SOLID STATE PHYSICS -II

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SOLID STATE PHYSICS II

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Magnetic susceptibility – magnetic permeability – magnetization- electron spin and magnetic moment – Diamagnetism – theory of diamagnetism – Para magnetism – Langevin’s theory of paramagnetism – Weiss theory – Hund’s rule – paramagnetic susceptibility of a solid – Quantum theory of paramagnetism – cooling by adiabatic demagnetization – Determination of susceptibility of para and dia magnetic materials – theory – Guoy method- Quincke’s method.

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Ferromagnetism – spontaneous magnetization in Ferro magnetic materials – quantum theory of Ferro magnetism – Weiss molecular field – curie Weiss law – temperature dependence of spontaneous magnetization – internal field and exchange interaction – Ferromagnetic domains –

domain theory – Spin waves – Magnons – Anti Ferromagnetism – Two sublattice model – anti Ferro magnetic order and magnons – Ferromagnetism (Ferrites) – Structure of Ferrites – magnetic materials – Soft and hard magnetic matials.

Book for study and reference:

1. Introduction to Solid state physics (7th edition) by Charles Kittle
2. Solid state physics by S.O. Pillai
3. Solid state physics by A.B. Gupta and Nurul Islam
4. Solid state physics by A.J. Dekker
5. Fundamentals of Solid state physics by B.S. Saxena, R.C. Gupta and P.N. Saxena
6. Elementary Solid state physics by Ali Omar

Unit I

Semiconductor crystals and Fermi surface

1. 1 Semiconductor crystals

Semiconductors are materials which have electrical conductivities lying between those of good conductors and insulators. The resistivity of semiconductors varies from 10^{-5} to 10^{-4} ohm-m as compared to the values ranging from 10^{-8} to 10^{-6} ohm- m for conductors and from 10^{7} 10^{8} for insulars. There are elemental semiconductors such as germanium and silicon which belong to group IV of the periodic table and have resistivity of about 0.6 and $1.5X10^{3}$ ohm-m respectively. Besides these there are certain compound semi conductors such as gallium arsenide (GaAs) indium phosphide (InP), cadmium sulphide (CdS) ect., which are formed from the combination of the group elements of III and V group or II and VI group .

Properties of semiconductor

1. The resistivity of the semiconductor is less than the insulator but more than the conductor.
2. The semiconductor have negative temperature coefficient of resistance.
3. Semiconductors are metallic on nature. But are generally hard and brittle.
4. Semiconductors have a filled valance band and empty conduction band at 0K.
5. When impurities are added to a semiconductor, its electrical conductivity will increase.

1.2 Band Gap theory of semiconductor

A semiconductor is a substance which has almost filled valence band and nearly empty conduction band with a very small energy gap ($\cong$ 1ev).

Figures1.1 (a) & 1.1(b) show the energy band diagram of germanium and silicon respectively. It may be seen that forbidden energy gap is very small; for silicon 1.1ev and for germanium 0.7ev. Therefore, a small amount of energy is needed for their valence electrons to cross over the conduction band. Even at room temperature some of the valence electrons may acquire sufficient energy and jump into the conduction band and become free. Therefore, at room temperature, germanium or silicon is neither conductor nor an insulator. For this reason such substances are called semiconductors.

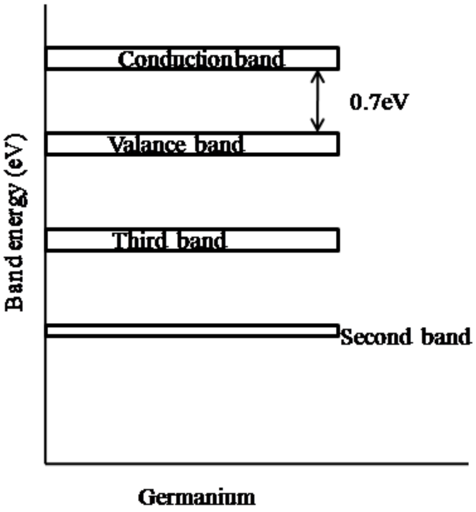


Fig.1.1(a)

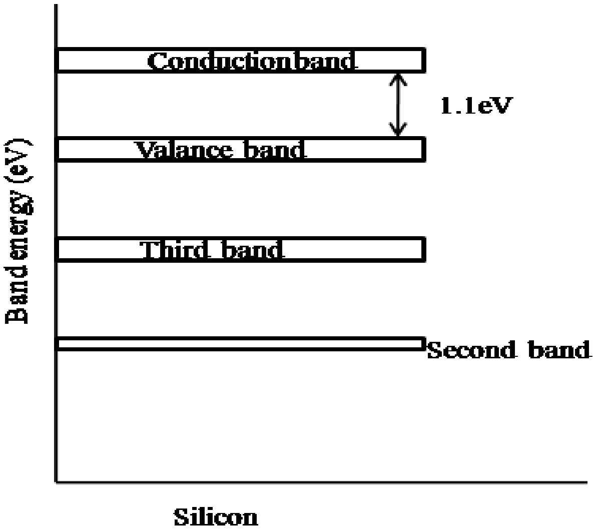


Fig.1.1(b)

1.3 Direct and indirect band gap

In semiconductor physics, the bands are represented by Energy (E) versus wave number (K) curve in Brillouin zones. If the K value corresponding to the minimum energy state in the conduction band and the K value corresponding to the maximum energy state in the valence band are the same, the band gap is said to be direct band gap. If these two K values are not same, the band gap is said to be indirect. The direct and indirect band gaps are illustrated in fig.1.2. The most accurate method of the measurement of band gap is the optical absorption method. In both the cases of direct and indirect band gaps, when light is incident on the system, electron- hole pairs are produced, that is an electron in the valence band absorbs the incident energy and goes to conduction band by leaving a hole in the valence band. After a short time back the electron combines with the hole giving out a photon of energy equal to the energy difference between the electron in the conduction band and hole in the valence band. This process is known as radioactive recombination.

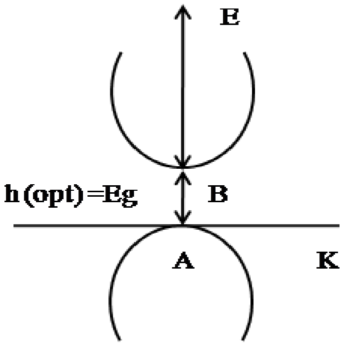


Fig.1.2

The radioactive recombination is much faster in the case of direct gap than in the case of indirect band gap. A photon of energy E_g (band gap energy) can produce an electron- hole pair in direct band semiconductors easily, because the electron does not undergo any change in its momentum. However in indirect band semiconductors, the electron has to undergo a significant change in momentum in the process of producing an electron- hole pair. The electron which is lifted to conduction band from valence band has to interact not only with photon but also with a phonon, which is the much slower process.

1.4 Equation of electron motion

Consider the motion of a wave packet in an applied electric field, which consists of wave functions with wave vector K and velocity v.

$$v= \frac{d\omega}{dK} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The frequency associated with a wave function of energy E is

$$\omega = \frac{E}{\hbar} \text{ and so}$$

$$v = \frac{d}{dK}\left(\frac{E}{\hbar}\right) = \hbar^{-1}\frac{dE}{dk} \quad \ldots\ldots\ldots (2)$$

$$v = \hbar^{-1}\nabla_k E \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

The work dE done on the electron by the electric field E in the interval dt is

$$dE = - eEvdt \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

From eqn (2)

$$dE = \left(\frac{dE}{dk}\right)dk = \hbar vdk\ldots\ldots(5)$$

on comparing (4) and (5) we have,

$$\hbar vdk = -eEvdt$$

$$dK = -\left(\frac{eE}{\hbar}\right)dt \qquad \ldots\ldots\ldots\ldots(6)$$

$$\left(\frac{dk}{dt}\right) = -\left(\frac{eE}{\hbar}\right)$$

$$\hbar\left(\frac{dk}{dt}\right) = -eE \qquad \ldots\ldots\ldots\ldots (7)$$

$\hbar\left(\frac{dk}{dt}\right) = \mathrm{F}$ → This is the equation of motion of electron.

Where $\mathrm{F} = -\mathrm{eE}$, is the external force.

When the electron moves in the magnetic field B, it experiences a force called Lorentz force. Thus the equation of motion of an electron with velocity v is

$$\hbar\left(\frac{dk}{dt}\right) = \frac{e}{c}(v \times B)$$

Substitute the value of v from eqn(3)

$$\hbar\left(\frac{dk}{dt}\right) = \frac{e}{c}(\hbar^{-1}\nabla_{\mathrm{k}}\mathrm{E} \times B)$$

$$\frac{dk}{dt} = \frac{e}{\hbar^2 c}(\nabla_{\mathrm{k}}\mathrm{E} \times B)\ldots\ldots\ldots\ldots(8)$$

It implies that, in a magnetic filed an electron moves in K space in a direction normal to the direction of the gradient of the energy E, so that the electron moves on a surface of constant energy.

1.5 Concept of hole

A allowed band where all the states are occupied can carry no electric current , since for every electron with a positive value of K there is another with the value of (-K).

Consider a band which is filled except for one state at the top of the band which has –k. if an electron occupies this state, it would have negative charge and negative mass. Its momentum p= $\hbar k$ will be negative but its velocity will be positive. So that it will carry a negative current. However, the presence of such an electron will fill the band and the net momentum and current will be zero. Hence the momentum and current due to all the other electrons must be equivalent to that of one particle with positive momentum giving a positive current and the mass$|m^*|$. Such a particle is called a positive hole.

The advantage of the concept of positive holes is that the momentum and current of a nearly filled band with n empty states can be attributed to the presence of an equivalent number n of entities which behave like particles with positive charge and effective mass m*.

Let us consider a single hole in a filled band of a one dimensional lattice. Let –e be the charge of electron and v_i be the velocity of electrons. In the absence of electric field, the current due to all the electrons in a completely filled band is

$$\mathrm{I} = -e\sum_i v_i \ = \ -e\left[v_j + \sum_{i\neq j} v_i\right] = 0 \text{ ……………………..(1)}$$

If the electron j is missing

$$I' = e\sum_{i\neq j} v_i = ev_j \text{ ………………… (2)}$$

Rate of change of current I' on applying the electric field f is

$$\frac{dI'}{dt} = e\frac{dv_j}{dt} = \frac{-e^2F}{m_j^*} = \frac{e^2F}{\left|m_j^*\right|} \text{ …………(3)}$$

Since holes tend to reside in the upper part of the nearly filled band, m_j^* is negative and the right hand side of the eqn (3) becomes positive. Thus a band in which an electron is missing behaves as a positive hole with an effective mass$\left|m_j^*\right|$.

1.6 Effective mass

It is a new concept and arises because of the interaction of the electron wave packet with the periodic lattice. If the interaction between them is very large or if there is a strong binding force between the electron and the lattice, it will be difficult for the electron to move, meaning thereby that the electron has acquired a large mass called effective mass.

Effective mass of electron

We know that the free electron energy in terms of K is given by

$$\mathrm{E} = \frac{h^2k^2}{8\pi^2m} \text{ …………..(1)}$$

m is the mass of the electron.

Differentiating the above eqn

$$\frac{dE}{dK} = \frac{h^2k}{4\pi^2m} \ and \ \frac{d^2E}{dk^2} = \frac{h^2}{4\pi^2m}$$

$$\mathrm{m} = \frac{h^2}{4\pi^2}\left(\frac{d^2E}{dk^2}\right)^{-1} \text{…………..(2)}$$

For a free electron model, where E versus K has a parabolic relationship. When the electrons move in a periodic potential of the crystal lattice the parabolic relation between E and k no longer exists. There is a breakup in the curve of various zone boundaries leading to the origin of allowed and forbidden bands. Near the forbidden band, the curvature of E versus K curve changes and become negative.

$\therefore \frac{d^2E}{dk^2}$ is no longer a constant and also the mass of the electron. Both are the function of k.

Thus under periodic potential, the mass of the electron given by the eqn (2) is known as effective mass and it is represented by the symbol m^*.

$$m^* = \frac{h^2}{4\pi^2}\left(\frac{d^2E}{dk^2}\right)^{-1}$$

1.7 Physical interpretation of effective mass

Consider an electron with K value less than π/a (K<π/a) at the boundary. It will manage to move through the crystal. But when a field is applied which should accelerate the electron and increase the k value, the electron will meet the condition for Bragg reflection and will be scattered back in the opposite direction. In this way, it behaves like a particle with negative charge and negative mass. The effective mass of an electron may be positive or negative and is shown in fig. 1.3 by plotting a curve between m* and K in the first brillouin zone for one dimensional lattice. The first figure shows that the effective mass is positive in the lower part of the band and negative close to the zone boundary. The figure also shows that, the curves E versus K, dE/dk versus K and d^2E/dK^2 versus K is in qualitative form.

The effective mass m* may be equal to m (m* =m) only when the energy is not near the edge of a band and E versus K is parabolic.

In most conductors, the band is only partially filled so m* =m. In semiconductors, insulators and certain conductors, valence bands are almost filled. So the effective mass differs from m.

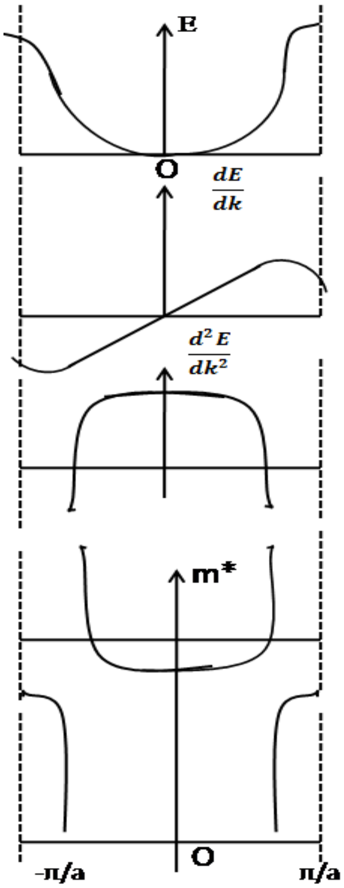


Fig.1.3

1.8 Effective masses in semiconductors

The determination of the energy surface is equivalent to the determination of the effective mass tensor. Cyclotron resonance in a semi conductor is carried out with centimeter wave or millimeter wave radiation at low carrier concentration.

The current carriers are accelerated in helical orbits about the axis of a static magnetic field with the angular frequency ω_c..

$$\omega_c = \frac{eB}{m^* c} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where m^* is the appropriate cyclotron effective mass. Resonant absorption of energy from an RF electric field perpendicular to the static magnetic field occurs when the RF frequency is equal to the cyclotron frequency.

At resonance if we consider $\frac{m^*}{m} = 0.1$ and

$\omega_c = 1.5X10^{11} s^{-1}$, we have B = 860G

In direct gap semiconductors, the band edges at the center of the brillouin zone have the structure as shown in fig 1.4. The conduction band edge is spherical with the effective mass m_e.

$$E_c = E_g + \frac{\hbar^2 K^2}{2m_e} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The valence bands are characteristic by three bands near the edge. They are heavy hole (hh) band, light hole (lh) band and spin-orbit hole band (soh) with energies.

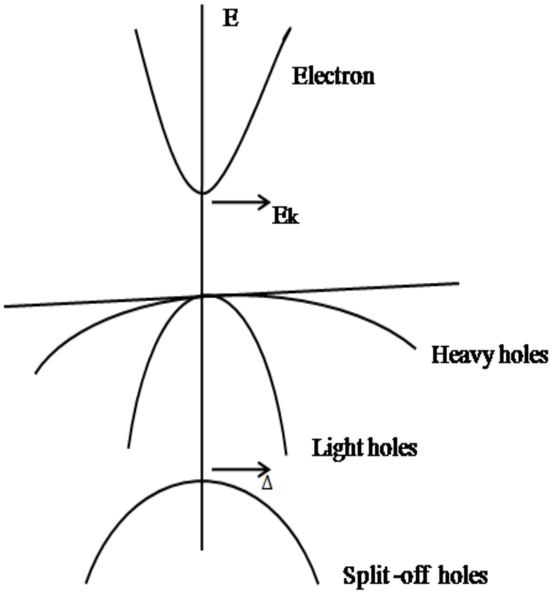


Fig.1.4

$$E_v(hh) \cong \frac{-\hbar^2 K^2}{2m_{hh}},\ E_v(lh) \cong \frac{-\hbar^2 K^2}{2m_{lh}} \text{ and } E_v(soh) \cong -\Delta - \frac{\hbar^2 K^2}{2m_{soh}}$$

The perturbation theory of band edges suggests that the electron effective mass should be proportional to the band gap for a direct gap crystal.

1.9 Fermi surface

The Fermi surface is defined as the surface of constant energy E_F in K- space inside which all the states are occupied by the valence electron, while all the states lying outside it are empty at zero temperature. The effect of temperature on the Fermi surface is very slight and the surface remains sharp even at room temperature or higher. The shape of the Fermi surface is determined by the geometry of the energy contours in a zone. For a free electron, the Fermi surface is a sphere of radius K_F when it lies well within the first Brillouin zone. However, non spherical and complicated shaper are observed when the Fermi surface and Brillouin zone are close to or touch one another under the effect of pseudo potential V_{eff} (r). Hence, a study of the shape of the Fermi surface and its proximity of the Brillouin zone is used to determine the properties of solids, such as heat capacity, pauli's paramagnetism , electrical conductivity, etc. Fig 1.5 shows the evolution of the shape of constant energy curve (fs) as the number of electrons are gradually increased. The kinetic energy of a free electron in K - space is given by the parabolic eqn.

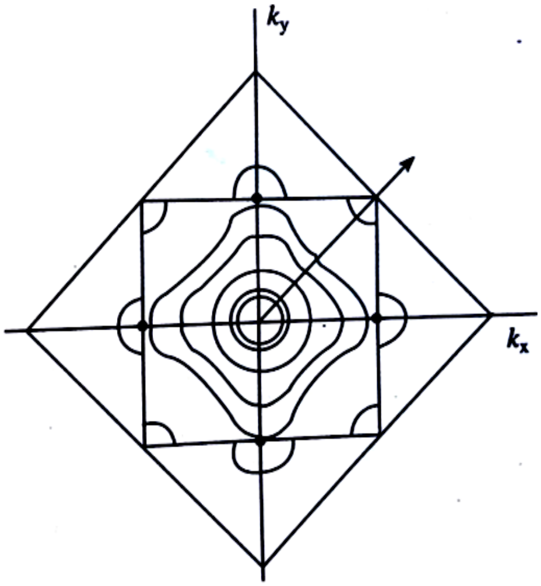


Fig.1.5

$$E_{(k)} = \frac{\hbar^2 k^2}{2m}$$

The center of the first BZ (where K=0) is a minimum energy position, E = 0. This implies that for K =0 all the states are empty inside the brillouin zone. For small number of valence electrons, only the states lying near the bottom of the band (ie. the centre of the first BZ) are filled and the occupied volume is a sphere of radius K_F . As the number of valence electrons is increased, more and more states are occupied and so the Fermi volume gradually expands. The Fermi surface begins to deform and loses its spherical shape near the zone boundary. The degree of distortion depends on (i) how near is the Fermi surface to the zone boundaries, (ii) the magnitude of the effective pseudo potential.

Characteristics of Fermi surfaces

1. The Fermi surface represents the dynamic and inertial properties of conduction electron in K- space.
2. The volume of the Fermi surface represents the number of conduction electrons.
3. The Fermi surface has spherical shape within the first brillouin zone and non- spherical in higher zones.
4. The Fermi surface always meets the zone boundary at right angles along the line of intersection.
5. For a spherical Fermi surface, the velocity of for a free electron is $v = \frac{\hbar K}{m_0}$.
6. For non- spherical Fermi surfaces, under periodic potential, the velocity of electron is a non linear function of K.

   $V = \frac{1}{\hbar} \nabla_k E$
7. Study of Fermi surface gives to know the important properties of solids, such as heat capacity, pauli's paramagnetism, electrical conductivity etc.

1.10 Harrison's method of constructing Fermi surface

Extended zone scheme

Harrison's method is based on a weak pseudo potential $V_{eff}(r)$. The effect of this potential causes the energy discontinuities ΔE as well as distortion in the Fermi surface at the zone boundaries. Therefore, if $V_{eff}(r)$ is made arbitrarily low , the energy discontinuities and the distortion in the Fermi surface can be removed. By taking arbitrarily low pseudo potential, we can describe the Fermi sphere of any radius K_F from the centre of the first Brillouin zone which will cross a whole nmber of zone boundaries without distortion. This representation is an example of extended zone scheme. Thus, using Harrison's method , let us construct Fermi surface for some simple lattice in two and three dimensions.

Fermi surfaces in two dimension (square lattice)

Consider a square lattice of lattice periodicity 'a'. In order to know the size of the Harrison's Fermi circle, let us consider the following cases of increasing electron concentration.

(a) Monovalent metal

The area of a first Brillion zone corresponding to a square lattice of parameter ‘a’ is given by A = $\frac{4\pi^2}{a^2}$. In a monovalent lattice, there is only one electron per unit cell. Thus only half the area in the first BZ will be occupied, and the rest will be vacant. The area of the Fermi circle (2D) equal to πK_F^2 must be equal to half the area of the first Brillouin zone.

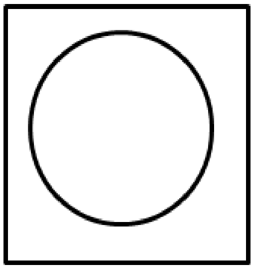


Fig.1.6

$$\pi K_F^2 = \frac{1}{2}\frac{4\pi^2}{a^2} \quad \text{……………(1)}$$

$$K_F = \sqrt{\frac{2}{\pi}}\left(\frac{\pi}{a}\right) = 0.798\,\frac{\pi}{a} \text{………(2)}$$

$K_F -$ Radius of Fermi circle.

Where π/a is the distance of the zone boundary from the centre of the zone. Since the value A k_f lies between 0<$k_f < \pi/a$, the Fermi circle lies well within the first BZ as shown in fig 1.6 Hence the Fermi surface remains undistorted.

(b) Divalent metal

If the atom of the metal is divalent in a square lattice, then from the same argument as given above

$$\pi K_F^2 = \frac{2}{2}\frac{4\pi^2}{a^2} \text{………(3)}$$

$$K_F = \frac{2}{\sqrt{\pi}}\left(\frac{\pi}{a}\right) = 1.228\ \pi/a \text{…………………(4)}$$

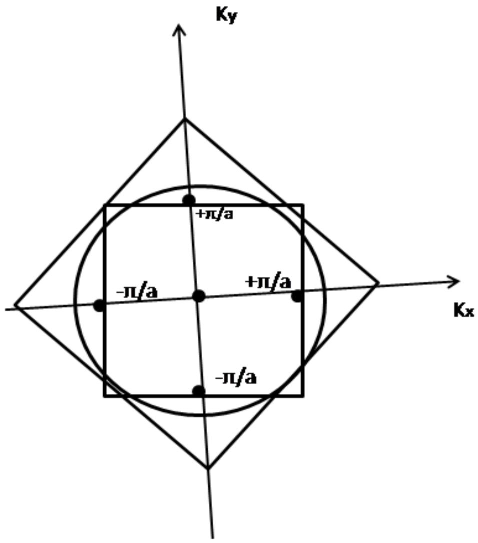


Fig.1.7 (a)

Distance of the first Brillouin zone boundary from the centre is equal to (π/a) and the corner of the first zone from the centre in equal to $\sqrt{2}\ \pi/a$ = 1.414 ……(5)

From eqn (3) and (4) , we have ,

$$\frac{\pi}{a} < k_f < 1.414\ \pi/a$$

This implies that a circle of radius K_F will go beyond the first zone boundary but will remain inside the corner of the first Brillouin zone as shown in fig 1.7(a).

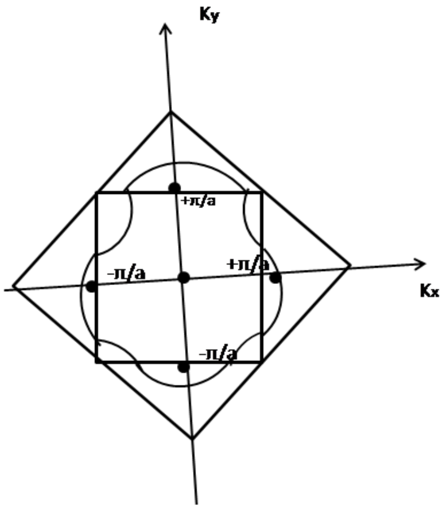


Fig.1.7(b)

If we translate the pieces of Fermi circle shown in fig1.8 through a distance $2(\pi/a)$ along k_x and k_y axes , we can construct closed curves around the corner and the boundaries of the first BZ as shown in the figure in a periodic zone scheme.

In fig 1.8 (a), the constant energy curves surround empty areas and are known as first zone holes and the constant energy curves in fig1.8 (b) surround the areas filled with electron and are known as the second zone electrons.

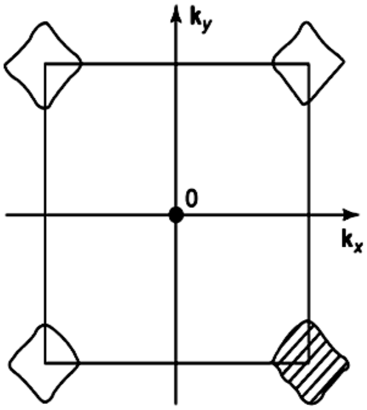


Fig 1.8(a)

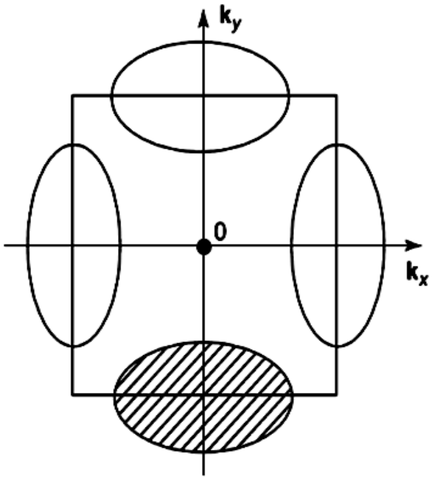


Fig. 1.8 (b)

(c) Trivalent metal

For the trivalent metal, the radius of the Fermi circle is found to be

$$\pi k_f^2 = \frac{3}{2}\,\frac{4\pi^2}{a^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$K_F = \sqrt{\frac{6}{\pi}}\,(\frac{\pi}{a}) = 1.38\,\frac{\pi}{a}\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

It means that $\frac{\pi}{a} < K_F < 1.414\frac{\pi}{a}$, which shows that the radius of the Fermi circle is still smaller than the distance of the corner of the first zone from the centre. Hence, the nature of the Fermi surface will be similar to the divalent case. The only difference will be that the size of the first zone holes will be smaller and the size of the second zone electrons bigger.

(d) Tetravalent metal

For the tetravalent metal, the radius of the Fermi circle is found to be

$$\pi k_f^2 = \frac{4}{2}\ \frac{4\pi^2}{a^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

$$K_F = \sqrt{\frac{8}{\pi}}\ (\frac{\pi}{a}) = 1.595\ \frac{\pi}{a} \qquad \ldots\ldots\ldots\ldots\ldots\ (9)$$

Now comparing eqn (5) and (9), we have

$$\frac{\pi}{a} < 1.414\ \pi/a < k_f.$$

This indicates that the Fermi circle for tetravalent case completely encloses the first BZ and passes through the second, third and fourth zones as shown in fig 1.9.

