Manonmaniam Sundaranar University,
Directorate of Distance & Continuing Education,
Tirunelveli - 627 012 Tamilnadu, India

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES
(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

II YEAR

M.Sc. Physics

Course Material

Condensed Matter Physics

Prepared
By

Dr. S. Shailajha
Dr. S. Arunavathi
Assistant Professor
Department of Physics
Manonmaniam Sundaranar University
Tirunelveli - 12

CONDENSED MATTER PHYSICS

UNIT I:

CRYSTAL PHYSICS

Types of lattices - Miller indices – Symmetry elements and allowed rotations Simple crystal structures – Atomic Packing Factor- Crystal diffraction - Bragg's law –Scattered Wave Amplitude - Reciprocal Lattice (sc, bcc, fcc). Structure and properties of liquid crystals. Diffraction Conditions – Laue equations - Brillouin zone - Structure factor - Atomic form factor - Inert gas crystals - Cohesive energy of ionic crystals - Madelung constant - Types of crystal binding (general ideas).

UNIT II:

LATTICE DYNAMICS

Lattice with two atoms per primitive cell - First Brillouin zone - Group and phase velocities - Quantization of lattice vibrations - Phonon momentum - Inelastic scattering by phonons - Debye’s theory of lattice heat capacity - Thermal Conductivity - Umkalapp processes.

UNIT III:

THEORY OF METALS AND SEMICONDUCTORS

Free electron gas in three dimensions - Electronic heat capacity - Wiedemann- Franz law - Band theory of metals and semiconductors - Bloch theorem - Kronig-Penney model - Semiconductors - Intrinsic carrier concentration – Temperature Dependence - Mobility - Impurity conductivity – Impurity states - Hall effect - Fermi surfaces and construction - Experimental methods in Fermi surface studies - de Hass-van Alphen effect .

UNIT IV:

MAGNETISM

Diamagnetism - Quantum theory of paramagnetism - Rare earth ion - Hund's rule - Quenching of orbital angular momentum - Adiabatic demagnetization - Quantum theory of ferromagnetism - Curie point - Exchange integral - Heisenberg's interpretation of Weiss field - Ferromagnetic domains – Bloch wall - Spin waves - Quantization - Magnons - Thermal excitation of magnons - Curie temperature and susceptibility of ferrimagnets - Theory of anti feromagnetism - Neel temperature.

UNIT V

Superconductivity

Experimental facts: Occurrence - Effect of magnetic fields - Meissner effect – Critical field – Critical current - Entropy and heat capacity - Energy gap - Microwave and infrared properties - Type I and II Superconductors.

Theoretical Explanation: Thermodynamics of super conducting transition - London equation - Coherence length – Isotope effect - Cooper pairs – Bardeen Cooper Schrieffer (BCS) Theory – BCS to Bose – Einstein Condensation (BEC) regime- Nature of paring and condensation of Fermions. Single particle tunneling - Josephson tunneling - DC and AC Josephson effects - High temperature Superconductors – SQUIDS.

TEXT BOOKS

C. Kittel, 1996, Introduction to Solid State Physics, 7 th Edition, Wiley, New York.

Rita John, Solid State Physics, Tata Mc-Graw Hill Publication.

A. J. Dekker, Solid State Physics, Macmillan India, New Delhi.

M. Ali Omar, 1974, Elementary Solid State Physics – Principle and Applications, Addison - Wesley

H. P. Myers, 1998, Introductory Solid State Physics, 2 nd Edition Viva Book, New Delhi.

UNIT I

CRYSTAL PHYSICS

Types of lattices - Miller indices – Symmetry elements and allowed rotations. Simple crystal structures – Atomic Packing Factor- Crystal diffraction - Bragg's law –Scattered Wave Amplitude - Reciprocal Lattice (sc, bcc, fcc). Structure and properties of liquid crystals. Diffraction Conditions – Laue equations - Brillouin zone - Structure factor - Atomic form factor - Inert gas crystals - Cohesive energy of ionic crystals - Madelung constant - Types of crystal binding (general ideas).

1.1 Lattice:

Lattice is defined as an array of points such that every lattice point has got the same environment or every point is indistinguishable from the other lattice point.

1.1.1Types of lattices:

The number of point groups in two and three dimensions are 10 and 32 respectively. The point groups form the basis for construction of different types of lattices. Only these lattices are permissible which are consistent with the point group operations. Such lattices are called Bravis lattices.

Bravis lattices stated that 10 and 32 point groups in two and three dimensions produce only 5 and 14 distinct Bravis lattices respectively. These Bravis lattices further become parts of 4 and 7 distinct crystal systems respectively

(i) Two dimensional Lattice:

The four crystal systems of two-dimensional space are oblique, rectangular, square and hexagonal. The rectangular crystal system has two Bravais lattices, namely rectangular primitive and rectangular centered. There are five Bravais lattices along with the corresponding point groups.

