

PH20017/63 Condensed Matter Physics 1

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Lecture notes set 4 - Magnetism

These are only summary notes – you should annotate, expand and supplement.

Magnetism

- ▶ Magnetic materials
- ▶ Curie paramagnetism
- ▶ Pauli paramagnetism
- ▶ Diamagnetism
- ▶ Origins of magnetic order
- ▶ Ferromagnetism

For alternative descriptions and explanations, often at a different level, plus further problems, see:

Hook and Hall (2nd Ed.)

Myers*

Kittel (5th ed.)

Ibach & Lüth (3rd Ed.)

Ashcroft & Mermin

Chs 7 & 8; p198–228; 248–251

Ch 11; p361–420

Chs 14 & 15; p433–466; 484–493

Ch 8; p191–201; 209–211

Chs 31 & 12; p644–681, 715–722

Magnetic materials

Magnetism concerns phenomena associated with forces on magnets due to other magnets.

The origins of magnetism are

- ▶ moving electric charges (e.g. electric currents in wires, “atomic currents” due to orbiting electrons), and
- ▶ fundamental magnetic moments of elementary particles (spin).

These create a magnetic field \vec{B} which can be measured through its effect on moving charges (e.g. Hall effect).

A magnetic solid can be thought of as consisting of many permanent or induced magnetic dipoles with dipole moments $\vec{\mu}_i$. The magnetisation $\vec{\mathcal{M}}$ is the average magnetic moment per unit volume, $\vec{\mathcal{M}} = (1/V) \sum_i \vec{\mu}_i$, and creates an average magnetic field

$$\vec{B}_{\mathcal{M}} = \mu_0 \vec{\mathcal{M}} \quad \begin{aligned} \mu_0 &= \text{permeability of free space} \\ &= 4\pi \times 10^{-7} \text{ in SI units (dimensionless).} \end{aligned}$$

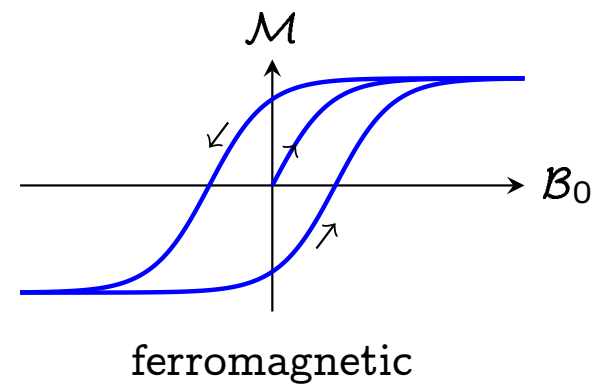
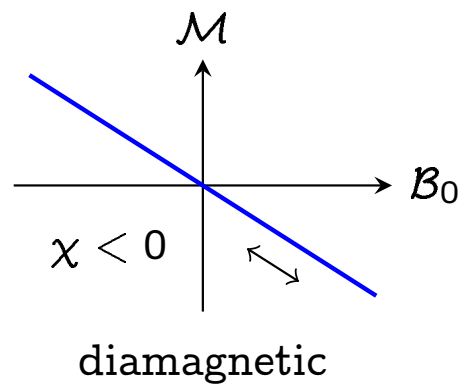
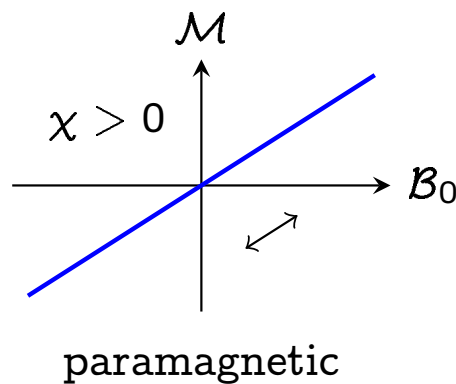
The magnetisation of a solid is often induced by an external field \vec{B}_0 . For weak fields one finds

$$\vec{B}_{\mathcal{M}} = \chi \vec{B}_0$$

$$\text{or } \vec{\mathcal{M}} = \chi \frac{\vec{B}_0}{\mu_0}$$

χ = magnetic susceptibility

χ can be positive (paramagnetic material), or negative (diamagnetic). In some materials magnetisation is observed in the absence of an external magnetic field: e.g. ferromagnetic.



Atomic theory of paramagnetism

Consider a solid containing atoms with permanent magnetic dipoles.

These are randomly aligned if there is no external magnetic field: $\vec{\mathcal{M}} = 0$.

If a field $\vec{\mathcal{B}}_0$ is applied, they experience a torque $\vec{\tau} = \vec{\mu} \times \vec{\mathcal{B}}_0$, tending to align $\vec{\mu}$ with $\vec{\mathcal{B}}_0$. This results in a non-vanishing $\vec{\mathcal{M}}$ parallel to $\vec{\mathcal{B}}_0$.

Thermal disorder acts to reduce $\vec{\mathcal{M}}$.

To model this, we assume a solid made of atoms with atomic moments

$$\vec{\mu} = -g\mu_B \vec{J}$$

[see Quantum and Atomic course] where

- ▶ $\hbar\vec{J} = \hbar\vec{L} + \hbar\vec{S}$ is the total angular momentum, the sum of the orbital and spin contributions.
- ▶ μ_B is the Bohr magneton
- ▶ $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$ is the Landé g-factor.
- ▶ J_z is quantised: $m_J = -J, -J+1, \dots, J-1, J$



Atomic moments — background

An electron undergoing circular motion, radius r , angular frequency ω , represents a current

$$i = \frac{\text{charge}}{\text{time}} = \frac{-e}{2\pi/\omega} = -\frac{e\omega}{2\pi}$$

enclosing an area $\mathcal{A} = \pi r^2$.

