

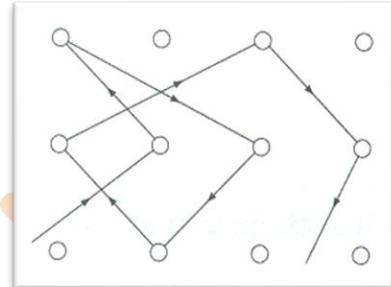
Contents

1. Review of classical free electron theory
2. Drawbacks of the classical free electron theory
 - a. *Temperature dependence of resistivity*
 - b. *Specific heat of electrons in a metal*
 - c. *Conductivity variations with electron concentrations*
3. Concepts of quantum free electron theory
4. Fermi Dirac statistics and Fermi factor
5. Density of states of valence electrons in a metal
6. Merits of the quantum free electron theory and short comings
 - a. *Temperature dependence of resistivity*
 - b. *Specific heat of electrons in a metal*
 - c. *Wiedemann-Franz law*
 - d. *Hall effect in certain metals*
7. Bloch Theorem and Electron wave functions in a periodic potential
8. Origin of energy bands – metals insulators and semiconductors
9. Effective mass of charge carriers.
10. Introduction to Magnetic materials
11. Atomic origin of magnetization
12. Diamagnetic materials, Paramagnetic materials , Ferro magnetic materials

1 Basics of CFET, expressions for electrical parameters

Drude and Lorentz proposed the classical free electron theory of electrical conductivity of metals (as early as 1904). The model of conductivity of free electrons is based on the following assumptions:

- (1) The valence electrons of the atoms of the metal contribute to the conduction process either electrical or thermal. The electrons move in an array of ion cores (which are nuclei surrounded by inner electrons excluding the valence electrons). All the valence electrons are free electrons and are treated as conduction electrons which are in a state of random motion (like the molecules in an ideal gas).
- (2) The effect of positive ion cores on the electrons is considered to be constant and hence neglected.
- (3) The electrostatic repulsion between the electrons is neglected.
- (4) The electrons in the metal are considered equivalent to molecules in a gas and the gas laws are made applicable to the electrons in a metal. Accordingly, the distribution of energy and velocity is assumed to follow Maxwell-Boltzmann statistics.



The average velocity of electrons in the metal is dependent on the temperature of the metal and is termed as the thermal velocity of electrons $v_{th} = \sqrt{\frac{3kT}{m}}$. At 300K the thermal velocity of the electrons is $v_{th} \approx 10^5 \text{ ms}^{-1}$.

However, this random motion of the electrons do not contribute to a net drift of electrons across the metal and hence no current flows through the material

The conduction electrons in the lattice are scattered by collisions with the ionic cores and other electrons. The mean time between collisions is the relaxation time of the electrons in the metal and the distance between successive collisions is the mean free path. Taking the mean lattice parameter of 10nm as the mean free path λ , the relaxation time can be estimated as $\tau = \frac{\lambda}{v_{th}} \approx 10^{-15} \text{ s}$.

Drift Velocity : In the presence of an Electric field E the electrons show a net drift across the metal in a direction opposite to that of the electric field. The velocity of the electrons across the metal in the presence is known as the drift velocity v_d .

The force equation for the electron's motion can be described by $m \frac{dv}{dt} = eE - kmv$ where the last term accounts for the loss of energy due to the scattering which is proportional to the momentum of the electrons and k is the coefficient of scattering loss.

In the equilibrium condition this leads to an average velocity for the electrons which is the drift velocity $v_d = \frac{eE}{km}$

Dimensionally k should be $(\text{time})^{-1}$.

The decay of the drift velocity to zero in the absence of the electric field yields that $k = \frac{1}{\tau}$ where τ is the relaxation time – the time between successive collisions or the time for the drift velocity to fall to $1/e$ times its steady value in the presence of an electric field.

The drift velocity $v_d = \frac{e\tau E}{m} = \mu E$ where $\mu = \frac{e\tau}{m}$ is the **electron mobility or the charge carrier mobility**. The mobility $\mu = \frac{v_d}{E} = \frac{e\tau}{m}$ is the drift velocity per unit electric field.

The drift velocity of electrons is extremely low compared to thermal velocity. To illustrate, the drift velocity of electrons experiencing an electric field of $1V/m$ is of the order of 10^{-4} ms^{-1} .

Expression for Electrical conductivity:

The current through a conductor with an electron concentration n of cross section A and length L at an applied electric field E can be evaluated as

$$I = nev_d A \text{ where } v_d \text{ is the drift velocity given by } v_d = \frac{e\tau E}{m}$$

$\therefore I = neA \frac{e\tau E}{m}$ or $J = \frac{I}{A} = \frac{ne^2\tau}{m} E = \sigma E$ where σ is a constant for a given metal and is the conductivity of the metal

$$\sigma = \frac{ne^2\tau}{m} = ne\mu$$

$$\text{The resistivity of the metal is } \rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} = \frac{1}{ne\mu}.$$

Thus the resistivity of a metal is inversely proportional to the concentration of free electrons and the relaxation time of electrons in the metal.

2 Experimental temperature dependence of the resistivity

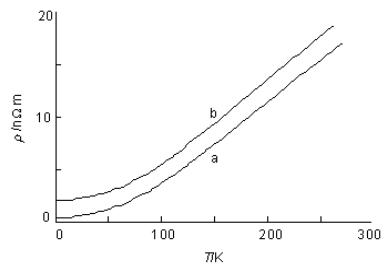
Experiments show that resistivity of metals in general vary linearly with temperature in the normal operating temperatures. At these temperatures the resistivity ρ_{sc} results from the scattering of the electrons moving with high thermal velocities in random directions.

However, at very low temperatures the resistivity ρ_{res} is found to saturate to a non zero finite value, which is dependent on the impurity concentration in the metal.

Hence two independent types of resistivities determine the total resistivity of the metal. Since the phenomena are independent of each other the net resistivity would be the sum of the two resistivity components which is known as the Mattheissen's rule.

$$\rho = \rho_{res} + \rho_{sc}$$

Hence $\frac{m}{ne^2\tau} = \frac{m}{ne^2\tau_{res}} + \frac{m}{ne^2\tau_{sc}}$. This gives us the effective relaxation time as $\frac{1}{\tau} = \frac{1}{\tau_{res}} + \frac{1}{\tau_{sc}}$



3 Draw backs of CFET and quantum corrections.

The classical free electron theory failed to correlate the experimental results of many phenomena such as the temperature dependence of resistivity, specific heat of electrons etc.

- According to the classical free electron theory the resistivity of a metal is given by $\rho = \frac{m}{ne^2\tau}$. For a given material the temperature dependence of resistivity arises from the temperature dependence of the relaxation time $\tau = \frac{\lambda}{v_{th}}$. Since the mean free path of the electrons is assumed to be a constant for a wide range of metals, the temperature dependence of the thermal velocity should affect the relaxation time. For a given temperature $v_{th} = \sqrt{\frac{3k_B T}{m}}$ and hence $v_{th} \propto \sqrt{T}$ or $\tau \propto T^{-\frac{1}{2}}$. Since the resistivity $\rho \propto \tau^{-1}$, the temperature dependence of resistivity can be inferred to be $\rho \propto \sqrt{T}$. But experimental observations show that $\rho \propto T$ and hence the classical free electron conduction model fails to explain the correct temperature dependence of resistivity of metals.
- The contribution of electrons to the specific heat of the metal can be estimated using the principle that the specific heat $C_{el} = \frac{dU}{dT}$. Considering one mole of a mono valent metal, the energy of the valence electrons is given by $U = \frac{3}{2} k_B T \cdot N_{avg}$. Hence the specific heat of the electrons should be equal to $C_{el} = \frac{dU}{dT} = \frac{3}{2} k_B \cdot N_{avg} = \frac{3}{2} R$ which is a constant. However experimental estimation of the specific heat of electrons is only approximately 1% of the theoretical value and is also found to be temperature dependent. Thus, the theory fails to explain the actual specific heat dependence of electrons in metals.
- The electrical conductivity of metals, given by $\sigma = \frac{ne^2\tau}{m}$, should be dependent on the free electron concentration for a given temperature, assuming that the relaxation time is more or less constant. However, it is found that mono valent Copper with lesser electronic concentration has a higher electrical conductivity as compared to trivalent Aluminum. Similarly Zinc with higher electronic concentration has lesser conductivity than Aluminum. Experimental results show that there is no linear dependence of the electronic concentration on the conductivity of metals.

Thus, the classical free electron theory fails to explain the experimental observations. It is obvious that some of the assumptions of the CFET are over estimations or under estimations of the physical parameters and hence need to be corrected.

4 Quantum model of valence electrons in a metal - Fermi energy

Metals have a very high concentration of valence electrons $\cong 10^{28} m^{-3}$. According to the quantum mechanical principles these valence electrons in a metal have to be in discrete energy states following Pauli's exclusion principle. This requires the energy states of the atomic levels to split into discrete closely spaced energy states to accommodate all the valence electrons. At 0K such an arrangement leads to a sea of energy levels which have a separation as small as $\cong 10^{-20} eV$. The upper most occupied energy state at 0K is then termed as the Fermi energy of the metal. Thus at 0K all the states below the Fermi energy are filled and all the states about the Fermi energy are empty.

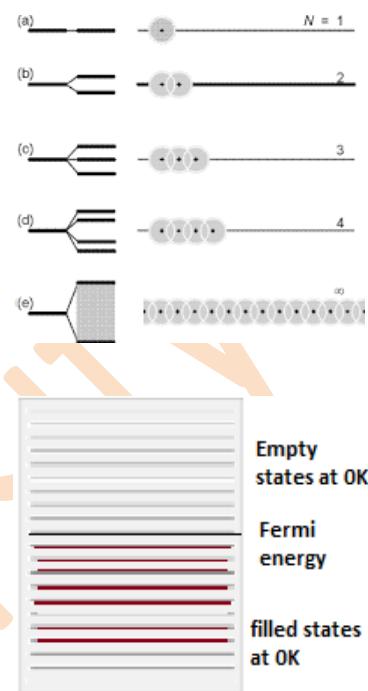
By convention electrons above the Fermi level should contribute to the conduction process and the valence electrons are below the Fermi level. (The electrons in states below the Fermi level do not contribute to the conduction process). Thus according to this model not all the valence electrons in a metal are conduction electrons.

The effective number of electrons above the Fermi level could be approximated as $n_{eff} = n \frac{kT}{E_f}$.

The effective number of electrons above the Fermi level for copper ($E_f=7eV$) at 300K can be calculated to be $n_{eff} = n \frac{kT}{E_f} = n * 0.0036 = n * 0.36\%$. Thus a small fraction of the available valence electrons are excited into states above the Fermi level, which contribute to the conductivity of the material.

This quantum model of the free electrons gives rise to the following modifications to the classical free electron theory:

- The valence electrons in the metal are arranged in discrete energy states following Pauli's exclusion principle. Only electrons close to the Fermi level participate in the conduction process
- The occupation probability of the electron states are described by the Fermi Dirac distribution function applicable to fermions.
- The conduction electrons in a metal move in array of positive ions, colliding with the ionic centers and other electrons resulting in the resistance of the material.



