Magnons and Magnetic Resonance

A. Diamagnetism and Paramagnetism

B. Ferromagnetic Order

C. Magnons

D. Antiferromagnetic Order

E. Ferromagnetic Domains

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Diamagnetism and Paramagnetism

The magnetic moment of a free atom has the nuclear and electronic magnetic moments. Magnetic moments of nuclei are of the order of 10^{-3} times smaller than the magnetic moment of the electron. The electronic magnetic moments has three principal sources: 1) the spin with which electrons are endowed; 2) the orbital angular momentum about the nucleus; 3) the change in the orbital moment induced by an applied magnetic field.

Diamagnetism is associated with the tendency of electrical charges partially to shield the interior of a body from an applied magnetic field. In an electron orbit within an atom, the magnetic field of the induced current is opposite to the applied field, and the magnetic moment associated with the current is a diamagnetic moment. Even in a normal metal there is a diamagnetic contribution from the conduction electrons, and this diamagnetism is not destroyed by collisions of the electrons.

The magnetization M is defined as the magnetic moment per unit volume. The **magnetic susceptibility** per unit volume is defined as

$$\chi = \frac{M}{B}$$

where B is the applied macroscopic magnetic field intensity.

Magnetic Susceptibility
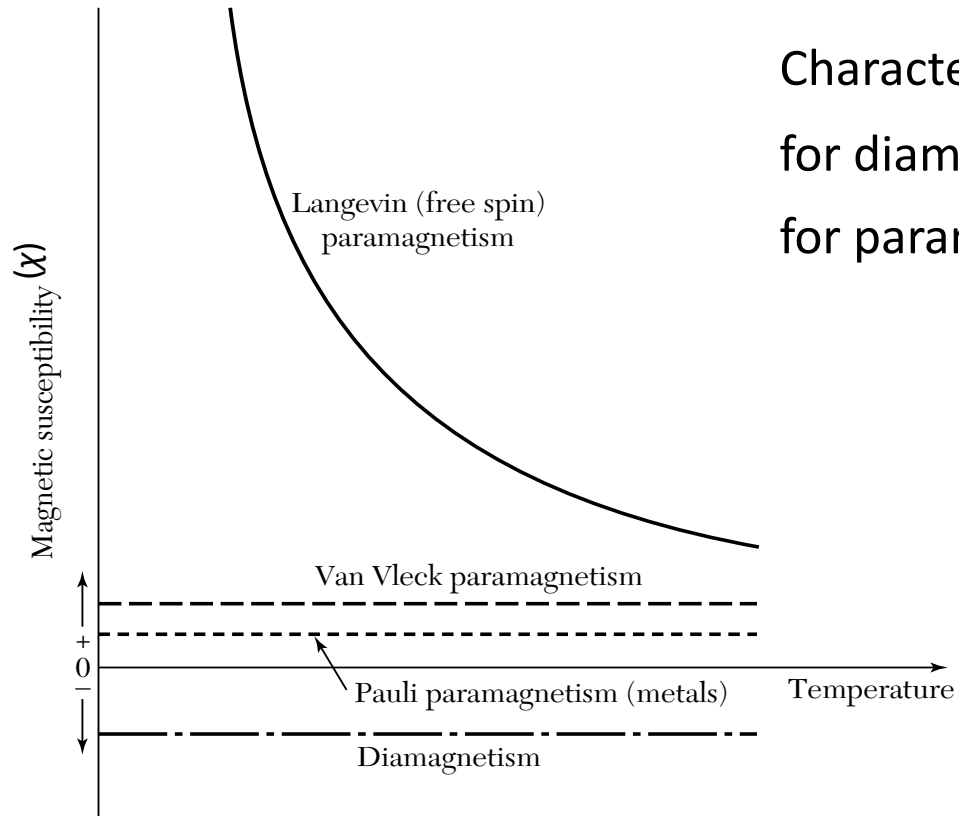
Characteristic magnetic susceptibilities:

for diamagnetic substances $\chi < 0$
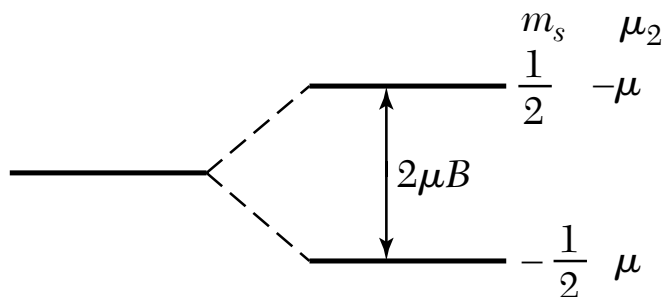
for paramagnetic substances $\chi > 0$

Langevin (free spin) paramagnetism

Van Vleck paramagnetism

Pauli paramagnetism (metals)

Diamagnetism

Magnetic susceptibility (χ)

Temperature

Magnetic Moment of an Atom

The magnetic moment of an atom or ion in free space is given by

$$\boxed{\boldsymbol{\mu} = \gamma\hbar\mathbf{J} = -g\mu_B\mathbf{J}} \;, \qquad \mathbf{J = L + S}$$

where the total angular momentum $\hbar\mathbf{J}$ is the sum of the orbital $\hbar\mathbf{L}$ and spin $\hbar\mathbf{S}$ angular momenta. For electronic systems a quantity g called the g factor or the spectroscopic splitting factor and the **Bohr magneton** μ_B is defined as $e\hbar/2mc.$ The energy levels of the system in a magnetic field are

$$U = -\boldsymbol{\mu}\cdot\mathbf{B} = m_J g\mu_B B \;,$$

where m_J is the azimuthal quantum number and has the values J, $J - 1, \dots, -J$. For a single spin with no orbital moment we have $m_J = \pm 1/2$ and $g = 2$, whence the energy level $U = \pm 1/2\ \mu_B B.$ The equilibrium populations of the two levels are
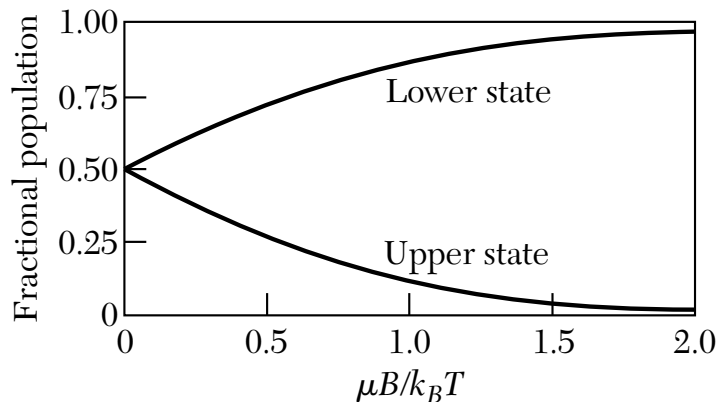

$$\frac{N_1}{N} = \frac{\exp(\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)} \quad \text{Lower state}$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)} \quad \text{Upper state}$$

$$N = N_1 + N_2 \quad \text{and} \quad \tau \equiv k_B T$$

The fractional populations of the two levels are shown below and the resultant magnetization M for N atoms per unit volume is, with $x = \mu B/k_B T$,

