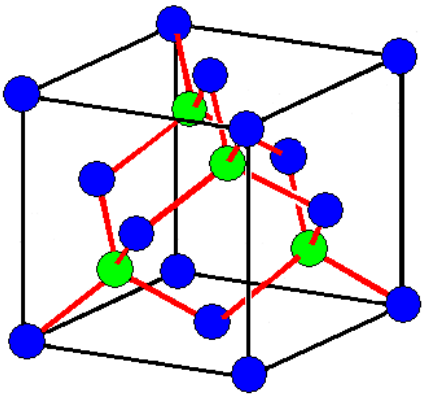
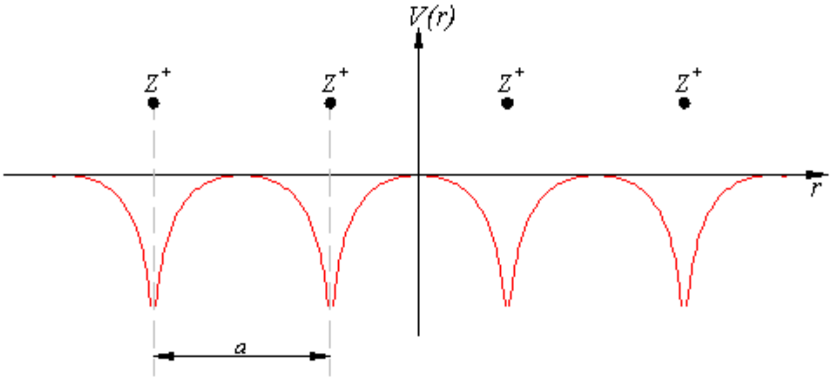
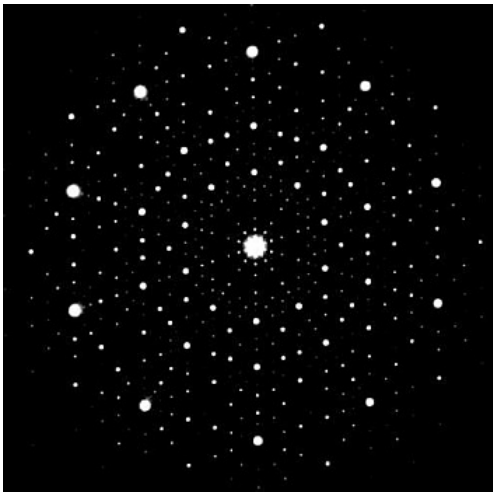






KYA322

Solid State Physics

Andrew Cole
andrew.cole@utas.edu.au

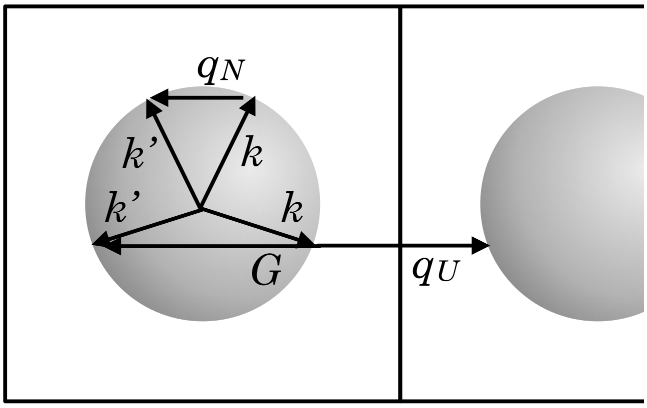
Umklapp Scattering

“Umklapp” scattering accounts for most of the electrical resistance of metals at temperatures below the Fermi temperature. These are generally *large scattering angle* collisions, in which the direction of electron motion is changed by amounts close to π.

When the Fermi surface is smaller than the first Brillouin zone, then there is a minimum phonon wavevector that can contribute to umklapp scattering.

For very low temperatures, the number of phonon modes available falls like $e^{-(\theta/T)}$, where θ is a parameter that depends on the geometry of the Brillouin zone.

Real Fermi surfaces are more complicated, but the principles are the same.



**Adjacent Brillouin zones of a bcc crystal
with Fermi sphere of a simple metal.**

The Wiedemann-Franz Law

The Wiedemann-Franz law is an empirical relationship stating that for **metals** at a moderate temperature, the ratio of thermal to electrical conductivity is directly proportional the temperature, with proportionality constant independent of the type of metal: $\mathbf{K/\sigma \propto T}$

This was interpreted as strong evidence in favour of the free electron gas model for metallic solids.

The proportionality constant is expressed in terms of the **Lorenz number**.

$\mathbf{L \equiv K/(\sigma T)}$.

Experimentally, L for many metals is found to have values in the range:

22–30 nW·Ω/K^2 at 0° C
23–33 nW·Ω/K^2 at 100° C

The Wiedemann-Franz Law

The electrical conductivity is predicted to be $\sigma = \dfrac{ne^2\tau}{m}$.

Thermal conductivity from basic kinetic theory is $K \approx \dfrac{1}{3}Cv\ell$.

C and v are known for a Fermi gas, with $C = \dfrac{1}{2}\pi^2 nk_B(T/T_F)$ and $v = v_F$.

Taking the mean free path $\ell = v_F\tau$, $K \approx \dfrac{1}{3}\pi^2 nk_B\left(\dfrac{v_F^2\tau}{2T_F}\right)$.

Kinetic theory lets us substitute $\epsilon_F = k_BT_F = \dfrac{1}{2}mv_F^2$,

so the electron contribution to the thermal conductivity works out to be

$$K \approx \frac{\pi^2 nk_B^2 T\tau}{3m}$$

The Weidemann-Franz Law

With the two predictions based on the Fermi gas model, it is predicted that:

$$\frac{K}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

This result involves neither the electron mass nor concentration. Under the assumption that the relaxation time $\boldsymbol{\tau}$ is identical for thermal and electrical processes, it does not involve the collision rate between electrons.