- The electrostatic interactions namely, the electron – electron interaction and the electron – ion interactions are negligible.
- The electrons undergo random scattering due to the vibrating ionic centers giving rise to resistance to flow of electrons.

5 Fermi Dirac statistics, Fermi factor

The occupation probabilities of electrons in the different energy state at different temperatures are estimated using the Fermi Dirac statistics for Fermions. (All particles with spin $\pm \frac{1}{2}$ are classified as Fermions. Fermions follow the Fermi Dirac statistics for particles which are indistinguishable.)

The Fermi factor $F_d = \frac{1}{\left(e^{\left(\frac{E-E_f}{k_B T}\right)}+1\right)}$ gives the probability of an energy state E to be occupied at a

temperature T

Estimation of the Fermi factor at T=0K gives distinct results for $E < E_f$ and $E > E_f$.

- If $E < E_f$ then for $E - E_f$ is negative, then the Fermi factor $F_d =$

$$\frac{1}{\left(e^{-\left(\frac{\Delta E}{k_B T}\right)}+1\right)}.$$

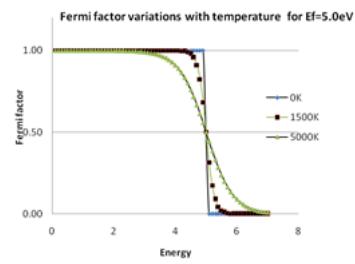
At 0K this becomes $F_d = \frac{1}{(e^{-(\infty)}+1)} = 1$. This implies that at 0K all electron states below the Fermi level are filled states.

- If $E > E_f$ then for $E - E_f$ is positive, then the Fermi factor $F_d =$

$$\frac{1}{\left(e^{\left(\frac{\Delta E}{k_B T}\right)}+1\right)}.$$

At 0K this becomes $F_d = \frac{1}{(e^{(\infty)}+1)} = 0$. This implies that at 0K all electron states above the Fermi level are empty states.

- For $T>0$ and $E=E_f$ the Fermi factor $F_d = \frac{1}{\left(e^{\left(\frac{E-E_f}{k_B T}\right)}+1\right)} = \frac{1}{e^0+1} = \frac{1}{2} = 0.5$. This gives a probability of occupation of 50% for the Fermi energy.



The Fermi energy has a weak temperature dependence and is given by

$$E_f = E_{f0} \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_{f0}} \right)^2 \right]$$

where E_{f0} is the Fermi energy at zero Kelvin. At normal temperature ranges the ratio of $\frac{k_B T}{E_{f0}}$ is very low and hence can be approximated to be a constant equal to the value at zero Kelvin.

6 Fermi temperature

The arrangement of electrons in discrete energy states leads to the concept that only electrons near the Fermi energy are excited into the conduction band and it may be really difficult to excite all the valence electrons into the conduction band. If the temperature of the metal is T then $k_B T$ is the thermal energy available to the electrons in the metal. The thermal energy required to excite the last electron at the bottom of the energy band if termed as $k_B T_f$, then at temperature T_f the electron would have an energy $E_f = k_B T_f$. This temperature is termed as the Fermi temperature of electrons in the metal.

Evaluating the temperature for Copper with Fermi energy as 7 eV gives the value of the Fermi temperature as approximately 81000K. It is obvious that at such high temperatures the metal cannot be in the solid state and hence this is only a representative temperature which highlights the point that all valence electrons cannot be conduction electrons.

7 Fermi velocity

From the above analysis only a small fraction of electrons close to the conduction band can be taking part in the conduction processes. The electrons excited into the conduction band have energies very close to the Fermi energy. These conduction electrons then possess a kinetic energy which may be equal to Fermi energy.

The kinetic energy of the electrons near the Fermi energy is $E_f = \frac{1}{2}mv_f^2$ where v_f the Fermi velocity of conduction electrons is $v_f = \sqrt{\frac{2E_f}{m}}$. Fermi velocity for conduction electrons in copper gives $v_f = 1.06 \times 10^6 \text{ ms}^{-1}$.

This velocity is greater than the thermal velocity of electrons (as per the CFET). The electrons in the conduction band are in a state of random motion and the scattering of the electrons by the lattice is the origin of the electrical resistance of the metal.

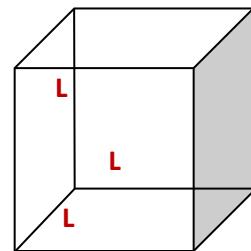
8 Density of states derivation

The electrons in a metal can be approximated to the particle in a box in three dimensions, since under normal conditions the electrons cannot escape the boundaries of the metal. Consider a mono-valent metal in the form of a cube of side L . Inside the metal the electrons can be assumed to be moving in a zero potential field.

The three-dimensional Schrödinger's wave equation can be written as three one dimensional Schrödinger's wave equation and their corresponding solutions analysed.

The x component of the particle motion can be described by the wave function which is the solution of the SWE

$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0$$



This gives the Eigen energy value for the x component as $E_{n_x} = \frac{\hbar^2 n_x^2}{8mL^2}$

Similarly the energy in the other two dimensions can be evaluated as $E_{n_y} = \frac{\hbar^2 n_y^2}{8mL^2}$ and $E_{n_z} = \frac{\hbar^2 n_z^2}{8mL^2}$

The total energy of the electron can be written as

$$E_n = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{8mL^2} R^2 \quad \text{----- (1) where } R^2 = n_x^2 + n_y^2 + n_z^2$$

The number of states with energy E can be evaluated by studying the variation of the combinations of n_x , n_y and n_z . It can be deduced that every combination of n_x , n_y and n_z result in an energy state as per equation (1).

(The n space corresponds to the momentum space since $k = n \frac{\pi}{L}$. Thus the combinations can give the picture of particles moving in different directions.) When n_x , n_y and n_z are equal the energy state is unique and is non degenerate. It is also noted that the energy states can be degenerate with degeneracy of 3 when two of the three n_x , n_y and n_z are equal and degeneracy of 6 when all the three are not equal.

The distribution of energy states depending of the combinations of n_x , n_y and n_z can be evaluated analyzing the n space formed by n_x , n_y and n_z .

It is observed that every combination of n_x , n_y and n_z gives additional unit volume in ***n space*** from which we conclude that evaluating the number of states is equivalent to evaluating the volume of the ***n space***.

It is also noticed that the degenerate energy states with the same energy values lie on the surface of an octant of a sphere with the center at the origin. Hence it is sufficient to find the volume of the octant of a sphere of radius R to evaluate the number of energy states up to R i.e., the combination of n_x , n_y and n_z .

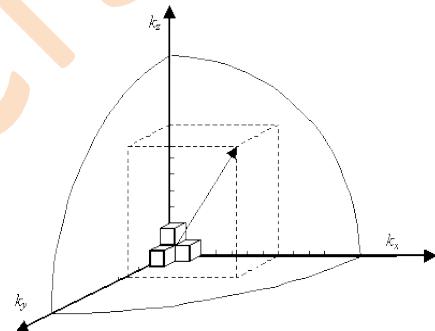
The sensitivity of the increase in the states with increasing n_x , n_y and n_z can be found from the change in the volume of the octant if the radius changes from R to $R+dR$ realizing that $R \gg dR$.

The volume of the shell of thickness dR is then given by $\frac{\pi R^2 dR}{2}$. This is also then the number of energy states available between R and $R+dR$.

The energy expression $E_n = E_0 R^2$ gives us $R^2 = \frac{E_n}{E_0}$ and $dR = \frac{dE}{2(E_n E_0)^{1/2}}$

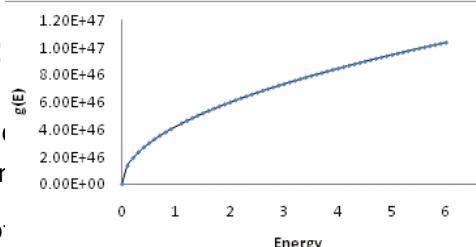
Therefore the number of energy states between E and $E+dE$ is given by

$$\frac{\pi R^2 dR}{2} = \frac{\pi}{4} \frac{E_n}{E_0} \frac{dE}{\{E_n E_0\}^{1/2}} = \frac{\pi}{4} \cdot \frac{E_n^{1/2}}{E_0^{3/2}} dE$$



Substituting for $E_0 = \frac{h^2}{8mL^2}$ we get the number of energy states between E and E+dE as

$$\frac{\pi}{4} \cdot \left(\frac{8mL^2}{h^2} \right)^{3/2} E^{1/2} dE$$



The number of electrons states per unit volume can be estimated by exclusion principle and allowing two electrons with opposite spins.

The density of states for electrons in a metal gives the number of states per unit volume.

$$g(E)dE = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE$$

This shows that the distribution of electrons in energy states vary non-linearly with increasing energy E.

The probability that an energy state is occupied is given by the fermi factor

$$F_d = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$$

And hence the occupancy of the states described by N(E) is determined.

$$N(E) = g(E) * F_d$$

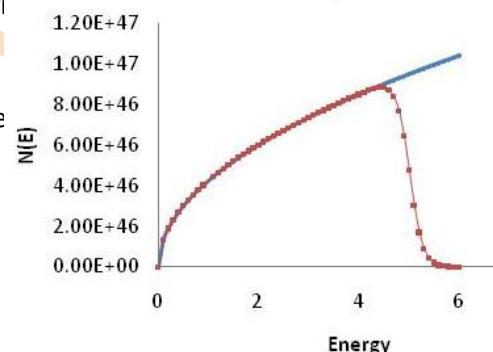
This is effect is multiplying g(E) by a number between 0 and 1 depending on the energy relative to the Fermi energy and the temperature.

The states below $E_f - k_B T$ are completely occupied as F_d is 1.

The states in the range of $k_B T$ below the Fermi level are emptied and the probability of occupancy F_d is between 1 and 0.5.

The states above E_f in a range $k_B T$ are now occupied and the probability of occupancy lies between 0.50 and 0.00.

The variation of N(E) with E can be graphically represented as shown for a representative material with Fermi energy of 5eV.



9 Expression for Fermi energy, average electron energy

The Fermi energy of metals can be evaluated from the fact that all available electrons occupy energy levels below the Fermi level E_f at 0K. This means that the density of occupied states $N(E) = g(E) * F_d$ when evaluated for all levels from 0 to E_f , should result in the total count of electrons in the metal, ie.,

$$\text{The total free electronic concentration } n = \int_0^{E_f} N(E) dE = \int_0^{E_f} g(E) * F_d dE .$$

We know that F_d has to be 1 for all energy levels below E_f at 0K and hence

$$n = \int_0^{E_f} N(E) dE = \int_0^{E_f} g(E) dE = \frac{\pi}{2} \left(\frac{8m}{h^2}\right)^{\frac{3}{2}} \int_0^{E_f} E^{\frac{1}{2}} dE = \frac{\pi}{3} \left(\frac{8m}{h^2}\right)^{\frac{3}{2}} E_f^{\frac{3}{2}}$$

This gives us a method of estimating the Fermi energy of the system if the number of valence electrons per unit volume is known.