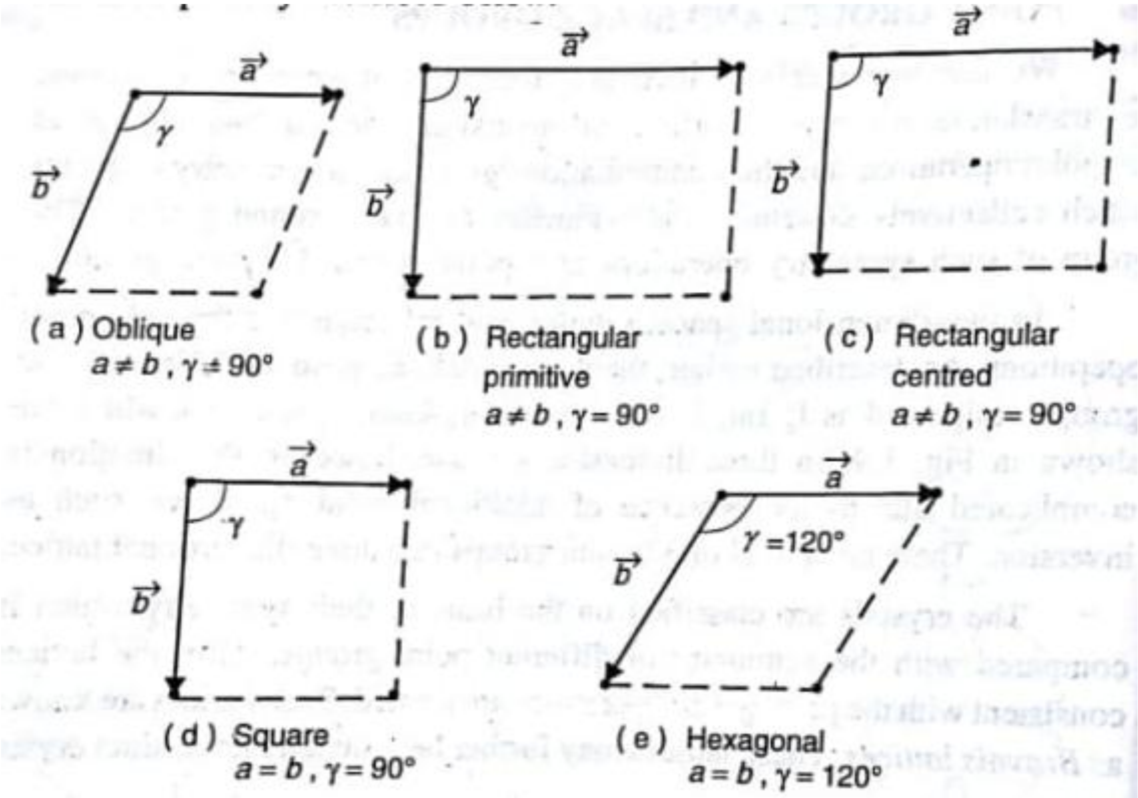
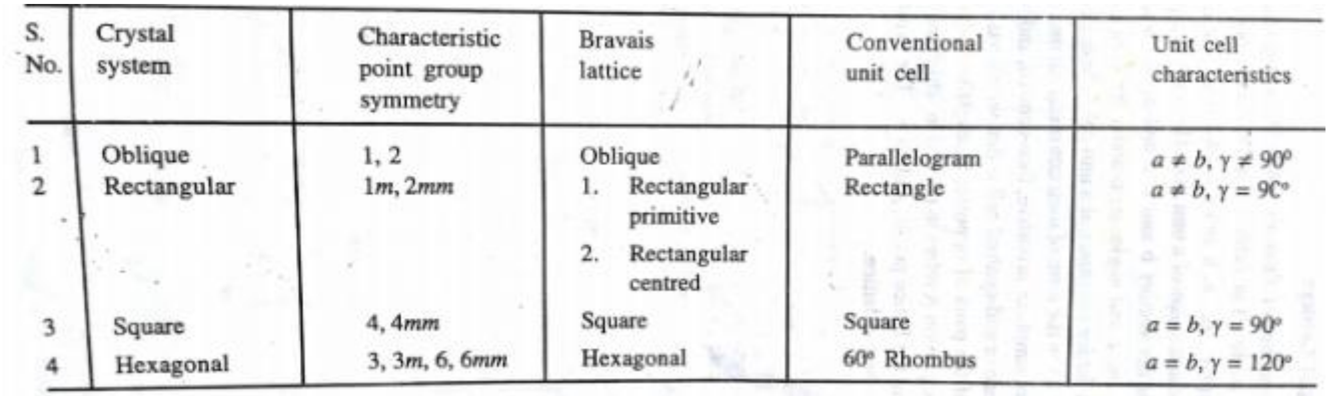


Figure 1.1 Bravis lattice in 2-dimensions

Table 1.1 Crystal system and bravis lattices in two dimensions



S. No.	Crystal system	Characteristic point group symmetry	Bravais lattice	Conventional unit cell	Unit cell characteristics
1	Oblique	1, 2	Oblique	Parallelogram	$a \neq b, \gamma \neq 90°$
2	Rectangular	1m, 2mm	1. Rectangular primitive 2. Rectangular centred	Rectangle	$a \neq b, \gamma = 90°$
3	Square	4, 4mm	Square	Square	$a = b, \gamma = 90°$
4	Hexagonal	3, 3m, 6, 6mm	Hexagonal	60° Rhombus	$a = b, \gamma = 120°$

(ii) Three dimensional lattices

All the seven crystal systems of three-dimensional space and the corresponding Bravais lattices are listed, in the decreasing order of symmetry.