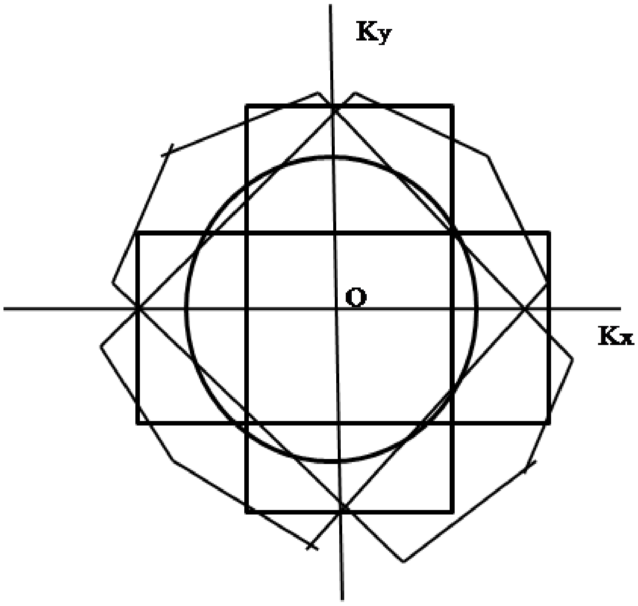


Fig. 1.9

1.11 Effect of magnetic field on Fermi surface: electron orbit

In the absence of collision, the equation of motion of an electron in a magnetic field is given by

$$\hbar\left(\frac{dk}{dt}\right) = e(v \times B)\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Where e (v×B) is Lorentz force experienced by the electrons moving with velocity V in a magnetic field B. In metals, since V is perpendicular to Fermi surface in K space, the force is parallel to the Fermi surface and perpendicular to both v and B. The component of K parallel to B is therefore constant. So that electron orbit in K space is obtained by taking the intersection of the Fermi surface with a plane normal to B. The shape of the electron orbit in k space depends on the shape of the Fermi surface and the orientation of the external magnetic field.

Let us consider two closely spaced electron orbits in k space with energies E and E+ dE as shown in fig 1.10. The shape of the electron orbit in r- space can be obtained by integrating eqn(1).

$$K = \frac{e}{\hbar}(r\times B)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

This shows that the electron orbit in r- space is similar in shape with the K space orbit but differs by a scale factor of $\frac{\hbar}{eB}$ and rotation of $\frac{\pi}{2}$. The period of electron orbit in a magnetic field is obtained as

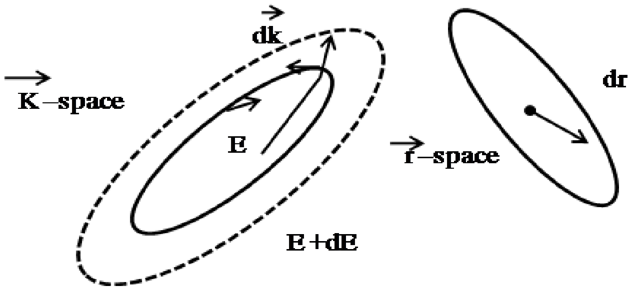


Fig.1.10

$$T= \oint dt = \oint \frac{dr}{V} \ldots\ldots\ldots\ldots(3)$$

The velocity of an electron in a band of energy E in K space is given by

$$V= \frac{dr}{dt} = \frac{1}{\hbar}\frac{dE(k)}{dk} = \frac{1}{\hbar}\frac{dE}{dk_{\perp}}\ldots\ldots\ldots\ldots\ldots(4)$$

Where $dk_{\perp}$ *is* the normal distance in k space.

Eqn (3) becomes

$$T = \hbar\oint dr.\frac{dk_{\perp}}{dE} = \frac{\hbar^2}{eB}\oint\frac{|dk\times dk_{\perp}|}{dE}$$

$$= \frac{\hbar^2}{eB}.\frac{dA_k}{dE} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

A is the area of the orbit in K space .

Therefore, the cyclotron frequency is $\omega_c = \frac{2\pi}{T} = \frac{2\pi eB}{\hbar^2}.\frac{dE}{dA_k}\ldots\ldots\ldots(6)$

Cyclotron frequency is also given by $\omega_c = v/r = eB/m_c$

Where m_c is the cyclotron effective mass and can be determined by comparing eqn (5) and (6)

cyclotron effective mass $m_c = \frac{\hbar^2}{2\pi}.\frac{dA_k}{dE}$.

1.12 Fermi surface in metals: construction of Fermi surface of metals

The procedure for constructing the Fermi surface in metal consists the following steps.

1. For a given metal lattice, construct the corresponding reciprocal lattice.
2. Near each reciprocal lattice point, construct a unit cell (brillouin zone) by the Wigner Seitz method.
3. For the given parameters of the Brillouin zone and valence of the metal, determine the radius of the Fermi sphere K_F . A sphere of this radius is drawn from the centre of the extended zone.
4. The Fermi surface formed by the intersection of the Fermi sphere is classified by the rules.

For constructing Fermi surface in 3D for metals having simple crystal structures, first we have to develop a formula connecting K_F and the dimension of the brillouin zones.

The expression for Fermi energy E_F in terms of electron density in the material is

$$E_F = \frac{\hbar^2}{2m\,(3n\pi^2\,)^{\frac{2}{3}}} \qquad \text{………………} \; (1)$$

Where n is the density of electron =N/V.

$$E_F = \frac{\hbar^2}{2m\,(3\pi^2\frac{N}{V})^{\frac{2}{3}}} \qquad \text{…………………..}(2).$$

E_F can be written as $\frac{\hbar^2 K_F^2}{2m}$ …………….(3)

$$\frac{\hbar^2 K_F^2}{2m} = \frac{\hbar^2}{2m\,(3\pi^2\frac{N}{V})^{\frac{2}{3}}}$$

$$K_F^2 = (3\pi^2\,\frac{N}{V})^{\frac{2}{3}}$$

$$K_F = (3\pi^2\,\frac{N}{V})^{\frac{1}{3}} \qquad \text{…………………..}(4)$$

Then substituting V= a^3 in eqn (4)

$$K_F = (3\pi^2\,\frac{N}{\mathrm{a}3})^{\frac{1}{3}} = \left[\left(\frac{3}{\pi}\right)\left(\frac{\pi^3}{a^3}\right)N\right]^{\frac{1}{3}}$$

$$K_F = \left(\frac{3N}{\pi}\right)^{\frac{1}{3}}\frac{\pi}{a} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Where $\frac{\pi}{a}$ is the distance between the centre of the first Brillouin zone and its boundary and N is the number of atoms.

1. Simple cubic lattice

In this case, N=1

$$K_F = \left(\frac{3X1}{\pi}\right)^{\frac{1}{3}}\frac{\pi}{a}$$

$$K_F = 0.985\left(\frac{\pi}{a}\right)\ldots\ldots\ldots\ldots\ldots(6)$$

Eqn (6) shows that the K_F is very close to the zone boundary.

If the effect of the weak pseudo potential is taken into account, the Fermi sphere will touch each other across the zone boundaries and will take the shape as shown in fig1.11. A surface of this type is called as monster.

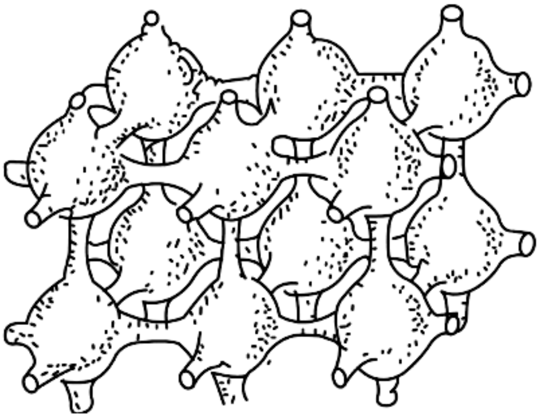


Fig. 1.11

2. Body centered cubic lattice

In this case N= 2

Eqn (5) can be written as

$$K_F = \left(\frac{3X2}{\pi}\right)^{\frac{1}{3}}\frac{\pi}{a} = 1.241\left(\frac{\pi}{a}\right)\ldots\ldots\ldots\ldots(7)$$

The first Brillouin zone of the BCC lattice has the form of rhombic dodecahedron. It has 12 identical faces and are located at the same distance $\sqrt{2}(\frac{\pi}{a})$ from the centre of the zone. The shortest distance d of a zone face from the centre of the zone is

$$d = \frac{2\pi}{a}\sqrt{\frac{1}{2}^2 + \frac{1}{2}^2 + 0} = \sqrt{2}\left(\frac{\pi}{a}\right) \ldots\ldots\ldots(8)$$

$$= 1.414(\frac{\pi}{a}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

From eqn (7) and (8) we have

$$0 < K_F < d$$

Further, we have $\frac{K_F}{d} = 0.88, d - K_F = 0.174\left(\frac{\pi}{a}\right)$

Thus, the Fermi sphere is entirely inside the first Brillouin zone and the Fermi surface is quite away from the zone faces. Due to the crystal potential, some distortions appear at 12 different points on the Fermi surface. These 12 points are located along the [110] directions of the first Brillouin zone boundaries.

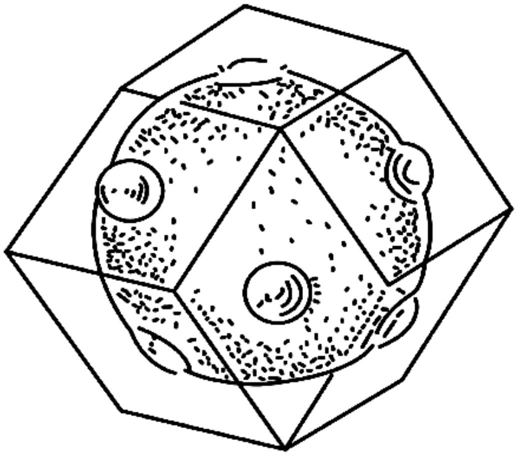


Fig.1.12

3. FCC lattice

For FCC lattice, N= 4

$$K_F = (\frac{3X4}{\pi})^{\frac{1}{3}}\frac{\pi}{a} = 1.563(\frac{\pi}{a}) \ldots\ldots\ldots\ldots(10)$$

The first Brillouin zone of a FCC lattice is a truncated octahedron with 14 faces, including 8 hexagonal faces and 6 square faces. The shortest distance d_s of a square face from the centre of the zone is

$$d_s = \frac{2\pi}{a}\sqrt{\frac{1}{2}^2+\frac{1}{2}^2+\frac{1}{2}^2} = \sqrt{3}\left(\frac{\pi}{a}\right)$$

$$= 1.732\left(\frac{\pi}{a}\right) \ldots\ldots\ldots\ldots \text{(11)}$$

From equations (8) , (10) and (11) we have

$$\frac{K_F}{d_s} = \frac{1.563}{2} = 0.782 \text{ and}$$

$$d_s - K_F = 0.437\left(\frac{\pi}{a}\right)\ldots\ldots\ldots\text{(12)}$$

$$\frac{K_F}{d_h} = \frac{1.563}{1.732} = 0.900 \text{ and}$$

$$d_h - K_F = 0.169\left(\frac{\pi}{a}\right) \ldots\ldots\ldots\ldots\text{(13)}$$

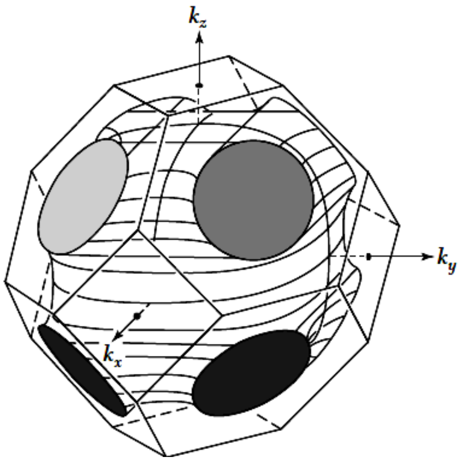


Fig.1.13

Thus, the Fermi surface is inside the first Brillouin zone. Due to the crystal potential, the Fermi face near the centers of the hexagonal faces are substantially distorted , but the Fermi surface near the centers of the square faces does not suffer distortions. It happens because the centers of the hexagonal faces from the Fermi surface are much nearer compare to the square faces.

1.13 Electron orbit, hole orbit and open orbit

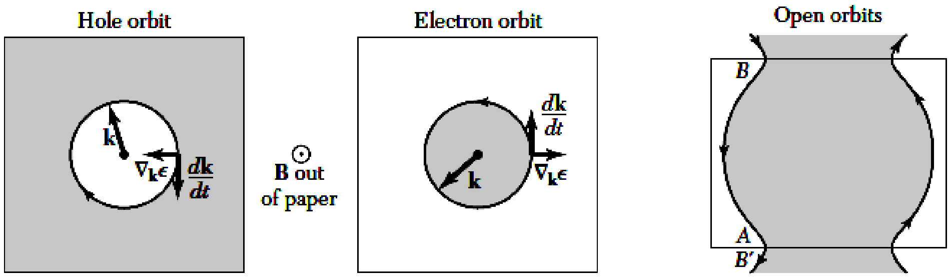


Fig. 1.14

The three types of orbits in a magnetic field are shown in fig 1.14. The three orbits are (1) electron orbit (2) hole orbit (3) open orbit. The first two orbits are closed orbits and are traversed in opposite manner. Because, particles of opposite charge moving in the magnetic field in opposite direction. Electrons in holes like orbits move in a magnetic field with a positive charge. The third orbit is not closed. The particle on reaching the zone boundary at A is instantly recoils back to B. such an orbit is called an open orbit. Open orbits have an important effect on the magneto resistance. Orbits that enclose filled states are electron orbits. Orbits that enclose the empty states are called hole orbits. Orbits that move from zone to zone without closing are open orbits.

1.14 De-Hass-van alphen effect (dHvA effect)

When a metal is placed in a magnetic field, the electrons do not move in straight path but rotate in quantized orbits around the Fermi surface in a plane perpendicular to the field. Based on this concept, de Hass and van Alphen discovered that, at low temperatures the diamagnetic susceptibility of pure bismuth as a function of magnetic field in high fields exhibits periodic oscillations. This effect is called as de Hass van Alphen effect.

This effect has been developed successfully in determining the external cross- sectional area of the Fermi surface. The basic idea of the de Hass van Alphen effect involves the quantization of electron orbits in a constant magnetic field applied in the Z- direction on such a way that the flux through the orbit is $\varphi = \frac{2\pi\hbar}{e}(n+\nu)$............(1)

Where $\nu = 0.5$, for free electrons.

The quantization of the area of the orbit in K-space is given as A = $\frac{2\pi eB}{\hbar}(n+\nu)$..........(2)

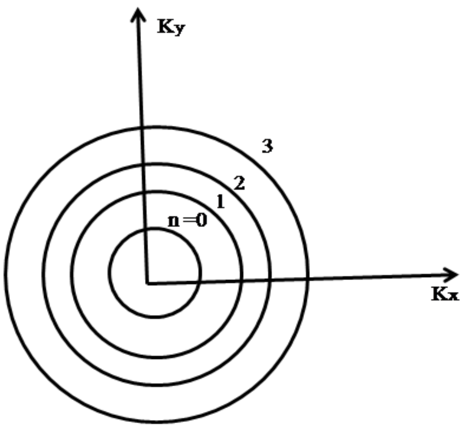


Fig.1.15(a)

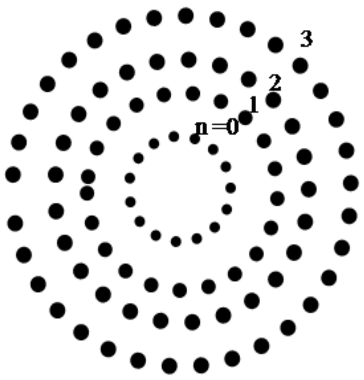


Fig.1.15(b)

The Bloch theorem is still applicable to K_Z component of K, but not to K_X and K_Y. Therefore the stationary allowed values specified by the square lattice of points are taken as shown in fig1.15 (a). They move round on one or other set of quantized circular orbits shown in fig1.15 (b). Each of these circular orbits has a considerable degree of degeneracy. When a magnetic field is applied along K_Z direction, it confines electrons to orbits of quantization area and these orbits lie on a set of coaxial cylinders of axis K_Z. On the application of magnetic field, the energy levels which are condensed in this way are termed as Landau levels. When the magnetic field is increased, the allowed area of the orbit increases. So that the cylinders which correspond to the Landau level expand in cross section. Near the Fermi surface, the nearest cylinder expands in areas with increasing field, cylinder crosses the Fermi energy and so the corresponding landau level becomes empty. The electrons then distribute themselves on other parts of the Fermi surface. The critical field at which this happens is obtained as $\frac{1}{B} = \frac{2\pi e}{\hbar A}(n + \nu)$

If ν Landu levels are below the Fermi energy, $(\nu - 1)$ levels will be below it. If ν is very large, the new state of the electron gas with $(\nu - 1)$ levels below E_F becomes equivalent to the earlier situation and, therefore the process repeats as field is increases further. The effect of this procession of Landau level through the Fermi level as the magnetic field is increased gives the periodic fluctuation of the energy of the electron about the zero filed. The magnetic moment is the rate of change of free energy with field. Therefore the magnetization and the susceptibility vary periodically with 1/B.

The period is $\delta(\frac{1}{B}) = \frac{2\pi e}{\hbar A}$

Thus the period of oscillations is inversely proportional to the cross- sectional area of the Fermi surface in a plane perpendicular to the magnetic field. The external area of the Fermi surface normal to the direction of applied field is measured using the above equation.

1.15 Wigner-Seitz method for energy band calculation

Wigner-Seitz considered alkali metal lies in the lowest energy level in the band i.e., K= 0 state. For this K= 0 state the wave function is simply the Bloch function having full symmetry of the lattice. Here, the crystal is divided into atomic cells, the cell associated with each atom containing all points nearest closer to that atom. The symmetry and periodicity of the wave function implies that the normal derivative of the wave function vanishes at the boundaries of atomic cells. For a free ion potential, they took a free ion potential in each cell and this ion potential was spherically symmetric. The atomic cells were replaced by a sphere of equal volume.

The boundary condition is given by $\left(\frac{\partial\psi_0}{\partial t}\right)_{r=r_0} = 0$…………(1)

Where r_0 is the radius of sphere.

With K= 0 and a spherically symmetric potential, the wave function is given by an expression

$$\left[-\frac{\hbar}{2mr^2}\cdot\frac{d}{dr}\left(r^2\cdot\frac{d}{dr}+V(r)\right)\right]\psi_0 = E\psi_0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

The simultaneous solutions of eqn (1) and (2) give both the eign function ψ_0 and the eign value. Once ψ_0 has been obtained, higher K value wave functions may be approximated by $\psi_k(r) \sim e^{ikr}\psi_0$.

UNIT II

IMPERFECTIONS IN CRYSTALS

2.1 INTRODUCTION

In an ideal crystal, the atomic arrangement is perfectly regular and continuous throughout. But real crystals are never perfect; lattice distortion and various imperfections, irregularities or defects generally present in them. The mechanical, electrical and magnetic properties of engineering crystalline solids, particularly metals and alloys, are affected by the imperfections in the crystals.

If atoms in the solid are not arranged in a perfectly regular manner, it is called defects in crystals.

2.2 CLASSIFICATION OF IMPERFECTIONS (Defects)

The various types of structural imperfections or defects in crystals are classified as follows:

1. Point defects (or) Zero dimensional defects
    - a. Vacancies
        - i. Schottky defect
        - ii. Frenkel defect
    - b. Interstitial atoms
    - c. Extrinsic defects (Impurities)
        - i. Substitutional Impurity
        - ii. Interstitial Impurity
2. Line defects (or) one dimensional defect
    - a. Edge dislocation
    - b. Screw dislocation
3. Surface defects (or) Plane defects (or) two dimensional defects
    - a. Grain boundaries
    - b. Tilt boundaries
    - c. Twin boundaries
    - d. Stacking faults

2.3 Point defects

Point defect is also called zero dimensional imperfections. In a crystal lattice, point defect is one which is completely local in its effect, e.g. a vacant lattice site. The introduction of point defect into a crystal increases its internal energy as compared to that of the perfect crystal. They change the electrical resistance of a crystal.

Point defects are created during crystal growth and application of thermal energy, mechanical stress or electric field. Further they are created by irradiating the crystal by x-ray, microwaves and light.

Different types of point defects are described below.

a. Vacancies

A vacancy is the simplest point defect in a crystal. This refers to a missing atom (or) a vacant atomic site. Such defects may arise either from imperfect packing density crystallization process or from thermal vibration of atoms at high temperature.

Vacancy may also occur if an atom leaves its own site and dissolved interstitially into the structures. The vacancies may be single or deviancies or trivacancies and so on.

Vacancies are classified into two types as follows.

(i) Schottky defect

(ii) Frenkel defect

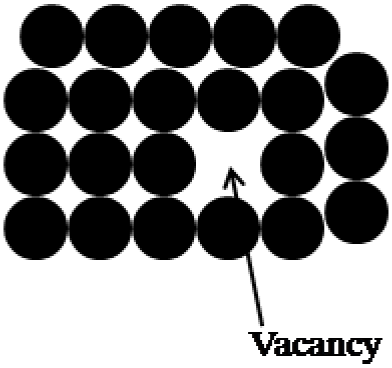


Fig. 2.1

(i) Schottky defects

Schottky vacancies refer to the missing of anion and cation. In general the missing of pair of ions in ionic crystal is called schottky defect. This defect is the combination of one cation vacancy and one anion vacancy. The concentration of Schottky defect decreases the density of the crystal. This type of point defect is dominant in alkali halides.

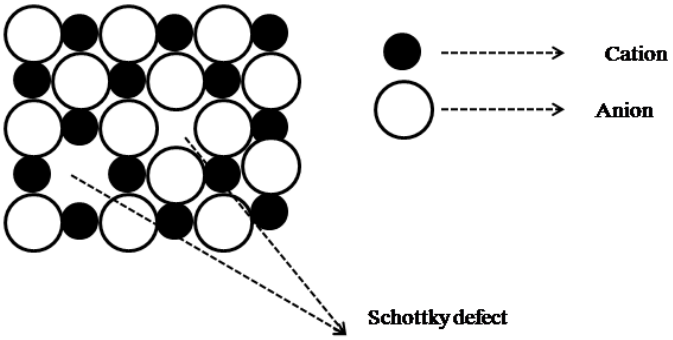


Fig.2.2

Consider an ionic crystal having equal number of positively and negatively charged ions. Let the crystal contain N ions and n schottky defects. The probability to generate the vacancy is

$$\frac{N!}{n!(N-n)!}$$

Let W is the number of ways in which n vacancies pair can be produced.

$$W = \left(\frac{N!}{n!(N-n)!}\right)^2$$

The entropy probability relation is $S = K_B \ln W$

Substituting the value of W, we get

$$S = K_B \ln\left(\frac{N!}{n!(N-n)!}\right)^2$$

$$S = 2K_B \ln\frac{N!}{n!(N-n)!}$$

The Helmholtz free energy F of the crystal is

$$F = U - TS = nE_v - 2K_B T \ln\frac{N!}{n!(N-n)!}$$

Where $U = nE_v$, the internal energy.

S - Entropy.

$$F = nE_v - 2K_B T\ [\ln N! - \ln n! - \ln (N-n)!]$$

Using sterling's approximation

$$F = nE_v - 2K_B T[N\ln N - N - n\ln n + n - (N-n)\ln (N-n) + (N-n)]$$

$$F = n E_v - 2K_B T[N\ln N - n\ln n - (N-n)\ln (N-n)]$$

In equilibrium, the Helmholtz free energy is constant and its first derivative related to n is zero.

$$\frac{\partial F}{\partial n} = 0$$

$$\frac{\partial F}{\partial n} = E_v - 2K_B T[0 - \ln n + \frac{(N-n)}{(N-n)} - \frac{n}{n} + \ln (N-n)]$$

$$0 = E_v - 2K_B T[-\ln n + \ln (N-n)]$$

$$0 = E_v - 2K_B T \ln\frac{N-n}{n}$$

$E_v = 2K_B T \ln \frac{N-n}{n}$ since n<< N

$E_v = 2K_B T \ln \frac{N}{n}$

n = N exp $[-\frac{E_v}{2K_B T}]$

The number of schottky defects depends on (a) total number of ion pairs N (b) the average energy required to produce a schottky defect (c) temperature; the fraction of schottky defect increases with increasing temperature.

(ii) Frenkel defects

Frenkel vacancies refer to the shift of cation from the regular site to interstitial site. As cations are generally the smaller ions, it is possible for them to get displaced into the void space present in the lattice. The concentration of Frenkel defects does not change the density of the crystal and the overall electrical neutrality of the crystal. The point defect in silver halides and calcium fluoride are of the Frenkel type.

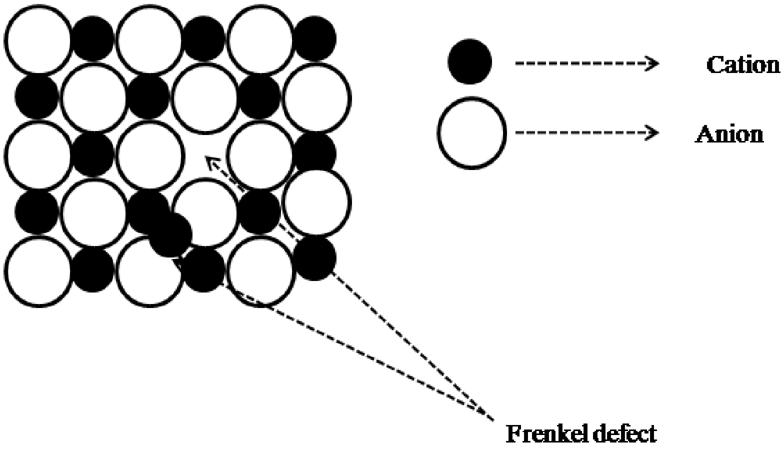


Fig.2.3

Consider a crystal composed of equal numbers of positively and negatively charged ions. Let N be the total number of atoms, N_i the number of interstitial sites and E_i is the energy required to displace a certain atom from its regular position to an interstitial position. The total number of ways in which an atom van be removed is given by

$\frac{N!}{n!(N-n)!}$ Where n is the number of interstitial defects. The number of different ways in which n interstitial defects can be formed is

$$W_i = \frac{N!}{n!(N-n)!} \times \frac{N_i!}{n!(N_i-n)!}$$

The corresponding increase in entropy increase in entropy from Boltzmann relation is

$$S = K_B \ \ln W_i$$

$$= K_B \ \ln[\frac{N!}{n!(N-n)!} \times \frac{N_i!}{n!(N_i-n)!}]$$

$$= K_B \ [\ln \frac{N!}{n!(N-n)!} + \ln \frac{N_i!}{n!(N_i-n)!}]$$

$$= K_B \ [\ln N! - \ln(N-n)! - \ln n! + \ln N_i\,! - \ln n! - \ln(N_i - n)!]$$

Using sterling's approximation

$$S = K_B \ [N\ln N - N - (N-n)\ln(N-n) + (N-n) - nlnn + n + N_i lnN_i - N_i - nln\, n + n - (N_i - n)\ln(N_i - n) + (N_i - n)]$$

$$S = K_B \ [N\ln N - (N-n)\ln(N-n) - 2nln\, n + N_i lnN_i - (N_i - n)\ln(N_i - n)]$$

The change in Helmholtz free energy is

$$F = U - TS$$

$$= n\,E_i - K_B\,T[N\ln N - (N-n)\ln(N-n) - 2nln\, n + N_i lnN_i - (N_i - n)\ln(N_i - n)]$$

In equilibrium,

$$\frac{\partial F}{\partial n} = 0$$

$$\frac{\partial F}{\partial n} = \ E_i \ - \ K_B\,T[0 + \frac{(N-n)}{(N-n)} + \ln(N-n) - 2ln\, n - 2 + 0 + \frac{(N_i-n)}{(N_i-n)} + \ln(N_i - n)]$$

$$0 = \ E_i \ - \ K_B\,T[\ln(N-n) - ln\, n^2 + \ln(N_i - n)]$$

$$E_i \ = \ K_B\,T \ln \frac{(N-n)(N_i-n)}{n^2}$$

For n<< N , N_i

$$E_i \ = \ K_B\,T \ln \frac{N\,N_i}{n^2}$$

$$\frac{n^2}{N\,N_i} = \exp\,[-\frac{E_i}{K_B\,T}]$$

$n = \sqrt{N\,N_i} \ \ \exp\,[-\frac{E_i}{2K_B\,T}]$. The concentration rises exponentially with the temperature.

2.4 Extrinsic vacancies (Impurities)

This is a defect in which a foreign atom occupies a regular lattice site. Foreign atoms generally have atomic radii and electronic structures differing from those of the host atoms and therefore act as centers of distortion. Basically there are two types of impurity defects.

(a) Substitutional impurity

It refers to a foreign atom substitutes or replaces a parent atom in the lattice.