The Lorenz number is predicted to be L = 24.5 nW · Ω/deg^2.
This works out to be 2.72×10^{-13} (erg/esu-K)^2 in cgs units.

The classical result from kinetic theory has no temperature dependence.

At very low temperatures the value of L is observed to decrease, e.g., for copper at 15 K the observed value is a factor of 10 less than at room temperature. This is because thermal and electrical relaxation times are no longer roughly equal.

The Fermi Liquid

A Fermi gas is a system of noninteracting identical particles subject to the Pauli exclusion principle. If the same system is extended to include interactions between the particles, it is described as a Fermi liquid.

Strictly speaking, the conduction electrons in a metal are a Fermi liquid. This causes the small deviations from the predictions of the Fermi gas model that become more obvious at low temperature. Non-nearest-neighbour interactions cannot be ignored in the liquid.

The theory of the Fermi liquid was developed by Landau and discusses the system in the language of “quasiparticles”. A quasiparticle is an excitation in a system of interacting electrons, analogous to a photon or a phonon. A single quasiparticle can be thought of as an electron plus an oscillating distortion to the nearby electron gas.

The main effect at reasonable temperatures is to increase the effective mass of the electron (e.g., by up to ~25% in alkali metals).

Realistic Fermi Surfaces

The presence of zone boundaries tends to lower the electron energy levels, so the Fermi surface “necks” out towards the centre of Brillouin zone faces.

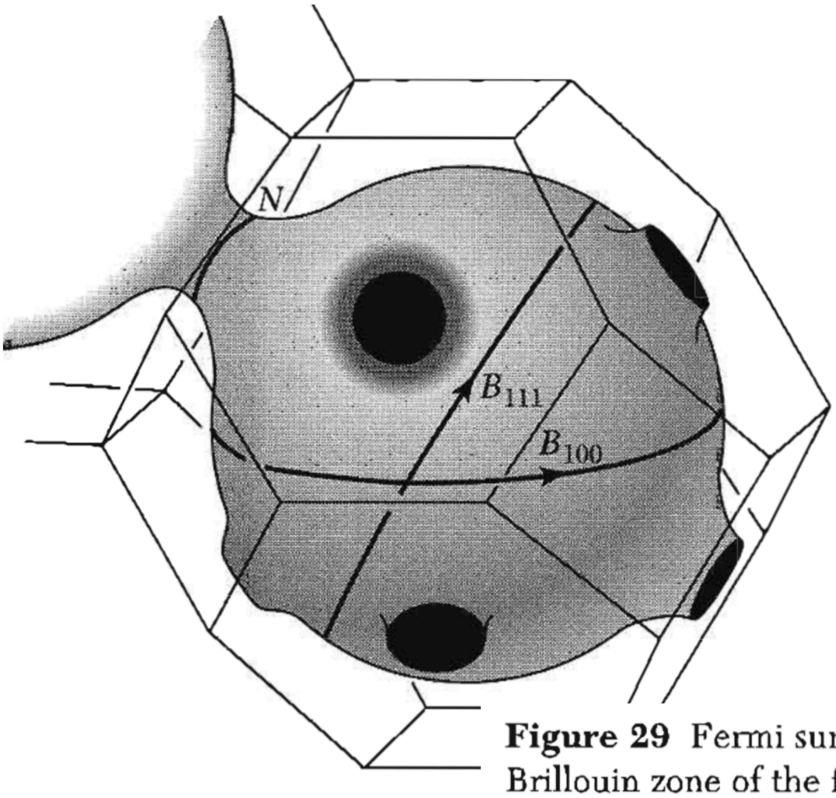


Figure 29 Fermi surface of copper, after Pippard. The Brillouin zone of the fcc structure is the truncated octahedron derived in Chapter 2. The Fermi surface makes contact with the boundary at the center of the hexagonal faces of the zone, in the [111] directions in **k** space. Two “belly” extremal orbits are shown, denoted by *B*; the extremal “neck” orbit is denoted by *N*.

Energy Bands

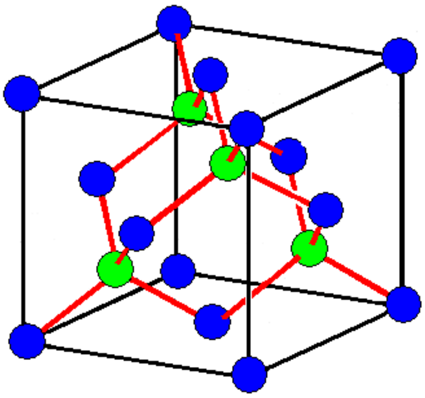
The free electron model did a reasonable job of calculating some properties of metals, but it doesn’t do a great job of explaining the differences between conductors and insulators, or the existence of semiconductors.

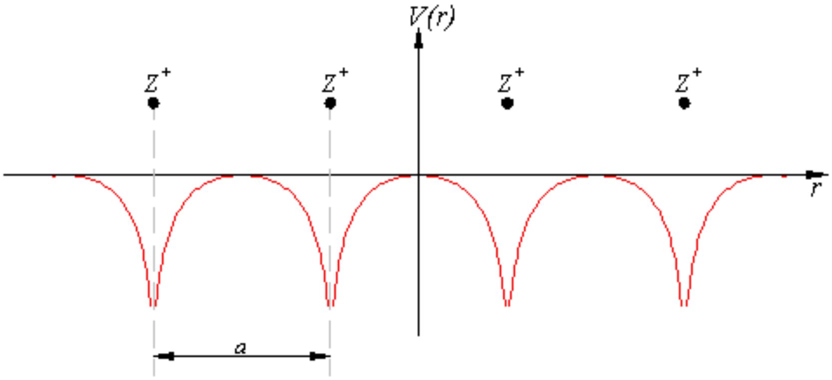
E.g., a conductor can have resistivity as low as $10^{-10}\ \Omega \cdot \mathrm{cm}$, but an insulator can be as high as $10^{22}\ \Omega \cdot \mathrm{cm}$. This is an enormously high range that the free electron model doesn’t account for.