The Fermi energy can be estimated if the concentration of free electrons is known and can be evaluated as

$$E_f = \left(\frac{3}{\pi}\right)^{2/3} \left(\frac{h^2}{8m}\right) n^{2/3}$$

Average energy of electrons in a metal at 0K

Since the distribution of electrons in the different energy states shows a non linear variation, the average energy of the electron is not the simple average of the electron's max and min energy. From the graph of $N(E)$ vs E we observe that $N(E)$ states have energy E which implies that the total energy of all electrons in filled states upto E_f should be the summation of all $N(E)*E$

The average energy of the electron = $\frac{\text{total energy of all electrons in different energy states}}{\text{total number of electrons}}$

$$\frac{\int_0^{E_f} g(E) * E * F_d dE}{\int_0^{E_f} g(E) * F_d dE} = \frac{\frac{\pi}{2} \left(\frac{8m}{h^2}\right)^{\frac{3}{2}} \int_0^{E_f} E^{\frac{1}{2}} dE * E}{\frac{\pi}{2} \left(\frac{8m}{h^2}\right)^{\frac{3}{2}} \int_0^{E_f} E^{\frac{1}{2}} dE}$$

This on integration gives the average energy $E = \frac{3}{5} E_f = 0.6 * E_f$

Merits of Quantum free electron theory:

Heat capacity due to free electrons

The electronic specific heat (contribution to the specific heat from the conduction electrons) can be evaluated in the light of the fact that only electrons close to the Fermi level participate in the conduction. Hence heat absorption happens due to that fraction of electrons. This number can be estimated as the effective number of electrons (in one mole of the metal for a mono valent metal) in the conduction process as $n_{eff} = \frac{N_a}{E_f} \cdot k_B T$.

Hence if the average thermal energy of the electrons is taken to be $\frac{3}{2} k_B T$ then the total energy of electrons in one mole of the material $U = n_{eff} \cdot \frac{3}{2} k_B T = \frac{3}{2} k_B T \cdot \frac{N_a}{E_f} \cdot k_B T = \frac{3}{2} \cdot \frac{N_a}{E_f} \cdot k_B^2 T^2$

Hence the specific heat $C_{el} = \frac{dU}{dT} = 3 \cdot \frac{N_a}{E_f} \cdot k_B^2 T = 3R \cdot \frac{kT}{E_f}$

Thus, the electronic specific heat is a fraction of the value predicted by the CFET (since $\frac{kT}{E_f}$ is a fraction less than 1% for most metals) and is temperature dependent. This analysis gives the correct correlation with the experimental results.

A more accurate evaluation of the electronic specific heat of mono valent metals (using the ideas of the number of electrons in the levels above E_f and their average energy values) results in the relation $C_{el} = \frac{\pi^2}{2} N * \frac{k_B^2 T}{E_f}$

Temperature dependence of resistivity

According to the classical free electron theory resistivity of the electrons originates from the scattering mechanism in which the ionic centers are stationary.

The quantum free electron theory takes into account the thermal vibrations of the ionic array which accounts for the scattering of electrons. The amplitude of the random vibrations of the lattice ions is proportional to temperature. When the ions vibrate the lattice presents an effective cross-sectional area for scattering of πr^2 where r is the amplitude of vibration. But the increasing amplitude also result in an increase in the probability of electron scattering.

Thus, the mean free path λ of the electrons reduces with increasing temperature. The electron mean free path λ is inversely proportional to the scattering cross section and hence $\lambda \propto 1/T$

The expression for conductivity $\sigma = \frac{ne^2\tau}{m} = \frac{ne^2\lambda}{mv_f}$ shows that conductivity is proportional to the mean free path. Hence the conductivity will be inversely proportional to temperature or resistivity $\rho \propto T$ as is found experimentally.

Relation between electrical conductivity and thermal conductivity (Wiedemann-Franz law and Lorenz number)

From the discussions of electronic arrangement, it is obvious that the electrons close to the Fermi energy are responsible for electrical or thermal conduction and hence it should be possible to find a relation between two seeming different physical phenomena.

It is known that the thermal conductivity of the metal $K = \frac{1}{3} \cdot \frac{C}{V} \cdot V \cdot L$

Where C is the electronic specific heat given by $C_{el} = \frac{\pi^2}{2} N \cdot \frac{k_B^2 T}{E_f}$,

V the volume, v is the velocity of electrons and L the mean free path. The mean free path of electrons is given by $L = v \cdot \tau$. Taking velocity to be the Fermi velocity v_F (since most of the conduction electrons are located about the Fermi energy) the expression for the thermal conductivity can be written as

$$K = \frac{1}{3} \cdot \frac{1}{V} \cdot \frac{\pi^2}{2} N \cdot \frac{k_B^2 T}{E_f} \cdot v_F \cdot v_F \tau = \frac{\pi^2}{6} \cdot n \cdot \frac{k_B^2 T}{E_f} \cdot v_F^2 \cdot \tau.$$

where $n = \frac{N}{V}$ is the concentration of free electrons.

$$K = \frac{\pi^2}{3} \cdot n \cdot \frac{k_B^2 T}{E_f} \cdot \frac{mv_F^2}{2m} \cdot \tau = \frac{\pi^2}{3} \cdot n \cdot \frac{k_B^2 T}{m} \cdot \tau$$

The electrical conductivity of the metal is then given by $\sigma = \frac{ne^2\tau}{m}$

The ratio of the thermal conductivity to electrical conductivity can be calculated as

$$\frac{K}{\sigma} = \frac{\pi^2}{3e^2} k_B^2 T.$$

This is the Wiedemann-Franz law. It was noticed by Lorenz that the ratio $\frac{K}{\sigma T} = \frac{\pi^2}{3e^2} k_B^2$ is a constant irrespective of the metal and is called the Lorenz number.

The Lorenz number has a value = $2.4 \times 10^{-8} \text{ W}\Omega\text{K}^2$.

Short comings of quantum free electron theory

The quantum free electron theory though successful in giving correct dependencies of some of the electrical parameters and the specific heat of electrons, **was not able** to explain differences in conduction in metal, semiconductor and insulator, and the origin of the band gap in semiconductors and insulators are not explained.

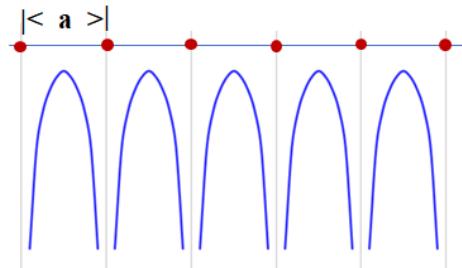
Experimentally observed positive Hall co-efficient observed in some metals like Zinc, Magnesium, lead etc.

These demerits could be reflective of the real potentials of the ionic centers in the lattice which was ignored in the development of the model. The presence of the potentials can significantly affect the wave function of the electrons.

14. Motion of electron in periodic potential (one dimensional treatment)

The free electrons in a metal are not free from electrostatic potentials and move in a periodic potential due to the regular arrangement of the ionic centers.

The potential is lower close to the positive ions in the lattice (and in some cases basis) positions. Electrons moving through the lattice experience a potential which has the same periodicity as the lattice. The columbic potential in the real crystal can be approximated by rectangular potentials.



If $V(x)$ is the potential at x then, it can be seen from the figure that $V(x + a) = V(x)$ which means that the potential is periodic and invariant under the translation through the lattice parameter.

However, the wave function of the free electrons $\Psi(x) = e^{ikx}$ is modulated by periodic potential and can be written as

$\Psi(x) = e^{ikx} \cdot V_k(x)$ where k is the wave number of the electron waves. This is known as the Bloch function.

Kronig Penny model, allowed energy zones/energy bands

In the Kronig-Penney model the periodic potential is approximated as a long chain of coupled finite square wells, of barrier height V_0 , with a period 'a', and barrier thickness c.

The wave function of the electron is a modulated wave of the form $\psi(x) = e^{ikx} \cdot V_k(x)$.

A solution to the Schrödinger's equation exists if the dispersive wave number of the electron k is related to the energy through the equation:

$$\cos(ka) = \frac{ma}{\hbar^2} V_0 \cdot c \cdot \frac{\sin(Ka)}{Ka} + \cos(Ka)$$

where $K = \sqrt{\frac{2m(E)}{\hbar^2}}$. We notice that the above is a transcendental equation and has approximate solutions.

The left-hand side of the equation is bound with upper and lower limits of +1 to -1.

The right side of the equation has oscillations of decreasing amplitude with increasing ka . However, the solutions exist only for those allowed range of $k = n\frac{\pi}{a}$. Thus, there exists a range of allowed energy states and forbidden energy states.

In the limit $\frac{ma}{\hbar^2} V_0 \cdot c$ tends to infinity $\sin(Ka) = 0$ which implies $K = \frac{n\pi}{a}$ and hence the energy $E_n = \frac{\hbar^2\pi^2}{2ma^2} n^2$.

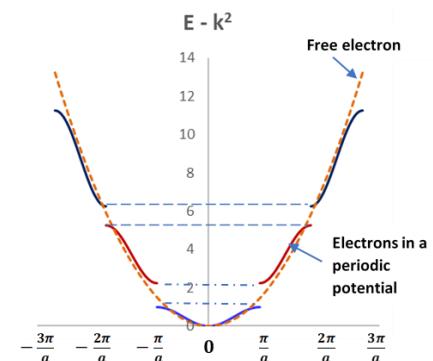
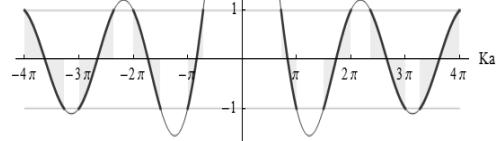
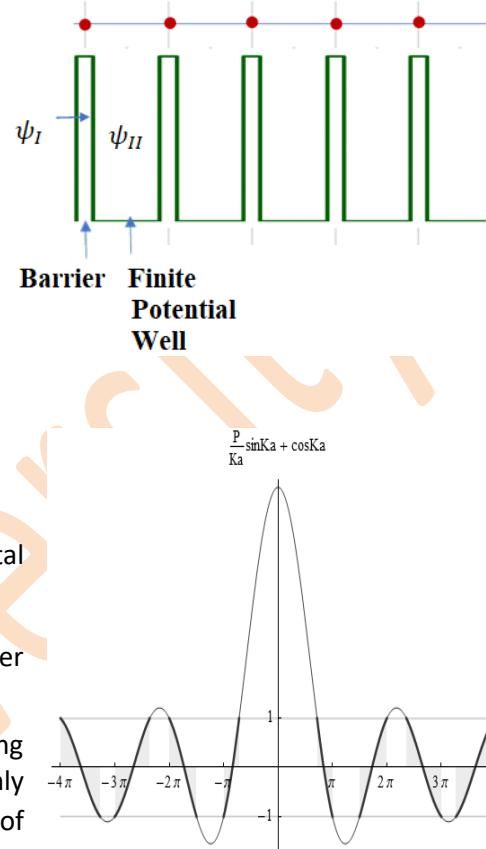
In the limit $\frac{ma}{\hbar^2} V_0 \cdot c$ tends to zero $\cos(Ka) = 1$ which implies $k = K$ and hence the energy $E = \frac{\hbar^2 K^2}{2m}$ which is the solution for a free particle.