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

At high temperature, we have $x \ll 1$, $\tanh x \cong x$, and

$$M \cong N\mu(\mu B/k_B T)$$

In general, an atom with angular momentum quantum number J in a magnetic field has $2J + 1$ equally spaced energy levels. The magnetization is thus given by

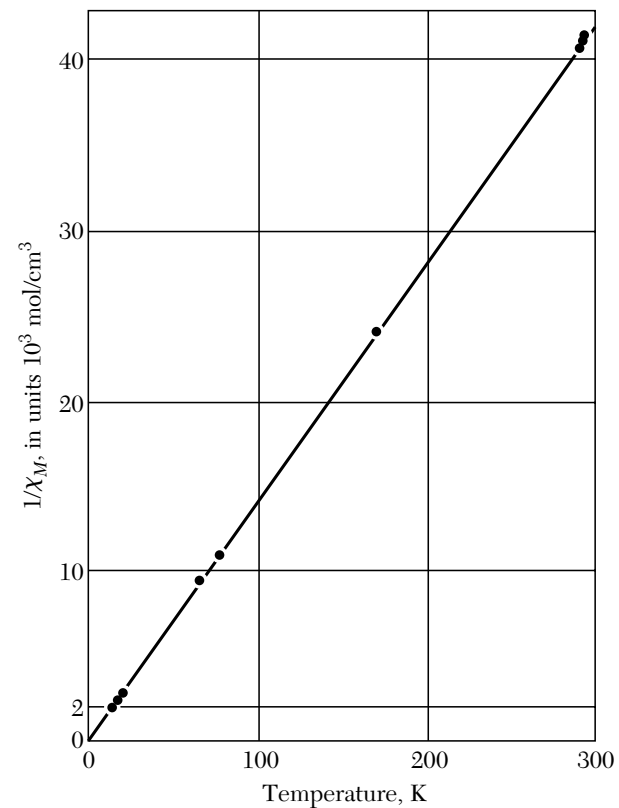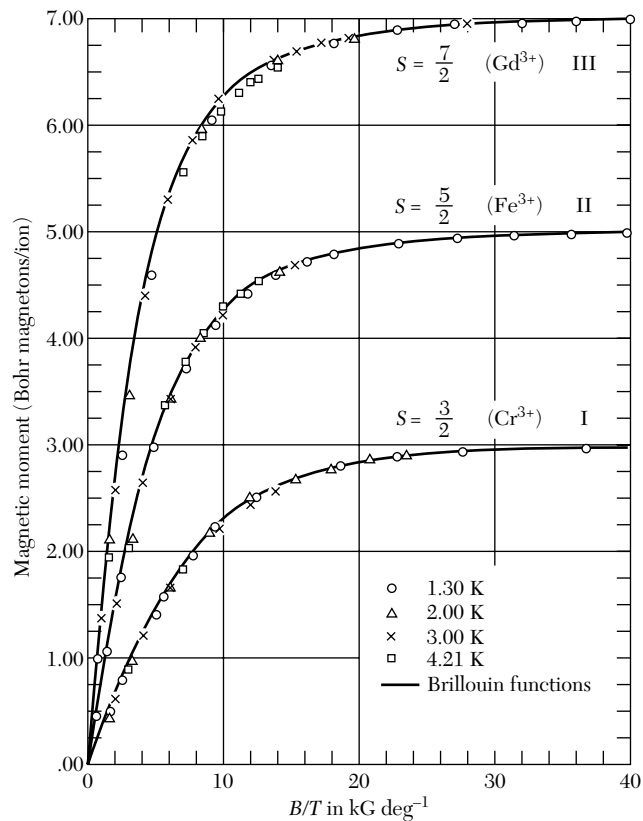$$M = NgJ\mu_B B_J(x) \quad , \qquad (x = gJ\mu_B B/k_B T) \quad ,$$

where the **Brillouin function** B_J is defined by

$$B_J(x) = \frac{2J + 1}{2J} \operatorname{ctnh}\left(\frac{(2J + 1)x}{2J}\right) - \frac{1}{2J} \operatorname{ctnh}\left(\frac{x}{2J}\right)$$

For $x = \mu B/k_B T \ll 1$, we have $\text{ctnh}\, x = \dfrac{1}{x} + \dfrac{x}{3} - \dfrac{x^3}{45} + \cdots$, and the susceptibility is

Curie law : $\dfrac{M}{B} \cong \dfrac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \dfrac{Np^2\mu_B^2}{3k_B T} = \dfrac{C}{T}$, C is the **Curie constant**.

Here p is the **effective number of Bohr magnetons**, $p \equiv g[J(J+1)]^{1/2}$.

Hund rules

The Hund rules as applied to electrons in a given shell of an atom affirm that electrons will occupy orbitals in such a way that the ground state is characterized by the following:

1. The maximum value of the total spin S allowed by the exclusion principle;
2. The maximum value of the orbital angular momentum L consistent with this value of S;
3. The value of the total angular momentum J is equal to $|L - S|$ when the shell is less than half full and to $L + S$ when more than half full. When the shell is just half full, the application of the first rule gives $L = 0$, so that $J = S$.

The first Hund rule has its origin in the exclusion principle and the coulomb repulsion between electrons. The second Hund rule is best approached by model calculations. The third Hund rule is a consequence of the sign of the spin-orbit interaction: For a single electron the energy is lowest when the spin is antiparallel to the orbital angular momentum.

Example of the Hund rules: The ion Ce^{3+} has a single f electron with $l = 3$ and $s = ½$. The J value by the preceding rule is $|L-S| = L-1/2 = 5/2$.

Ferromagnetic Order

Given an internal interaction tending to line up the magnetic moments parallel to each other, we shall have a ferromagnet. Let us postulate such an interaction and call it the exchange field $\mathbf{B}_E$. We treat the exchange field as equivalent to a magnetic field and, in the **mean-field approximation**, we assume each magnetic atom experiences a field proportional to the magnetization: $\mathbf{B}_E = \lambda \mathbf{M}$, where $\lambda$ is a constant, independent of temperature. The **Curie temperature** T_c is the temperature above which the spontaneous magnetization vanishes; it separates the disordered paramagnetic phase at $T > T_c$ from the ordered ferromagnetic phase at $T < T_c$. We can find T_c in terms of the constant λ. Consider the paramagnetic phase: an applied field B_a will cause a finite magnetization and this in turn will cause a finite exchange field B_E. If χ_p is the paramagnetic susceptibility, $\quad M = \chi_p(B_a + B_E)$

The paramagnetic susceptibility is given by the Curie law $\chi_p = C/T$, where C is the Curie constant. Then, we have the **Curie-Weiss law**

$$\chi = \frac{M}{B_a} = \frac{C}{(T - C\lambda)} = \frac{C}{T - T_c} \; ; \qquad T_c = C\lambda \; .$$