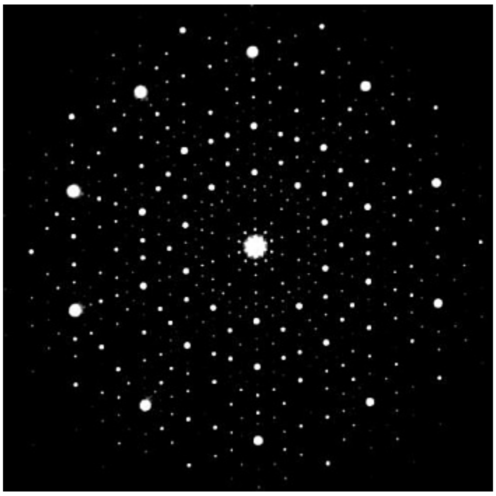
The most general treatment uses the Schrödinger equation for electrons in the presence of a strictly periodic lattice of atomic potentials.

Model the electrons as moving independently of each other in an average field that is determined by the symmetries of the crystal structure.

There are a few different approximate analytical techniques, and computational techniques based on them that add complexity.







KYA322

Solid State Physics

Andrew Cole
andrew.cole@utas.edu.au

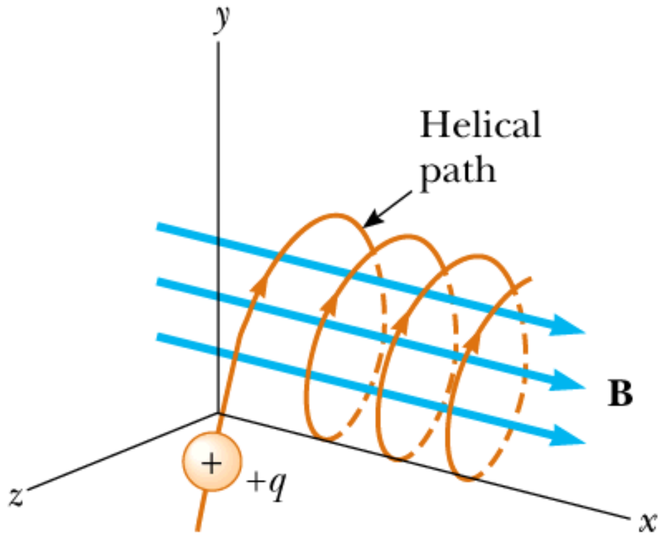
Magnetic Fields

For a Fermi sphere of particles acted on by a force F and with time between collisions equal to $\boldsymbol{\tau}$, the equation of motion is $\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)\delta k = F$.

In the presence of a magnetic field, this becomes

$$\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)\delta k = -e\left(\vec{E}+\frac{1}{c}\vec{c}\times\vec{B}\right)$$

If there is a steady state in a constant field, the drift velocities now have a helical form instead of following the E field.



Magnetic Fields

For the B field directed along the z axis, the drift velocities are:

$$v_x = -\frac{e\tau}{m}E_x - \omega_c \tau v_y \qquad v_y = -\frac{e\tau}{m}E_y + \omega_c \tau v_x \qquad v_z = -\frac{e\tau}{m}E_z$$

where $\omega_c = eB/mc$ is the cyclotron frequency and cgs units are used.

Magnetoresistance is the term for a variety of effects that are observed when magnetic fields increase or decrease the resistance of materials to current flow.

The simplest type of magnetoresistance, geometric magnetoresistance, is explained by the effect of a static B field on the kinetics of electron collisions within a material. It was observed in iron and nickel by Kelvin in 1856.

Kelvin found that resistance increases by a few percent when E and B are aligned, and decreases by a similar amount when E and B are perpendicular.

The Hall Effect

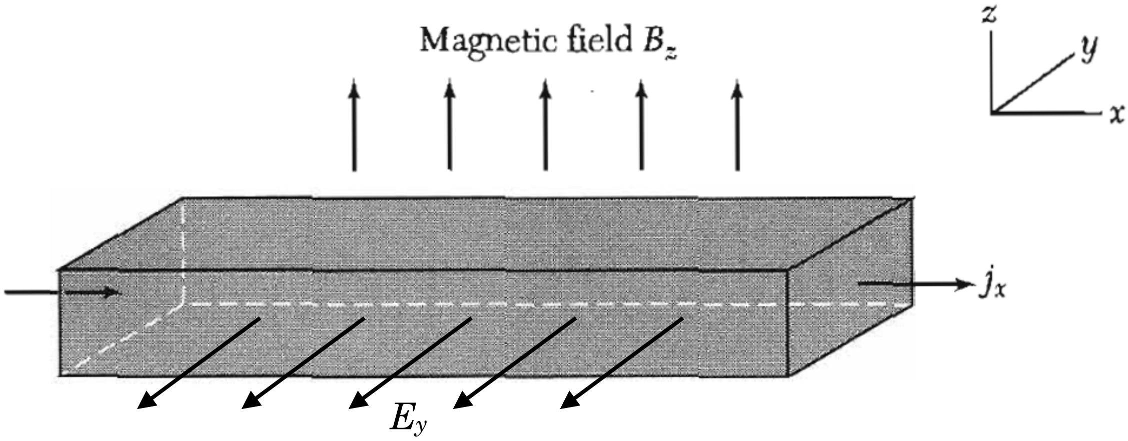
The Hall effect was first discovered in 1879. Like magnetoresistance, there are several different varieties of the Hall effect due to different terms in the equations governing electron motion in combined E and B fields.