The $E(k)$ – k diagram for the system show discontinuity in the energy at the zone boundary of $k = \pm n\frac{\pi}{a}$. (The parabolic variation of E for the free electrons is shown for comparison).

Since the functions are symmetric (and periodic with period of $2\frac{\pi}{a}$), it is possible to represent the energy band diagram in a single zone of $+\frac{\pi}{a}$ to $-\frac{\pi}{a}$.

The lowest allowed energy state is non-zero. The lowest band is the completely filled inner band followed by a band of forbidden energy states (shaded).

The next band of allowed states represents the valence band.



The upper most occupied states form the conduction band.

Thus, we observe allowed and forbidden energy states for the electrons in the material.

Materials are then classified as metals, semiconductors or insulators on the basis of the Fermi energy of the material.

In the case of conductors, the Fermi level is in the uppermost band the conduction band. All states below the Fermi level are filled and all levels above the Fermi energy are empty. Thus, metal are characterized by a partially filled conduction band.

In the case of materials with a completely filled valence band and completely empty conduction band, the Fermi energy is theoretically the midpoint of the energy band gaps. Materials with energy gap of 3-5 eV are classified as semiconductors. At normal temperatures it is possible for the electrons in the valence band to move into the conduction in the case of metals and semiconductors.

Materials with energy band gap greater than 5eV are classified as Insulators in which the electron conduction is impossible and attempts to excite the electrons lead to a dielectric breakdown.

Concept of Effective mass

The motion of electrons in the crystal is governed by the energy equation $E = \frac{\hbar^2 k^2}{2m}$ which shows that the energy is nonlinearly dependent on the propagation constant k .

Differentiating the expression twice with respect to k

$$\frac{d^2E}{dk^2} = \frac{\hbar^2}{m^*}$$

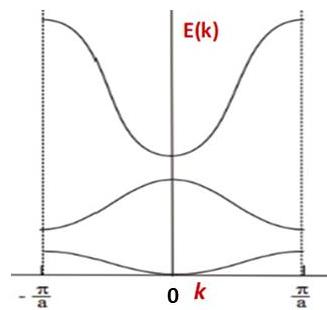
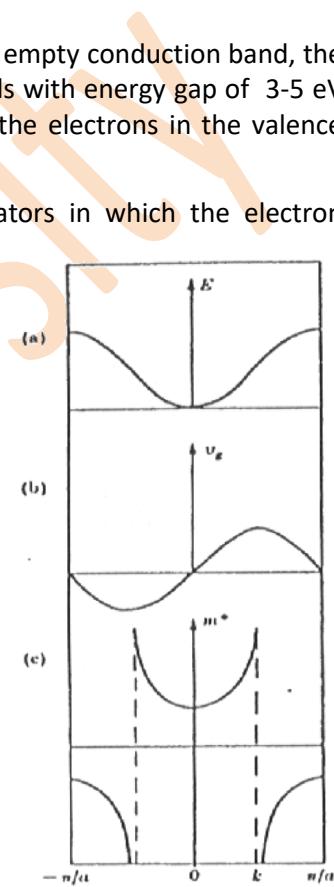
it is observed that $m^* = \left(\frac{1}{\hbar^2} \frac{d^2E}{dk^2}\right)^{-1}$ is not a constant and depends on the nonlinearity of E . This means that the charge carriers have an effective mass which depends on the curvature of $E-k$.

Higher curvature (larger $\frac{d^2E}{dk^2}$) means smaller effective mass and smaller curvature results in higher effective mass.

It can be seen that the slope of the E-K curve is minimum at the band edges and hence the effective mass of the charge carriers are highest at the band edges.

Since curvature of the $E-k$ is positive in the conduction band the effective mass is +ve and the curvature in the valence band is negative indicating a negative mass. However, this can be construed to be the motion of a charge carrier with a charge of the opposite type as that of electrons. This leads to the concept of hole conduction in the valence band. The effective mass of electrons can be higher or lower than the rest mass of the electrons and depends on the position of the electron in the particular band.

The concept of the effective mass helps understand the mobility of charge carriers in a system particularly in semiconductors. In most compound semiconductors the effective mass of electrons and holes are much smaller than the rest mass of electrons. These materials exhibit a higher mobility of charge carriers.



Quantum treatment of Magnetism

1. Introduction to Magnetic Materials

Every material when placed in an external magnetic field H responds in different magnitudes and different ways. Some materials get magnetized either temporarily or permanently, others do not get magnetized but repulse the external magnetic fields. Materials are classified according to the magnetization state of the material.

The intensity of magnetization (M) of a material is defined as the dipole moment per unit volume of the material.

$$M = \frac{m * 2l}{2l * a} = \frac{m}{a}$$
 which is the dipole strength per unit area of cross section.

*The first truly scientific study of magnetism was made by the Englishman William Gilbert (1540–1603), who published his classic book *On the Magnet* in 1600. He experimented with lodestones (magnetite) and iron magnets, formed a clear picture of the Earth's magnetic field, and cleared away many superstitions that had clouded the subject. From his experiments, he concluded that the Earth was itself magnetic and that this was the reason compasses pointed north (previously, some believed that it was the pole star (Polaris) or a large magnetic island on the north pole that attracted the compass).*

The existence of isolated magnetic poles, or monopoles, is not forbidden by any known law of nature, and serious efforts to find monopoles have been made [P. A. M. Dirac, Proc. R. Soc. Lond., A133 (1931) p. 60; H. Jeon and M. J. Longo, Phys. Rev. Lett., 75 (1995) pp. 1443–1446]. The search has not so far been successful.

$$\text{The magnetization of the material } M = \chi_m H$$

where the magnetic susceptibility χ_m of the material is the ratio of the magnetization B to the magnetic field H ie., $\chi_m = \frac{M}{H}$

Consider a long solenoid of length l with air as the core and having n turns. The magnetic field strength when a current I flows through the solenoid $H = \frac{nI}{l}$ A/m.

$$\text{The magnetic flux density } B_o = \mu_0 H \quad \text{Tesla (Wb /m}^2\text{)}$$

$$\text{Where } \mu_0 = 4\pi \times 10^{-7} \text{ H/m or } (4\pi \times 10^{-7} \text{ TmA}^{-1})$$

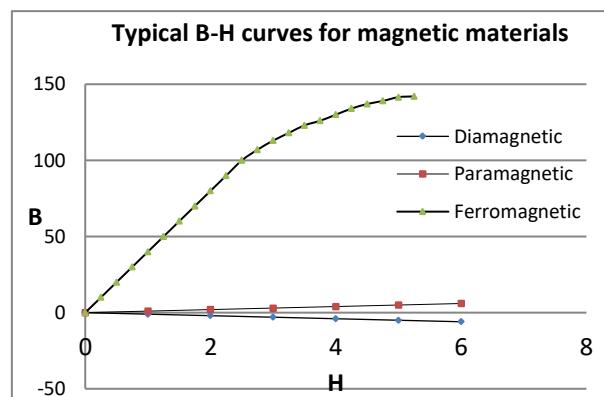
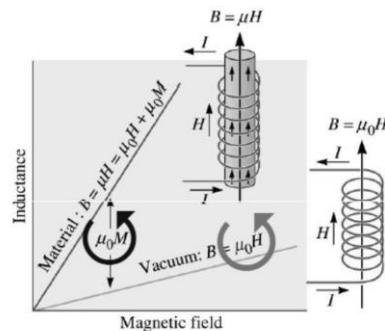
When a material of susceptibility χ_m is introduced inside the solenoid the total magnetic flux of the system is the sum of the flux due to the coil and the flux due to the magnetization of the material.

$$\begin{aligned} B &= \mu_0 H + \mu_0 M = \mu_0 (H + M) = \mu_0 (H + \chi_m H) \\ &= \mu_0 (1 + \chi_m) H \end{aligned}$$

Defining the relative permeability of the material $\mu_r = (1 + \chi_m)$

The magnetic flux density $B = \mu_0 \mu_r H = \mu H$, where $\mu = \mu_0 \mu_r$ is the permeability of the material.

Magnetic materials can be classified on their susceptibility to be magnetized by an external



magnetic field and on their relative permeability.

Materials with susceptibilities less than 0 (χ_m negative) are classified as diamagnetic materials. They tend to repel the lines of force of the external magnetic field. The diamagnetic susceptibilities are in the range of -10^{-3} to -10^{-6} . Diamagnetic materials possess a relative permeability less than 1.

Materials with a small positive susceptibility >0 (χ_m positive) are classified as paramagnetic materials. Paramagnetic materials tend to show feeble magnetization in the presence of an external field. The susceptibility of the material is of the order of 10^{-4} to 10^{-5} and relative permeability is slightly more than 1.

Materials with a large positive susceptibility $>>0$ (χ_m positive and large) are classified as ferromagnetic materials. Ferromagnetic materials are easily magnetized in the presence of an external magnetic field and exhibit a large relative permeability of the order of 10^5 - 10^6 .

2. Origin of Magnetism in materials

Any current loop creates a magnetic field with the direction of the current deciding the direction of the field. It is imperative that the atomic level currents due to the electrons in the orbits could result in magnetic fields. The spin of the electrons can also be one of the major contributors to the magnetization in materials. In addition, there is also a feeble contribution from the nuclei as well which could be neglected for all practical evaluations. The net contribution from an atom to the magnetization would depend on the magnitudes of the individual components and the statistical behavior of the collection of atoms would decide the magnetic susceptibility of the material.

The basic atomic model of orbiting electrons around the nucleus constitutes tiny current loops at atomic levels. If the electrons are assumed to move in an orbit of radius r with a constant speed v , the period of rotation T , then the current $I = \frac{e}{T} = \frac{e\omega}{2\pi} = \frac{ev}{2\pi r}$

The magnetic moment associated with the electron's moment in the orbit

$$\mu_e = I \cdot A = I * \pi r^2 = \frac{ev}{2\pi r} \pi r^2 = \frac{1}{2} evr = \frac{1}{2} e\omega r^2$$

The angular momentum of the orbiting electron $L = m_e vr$ and the magnetic moment can be written as

$$\mu_{\text{orb}} = \left(\frac{e}{2m_e}\right) L$$

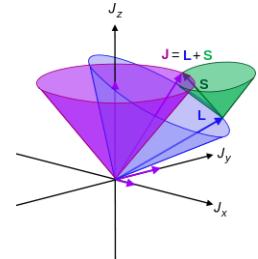
Thus, the magnetic moment of the electron is proportional to its angular momentum. The ratio of the magnetic moment to the angular momentum $\gamma = \frac{\mu_{\text{orb}}}{L} = \left(\frac{e}{2m_e}\right)$ is known as the gyro magnetic ratio.