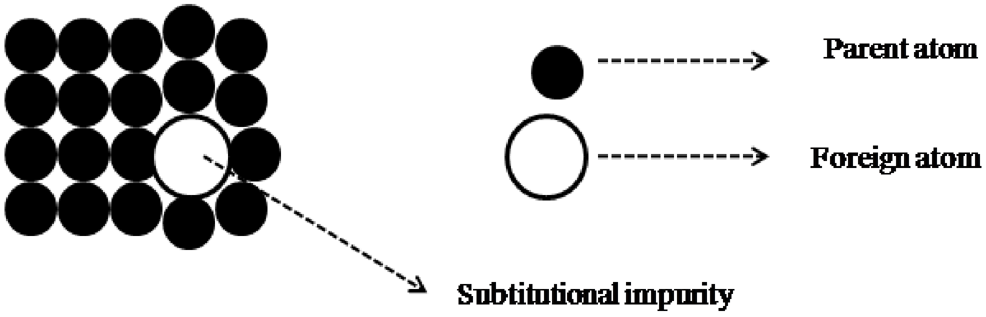


Fig.2.4

Example: In the case of semiconductor technology, Aluminum and phosphorus doped in silicon are substitutional impurities in the crystal.

(b) *Interstitial impurity*

It is a small sized atom occupying the void space in the parent crystal, without dislodging any of the parent atoms from their sites. An atom can enter the interstitial or void space only when it is substantially smaller than the parent atom.

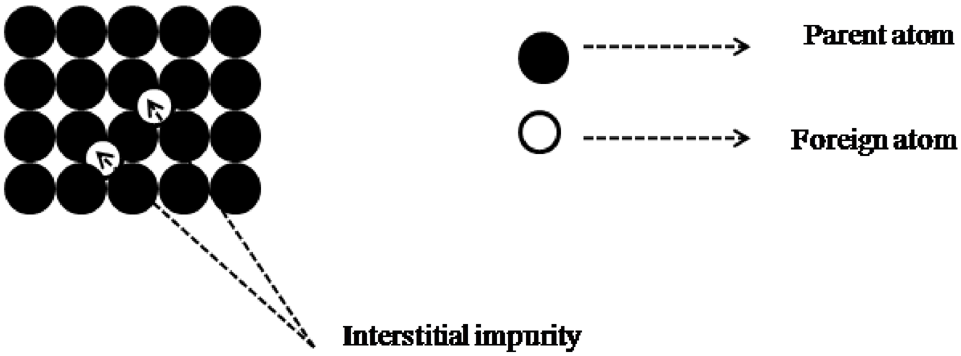


Fig.2.5

Example: Presence of carbon in iron.

2.5 Colour centers

The defects introduced in the crystal, selectively absorb certain colors in the visible light. The combination of the remaining colors provides a new color to the crystal. The defects that change the color of crystal are known as the color centers.

Types of color centers

1. Electronic centers.
2. Hole centers(v- center)

1. Electronic centers

Electronic centers are divided in to 4 types.

a. F – center b. F_A center c. M – center d. R- center

(a) F –center

In a alkali halide crystal, KCl, the atoms K and Cl exist in the form of K^+ and Cl^- ions. If from the KCl lattice one of the Cl^- ions is missing, then the site of the missing ion will behave like a positive charge and will try to attract an electron to its place. The electron occupying the site of the Cl^-ion is the F – center.

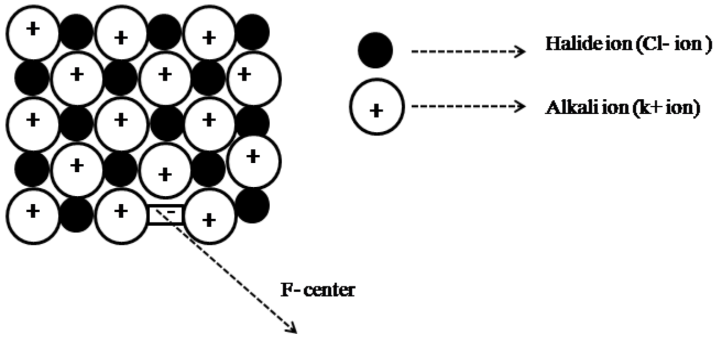


Fig.2.6

When alkali halide KCl is heated in excess potassium vapor, some K^+ions are deposited on the crystal surface. The Cl^- ions from the interior migrate to the surface to combine with the K^+ions. These create Cl^- ion vacancies in the interior. In order to maintain the charge neutrality of the crystal, free electrons get trapped in these Cl^- ion vacancy is called F – center.

(b) F_A- center

An F- center in which the five neighbors are of one kind of alkali ions and the sixth one is of a different kind is known as the F_A- center.

(c) M- center

Two f- centers joined together from an m-center.

(d) R- center

Three F- centers joined together form the R- center.

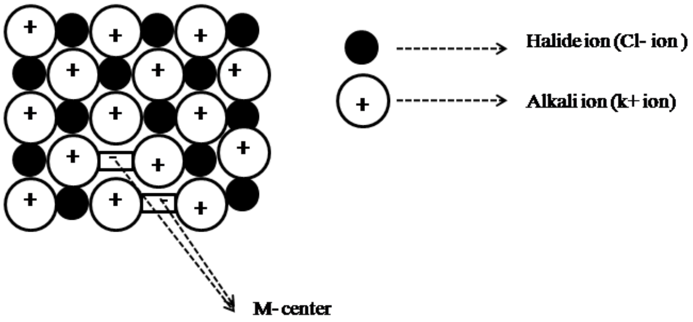


Fig.2.7

2. Hole center (V- center)

V- Centers are formed at the sites of positive ion vacancies. Positive ion vacancy means a site of negative charge. In order to maintain the charge neutrality, a positive charge is captured. The positive charge occupying the site of the positive ion is the V- center.

When KCl crystal is heated in an atmosphere of halogen (Cl) vapor, Cl atoms are adsorbed on the surface of the crystal. Thus, the Cl atom on the surface of the crystal may migrate to the positive ion vacancy shown by a square with a plus sign inside it, in fig.2.8. Hence the replacement of the Cl atom because of its association with a hole at the site of the positive ion vacancy may be treated as the creation of the V- center in the crystal.

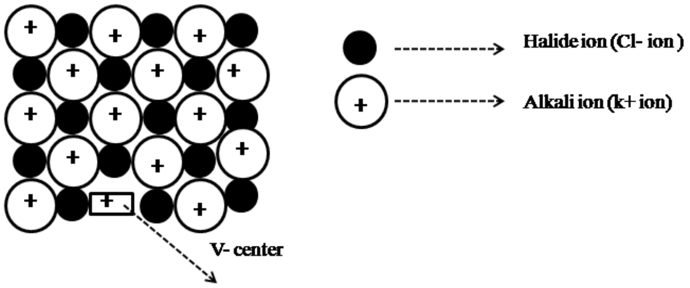


Fig.2.8

2.6 Excitons

When a semiconductor (or) insulating material is irradiated with an electromagnetic wave of energy greater than the band gap of the material, the electron is lifted from the valence band to the conduction band leaving behind a hole in the valence band. The electrons on reaching the conduction band are free to move and also the holes in the valence band can move. If the velocity of the electron in the conduction band and the hole in the valence band is the same, a force of attraction between the negatively charged electron and the positively charged hole will develop and the pair of electron and hole act as a system called exciton. Due to this attractive energy, the energy of the electron will be lowered down and its energy level will be below the bottom of the conduction band. In this bound condition, the electron- hole combinations named as excitons will travel in the crystal for some time and then recombine and emit the energy in the form of radiation. They travel in the crystal but cannot contribute to current, because the total charge associated with the exciton is zero. They can carry energy but no charge. The appearance of sharp absorption lines below the edge of the continuum in optical absorption spectrum is the proof of the existence of the excitons. The binding energy of excitons varies from a few meV to 1eV. The excitons that having lower range binding energy are known as the Mott and Wannier excitons. The excitons having high binding energy are known as Frenkel excitons.

2.7 Line defects or **dislocation**

Line defects are called dislocations. A dislocation may be defined as a disturbed region between two substantially perfect parts of a crystal. It is a line defect in a crystal structure whereby a part-plane of atoms is displaced from its symmetrically stable positions in the array. Dislocation is the region of localized lattice disturbance separating the slipped and unslipped regions of a crystal. Movement of dislocation is necessary for plastic deformation.

The two basic types of dislocations are:

a) Edge dislocation

b) Screw dislocation

a) Edge dislocation

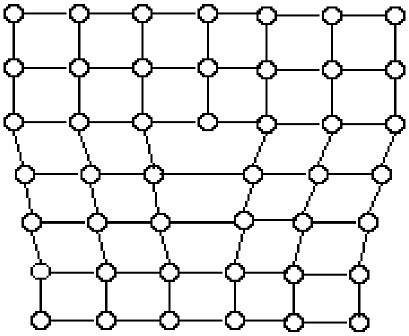


Fig.2.9

An edge dislocation is a defect where an extra half-plane of atoms is introduced mid way through the crystal, distorting nearby planes of atoms. The atoms below the edge of dislocation are squeezed together and are in a state of compression. The band lengths are small than the equilibrium value. Just above the edge of the extra plane, the atoms are pulled apart and are in a state of tension. Here the bond lengths are above the normal values. There is an extra energy due to the distortion in the region immediately surrounding the edge of the incomplete plane. If the insertion of the extra plane in the crystal is from the bottom of the crystal, the edge dislocation is said to be negative and it is denoted by T. when the insertion of the extra plane in the crystal is from the top of the crystal, the edge dislocation is said to be positive and it is denoted by $\perp$.

b) Screw dislocation

Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line. When the atoms are displaced in two separate planes perpendicular to each other, the imperfection produced is called screw dislocation.

The diagram shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminates within the crystal. The row of atoms marking the termination of the displacement is the screw dislocation.

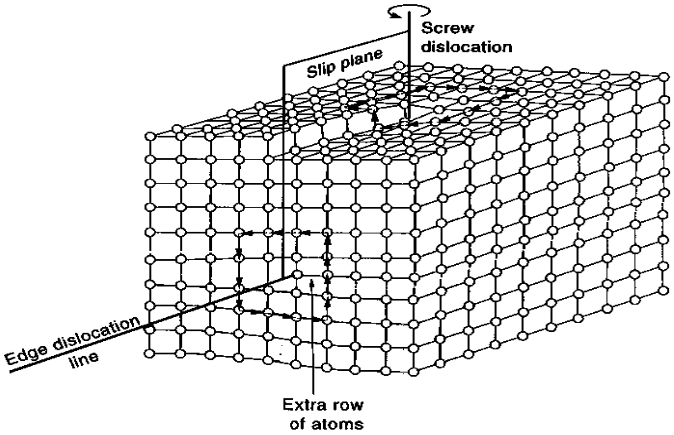


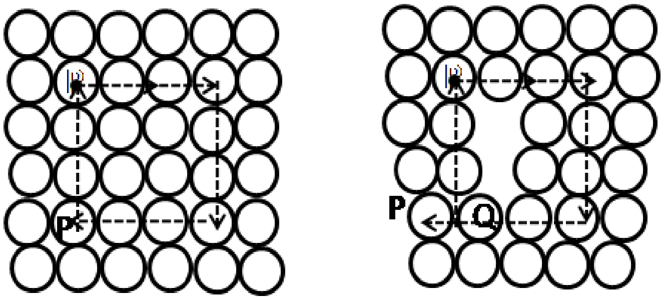
Fig.2.10

2.8 Burger’s vector

The magnitude and the direction of the dislocation are determined by a vector called burger’s vector.

Burger circuit

Let us consider two crystals one perfect and another with edge dislocation as shown in fig2.11



Perfect crystal

Edge dislocation

Fig.2.11

In perfect crystal, consider a point ‘P’ and starting from P move x times the atomic distance in positive x direction. Then move y times the atomic distance in positive Y axis and then move x times the atomic distance in the negative x direction then move y times the atomic distance in negative Y axis. After these movements, we can reach the original staring point P. The circuit is a closed one in perfect crystal. This type of circuit is called Burger’s circuit.

When we draw Burger’s circuit in the edge dislocation crystal, the circuit would not be completed. Since the end point Q and the starting point P are not located at the same place. To reach the starting point, we have to move an extra distance ‘b’ as shown in fig.2.11.

$\vec{b} = \overrightarrow{PQ}$ is called the Burger vector of the dislocation.

2.9 Dislocation energy

The process of dislocation always increases the free energy of the crystal. In order to calculate the energy of a dislocation, let us consider a cylindrical crystal of length l with a screw dislocation of Burger vector b along its axis. The elastic shear strain γ in a thin annular section of radius r and thickness dr is

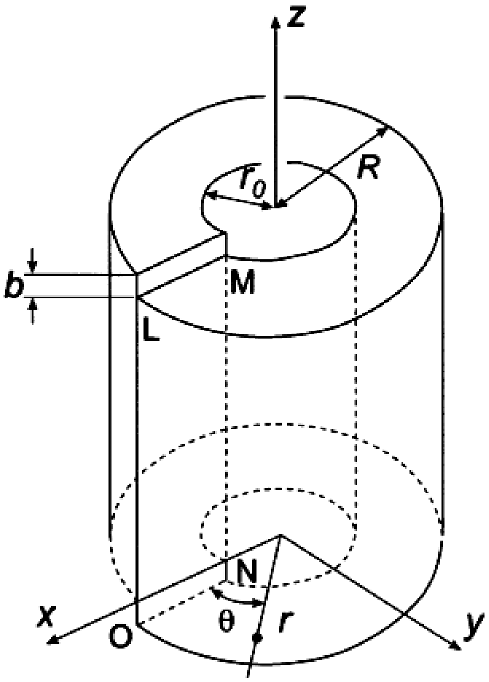


Fig.2.12

$$\gamma = \frac{b}{2\pi r}$$

the elastic energy per unit volume $\frac{dE}{dV}$ of thin annular region is

$$\frac{dE}{dV} = \frac{1}{2}\tau\lambda = \frac{1}{2}G\gamma^2 = \frac{G}{2}\left(\frac{b}{2\pi r}\right)^2$$

Where G – elastic shear modulus.

The volume of the annular ring is dv

$$dv = 2\pi r.dr \quad \text{and}$$

Thus the elastic energy per unit length of the shell is

$$dE = \frac{lGb^2}{4\pi}.\frac{dr}{r}$$

The strain energy due to the presence of this dislocation is

$$E = \int_{r_o}^{R} dE = \int_{r_o}^{R} \frac{lGb^2}{4\pi}.\frac{dr}{r}$$

$$= \frac{lGb^2}{4\pi}.\ln\frac{R}{r_o}$$

Where $\ln\frac{R}{r_o} = 4\pi$

$$\therefore \qquad E = lGb^2$$

Similarly, the energy of an edge dislocation is

$$E = \frac{1}{1-V}\frac{lGb^2}{4\pi}.\ln\frac{R}{r_o} \approx \frac{lGb^2}{1-V}$$

Where, v is the Poisson's ratio. If V = 1/3, the energy of an edge dislocation is 3/2 times that of screw dislocation of the same length. The above equations show that the energy of the dislocation is proportional to its length i.e. the line energy is equivalent to line tension. Thus a curved dislocation will have a line tension T, a vector acting along the line so that

$$T = \frac{\partial F}{\partial l} = Gb^2.$$

2.10 Shear strength of single crystals

Plastic deformation in crystals occurs by slip. In slip one part of the crystal slides as a unit across an adjacent part. The surface on which slip takes place is known as the slip plane. The direction of motion is known as the slip direction.

Consider two neighboring atomic planes separated by a distance'd', and 'a' is the separation between two atoms in the same plane. A stress τ is applied on the upper plane of atoms, so that it is displaced with respect to the lower plane of atoms by a distance x. For small elastic strains, the relation between the stress and the displacement is given by the equation

$$\tau = \frac{\mu x}{d} \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where μ is the shear modulus.

We can represent the stress –displacement by a periodic function as

$$\tau = K \sin\frac{2\pi x}{a}$$

For small displacements, (x<<a) $\sin\frac{2\pi x}{a} = \frac{2\pi x}{a}$

$$\therefore \quad \tau = k\frac{2\pi x}{a} \ldots\ldots\ldots\ldots\ldots(2)$$

Comparing eqns (1) and (2)

$$K\frac{2\pi x}{a} = \frac{\mu x}{d}$$

$$K = \frac{\mu a}{2\pi d}$$

Substituting the K value in eqn (2), we have

$$\tau = \frac{\mu a}{2\pi d} \sin \frac{2\pi x}{a}$$

The stress required for large displacement is called critical shear stressτ_c.

$$\tau_c = \frac{\mu a}{2\pi d}$$

If a = d

$$\tau_c = \frac{\mu}{2\pi} .$$

2.11 Surface Defects or plane defects

The defects, which take place on the surface of a material, are known as surface defects or plane defects. The surface defects take place either due to imperfect packing of atoms during crystallization or defective orientation of the surface.

a. ***Grain Boundary***

It is a general planar defect that separates regions of different crystalline orientation (i.e., grains) within a polycrystalline solid. The atoms in the grain boundary will not be in perfect crystalline arrangement. Grain boundaries are observed during the solidification of polycrystalline material. Grain boundary area depends on the grain size of the material and increases with decrease in grain size and vice versa.

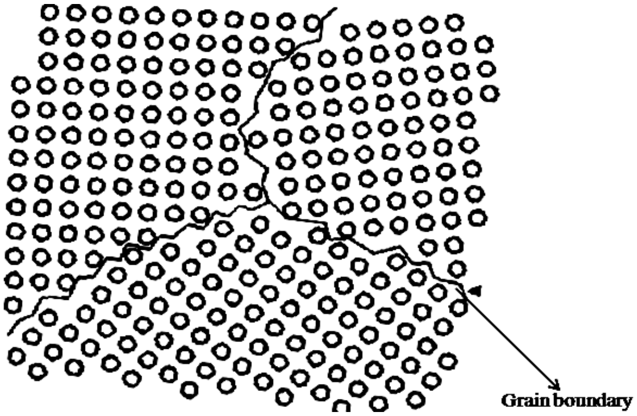


Fig.2.13

b. ***Tilt Boundaries***

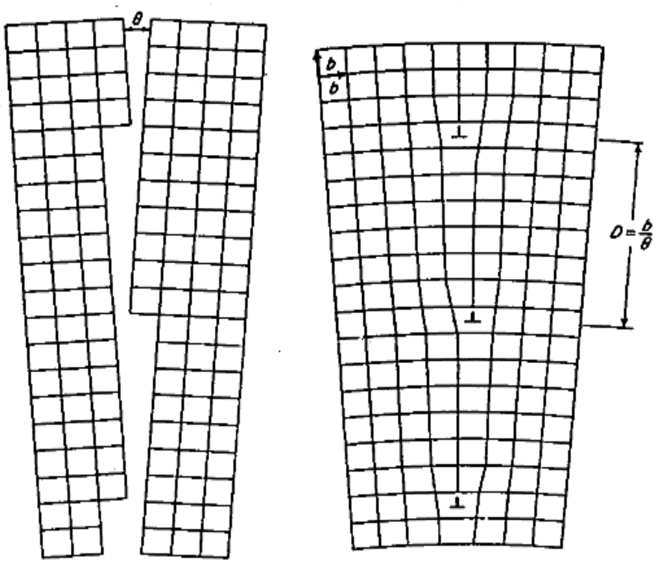


Fig.2.14

It is also called as a small angle boundary as the orientation of grains in two neighboring crystals differs by only a few degrees. By rotation of an axis in the boundary it is possible to bring the axis of two ordering grains into coincidence, i.e., a tilt boundary, in which case

Tan $\theta = b/h$ (or) $\theta = b/h$

Where, b is the length of the Burgers vector h is the vertical spacing between two neighboring edge dislocations. θ is the angle of tilt

These defects affect the deformation behavior, mechanical properties and recrystallisation temperature of materials. They also have an influence on electrical properties and corrosion resistance.

c. Twin boundaries

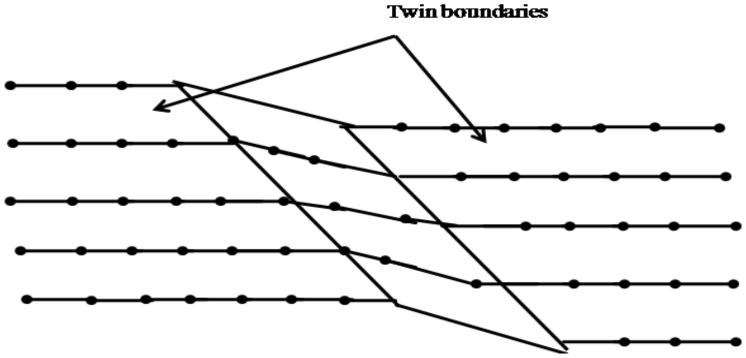


Fig.2.15

A ‘twin’ is an area defect where a mirror image of the regular lattice is formed during the growth of the silicon ingot, usually caused by a perturbation. The twin boundary is the mirror plane of the twin formation.

d. Stacking faults

A defect in a face – centered cubic or hexagonal close – packed crystal in which there is a change from the regular sequence of positions of atomic planes is called stacking fault.

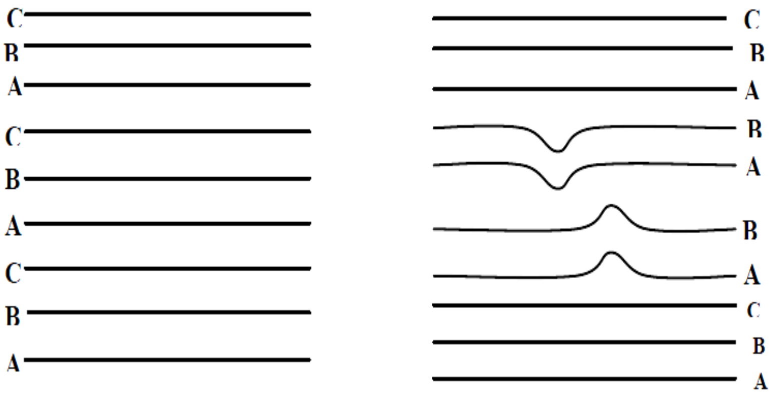


Fig.2.16

For example in the case of closed packed FCC structure the stacking sequence can be written as ABC ABC ….. In that sequence, it is possible in one atom layer 'A' the atoms are not positioned properly in a small region and hence deviates from the sequence, relative to the atoms of the layers above and below giving a defect, since now there is sequence of ABAB… which belongs to HCP structure instead of ABC ABC…. . The above diagram shows the stacking fault in FCC metal. So, stacking fault arises when there is only small dissimilarity between the stacking sequences of closed planes in FCC and HCP metals. Stacking faults are more frequently found in deformed metals than in annealed metals.

2.12 Sonder- Sibley notation rules for point defects in insulators

1. The basic atomic character of the defect is represented by a letter:
   (a) F is used for negative ion(anion) vacancies
   (b) V for positive ion (cation) vacancies
   (c) I is for interstitial species
2. The electronic character of the defects is given by a superscript charge. Thus an oxygen vacancy has an effective positive charge, since an anion has been removed from the neutral lattice and it is designated as F^{2+} .If charge neutrality is obtained by the capture of two electrons in the same vacancy, the defect becomes an F center.
3. In atomic crystal, the two neighboring F centers are denoted asF_2.
4. Impurity atoms are included as a subscript. An F center next to an impurity atom will be called as F_A and a cation vacancy next to an OH^- ion and having a trapped hole in an alkaline earth oxide would be a V_{oH}center.

UNIT III

DIELECTRICS AND FERRO ELECTRICS

3.1 Basic definitions

Electric dipole

Two equal and opposite charges (+q, -q) separated by a distance is called an electric dipole.

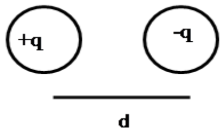


Fig.3.1

Dipole moment (μ)

The product of the magnitude of the charge and the distance between two charges is called as dipole moment. $\mu = qd$

Polarization

The process of producing electrical dipoles inside the dielectric by the application of an external electric field is called polarization .

The polarization p is thus defined as the dipole moment per unit volume. ie,

$$P = \frac{p}{\Delta V}$$

If the number of molecules per unit volume is N and if each has a moment p, then the polarization is given as P=N p

3.2 The electric field of a dipole

Consider the coordinates such that polarization vector p lies at the origin and points in the z-direction, then the potential at a point (r,θ) from the centre of the dipole is given as

$$V_{dip} = \frac{\hat{r}.P}{4\pi\varepsilon_0 r^2} = \frac{P\cos\theta}{4\pi\varepsilon_0 r^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The various components of the electric field in the spherical polar coordinate system can be written as,

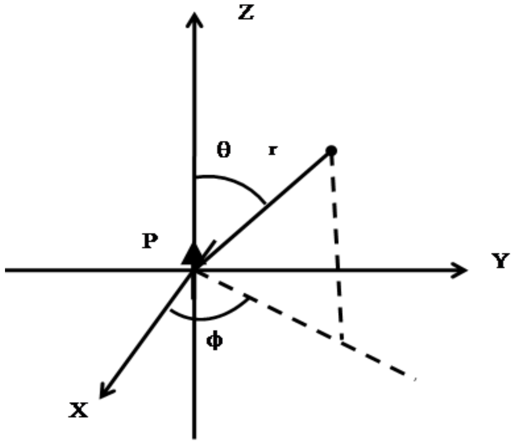


Fig.3.2

$$E_r = \frac{-\partial V}{\partial r} = \frac{2Pcos\theta}{4\pi\varepsilon_0 r^3} \text{......................(2)}$$

$$E_\theta = \frac{-1}{r}\frac{\partial V}{\partial \theta} = \frac{Psin\theta}{4\pi\varepsilon_0 r^3} \text{..................(3)}$$

$$E_\emptyset = \frac{-1}{rsin\theta}\frac{\partial V}{\partial \emptyset} = 0 \text{.....................(4)}$$

Thus, $E_{dip}\,(r,\theta) = \frac{P}{4\pi\varepsilon_0 r^3}(2\cos\theta\hat{r} + sin\theta\hat{\theta})$…………..(5)

In order to simplify this, let y = r sinθ and z = r cos θ

The radius vector r lying in the YZ - plane can be written as

$$\vec{r} = \hat{J}y + \widehat{K}z$$

$$= \hat{J}rsin\theta + \widehat{K}rcos\theta$$

Therefore, $\hat{r} = \frac{\vec{r}}{r} = \hat{J}sin\theta + \widehat{K}cos\theta$ ……………(6)

Similarly, $\hat{\theta} = \hat{J}cos\theta - \widehat{K}sin\theta$…………………(7)

Where $\hat{r}, \hat{\theta}$ are the unit vectors. Substituting the eqns (6) and (7) in eqn (5) we get,

$$E_{dip}\,(r,\theta) = \frac{P}{4\pi\varepsilon_0 r^3}(2\cos\theta(\hat{J}sin\theta + \widehat{K}cos\theta) + sin\theta(\hat{J}cos\theta - \widehat{K}sin\theta))$$

$$E_{dip}\,(r,\theta) = \frac{P}{4\pi\varepsilon_0 r^3}(2\hat{J}sin\theta\cos\theta + 2\widehat{K}\cos\theta^2 + \hat{J}sin\theta cos\theta - \widehat{K}sin\theta^2)$$

$$= \frac{P}{4\pi\varepsilon_0 r^3}\left(3\hat{J}sin\theta\cos\theta + \widehat{K}\ (2\cos\theta^2 - sin\theta^2)\right)$$

$$= \frac{P}{4\pi\varepsilon_0 r^3}\left(3\hat{J}sin\theta\cos\theta + \widehat{K}\ (3\cos\theta^2 - 1)\right)$$

$$= \frac{P}{4\pi\varepsilon_0 r^3}\left(3\cos\theta\left(\hat{J}sin\theta + \widehat{K}\ \cos\theta\right) - \widehat{K}\right)$$

$$= \frac{1}{4\pi\varepsilon_0 r^5}\left(3r^2\cos\theta\ P\left(\hat{J}sin\theta + \widehat{K}\ \cos\theta\right) - \widehat{K}\ r^2 P\right)$$

$$E_{dip}(r,\theta) = \frac{1}{4\pi\varepsilon_0 r^5}\left(3(\vec{P}.\vec{r})\vec{r} - r^2\vec{P}\right)$$

3.3 Dielectric susceptibility

The polarization P is directly proportional to the applied electric field E,

$$P \propto E$$

$$P = \varepsilon_0 \chi_e E$$

$$\chi_e = \frac{P}{\varepsilon_0 E}$$

Where, χ_e is a constant called the dielectric susceptibility of the medium.