The “ordinary” Hall effect refers to the appearance of a voltage perpendicular to the current in a conductor and to an applied B field.

The strength of the Hall effect depends on the electron density in the conductor and the kinetics of the electron motion. In some materials it can be convenient to describe the Hall effect in terms of the motion of holes instead of electrons.

Hall effect sensors are frequently used for sensitive position sensing, as ferromagnets can be moved to change a voltage. The voltages are very small so require large amplification.

The Hall Effect

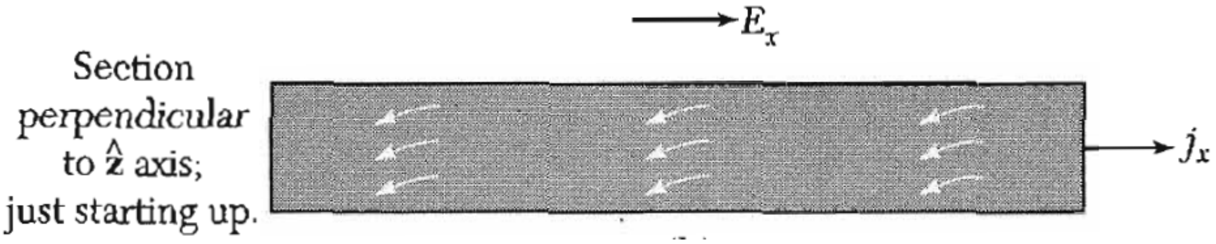


When a current flows across a magnetic field B, an electric field develops across conductor with direction given by *j*×B.

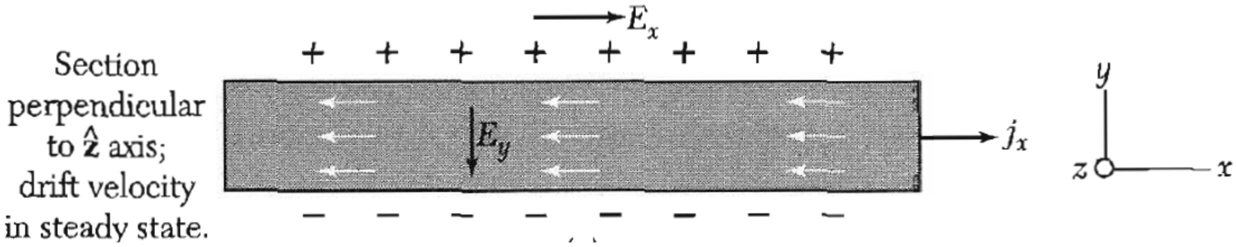
If current cannot flow out of the conductor in the *y* direction, then the drift velocity in *y* must be zero.

This can only happen if there is an electric field $E_y = -\omega_c \tau E_x = -\dfrac{eB\tau}{mc} E_x$

The Hall Effect



When the current is turned on at *t* = 0, the electrons respond to the B field by beginning to drift in the –*y* direction.



Because current cannot leave the conductor through the *y* direction, charge builds up on the opposite surfaces, establishing the Hall effect voltage.

Hall Effect

The strength of the Hall effect in a metal is given by $R_H = E_y/j_xB$.

From the simple equation of motion, $R_H = -1/ne$. This is negative for electrons. Historically the Hall effect was taken as evidence that the charge carriers are negative, due to the direction of the voltage appearing.

The size of R_H can be used to infer the number of conduction electrons per atom and as a test of the free electron theory for solids.

Experimental measures of R_H are typically around several 10^{-24} in cgs units, and in reasonable agreement with theory for many metals.

In some metals (e.g., aluminium, indium, arsenic) the sign of R_H is positive, indicating that the material behaves as though the unoccupied orbitals ("holes" in the electron distribution) are mobile, behaving as pseudo-particle carrying the charge. This is a failure of the free electron model and requires (quantum) band theory to explain.

Magnetic Properties

Magnetism is fundamentally a quantum mechanical phenomenon, because it relates to electron spin. In most contexts, we can ignore the magnetic properties of the nucleus.

Magnetic moments can arise from electron orbital motion, electron spin, and from the *change* in magnetic moment induced by an applied external field.

Finite magnetic moments are associated with incompletely filled electron orbital shells.

Materials may have a permanent magnetic moment (**ferromagnetic** and **ferrimagnetic** materials), or they may have a moment only in the presence of an external field.

Materials in which the induced response is aligned with the external field are called **paramagnetic**; if the magnetization is opposite the applied field, they are called **diamagnetic**.

Magnetization

The fundamental quantity in discussing the magnetic properties of solids is the magnetization per unit volume, M(r). For a crystal, the magnetization is the total dipole moment of a primitive unit cell divided by the cell volume.