The resulting magnetic dipole moment is

$$\vec{\mu} = i\vec{\mathcal{A}} = -\frac{e\omega}{2\pi} \times \pi r^2 \hat{\mathcal{A}} = -\frac{e\hbar}{2m} \vec{\ell}$$

with $\hbar\vec{\ell}$ the orbital angular momentum of the electron: $|\hbar\vec{\ell}| = m\omega r^2$. The direction of $\vec{\mu}$ is such that i is **clockwise looking along $\vec{\mu}$** .

We see the natural unit for magnetic moments is the **Bohr magneton**

$$\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J T}^{-1} = 5.79 \times 10^{-5} \text{ eV T}^{-1}.$$

The total orbital moment of an atom with several electrons follows by addition:

$$\vec{\mu} = -\mu_B \sum \vec{\ell} = -\mu_B \vec{L}$$

where $\hbar \vec{L} = \hbar \sum \vec{\ell}$ is the total orbital angular momentum of the atom.

The **intrinsic spin** of the electron also contributes to the magnetic moment. For a stationary electron with spin angular momentum $\hbar \vec{s}$,

$$\vec{\mu} = -g_0 \mu_B \vec{s}$$

where $g_0 = 2$ is the electron spin g-factor (actually 2.0023193043622... — QED); spin angular momentum is twice as effective as orbital angular momentum in generating magnetic moment.

Spin and orbital angular momentum combine. The total moment $\vec{\mu} = -g\mu_B \vec{J}$, where $\hbar \vec{J} = \hbar \vec{L} + \hbar \vec{S}$ is the total angular momentum.

For a closed shell of electrons, \vec{L} and \vec{S} are zero, and there is no permanent magnetic moment.

Quantum theory of paramagnetism

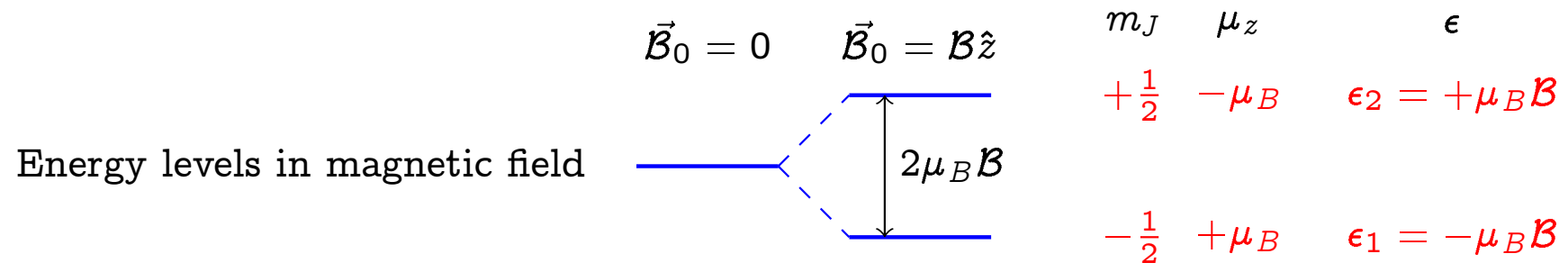
What happens when an atomic moment is placed in an applied magnetic field?

The energy levels of the (quantum) moment in the field $\vec{B}_0 = B\hat{z}$ are

$$U = -\vec{\mu} \cdot \vec{B}_0 = m_J g \mu_B B \quad m_J = -J, -J+1, \dots, J-1, J$$

The field tends to align the moments. However, thermal fluctuations will tend to randomise them.

To see this, consider the simplest case: no orbital moment ($L = 0$) and a single spin ($S = 1/2$). Then $J = 1/2$, $m_J = \pm \frac{1}{2}$, $g = 2$ and $U = \pm \mu_B B$.



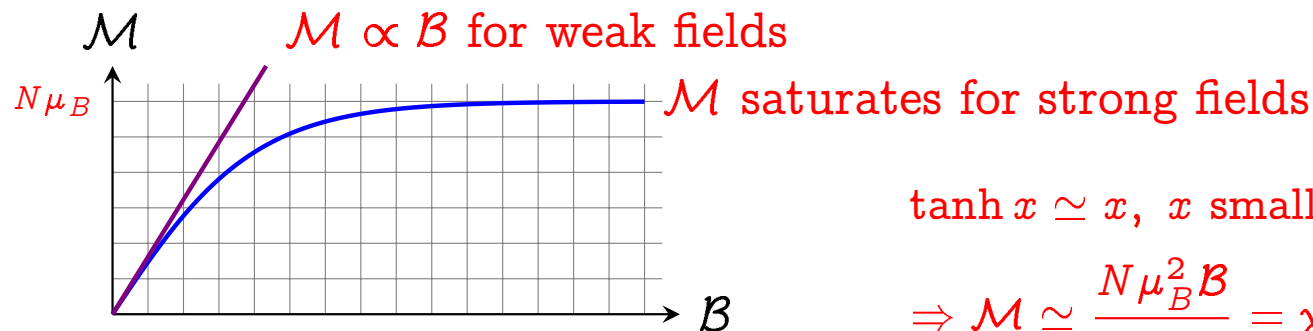
At temperature T , the probability p_i of occupying level i with energy ϵ_i is $\propto \exp -\epsilon_i/k_B T$, so

$$p_1 = \frac{1}{Z} e^{+\mu_B \mathcal{B}/k_B T} \quad p_2 = \frac{1}{Z} e^{-\mu_B \mathcal{B}/k_B T}$$

where Z normalises: $p_1 + p_2 = 1$. The average moment of the atom is

$$\langle \mu \rangle = (+\mu_B)p_1 + (-\mu_B)p_2 = \dots = \mu_B \tanh \left(\frac{\mu_B \mathcal{B}}{k_B T} \right).$$