3.4 Dielectric constant and its measurement

It is the ratio between permittivity of the medium (ε) and permittivity of free space ε_0.

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

Fig 3.3 shows an experimental setup for measuring dielectric constant. The plates of a capacitor are connected to a battery. In the absence of a dielectric inside the capacitor, the field produced by the charges is $E_{0.}$ the potential difference V_o across the capacitor is

$$E_o = \frac{V_o}{L} \text{……………..} (1)$$

Where, L is the distance between the plates.

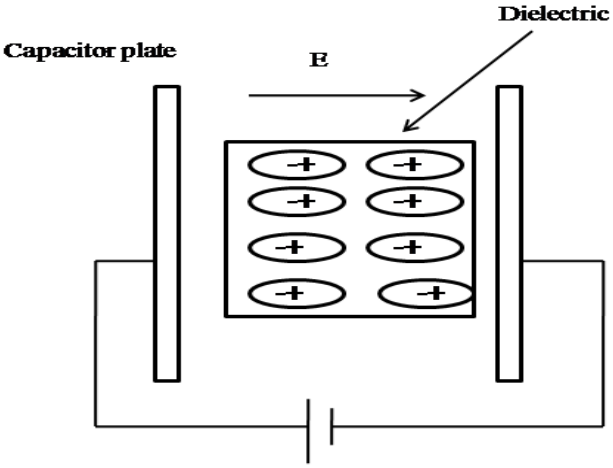


Fig.3.3

When a dielectric slab is placed between the plates, the field E_o polarizes the medium, which in turn modifies the field to a new value E.

$$E = \frac{V}{L} \text{………………..} (2)$$

The dielectric constant in terms of the fields E_o and E is given by the relation

$$\varepsilon_r = \frac{E_o}{E} \ldots\ldots\ldots\ldots\ldots(3)$$

From eqns (1), and (2)

$$\varepsilon_r = \frac{V_o}{V} \ldots\ldots\ldots\ldots\ldots(4)$$

Thus we can obtain the dielectric constant by measuring the potential difference across the capacitor with and without a dielectric.

We know that the capacity of the capacitor is $C = \frac{Q}{V}$; Q= CV

The above equation indicates that the increase in the capacity by a factor ε_r means a decrease in the potential difference as well as in the field by the same factor.

The decrease in the field in the presence of a dielectric medium is,

$$E = \frac{E_o}{\varepsilon_r}$$

This decrease in the field in turn induces dipoles and the medium gets polarized. The polarization produced in the material is a measurement of the charge in the capacitance.

$$P = (C - C_o)V$$

$$= (\varepsilon - \varepsilon_o)E$$

$$= (\varepsilon_r - 1)\ \varepsilon_o E$$

Rearranging the terms, we get

$$\varepsilon_r = 1 + \frac{P}{E\varepsilon_o} = 1 + \chi_e .$$

Where χ_e *is the electric susceptibility*.

Polarizability

It is the ratio of average dipole moment to the electrical field applied

$$\alpha = \frac{\mu}{E}$$. Unit :- Farad m^2

3.5 Internal field or local field

The long range coulomb field produced due to dipoles is known as internal field or local field.

Derivation

Let us assume a dielectric material is placed in an external field. Consider an imaginary sphere in the dielectric of radius r. The electric field acting on the atom A at the centre of the sphere is called internal field.

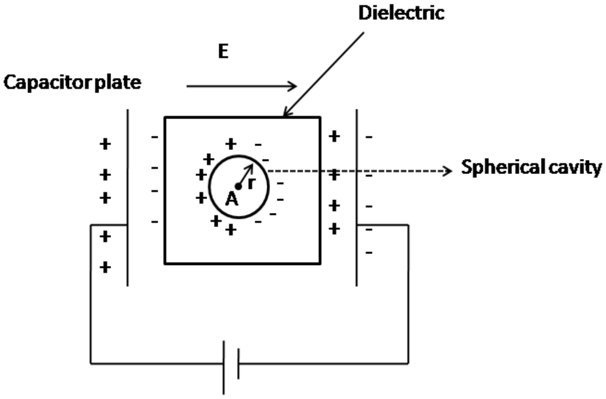


Fig.3.4

$E_{int} = E_1 + E_2 + E_3 + E_4$

Where,

E_1-------- Field due to the charge on the plates.

E_2--------Field due to the polarization charges.

E_3-------Field due to the polarized charges induced at the spherical surface.

E_4-- -----Field due to the atomic dipoles inside the sphere considered.

We take $E = E_1 + E_2$

If the dielectric is highly symmetric then the dipoles will cancel with each other. We can take $E_4 = 0$.

$E_{int} = E + E_3$…............(1)

To find E_3

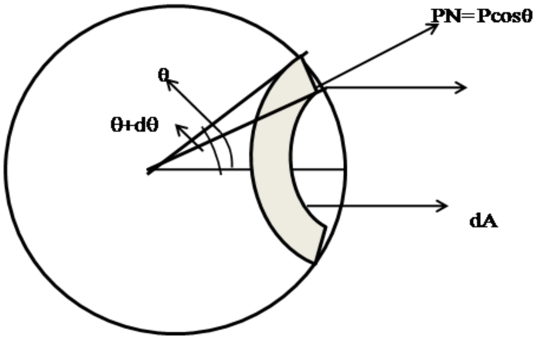


Fig.3.5

Let us consider small area ds on the surface of the sphere between θ and θ + dθ as shown in fig. 3.5. Let q' is the charge on the area ds. Polarization is defined as the surface charges per unit area.

If P_N is the component of polarization perpendicular to the area ds

$$P_N = Pcos\theta = \frac{q'}{ds}$$

$$q' = Pcos\theta ds \ldots\ldots\ldots\ldots\ldots(2)$$

Therefore electric field intensity at A due to a charge q’ is given by $E = \frac{q'}{4\pi\varepsilon_0 r^2}$………..(3)

Substitute eqn (2) in (3), $E = \frac{Pcos\theta ds}{4\pi\varepsilon_0 r^2}$

This field is along the radius r. Resolving the field intensity in to two components.

Parallel component $E_x = Ecos\theta$

$$\therefore E_x = \frac{Pcos\theta ds \times cos\theta}{4\pi\varepsilon_0 r^2}$$

$$= \frac{Pcos^2\theta ds}{4\pi\varepsilon_0 r^2}\ldots\ldots\ldots\ldots\ldots(4)$$

Perpendicular component $E_y = Esin\theta$

The perpendicular components are in opposite direction and hence cancel each other.

Now consider a ring of area dA and let Y be the radius of the ring.

Ring area dA = circumference $\times$ $thickness$

$$dA = 2\pi y \times rd\theta \ldots\ldots\ldots(6)$$

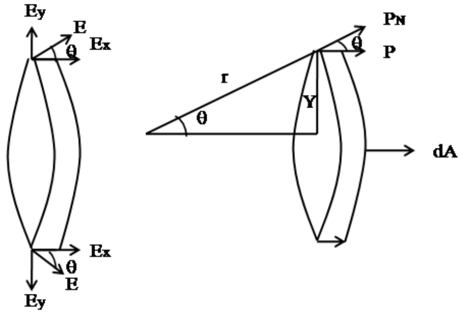


Fig.3.6

From the fig.3.6.

$$Y = rsin\theta$$

$$\therefore dA = 2\pi rsin\theta \times rd\theta$$

$$= 2\pi r^2 sin\theta d\theta \ldots\ldots\ldots(7)$$

Electric field intensity at A due to elemental ring dA,

$$E = \frac{Pcos^2\theta dA}{4\pi\varepsilon_0 r^2}\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Substitute eqn (7) in (8),

$$E = \frac{Pcos^2\theta \times 2\pi r^2 sin\theta d\theta}{4\pi\varepsilon_0 r^2}$$

E = $\frac{Pcos^2\theta sin\theta d\theta}{2\varepsilon_0}$……………(9)

Electric field intensity (E_3) due to the whole sphere can be obtained by integrating eqn (9) within the limits 0 to π.

$$E_3 = \int_0^\pi \frac{Pcos^2\theta sin\theta d\theta}{2\varepsilon_0}$$

$$= \frac{P}{2\varepsilon_0}\int_0^\pi cos^2\theta sin\theta d\theta \qquad \int_0^\pi cos^2\theta sin\theta d\theta = \frac{2}{3}$$

$$= \frac{P}{2\varepsilon_0} \times \frac{2}{3}$$

$$E_3 = \frac{P}{3\varepsilon_0} \text{ ………………(10)}$$

Substituting eqn (10) in (1)

E_{int} = E+$\frac{P}{3\varepsilon_0}$………….. (11). this is the expression for internal or local field.

3.6 Clausius –Mosotti equation

Let N be the number of atoms per unit volume.

Total polarization P = $N\alpha E_{int}$

$$E_{int} = \frac{P}{N\alpha} \text{………………… (1)}$$

We know that,

$$P = (\varepsilon_r - 1)\ \varepsilon_o E$$

$$P = (\varepsilon_o\varepsilon_r - \varepsilon_o)E$$

$$P = (\varepsilon - \varepsilon_o)E \qquad \varepsilon_o\varepsilon_r = \varepsilon$$

$$E = \frac{P}{\varepsilon - \varepsilon_o} \text{……………..(2)}$$

Substitte eqn (2) in the eqn $E_{int} = E + \frac{P}{3\varepsilon_0}$

$$E_{int} = \frac{P}{\varepsilon - \varepsilon_o} + \frac{P}{3\varepsilon_0}$$

$$E_{int} = \mathrm{P}(\frac{1}{\varepsilon - \varepsilon_o} + \frac{1}{3\varepsilon_0})$$

$$= \mathrm{P}\left(\frac{3\varepsilon_0 + \varepsilon - \varepsilon_o}{3\varepsilon_0(\varepsilon - \varepsilon_o)}\right)$$

$$E_{int} = \frac{P}{3\varepsilon_0}\left(\frac{2\varepsilon_0 + \varepsilon}{(\varepsilon - \varepsilon_o)}\right) \ldots\ldots\ldots\ldots (3)$$

Equating (1) and (3)

$$\frac{P}{\mathrm{N}\alpha} = \frac{P}{3\varepsilon_0}\left(\frac{2\varepsilon_0 + \varepsilon}{(\varepsilon - \varepsilon_o)}\right)$$

$$\frac{\mathrm{N}\alpha}{3\varepsilon_0} = \left(\frac{\varepsilon - \varepsilon_o}{2\varepsilon_0 + \varepsilon}\right)$$

Divide the numerator and denominator by ε_o

$$\frac{\mathrm{N}\alpha}{3\varepsilon_0} = \frac{\frac{\varepsilon}{\varepsilon_o} - 1}{\frac{\varepsilon}{\varepsilon_o} + 2}$$

$\frac{\mathrm{N}\alpha}{3\varepsilon_0} = \frac{\varepsilon_r - 1}{\varepsilon_r + 2}$ .This is known as Clausius –Mosotti equation.

3.7 Electronic polarization

The electronic polarization occurs due to the displacement of positively charged nucleus and negatively charged electrons in opposite direction when an external field is applied. Thus the separation created between the charges induces a dipole. This process occurs throughout the material and the material will be polarized.

The induced dipole moment $\mu = \alpha_e E$

Where α_e is electronic polarisability.

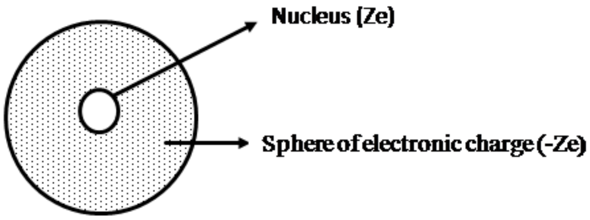


Fig.3.7

Consider an atom of a dielectric material. Let the charge of the nucleus is Ze. The electrons of charge (-Ze) are distributed uniformly throughout the atom of radius R. in the absence of an electric field the centre of gravity of the electron distribution coincides with the nucleus. Negative charge density of the atom is

$$\rho = \frac{\text{total } -\text{ve charge}}{\text{volum e of the atom}}$$

$$\rho = \frac{-Ze}{\frac{4}{3}\pi R^3}$$

$$\rho = \frac{-3Ze}{4\pi R^3} \text{ …………(1)}$$

When the dielectric is placed in a electric field of strength E, two phenomena occur. a) Lorentz force due to the electric field tends to separate the nucleus and the electron cloud from their equilibrium position. B) After separation, an attractive coulomb force arises between the nucleus and the electron cloud which tries to maintain the original equilibrium position.

Lorentz force = charge X field

$$F_L = ZeE \text{ ………..(2)}$$

Coulomb force $F_c = \frac{1}{4\pi\varepsilon_0}\left(\frac{q_p\, q_e}{x^2}\right)$…………….(3)

Where q_p = Ze -----charge of the nucleus.

q_e--------- Total negative charge enclosed in sphere of radius x.

$$q_e = \frac{4\pi x^3}{3} \times \frac{-3}{4}\frac{Ze}{\pi R^3}$$

$$= -Ze\frac{x^3}{R^3} \text{ ……………….(4)}$$

$$\therefore \quad F_c = \frac{1}{4\pi\varepsilon_0 x^2} \times \text{Ze} \times -Ze\frac{x^3}{R^3}$$

$$F_c = \frac{-1}{4\pi\varepsilon_0} \times \frac{Z^2\text{e}^2\text{x}}{R^3}$$

In equilibrium position

Lorentz force = - Coulomb force

$$F_L = F_c$$

$$\text{ZeE} = \frac{-1}{4\pi\varepsilon_0} \times \frac{Z^2\text{e}^2\text{x}}{R^3}$$

$$\text{E} = \frac{Z^2\text{e}^2\text{x}}{4\pi\varepsilon_0 R^3} \times \frac{1}{Ze}$$

$$E = \frac{Zex}{4\pi\varepsilon_0 R^3}$$

$$x = \frac{4\pi\varepsilon_0 R^3 E}{Ze}$$

The induced dipole moment $\mu = \text{charge} \times \text{displacement}$

$$= Ze \times x$$

$$= Ze \times \frac{4\pi\varepsilon_0 R^3 E}{Ze}$$

$$\mu = 4\pi\varepsilon_0 R^3 E$$

$$\mu = \alpha_e E$$

Where $\alpha_e = 4\pi\varepsilon_0 R^3$ is called electronic polarization.

3.8 The classical theory of electronic polarisability

According to classical theory, atom is that there is a heavy, immobile nucleus of charge Ze surrounded by an electronic shell of charge Ze connected to the nucleus by a harmonic spring or a force F = $-$Kx

Let the external electric field is taken in the form of E=$E_0 \exp(-i\omega t)$ where ω is the angular frequency of the variation of electric field. The equation of motion of the electron shell of mass m will be m $\frac{d^2r}{dt^2}$ = $-$Kr$-$ e$E_0 \exp(-i\omega t)$…………..(1)

Where r = $r_0 \exp(-i\omega t)$

$$\frac{d^2r}{dt^2} = -\omega^2 r \text{ …………………(2)}$$

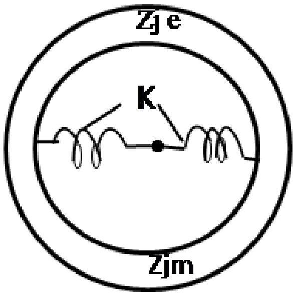


Fig.3.8

Eqn (1) becomes,

$$-m\omega^2 r = -Kr - eE_0 \exp(-i\omega t)$$

Where k is the force constant between the positive heavy nucleus and the electron cloud

$$-m\omega^2 r_0 \exp(-i\omega t) = -Kr_0 \exp(-i\omega t) - eE_0 \exp(-i\omega t)$$

$$-m\omega^2 r_0 = -Kr_0 - eE_0$$

$$\omega^2 r_0 = \frac{K}{m} r_0 - \frac{e}{m} E_0$$

$$\omega^2 r_0 = -\omega_0^2 r_0 - \frac{e}{m} E_0$$

Where $\omega_0^2 = \frac{K}{m}$ is the natural frequency of deformation of electron cloud . Thus

$$r_0(\omega_0^2 - \omega^2) = -\frac{e}{m} E_0$$

$$r_0 = -e \frac{E_0}{m(\omega_0^2 - \omega^2)}$$

As $'r'$ is the separation of electronic shell from the nucleus, which is the type of

r = r_0 exp$(-i\omega t)$, the corresponding dipole moment is taken in the form of

P = e r = e r_0 exp$(-i\omega t)$

P = p_0 exp$(-i\omega t)$ and $p_0 = \alpha_{at}(\omega)\, E_0$

Where α_{at} is the atomic or electronic polarisability

$$\alpha_{at}(\omega) = \frac{e^2}{m(\omega_0^2 - \omega^2)}$$

3.9 Structural phase transition

The structural transition of crystal from one structure to another with the variation of temperature or pressure is called structural phase transition. Some structural phase transition has small effect on the macroscopic physical properties of the material. Some other structural phase transitions may have spectacular effects on the macroscopic electrical properties. Ferroelectric transitions are experienced by the appearance of spontaneous dielectric polarization in the crystal.

3.9.1 Ferro electric material

Materials which exhibit electronic polarization even in the absence of the applied field are called as ferroelectric materials. The electricity produced by the ferroelectric material is called Ferro electricity.

Examples; Barium titanate ($BaTiO_3$), potassium Dihydrogen phosphate (KDP)

Properties of ferroelectric materials

1. The ferroelectric materials exhibits domain structures similar to ferromagnetic materials.
2. They possess spontaneous polarization.
3. They exhibit Ferro electricity only when T≤ T_c , T_c is called the Ferroelectric Curie temperature or transition temperature.
4. Above T_c, the Ferro electricity disappears and the material converted to para electric material. i.e. Above T_c the spontaneous polarization is destroyed by the thermal disorder.
5. The condition for spontaneous polarization is given by $\frac{N\alpha_e}{3\varepsilon_0} = 1$
6. Ferroelectric materials exhibit piezoelectric and pyroelectricity.

Classification of ferroelectric materials

Ferroelectric materials may be classified in to three groups depending on their chemical composition and structure.

1. Tartrate group
2. Dihydrogen phosphates and arsenates alkali metals
3. Oxygen octahedrogen group

1. Tartrate group

Rochelle salt, which is the sodium – potassium salt of tartaric acid Na K $(C_4H_4O_6)4H_2O$ is the typical example of tortrate group ferroelectric material. This material has the unique property that it is ferroelectric only in the temperature range from -18°C to 23°C. Thus this material has two transition regions.

Figure 3.9 shows the variation of spontaneous polarization P of Rochelle salt with temperature. The other materials belongs to this group of ferroelectric material are N H_6 K $(C_4H_4O_6)$ $4H_2O$, Rb K $(C_4H_4O_6)$ $4H_2O$

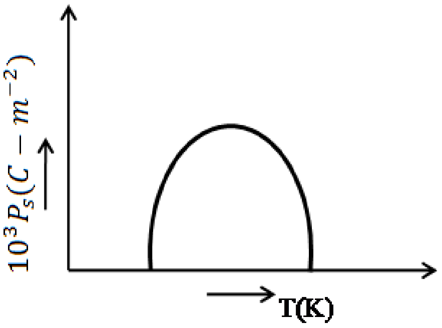


Fig.3.9

2. Dihygrogen phosphate and Arsenates of alkali metals

A typical example of this group is K$H_2P\,O_4$. In this case, there is only one curie temperature namely 123K. Figure3.10 shows the spontaneous polarization versus temperature curve of this material.

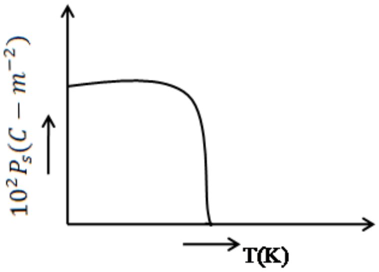


Fig.3.10

3. oxygen octahedron group

Ba Ti O_3 is the best example of oxygen octahedron group of ferroelectric materials. Above the Curie temperature (120°c), Ba Ti O_3 has cubic structure as shown in fig 3. 11.

In this structure, the Ba^{2+} ions occupy the corner of a cube, the centers of the cube faces are occupied by O^{2-}ions. The oxygen ions form an octahedron, at the centre of which the small Ti^{4+}ion is located. The Ti^{4+} ion causes a high ionic polarisability by two reasons; a) It has a charge of 4e and b) it can be displaced over a relatively large distance.

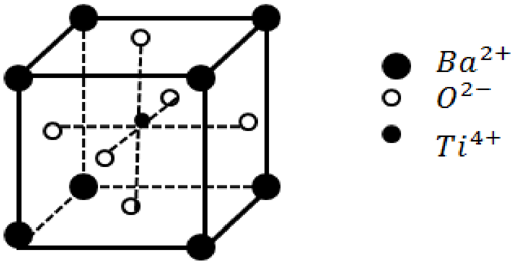


Fig.3.11

When the temperature is lowered through the critical temperature of 120°C, the material becomes spontaneously polarized along any of the cube edges and the structure also charged into tetragonal structure. BaTi O_3 has two more transition temperatures. One at 5°c, where the spontaneous polarization changes its direction from one of the cube edges to a direction along the face diagonal and one at -80°C where the spontaneous polarization changes from a direction corresponding to a face diagonal to one along a body diagonal. Associated with each of these ferroelectric transitions is a change in the crystal structure of the material.

3.9.2 Landau theory of phase transition

A first – order phase transition between the ferroelectric and the para electric state is distinguished by a discontinuous change of the saturation polarization at the transition temperature. The transition between the normal and superconducting states is a second – order transition. In this transition the degree of order goes to zero without a discontinuous change as the temperature is increased.

To obtain the thermodynamic theory of behavior of a ferroelectric crystal, we assume that the Landau free energy density $\hat{F}$ in one dimension may be expanded as

$$\hat{F}(P,T,E) = -EP + g_0 + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 + \frac{1}{6}g_6P^6 + \ldots\ldots\ldots \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

In thermal equilibrium, the value of polarization is given by the minimum value of $\hat{F}$ called Helmholtz free energy F(T,E) .

In an applied electric field E, the equilibrium polarization satisfies the condition

$$\frac{d\hat{F}}{dP} = 0 = -E + g_2P + g_4P^3 + g_6P^5 + \ldots\ldots \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

To obtain a ferroelectric state, the coefficient of the term P^2 in equation (1) must be zero at some temperatureT_0.

$$g_2 = \gamma(T - T_0) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where γ is taken as a positive constant and T_0 may be equal to or lower than the transition temperature. A positive value of g_2 means that the lattice is soft and is close to in stability. A negative value of $g_2$means that the unpolarised lattice is unstable.

Second-order transition

If g_4 in equation (1) is positive, the term g_6 is neglected. From eqn (2), the polarization for zero applied electric field can be written as

$$\gamma\,(T - T_0)\,P_s + g_4{P_s}^3 = 0 \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$${P_s}^2 = \frac{\gamma}{g_4}\,(T - T_0)$$

$|P_s| = \left[\frac{\gamma}{g_4}\,(T - T_0)\right]^{\frac{1}{2}}$The phase transition is a second – order transition because the polarization goes continuously to zero at the transition temperature. The transition Li Ta O_3 is an example of a second order transition.

First – order transition

The transition is first order if g_4 in equation (1) is negative. The equilibrium condition for E =0 is given by eqn (2).

$$\gamma\,(T - T_0)\,P_s - g_4 P_s^{3} + g_6\,P_s^{5} = 0$$

so that either $P_s = 0$ or

$$\gamma\,(T - T_0) - |g_4| P_s^{2} + g_6\,P_s^{4} = 0 \;\ldots\ldots\ldots(5)$$

At the transition temperatureT_C, the free energies of the Para electric and ferroelectric phases will be equal. The transition in Ba Ti O_3 is first order transition.

3.9.3 AntiFerroelectricity

AntiFerro electricity is an analogue of anti ferromagnetism. Hence like anti Ferro magnets, in antiferroelectric materials, each dipole is anti parallel to its neighboring dipoles hence has no bulk polarization and do not exhibit hysteresis effect. However anti Ferro electric state may be changed in to ferroelectric state under the influence of strong external field or upon cooling to a very low temperature.

3.9.4 Ferro electric domain

A Ferro electric crystal consists of a number of domains; within each domain the polarization has a specific direction. However, this direction varies from one domain to another. In the absence of an applied electric field all the dipoles are randomly oriented resulting in net zero. When an electric field is applied, the domain with polarization making an angle with the electric field tries to orient along the direction of electric field. With increasing electric field the number of domains align with it also increases at the expense of domains whose polarization direction is anti parallel to the electric field. Thus polarization increases with electric field as shown OC in fig 3.12.

When the polarization of all the domains align parallel to the electric field (AB), there is no further increase in the polarization with increasing electric field and polarization saturates and the crystal behaves as it has only a single domain. The value of spontaneous polarization P_s is determined by extrapolation of the linear part BC to the zero electric field. If electric field is now decreased, the polarization of the crystal also decreases but does not follow exactly the same path as for with increasing electric field . During decrease of the applied electric field the value of polarization does not vanish at zero magnetic field but their remains the polarization called remanent polarization P_r.

Now if the direction of the applied electric field is reversed, the polarization decreases from value P_r to zero. The electric field necessary to make polarization zero again is known as coercive field E_c. A further increase in the electric field in the opposite direction causes the polarization to grow in the reverse direction and a saturation value of polarization is obtained (EF) and curve FED is obtained. If the electric field necessary to obtain zero polarization is large than the breakdown field of the crystal, no change in the direction of spontaneous polarization can be reached and solid cannot be treated as ferroelectric. Since the relation between P and E is nonlinear therefore the dielectric constant of a ferroelectric depends on the electric field strength and temperature at which it is measured.

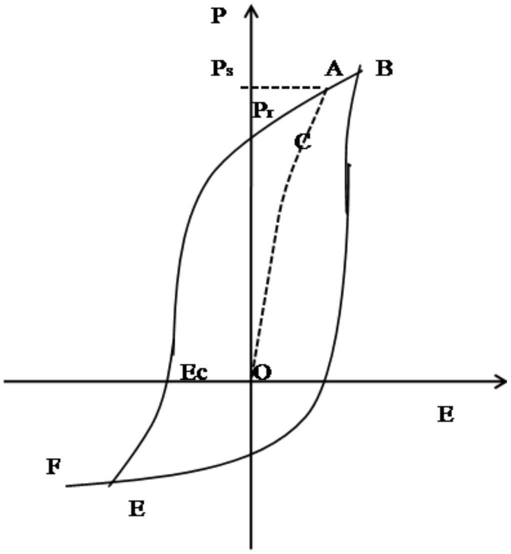


Fig.3.12

Clausius –Mosotti equation is

$$\frac{\mathrm{N}\alpha}{3\varepsilon_0} = \frac{\varepsilon_r - 1}{\varepsilon_r + 2}$$

$$\varepsilon_r - 1 = (\varepsilon_r + 2)\frac{\mathrm{N}\alpha}{3\varepsilon_0}$$

$$\varepsilon_r = \frac{2\mathrm{N}\alpha + 3\varepsilon_0}{3\varepsilon_0 - \mathrm{N}\alpha} \text{…………………………..(1)}$$

From the above equation, it is seen that the dielectric constant is very sensitive to small deviation of $\mathrm{N}\alpha$ from$3\varepsilon_0$. The deviation is represented as

$$\mathrm{N}\alpha = 3\varepsilon_0(1-\delta) \qquad \text{For } \delta \ll 1 \text{ ……(2)}$$

From eqns (1) and (2)

$$\varepsilon_r = \frac{6\varepsilon_0(1-\delta) + 3\varepsilon_0}{3\varepsilon_0 - 3\varepsilon_0(1-\delta)} = \frac{3-2\delta}{\delta} = \frac{3}{\delta} \text{ ………..(3)}$$

The deviation of δ is linear dependent on the temperature nearT_c, we assume that

$$\delta = \frac{3}{C}(\mathrm{T} - T_c) \text{ …………………………(4)}$$

where C is constant of proportionality.

Substituting eqn (4) in eqn (3)

$$\varepsilon_r = \frac{C}{\mathrm{T} - T_c}$$

This is known as Curie Weiss law for ferroelectrics.