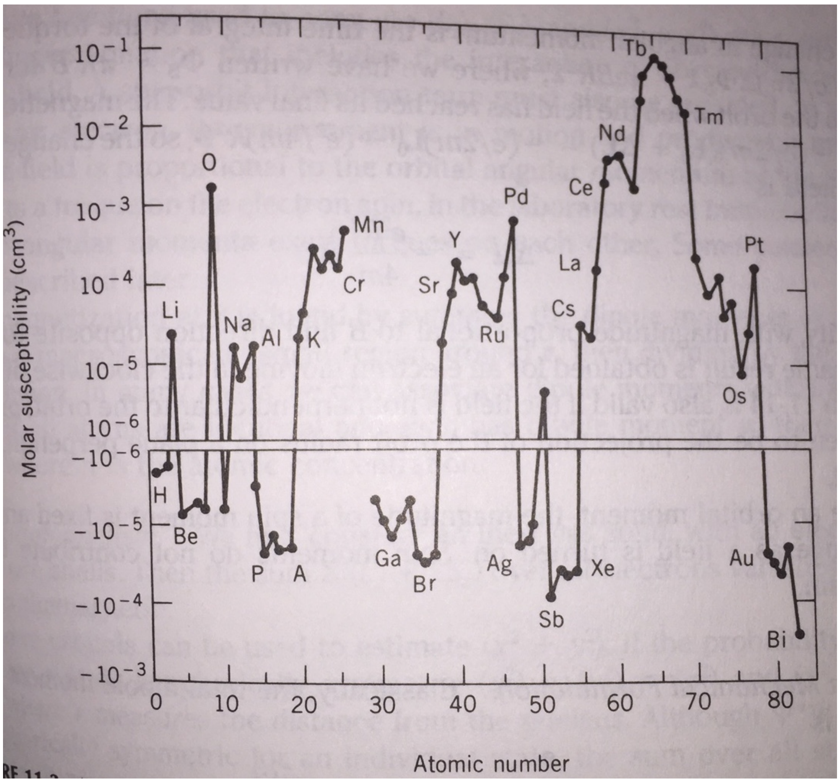
In paramagnets and diamagnets, the **magnetic susceptibility** is defined in terms of the magnetic field by $\chi = M/H$. This relation is normally linear. In ferromagnets, there is no one to one relation because of hysteresis.

To express the susceptibility in terms of the induction field, $M = \dfrac{\chi B}{\mu_0(1+\chi)}$

A paramagnetic material has $\chi > 0$.

Susceptibilities are typically << 1.

Magnetic Susceptibilities



Elements with partially filled electron subshells tend to be paramagnetic, especially the transition and rare earth elements with partially filled *d* and *f* subshells.

The rare earths have nonzero angular momentum and a permanent dipole moment.

When the spin and orbital contributions each sum to 0, only the induced moments remain- these tend to be <0.

Diamagnetism

Alkali metals tend to be weakly paramagnetic: individual atoms do not have permanent dipole moments, but they tend to align with an applied field.

Noble metals and most nonmetals are diamagnetic.

Diamagnetism can be partially explained by a classical calculation: the response of electrons to an applied field is to partially shield the region interior to the electron orbits from field changes.

Application of an external field will cause the electron motion to precess at the Larmor frequency. The application of the field causes a circular current around the nucleus, which induces a magnetic field that tends to oppose the original field.

When the applied field is weak, the Larmor frequency is small compared to the frequency of the original motion.

Langevin Diamagnetism Equation

Classically, the current arising from the Larmor precession of Z electrons is

$$I = (-Ze)\left(\frac{1}{2\pi} \cdot \frac{eB}{2m}\right)$$

which produces a magnetic moment $\mu = IA$ for a loop of area A.

If $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$ is the mean square value of the orbital radius in a plane, the resulting moment is $\mu = -\frac{Ze^2 B}{4m}\langle \rho^2 \rangle$

For a spherically symmetric distribution, $\langle r^2 \rangle = 3\langle \rho^2 \rangle / 2$

and for N atoms for unit volume, the susceptibility is then $\chi = -\frac{\mu_0 N Z e^2}{6m}\langle r^2 \rangle$

When conduction electrons are negligible, this formula gives roughly correct results if $\langle r^2 \rangle$ is calculated quantum mechanically, but it fails for metals.

Paramagnetism

Paramagnetism is found anywhere the total spin or orbital angular momentum of electrons is nonzero, and in metals. In metals, the conduction electrons are free to align their dipole moments with any external field.

- Any substance with an odd number of electrons, e.g., sodium atoms, gaseous nitric oxide.
- Free atoms and ions with partly filled electron subshells. Paramagnetism is often weaker in the solid state than in gaseous states because the solid has more limited ability to respond to applied fields.
- A few compounds with an even number of electrons, notably molecular oxygen.

Paramagnetism is inherently quantum mechanical.

Quantum Theory of Paramagnetism

For an atom or ion in free space with total angular momentum J, the magnetic moment is a multiple of the Bohr magneton

$$\mu = g_L \mu_B J$$

where the Landé g-factor accounts for the varying strength of the spin and orbital contributions to the magnetic moment:

$$g_L = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

The quantum numbers for the ground state of a multi-electron atom or ion are determined by the solution of the Schrödinger equation, and are summarized in *Hund's rules* for assigning quantum numbers to electrons in the way that minimizes the total energy.

Quantum Theory of Paramagnetism

In a magnetic field, the energy levels are split by an amount proportional to the projection of the dipole moment in the field direction,

$$U = -\mu \cdot B \;= m_j\, g_L \mu_B B$$

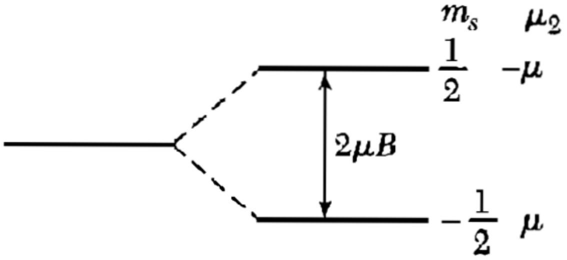


Figure shows the energy levels of a system with *l* = 0 and *s* = 1/2 in a magnetic field along the *z*-axis.

For electrons, the magnetic moment is opposite to the spin, so the low-energy state has μ aligned with B, and the high-energy state anti-aligned with B.