For N indep. atoms per unit volume $\mathcal{M} = N \langle \mu \rangle = N \mu_B \tanh \left(\frac{\mu_B \mathcal{B}}{k_B T} \right)$.



$$\tanh x \simeq x, \quad x \text{ small}$$

$$\Rightarrow \mathcal{M} \simeq \frac{N \mu_B^2 \mathcal{B}}{k_B T} = \chi \frac{\mathcal{B}}{\mu_0}, \quad \mathcal{B} \text{ small}$$

$$\Rightarrow \chi = \frac{C}{T} \quad \text{Curie's Law}$$

More generally, an atom with angular momentum quantum number J results in $(2J + 1)$ equally spaced energy levels and

$$\mathcal{M} = Ng\mu_B JB_J(x), \quad x = \frac{g\mu_B J\mathcal{B}}{k_B T}$$

where the Brillouin function $B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$.

Then for small x , $\mathcal{M} \simeq \frac{Ng^2\mu_B^2 J(J+1)\mathcal{B}}{3k_B T}$.

In weak fields the susceptibility is

$$\chi = \mu_0 \frac{\mathcal{M}}{\mathcal{B}_0} = \dots = \frac{Np^2\mu_B^2\mu_0}{3k_B T} \quad \text{so} \quad \chi = \frac{C}{T} \quad \text{Curie's Law} \quad \text{► Curie}$$

again. C is the Curie constant, $p = g\sqrt{J(J+1)}$ an effective number of Bohr magnetons.

Experimental results [from Kittel]

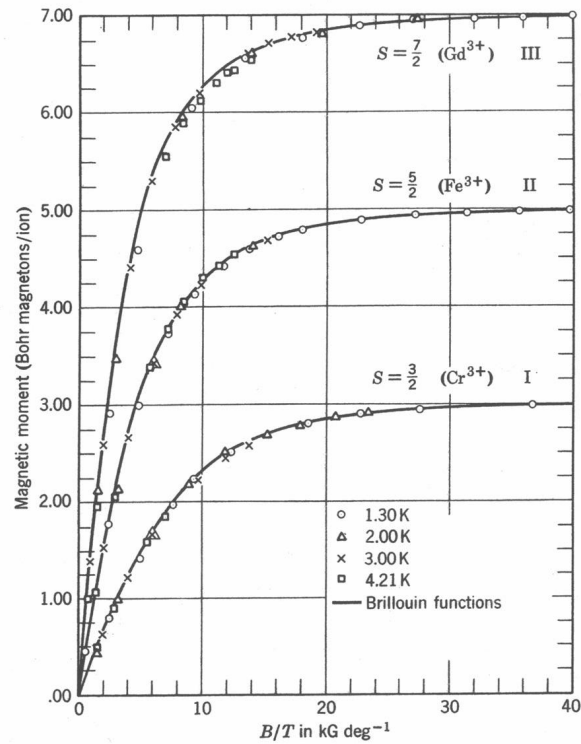


Figure 4 Plot of magnetic moment *versus* B/T for spherical samples of (I) potassium chromium alum, (II) ferric ammonium alum, and (III) gadolinium sulfate octahydrate. Over 99.5% magnetic saturation is achieved at 1.3 K and about 50,000 gauss. [After W. E. Henry, Phys. Rev. **88**, 559 (1952).]

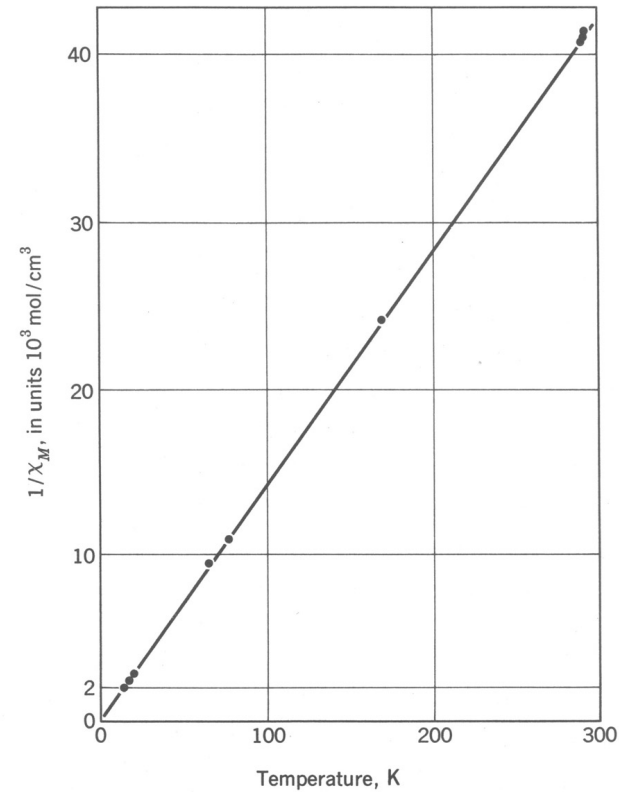


Figure 5 Plot of $1/\chi$ *vs* T for a gadolinium salt, $\text{Gd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The straight line is the Curie law. (After L. C. Jackson and H. Kamerlingh Onnes, Leiden Communications 168a.)

Paramagnetism of conduction electrons

What about conduction electrons, which no longer orbit as in atoms?