3.9.5 Piezoelectricity

When an external force is applied to the opposite sides of the crystalline material, polarization is induced and an electric field is established across the material. If the sign of the external fore is reversed, the direction of the field is reversed. The converge effect of piezoelectricity effect is that when the crystal is subjected to an external field along specific orientations, and then it gets strained. Titanates of Barium and lead, tourmaline, lead zerconate, quart are the examples of piezoelectric materials.

3.9.6 Ferro elasticity

Ferro elasticity is a phenomen on in which a material may exhibit a spontaneous strain. When stress is applied to a Ferro elastic material, a phase change will occur in the material from one phase to an equally stable phase, either of different crystal structure (e.g. cubic to tetragonal), or of different orientation (a 'twin' phase). This stress-induced phase change results in a spontaneous strain in the material.

The shape memory effect and super elasticity are manifestations of Ferro elasticity. Nitinol (nickel titanium), a common Ferro elastic alloy, can display either super elasticity or the shape-memory effect at room temperature, depending on the nickel/titanium ratio.

UNIT IV

MAGNETISM 1

4.1 Basic definitions and units

Magnetic field

Magnetic field is the space around a magnet where its magnetic effect is felt. The magnetic field is represented by magnetic lines of force emanate from north pole and pass through the surrounding medium and then re-enter the south pole.

Magnetic flux (φ)

Total number of magnetic lines of forces passing through a surface is known as magnetic flux. It is represented by the symbol φ and its unit is weber (Wb).

Magnetic flux density (or) Magnetic induction (B)

Magnetic flux density (B) is defined as the magnetic flux (φ) passing normally through unit area of cross section at that point. The unit is Wb/m^2 or tesla.

Thus $B = \frac{\varphi}{A}$

Magnetic field intensity (H)

Magnetic field intensity at any point in a magnetic field is the force experienced by a unit North Pole placed at that point. It is denoted by H and its unit is N/Wb.

Magnetic moment (μ_m)

Magnetic moment is a measure of the strength of a magnet. It is the product of strength of one of the poles and the distance between the two poles of a magnet.

Magnetisation (M)

When a solid is placed in a magnetic field, it gets magnetized. The magnetic moment per unit volume developed inside the solid is called magnetization and is denoted by M. It is measured in amperes per meter (am^{-1}).

Magnetic permeability (μ)

It is defined as the ratio of magnetic induction B to the applied field H. i.e.,

$$\mu = \frac{B}{H}$$

Rearranging the above equation, we get, $B = \mu_0 (M+H)$

The permeability of vacuum of free space is $\mu_0 = 4X10^{-7}$ H/m.

Relative permeability (μ_r)

Relative permeability (μ_r) of a medium is defined as the ratio between the absolute permeability (μ) to the permeability of the free space (μ_0) .

$$\mu_r = \frac{\mu}{\mu_0}$$

Magnetic susceptibility (χ)

It is defined as the ratio of the intensity of magnetization M to the magnetic field strength H.

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

Relation between magnetic parameters:

Relative permeability $\mu_r = \frac{\mu}{\mu_0}$

Substituting the value of $\mu = \frac{B}{H}$,we get

$$\mu_r = \frac{B}{H\mu_0}$$

substituting the magnetic induction $B = \mu_0(M+H)$

$$\mu_r = \frac{\mu_0(M+H)}{H\mu_0}$$

$$\mu_r = 1 + \chi$$

4.2 Origin of magnetic moments

The magnetic property of matter arises due to the orbital and spin angular motion of charged particles in an atom. i.e., whenever a charged particle has an angular momentum it contributes to the magnetic moment. In an atom we have two kinds of charges; namely, positively charged nucleus and negatively charged electrons. Thus, there are three contributions to the magnetic moments of the material.

1. Due to the orbital motion of electrons.
2. Due to the spin of the electrons, and
3. Due to the spin of the nucleus.

Since the mass of the nucleus is very large as compared to that of the electrons, nuclear magnetic moment becomes negligibly small and hence neglected. Thus, the magnetic moment of the atom is therefore considered as mainly due to the orbital and the spin motion of the electrons.

4.3 Magnetic moment due to electrons

Each electron in an atom has magnetic moments that originate from two sources.

1. Due to the orbital motion of electron around the nucleus and
2. Due to the spinning of an electron around its own axis.

4.3.1 Magnetic moment due to orbital angular momentum of electrons

Let us consider an electron moving in a circular orbit of radius r with a constant velocity v. let T be the time taken for one rotation and e be the magnitude of charge of the electron. Thus an electron's orbit may be considered to be a small current loop generating a very small magnetic field and having a magnetic moment along its axis of rotation.

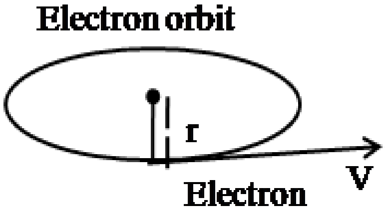


Fig.4.1

Therefore the current across any point in the orbit is

$$I = \frac{-e}{T}………………(1)$$

The area of the orbit is $A = \pi r^2$

The magnetic moment associated with the orbit is $\mu_e = IA$

$$= \frac{-e}{T}\pi r^2 \ldots\ldots\ldots\ldots (2)$$

Since T is the time taken for one revolution, the angle covered in time T is 2π.

Angular velocity $\omega = \frac{2\pi}{T}$

$$T = \frac{2\pi}{\omega} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Substituting the value of T in equation (2)

$$\mu_e = \frac{-e}{2\pi}\pi r^2 \omega$$

$$\mu_e = \frac{-e\omega r^2}{2} \ldots\ldots\ldots\ldots (4)$$

But from the theory of circular motion, the angular momentum L is given by

$$L = m_e \omega r^2 \ldots\ldots\ldots\ldots\ldots (5)$$

Substituting equation (5) in (4) we get,

$$\mu_e = \frac{-e}{2m_e} L \ldots\ldots\ldots\ldots\ldots (6)$$

Equation (6) gives the expression for the magnetic moment associated with the orbital motion of the electron .The negative sign indicates that, the magnetic moment vector and the angular velocity are aligned in opposite directions.

4.3.2 Magnetic moment due to spin of the electron

According to quantum theory, the magnetic moment associated with the spin of the electron is given by $\mu_s = \frac{e}{m_e} S$ ……………… (7)

Where S the spin angular momentum $= \frac{1}{2}(\frac{h}{2\pi})$

ie,. $\mu_s = \frac{e}{m_e} \cdot \frac{1}{2}(\frac{h}{2\pi})$

$$\mu_s = \frac{e}{2m_e} \cdot (\frac{h}{2\pi}) \ldots\ldots\ldots\ldots (8)$$

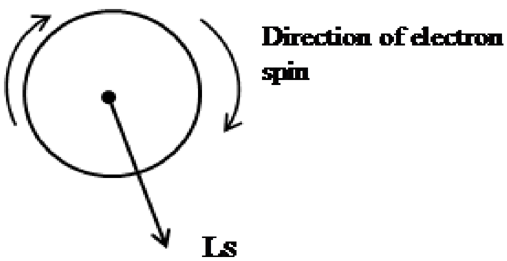


Fig.4.2

$\mu_B = \frac{e\hbar}{2m_e}$ $(\mu_S = \mu_B)$

Substituting the values in equation (8), we have

$$\mu_B = \frac{1.6\times10^{-19}\times6.625\times10^{-34}}{4\times3.14\times9.1\times10^{-31}}$$

$\mu_B = 9.274\times10^{-24}$ ampere meter^2

Where μ_B is known as Bohr magneton.

4.4 Classification of magnetic materials

Magnetic materials are classified into different categories based on their magnetic parameters like susceptibility, dipole moment, temperature dependence and permeability.

1. Diamagnetic materials

2. Paramagnetic materials

3. Ferromagnetic materials, and

4. Antiferromagnetic materials

5. Ferromagnetic materials

4.4.1 Diamagnetic materials

Definition

Dia magnetic materials are the magnetic materials having the dipoles oriented in such a way that the resultant dipole moment is zero. The external magnetic field changes the rotation of the individual dipoles. This produces an induced magnetic moment and it opposes the applied field. This is weak effect and decreases the magnetic induction present in the material. This effect is known as diamagnetism.

Examples: Bismuth, antimony, mercury, copper, and gold.

Properties

- Dia magnetic materials repel the magnetic lines of force.
- There is no permanent dipole moment. Therefore, the magnetic effects are very small.

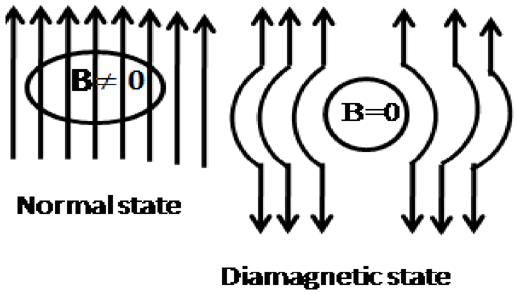


Fig.4.3

- Magnetic susceptibility is negative and is independent of temperature and applied magnetic field strength.
- Magnetic permeability is less than one

4.4.2 Paramagnetic materials

Definition

In paramagnetic material, the dipoles are randomly oriented in such a way that the resultant dipole moment is not equal to zero. There is a small amount of resultant magnetic moment in each atom even in the absence of magnetic field.

When an external magnetic field is applied, the magnetic moments of individual atom reoriented itself along the direction of the applied field and the material is magnetized.

Examples: ferric oxide, nickel sulphate, ferrous sulphate, chromium etc.

Dipole alignment

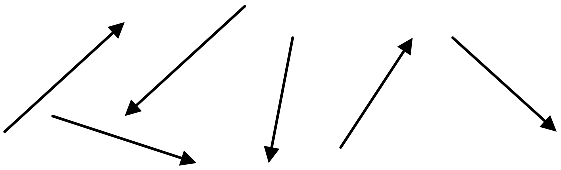


Fig.4.4

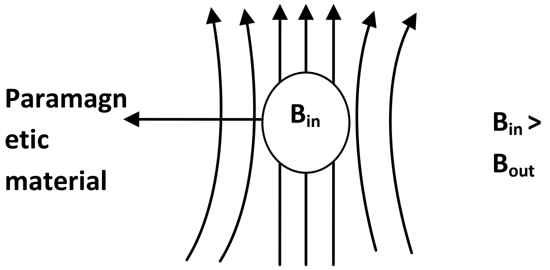


Fig.4.5

Properties

- Paramagnetic materials attract the magnetic lines of force.
- They possess permanent dipole moment.
- Magnetic susceptibility is positive and is given by,

$$\chi = \frac{C}{T-\theta} \quad \text{(Curie – Weiss law)}$$

Where, C → Curie constant

T → absolute temperature

θ → Curie temperature

Magnetic susceptibility is independent of applied magnetic field strength and it depends on the temperature.

- Magnetic permeability is greater than 1.
- When the temperature is less than Curie temperature, the paramagnetic materials change as diamagnetic materials.

4.4.3 Comparison of dia, para and ferromagnetic materials

S.No.	Dia	Para	Ferro
1.	Diamagnetic materials are the magnetic materials, having the dipoles oriented in such a way that the resultant dipole moment is zero.	In paramagnetic material, the dipoles are randomly oriented in such a way that the resultant dipole moment is not equal to zero. There is a small amount of resultant magnetic moment in each atom even in the absence of magnetic field.	In ferro magnetic material, the magnetic interaction between any two dipoles aligns themselves parallel to each other. The materials which have finite values of magnetization even if the external magnetic field is absent are called ferromagnetic material.
2.	When the material is placed in the magnetic field the magnetic flux lines are repelled away from the material.	When the material is placed in the magnetic field the magnetic flux line pass through the material.	When the material is placed in the magnetic field the magnetic flux lines are highly attracted towards the centre of the material.
3.	Susceptibility is negative.	Susceptibility is positive and small.	Susceptibility is positive and large.
4.	Susceptibility is independent of temperature.	Susceptibility is independent of temperature.	Susceptibility depends on temperature.
5.	Permeability is less than one	Permeability is greater than one	Permeability is very much greater than one
6.	When the temperature is less than the Curie temperature the diamagnetism suddenly disappear and the material becomes normal material.	When the temperature is less than the Curie temperature the paramagnetic material is converted into diamagnetic material.	When the temperature is greater than the Curie temperature the ferromagnetic material is converted into paramagnetic material.
7.	No spin or magnetic moment.	All spins are randomly oriented.	All spins are orderly oriented.
8.	**Examples:** Hydrogen, Bismuth, Gold, water, germanium, silicon etc.,	**Examples:** Platinum, Aluminium, Chromium etc.,	**Examples:** Iron, Nickel, Cobalt, Steel etc.,

4.5 Langevin diamagnetism theory

Consider an electron of mass m and charge e rotating about the nucleus of charge Ze in a circular orbit of radius r. If ω_0 is the angular velocity of electron in the absence of an applied field then we have,

$$F = m\omega_0^2 r = \frac{Ze^2}{4\pi r^2\ \varepsilon_0} \ldots\ldots\ldots\ldots\ldots (1)$$

$$\omega_0^2 = \frac{Ze^2}{4\pi r^2\ \varepsilon_0 m r} = \frac{Ze^2}{4\pi r^3\ \varepsilon_0 m}$$

$$\omega_0 = \sqrt{\frac{Ze^2}{4\pi r^3\ \varepsilon_0 m}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The magnetic moment of the electron is m = current X area = $\frac{e\omega_0}{2\pi} \times \pi r^2 = \frac{e}{2}\omega_0 r^2$

In the presence of a magnetic induction, the Lorentz force on an electron moving with velocity v is given by

$$F = -e\,(v\times B) \ldots\ldots\ldots\ldots\ldots (3)$$

$$F = -eBr\omega \qquad\qquad (\omega = v/r)$$

If ω is the angular velocity of electron in the presence of field, the condition for stable motion is

$$m\omega^2 r = \frac{Ze^2}{4\pi r^2\ \varepsilon_0} - eBr\omega$$

Using the equation (1) we get

$$m\omega^2 r = m\omega_0^2 r - eBr\omega \ \ldots\ldots\ldots\ldots (4)$$

Divide the eqn (4) by mr

$$\omega^2 = \omega_0^2 - \frac{eB\omega}{m}$$

$$\omega^2 + \frac{eB\omega}{m} - \omega_0^2 = 0 \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Solving this eqn

$$\omega = \frac{\frac{-eB}{m} \pm \sqrt{(\frac{eB}{m})^2) + 4{\omega_0}^2}}{2}$$

$$= \pm\sqrt{(\frac{eB}{2m})^2) + {\omega_0}^2} - \frac{eB}{2m}$$

$$\frac{eB}{2m} \ll \omega_0$$

So, $\omega = \pm\ \omega_0 - \frac{eB}{2m}$ …………….. (6)

This shows that the angular velocity of revolution of an electron changes by a factor of $\frac{eB}{2m}$ in the presence of magnetic induction B. this result is called the Larmor theorem.

The change in frequency produces as additional current I =charge × revolution per unit time.

$$I = -e\,(\frac{1}{2\pi}\frac{eB}{2m})$$

$$= -\frac{e^2B}{4\pi m}$$

The corresponding change in the magnetic moment of the electron is

$$\Delta m = current\ \times area$$

$$= -\frac{e^2B}{4\pi m} X\pi r^2 \ = -\frac{e^2Br^2}{4m} \text{ ………………… (7)}$$

On summing over all electrons in the atoms, the induced moment /atom becomes

$$\Delta m_{atom} = -\frac{e^2B\sum r^2}{4m}$$

Let Z be the number of electrons in the atom. Then,

The magnetization $M = -\frac{Ze^2B\sum r^2}{4m}$……………….. (8)

All the electron orbits are not oriented normal to the magnetic field hence r^2 in eqn (8) should be replaced by $\frac{2}{3}r^2$

$$\therefore\ M = -\frac{Ze^2B\sum r^2}{6m}$$

For the solid consisting of N atom per unit volume,

The susceptibility of the material $\chi = \frac{M}{H} = -\frac{ZNe^2B\sum r^2}{6mH}$ ($B = \mu_0 H$)

$$\chi = -\frac{ZNe^2\mu_0 \sum r^2}{6m} = -\frac{e^2\mu_0}{6m} ZN \sum r^2$$

$$\chi = -\frac{e^2\mu_0}{6m} ZN < r^2 > \ldots\ldots\ldots\ldots\ldots\ldots(9)-$$

This shows χ is independent of the field strength and temperature. This is the classical langevin result.

4.6 Langevin theory of paramagnetism

Consider a paramagnetic gas containing N atoms per unit volume, each having a permanent magnetic moment. The mutual interaction between the magnetic dipoles is neglected. In the presence of the magnetic induction B, the dipoles tend to orient themselves in the field direction. The thermal energy at ordinary temperature resists the alignment of dipoles. In thermal equilibrium, the dipoles orient themselves at an angle θ with the direction of the applied field.

The magnetic potential energy of each dipole in this position is given by

$$E = -\mu_m . B = -\mu_m B\cos\theta \ldots\ldots\ldots\ldots\ldots.. (1)$$

Let N be the number of dipoles in unit volume. If dN is the number of dipoles having inclination θ and $(\theta + d\theta)$and energy value E. then,

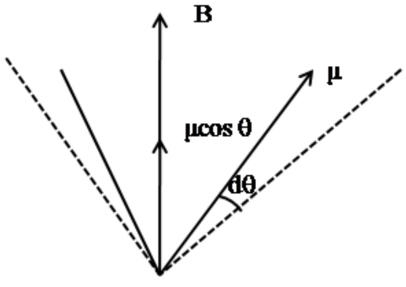


Fig.4.6

$$dN \propto \exp(-\frac{E}{K_B T}) \sin\theta d\theta$$

$$dN = c \exp(-\frac{E}{K_B T}) \sin\theta d\theta \ldots\ldots\ldots\ldots\ldots(2)$$

Substituting eqn(1) in eqn (2)

$$dN = c \exp(\frac{\mu_m B\cos\theta}{K_B T}) \sin\theta d\theta$$

$$dN = c \exp(a\cos\theta) \sin\theta d\theta \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$a = \frac{B\mu_m}{K_B T}$$

$$N = \int dN = \int_0^{\pi} c \exp(a\cos\theta) \sin\theta d\theta$$

Put cos $\theta = x$; sin$\theta d\theta = -dx$

$$N = c\int_{+1}^{-1} e^{ax}(\text{-dx}) = c\left[\left[\frac{e^{ax}}{a}\right]_{-1}^{1}\right]$$

$$N = \frac{c}{a}[e^{a} - e^{-a}]$$

$$c = \frac{Na}{e^{a}-e^{-a}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The total magnetic moment due to N molecules in one cubic meter is

$$M = \int_0^{\pi} \mu_m cos\,\theta dN \ldots\ldots\ldots\ (5)$$

Where, M – magnetization.

Substituting eqn (3) in (5)

$$M = \int_0^{\pi} c\mu_m cos\,\theta \text{exp}(\text{acos}\theta)\ \text{sin}\theta d$$

Let x = cosθ

dx = $-sin\theta d\theta$

$$\therefore \quad M = c\mu_m \int_1^{-1} xe^{ax}(-dx)$$

$$= c\mu_m \int_{-1}^{+1} xe^{ax}(dx) = c\mu_m \int_1^{-1}(x/a)d(e^{ax})$$

$$= c\mu_m \left[\frac{xe^{ax}}{a}\right]_{-1}^{1} - \frac{c\mu_m}{a}\int_{-1}^{1} e^{ax}\,dx$$

$$= \frac{c\mu_m}{a}\left[(e^{a} + e^{-a}) - \left(\frac{e^{a}-e^{-a}}{a}\right)\right]$$

$$c = \frac{aN}{e^{a}-e^{-a}}$$

$$M = \frac{\frac{aN}{e^{a}-e^{-a}}}{a}\mu_m \left[(e^{a} + e^{-a}) - \left(\frac{e^{a}-e^{-a}}{a}\right)\right]$$

$$= \frac{aN\mu_m}{a}\left[\frac{e^{a}+e^{-a}}{e^{a}-e^{-a}} - \frac{e^{a}-e^{-a}}{a(e^{a}-e^{-a})}\right]$$

$$= N\mu_m \left[\frac{e^{a}+e^{-a}}{e^{a}-e^{-a}} - \frac{1}{a}\right]$$

$$\mathrm{M} = \mathrm{N}\mu_{\mathrm{m}} \left\{\mathrm{cotha} - \frac{1}{\mathrm{a}}\right\}$$

$$\mathrm{M} = \mathrm{N}\mu_{\mathrm{m}}\,\mathrm{L(a)} \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

L(a) – Langevin function.

Case1

At low temperature or large applied field (x)→ 1. Hence the magnetization M in this case will be

$$\mathrm{M} = N\mu_m$$

So saturation is reached when all the atomic dipoles are parallel to B.

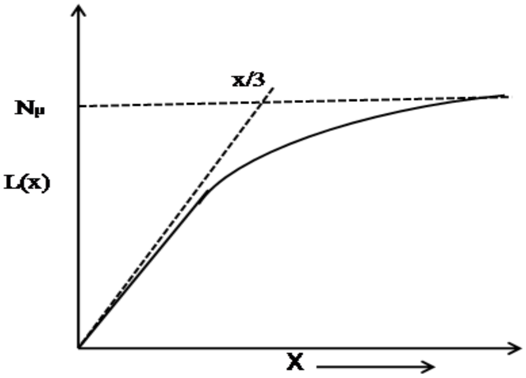


Fig.4.7

Case 2

At high temperature, K_B T is high. Therefore a is very small (a≪ 1) then

$$\mathrm{L(a)} = \left\{cotha - \frac{1}{a}\right\} = \frac{a}{3}$$

$$M = N\mu_m \frac{a}{3} = N\mu_m \frac{\frac{B\mu_m}{K_B T}}{3}$$

$$\mathrm{M} = \frac{N\mu_m^2 B}{3K_B T}$$

The paramagnetic susceptibility $\chi = \frac{\mu_0}{B} M$

$$= \frac{\mu_m^2 N\mu_0}{3K_B T}$$

Which shows that, the susceptibility is inversely proportional to the temperature. It can be written as

$\chi_{para} = \frac{C}{T}$ where C = $\frac{\mu_m^2 N\mu_0}{3K_B}$ is called curie constant.

4.7 Weiss theory of paramagnetism

In order to remove the failures of langevin theory, Weiss introduce the concept of internal molecular field. In real gas the molecules are mutually influenced by their magnetic moments and consequently there should exist within the gas a molecular field. This field produced at any point by all the neighboring molecules is proportional to the intensity of magnetization.

The molecular field $H_i = \lambda M$ where λ is molecular field coefficient.

The effective field $H_{eff} = H + H_i$

Following the langevin theory along with this effective field,

$$M = \frac{N\mu_m^2 B}{3K_B T} \quad \text{since } B = \mu_0 H \text{ then,}$$

$$M = \frac{N\mu_m^2\ \mu0Heff}{3K_B T} = \frac{N\mu_m^2\ \mu0(H + Hi)}{3K_B T}$$

$$= \frac{N\mu_m^2\ \mu0(H + \lambda M)}{3K_B T}$$

Rearranging the terms we get,

$$M = \frac{NH\mu_m^2\mu_0}{3K_B T} + \frac{NH\lambda M\mu_m^2\mu_0}{3K_B T}$$

$$M - \frac{NH\lambda M\mu_m^2\mu_0}{3K_B T} = \frac{NH\mu_m^2\mu_0}{3K_B T}$$

$$M\left[1 - \frac{NH\lambda\mu_m^2\mu_0}{3K_B T}\right] = \frac{NH\mu_m^2\mu_0}{3K_B T}$$

Let $C = \frac{N\mu_m^2\mu_0}{3K_B}$ and $\theta = C\lambda$

$$M\left[1 - \frac{\theta}{T}\right] = \frac{CH}{T}$$

But $\chi = \frac{M}{H} = \frac{C}{\left[1 - \frac{\theta}{T}\right]T}$

$\chi = \frac{C}{T - \theta}$. This equation is called curie Weiss law.

This equation shows that below Curie temperature ($T<\theta$), the susceptibility becomes negative. i.e. Paramagnetic material becomes diamagnetic material.

4.8 Quantum theory of paramagnetism

Quantum theory assumes that the permanent magnetic moment of a given atom is limited to a finite set of orientations related to the applied field. Let N be the number of atom/m^3.

J--- Total angular momentum quantum number of each atom. J = L+S

The magnetic moment of each atom is $\mu_J = gM_J\mu_B$

M_J – magnetic quantum number = J,(J-1),(J-2),…..-(J-1),-J

According to statistical mechanics, the magnetization

$$M = N\frac{\sum_{-J}^{J} gM_J\mu_B \exp(gM_J\mu_B H\mu_0/K_B T)}{\sum_{-J}^{J} \exp(gM_J\mu_B H\mu_0/K_B T)} \text{……………..(1)}$$

At high temperature $\frac{gM_J\mu_B H\mu_0}{K_B T} \ll 1$

$$\therefore \exp\left(\frac{gM_J\mu_B H\mu_0}{K_B T}\right) = 1 + \frac{gM_J\mu_B H\mu_0}{K_B T}$$

Higher terms neglected.

Eqn(1) becomes

$$M = N\frac{\sum_{-J}^{J} gM_J\mu_B (1+\frac{gM_J\mu_B H\mu_0}{K_B T})}{\sum_{-J}^{J}(1+\frac{gM_J\mu_B H\mu_0}{K_B T})}$$

$$M = N\left[\frac{\sum_{-J}^{J} gM_J\mu_B + \sum_{-J}^{J}\frac{M_J^2 g^2\mu_B^2\mu_0}{K_B T}}{\sum_{-J}^{J} 1 + \sum_{-J}^{J}\frac{gM_J\mu_B H\mu_0}{K_B T}}\right] \text{……………(2)}$$

Substitute $\sum_{-J}^{J} M_J = 0$, $\sum_{-J}^{J} 1 = (2J+1)$, and $\sum_{-J}^{J} M_J^2 = \frac{J(J+1)(2J+1)}{3}$

Eqn(2) becomes

$$M = N\left[\frac{0+\left[\frac{Hg^2\mu_B^2\mu_0}{K_B T}\right] X \sum_{-J}^{J} M_J^2}{(2J+1)+\frac{g\mu_B H\mu_0}{K_B T}\sum_{-J}^{J} M_J}\right]$$

$$= N\left[\frac{\left[\frac{Hg^2\mu_B^2\mu_0}{K_BT}\right]X\frac{J(J+1)(2J+1)}{3}}{(2J+1)+0}\right]$$

$$M = N\frac{Hg^2\mu_B^2\mu_0\frac{J(J+1)}{3}}{K_BT}$$

$$M = \left[\frac{NHg^2\mu_B^2\mu_0}{K_BT}\right]\frac{J(J+1)}{3}\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Susceptibility $\chi = \frac{M}{H} = \left[\frac{NHg^2\mu_B^2\mu_0}{K_BTH}\right]\frac{J(J+1)}{3}$

$$=J(J+1)\frac{Ng^2\mu_B^2\mu_0}{3K_BT} = \frac{N\mu_J^2\mu_0}{3K_BT}$$

$$\chi = \frac{C}{T}\ \ldots\ldots\ldots..(4)$$

Where,

$$\mu_J = g^2J(J+1)\mu_B^2$$

$$\mu_J = \mu_B Xg\sqrt{J(J+1)}$$

$$= \mu_B \times P_{eff}$$

P_{eff} − effective bohr magneton

$$\chi = \frac{NP_{eff}^2\mu_B^2\mu_0}{3K_BT} = \frac{C}{T}$$

4.9 Para magnetic susceptibility of solid

Consider a solid in which the magnetic dipole moments are due to pure electron spin and assume that they do not interact with one another.

The spin quantum number S =1/2

So there are two possible orientations of magnetic moment, one parallel to magnetic field and the other antiparallel.

Let there are N spins/m^3 in the material. When the applied field is zero, the up and down spin moments are equal in numbers. So, the total magnetization M is zero.

In the presence of the applied magnetic field, let N_P is the number of dipoles aligned parallel to the field. N_a is the number of dipoles aligned antiparallel to the field at a temperature t Kelvin.

