron band is spin-split into two spin sub-bands separated by $g\mu_{\rm B}B = 2\mu_{\rm B}B$. The number of extra electrons with spin-up is $\delta n_\uparrow = \frac{1}{2}g(E_F)\mu_{\rm B}B$. This is also the number of the deficit of electrons with spin-down, $\delta n_\downarrow = \frac{1}{2}g(E_F)\mu_{\rm B}B$. Thus the magnetisation is given by

$$M = \mu_{\rm B}(\delta n_\uparrow - \delta n_\downarrow) = g(E_F)\mu_{\rm B}^2 B$$

and the susceptibility by

$$\chi = \frac{\mu_0 M}{B} = g(E_F)\mu_0\mu_{\rm B}^2 = \frac{3\mu_0\mu_{\rm B}^2 n}{2E_F}$$

using the result $g(E_F) = 3n/2E_F$ where $n = N/V$, the number of electrons per unit volume.



Density of states showing splitting of energy bands in a field B

Band ferromagnetism and spontaneously-split bands

The $\uparrow$ and $\downarrow$ spin bands can also split in the absence of an external field as in Fe, Ni, Co. When bands are split electrons move from one band to the other to equalize the chemical potential leading to an imbalance between the $\uparrow$ and $\downarrow$ populations and to a net magnetization $M = \mu_B(n_\uparrow - n_\downarrow)$. The band splitting occurs because of the internal field due to exchange interactions and the criterion for this to be energetically favourable is $Ug(E_F) \geq 1$, where U is a measure of the strength of the magnetic interactions and $g(E_F)$ is the density of states at the Fermi energy. This condition is satisfied in the metallic ferromagnets Fe, Ni, Co. When this condition is not satisfied, i.e. $Ug(E_F) < 1$ bands do not split spontaneously in zero field, but in applied field the susceptibility χ is enhanced compared to the bare Pauli value $\mu_0\mu_B^2 g(E_F)$ by a factor $[1 - Ug(E_F)]^{-1}$.

	Fe	Ni	$ZrZn_2$
μ/μ_B	2.12	0.6	0.17
Δ (eV)	2.2	0.6	0.07
T_c (K)	1043	627	28

Magnetization per formula unit μ/μ_B, band splitting Δ and ordering temperature T_c of some band ferromagnets.

1. Show that the magnetization M of an assembly of N independent atoms of total electronic angular momentum J, in thermal equilibrium at temperature T, is given by

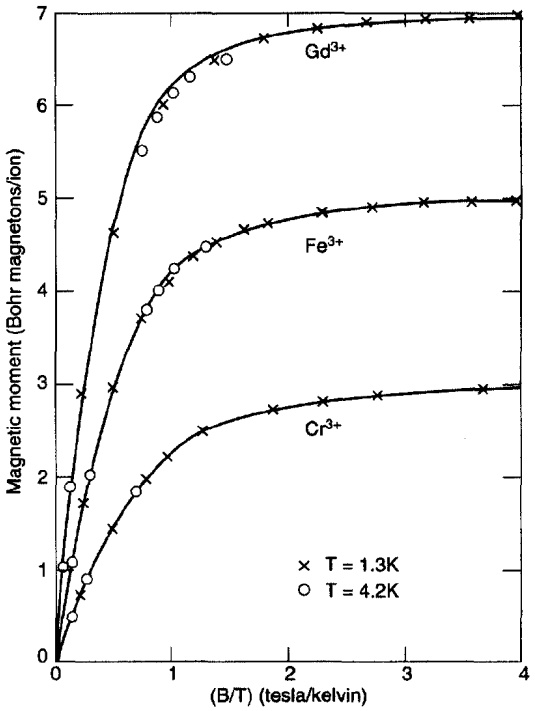
$$M = N g_J \mu_B J B_J(y) \tag{1}$$

with $y = g_J \mu_B J B / k_B T$, B is the magnetic flux density, g_J is the Landé g-factor and $B_J(y)$ is the Brillouin function

$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right).$$

The figure shows the magnetic moment m per ion plotted versus B/T for the paramagnetic salts $KCr(SO_4)_2.12H_2O$ (Cr^{3+}), $NH_4Fe(SO_4)_2.12H_2O$ (Fe^{3+}) and $Gd_2(SO_4)_3.8H_2O$ (Gd^{3+}). Show that equation (1) has the same form as the data at both low and high B/T.

The $3d$ shells of free Cr^{3+} and Fe^{3+} ions contain 3 and 5 electrons respectively, and the $4f$ shell of Gd^{3+} contains 7. Using Hund's rules, calculate the values of S, L, J and g_J for these ions, and show that the values you obtain account well for the data in the figure for Gd^{3+} and Fe^{3+}, but not for Cr^{3+}. Infer the actual g-factor and ground-state configuration for Cr^{3+} from the experimental data, and describe briefly the reason for the discrepancy between the data and your initial calculation.



2. a) Determine the ground state according to Hund's rules for isolated ions of Co^{2+} ($3d^7$) and Co^{3+} ($3d^6$).

b) Discuss the magnetic ground states of Co^{2+} and Co^{3+} ions located at the centre of (i) a regular octahedron, and (ii) a regular tetrahedron of O^{2-} ions. Consider separately the cases of weak and strong crystal fields.

The insulator Co_3O_4 contains Co^{3+} ions in octahedral coordination and Co^{2+} ions in tetrahedral coordination. Account for the experimental finding that Co^{3+} ions carry no magnetic moment, while Co^{2+} ions have a moment of $\sim 3\mu_B$ per ion.

c) Elemental Co is a ferromagnet. The saturated magnetic moment is $M = 1.7\mu_B$ per cobalt atom. Explain the physical origin of the non-integer value of the magnetic moment M/μ_B.