A free electron has a magnetic moment μ_B due to its spin. One might therefore expect a Curie-type paramagnetic contribution to the magnetisation

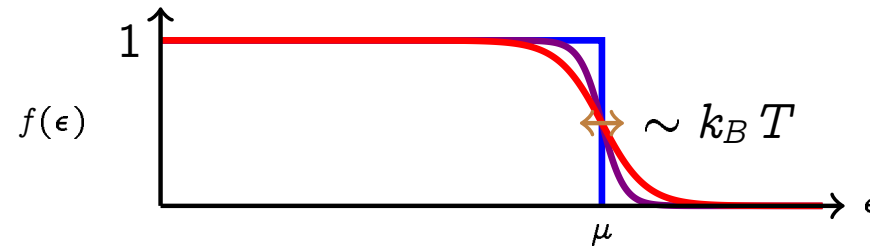
$$\mathcal{M} = \frac{N \mu_B^2 \mathcal{B}}{k_B T}.$$

from N conduction electrons per unit volume.

However, for most non-ferromagnetic metals it is found to be much smaller, and independent of T . Why?

The reason is similar to the explanation used for the electronic heat capacity.

Most electrons cannot align to an external field because the Pauli exclusion principle forbids it — the necessary states are already occupied.



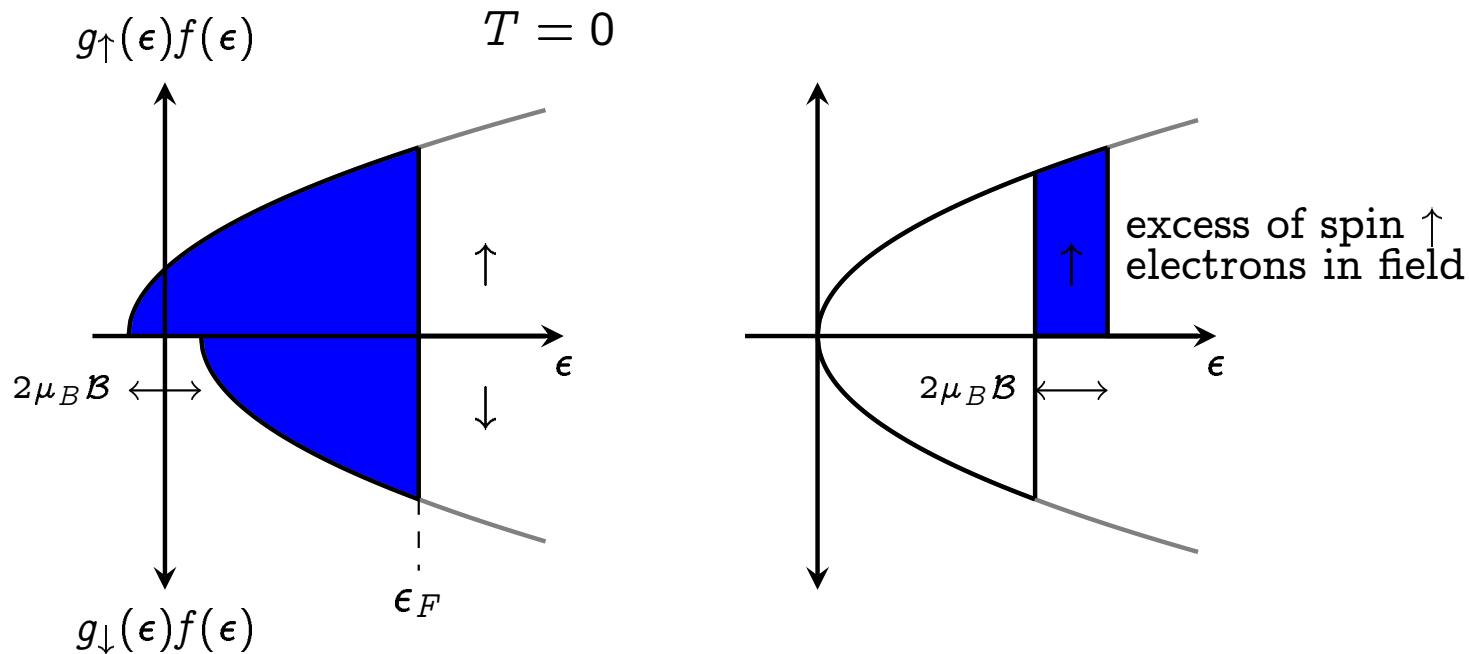
The electron can only align its moment with the field if the aligned state is initially unoccupied — which means the electron must be in a state within $\sim k_B T$ of the Fermi level. Only a fraction T/T_F of the electrons are within $k_B T$ of the Fermi level. Therefore the magnetisation is

$$\mathcal{M} \simeq \frac{N \mu_B^2 \mathcal{B}}{k_B T} \times \frac{T}{T_F} = \frac{N \mu_B^2 \mathcal{B}}{k_B T_F}$$

— independent of temperature, and with the observed magnitude.

More quantitative

States with spin \uparrow lowered in energy by $\mu_B \mathcal{B}$, states with spin \downarrow raised in energy by $\mu_B \mathcal{B}$. Let the density of states of spin up (down) electrons be $g_{\uparrow}(\epsilon)$ ($g_{\downarrow}(\epsilon)$), and fill the lowest N states with electrons.



$$\mathcal{M} = \mu_B(N_{\uparrow} - N_{\downarrow}) \simeq \mu_B \times (2\mu_B \mathcal{B} \times g_{\uparrow}(\epsilon_F)) = \mu_B^2 \mathcal{B} g(\epsilon_F).$$

We derived the following results when we looked at the quantum free electron gas:

$$\left. \begin{aligned} g(\epsilon) &= \alpha \epsilon^{1/2} \\ N &= \frac{2}{3} \alpha \epsilon_F^{3/2} \end{aligned} \right\} \Rightarrow g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2k_B T_F}$$

Therefore the Pauli paramagnetic magnetisation of the quantum free electron gas is

$$\mathcal{M} = \frac{3N\mu_B^2 \mathcal{B}}{2k_B T_F}$$

– a factor 3/2 times our simple estimate.