Quantum Theory of Paramagnetism

If atoms are oriented randomly with respect to the field, then there are just as many positive as negative dipole moments, and the magnetization will be zero.

If an external induction field is applied, atoms will tend to align with B in order to lower their energy. A net magnetization in the same direction as B will result.

At absolute zero, all the atoms/ions should be in the lowest-energy state, but for non-vanishing temperature there is a finite probability that a given atom/ion will be found in the higher energy state.

A basic prediction of quantum mechanics is that the paramagnetic response of a collection of electrons will be a function of temperature. The specific details can be calculated from Fermi-Dirac statistics.

Quantum Theory of Paramagnetism

The probability for a system to be in a state with $J_z = m_j \hbar$ is given by the distribution $e^{-m_j g_L \mu_B B/k_B T}$.

More atoms are in the lowest energy state than any other.

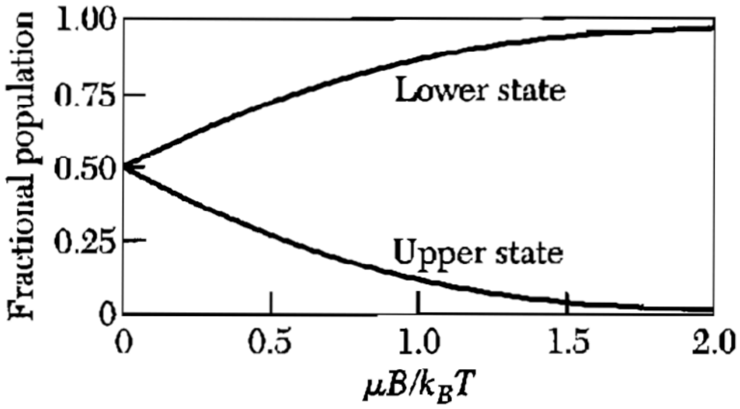


Figure 3 Fractional populations of a two-level system in thermal equilibrium at temperature T in a magnetic field B. The magnetic moment is proportional to the difference between the two curves.

The expectation value of the dipole moment is found by summing over the range of possible m_j values from –*j* to +*j:*

$$\langle \mu_z \rangle = \frac{-\sum m_j g_L \mu B \, e^{-m_j g_L \mu_B B/k_B T}}{\sum e^{-m_j g_L \mu_B B/k_B T}}$$

Brillouin Functions

The summation can be expressed in closed form using the Brillouin functions, $B_J(x)$, as $\langle \mu_z \rangle = \; g_L \mu_B j \, B_J(x)$

where $x = g_L \mu_B j \, B/k_B T$ and *j* has its usual meaning as the total angular momentum quantum number. The Brillouin function is

$$B_J(x) = \frac{2j+1}{2j} \coth\left[\frac{(2j+1)x}{2j}\right] - \frac{1}{2j} \coth\left[\frac{x}{2j}\right]$$

If the concentration of magnetic ions is *n,* then $M = n\, g\, \mu_B\, j\, B_J(x)$.

When $g\mu_B jB >> k_B T$, this corresponds to $x >> 1$, and the level splittings are much larger than the mean thermal energy. Nearly all ions are then in their lowest energy state and the dipoles are nearly all aligned with the B field.

In that case, the magnetization is *saturated*. B_J —> 1 and M —> $ng\mu_B B$

Magnetic moment of paramagnetic ions.

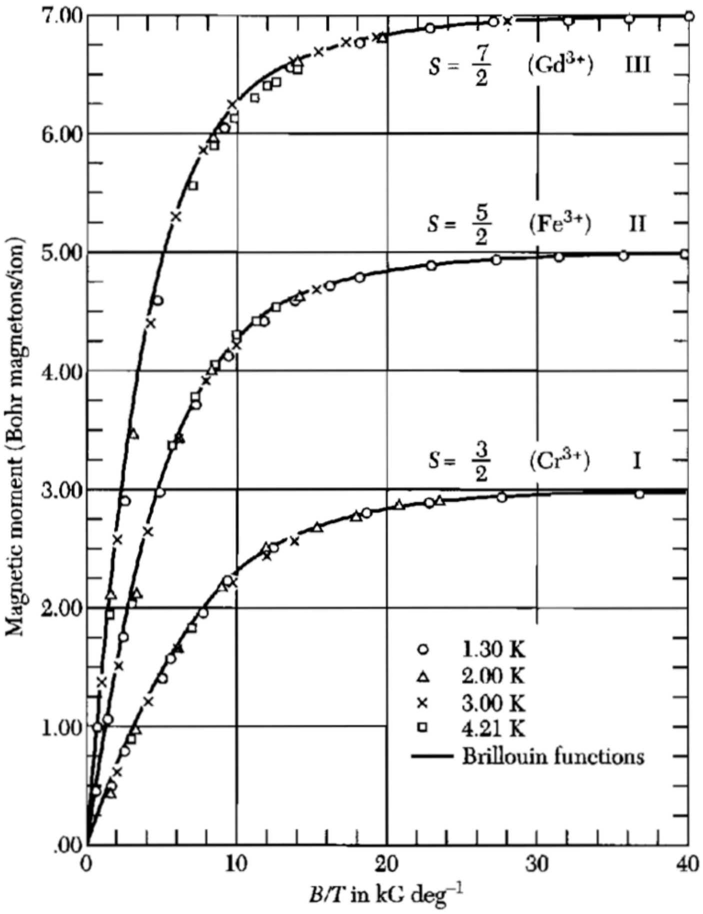
Expressed in units of "Bohr magnetons per ion", plotted against the ratio of B field to absolute temperature.

One complication: If there are other energy levels nearby that have different values of *j*, then the summation must include those as well.