Heisenberg model

The exchange field gives an approximate representation of the quantum mechanical exchange interaction. On certain assumptions it is shown in texts on quantum theory that the energy of interaction of atoms i, j bearing electron spins S_i, S_j contains a term $U = -2J\mathbf{S}_i \cdot \mathbf{S}_j$, where J is the exchange integral and is related to the overlap of the charge distributions of the atoms i, j. This is called the **Heisenberg model**.
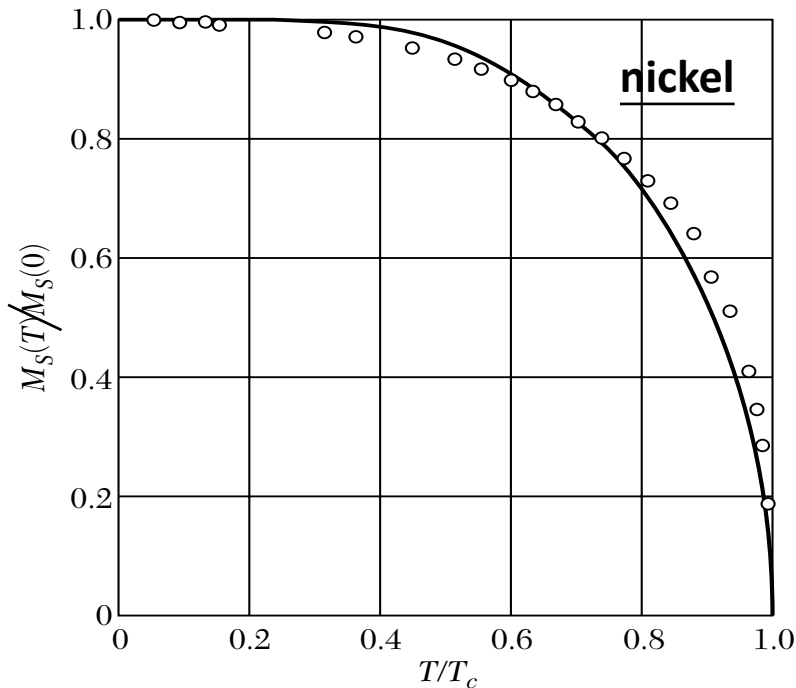
The curves of M versus T obtained in this way reproduce roughly the features of the experimental results, as shown in the left for nickel. As T increases, the magnetization decreases smoothly to zero at $T \simeq T_c$. This behavior classifies the usual ferromagnetic/paramagnetic transition as a second-order transition.

nickel

$M_S(T)/M_S(0)$

T/T_c

Exchange Interaction Between Free Electrons

Consider two free electrons i and j and their pair wavefunction ψ_{ij},

$$\psi_{ij} = \psi_i(\boldsymbol{r}_i)\psi_j(\boldsymbol{r}_j) - \psi_i(\boldsymbol{r}_j)\psi_j(\boldsymbol{r}_i) = \frac{1}{\sqrt{2V}}(e^{i\,\boldsymbol{k}_i\cdot\boldsymbol{r}_i}e^{i\,\boldsymbol{k}_j\cdot\boldsymbol{r}_j} - e^{i\,\boldsymbol{k}_i\cdot\boldsymbol{r}_j}e^{i\,\boldsymbol{k}_j\cdot\boldsymbol{r}_i})$$

$$= \frac{1}{\sqrt{2V}}e^{i(\boldsymbol{k}_i\cdot\boldsymbol{r}_i+\boldsymbol{k}_j\cdot\boldsymbol{r}_j)}\left(1 - e^{-i(\boldsymbol{k}_i-\boldsymbol{k}_j)\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\right)$$

The probability that electron i is to be found in volume element $d\boldsymbol{r}_i$ and that electron j is to be found in volume element $d\boldsymbol{r}_j$ is then equal to $|\psi_{ij}|^2$ $d\boldsymbol{r}_i d\boldsymbol{r}_j$:

$$|\psi_{ij}|^2 \, d\boldsymbol{r}_i d\boldsymbol{r}_j = \frac{1}{V^2}[1 - \cos(\boldsymbol{k}_i - \boldsymbol{k}_j) \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j)]d\boldsymbol{r}_i d\boldsymbol{r}_j$$

This expression shows all of the crucial features: the probability of finding two electrons with the same spin at the same place vanishes for every $\boldsymbol{k}_i$ and $\boldsymbol{k}_j$. For a particular spin-up electron, the other electrons with the same spin cannot screen the Coulomb potential of the ion cores so well locally, which leads to a reduction of the energy of the spin-up electron. This energy reduction is reinforced if the highest possible percentage of all the electrons have the same spin as the spin-up electron.

Let's consider the Fermi electrons and introduce relative coordinates between the electrons i and j with $\boldsymbol{r} = \boldsymbol{r}_i - \boldsymbol{r}_j$. We then ask what is the probability that a second spin-up electron is at a distance $\boldsymbol{r}$ in a volume element $d\boldsymbol{r}$. The probability and effective electron density acting on the spin-up electron are then

$$P(r)_{\uparrow\uparrow} d\boldsymbol{r} = n_\uparrow d\boldsymbol{r} \overline{[1 - \cos(\boldsymbol{k}_i - \boldsymbol{k}_j) \cdot \boldsymbol{r}]}$$
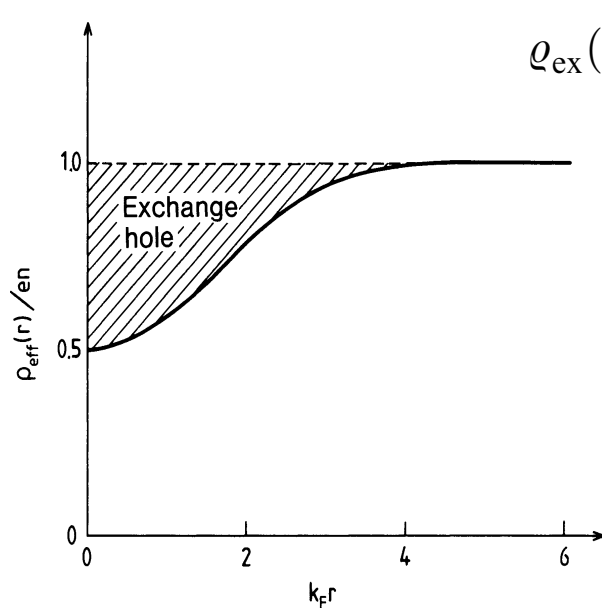
$$\varrho_{\mathrm{ex}}(\boldsymbol{r}) = \frac{e\,n}{2} \overline{[1 - \cos(\boldsymbol{k}_i - \boldsymbol{k}_j) \cdot \boldsymbol{r}]} \quad \text{with} \quad n_\uparrow = n/2$$

$$= \frac{e\,n}{2} \left[1 - \frac{1}{\left(\dfrac{4\pi}{3} k_{\mathrm{F}}^3\right)^2} \int d\boldsymbol{k}_i \int d\boldsymbol{k}_j \frac{1}{2} \left(\mathrm{e}^{\mathrm{i}(\boldsymbol{k}_i - \boldsymbol{k}_j)\cdot\boldsymbol{r}} + \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}_i - \boldsymbol{k}_j)\cdot\boldsymbol{r}}\right) \right]$$

$$\varrho_{\mathrm{eff}}(\boldsymbol{r}) = e\,n \left(1 - \frac{9}{2} \frac{(\sin k_{\mathrm{F}} r - k_{\mathrm{F}} r \cos k_{\mathrm{F}} r)^2}{(k_{\mathrm{F}} r)^6} \right)$$

The existence of an exchange hole implies a positive exchange coupling, i.e., the exchange integral J is positive in the exchange energy $U = -2J\boldsymbol{S}_i \cdot \boldsymbol{S}_j$.