Due to the negative charge of the electron, the vectors $\vec{\mu}$ and \vec{L} point in opposite directions and are perpendicular to the plane of the orbit. The angular momentum of the electron is a multiple of \hbar (quantum mechanical concepts).

The magnetic effect of the orbital motion of the electron is either zero or very small because of the cancellation of the magnetic moments of electrons orbiting in opposite directions.

Apart from the orbital magnetic moments, electrons have the property of spin and a spin angular momentum \vec{S} associated with it. \vec{S} is of the same order as the angular momentum \vec{L} .

The magnetic moment due to the spin of the electrons is almost twice that of the orbital movement and the contribution from the spin to the magnetic moment can be written as $\mu_{\text{spin}} = \sqrt{s(s+1)} \frac{e\hbar}{2m}$.



The total magnetic moment of an atom is the vector sum of orbital and spins magnetic moments.

The net magnetic moment due to electrons

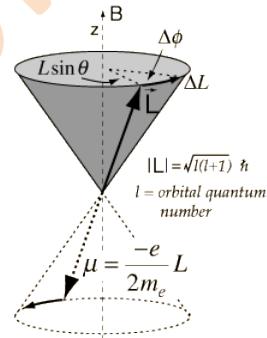
$$\mu_e = g_e \frac{e\hbar}{2m}$$

where g_e is the Lande g factor (spectroscopic splitting factor of the energy levels) given by $g_e = 1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$

From this the smallest non zero value of the spin magnetic moment due to electrons (when $s=j$ and $l=0$) is obtained as $\mu_s = \frac{e\hbar}{m}$

This is twice the orbital magnetic moment and hence determines the susceptibility of materials. The magnetic moment being quantized; the smallest unit of magnetic moment $\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T}$ is called the Bohr magneton.

The magnetic moments of protons and neutrons are much smaller than the electron magnetic moment and are usually neglected.



3. Larmor precession

A magnetic moment directed at some finite angle with respect to the applied magnetic field direction, experiences a torque $\mu \times B$. This causes μ to precess (rotate) the magnetic field direction. (This is analogous to the precession of a spinning top around the gravity field.)

For static magnetic moments or classical current loops, the torque tends to line up the magnetic moments with the magnetic field B , so this represents its lowest energy configuration.

In the case of an electron in orbit around a nucleus, the magnetic moment is proportional to the angular momentum of the electron. The torque exerted the external field produces a change in angular momentum which is perpendicular to that angular momentum, causing the magnetic moment to precess around the direction of the magnetic field rather than settle down in the direction of the magnetic field. This is called Larmor precession.

When a torque is exerted perpendicular to the angular momentum L , it produces a change in angular momentum ΔL which is perpendicular to L , causing it to precess about the z axis. The effect of the torque as follows:

$$\tau = \mu \times B = |\mu B \sin \theta| = \frac{\Delta L}{\Delta t} = \frac{L \sin \theta \Delta \phi}{\Delta t} = L \sin \theta \omega_L$$

The precession angular velocity (Larmor frequency) is given by $\frac{d\phi}{dt} = \omega_L = \frac{e}{2m_e} B$ since $\frac{\mu}{L} = \left(\frac{e}{2m_e}\right)$.

The Larmor frequency forms the basis for magnetic resonance.

The Larmor precession frequency for electrons is 14GHz/ T which forms the basis of the electron spin resonance.

The Larmor precession frequency for protons is 7.8 MHz/ T which forms the basis of the Nuclear magnetic resonance.

Thus, the magnetic moment due to a precessing charge can be evaluated as

$\mu_{ind} = \frac{1}{2} e\omega r^2 = \frac{Be^2r^2}{4m}$ where r is the radius of the precessing orbit. The sign of this induced magnetic moment is negative by Lenz's law (it opposes the magnetic field that induced the precession).

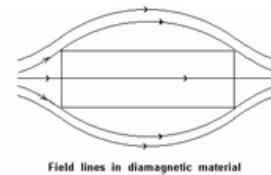
If there are N_a number of atoms per unit volume and each atom contains Z electrons we can estimate the total induced magnetisation as $M = N_a Z \mu_{ind} = -\frac{N_a Ze^2 \langle \rho^2 \rangle B}{4m} = -\frac{N_a Ze^2 \langle \rho^2 \rangle \mu_0 H}{4m}$

Hence the induced susceptibility $\chi_m = \frac{M}{H} = -\frac{N_a Ze^2 \langle \rho^2 \rangle \mu_0}{4m}$.

This will yield an extremely small negative value of the order of 10^{-5} for most materials and is recognized as the diamagnetic response of all materials.

4. Diamagnetic materials

Diamagnetism is a property due to which certain materials are repelled by both poles of a magnet. When a short rod of diamagnetic material is placed in a magnetic field, it aligns itself at right angles to or across the direction of the magnetic lines of force. The meaning of term "diamagnetic" in Greek is "across magnetic".



The orbital motion of electrons is equivalent to tiny atomic-current loops, producing magnetic fields. In most materials, the magnetic fields of orbiting electrons balance each other and add up to zero in the absence of an external field. However, in the presence of an external magnetic field, the interaction of external field with the electrons induces an internal field which tends to align the current loops in a direction opposite to the applied field.

This effect on the atomic scale is similar to that due to Lenz's law - induced magnetic fields tend to oppose the change which created them. If magnetic response is only due to these phenomena, then the material is classified as diamagnetic. Diamagnetism is exhibited by a substance only in the presence of an externally applied magnetic field.

Atoms with closed electronic shells and sub shells are diamagnetic (-ve χ_m and $\mu_r < 1$). The classical expression for diamagnetic susceptibility is

$$\chi_{dia} = -\frac{Ne^2\mu_0}{6m} \langle r^2 \rangle$$

where N is the number of atoms per unit volume and $\langle r^2 \rangle$ is the average value of the square of the radius of the current loops. The above expression for susceptibility shows that the diamagnetic susceptibility is temperature independent.

All materials have inherent diamagnetism. Diamagnetism is detectable and observable only with sensitive instruments and in the presence of powerful magnets. Examples of diamagnetic substances include water, wood, sodium chloride, most organic compounds such as petroleum, some plastics, and many metals including copper, particularly the heavy metals with many core electrons, such as mercury, gold, bismuth and antimony. Most substances usually considered nonmagnetic may be strictly called diamagnetic.

Pierre Curie (1859–1906) was a French physicist who worked extensively on magnetic materials. He and his wife, Marie (Skłodowska) Curie (1867–1934), later became famous for their research on radioactivity.

The volume magnetic susceptibility of water is $= -9.05 \times 10^{-6}$

Bismuth, the most strongly diamagnetic material has $= -1.66 \times 10^{-4}$.

However, superconductors show strong diamagnetic effect (and offer no resistance **to** the formation of the current loops and conduction of electricity). Lines of external magnetic flux are expelled entirely from the material due to the strong diamagnetic behavior of these systems. These materials are used in creating strong repulsive magnetic fields which are used in levitation experiments / applications.

5. Para magnetism

Paramagnetic materials are weakly attracted by magnetic fields. When a small rod of paramagnetic material is placed in a magnetic field, it aligns with or alongside the lines of force. The term paramagnetic is derived from a Greek word meaning “alongside magnetic”.

Para magnetism is a characteristic of materials with partially filled 3d shells, where Hund’s rule restricts the anti-parallel alignment resulting in the net spin magnetic moment for the atoms.

Materials with unpaired electron spins in the atomic / molecular orbitals have permanent magnetic dipoles even in the absence of an applied field. These dipoles are randomly oriented and do not interact with one another. The thermal energy of the system being greater than the magnetic energy $k_B T > \mu \cdot B$, the thermal agitation result in random ordering and a net zero magnetic moment.



In the presence of an external magnetic field these dipoles tend to align to the applied direction leading to a net magnetic moment in the direction of the applied field. The induced magnetization is weak and linearly dependent on the applied magnetic field. When the magnetic field is removed, the dipoles relax back to their normal random orientation, and the magnetization becomes zero. Aluminum, Oxygen, titanium, FeO are examples of materials which are weakly magnetized and are attracted by a magnetic field.

6. Quantum theory of Paramagnetic materials (solids).

Some of the features of the quantum theory of Para magnetism are:

The magnetic dipoles of a molecule / atom /ion in a material can be written as

$$\mu = g\mu_B m_j$$

where g_e is the Lande g factor and μ_B is the Bohr magneton. In an external magnetic field B the dipoles are allowed only certain fixed orientations of the total angular momentum J and described by M_J .

For a given J (the total angular momentum) the allowed orientations are $2j+1$ ($j, j-1, j-2, \dots, 0, \dots, -j$)

and the energy of interaction with an external magnetic field B is given by

$$E_j = \mu \cdot B = g\mu_B m_j \cdot B = g\mu_0 \mu_B H m_j$$

For a material with N dipoles per unit volume, the net magnetization is the statistical average of the allowed m_j orientations and is given by

$$M = N \left[\frac{\sum_{-j}^{+j} m_j g \mu_B * \exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)}{\sum \exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)} \right] \quad \text{eqn. 1.0}$$

Clearly the magnetization will depend on the value of the exponent $\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)$.

Case 1: If $m_j g \mu_0 \mu_B H \ll kT$ i.e. the thermal energy is significantly higher (high temperatures) than the magnetic interaction energy with field, the ratio will be much less than 1.

Expanding the exponential terms as a power series and simplifying the terms the net magnetization

$$M = Ng\mu_B * \frac{g\mu_0 \mu_B H}{KT} \frac{j(j+1)}{3} = \frac{Ng^2 \mu_0 \mu_B^2 H}{KT} \frac{j(j+1)}{3}$$

The magnetic susceptibility $\chi = \frac{M}{H} = \frac{Ng^2\mu_0\mu_B^2}{KT} \frac{j(j+1)}{3} = \frac{C}{T}$ which is the classical Curie's law of

$$\left\{ \begin{array}{l} \text{Simplification of the expression} \left[\frac{\sum_{-j}^{+j} m_j g \mu_B * \exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)}{\sum \exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)} \right] \end{array} \right.$$

$$\text{Let } \exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right) = \exp^{m_j x}, \text{ then the expression simplifies to} \frac{\sum_{-j}^{+j} m_j * \exp(m_j x)}{\sum \exp(m_j x)}$$

Since the exponent is small we can expand the exponential term as a series (summation neglecting the higher order term in x , $\frac{\sum_{-j}^{+j} m_j (1 + m_j x)}{\sum (1 + m_j x)} = \frac{\sum_{-j}^{+j} m_j + \sum_{-j}^{+j} m_j^2 x}{\sum_{-j}^{+j} 1 + \sum_{-j}^{+j} m_j x}$

m_j can take values from $-j$ to $=j$ including 0 and x is independent of j and hence

$$\sum_{-j}^{+j} m_j = j + (j - 1) + \dots + 1 + 0 - 1 - 2 \dots - (j - 1) - j = 0$$

$$\sum_{-j}^{+j} m_j^2 = 2 \times [1^2 + 2^2 + \dots + (j - 1)^2 + (j)^2] = 2 \times \frac{j(j+1)(2j+1)}{6} = \frac{j(j+1)(2j+1)}{3}$$

$$\sum_{-j}^{+j} 1 = 2j + 1$$

$$\text{Hence } \frac{\sum_{-j}^{+j} m_j (1 + m_j x)}{\sum (1 + m_j x)} = \frac{0 + \frac{j(j+1)(2j+1)}{3}x}{(2j+1)+0} = x \frac{j(j+1)}{3} \quad \left. \right\}$$

paramagnetic materials where the Curie constant $C = \frac{Ng^2\mu_0\mu_B^2}{K} \frac{j(j+1)}{3}$.