The total magnetization $M = N_p\mu_B - N_a\mu_B$

$$= \mu_B(N_p - N_a) \ldots\ldots\ldots.(1)$$

Where μ_B – Bohr magneton $= \frac{eh}{4\pi m}$

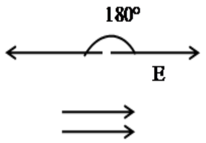


Fig.4.8

The energy of a dipole (E) $= \int_{90}^{\theta} \mu_0\mu_m H\sin\theta d\theta$

$$E = -\mu_0\mu_m H\cos\theta$$

Energy of antiparallel dipoles is obtained by putting $\theta = 180°$

$$E_a = -\mu_0\mu_m H(-1)$$

$$E_a = \mu_0\mu_m H$$

Energy of parallel dipole $E_p = -\mu_0\mu_m H(1)$

$$= -\mu_0\mu_m H$$

Energy difference between antiparallel and parallel dipoles is

$$Ea - Ep = \mu_0\mu_m H - (-\mu_0\mu_m H)$$

$$Ea - Ep = 2\mu_0\mu_m H \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

By Boltzmann statistics,

$$N_a \propto exp\left(\frac{-E_a}{K_B T}\right)$$

$$N_p \propto exp\left(\frac{-E_p}{K_B T}\right)$$

$$\frac{N_a}{N_p} = exp\left(\frac{-E_a-(-E_p)}{K_B T}\right) = exp\left(\frac{-(E_a-E_p)}{K_B T}\right)$$

$$= exp\left(\frac{-2\mu_0\mu_m H)}{K_B T}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$N = N_a + N_P$$

Divide the above equation by N_P

$$\frac{N}{N_p} = \frac{N_a}{N_p} + \frac{N_p}{N_p} \ = \frac{N_a}{N_p} + 1$$

$$\frac{N}{N_p} = 1 + exp\left(\frac{-2\mu_0 \mu_B H}{K_B T}\right)$$

$$N_p \ = \frac{N}{1 + exp\left(\frac{-2\mu_0 \mu_B Hz}{K_B T}\right)}$$

Multiply and divide by exp $\left(\frac{\mu_0 \mu_B H}{K_B T}\right)$

$$N_p \ = \frac{N \times exp\,(\frac{\mu_0 \mu_B H}{K_B T})}{exp\,(\frac{\mu_0 \mu_B H}{K_B T})\left(1 + exp\left(\frac{-2\mu_0 \mu_B H}{K_B T}\right)\right)}$$

$$\mathrm{N_p} \ = \frac{\mathrm{N} \times \exp\,(\frac{\mu_0 \mu_B H}{K_B T})}{\left(\exp\,(\frac{\mu_0 \mu_B H}{K_B T}) + \exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)\right)} \ldots\ldots\ldots\ldots(4)$$

$N = N_a + N_P$

Divide by N_a

$$\frac{N}{N_a} = \frac{N_a}{N_a} + \frac{N_p}{N_a} \ = \frac{N_p}{N_a} + 1 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Eqn(3) $\frac{N_a}{N_p} = \exp\left(\frac{-2\mu_0 \mu_B H}{K_B T}\right)$

$$\frac{N_p}{N_a} = \exp\left(\frac{2\mu_0 \mu_B H}{K_B T}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Apply eqn (6) in eqn (5)

$$\frac{N}{N_a} = 1 + \exp\left(\frac{2\mu_0 \mu_B H}{K_B T}\right)$$

$$N_a \ = \frac{N}{1 + \exp\left(\frac{2\mu_0 \mu_B H}{K_B T}\right)}$$

Multiply and divide by exp $(\frac{-\mu_0 \mu_B H}{K_B T})$

$$N_a = \frac{N \times \exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)}{\exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)\left(1+\exp\left(\frac{2\mu_0 \mu_B H}{K_B T}\right)\right)}$$

$$N_a = \frac{N \times \exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)}{\left(\exp\left(\frac{\mu_0 \mu_B H}{K_B T}\right)+\exp\left(\frac{-\mu_0 \mu_B H)}{K_B T}\right)\right)}$$

$$N_p - N_a = \frac{N \times \exp\left(\frac{\mu_0 \mu_B H}{K_B T}\right)}{\left(\exp\left(\frac{\mu_0 \mu_B H}{K_B T}\right)+\exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)\right)} - \frac{N \times \exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)}{\left(\exp\left(\frac{\mu_0 \mu_B H}{K_B T}\right)+\exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)\right)}$$

$$N_p - N_a = N\left[\frac{\exp\left(\frac{\mu_0 \mu_B H}{K_B T}\right)-\exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)}{\exp\left(\frac{\mu_0 \mu_B H}{K_B T}\right)+\exp\left(\frac{-\mu_0 \mu_B H}{K_B T}\right)}\right]$$

$$N_p - N_a = N \tanh\left(\frac{\mu_0 \mu_B H}{K_B T}\right) \ldots\ldots\ldots\ldots\ldots(8)$$

Substitute eqn (8) in eqn (1)

$$M = \mu_B (N_p - N_a)$$

$$= \mu_B \left(N \tanh\left(\frac{\mu_0 \mu_B H}{K_B T}\right)\right)$$

Let $\alpha = \frac{\mu_0 \mu_B H}{K_B T}$

$$M = \mu_B N \tanh\alpha \ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

For normal temperature and weak field, $\mu_0 \mu_B H \ll 1$

$\therefore$ $\alpha \ll 1$. So that $\tanh\alpha = \alpha$

Eqn (9) can be written as

$$M = \mu_B N \alpha$$

$$M = \mu_B N \frac{\mu_0 \mu_B H}{K_B T}$$

$$M = \frac{N \mu_0 H {\mu_B}^2}{K_B T}$$

Susceptibility $\chi = \frac{M}{H}$

$$\chi = \frac{N\mu_0 H\mu_B{}^2}{K_B TH} = \frac{N\mu_0\mu_B{}^2}{K_B T} = \frac{C}{T}$$

$\chi = \frac{C}{T}$ curie law. Many paramagnetic materials do not obey this curie law. They obey the modified curie law called curie Weiss law.

$$\chi = \frac{C}{T-\theta}$$

θ - Constant with dimensions of temperature.$\theta = 0$ For the substance which obey curie law.

4.10 Hund's rules

The ground state of the atom is characterized by the following three rules called Hund's rules.

First rule

The maximum value of the total spin S allowed by the exclusion principle. This rule has its origin in the exclusion principle and the coulomb repulsion between electrons. The exclusion principle prevents two electrons of the same spin being at the same place at same time. Thus electrons of the same spin are kept apart than the electrons of opposite spin. Because of the coulomb interaction the energy of the same spin is lower; the average potential energy is less positive for parallel spin than for anti parallel spin.

Example: Mn^{2+} ion has five electrons in the 3D shell. Therefore 3D shell is half filled. There are 5 different orbits available. The spin can be parallel if each electron enters different orbits. The orbits are characteristics by orbital quantum number. m_L = 2,1,0, -1, -2.

Second rule

The maximum value of the orbital angular momentum L consistent with the value of S. This rule is approached by model calculations.

Third rule

The value of the total angular momentum $J = |L - S|$ when the shell is less than half full. J = L+s when the shell is more than half full. When the shell is just half full, the application of the first rule gives L =0, so that J =S.

4.11 Cooling by adiabatic demagnetization

The process which can give the temperature of the substance below 1K is called adiabatic demagnetization. The paramagnetic salt is used in this process for which the energy versus temperature curve is shown in fig 4.9. The curve OCA represents the variation of entropy without an external magnetic field.

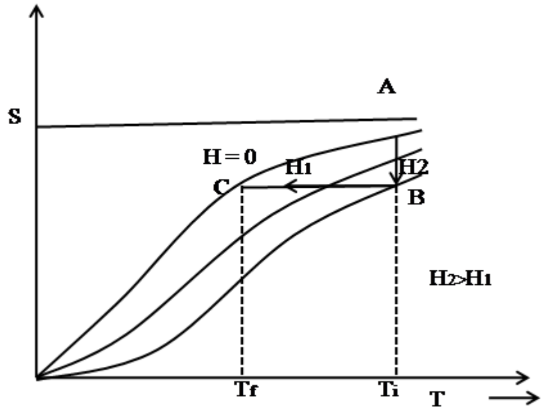


Fig.4.9

Let at initial temperature T_i, magnetic field be applied isothermally, then the magnetic dipoles will tend to line along the direction of the field. The spins will become more orderly decreasing the entropy of the system from A to B. Now if the paramagnetic salt is isolated from its surroundings and the magnetic field is removed, then we go from B to C along an adiabatic with no change in entropy. By successive steps of this kind, temperatures of the order of 0.001K have been obtained. Thermodynamically with the help of Maxwell's relations the entropy given as

$$\text{Entropy } S = S_0 + \int_0^H \left[\frac{\partial M}{\partial T}\right]_H dH \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

where S_0 is the entropy without magnetic field. According to curie's law,

$$M = \frac{Ng^2\mu_B^2\mu_0 J(J+1)}{3K_B T} H \ldots\ldots\ldots\ldots\ldots\ \ldots\ldots\ldots\ldots\ldots..(2)$$

$$S = S_0 - \frac{Ng^2\mu_B^2\mu_0 J(J+1)}{6K_B T^2} H^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

This shows that entropy with magnetic field at $T=T_i$ will be lower than S_0 and to will actually correspond to S_0 at $T=T_f$ where T_f is s lower T_i. The last step is obtained by adiabatically moving along BC (ds = 0) removing the magnetic field, thus the name adiabatic demagnetization bringing the temperature below 1k by successive steps of the kind described above.

4.12 Determination of susceptibilities of para and diamagnetic materials

Theory

Let a body of permeability μ_2 and volume V be placed in a magnetic field with permeability of the medium as μ_1. The broken line indicates the direction along which the body is free to move. Let the permeability of the region surrounding the medium is unity, then the potential energy of the body will be $\frac{-\mu_2 H^2 v}{2}$. Since the body is situated in a medium of permeability μ_1, it displaces a volume of the medium whose potential energy will be $\frac{-\mu_1 H^2 v}{2}$

The total change in potential energy due to the introduction of the body is,

$$-(\mu_2 - \mu_1)H^2 v/2$$

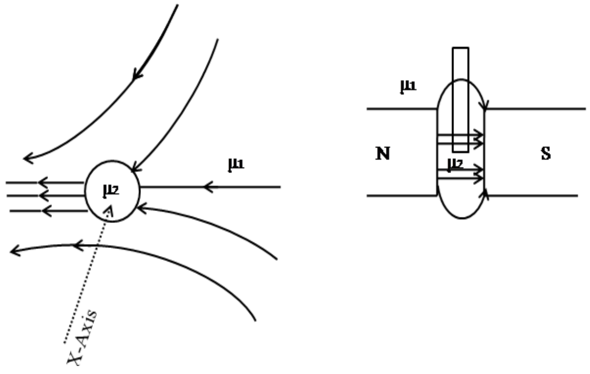


Fig.4.10

Thus the force which tends to move the body along the x- direction will be

$$F_x = -\frac{d}{dx}\left[-(\mu_2 - \mu_1)H^2 v/2\right]$$

$$= \frac{(\mu_2 - \mu_1)}{2}\left[\frac{d(H^2)v}{dx}\right] \text{……………….(1)}$$

Putting $\mu_{r2} = 1 + \chi_2$,

$\mu_{r1} = 1 + \chi_1$ and $\mu_2 = \mu_0\mu_{r2}$ and

$\mu_1 = \mu_0\mu_{r1}$, one gets

$$(\mu_2 - \mu_1) = \mu_0(\mu_{r2} - \mu_{r1}) = \mu_0(\chi_2 - \chi_1)$$

Substituting this value of $(\mu_2 - \mu_1)$ in equation (1)

$$F_x = \left[\frac{\mu_0 v(\chi_2 - \chi_1)}{2}\right]\frac{d}{dx}(H^2) \text{………………..(2)}$$

$$F_x = \frac{\mu_0 v(\chi_2 - \chi_1)}{2}\left[\frac{d}{dx}(H_x^2) + \frac{d}{dx}(H_y^2) + \frac{d}{dx}(H_z^2)\right]$$

Where $H^2 = (H_x^2) + (H_y^2) + (H_z^2)$. H_x, H_y, H_z are the components of the fields along the x- axis and any mutual perpendicular axes y and z.

4.13 Guoy method

It is one of the best methods to determine the susceptibility of the material whose susceptibility varies with temperature. The material whose susceptibility is required must be in the form of a circular rod or as solution or very finely ground powder taken in a glass tube of uniform cross section. The specimen is suspended with its axis vertical from one arm of a sensitive microbalance. The lower end of the specimen is kept between two flat pole tips of field H, the field strength at the upper end H_0 less than 1% of H. Due to this field a vertical force, acting on an element of the specimen of length dx and volume dV is

$$dF_x = \frac{\mu_0(\chi_2-\chi_1)}{2}\left[\frac{d}{dx}(H_x^2)+\frac{d}{dx}(H_y^2)+\frac{d}{dx}(H_z^2)\right]dv \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Where χ_2 and χ_1 are the susceptibilities of specimen and surrounding medium respectively.

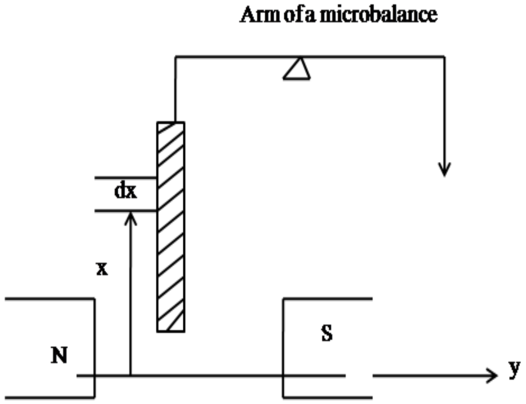


Fig.4.11

Since in the gap flux lines will be direct from one pole piece to another i.e., in y direction, we can neglect H_x, H_z .

$$dF_x = \frac{\mu_0(\chi_2-\chi_1)}{2}\left[\frac{d}{dx}(H_y^2)\right]dv \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

If 'a' is the area of cross section of the specimen, then

$$dv = a\,dx$$

The total vertical force on the specimen due to the whole field along its length from region where

$H_y = H$ to $H_y = H_0$ will be

$$F_x = \frac{\mu_0(\chi_2-\chi_1)a}{2}\int_{H_0}^{H}\frac{d}{dx}(H_y^2)dx$$

$$F_x = \frac{\mu_0(\chi_2-\chi_1)a[H^2-H_0^2]}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

This force will be downwards if the material is paramagnetic and upwards if diamagnetic. In eqn (3) H_0^2 is small and can be neglected. Thus

$$F_x = \frac{\mu_0(\chi_2-\chi_1)aH^2}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

This pull can be calculated by the microbalance. The specimen is weighed in the absence of field and again when the current is switched on. The difference in weights in m kg represents the pull on the specimen.

$$\therefore \quad mg = \frac{\mu_0(\chi_2 - \chi_1)aH^2}{2} \quad \ldots\ldots\ldots(5)$$

$$\chi_2 - \chi_1 = \frac{2mg}{\mu_0 aH^2}$$

The value of susceptibility will be accurate. This method can be used at low temperature.

4.14 Quincke's method

This method is suitable for the susceptibility measurements of aqueous solutions, many liquid and liquefied gases. The experimental liquid is placed in a vertical U- tube with one limb of wide bore and the other narrow . The narrow limb is placed in between the poles of the electromagnet such that the surface of the liquid in the limb lies at the line of centers of the pole pieces when the field is off as shown in fig 4.12.

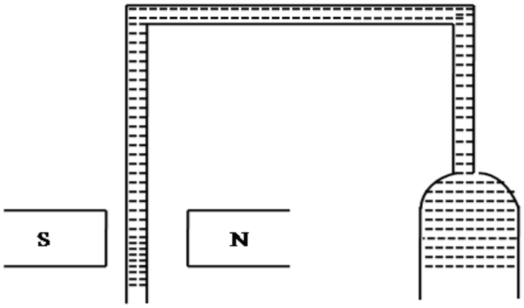


Fig.4.12

When the energizing current is switched on, a strong uniform field is established at the upper surface of the narrow column of the liquid, while lower portion of the column is in a region of weak field.

Consequently a force will act upon the column and if the liquid is paramagnetic, it will rise.

Let x be the vertical direction and y be the direction perpendicular to the pole pieces, the vertical force on a small volume dv of liquid of length dx will be

$$dF_x = \frac{\mu_0(\chi_2 - \chi_1)}{2}\left[\frac{d}{dx}\left(H_y^2\right)\right] dv \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

if 'a' is the area of cross section of the narrow limb then,

$$dv = a\,dx$$

$$dF_x = \frac{\mu_0(\chi_2 - \chi_1)}{2}\left[\frac{d}{dx}\left(H_y^2\right)\right] a\,dx$$

Thus the total vertical force acting on the liquid column is

$$F_x = \frac{\mu_0(\chi_2-\chi_1)a}{2}\int_0^{H_m}\frac{d}{dx}\left(H_y^2\right)dx$$

$$F_x = \frac{\mu_0(\chi_2-\chi_1)aH_m{}^2}{2} \text{ ....}(2)$$

Where H_m is the final field applied.

The rise in the surface of the liquid is noted with travelling microscope. There will be no appreciable change in the level of the liquid column of the wider limb because of the large cross-section. If ρ be the density of the liquid and σ the density of air.

The change in hydrostatic pressure when the liquid rises to a height h will be $(\rho-\sigma)gh$

Thus the corresponding change in force acting vertically will be $(\rho-\sigma)gha$

And this must be equal to F_x

$$\text{ie., } \frac{\mu_0(\chi_2-\chi_1)aH_m{}^2}{2} = (\rho-\sigma)gha$$

$$\chi_2-\chi_1 = \frac{2hg(\rho-\sigma)}{\mu_0 H_m{}^2} \text{ .... } (3)$$

χ_1 is the susceptibility of air whose value can be taken from tables and χ_2 can be calculated.

UNIT V

MAGNETISM 2

5.1 Ferromagnetic materials

Definition

The materials which have finite value of magnetization even if the external magnetic field is absent are called ferromagnetic materials.

In a ferromagnetic material, the magnetic interaction between any two dipoles aligns themselves parallel to each other. Due to the parallel alignment, even for a smaller value of applied magnetic field, a large value of magnetization is produced.

Examples: Iron, Cobalt, Nickel, etc.

Diploe alignment

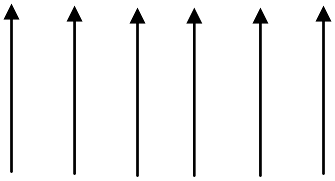


Fig.5.1

Properties

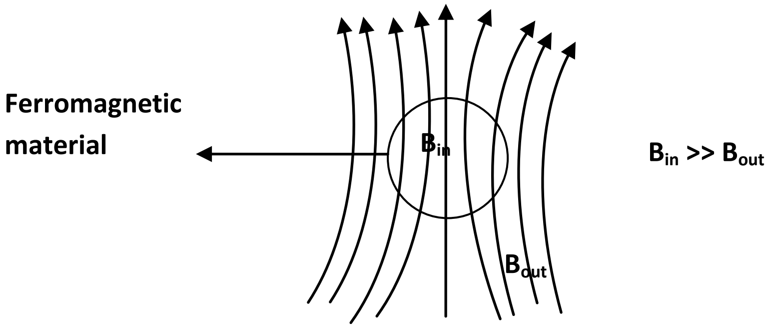


Fig.5.2

- Ferro magnetic materials have permanent dipole moment and they attract the magnetic field strongly.

- All the dipoles are aligned parallel to each other due to the magnetic interaction between any two dipoles.
- They exhibit magnetization even in the absence of magnetic field. This property of ferromagnetic material is called spontaneous magnetization. They exhibit hysteresis curve.
- During heating, they lose magnetization slowly.
- It consists of number of small spontaneously magnetized regions called domains.
- Each ferromagnetic material has a particular ferromagnetic Curie temperature. (θ_f)
- When the temperature is less than θ_f, the material is in ferromagnetic state.
- When the temperature is greater than θ_f, the material is converted into paramagnetic state.
- Magnetic susceptibility is very large and positive. It depends on temperature.

$$\chi = \frac{C}{T-\theta} \quad \text{(For T > }\theta\text{)}$$

- Magnetic permeability is very much greater than one.

5.2 Spontaneous magnetization in ferromagnetic materials

In ferromagnetic materials the existence of an internal molecular field H_m is proportional to the magnetization M. $H_m = \lambda M$

Where λ is called the Weiss molecular field coefficient, it determines the strength of the interaction between the magnetic dipole moments in the material.

The effective magnetic field H_{eff} on an atomic dipole is

$$H_{eff} = H + H_m \text{……………}(1)$$

$$H_{eff} = H + \lambda M \text{…………… ….}(2)$$

The Weiss field λM has a tendency to align the dipoles and is opposed by the thermal agitation of the elemental moments.

The magnetization $M = N\mu_B \tanh\left(\frac{\mu_B H \mu_0}{K_B T}\right)$

For the spontaneous magnetization the magnetic field H in the above eqn is replaced by H_{eff}

$$\mathrm{M} = N\mu_B \tanh\left(\frac{\mu_B\mu_0(H+\lambda\mathrm{M})}{K_BT}\right)\ldots\ldots\ldots\ldots(3)$$

At high temperature, $\mu_B\mu_0(H+\lambda\mathrm{M}) \ll 1$

Thus,

$$\tan\mathrm{h}\left(\frac{\mu_B\mu_0(H+\lambda\mathrm{M})}{K_BT}\right) = \left(\frac{\mu_B\mu_0(H+\lambda\mathrm{M})}{K_BT}\right)$$

$$\mathrm{M} = \left[\frac{N\mu_B^2\mu_0}{K_BT}\right](H+\lambda\mathrm{M})\ldots\ldots\ldots\ldots\ldots..(4)$$

$$= \frac{N\mu_B^2\mu_0 H}{K_BT} + \frac{N\lambda\mathrm{M}\mu_B^2\mu_0}{K_BT}$$

$$\mathrm{M}\left[1 - \frac{N\mu_B^2\lambda\mu_0}{K_BT}\right] = \frac{N\mu_B^2\mu_0 H}{K_BT}$$

$$\mathrm{M} = \frac{N\mu_B^2\mu_0 H}{K_BT}\left[\frac{1}{1-\frac{N\mu_B^2\lambda\mu_0}{K_BT}}\right]\ldots\ldots\ldots\ldots\ldots(5)$$

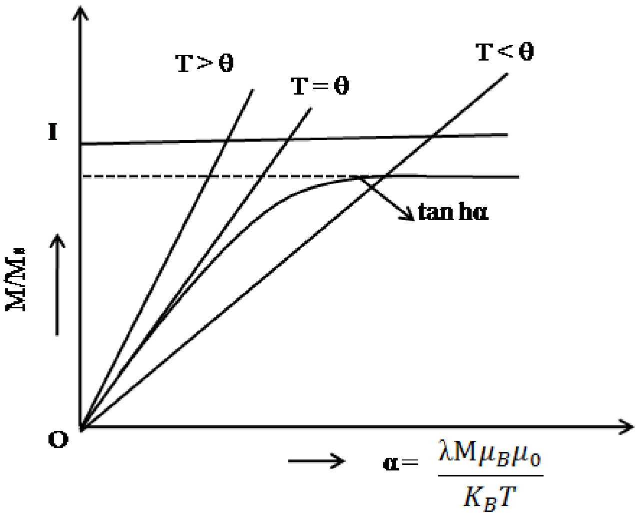


Fig.5.3

The susceptibility $\chi = \frac{M}{H}$

$$= \frac{N\mu_B^2\mu_0}{K_BT}\left[\frac{1}{1-\frac{N\mu_B^2\lambda\mu_0}{K_BT}}\right]$$

$$\chi = \frac{N\mu_B^2\mu_0}{K_B\left(T-\frac{N\mu_B^2\lambda\mu_0}{K_B}\right)} = \frac{C}{T-\theta}\ldots\ldots\ldots\ldots\ldots..(6)$$

Where C = $\frac{N\mu_B^2\mu_0}{K_B}$

Equation (5) is identical with the curie – Weiss law of paramagnetism. Thus we conclude that ferromagnetic materials behave as paramagnetic materials for T>> θ . The eqn (5) cannot hold good for (T≤ θ). Then the magnetic susceptibility will pass through a pole and become negative.

For T = θ, the susceptibility becomes infinite. This fact suggests that when T= θ , spontaneous magnetization may occur, when H= 0, M is non-vanishing.

When H= 0, the eqn (3) becomes

$$\mathrm{M} = N\mu_B \tanh\left(\frac{\lambda \mathrm{M}\mu_B\mu_0}{K_B T}\right)$$

Let $\alpha = \frac{\lambda \mathrm{M}\mu_B\mu_0}{K_B T}$

$$\mathrm{M} = N\mu_B \tanh\alpha \text{……………….(7)}$$

$$\frac{M}{N\mu_B} = \tanh\alpha$$

$$\frac{M}{Ms} = \tanh\alpha \text{ ………………….(8)}$$

Where $M_s = N\mu_B$ is the saturation value of magnetization.

From eqn (4) and (6) we can write

$$\frac{M}{M_s} = \frac{M}{N\mu_B} = \frac{K_B T\alpha}{\mathrm{N}\lambda\mu_B^2\mu_0} = \frac{T\alpha}{\lambda c}$$

$$\frac{M}{M_s} = \frac{T\alpha}{\lambda c}\text{……………(9)}$$

Where C = $\frac{\mathrm{N}\mu_B^2\mu_0}{K_B}$; $\lambda c = \theta$ is called paramagnetic curie temperature.

Eqn (9) can be written as

$$\frac{M}{Msat} = \frac{T\alpha}{\theta} \text{ ……………(10)}$$

For a given value of temperature T, the eqn (10) is a plot of $\frac{M}{M_s}$ versus αrepresents a straight line with slope $\frac{T}{\theta}$ as shown in fig.

Since $\frac{M}{M_s}$ satisfy both eqns (8) and (10) the value of $\frac{M}{M_s}$ for the temperature T is given by the intersection of the straight line and the tan hα curves as shown in figure.

5.3 Quantum theory of ferromagnetism

According to quantum theory, the magnetic dipole moment μ and its component μ_z in the direction of the applied field cannot have arbitrary values.

In general, a direct relation between the magnetic dipole moment μ of an atom in free space and its angular momentum J as $\mu = -g\,\mu_B J$…………(1)

$\mu_B = \frac{e\hbar}{2m}$ is called bohr magnetron; g is known as the Lande's g factor.

$$g = \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \text{ ……………………(2)}$$

Where s and L represent the spin and orbit quantum numbers. Magnetic moment μ with respect to the direction of the applied field is $\mu_z = -g\,\mu_B M_J$ ……..(3)

M_J – magnetic quantum number =-J,-(J-1),….(J-1),J.

For each values of J, the magnetic moments of the atom can have (2J+1) different orientations.

The potential energy of a magnetic dipole in the presence of a magnetic field h is given by

$$U = -\mu.H = m_J\ \mu_B g H_{eff} \text{ ……………………………(4)}$$

Where $H_{eff} = H + \lambda M$

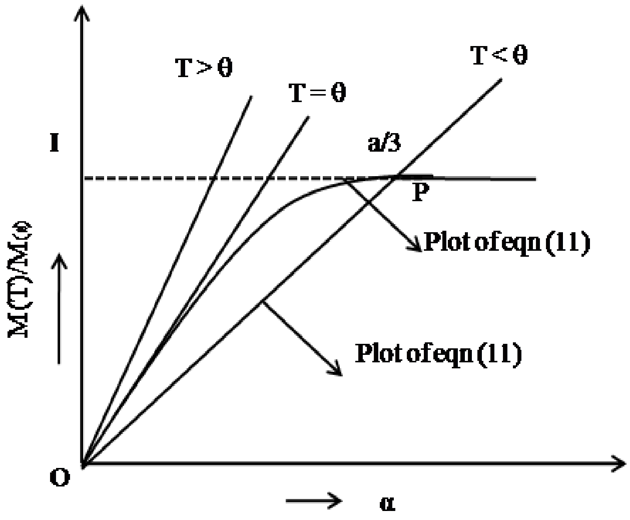


Fig.5.4

Consider ferromagnetic solid containing N atoms per unit volume each having a total angular momentum number J.