Magnons

A magnon is a quantized spin wave. It can be treated classically, just as we did for phonons. The ground state of a simple ferromagnet has all spins parallel, as in Fig. (a). Consider N spins each of magnitude S on a line, with nearest-neighbor spins coupled by the Heisenberg interaction:

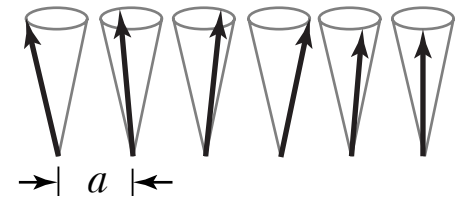$$U = -2J \sum_{p=1}^{N} \mathbf{S}_p \cdot \mathbf{S}_{p+1}$$

In the ground state, $\mathbf{S}_p \cdot \mathbf{S}_{p+1} = S^2$ and the energy of the system is $U_0 = -2NJS^2$.

(a)

(a)

(b)

(b)

(c)
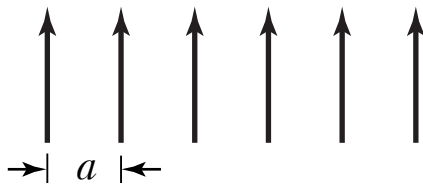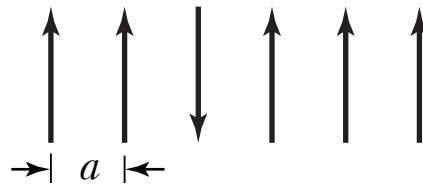
(c)

Consider an excited state with one particular spin reversed, as in Fig. (b). This increases the energy by $8JS^2$, so that $U_1 = U_0 + 8JS^2$. But we can form an excitation of much lower energy if we let all the spins share the reversal, as in Fig. (c).

The elementary excitations of a spin system have a wavelike form and are called magnons as shown below. Spin waves are oscillations in the relative orientations of spins on a lattice; lattice vibrations are oscillations in the relative positions of atoms on a lattice.

Side View (a)

Top View (b)
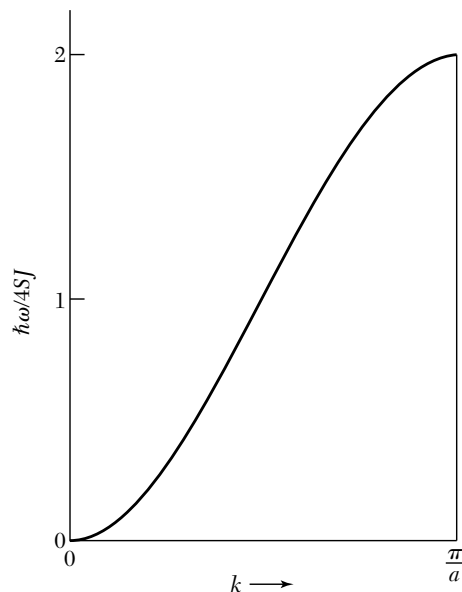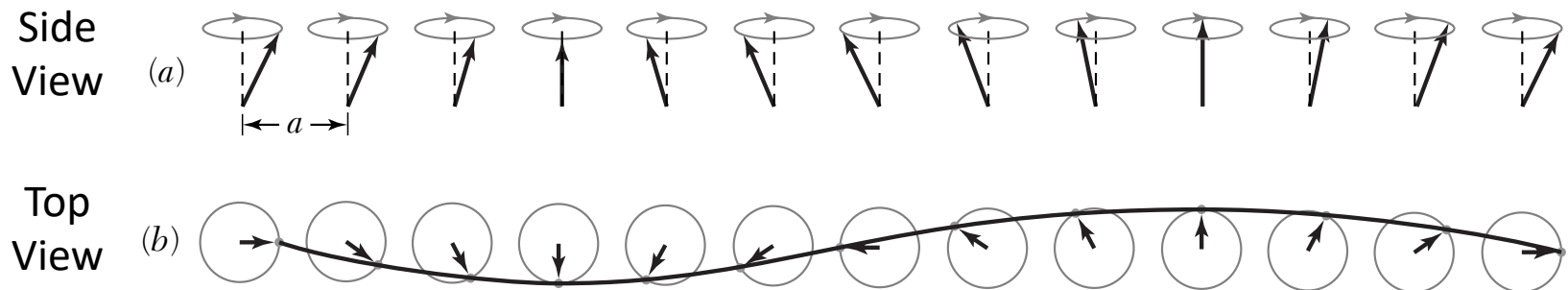
The dispersion relation for magnons in a ferromagnet in one dimension with nearest neighbor interactions is

$$\hbar\omega = 4JS(1 - \cos ka)$$

At long wavelength, $ka<<1$, and $(1-\cos ka)\simeq 1/2(ka)^2$, $\hbar\omega \cong (2JSa^2)k^2$, the frequency is proportional to k^2.
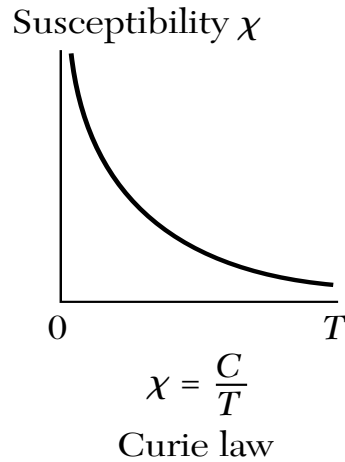
Antiferromagnetic Order