Paramagnetic susceptibility is thus inversely proportional to the absolute temperature.

Curie's law is obeyed under generally prevailing conditions of low magnetization ($\mu H < k_B T$), i.e., when only a relatively small fraction of atomic dipoles are aligned, with the magnetic field. Curie's law indicates that Magnetization M depends on the applied field H (the stronger magnetic field aligns more dipoles) and the susceptibility χ . However, χ is inversely proportional to the temperature i.e., the magnetization decreases if the temperature is increased (increased thermal agitation prevents alignment of dipoles).

Case 2: If $m_j g \mu_0 \mu_B H \gg KT$ i.e. the magnetic interaction energy is much greater than the thermal energy the exponent will be greater than 1.

Equation 1 can be written as

$$M = Ng\mu_B \left[\frac{\sum_{-j}^j m_j * \exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)}{\exp\left(\frac{m_j g \mu_0 \mu_B H}{kT}\right)} \right] = Ng\mu_B \frac{\sum_{-j}^j m_j * \exp(m_j x)}{\sum \exp(m_j x)} \text{ where } x = \frac{g\mu_0\mu_B H}{kT}$$

This can be simplified by taking $a = xj$ to

$$M = Ng\mu_B j \left[\frac{2j+1}{2j} \coth \left(\frac{2j+1}{2j} a \right) - \frac{1}{2j} \coth \left(\frac{a}{2j} \right) \right] = Ng\mu_B j \cdot B_j(a)$$

where $B_j(a) = \left[\frac{2j+1}{2j} \coth \left(\frac{2j+1}{2j} a \right) - \frac{1}{2j} \coth \left(\frac{a}{2j} \right) \right]$ is the **Brillouin function** which describes the probability of all the dipoles to orienting in the direction of the external field.

When the dipoles are aligned completely in the direction of the external field, the magnetization of the material is saturated, and the saturation magnetization is given by $M_s = Ng\mu_B j$.

Hence the magnetization can be written as $M = M_s B_j(a)$.

When $j = \frac{1}{2}$ the Brillouin function reduces to $\tanh(a)$.

The limit of large j the Brillouin function converges to the classical Langevin's function $L(a) = \coth(a) - \frac{1}{a}$.

[$L(a)$ can be written as a series expansion in a as $\frac{a}{3} - \frac{a^3}{45} + \frac{2a^5}{945} - \dots$. For small values of a , the function then converges to $\frac{a}{3}$.]

For small values of a (large values of T) the magnetization reduces to $M = M_s \frac{a}{3}$ and the susceptibility is given by $\chi = \frac{Ng^2 \mu_0 \mu_B^2}{3KT}$ which is like the Curie's theory of Paramagnetism.

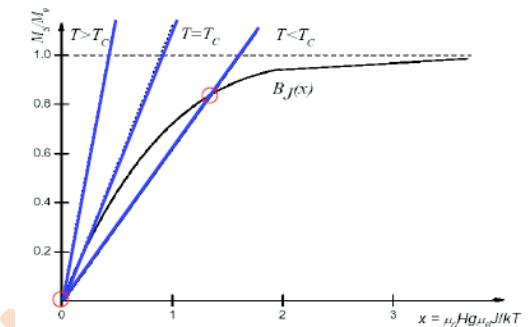
The variation of $\frac{M}{M_s}$ is represented in the figure for three different cases of the temperature (as compared to T_c the curie temperature of the material)

Examples of paramagnetic materials at room temperature include Aluminum (Al), Manganese (Mn), platinum (Pt), Oxygen (gas and liquid), and rare earth ions Ce, Nd.

7. Weiss Molecular field concept.

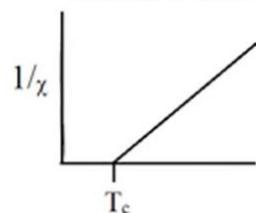
The variation of $\frac{1}{\chi}$ vs T is expected to be a straight line passing through the origin. However, some materials show a variation in this behaviour with the straight line showing a positive intercept T_c on the temperature axis.

Weiss in 1907 showed that this could be due to a molecular field which is the field at any point due to the neighbouring dipoles. If M is the magnetization in the material, then the magnetic field at any point is proportional to M and hence the field at any point in the material could have an additional contribution = λM . This field has the tendency to align the dipoles in the direction of the field and hence it would be a case of spontaneous magnetisation. Therefore, the Curie's law is modified as $\frac{M}{H+\lambda M} = \frac{C}{T}$ which gives us $\chi = \frac{C}{T-T_c}$ where $T_c =$



Pierre Weiss (1865–1940), French physicist deserves to be called the “Father of Modern Magnetism” because almost the whole theory of ferromagnetism is due to him, and his ideas also permeate the theory of ferrimagnetism. Most of his work was done at the University of Strasbourg.

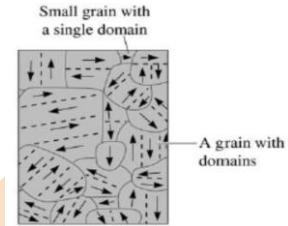
Ferromagnet (Fe) or Ferrimagnet (Fe_3O_4)



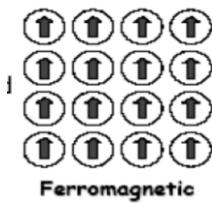
λC is the Curie temperature above which the materials show the paramagnetic behaviour. Below T_c the material behaves as a ferromagnetic material. However, most of the common materials have a low T_c and hence at normal temperatures does not show spontaneous magnetization.

8. Ferromagnetism

Ferromagnetism is the property by which certain materials are attracted by a magnet and form permanent magnets. Ferromagnetic materials have very high magnetic susceptibilities, ranging from 1000 up to 100,000. The ferromagnetic behavior can be explained by the formation of domains of spins ordered in the immediate neighborhood. The formation of domains to minimize the total energy of the ferromagnetic material.



Consider a material consisting of a single domain (i.e., all of it is magnetized in the same direction). The magnetization changes discontinuously at the surfaces, forming free poles. These poles are sources of a magnetic field (called the *demagnetization field*) that fills all of space. The energy associated with this field, called magnetostatic or demagnetization energy, is proportional to the square of magnetization. Thus, for a single domain with a large magnetization, the magnetostatic energy is large. This energy can be reduced by the formation of domains. Domains form in such a way that opposite poles are close to each other thereby confining the path of the flux lines and reducing the net magnetization to a value close to zero.



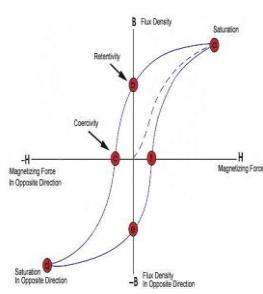
$$T < T_c \quad H = 0, \quad M \neq 0$$

Ferromagnetic materials exhibit spontaneous magnetization and exhibit sharp hysteresis characteristics in the magnetization versus magnetizing field. Ferromagnetism can be considered as a case of a Paramagnetic material with a high molecular field constant λ and a very high T_c .

The local molecular field can result in a high ordering of spins in certain materials like Fe, Co, Ni etc, result in the materials being easily magnetized).

The presence of unpaired spins in the 3d shells of these materials gives a large dipole moment for the atom. (Cobalt has a $T_c > 1000K$, Fe has a $T_c > 750K$ and Ni has a $T_c > 350K$)

In Ferromagnetic materials when an external magnetic field is applied the magnetic moments are aligned in the direction of the applied field and domains grow at the expense of their neighbours. Microscopic regions in which large numbers of dipoles are aligned are called magnetic domains. The unpaired electron spins to line up parallel with each other. This quantum mechanical interaction at the atomic level gives rise to long range order and creates magnetic domains. The alignment directions of the individual regions are random throughout the material. Hence the bulk of the material is usually unmagnetized or weakly magnetized in the absence of magnetic field.



The magnetization of the material in the presence of an external magnetic field tends to exhibit classic M-H hysteresis. When the external field is strong and all the spins are aligned the magnetization shows a saturation value. When the external field is removed, sizable number of dipoles still maintains the alignment resulting in

a net magnetization which is the retentivity of the material. Thus, the material gets permanently magnetized. This remnant magnetization can be removed if a coercive field H_c is applied in the reverse direction. Since the material exhibits hysteresis, it is obvious that it has a memory of the previous experience of external fields and hence can be used as memory materials. The flipping of the magnetization in opposite directions is achieved by applying a saturation magnetization field H_s in the appropriate direction.

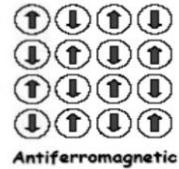
All ferromagnets have a maximum temperature at which the thermal motion of the dipoles becomes violent, the alignment of dipole moments and spontaneous magnetization cannot be maintained. Phase change from ferromagnetic to paramagnetic behaviour with the usual weak magnetization occurs. This critical temperature is called Curie temperature. The magnetic susceptibility above the Curie temperature is given by $\chi = \frac{C}{T-\theta}$ where θ is the transition temperature constant.

Ferromagnetic materials can be characterized by their Curie temperature in addition to their Permeability, Coercive field and Remnant Magnetization.

Apart from iron, other materials exhibiting ferromagnetic property are nickel, cobalt, some of the rare earths gadolinium, dysprosium, samarium and neodymium in alloys with cobalt. They have important applications in fabrication of magnets, electromagnets, transformers; magnetic storage media e.g. tape recording, computer hard disks etc.

9. Anti-ferro magnetic materials

The magnetization of a material also depends on the type of ordering that exist in some of the ordered materials. In the case of ferro magnetic materials it is seen that there is a long-range ordering of the magnetic dipoles that lead to strong magnetization.

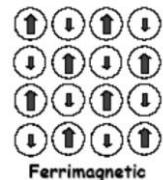


$$T < T_N \quad H = 0 \quad M = 0$$

The class of anti-ferro magnetic materials such as MnO, NiO, CoO etc in which the electron spins associated with the atoms at different crystallographic sites are ordered such that the net magnetization of the material is zero below a certain temperature called the Neel temperature T_N . Above the Neel temperature the materials behave as paramagnetic with the magnetic susceptibility inversely proportional to temperature.