3. MnF_2 has a tetragonal crystal structure in which the Mn ions are situated at the corners of the tetragonal unit cell $a = b$ =0.5 nm and c =0.3 nm, and at the body centred position in the unit cell. Below 70 K the spins of the Mn ions become antiferromagnetically aligned along the $c-$axis with the spins of the ions at the centre of the unit cell aligned opposite to those at the corners. The neutron scattering from a powdered sample of MnF_2 is measured using an incident neutron wavelength of 0.3 nm and an angle of scattering between 0° and 90°. Sketch the results you would expect to observe at (a) 100 K and (b) 10 K. You can neglect the scattering from the F ions.

4. The Landau theory of a ferromagnet in a magnetic field H implies that the free energy is given by

$$F(M) = F_0 + a_0(T - T_C)M^2 + bM^4 - \mu_0 MH$$

where a_0 and b are positive constants.

a) By evaluating $\partial F/\partial M$, and setting it equal to zero, show that for no applied field ($H = 0$) the magnetization M is zero above T_C and is proportional to $(T_C - T)^{1/2}$ below T_C.

b) Show also that at $T = T_C$, $M \propto H^{1/3}$.

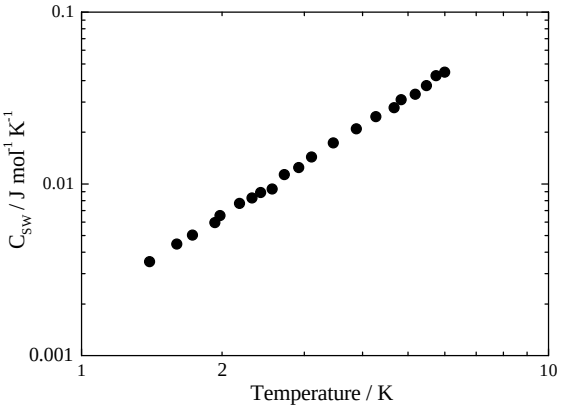
c) Show that the form of the free energy also implies that

$$M^2 = u + v\frac{H}{M}$$

where u and v are constants that you should determine. By sketching M^2 against H/M for T just above T_C, just below T_C, and exactly at T_C, show how this method can be used to determine T_C. This idea is the basis of the so-called *Arrott plot* which is a plot of M^2 against H/M which is used experimentally to locate T_C from $M(H)$ data measured at different temperatures.

5. At low temperatures, the energy $\hbar\omega$ of a long-wavelength spin wave in a ferromagnet is related to the magnitude of the wavevector k by $\hbar\omega = Dk^2$, where D is a constant. Show that the contribution to the heat capacity from spin wave excitations, C_{SW}, varies with temperature T as $C_{SW} \propto T^\alpha$, and determine α for a three-dimensional system.

   To what extent is this prediction valid for the measurements on gadolinium shown in the figure ? [Note log-log plot].



   [Gadolinium is a ferromagnet with a Curie temperature of 292 K.]

6. A square-lattice anisotropic magnet is described by the Hamiltonian

$$\mathcal{H} = \frac{1}{2}\sum_{ij}\left[J_\parallel S_i^z S_j^z + J_\perp\left(S_i^x S_j^x + S_i^y S_j^y\right)\right] + g\mu_B B\sum_i S_i^z,$$

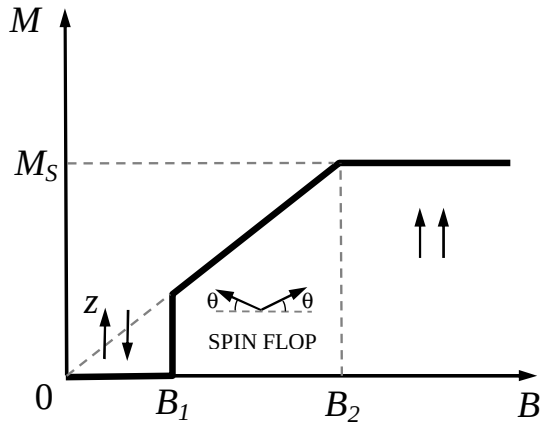
where in the first sum i and j are nearest-neighbour sites, $J_\parallel, J_\perp > 0$, and the last term is the Zeeman energy in an external magnetic field B applied along the z-axis. When $J_\parallel > J_\perp$ the ground state at $B = 0$ is a collinear antiferromagnet in which neighbouring spins point alternately along the positive and negative z-direction. Calculate the mean-field energy per spin of this state at non-zero applied field B (the mean-field energy is calculated by replacing spin operators by their expectation values).

Consider an alternative magnetic structure in which the magnetic moments have their z components aligned ferromagnetically along the applied field B, and the components in the xy plane ordered antiferromagnetically, as illustrated in the figure below.

Show that mean-field energy of this (spin-flop) state is

$$E_{\mathrm{SF}}(\theta) = -g\mu_{\mathrm{B}}BS\sin\theta + \frac{n}{2}(J_{\parallel} + J_{\perp})S^2 f(\theta) - \frac{n}{2}J_{\perp}S^2 \qquad \text{(per spin)},$$

where n is the number of nearest neighbours and $f(\theta)$ is a function to be determined. Find how the equilibrium angle θ varies with the applied field B, and show that the spin-flop state becomes energetically more favourable than the collinear antiferromagnetic state above a critical field B_1 to be determined.



Account for the shape of the magnetization curve plotted in the figure, and determine the values of $J_{\parallel}$ and $J_{\perp}$ for the square-lattice antiferromagnet K_2CoF_4, for which $B_1 = 80\,\mathrm{T}$, $B_2 = 130\,\mathrm{T}$, $g = 2.1$ and $S = 3/2$.