In real metals, corrections to this result arise due to the band properties of electrons, and due to interactions between electrons that are not included in the free-electron model.

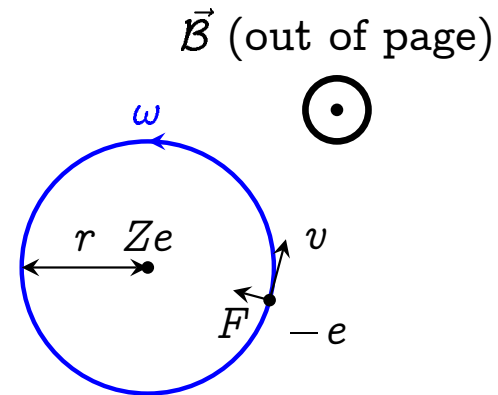
Diamagnetism - classical treatment

Diamagnetism occurs because **an applied field *changes* electron motion.**

Consider an electron orbiting the nucleus.

When $\vec{B} = 0$, balancing forces

$$\underbrace{\frac{Ze^2}{4\pi\epsilon_0 r^2}}_{\text{electrostatic}} = \underbrace{m\omega_0^2 r}_{\text{centrepetal}} \Rightarrow \omega_0^2 = \frac{Ze^2}{4\pi\epsilon_0 m r^3}$$



When $\vec{B} \neq 0$, an additional Lorentz force $\vec{F}_L = -e\vec{v} \times \vec{B}$ acts on the electron:

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} + \underbrace{e\omega r B}_{\text{Lorentz}} = m\omega^2 r \quad \text{or} \quad \omega^2 - \frac{eB}{m}\omega - \omega_0^2 = 0$$

Solving [with $(-b \pm \sqrt{b^2 - 4ac})/2a$] for small B gives $\omega \simeq \omega_0 + \frac{eB}{2m}$

The B -field induces additional precession at angular frequency $\omega_{\text{ind}} = \frac{eB}{2m}$.

Here, ω is increased so the induced rotation of the electron is anti-clockwise. The corresponding induced current is clockwise:

$$i_{\text{ind}} = \frac{\text{charge}}{\text{time}} = \frac{-e}{2\pi/\omega_{\text{ind}}} = -e \frac{\omega_{\text{ind}}}{2\pi} = -\frac{e^2 \mathcal{B}}{4\pi m}.$$

The induced moment is into the page, **opposite** to the \mathcal{B} -field.

$$|\vec{\mu}| = i_{\text{ind}} \mathcal{A} = -\frac{e^2 \mathcal{B}}{4\pi m} \times \pi r^2 = -\frac{e^2 \mathcal{B}}{4m} r^2.$$

For an atom with Z electrons, this generalises to $\mu = -\frac{Ze^2 \mathcal{B}}{4m} \langle \rho^2 \rangle$ where $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle = \frac{2}{3} \langle r^2 \rangle$ for a spherically symmetric charge distribution. With N atoms per unit volume

$$\vec{\mathcal{M}} = N\vec{\mu} \quad \Rightarrow \quad \chi = \frac{\mu_0 N \mu}{\mathcal{B}} = -\frac{\mu_0 N Z e^2}{6m} \langle r^2 \rangle$$

— the classical **Langevin diamagnetic susceptibility**.

► Langevin

[Question: what if $\vec{\mathcal{B}}$ is into the page? or if the electron rotates clockwise?]

Diamagnetic susceptibilities of materials

With $\langle r^2 \rangle \sim 1 \text{ \AA}^2 = 10^{-20} \text{ m}^2$, $m \sim 10^{-30} \text{ kg}$, NZ = no. electrons per unit volume $\sim 1/\text{\AA}^3 = 10^{30}/\text{m}^3$ and $e \sim 10^{-19} \text{ C}$,

$$\chi = -\frac{\mu_0 NZ e^2}{6m} \langle r^2 \rangle \sim 10^{-5} \quad \text{— typical magnitude.}$$

Weak. Only evident if no paramagnetism, i.e. no permanent moments.

For metals, the diamagnetic contribution from conduction electrons is more difficult to calculate due to the complicated orbits of band electrons – but similar in magnitude.

material	$\chi(10^{-5})$	material	$\chi(10^{-5})$
Bismuth	−16.6	Carbon (graphite)	−1.6
Water	−0.9	Mercury	−2.9
Copper	−1.0	Superconductor*	−10 ⁵

* Superconductors have $\chi = -1$. They are perfect diamagnets, perfectly screening an applied field due to surface currents. See PH30079.

Magnetic levitation

Diamagnetic materials can be levitated.