10. Ferri magnetic materials

Ferri magnetic materials are a class of ordered structures in which the magnetic moments at crystal sites are anti parallel and unequal. These materials are treated as two sub lattices of a crystal with different magnetic moments and anti-parallel alignments. Generally, these materials contain cations of two or more types with different magnetic moments and hence show a net magnetization not equal to zero. Examples of such materials are NiFe_2O_4 , CoFe_3O_4 , and $\text{BaFe}_{12}\text{O}_{19}$ etc.

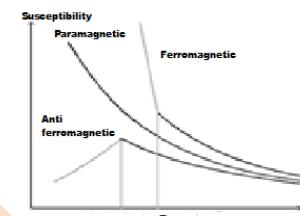


$$T < T_c \quad H = 0 \quad M \neq 0$$

Ferri magnetic materials like ferro magnetic materials show significant magnetization below the transition temperatures. Above T_c the materials display paramagnetic behaviour.

11. Magnetic susceptibility vs temperature

The temperature dependence of the susceptibility for the Para, Ferro and anti-ferro magnetic materials are summarized as shown. For paramagnetic materials the susceptibility χ_m varies monotonically as $1/T$ following the Curie's law.

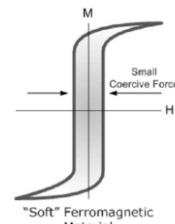


Ferromagnetic materials follow the Curie Weiss law and exhibit a paramagnetic behavior above the Curie temperature.

Anti-ferromagnetic materials show an increase in susceptibility till the Neel temperature above which the material behaves as a paramagnetic material.

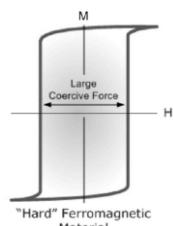
12. Soft and Hard Magnetic materials

Ferromagnetic materials can be classified as soft and hard materials depending on the nature of the hysteresis displayed by the material.



Soft magnetic materials are easily magnetisable and de-magnetisable. They are characterized by small coercivity and large saturation magnetization. The hysteresis loop is narrow and has low losses.

Soft magnetic materials find application in high frequency switching of magnetization and are used in transformers, motors and generators.

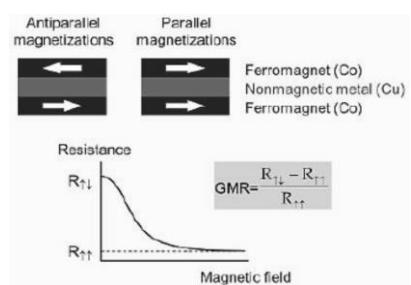


Hard magnetic materials on the other hand are difficult to magnetize and demagnetise. They exhibit very high retentivity and require a large coercive field to demagnetise the material. The area under the hysteresis curve is large, indicating the large amount of energy loss.

The high retentivity of the material makes it ideal for magnetic storage of information as in hard disk drives. The current capabilities are close to 1 Terra bits per square inch.

13. Giant Magneto Resistance device.

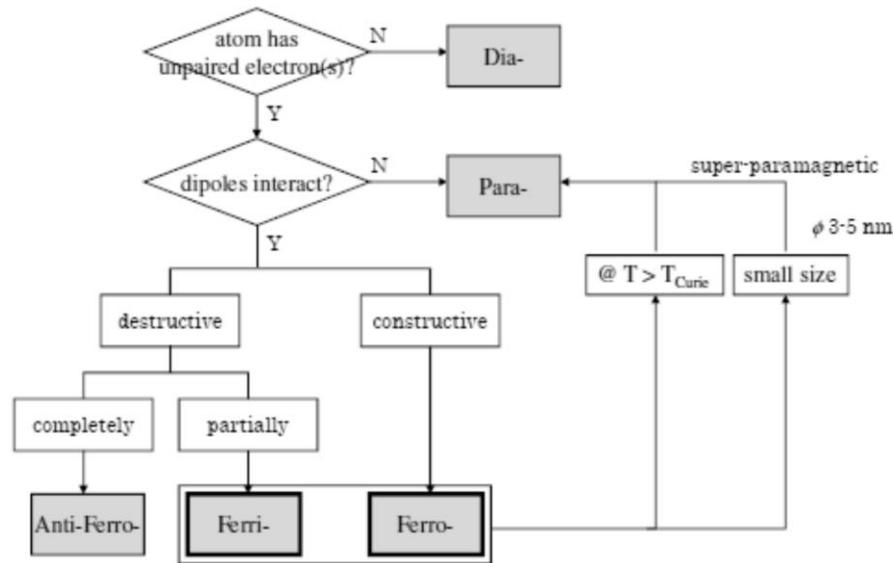
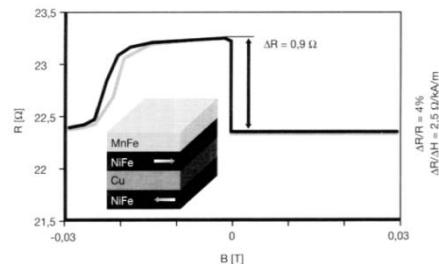
Magneto resistance has been observed in layered magnetic materials where the resistance across the thickness of two magnetic layers (generally Cobalt) separated by a non-magnetic layer (generally Copper) shows a dependence on the magnetization states of the individual layers. Resistance to current flow depends on the direction of magnetization of the two layers and can show large variations in the resistance. The effect has been attributed to the spin scattering of the electrons when they flow through the



material. Electron scattering is reduced when the magnetization of the two layers is parallel leading to a low resistance state. When the spin states of the two layers are anti parallel the electron scattering is increased and hence the resistance increases.

When the magnetic layers are in the range of 3 – 5nm with the separation layer about 25nm, it has been observed that the change in resistance can be as high as 50% of which is significant for any practical measurements and applications.

The Giant Magneto Resistor finds application in the read head of magnetic memories. One of the ferromagnetic layers is pinned to an anti-ferro magnetic material and the other (soft magnetic material) free layer's spin orientation is flipped by the magnetization of the domain (hard magnetic material) on the recording media.



14. General classification of magnetic materials

A general scheme for classifying materials according to the atomic characteristics is represented.

PES University

Superconductivity

Superconductivity was first discovered by H. Kammerlingh Onnes in 1911 while studying the resistivity of Mercury. He observed that if Mercury is cooled below 4.1K its electrical resistance falls by a factor of 10^6 . This drastic increase in the conductivity of certain metals has been termed superconductivity. The temperature at which the conductivity of the metal increases sharply is known as the transition temperature T_c . About 30 metals exhibit superconductivity, with superconducting transition temperatures between 0K and 9.3K.

Some of the key observations about superconductors are:

- Superconductivity is not observed in Mono valent metals
- The phenomena is exhibited by metals for which the valence electrons number are between 2 & 6.
- Metals which are highly resistive at normal temperatures show superconductivity at very low temperatures.
- The current in the super conductor persists for a long time of the order of 10^5 years.
- Superconductivity is destroyed by a high magnetic field or excessive currents through the superconductor.
- Ferromagnetic and anti-ferromagnetic materials are not superconductors

Meissner effect.

A superconducting material when subjected to a magnetic field and cooled to temperatures below the critical temperatures, it expels the magnetic lines of flux from its interior. The material then behaves as a perfect diamagnetic. This effect is called the Meissner effect.

When the material is in the normal conducting state, it allows the magnetic lines of force to pass through the material.

Critical Field

A critical temperature T_c of superconducting material is dependent on the strength of the external magnetic fields. The presence of a strong external field drives the material into the normal conducting state. The strength of the magnetic field at which the material loses its superconducting state is known as the Critical Field H_c . The critical field strength is temperature dependent and is related to the Critical temperature by the relation

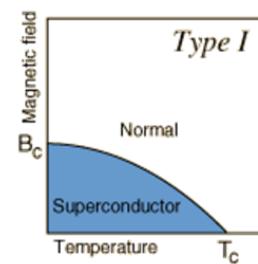
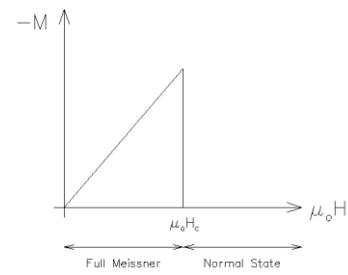
$$H_{c(T)} = H_{c(0)} \left[1 - \left(\frac{T}{T_c} \right)^2 \right]$$

Type I and type II superconductors

Superconductors are classified into two major categories as type I and type II superconductors based on the Meissner effect exhibited by the material.

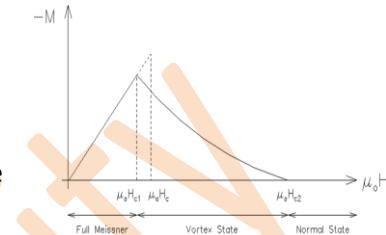
Type I superconductors are generally pure metals which behave like a perfect diamagnetic material in the superconducting state (exhibiting a complete Meissner effect).

In the case of type I superconductors the critical temperature is dependent on



the magnitude of an applied external magnetic field. Higher magnetic fields lower the critical field at which the material remains as a super conductor as shown.

External fields tend to induce an opposing magnetization in superconducting materials like diamagnetic materials. In the superconducting state, the induced negative magnetic moment of the material increases with the applied external magnetic fields. At the critical magnetic field, the material loses diamagnetic behavior, and the net magnetic moment falls to zero. The critical magnetic field strength for Type I superconductors is low. Type I superconductors are also known as soft superconductors.

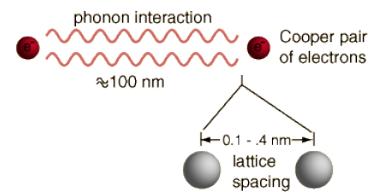


Type II superconductors are generally alloys of different metals. They were found to have much higher critical fields and therefore could carry much higher current densities while remaining in the superconducting state.

External magnetic fields induce magnetization of the material in the superconducting state and remain in the normal superconducting state up to a critical field H_{c1} . As the field is increased further, it is observed that the material partially allows the magnetic lines of force to penetrate the material, indicating the simultaneous presence of normal and superconducting states in the material up to a second critical field H_{c2} beyond which the material reverts to its normal conducting states.

BCS theory

The properties of Type I superconductors were modeled successfully by the efforts of John Bardeen, Leon Cooper, and Robert Schrieffer in what is commonly called the BCS theory. A key conceptual element in this theory is the pairing of electrons close to the Fermi level into Cooper pairs through interaction with the crystal lattice. This pairing results from a slight attraction between the electrons related to lattice vibrations; the coupling of the electrons to the lattice is called a phonon interaction.



Electron pairs behave very differently from single electrons (which are fermions and must obey the Pauli exclusion principle), whereas electron pairs act more like bosons (which can condense into the same energy level).

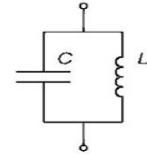
The electron pairs have slightly lower energy and hence are delicately stable. The pairs require an energy of about 0.001eV to be separated which is referred to as the energy gap for the paired state to the unpaired state.

In the paired state the charge carriers do not show the kind of collision interactions which lead to ordinary resistivity. Below the critical temperature, the system is then in an extremely low resistive state.