A classical example of magnetic structure determination by neutrons is shown below for MnO, which has the NaCl structure. At 80 K there are extra neutron reflections not present at 293 K. The reflections at 80 K may be classified in terms of a cubic unit cell of lattice constant 8.85 Å. At 293 K the reflections correspond to an fcc unit cell of lattice constant 4.43 Å.
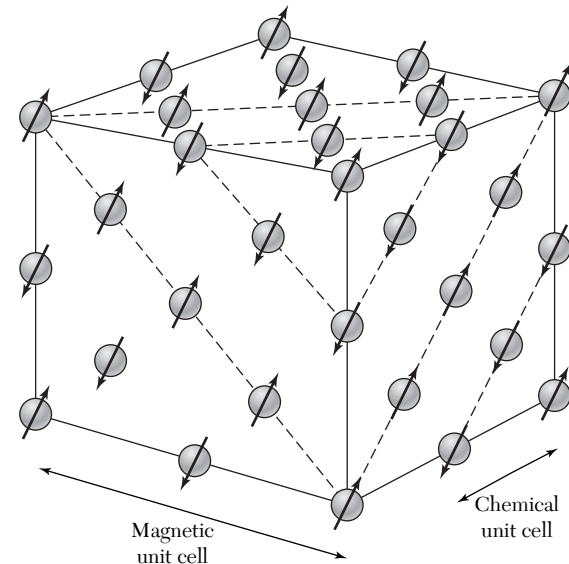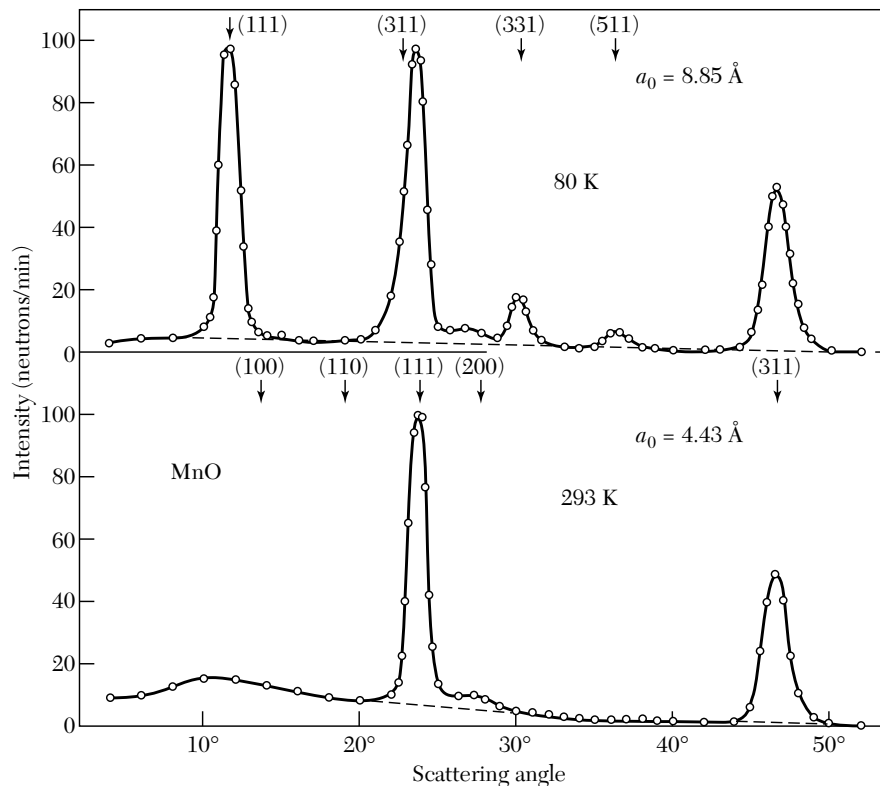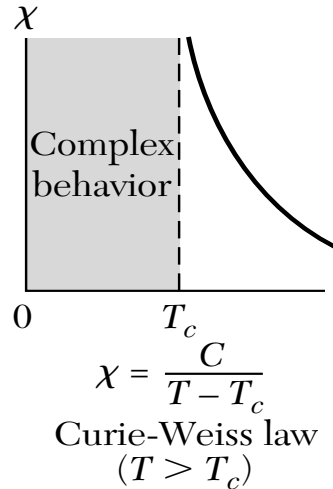

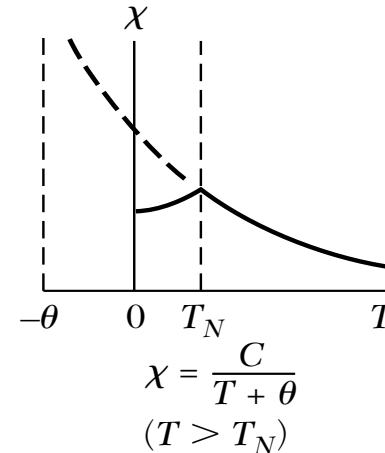The spins in a single [111] plane are parallel, but are antiparallel in adjacent [111] planes.
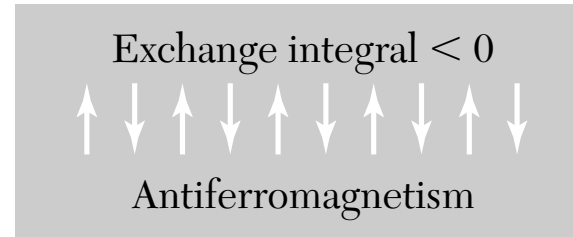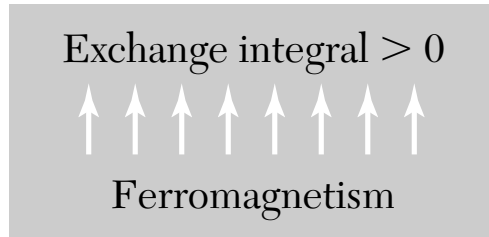
Materials are only antiferromagnetic below their corresponding **Néel temperature**, T_N. This is similar to the Curie temperature as above the Néel Temperature the material undergoes a phase transition and becomes paramagnetic.

Antiferromagnetic Magnons

By making the appropriate substitutions in the treatment of the ferromagnetic line, let spins with even indices 2*p* compose sublattice *A*, that with spins up ($S^z = S$); and let spins with odd indices 2*p*+1 compose sublattice *B*, that with spins down ($S^z = -S$). We consider only nearest-neighbor interactions, with *J* negative, and obtain the dispersion relation of magnons in a one-dimensional anti- ferromagnet.
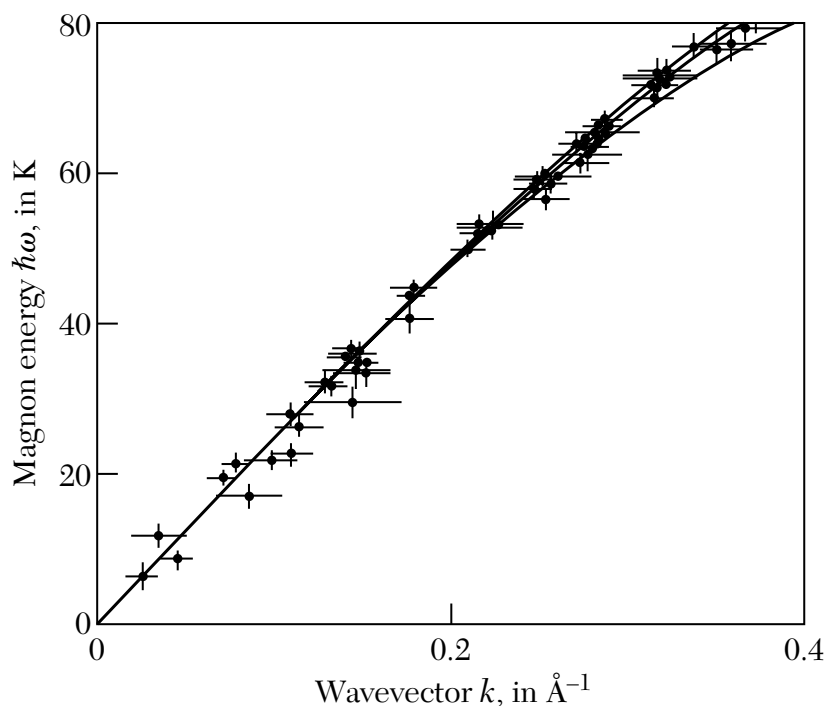

$$\omega = \omega_{\text{ex}}\left|\sin ka\right|$$

The dispersion relation for magnons in an antiferromagnet is quite different from that for magnons in a ferro-magnet. The graph on the left is the magnon dispersion relation in the simple cubic antiferromagnet RbMnF$_3$ as determined at 4.2 K by inelastic neutron scattering.