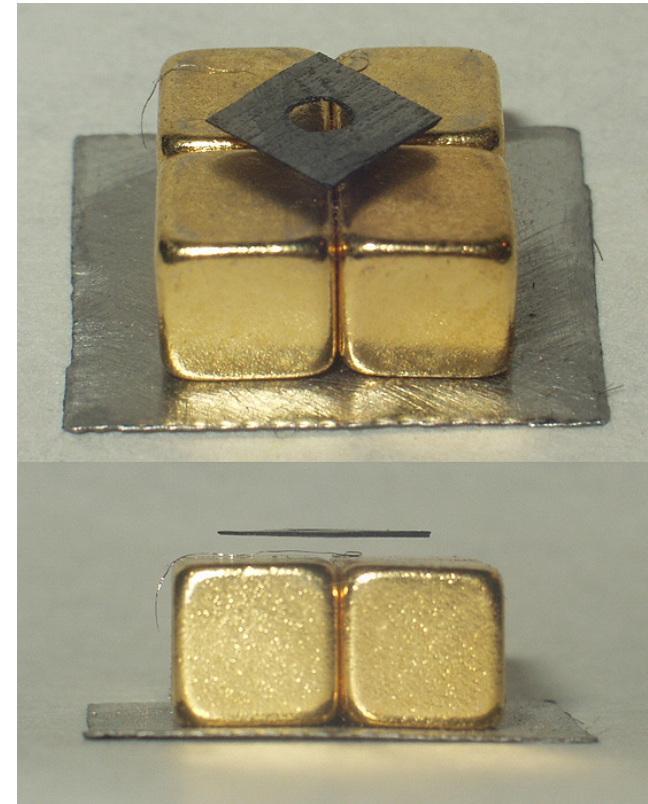
The magnetic force

$$\vec{F} = \vec{\nabla}(\vec{\mathcal{M}} \cdot \vec{\mathcal{B}}) = (\chi/\mu_0)\vec{\nabla}\mathcal{B}^2.$$

means diamagnets are attracted to field minima, which exist. (Field maxima do not exist in free space, so paramagnets cannot be levitated by static fields.)

The figure shows a 6mm \times 6mm graphite square levitating over a permanent neodymium magnet array (5mm cubes, poles orientated vertically in checkerboard pattern).

Applications include microgravity experiments (NASA, levitating mice to study effects on bone and muscle) and the growth of high-quality protein crystals countering gravitational influences.



Magnetic order

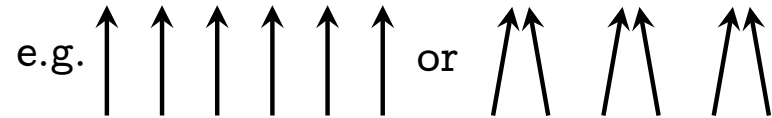
At low temperatures some materials exhibit a finite magnetisation \mathcal{M} even in the absence of an applied field — a **spontaneous magnetisation**.

As a result of interactions, the individual dipoles are sensitive to the alignment of their neighbours.

Examples of this magnetic order are:

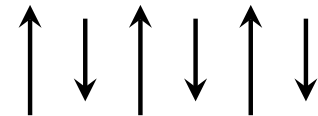
Ferromagnetic order

— all moments contribute equally



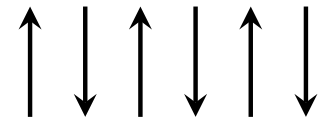
Ferrimagnetic order

— some cancellation, but overall finite \mathcal{M}



Antiferromagnetic order

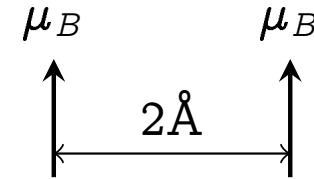
— no spontaneous magnetisation, but magnetic order



Interactions between dipoles cannot explain magnetic order

What causes the spontaneous ordering?

Consider two dipoles of magnitude μ_B separated by a typical interatomic distance $r \sim 2 \text{ \AA}$.



The \mathcal{B} field at one moment due to the other is

$$\mathcal{B} \sim \mu_0 \frac{\mu_B}{4\pi r^3}$$

so the interaction energy is

$$E \sim \mu_B \mathcal{B} = \frac{\mu_0}{4\pi} \frac{\mu_B^2}{r^3} \sim 10^{-7} \times \frac{(10^{-23})^2}{(2 \times 10^{-10})^3} \sim 10^{-24} \text{ J}$$

In temperature units ($E = k_B T$) this is 0.1 K. So above $T = 0.1 \text{ K}$ we expect thermal disorder will destroy the magnetic order. This is inconsistent with observations.

	Fe	Co	Ni	Gd	Dy	Eu0
Observed T_C (K)	1043	1388	627	292	88	69

The exchange interaction

Magnetic ordering at $T \sim 1000$ K requires another origin – **exchange**, also called the exchange interaction.

This arises because the **electrostatic interaction** between two electrons depends upon the relative alignment of their magnetic moments.

Electrons are fermions, so the wave function of two electrons must be antisymmetric under particle exchange:

$$\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = -\psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1).$$

If $\vec{r}_1, \vec{s}_1 = \vec{r}_2, \vec{s}_2$, the wave function **must** vanish. So electrons with the same spin cannot occur at the same point in space, and are kept apart. This is not the case if $\vec{s}_1 \neq \vec{s}_2$.

So electrons with parallel spins spatially avoid one another, making the Coulomb repulsion $\langle e^2/4\pi|\vec{r}_1 - \vec{r}_2| \rangle$ smaller when the spins are parallel than when they are anti-parallel — this is termed the exchange interaction.

This exchange interaction can be written $-2\mathcal{J}\vec{s}_1 \cdot \vec{s}_2$, where \mathcal{J} is the energy difference between parallel and antiparallel alignment of the moments.

The exchange field

More generally, the exchange energy of a solid can be approximated as

$$\mathcal{H} = - \sum_i \sum_{j \neq i} \mathcal{J}_{ij} \vec{S}_i \cdot \vec{S}_j \quad \text{Heisenberg Hamiltonian}$$

where i, j run over atoms and \vec{S}_i is the total effective spin of atom i (actually total angular momentum \vec{J}).