Then, the magnetization in the field direction is given by

$$M = N\frac{\sum_{-J}^{J} gM_J\mu_B \exp(gM_J\mu_B\mu_0 H_{eff}/K_BT)}{\sum_{-J}^{J}\exp(gM_J\mu_B H_{eff}\mu_0/K_BT)}$$

Let $x = \frac{g\mu_B\mu_0 H_{eff}}{K_BT}$

$$M = N\frac{\sum_{-J}^{J} gM_J\mu_B \exp(M_J x)}{\sum_{-J}^{J}\exp(M_J x)}$$

$$M = Ng\mu_B\frac{\sum_{-J}^{J} M_J \exp(M_J x)}{\sum_{-J}^{J}\exp(M_J x)} \qquad \text{……………………(5)}$$

After some algebraic manipulations eqn (5) reduces to

$$M = Ng\mu_B\left(\frac{2J+1}{2}\coth\frac{2J+1}{2}x - \frac{1}{2}\coth\frac{x}{2}\right)$$

Substituting x =a/J in the above eqn, we get

$$\mathrm{M} = Ng\mu_B\left(\frac{2J+1}{2}\cot\mathrm{h}\frac{2J+1}{2J}a - \frac{1}{2}\cot h\ \frac{a}{2J}\right)$$

$$\mathrm{M} = NgJ\mu_B\left(\frac{2J+1}{2J}\cot\mathrm{h}\frac{2J+1}{2J}a - \frac{1}{2J}\cot h\ \frac{a}{2J}\right)$$

$$\mathrm{M} = NgJ\mu_B B_J(a)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

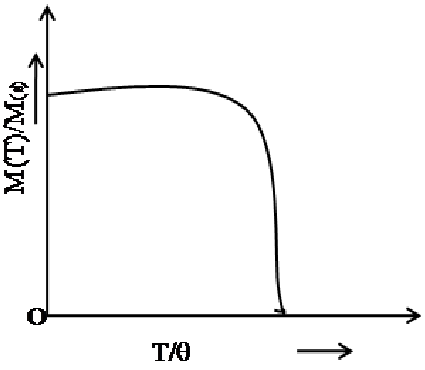


Fig.5.5

Where $B_J(a) = \left(\frac{2J+1}{2}\cot\mathrm{h}\frac{2J+1}{2J}a - \frac{1}{2}\cot h\ \frac{a}{2J}\right)$ is Brillouin function

$$\mathrm{X} = \frac{a}{J} = \frac{g\mu_0\mu_B H_{eff}}{K_B T}$$

$$\mathrm{a} = \frac{gJ\mu_0\mu_B H_{eff}}{K_B T} = \frac{gJ\mu_0\mu_B(H+\lambda\mathrm{M})}{K_B T}\ldots\ldots\ldots\ldots(7)$$

In the case of spontaneous magnetization H=0, therefore eqn (7) can be written as

$$\mathrm{a} = \frac{gJ\mu_0\mu_B\lambda\mathrm{M}}{K_B T}$$

$$\mathrm{M\ (T)} = \frac{aK_B T}{gJ\mu_0\mu_B\lambda} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

At T = 0k; a = ∞; $\mathrm{B_J(a)} = 1$; the magnetic moments align themselves parallel to the field and the magnetization M becomes the saturation magnetization $M_{s(0)}$From eqn (6)

The saturation magnetization $M_{s(0)}\ = NgJ\mu_B\ldots\ldots\ldots\ldots(9)$

from eqns (8) and (9)

$$\frac{\mathrm{M(T)}}{M_{s(0)}} = \frac{aK_B T}{N\lambda g^2 J^2\mu_0\mu_B^2}\ \ldots\ldots\ldots\ldots\ldots\ldots\ (10)$$

Also eqns (6) and (9) gives,

$$\frac{\mathrm{M(T)}}{M_{s(0)}} = B_J(a)\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

The magnetization M (T) at a given temperature can be obtained by solving eqns (10) and (11). The plots of $\frac{\mathrm{M(T)}}{M_{s(0)}}$ versus x representing eqns (10) and (11) are shown in figure.

The eqn (10) represents a straight line passing through the origin. At T $=\theta$, this line is tangent to the brillouin function at the origin. At the point o of intersection of the two plots, the magnetization is unstable. For T< θ , the point p of intersection indicate a non zero value of M even for zero external magnetic field and hence corresponds the spontaneous magnetization. It also follows that the spontaneous magnetization decreases with increase in temperature and vanishes beyond the temperature θ which is known as ferromagnetic curie temperature. The variation of continuous magnetization with temperature is shown in figure 5.5.

5.4 Weiss molecular field

To explain the spontaneous magnetization of a ferromagnetic material, Weiss assumed that there exists internal molecular field (exchange field) acting on a given dipole.

$$H_{ex} = H + \lambda M \text{ ....(1)}$$

Where λ is Weiss constant; H is applied field.

In ferromagnet the curie law holds for exchange field as well.

$$\therefore \frac{M}{H_{ex}} = \frac{c}{T} \quad \text{.................(2)}$$

$$\frac{M}{H+\lambda M} = \frac{c}{T}$$

$$M = \frac{c(H+\lambda M)}{T}$$

$$M = \frac{cH+c\lambda M}{T}$$

$$MT = cH + c\lambda M$$

$$MT - c\lambda M = cH$$

$$M(T - c\lambda) = cH$$

$$M = \frac{cH}{T-c\lambda}$$

The ferromagnetic susceptibility becomes

$$\chi = \frac{M}{H} = \frac{c}{T-c\lambda} = \frac{c}{T-T_c}$$

$T_c = c\lambda$ is called the Curie temperature.

5.5 Curie – Weiss law (Behavior of ferromagnetic materials for *T*> θ_f)

Brillouin function $B_J(a) = \left(\frac{a(J+1)}{3}\right)$ …………(1)

According to quantum theory of ferromagnetic materials,

$$M = NgJ\mu_B B_J(a)$$

$$= \frac{NgJ\mu_B a(J+1)}{3}$$

Substitute the value of $a = \frac{gJ\mu_0\mu_B(H+\lambda M)}{K_B T}$

$$M = \frac{NgJ\mu_B(J+1)}{3}\left(\frac{gJ\mu_0\mu_B(H+\lambda M)}{K_B T}\right)$$

$$= \frac{Ng^2\mu_0\mu_B^2 J(J+1)(H+\lambda M)}{3K_B T}$$

Multiply and divide the above eqn by J

$$M = \frac{Ng^2\mu_0\mu_B^2 J^2(J+1)(H+\lambda M)}{3JK_B T}$$

Let $\mu_J^2 = g^2\mu_B^2 J^2$

$$M = \frac{N\mu_0\mu_J^2(J+1)(H+\lambda M)}{3JK_B T}$$

$$M= \frac{N\mu_J^2\mu_0(J+1)H+N\mu_0\mu_J^2(J+1)\lambda M}{3JK_B T}$$

$$M-\frac{N\mu_J^2\mu_0(J+1)\lambda M}{3JK_B T} = \frac{N\mu_0\mu_J^2(J+1)H}{3JK_B T}$$

$$M[1-\frac{N\mu_0\mu_J^2(J+1)\lambda}{3JK_B T}] = \frac{N\mu_0\mu_J^2(J+1)H}{3JK_B T}$$

$$\theta = \frac{N\mu_0\mu_J^2(J+1)\lambda}{3JK_B}$$

$$M[1-\theta/T] = \frac{\theta}{\lambda}\frac{H}{T}$$

$$M = \frac{CH}{T(1-\theta/T)}$$

$$= \frac{CH}{T(1-\frac{\theta}{T})}$$

Where $C = \frac{\theta}{\lambda}$

Thus $\chi = \frac{M}{H} = \frac{c}{T-\theta}$ this is the curie – weiss law of ferromagnetic materials.

5.6 Temperature dependence of spontaneous magnetism

According to quantum theory of ferromagnetic materials,

$$M = NgJ\mu_B B_J(a)$$

Because a → ∞, $B_J(a) = 1$

The maximum spontaneous magnetization occur at T =0k is

$$M_{s(0)} = NgJ\mu_B$$

Hence $\frac{M(T)}{M_{s(0)}} = B_J(a)$……………(1)

But as long as we are interested in spontaneous magnetization, H =0 and we know that

$$a = \frac{gJ\mu_0\mu_B\lambda M}{K_B T}$$

$$M(T) = \frac{aK_B T}{gJ\mu_0\mu_B\lambda}$$

$$\frac{M(T)}{M_{s(0)}} = \frac{aK_B T}{N\lambda g^2 J^2 \mu_0 \mu_B^2}$$

For λ, substitute the value $\frac{3K_B\theta_f}{N\mu_0\mu_J^2}$

$$\frac{M(T)}{M_{s(0)}} = \frac{aK_B T}{Ng^2 J^2 \mu_0 \mu_B^2}\left[\frac{N\mu_0\mu_J^2}{3K_B\theta_f}\right]$$

$$= \frac{a\mu_J^2 T}{3g^2 J^2 \mu_B^2 \theta_f}$$

$$\mu_J^2 = g^2 J(J+1)\mu_B^2$$

Thus

$$\frac{\mathrm{M(T)}}{M_{s(0)}} = \frac{\mathrm{ag^2J(J+1)\mu_B^2T}}{\mathrm{3g^2J^2\mu_B^2\theta_f}}$$

$$\frac{\mathrm{M(T)}}{M_{s(0)}} = \frac{\mathrm{aTJ\,(J+1)}}{\mathrm{3J^2\theta_f}} \text{ ……….………….(2)}$$

The quantity $\frac{\mathrm{M(T)}}{M_{s(0)}}$ must satisfy both equations (1) and (2).

5.7 Internal field and exchange interaction

Consider a paramagnet with N number of ions of spins. If the given internal interaction tending to line up the magnetic moments parallel to each other paramagnet becomes to Ferro magnet. This interaction is as exchange field. The orientation of magnetic moment is opposed by thermal agitation. At high temperature, the spin order is destroyed.

Let exchange field B_E is the magnetic field. And

$$B_E \infty M$$

Where M = Magnetization.

$$B_E = \lambda M$$

λ is a constant, independent of temperature.

The curie temperature T_C is the temperature above which the spontaneous magnetization vanishes, and the ferromagnetic material becomes to paramagnetic .when a field B_a is applied , it is magnetized and this will cause a finite exchange field B_E .

$$\mathrm{M} = \chi_p(\mathrm{B_a} + \mathrm{B_E})$$

$$= \chi_p(\mathrm{B_a} + \lambda\mathrm{M})$$

By curie law $\chi = \frac{c}{T}$

$$\therefore \mathrm{M} = \frac{c}{T}(\mathrm{B_a} + \lambda\mathrm{M})$$

$$\mathrm{MT} = \mathrm{C}(\mathrm{B_a} + \lambda\mathrm{M})$$

$$\mathrm{MT} - \mathrm{C}\lambda\mathrm{M} = \mathrm{CB_a}$$

$$\frac{M}{B_a} = \frac{C}{T - C\lambda}$$

$$\chi = \frac{C}{T - C\lambda}$$

At T = Cλ, there exists a spontaneous magnetization.

$$\chi = \frac{C}{T - T_c}$$ is called curie law.

Where $T_c = C\lambda$.

$$\lambda = \frac{T_c}{c} = \frac{3K_B T_c}{Ng^2 s(s+1)\mu_B^2}$$

λ is the mean value of the field constant .

The exchange field gives the representation of the quantum mechanical exchange interaction. The energy of interaction of atom i,j with electron spins S_i , S_j is U =-2J S_i S_j ,from Heisenberg model. J is exchange integral.

The Pauli Exclusion Principle prevents two electrons of the same spin being at the same place at same time. Thus the electrostatic energy of a system will depend on the relative orientation of the spins. The difference in energy is called exchange energy.

The exchange energy of two electrons = =-2J S_1 S_2

If the atom has z nearest neighbors, each connected with the central atom by the interaction J.

$$J = \frac{3K_B T_c}{2ZS(S+1)}$$

This eqn connecting Curie temperature T_C and exchange integral J. For ferromagnetic substance J is positive.

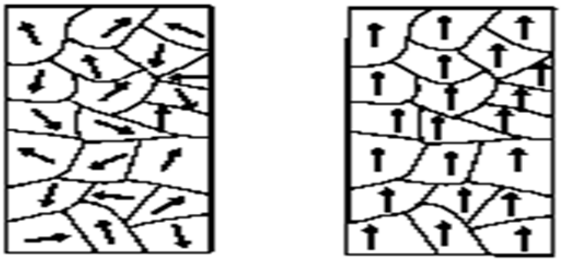
5.8 Origin of ferromagnetic domain

The small region within which all spin magnetic moments are aligned in specific direction is known as the magnetic domain. Ferromagnetic material consists of a number of domains. The size of the domain will be in the order of 10^{-6} m or larger. Each domain acts as a single magnetic dipole and is oriented in random direction. Therefore, in the absence of a magnetic field the net magnetization is zero.

Each domain is separated from the other domains by a wall known as bloch wall. When external field is applied, which are parallel or nearly parallel to the field grow in size at the expense of other domains. The domains which are not parallel to the field decreases in size.

5.8.1 Domain theory

- According to Weiss theory, a single crystal of ferromagnetic material is divided into large number of small regions called **domains**.
- These domains have spontaneous magnetization due to parallel alignment of spin magnetic moments in each domain.
- The direction of spontaneous magnetization varies from domain to domain and the net magnetization of the specimen is zero in the absence of external magnetic field.
- The size of a domain varies from 10^{-6}m to the entire size of the crystal.
- A domain acts as a single magnetic dipole.
- The dipole moments of each and every domain are pointed in random direction and the net magnetization is zero in the absence of field.



Absence of field

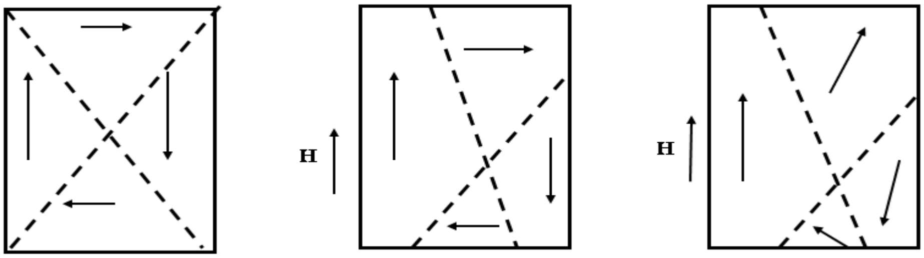
Presence of field

Fig.5.6

- These domains are separated from other domain by a wall known as **domain wall** or **Bloch wall**.
- When magnetic field is applied to a magnetic material, the domains that are parallel to the applied field increase in size at the expense of the other domains.
- The size of the domains which are not parallel to the applied field decreases.

When an external magnetic field is applied, there are two possible ways to align a random domain structure.

1. By the movement of domain walls
2. By rotation of domains



H=0
Fig.5.7(a)

Domain wall movement
Fig.5.7(b)

Domain rotation
Fig.5.7(c)

Fig.5.7

i. By the movement of domain walls

Fig.5.7 (a) shows the arrangement of domains in a ferromagnetic material without any external field. When a small magnetic field is applied, the domains with magnetization direction becomes parallel or nearly parallel to the field grow at the expense of others. (Fig.5.7 (b))

Ii. By rotation of domains

As the magnetic field is increased to a larger value (near saturation) further domain growth becomes impossible. Therefore, most favorably oriented and fully grown domains tend to rotate so as to be in complete alignment with the field direction. (Fig 5.7(c))

5.8. 2 Energies involved in domain growth

The total internal energy of a domain is contributed by the following energies.

1. Magnetostatic energy (or) Exchange energy
2. Crystalline energy (or) Anisotropy energy
3. Domain wall energy (or) Bloch wall energy
4. Magnetostriction energy.

1. Magnetostatic energy

It is defined as the energy required aligning the atomic magnets into a single domain. This work done is stored as potential energy. This energy arises from the interaction of electron spins. This interaction energy makes the adjacent dipoles align themselves. It depends on the interatomic distance.

Consider a single domain in a magnetic material. The orientation of dipole and the direction of magnetic lines of force in a single domain are shown in figure 5.8(a). The potential energy stored inside the magnetic material is known as magneto static energy and very high. This energy is reduced by splitting into two domains (fig5.8 (b))

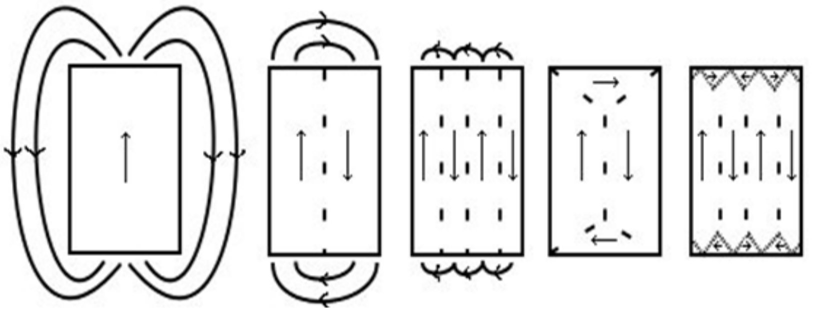


Fig.5.8(a) Fig.5.8(b) Fig.5.8(c) Fig.5.8(d) Fig.5.8(e)

Fig 5.8

The second domain consists of two dipoles with anti spin alignment. The magneto static energy of the domain is further reduced by creating another domain as shown in fig.5.8(c). During this process, domain wall known as Bloch wall is created. The energy is further reduced to a larger value by creating larger number of domains (figures 5.8(d), (e)). The domain attains an optimum size at equilibrium state.

2. Anisotropy energy

It is found that the ferromagnetic crystals have easy and hard directions of magnetization.ie) higher fields are required to magnetise a crystal in a particular direction than others. For example, in bcc iron the easy direction is [100], the medium direction is [110] and the hard direction is [111]. In nickel, easy direction is [111], the medium direction is [110] and the hard direction is [100]. The difference between the easy and hard directions is that for producing the same saturation magnetization, stronger fields are required in the hard direction than in the easy direction. The excess of energy required to magnetise a specimen in a particular direction over that required to magnetise it along the easy direction is called the crystalline anisotropy energy.

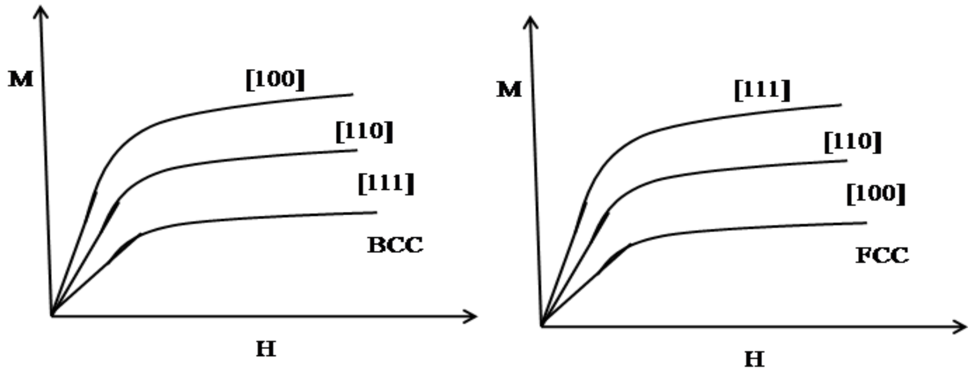


Fig.5.9

3. Bloch wall or domain wall

The equilibrium thickness of the domain wall should have a minimum potential energy which is the sum of exchange energy and the anisotropy energy. The minimum potential energy of a domain wall is known as the **domain wall energy.**

Consider a magnetic material consisting of two domains. These two domains are perpendicular to each other. The second domain is obtained by rotating the first domain by 180˚. The domain rotates gradually due to the existence of the exchange force and anisotropy energy.

The anisotropy energy demands very less thickness of domain wall whereas the exchange energy demands very large thickness. Therefore, there is a compromise between the two energies.

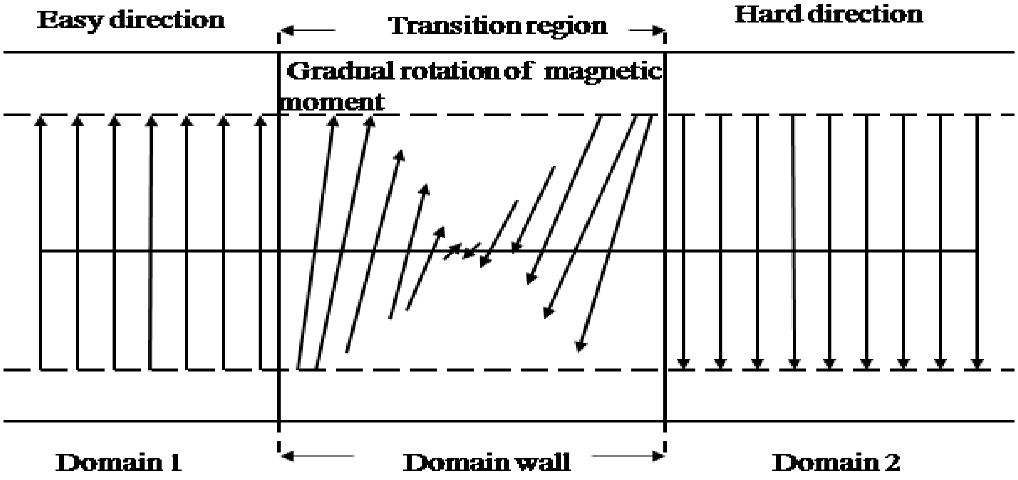


Fig.5.10

4. Magnetostriction energy

When a specimen is magnetized it is found that, it suffers a change of dimensions and this phenomenon is known as magnetostriction. When the magnetic field is applied in the hard direction, the material will experience a decrease in length. Let ‘l’ be the original length of the ferromagnetic material and Δl be the change in length.

Magnetostriction constant (λ) $= \frac{\Delta l}{l}$. The energy associated with the magnetostriction is called magnetostriction energy.

5.9 Spin wave (magnon)

Let us consider a ferromagnetic crystal with N atoms. At absolute zero temperature, all the spins are aligned. The total magnetic moment = Nμ

When the temperature increases from zero, one spin changes its direction with respect o the others. Now, the total magnetic moment is given by Nμ- μ. The change of energy is $2\mu_B H_{ex}$

H_{ex} is the exchange field.

Because of all the spins in the ferromagnetic crystal are connected by the exchange interaction, the change of the direction of one spin by 180^0 will not be confined to a particular spin but will be distributed over all the spins in one line like a wave called spin wave. This spin wave is similar to the de Broglie wave. Thus it has a momentum P=ħK and the energy $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$ as a particle.

Fig.5.11

The particle that is associated with the spin wave is called the magnon. Magnon is an ordinary excitation of the ordered magnetic moments of the materials. Once a ferromagnetic material drops to its ground state, the magnon disappears. Thus magnon is called as quasi particle. It has spin and the spin momentum is equal to one. Magnon propagation should be affected the magnetic properties of the medium.

5.10 Dispersion relation (ω-k) for magnon in ferromagnetic materials

For wave motion, the relation between frequency 'ν', wave length 'λ' and the velocity of propagation v is $\lambda\nu = v$; $2\pi\nu = v2\pi/\lambda$

$\omega = vK$; $K = 2\pi/\lambda$

$\omega \alpha K$

Let us consider, a one dimensional ferromagnetic lattice, where the spins are aligned along a line on atom site in the lattice.

By Heisenberg exchange interaction; the interaction between the nearest spins is given as $-2J_{ij} \sum s_i s_j$

Now consider the pth Spin, it is connected to the (p-1)th and (p+1)th spins by interactions as

$$-2Js_p\left(s_{p-1}+s_{p+1}\right)\ldots\ldots\ldots.(1)$$

We know,

$$\mu_P=-g\mu_P s_P$$

$$s_P=-\frac{\mu_P}{g\mu_B}$$

Substitute s_P in eqn (1)

$$-2J\frac{-\mu_P}{g\mu_B}\left(s_{p-1}+s_{p+1}\right)$$

$$-\mu_P\left[\frac{-2J}{g\mu_B}\right]\left(s_{p-1}+s_{p+1}\right)$$

$$-\mu_P B_p\ \ldots\ldots\ldots..(2) \qquad B_p=\left[\frac{-2J}{g\mu_B}\right]\left(s_{p-1}+s_{p+1}\right) \rightarrow \text{magnetic field.}$$

From mechanics, the rate of change of angular momentum = torque

$$\hbar\frac{ds_p}{dt}=\mu_P B_p$$

$$\frac{ds_p}{dt}=\frac{\mu_P B_p}{\hbar}$$

$$=\frac{-g\mu_B}{\hbar}S_p B_p \qquad \mu_P=-g\mu_B S_P$$

$$\frac{ds_p}{dt}=\frac{-g\mu_B}{\hbar}\left[\frac{-2J}{g\mu_B}\right]S_p\left(s_{p-1}+s_{p+1}\right)$$

$$\frac{ds_p}{dt}=\frac{2J}{\hbar}S_p\left(s_{p-1}+s_{p+1}\right)\ \ldots\ldots\ldots\ldots..(3)$$

In Cartesian form; $\frac{ds_p{}^x}{dt}=\frac{2J}{\hbar}\left[s_p{}^y\left(s_{p-1}{}^z+s_{p+1}{}^z\right)-s_p{}^z\left(s_{p-1}{}^y+s_{p+1}{}^y\right)\right]\ldots\ldots\ldots..(3a)$

$$\frac{ds_p{}^y}{dt} = \frac{2J}{\hbar}\left[s_p{}^z\left(s_{p-1}{}^x + s_{p+1}{}^x\right) - s_p{}^x\left(s_{p-1}{}^z + s_{p+1}{}^z\right)\right] \ldots\ldots\ldots\ldots\ldots\ldots..(3b)$$

$$\frac{ds_p{}^z}{dt} = \frac{2J}{\hbar}\left[s_p{}^x\left(s_{p-1}{}^y + s_{p+1}{}^y\right) - s_p{}^y\left(s_{p-1}{}^x + s_{p+1}{}^x\right)\right] \ldots\ldots\ldots\ldots\ldots\ldots.(3c)$$

Let $s_p{}^z = s_{p+1}{}^z = s_{p-1}{}^z = S$; $s_p{}^x s_p{}^y$ neglected

Eqn (3a)

$$\frac{ds_p{}^x}{dt} = \frac{2J}{\hbar}\left[s_p{}^y(S + S) - S\left(s_{p-1}{}^y + s_{p+1}{}^y\right)\right]$$

$$\frac{ds_p{}^x}{dt} = \frac{2JS}{\hbar}\left[2s_p{}^y - s_{p-1}{}^y - s_{p+1}{}^y\right] \ldots\ldots\ldots\ldots..(4a)$$

Similarly, eqn (3b) and (3c) become

$$\frac{ds_p{}^y}{dt} = \frac{-2JS}{\hbar}\left[2s_p{}^x - s_{p-1}{}^x - s_{p+1}{}^x\right] \ldots\ldots\ldots\ldots.(4b)$$

$$\frac{ds_p{}^z}{dt} = 0 \ldots\ldots\ldots\ldots\ldots\ldots..(4c)$$

A traveling wave solution of eqns (4a), (4b), (4c)

$$s_p{}^x = U\exp[i(pka - \omega t)] \ldots\ldots\ldots.(5a)$$

$$s_p{}^y = V\exp[i(pka - \omega t)] \ldots\ldots\ldots(5b)$$

$$\frac{ds_p{}^x}{dt} = U\exp[i(pka - \omega t)]\ (-i\omega)$$

$$\frac{ds_p{}^y}{dt} = V\exp[i(pka - \omega t)]\ (-i\omega)$$

Eqn (4a) becomes

$$-i\omega U\exp[i(pka - \omega t)] = \frac{2JS}{\hbar}[2V\exp[i(pka - \omega t)] - V\exp[i((p + 1)ka - \omega t)] - V\exp[i(p-1)ka-\omega t]$$

$$i\omega U\exp[i(pka - \omega t)] = \frac{2JS}{\hbar}[2Ve^{i(pka-\omega t)} - Ve^{i(pka-\omega t)}.e^{ika} - Ve^{i(pka-\omega t)}.e^{-ika}]$$

$$= \frac{2JS}{\hbar}V[2e^{i(pka-\omega t)} - e^{i(pka-\omega t)}.e^{ika} - e^{i(pka-\omega t)}.e^{-ika}]$$

$$-i\omega U\exp[i(pka - \omega t)] = \frac{2JS}{\hbar}Ve^{i(pka-\omega t)}[2-e^{ika} - e^{-ika}]$$

$$-i\omega U = \frac{2JS}{\hbar}2V\left(1-\frac{e^{ika}+e^{-ika}}{2}\right)$$

$$-i\omega U = \frac{4JSV}{\hbar}(1-\cos ka)\text{.............}(6a)$$

Eqn (4b) becomes

$$-i\omega V = -\frac{4JSU}{\hbar}(1-\cos ka)\text{............}(6b)$$

Let the determinants of coefficients of U,V is zero.

$$\begin{vmatrix} -i\omega & \frac{4JS}{\hbar}(1-\cos ka) \\ \frac{-4JS}{\hbar}(1-\cos ka) & -i\omega \end{vmatrix} = 0$$

$$\omega^2 = \left[\frac{4JS}{\hbar}(1-\cos ka)\right]^2$$

$$\hbar\omega = 4JS(1-\cos ka)\ \text{.................}(7)$$

For long wavelength ka<< 1

$$1-\cos ka = \frac{1}{2}(ka)^2$$

eqn (7),

$$\hbar\omega = 4JS\frac{1}{2}(ka)^2$$

$\hbar\omega = 2JSa^2k^2$ This is the dispersion relation equation.