Ferromagnet Domains

At temperatures well below the Curie point the electronic magnetic moments of a ferromagnet are essentially parallel on a microscopic scale. Actual specimens are composed of small regions called domains, within each of which the local magnetization is saturated. The directions of magnetization of different domains need not be parallel, and the application of an external magnetic field may be required to saturate the specimen.
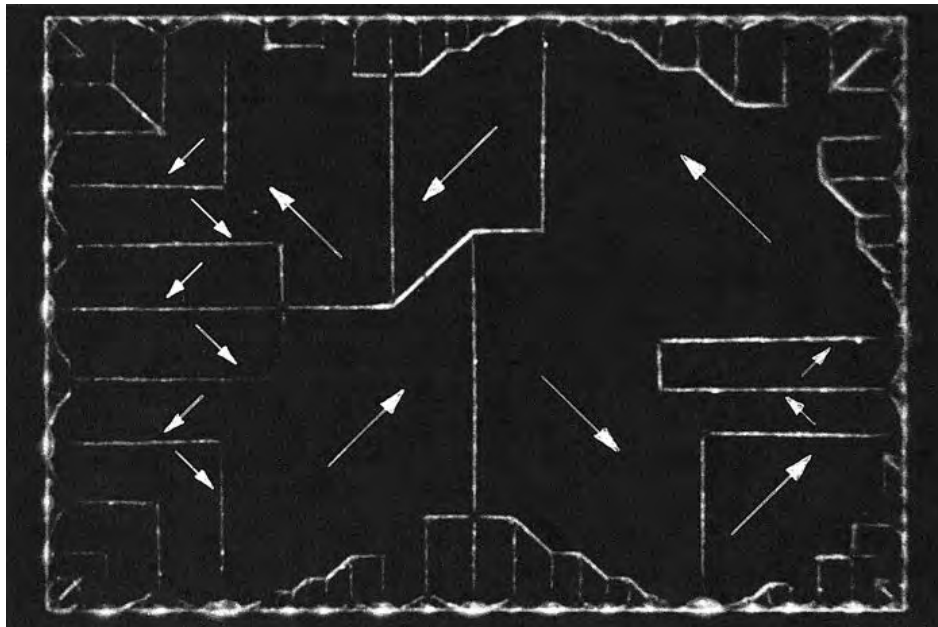
Ferromagnetic domain pattern on a single crystal platelet of nickel. The domain boundaries are made visible by the Bitter magnetic powder pattern technique. The direction of magnetization within a domain is determined by observing growth or contraction of the domain in a magnetic field.
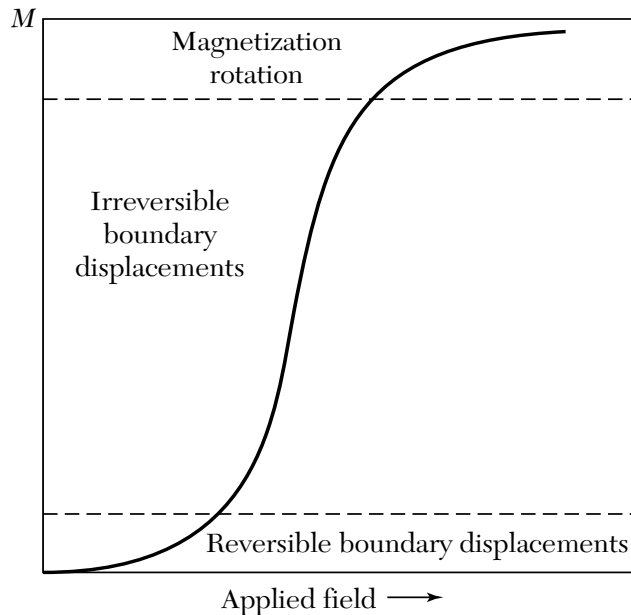
- In weak applied fields the volume of domains favorably oriented with respect to the field increases at the expense of unfavorably oriented domains;
- In strong applied fields the domain magnetization rotates toward the direction of the field.
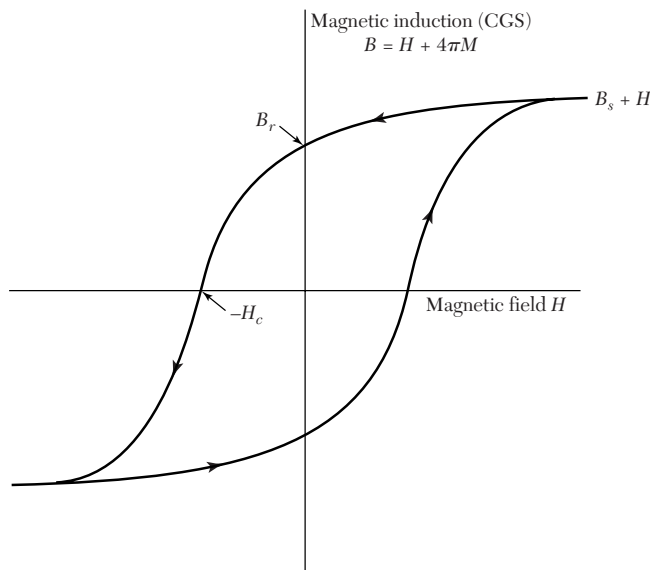

Technical terms defined by the hysteresis loop are shown in Fig. The coercivity H_c is the reverse field that reduces B to zero; a related coercivity H_{ci} reduces M or $B - H$ to zero. The **remanence** B_r is the value of B at $H = 0$. The saturation induction B_s is the limit of $B - H$ at large H, and the saturation magnetization $M_s = B_s/4\pi$.

Anisotropy Energy

There is an energy in a ferromagnetic crystal which directs the magnetization along certain crystallographic axes called directions of easy magnetization. This energy is called the **magnetocrystalline** or **anisotropy energy**.
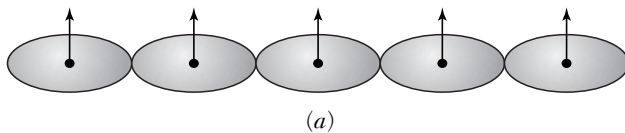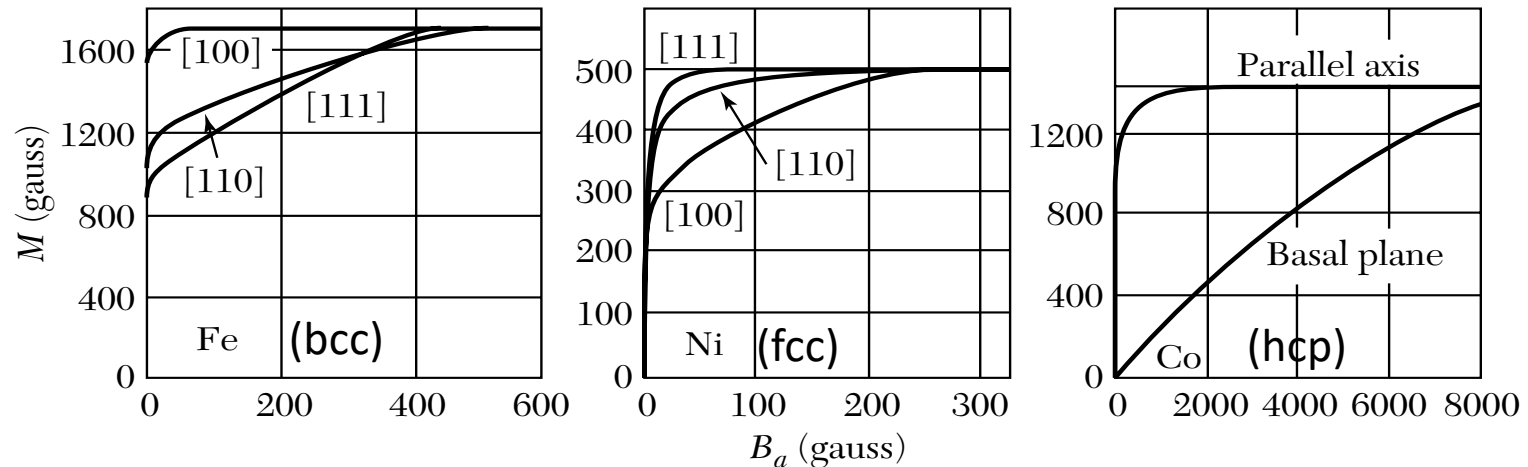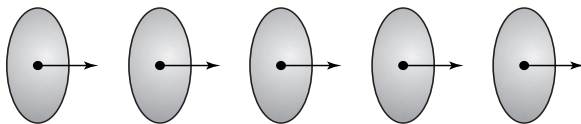