In the **mean field approximation** we replace each \vec{S}_j by the average value $\langle \vec{S} \rangle = (1/N) \sum_j \vec{S}_j$. Since the moment of atom j is $\vec{\mu}_j = -g\mu_B \vec{S}_j$, the magnetisation of the solid $\vec{\mathcal{M}} = (1/V) \sum_j \vec{\mu}_j$ is proportional to $\langle \vec{S} \rangle$. Then

$$\mathcal{H} = - \sum_i \vec{\mu}_i \cdot (\lambda \mu_0 \vec{\mathcal{M}}) \quad \text{where} \quad \lambda = \frac{\sum_{j \neq i} \mathcal{J}_{ij}}{\mu_0 g^2 \mu_B^2 (N/V)}$$

The exchange interaction acts like an extra magnetic field,

$$\vec{\mathcal{B}}_E = \lambda \mu_0 \vec{\mathcal{M}}$$

(subscript E for exchange). Note: It behaves like a magnetic field, but is not a real magnetic field.

Mean field analysis

What is the effect of the exchange field? Let us revisit our atomic theory of paramagnetism, but now include the exchange field.

In the case considered there ($L = 0, J = S = \frac{1}{2}, g = 2$)

$$\underbrace{\mathcal{M} = N\mu_B \tanh\left(\frac{\mu_B \mathcal{B}}{k_B T}\right)}_{\text{before}} \rightarrow \underbrace{\mathcal{M} = N\mu_B \tanh\left(\frac{\mu_B (\mathcal{B} + \mu_0 \lambda \mathcal{M})}{k_B T}\right)}_{\text{now}}.$$

At high T when $\mu_B (\mathcal{B} + \mu_0 \lambda \mathcal{M}) / k_B T \ll 1$ and using $\tanh x \simeq x$

$$\mathcal{M} = \frac{N\mu_B^2}{k_B T} (\mathcal{B} + \lambda \mu_0 \mathcal{M}).$$

Solving for \mathcal{M} gives the modified susceptibility

$$\chi = \mu_0 \frac{\mathcal{M}}{\mathcal{B}} = \frac{C}{T - T_C} \quad \text{Curie-Weiss "law"}$$

► Weiss

where $C = N\mu_B^2 \mu_0 / k_B$ is the Curie constant from before and $T_C = \lambda C$.

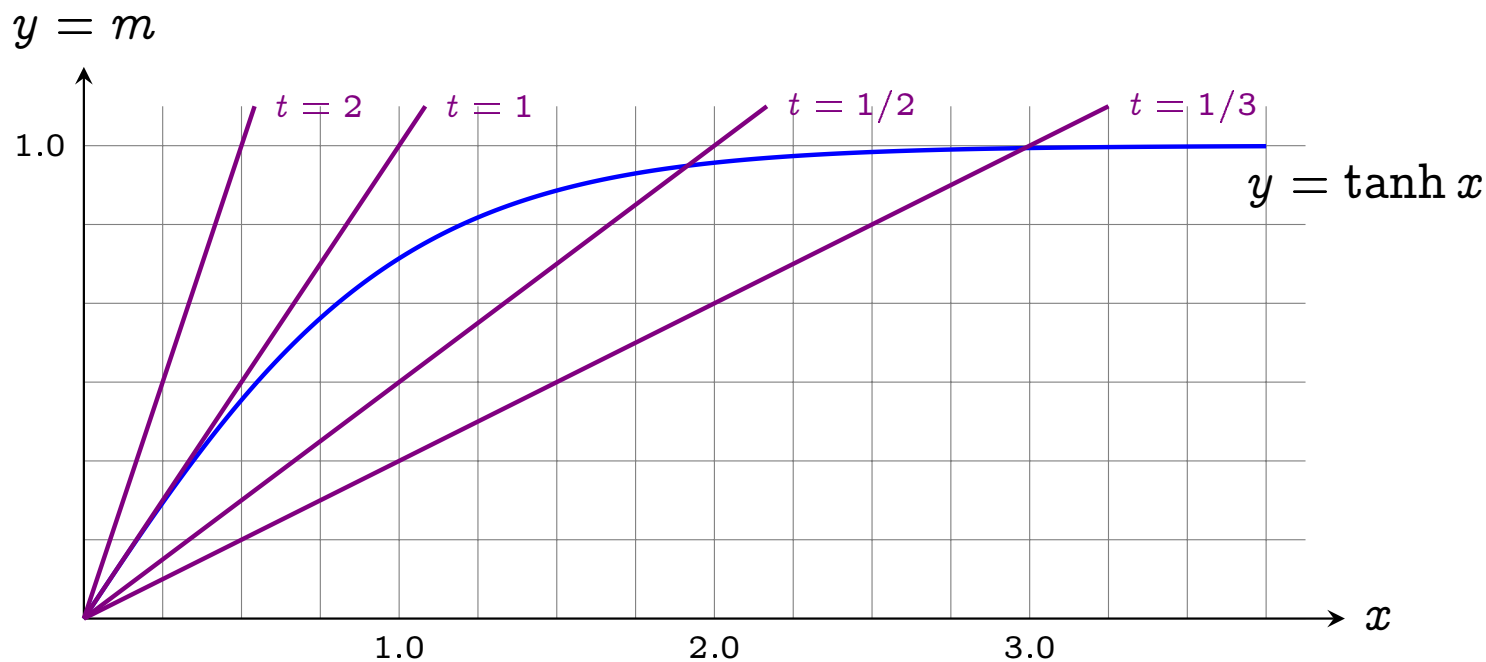
At the **Curie temperature** T_C , the susceptibility $\chi \rightarrow \infty$. Then, since $\mathcal{M} = \chi \mathcal{B} / \mu_0$, a finite \mathcal{M} can occur even if the applied $\mathcal{B} = 0$ – spontaneous magnetisation.