One simplification: for a two-level atom,

$$M = n\mu \tanh x$$

(for dipole moment μ)



The Curie Law

In the limit of small *x*, the Brillouin function tends to become linear in *x*,

$$B_J(x) \approx (j+1)x/(3j)$$

In this limit, the magnetization is $M = n g_L^2 \mu_B^2 \frac{j(j+1)}{3k_BT} B$

this represents *linear paramagnetism*. The total magnetization must account for any diamagnetic contributions, but these are frequently quite small.

This limit is approximately valid for many ionic solids (known as "paramagnetic salts") at room temperature. In the limit of small *x*, we can express this as the **Curie Law** for magnetic susceptibility: $\chi = \frac{mu_0 M}{B} = \frac{C}{T}$

using the Curie constant, $C = \mu_0 n g_L^2 \mu_B^2\, j(j+1)\,/3k_B$

The Curie Law

The Curie Law is often encountered with the substitution $p^2 = g_L^2\,(j+1)j$, where p is the "effective Bohr magnetons per ion".

When the magnetization is measured, the result can be compared to the predicted value of p as a test of the theory. Values typically range from around 1.5-10.

For rare earth ions, the data agrees with the Curie law in the weak field limit. These ions have their valence electrons in the *f*-subshell.

For the transition metals, the agreement is not as good. This is because the *d*-subshell wavefunctions are not well approximated by the equivalent single electron orbitals. The total electron probability distribution in these cases is represented by linear combinations of orbitals in which the contribution of L to the dipole moment is said to be *quenched*. (i.e., J ≈ S and $g_L \approx 2$).

Spontaneous Magnetization

In some atoms with unfilled electronic subshells, long-range order is exhibited in the arrangement of dipole moments.

Long range magnetic order is interpreted in terms of local induction fields produced at the site of each dipole - every point in the crystal lattice has an associated dipole moment, and their orientations are correlated. This local field is called the "Weiss effective field".

In **ferromagnetism**, the moments are aligned, resulting in spontaneous magnetization.

In **antiferromagnetism**, moments are anti-correlated, causing the net magnetization to vanish.

In **ferrimagnetism**, moments are anti-correlated, but have unequal magnitudes, so they do not completely vanish.

Magnetic Materials

Iron, nickel, and cobalt are ferromagnetic at room temperature.

Gadolinium and terbium at low temperatures. Other rare earths become ferromagnetic only at temperatures approaching absolute zero. At intermediate temperatures, these rare earths are antiferromagnetic.

At high temperatures, these materials become paramagnetic, as the high thermal energies randomize correlations between nearby dipoles.

The changes with temperature can be described as a phase change that occurs a the **Curie Temperature, T_C**.

Above the Curie temperature, all spontaneously magnetized materials become paramagnetic (no magnetization except in response to an appleid field).

Curie Temperature

Suppose the local field at any point in a solid can be written as the sum of an applied field and a field proportional to the local magnetization:

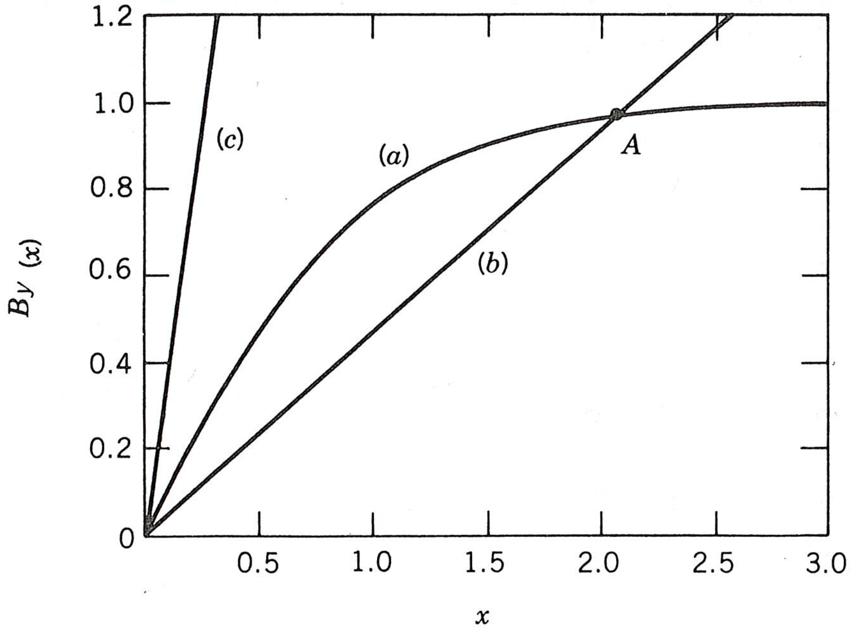
$$B = B_a + \mu_0 \gamma M$$

If we have *n* identical atoms per unit volume, with total angular momentum given by the quantum number *j*. The magnetization is $M = n g_L \mu_B j \, B_J(x')$, where we define $x' = \left[g_L \mu_B j (B_a + \mu_0 \gamma M) \right] / k_B T$.

To find the spontaneous magnetization, set $B_a = 0$ and solve for M. This is easiest to do graphically. Graph $B_J(x')$ vs. $M / n g_L \mu_B j$, and where these points intersect we have a solution for spontaneous magnetization.

Curie Temperature

Line (a) shows the Brillouin function. Line (b) shows a low temperature solution. The curves intersect at A, showing that spontaneous magnetization can occur. At high temperature, the appropriate line is given by (c), which only intersects at M = 0.



Curie Temperature

The Curie temperature can be found by equating the limiting slope of the Brillouin function to the slope of the linear curves in the graphic solution for M, and solving for T. The result is

$$T_C = \frac{\mu_0 n g_L^2 \mu_B^2 \gamma}{3k_B} j(j+1)$$

and we can also find the parameter $\gamma = T_C / C$.