5.11 Antiferromagnetic materials

Definition

In this magnetic material, the magnetic interaction between any two dipoles aligns themselves antiparallel to each other. All the dipoles are equal in magnitude. Therefore, the resultant magnetization is zero.

Examples: Manganese oxide, Chromium oxide, ferrous oxide etc.

Dipole alignment

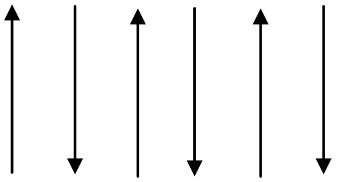


Fig.5.12

Properties

- The dipoles are aligned themselves antiparallel to each other; therefore, the resulting net magnetization is zero.
- The antiparallel alignment of adjacent dipoles is due to an exchange interaction.
- Magnetic susceptibility is small and positive and it is given by,

$$\chi = \frac{C}{T+\theta} \quad \text{(For } T > T_N\text{)}$$

- Initially, susceptibility increases slightly as the temperature increases and beyond Neel temperature (T_N), the susceptibility decreases with the temperature.
- Neel temperature is the temperature at which the susceptibility is maximum.

5.12 Two sub lattice model

Based on the quantum mechanical exchange interaction, when the distance between interacting atoms is very small, the exchange force produces a tendency to anti parallel alignment of the neighboring spin dipole moment. The substance now called as anti ferromagnetic substance. The most characteristic property of anti ferromagnetism is that its susceptibility shows a maximum as function of temperature.

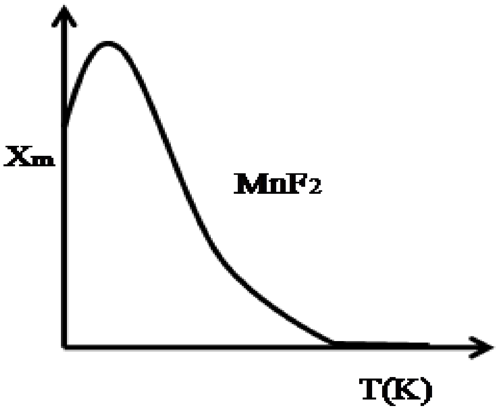


Fig.5.13

Consider a crystal containing two types of atoms A and B. Let A atoms occupy the corner points of the cube, the B atoms located at the center. Let the interaction between the atoms. A spins tends to line up anti parallel to the b spins. At low temperature, this interaction is very effective and in an external field, the resulting magnetization will be small. As the temperature is raised, the efficiency of the interaction becomes less pronounced and the susceptibility increases. Finally a critical temperature T_N known as Neel temperature is reached above which the spins are free and the anti ferromagnetic material becomes paramagnetic i.e. χ decreases with increase in temperature.

Let there are anti ferromagnetic A-B interaction as well as A-A interaction and B-B interaction.

$$H_a = H - \alpha M_a - \beta M_b$$

$$H_b = H - \alpha M_b - \beta M_a$$

Where, H_a, H_b --- the net molecular field at the A site and B site; H is the applied field.

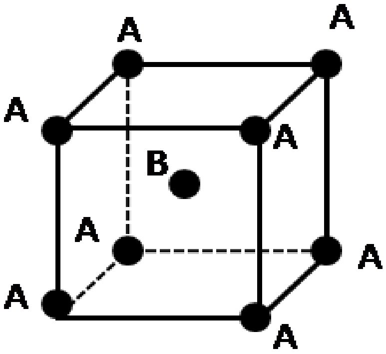


Fig.5.14

M_a, M_b are the magnetization of A and B lattice.
α, β are the weiss constants.

Case 1 : **$T > T_N$**

When the temperature is above the Neel temperature, Magnetization of the lattice A is given by

$$M_a = \left(\frac{N\mu_J^2}{3K_B T}\right) H_a$$

$$M_b = \left(\frac{N\mu_J^2}{3K_B T}\right) H_b$$

$$M = M_a + M_b$$

$$= \left(\frac{N\mu_J^2}{3K_B T}\right) H_a + \left(\frac{N\mu_J^2}{3K_B T}\right) H_b$$

$$= \left(\frac{N\mu_J^2}{3K_B T}\right) (H_a + H_b)$$

$$= \left(\frac{N\mu_J^2}{3K_B T}\right) [(H - \alpha M_a - \beta M_b) + (H - \alpha M_b - \beta M_a)]$$

$$= \left(\frac{N\mu_J^2}{3K_B T}\right)[2H - \alpha M_a - \beta M_b - \alpha M_b - \beta M_a]$$

$$= \left(\frac{N\mu_J^2}{3K_B T}\right)[2H - \alpha(M_a + M_b) - \beta(M_a + M_b)]$$

$$= \left(\frac{N\mu_J^2}{3K_B T}\right)[2H - \alpha M - \beta M$$

$$M = \left(\frac{N\mu_J^2}{3K_B T}\right)[2H - M(\alpha + \beta)]$$

$$M = \left(\frac{N\mu_J^2}{3K_B T}\right)[2H - M(\alpha + \beta)]$$

$$M = \left[\frac{2HN\mu_J^2}{3K_B T} - \frac{MN\mu_J^2}{3K_B T}(\alpha + \beta)\right]$$

$$M \quad + \frac{MN\mu_J^2}{3K_B T}(\alpha + \beta) = \left[\frac{2HN\mu_J^2}{3K_B T}\right]$$

$$M\,[1 + \frac{N\mu_J^2}{3K_B T}(\alpha + \beta)\,] = \left[\frac{2HN\mu_J^2}{3K_B T}\right]$$

Susceptibility $\chi = \frac{M}{H} = \dfrac{\frac{2HN\mu_J^2}{3K_B T}}{H\left[1 + \frac{N\mu_J^2}{3K_B T}(\alpha + \beta)\right]}$

$$= \frac{\frac{2N\mu_J^2}{3K_B}}{T[1 + \frac{N\mu_J^2}{3K_B T}(\alpha + \beta)\,]}$$

$$= \frac{\frac{2N\mu_J^2}{3K_B}}{T + \frac{N\mu_J^2 T}{3K_B T}(\alpha + \beta)} = \frac{\frac{2N\mu_J^2}{3K_B}}{T + \frac{N\mu_J^2}{3K_B}(\alpha + \beta)}$$

$\chi = \frac{C}{T + \theta}$ where $C = \frac{2N\mu_J^2}{3K_B}$; $\theta = \frac{N\mu_J^2}{3K_B}(\alpha + \beta)$

case 2:

In the absence of applied field at $T < T_N$

The eqn $M_a = \left(\frac{N\mu_J^2}{3K_B T}\right) H_a$ can be written as

$$M_a = -\left(\frac{N\mu_J^2}{3K_BT_N}\right)(\alpha M_a + \beta M_b)$$

$$M_a = -\left(\frac{N\mu_J^2\alpha M_a}{3K_BT_N}\right) - \left(\frac{N\mu_J^2\beta M_b}{3K_BT_N}\right)$$

$$M_a + \left(\frac{N\mu_J^2\alpha M_a}{3K_BT_N}\right) + \left(\frac{N\mu_J^2\beta M_b}{3K_BT_N}\right) = 0$$

$$M_a\left(1 + \left(\frac{N\mu_J^2\alpha}{3K_BT_N}\right)\right) + \left(\frac{N\mu_J^2\beta M_b}{3K_BT_N}\right) = 0 \text{ …………(A)}$$

Similarly,

$$M_b\left(1 + \left(\frac{N\mu_J^2\alpha}{3K_BT_N}\right)\right) + \left(\frac{N\mu_J^2\beta M_a}{3K_BT_N}\right) = 0 \text{ ……….(B)}$$

Solving these eqns we get,

$$M_a = M_b = 0$$

Spontaneous magnetization would take place if there existed a solution of the simultaneous equations for a finite value of M_a and M_b. This possible if

$$\begin{vmatrix} [1 + \left(\frac{c\alpha}{2T_N}\right)] & \frac{c\beta}{2T_N} \\ \frac{c\beta}{2T_N} & [1 + \left(\frac{c\alpha}{2T_N}\right)] \end{vmatrix} = 0$$

Thus

$$\left(1 + \left(\frac{c\alpha}{2T_N}\right)\right)^2 - \frac{c^2\beta^2}{4T_N^2}] = 0$$

$$\left(1 + \left(\frac{c\alpha}{2T_N}\right)\right)^2 = \frac{c^2\beta^2}{4T_N^2}$$

$$1 + \left(\frac{c\alpha}{2T_N}\right) = \frac{c\beta}{2T_N}$$

$$1 + \frac{c}{2T_N}(\alpha - \beta) = 0$$

$$T_N + \frac{c}{2}(\alpha - \beta) = 0$$

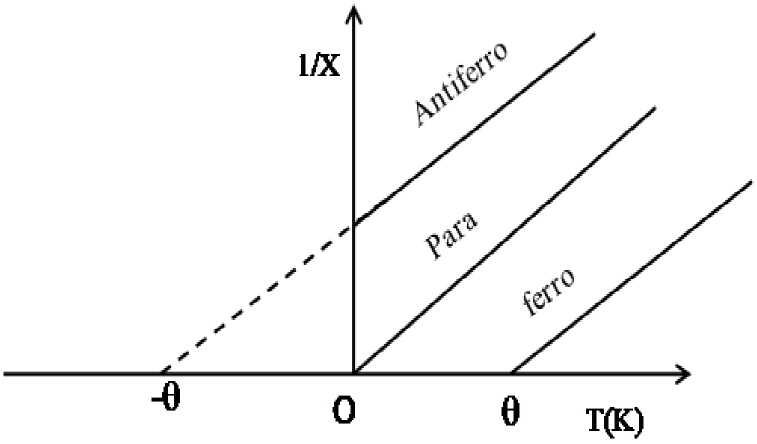


Fig.5.15

$$T_N = \frac{c}{2}(\beta - \alpha)$$

From this eqn, the Neel temperature T_N increases with β is stronger and decreases with α increasing.

From the eqn $\chi = \frac{C}{T+\theta}$; $\theta = \frac{N\mu_J^2}{3K_B}(\alpha + \beta) = \frac{C(\alpha+\beta)}{2}$

$$\frac{T_N}{\theta} = \frac{c(\beta-\alpha)}{2\frac{C(\alpha+\beta)}{2}} = \frac{\beta-\alpha}{\beta+\alpha}$$

$$\frac{T_N}{\theta} = \frac{\beta-\alpha}{\beta+\alpha}\,.$$

5.13 Antiferromagnetic order

In an antiferromagnet the spins are ordered in an anti parallel arrangement with zero net moment at temperatures below the Neel temperature. The susceptibility of antiferromagnet is not infinite at $T = T_N$.

Antiferromagnet is a special case of a ferromagnet for which both sub lattices A and B have equal saturation magnetizations. The Neel temperature in the mean field is given by $T_N = \mu c$ where c refers to single lattice. The susceptibility in the paramagnetic region $T > T_N$ is obtained as

$$\frac{2c}{T+\mu c} = \frac{2c}{T+TN}$$

The value of $\frac{\theta}{T_N}$ of the observed magnitude may be obtained when next – nearest – neighbor interactions are provided for, and when possible sublattice arrangements are considered. If a mean field constant –ε is introduced to describe interactions within a sub lattice, then $\frac{\theta}{T_N} = \frac{\mu+\varepsilon}{(\mu-\varepsilon)}$.

5.13.1 Susceptibility below the Neel temperature

There are two situations; with the applied magnetic field perpendicular to the axis of the spins; and with the field parallel to the axis of the spins. At and above the Neel temperature the susceptibility is nearly independent of the direction of the field relative to the spin axis.

For B_a perpendicular to the axis of the spins, the susceptibility is $\chi_{\text{perpendicular}} = \frac{2M\varphi}{B_a}$

In the parallel orientation, the magnetic energy is not changed, thus the susceptibility at T= oK is zero $\chi_{\text{parallel}} = 0$.

The parallel susceptibility increases with temperature up to T_N .in very strong fields the spin system will turn discontinuously from the parallel orientation to the perpendicular orientation where the energy is lower.

5.13.2 Magnons in antiferromagnets

Consider a one dimensional antiferromagnetic crystal. The spins are aligned alternatively up an down. Let,

2P even numbered spins have S^z=S.

(2p+1) odd numbered spins have $S^z = -S$

The spins interact with the nearest neighbors only,ie., pth spin interacts with (P+1)th spin and (P-1)th spin. In the anti ferromagnetic crystal, Heisenberg exchange interaction is $-2J_{12} \sum s_1 s_2$, where J is negative.

The Cartesian form of the relation between the rate of change of angular momentum and the torque is

$$\frac{ds_p{}^x}{dt} = \frac{2J}{\hbar}\left[s_p{}^y\left(S_{p-1}^z + S_{p+1}^z\right) - s_p{}^z\left(S_{p-1}^y + S_{p+1}^y\right)\right] \dots\dots\dots\dots(1)$$

$$\frac{ds_p{}^y}{dt} = \frac{2J}{\hbar}\left[s_p{}^z\left(S_{p-1}^x + S_{p+1}^x\right) - s_p{}^x\left(S_{p-1}^z + S_{p+1}^z\right)\right] \dots\dots\dots\dots(2)$$

$$\frac{ds_p{}^z}{dt} = 0\dots\dots\dots\dots(3)$$

Substituting the special conditions in these eqns;

For even numbered A spins S^z = S

For odd numbered B spins S^z = -S

We wil get two sets of equations, one set for A spins 2p atoms and other set for B spins (2p+1) atoms . For A spins, in eqns (1) and (2)

Put, S_{2p}^z= S; S_{2p+1}^z and $S_{2p-1}^z = -S$; P = 2p, P+1 = 2p+1, P-1= 2p-1.

$$\frac{\mathrm{d}s_{2p}{}^{x}}{\mathrm{dt}} = \frac{2J}{\hbar}\left[S^{y}_{2p}\left(S^{z}_{2p-1} + S^{z}_{2p-1}\right) - S^{z}_{2p}\left(S^{y}_{2p-1} + S^{y}_{2p-1}\right)\right]$$

$$\frac{\mathrm{d}S^{x}_{2p}}{\mathrm{dt}} = \frac{2JS}{\hbar}\left[-2s_{2p}{}^{y} - S^{y}_{2p-1} - S^{y}_{2p+1}\right] \ldots\ldots\ldots\ldots\ldots(4a)$$

Eqn (2) becomes,

$$\frac{\mathrm{d}S^{y}_{2p}}{\mathrm{dt}} = \frac{-2JS}{\hbar}\left[-2s_{2p}{}^{x} - S^{x}_{2p-1} - S^{x}_{2p+1}\right] \ldots\ldots\ldots\ldots..(4b)$$

For B atoms, in eqns (1) (2) substitute $S^{z}_{2p} = S^{z}_{2p+2} = S;\ S^{z}_{2p+1} = S^{z}_{2p-1} = -S, P = 2P + 1$

Eqn (1) becomes,

$$\frac{\mathrm{d}S^{x}_{2p+1}}{\mathrm{dt}} = \frac{2JS}{\hbar}\left[2S^{y}_{2p+1} + S^{y}_{2p} + S^{y}_{2p+2}\right] \ldots\ldots\ldots\ldots..(5a)$$

Eqn (2) becomes,

$$\frac{\mathrm{d}S^{y}_{2p+1}}{\mathrm{dt}} = \frac{-2JS}{\hbar}\left[2S^{x}_{2p+1} + S^{x}_{2p} + S^{x}_{2p+2}\right]\ldots\ldots\ldots\ldots\ldots(5b)$$

If $S^x + i\,S^y = s^+$, $\frac{\mathrm{d}S^{+}}{\mathrm{dt}} = \frac{\mathrm{d}S^{x}}{\mathrm{dt}} + i\frac{\mathrm{d}S^{y}}{\mathrm{dt}}$

$$\frac{\mathrm{d}S^{+}_{2p}}{\mathrm{dt}} = \frac{\mathrm{d}S^{x}_{2p}}{\mathrm{dt}} + i\frac{\mathrm{d}S^{y}_{2p}}{\mathrm{dt}}\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Substitute eqn (4a) and (4b) and simplify the eqn (6)

$$\frac{\mathrm{d}S^{+}_{2p}}{\mathrm{dt}} = \frac{2iJS}{\hbar}\left[2S^{+}_{2p} + S^{+}_{2p-1} + S^{+}_{2p+1}\right]\ldots\ldots\ldots\ldots\ldots(7a)$$

$$\frac{\mathrm{d}S^{+}_{2p+1}}{\mathrm{dt}} = -\frac{2iJS}{\hbar}\left[2S^{+}_{2p+1} + S^{+}_{2p} + S^{+}_{2p+2}\right] \qquad \ldots\ldots\ldots\ldots\ldots(7b)$$

The solutions of eqn (7a) and (7b) are

$$S^{+}_{2p} = U\exp[i2pka - i\omega t] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8a),$$

$$S^{+}_{2p+1} = V\exp[i(2p+1)ka - i\omega t] \qquad \ldots\ldots\ \ldots\ldots\ldots\ldots....(8b)$$

On substituting eqn(8a) and (8b) in eqn(7a) and (7b), we get,

$$\omega U = \frac{1}{2}\omega_{ex}\left[2U + V\exp(-ika) + V\exp(ika)\right] \quad \ldots\ldots\ldots(9a)$$

$$-\omega V = \frac{1}{2}\omega_{ex}[2V + U\exp(-ika) + U\exp(ika)] \ldots\ldots\ldots..(9b)$$

Where $\omega_{ex} = \frac{-4JS}{\hbar}$

Eqns (9a), (9b) have a solution when $\begin{vmatrix} \omega_{ex} - \omega & \omega_{ex}(\cos ka) \\ \omega_{ex}(\cos ka) & \omega_{ex} + \omega \end{vmatrix} = 0$

$$\omega_{ex}{}^2 - \omega^2 = \omega_{ex}{}^2\cos^2 ka$$

$$-\omega^2 = \omega_{ex}{}^2\cos^2 ka - \omega_{ex}{}^2$$

$$\omega^2 = \omega_{ex}{}^2(1 - \cos^2 ka)$$

$\omega = \omega_{ex}|\sin ka| \ldots\ldots\ldots\ldots(10)$. This is the dispersion relation for anti ferromagnetic material.

If $ka \ll 1$, then $\sin ka = ka$.

The dispersion relation becomes $\omega = |ka|$.

5 .14 Ferrimagnetic materials

Definition

Here, the magnetic interaction between any two dipoles aligns themselves antiparallel to each other. But the magnitude of two adjacent dipoles is not equal. Therefore, if we apply a small value of magnetic field, it will produce large value of magnetization.

Examples: ferrous ferrite, nickel ferrite etc.

Dipole alignment

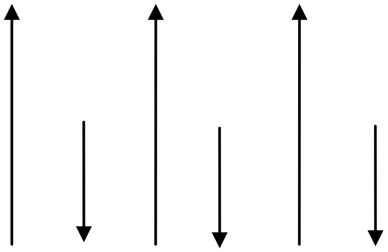


Fig.5.16

5.15 Ferrites

Definition

Ferrimagnetic materials are also called as ferrites. Ferrites are modified structures of iron with no carbon. They are made by two different kinds of atoms.

The general formula for ferrite molecule is $A^{2+}Fe_2^{3+}O_4^{2-}$ where, A^{2+} represents a divalent metal ion. It may be Zn^{2+}, Cd^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+} etc.

Examples: Manganese ferrite, Cadmium ferrite, Zinc ferrite etc.

5.15.1 Structure of ferrite

Normally, there are two types of structures present in the ferrites,

i. Regular spinel
ii. Inverse spinel

i. Regular spinel

Example: $Mg^{2+}Fe_2{}^{3+}\ O_4{}^{2-}$

In this type, each Mg^{2+} ions (divalent) is surrounded by four O^{2-} ions in tetragonal fashion**.** Totally, there will be 8 tetrahedral sites in the unit cell**.** This is indicated by A – site.

Each Fe^{3+} ions (trivalent) is surrounded by six O^{2-} ions in octahedral fashion. Totally, there will be 16 octahedral sites in the unit cell. This indicated by B – site. Thus in a regular spinel, each divalent metal ion Mg^{2+} exists in a tetrahedral form (A – site) and each trivalent metal ion Fe^{3+} exists in an octahedral form (B – site). The sites A & B combine together to form a regular spinel ferrite structure as shown in fig. 5.18.

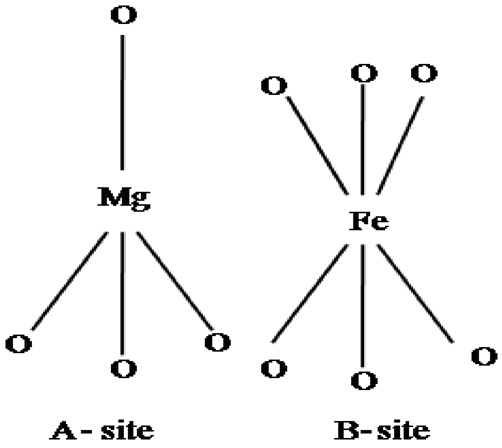


Fig.5.17

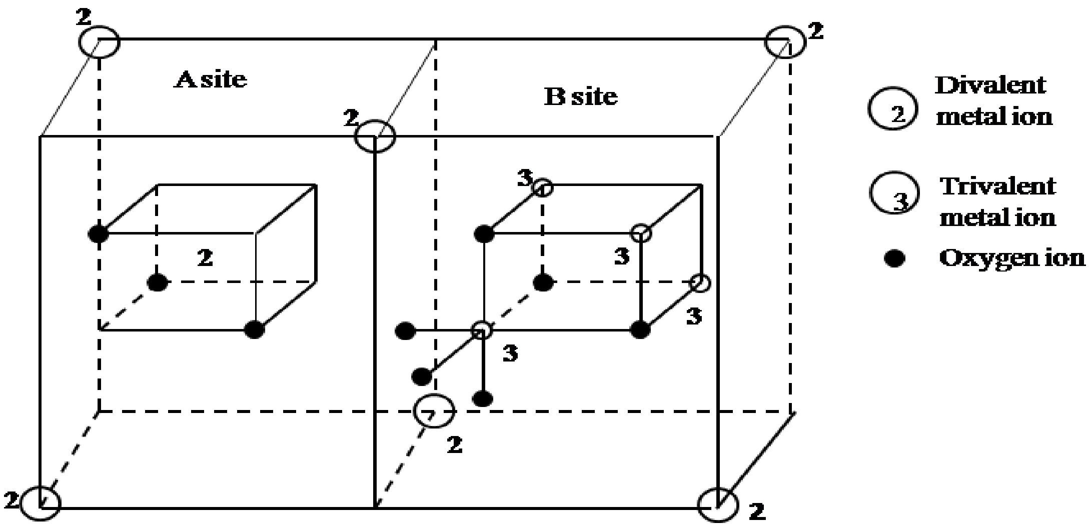


Fig.5.18

ii. Inverse spinel

Example: $Fe^{3+}[Fe^{2+}Fe^{3+}]\ O_4{}^{2-}$

In this type, Fe^{3+} ions (trivalent) occupy all the A – sites (tetrahedral) and half of the B – sites (octahedral) also. The remaining half of the B – sites will be occupied by the Fe^{2+} (divalent) atoms.

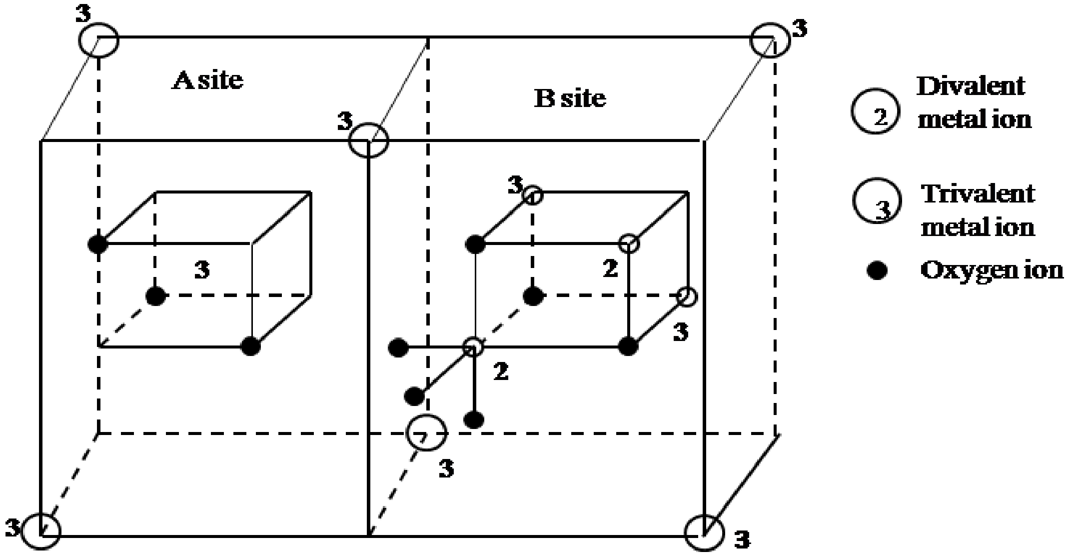


Fig.5.19

5.15.2 Properties

- The dipoles are aligned antiparallel to each other and the magnitude of any two magnetic dipoles is not equal.
- It has pure iron character.
- It has low tensile strength, brittle, soft and non-machinable one.
- They are bad conductors.
- They have low eddy current losses and low hysteresis losses.
- They have high resistivity and high permeability.

5.15.3 Applications

- Ferrites are used to produce low frequency ultrasonic waves.
- Hard ferrites are used for the preparation of permanent magnets, which is used in loudspeakers, wind screens and telephone etc.
- Ferrites are used to prepare the low power transformers and high flux transformers.
- Ferrites are used for the preparation of microwave devices like isolators, circulators and gyrator.
- Ferrites are used to increase the sensitivity of radio receivers.
- They are used as cores in audio and TV transformers.
- They are used in digital computers and data processing circuits as a magnetic storage element.
- The non-volatile memories made up of ferrites are used in military field.
- Ferrites powders are used in the coatings of magnetic recording tapes.
- Ferrites are used for power limiting and harmonic generation.

5.16 Soft and Hard magnetic materials

Hard magnetic materials	Soft magnetic materials
1. It is hard to magnetise and demagnetise. 2. It shows fat hysteresis loop. 3. They have small hysteresis loss due to small hysteresis loop area. 4. The susceptibility and permeability values are low. 5. The eddy current loss is more due to its smaller resistivity. 6. Domain wall movement is difficult due to crystal imperfections and is irreversible in nature. 7. The coercivity and retentivity are large. 8. Its magnetostatic energy is large. 9. These are used to produce permanent magnets. 10. Examples: Alnico alloys, cunifies, cunico and silmanal	1. It is easy to magnetise and demagnetise. 2. It shows thin hysteresis loop. 3. They have small hysteresis loss due to small hysteresis loop area. 4. The susceptibility and permeability values are very high . 5. The eddy current loss is small due to its higher resistivity. 6. Domain wall move easily and reversible so that magnetisaion changes by large amount. 7. The coercivity and retentivity are small. 8. Its magnetostatic energy is small. 9. These are used in electro-magnets. 10. Examples: iron silicon alloy , ferrous nickel alloys, ferrites and garnets.