In cobalt, the anisotropy energy density is given by $U_K = K_1' \sin^2 \theta + K_2' \sin^4 \theta$, where θ is the angle the magnetization makes with the hexagonal axis. At room temperature, the anisotropic constants: $K_1' = 4.1 \times 10^6$ erg/cm³; $K_2' = 1.0 \times 10^6$ erg/cm³.

Bloch Wall

A **Bloch wall** in a crystal is the transition layer that separates adjacent domains magnetized in different directions. The entire change in spin direction between domains does not occur in one discontinuous jump across a single atomic plane, but takes place gradually over many atomic planes.
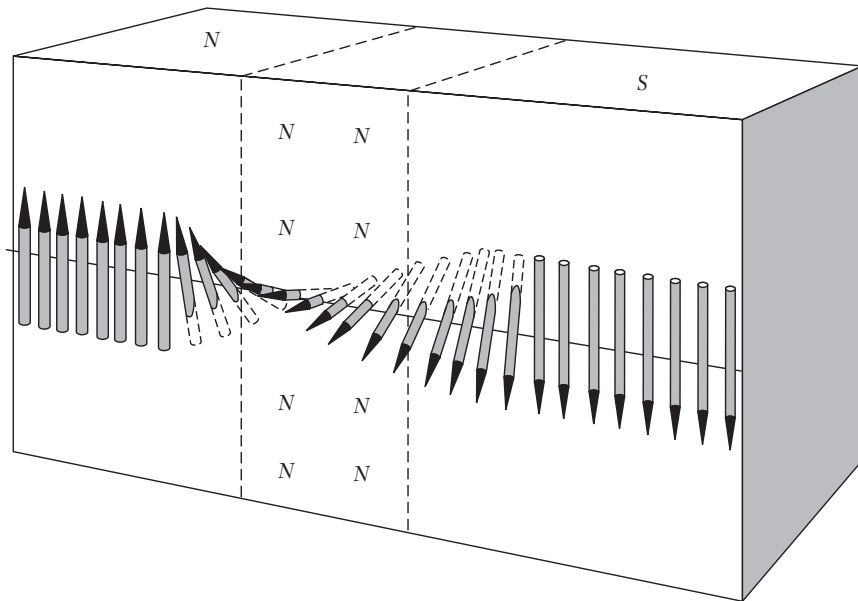
From Heisenberg equation, the extra exchange energy, $w_{ex} = JS^2\varphi^2$, generated between two spins making a small angle φ with each other. Here J is the exchange integral and S is the spin quantum number. If a total change of π occurs in N equal steps, $\varphi = \pi/N$, and the exchange energy per pair of neighboring atoms is $w_{ex} = JS^2 (\pi/N)^2$.

The total exchange energy of a line of N +1 atoms is $Nw_{ex} = JS^2\pi^2/N$.

Thickness of Bloch Wall

The wall would thicken without limit were it not for the anisotropy energy, which acts to limit the width of the transition layer. Consider a wall parallel to the cube face of a simple cubic lattice and separating domains magnetized in opposite directions. We wish to determine the number N of atomic planes contained within the wall. The energy per unit area of wall is the sum of contributions from exchange and anisotropy energies: $\sigma_w = \sigma_{ex} + \sigma_{anis}$.

With a as the lattice constant, there are $1/a^2$ lines per unit area,

$$\sigma_{ex} = \pi^2 J S^2 / N a^2$$

The anisotropy energy is of the order of the anisotropy constant (K) times the thickness Na, or $\sigma_{anis} = KNa$; therefore

$$\sigma_w \approx (\pi^2 J S^2 / N a^2) + KNa$$

Take derivative to find minimum N,

$$\partial \sigma_w / \partial N = 0 = -(\pi^2 J S^2 / N^2 a^2) + Ka \qquad \Longrightarrow \qquad N = (\pi^2 J S^2 / K a^3)^{1/2}$$

For order of magnitude, $N \sim 300$ in iron.

The total wall energy per unit area on this model is $\sigma_w = 2\pi (K J S^2 / a)^{1/2}$.

Origin of Domains

Landau and Lifshitz showed that domain structure is a natural consequence of the various contributions to the energy --exchange, anisotropy, and magnetic-- of a ferromagnetic body. We may understand the origin of domains by considering the structures shown below:


(a) (b) (c) (d) (e)
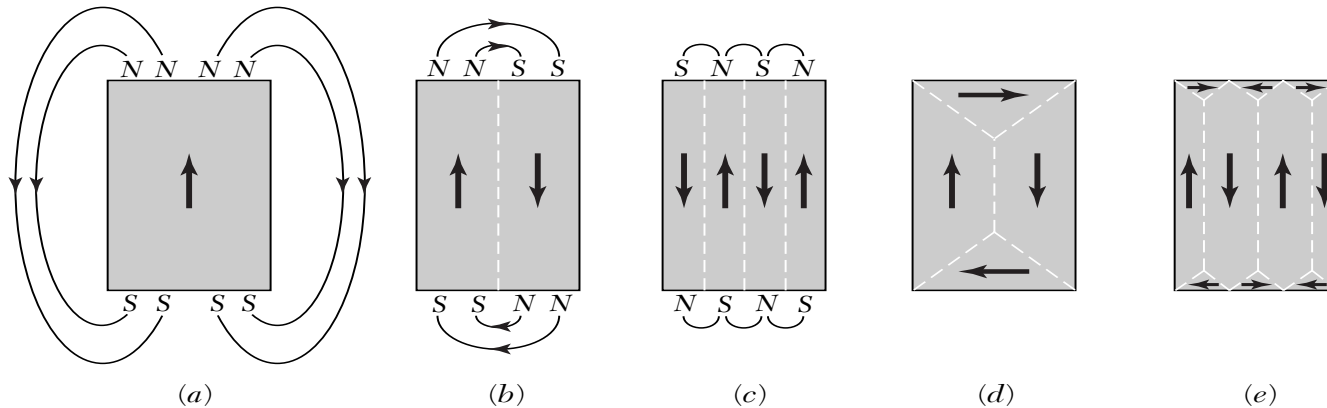
In (a) we have a single domain; as a consequence of the magnetic "poles" formed on the surfaces of the crystal with a high value of the magnetic energy $(1/8\pi)\int B^2 dV$. In (b) the magnetic energy is reduced by roughly one-half by dividing the crystal into two domains magnetized in opposite directions. In (c) with N domains the magnetic energy is reduced to approximately $1/N$ of the magnetic energy of (a). In domain arrangements such as (d) and (e) the magnetic energy is zero.