If an external field is applied, the Brillouin function shifts to the left and intersects the linear curves for any value of T. For small fields typical in lab circumstances, this intersection typically happens where the Brillouin function is linear.

For small fields and high temperatures, the resulting magnetization is $M = \dfrac{C}{\mu_0(T - T_C)} B_a$, which gives the Curie-Weiss law for ferromagnets above the Curie temperature: $\chi = C/(T - T_C)$

Experimental Data

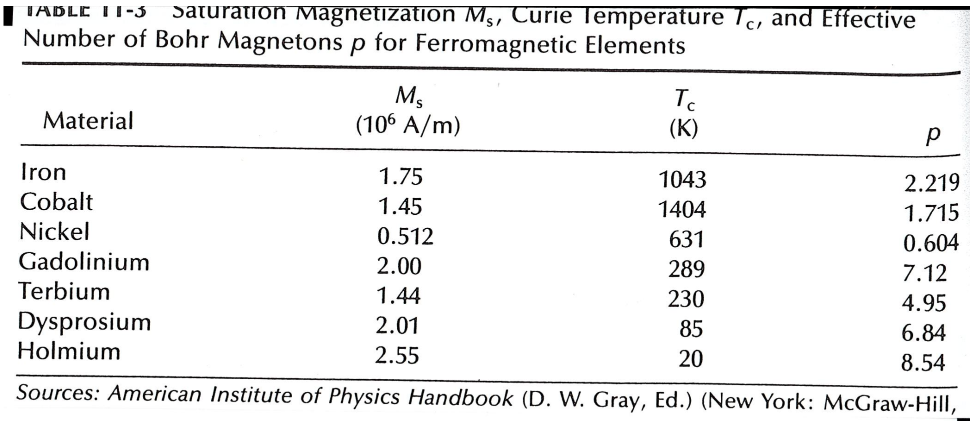


TABLE 11-3 Saturation Magnetization M_s, Curie Temperature T_c, and Effective Number of Bohr Magnetons p for Ferromagnetic Elements

Material	M_s (10^6 A/m)	T_c (K)	p
Iron	1.75	1043	2.219
Cobalt	1.45	1404	1.715
Nickel	0.512	631	0.604
Gadolinium	2.00	289	7.12
Terbium	1.44	230	4.95
Dysprosium	2.01	85	6.84
Holmium	2.55	20	8.54

Sources: American Institute of Physics Handbook (D. W. Gray, Ed.) (New York: McGraw-Hill,

Because the ferromagnetic behaviour is such a complicated function of electron angular momentum and energy, these values vary significantly between different ions and compounds of the same elements.

The saturation magnetization is the asymptotic value of M as T —> 0.

Origin of the Weiss Field

Atomic dipoles cannot account for the Weiss local field of a ferromagnet.

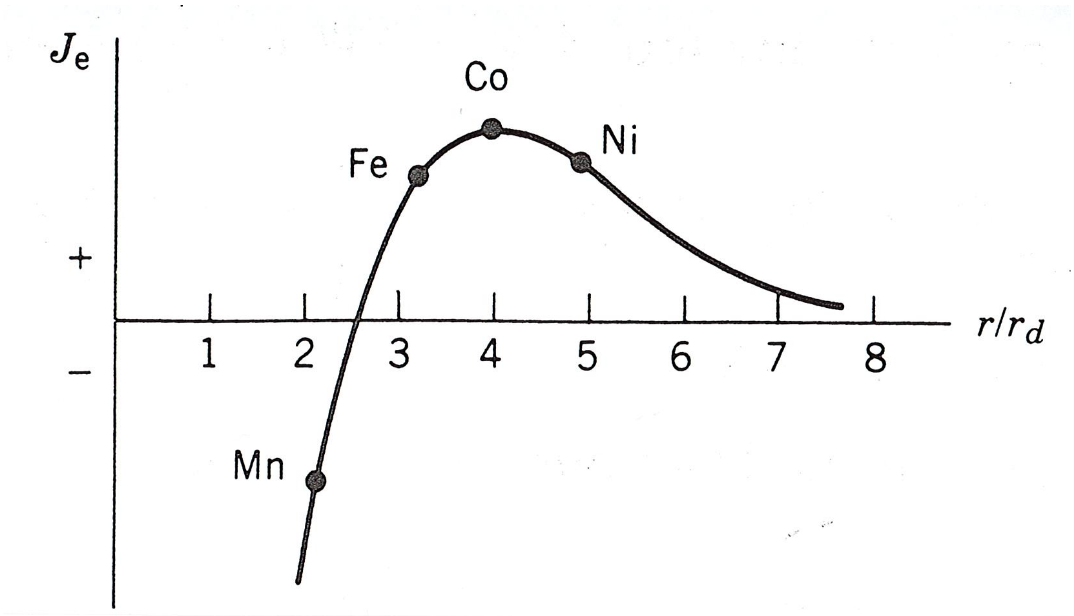
The Weiss field does not arise from Maxwell's equations. It arises due to Pauli exclusion principle interactions between charged particles, and can be expressed as a potential energy term involving spin-spin interactions between pairs of atoms.

The exclusion principle requires the total wave function for a collection of electrons to be antisymmetric under the exchange of particle coordinates and spins.

This produces the well-known triplet and singlet states in multi-electron atoms. In the triplet state the spins are aligned, and the potential energy is lower, but the mean separation is wider.

The exchange energy term can either be positive or negative.

Heisenberg Exchange Coefficient



Exchange energy can be written as $E = -J_e\, S_i \cdot S_j/\hbar$. The sign change indicates the difference between ferromagnetic and antiferromagnetic materials. The elements are plotted according to their interatomic distance, scaled to the average distance of $4d$ electrons from a nucleus.