In the absence of an applied field ($\mathcal{B} = 0$) we can solve graphically.

$$\mathcal{M} = N\mu_B \tanh\left(\frac{\mu_B \mu_0 \lambda \mathcal{M}}{k_B T}\right) \rightarrow m = \tanh(m/t)$$

with reduced magnetisation $m = \frac{\mathcal{M}}{N\mu_B}$, reduced temperature $t = \frac{T}{T_C}$.

Let $x = m/t$. Then $tx = \tanh x$ and plotting $y = tx$ and $y = \tanh(x)$ on the same axes, where they cross we have a solution.



Spontaneous magnetisation

For $t = T/T_C > 1$ the straight line and curve only cross at the origin – $m = 0$, and no spontaneous magnetisation exists.

For $t = T/T_C < 1$ the straight line and curve cross at finite y . The y value at which they cross gives the (reduced) magnetisation as predicted by the mean field theory.

The magnetisation is seen to increase rapidly as t drops below 1 (T drops below T_C) then saturates as the temperature approaches zero.

The theory gives qualitative agreement with experiment.

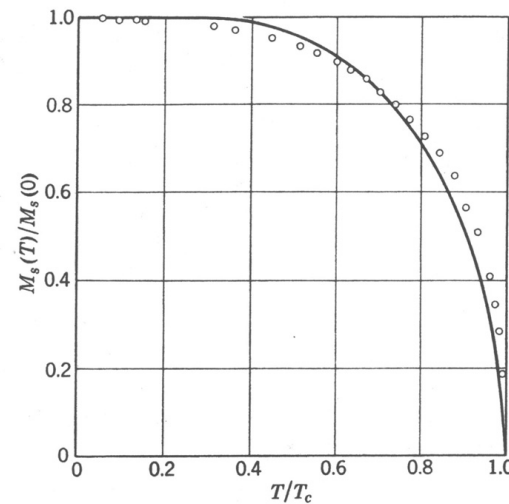


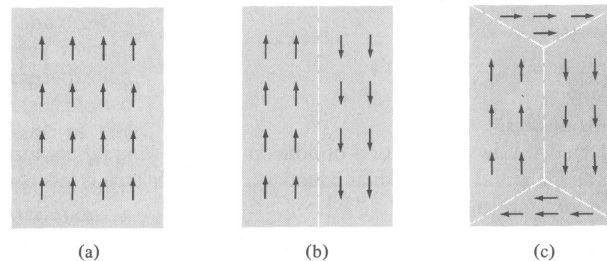
Figure 4 Saturation magnetization of nickel as a function of temperature, together with the theoretical curve for $S = \frac{1}{2}$ on the mean field theory. Experimental values by P. Weiss and R. Forrer, Ann. Phys. 5, 153 (1926).

Magnetic domains

Although for iron $T_C > 1000$ K, a piece of iron normally appears “unmagnetised”. Why?

It is attracted strongly by magnetic fields though, and can be “magnetised” by stroking with a “permanent” magnet. Why?

We saw the dipolar interaction is too weak to explain spontaneous magnetisation. However, it is much longer ranged ($\sim 1/r^3$) than the exchange interaction (\sim nearest neighbours) and can be significant when summed over large numbers of spins. In fact, the dipolar interactions can govern the macroscopic magnetisation whilst the exchange interaction governs the typical local magnetic order. This leads to the formation of **domains**.



The energy in (b) is lower than (a) because large numbers of spins reducing the small dipolar energy outweighs the small number of spins with increased exchange energy at the domain boundary. [(b) is like 2 bar magnets; to get to (a) you need to reverse one and unfavourably line up the poles].

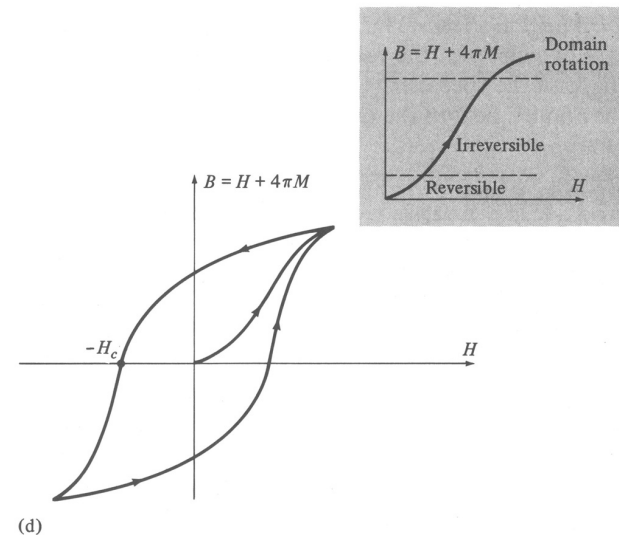
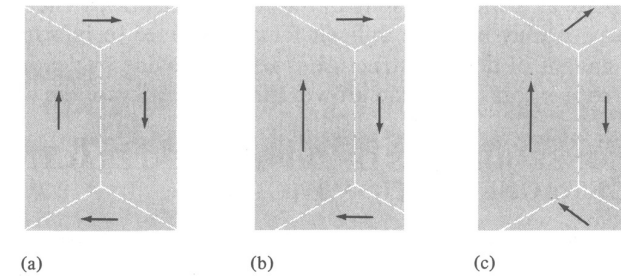
The energy can be further reduced by creating additional domains as in (c).

In (a) the sample is “unmagnetised” – “off the shelf” iron.

In (b) a weak field favouring spin up is applied, and the spin-up domains grow. In (c) an even stronger field causes domain rotation.

Strong fields cause irreversible domain changes, so that after removal of the applied field the magnetisation does not return to the original state, leading to a hysteresis curve.

Imperfections/defects in the crystal can **pin** domains, so that without a strong field in the opposite direction it is hard for the spins to return to their original state.



- end -