Bardeen, Cooper, and Schrieffer received the Nobel Prize in 1972 for the development of the theory of superconductivity.

Superconducting QUBITS

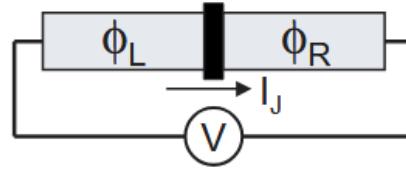
A simple LC circuit can be modelled on the ideas of a simple harmonic oscillator whose energy states are equally spaced. In the case of the LC circuit the total energy in the circuit is $\frac{1}{2}Li^2 + \frac{1}{2}CV^2$ which can be written in terms of the magnetic flux and the charges as is $H = \frac{1}{2L}\phi^2 + \frac{1}{2C}q^2$. This circuit however can be excited by the harmonic frequencies as well and is not suitable for Quantum computing circuit elements. In this case also a nonlinear element in the place of the inductor element can create the equivalent of an anharmonic oscillator, wherein the adjacent levels are going to be having slightly different excitation energies and thus one can realise the equivalent of an artificial atom.



The nonlinear element in this case can be a superconducting Josephson junction circuit element which is a superconducting current loop with a thin layer of insulating material introduced in the current path. The current continues to flow through the element despite the oxide layer, by the process of tunnelling of the Cooper pairs whose coherence length is large compared to the oxide layer thickness.

Josephson Junction as a nonlinear Inductor

A Josephson tunnel junction is formed by separating two superconducting electrodes with an insulator thin enough so that electrons can quantum-mechanically tunnel through the barrier, as shown:



The Josephson effect describes the supercurrent I_J that flows through the junction according to the classical equations

$$I_J = I_o \sin \delta \quad (1)$$

$$V = \frac{\Phi_0}{2\pi} \frac{d\delta}{dt}, \quad (2)$$

where $\Phi_0 = h/2e$ is the superconducting flux quantum, I_o is the critical-current parameter of the junction, $\delta = \phi_L - \phi_R$ and V are respectively the superconducting phase difference and voltage across the junction. The dynamical behavior of these two equations can be understood by first differentiating Eq. 1 and replacing $\frac{d\delta}{dt}$ with V according to Eq. 2

$$\frac{dI_J}{dt} = I_o \cos(\delta) \frac{2\pi}{\Phi_0} V \quad (3)$$

With $\frac{dI_J}{dt}$ proportional to V , this equation describes an inductor. By defining a Josephson inductance L_J according to the conventional definition $V = L_J \frac{dI_J}{dt}$, the inductance can be obtained as

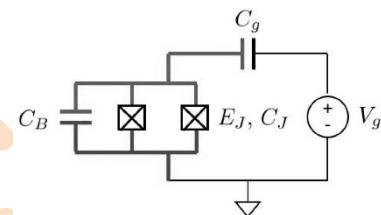
$$L_J = \frac{\Phi_0}{2\pi I_o \cos \delta} \quad . \quad (4)$$

The inductance at zero bias is $L_{J0} = \frac{\Phi_0}{2\pi I_0}$.

The $1/\cos \delta$ term reveals that this inductance is nonlinear. It becomes large as $\delta \rightarrow \pi/2$, and is negative for $\pi/2 < \delta < 3\pi/2$. The nonlinearity of the Josephson inductance breaks the degeneracy of the energy level spacings, allowing dynamics of the system to be restricted to only the two states which is essential for a qubit.

A pair of JJ in parallel with the capacitor element effectively creates what is referred to as a Cooper Pair Box, which has a pair of distinct energy states between which the switching can take place.

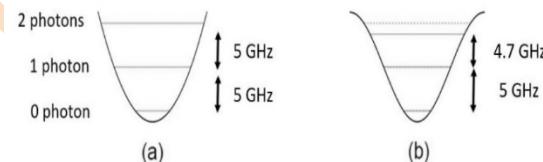
The graphical representation shows the differences in the excitation energy states of the LC oscillator and that of the CPB. Typically, a superconducting with a pair of nonlinear elements is referred to as a Transmon qubit.



The ground state and the first excited states in the transmon qubit correspond to the $|0\rangle$ and $|1\rangle$ states. The qubit excitation is achieved using microwave pulses of the precise frequency. Thus, the qubit in the $|0\rangle$ state can be excited to the $|1\rangle$ using electromagnetic energy pulses.

Transmon qubits are preferred over atomic, nuclear, molecular, spin or polarization states because of the following reasons:

- These elements are easier to fabricate and scale up to circuit level electronics
- They are noise resistant by providing sufficient isolation from the environment
- They can be controlled accurately with microwave pulses
- And easy integration of the technology with standard IC fabrication methods



Applications of Superconductivity:

Superconductors find extensive applications in a variety of fields. Some of the significant applications are:

SQUIDS which are superconducting quantum interference devices are capable of sensing extremely weak magnetic fields. They form the sensors in the MRI scanning used in the medical fields.

Strong magnets made using superconducting materials are used for magnetic levitation. Such magnets also form the core of the magnetic confinement that is required to contain plasma in fusion experiments.

Superconducting systems are potential candidates for creating QUBITs which are fundamental to creating quantum computers.

Research is on to create room temperature superconductors which can then reduce the loss of energy in power transmission.

PES University

Solved Numericals:

1. Estimate the Fermi factor of an energy state 0.01eV below the Fermi level at 500K

The Fermi factor $f_D = \frac{1}{e^{(E-E_f)/kT} + 1}$ gives the probability of occupancy of an energy state E above or below the Fermi energy at temperature T.

The Fermi factor for an energy state 0.01 eV below the Fermi level at 500 K

$$f_d = 1/(e^{((-0.01 * [1.6 \times 10] ^{-19}) / (1.38 \times 10^{-23} * 500))} + 1) = 0.558$$

2. If the Fermi energy of the metal is 3.75 eV calculate the molar specific heat at 500 K

The molar electronic specific heat is given by $C_{el} = dU/dT = 3N_a/E_f \cdot k_B^2 T$

At 500K the electronic specific heat = 0.29 J/mol

3. Determine the free electron concentration, the Fermi velocity for electrons in a metal with Fermi energy of 5.10 eV.

The concentration of free electrons in a metal is related to the Fermi energy as

$$n = \pi/3 (8m/h^2)^{3/2} \times E_f^{3/2}$$

For E=5.10eV n = $5.211 \times 10^{28} \text{ m}^{-3}$.

The Fermi velocity of electrons is given by $E_f = 1/2 m [v_f]^2$ Hence $v_f = \sqrt{(2E_f/m)} = 1.34 \times 10^6 \text{ ms}^{-1}$.

4. A mono valent metal has 5×10^{28} valence electrons per m³. Estimate the number of electron energy states per unit volume in the metal between 2eV and 2.005eV from the concept of the density of states.

The density of states for electrons in a metal gives the number of electron states per unit volume with

$$\text{energy } E \quad g(E)dE = \frac{\pi}{2} \left(\frac{8m}{h^2}\right)^{3/2} E^{1/2} dE$$

$$E = 2.00 \text{ eV} \quad dE = 0.005 \text{ eV}$$

$$\text{Hence } g(E)dE = \frac{\pi}{2} (8m/h^2)^{3/2} E^{1/2} dE = 4.80 \times 10^{25} \text{ per m}^3.$$

Problem set.

1. A certain conductor has a free electron concentration of $5.9 \times 10^{28} \text{ m}^{-3}$. What current density in the conductor will correspond to a drift velocity of $1/1.6 \text{ mm s}^{-1}$? Calculate the mobility of charge carriers given conductivity as $6.22 \times 10^7 (\Omega\text{m})^{-1}$. (Ans :)
2. Calculate the free electron concentration, mobility and drift velocity of electrons in an Al wire of diameter 0.5mm, length 5m, resistance of 60 milli ohms that carries a current of 15A . Al has 3 free electrons At wt of Al=26.98 and density $2.7 \times 10^3 \text{ kg m}^{-3}$.
3. Find the relaxation time and mobility of conduction electrons in a metal having $6.5 \times 10^{28} \text{ electrons m}^{-3}$ if the resistivity of the metal is $1.43 \times 10^{-8} \text{ ohm m}$
4. There are 10^{20} electrons per m^{-3} in a material having a resistivity of 0.1 ohm m . Find the charge mobility and the electric field needed to produce a drift velocity of 1 ms^{-1} .
5. A copper wire of radius 1mm and 10-meter length carries a direct current of 5 ampere. Calculate the drift velocity of electrons in copper if $n = 5 \times 10^{28}/\text{m}^3$.
6. Silver has a density of $10.5 \times 10^3 \text{ Kgm}^{-3}$ and atomic weight of 107.9. If the conductivity of silver at 27°C is $6.8 \times 10^7 (\text{ohm-m})^{-1}$, find the mean free path of electrons as per the classical free electron theory.
7. Calculate the relaxation time of conduction electrons in a metal of resistivity of $1.55 \times 10^{-8} \Omega - \text{m}$ and an electronic concentration of $6 \times 10^{28} \text{ per m}^3$.
8. Calculate the Fermi energy of electrons in a mono valent metal with atomic weight $132.9 \times 10^{-3} \text{ kg / mol}$ and density of $1.9 \times 10^3 \text{ kg/m}^3$ at 0K.
9. Estimate the energy for which the probability of occupation at 300K is 0.1 for copper with Fermi energy of 7.0eV. Comment on the probability of this level to be 0.5.
10. The Fermi temperature of two metals A and B are in the ratio 1.103. If the electron concentration of metal A is $5.86 \times 10^{28} \text{ m}^{-3}$, find the Fermi velocity of electrons in metal B. (Ans: $1.325 \times 10^6 \text{ ms}^{-1}$.)
11. Calculate the density of states with energy between 4eV and 4.005eV in copper with Fermi energy of 7.02eV. ($E = 4\text{eV} = 4 * 1.6 \times 10^{-19} \text{ J}$ and $dE = .005 * 1.6 \times 10^{-19} \text{ J}$ mass of electron = $9.1 \times 10^{-31} \text{ kg}$)
12. Derive an expression for the Bohr Magneton and calculate the value.
13. Discuss the concepts of Larmor precession and gyromagnetic ratio.
14. Elaborate on two tests which can differentiate a paramagnetic material from a diamagnetic material.
15. Discuss the parameters that distinguish ferro, antiferro and ferri magnetic materials.
16. Classify magnetic materials based on the magnetic susceptibility.
17. Bring out the differences between soft and hard magnetic materials.
18. Write a note on applications of magnetic materials.
19. Discuss the magnetic hysteresis of materials.
20. Discuss magnetic memory materials.
21. An electron in a hydrogen atom moves in a circular orbit of radius 0.065nm. The electron makes 10^{16} revolutions per second. Calculate the orbital magnetic moment.
22. The saturation magnetic induction of nickel is 0.65 Wbm^{-2} . If the density of nickel is 8906 kgm^{-3} and atomic weight is 514.7. Calculate the magnetic moment of nickel in Bohr magneton.