Nuclear Magnetic Resonance

The magnetogyric ratio of a particle or system is the ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ. We can then write the magnetic moment of a nucleus as $\boldsymbol{\mu} = \gamma\hbar\mathbf{I}$,

here $\mathbf{I}$ is angular momentum of the nucleus measured in $\hbar$.
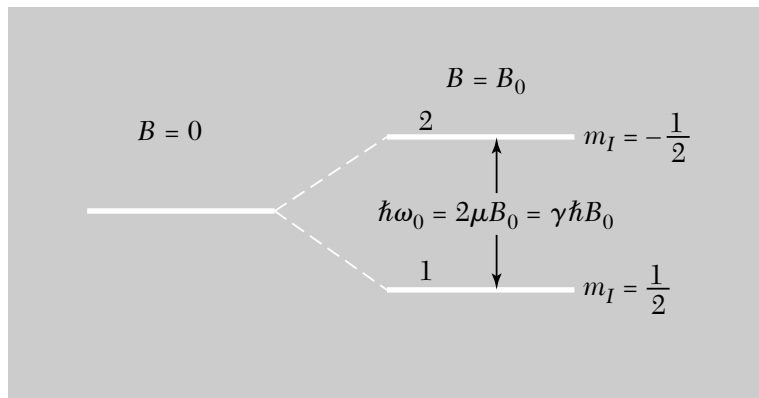
With a applied magnetic field $\mathbf{B}_a = B_0\hat{\mathbf{Z}}$, then

$$U = -\mu_z B_0 = -\gamma\hbar B_0 I_z = -m_I\gamma\hbar B_0$$
$$m_I = I, I - 1, \ldots, -I,$$

are the allowed values of I_z .

A nucleus with $I = \frac{1}{2}$, has two energy levels corresponding to $m_I = \pm\frac{1}{2}$, In a magnetic field B_0 as in the above figure. If $\hbar\omega_0$ denotes the energy difference between the two levels, then $\hbar\omega_0 = \gamma\hbar B_0$ or $\omega_0 = \gamma B_0$.

For the proton, $\gamma = 2.675 \times 10^8 \text{ s}^{-1} \text{ tesla}^{-1}$, $\nu(\text{MHz}) = 42.58\, B_0(\text{tesla})$

For the electron, $\nu(\text{GHz}) = 28.0\, B_0(\text{tesla})$, ν is magnetic absorption freqency.

The principle of NMR usually involves three sequential steps:
1. The alignment (polarization) of the magnetic nuclear spins in an applied, constant magnetic field B_0.
2. The perturbation of this alignment of the nuclear spins by a weak oscillating magnetic field, usually a radio-frequency (RF) pulse. The oscillation frequency required for significant perturbation is dependent upon the static magnetic field (B_0) and the nuclei of observation.
3. The detection of the NMR signal during or after the RF pulse, due to the voltage induced in a detection coil by precession of the nuclear spins around B_0. After an RF pulse, precession usually occurs with the nuclei's intrinsic Larmor frequency and, in itself, does not involve transitions between spin states or energy levels.
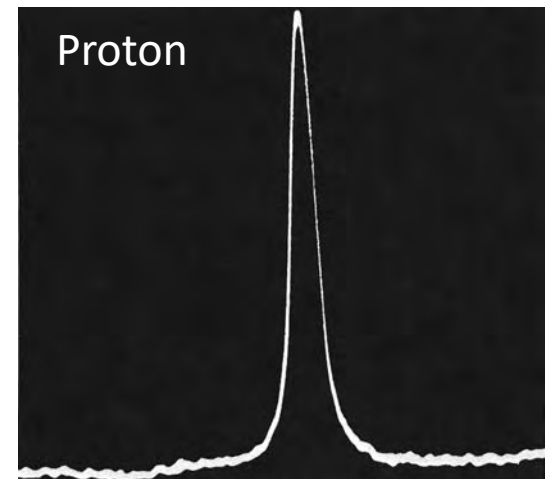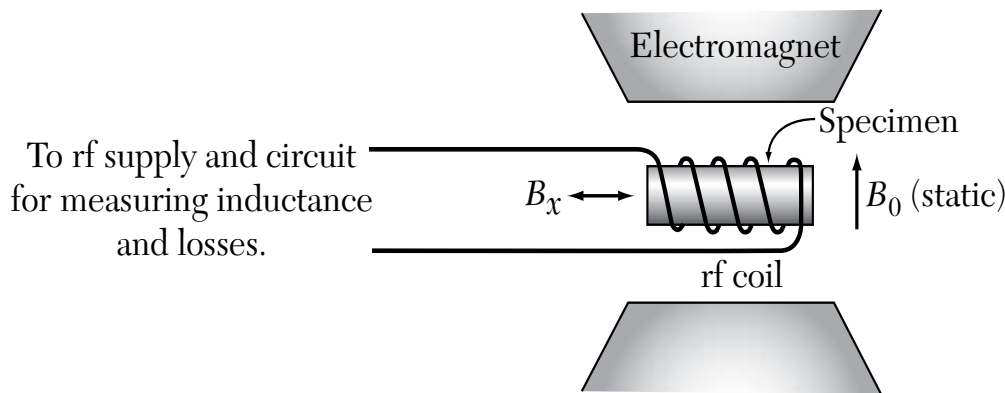
Problems

1. ***Diamagnetic susceptibility of atomic hydrogen.*** The wave function of the hydrogen atom in its ground state (1s) is $\psi = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$, where $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}\,\mathrm{cm}$. The charge density is $\rho(x,\,y,\,z) = -e|\psi|^2$, according to the statistical interpretation of the wave function. Show that for this state $\langle r^2 \rangle = 3a_0^2$, and calculate the molar diamagnetic susceptibility of atomic hydrogen $(-2.36 \times 10^{-6}\,\mathrm{cm}^3/\mathrm{mole})$.

2. ***Magnon dispersion relation.*** Derive the magnon dispersion relation for a spin S on a simple cubic lattice, $z = 6$. Hint: Show first that

$$dS_{\boldsymbol{\rho}}^x/dt = (2JS/\hbar)(6S_{\boldsymbol{\rho}}^y - \sum_{\delta} S_{\boldsymbol{\rho}+\delta}^y) \ ,$$

where the central atom is at $\boldsymbol{\rho}$ and the six nearest neighbors are connected to it by six vectors $\boldsymbol{\delta}$. Look for solutions of the equations for $dS_{\boldsymbol{\rho}}^x/dt \ \mathrm{and} \ dS_{\boldsymbol{\rho}}^y/dt$ of the form $\exp(i\mathbf{k} \cdot \boldsymbol{\rho} - i\omega t)$.

3. Néel temperature. Taking the effective fields on the two-sublattice model of an antiferromagnetic as

$$B_A = B_a - \mu M_B - \epsilon M_A \; ; \quad B_B = B_a - \mu M_A - \epsilon M_B \; ,$$

show that

$$\frac{\theta}{T_N} = \frac{\mu + \epsilon}{\mu - \epsilon} \; .$$