The crystallographic axes a, b and c drawn from one of the lattice points determine the size and shape of a unit cell. The angles α,β and γ are collectively known as lattice parameters or lattice constants of unit cell.

These Bravis lattice are also shown in figure in the form of their conventional unit cells.

The symbols P, F and I represent simple or primitive, face-centered and body-centered cells respectively.

A base or end-centered cell is that which has lattice points at corners and at one of the pairs of opposite faces. It is designated by the letter A, B or C. a designation A refers to the cell in which the faces defined by b and c axes contain the lattice points, and so on. The symbol R is specifically used for rhombohedral lattice.

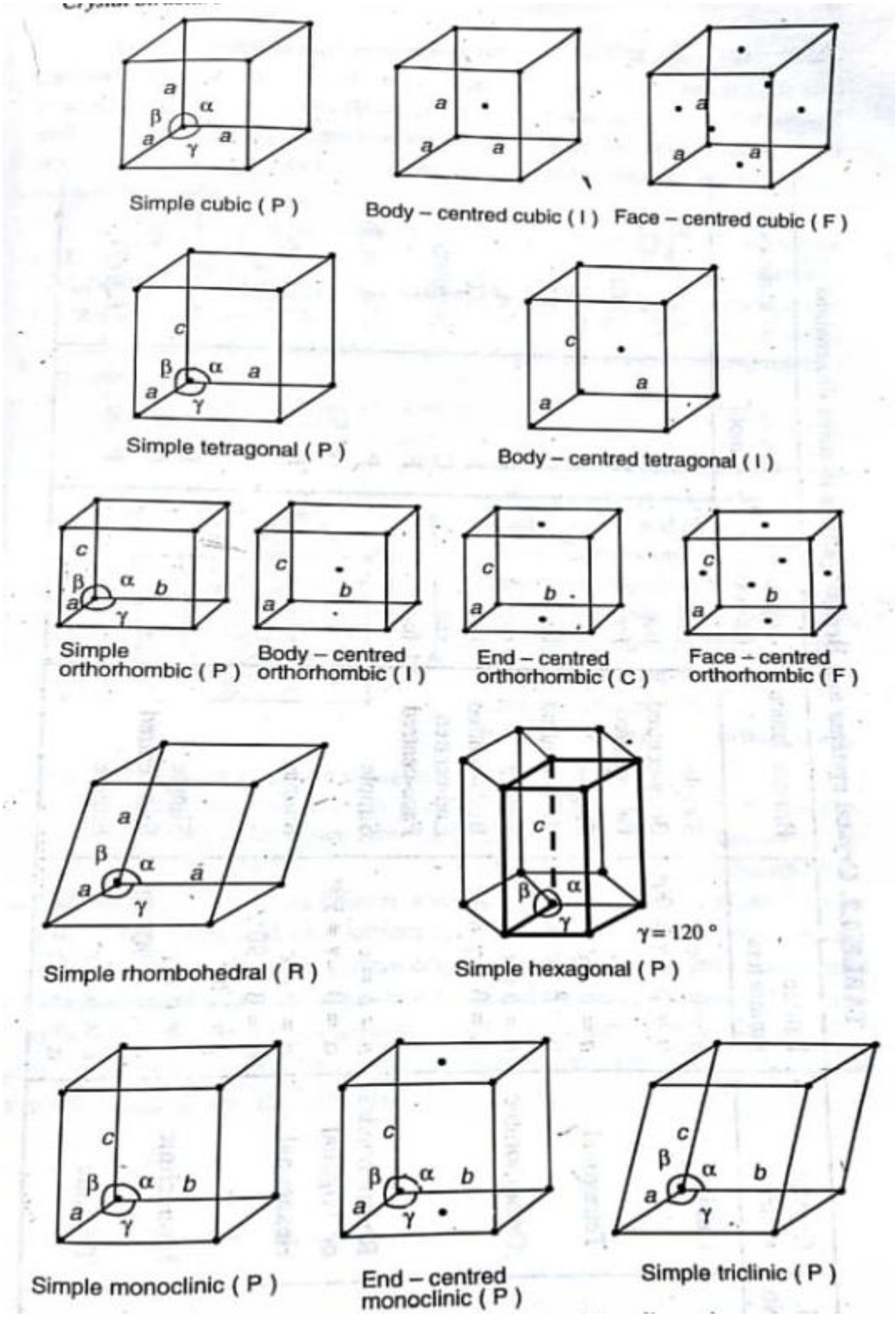
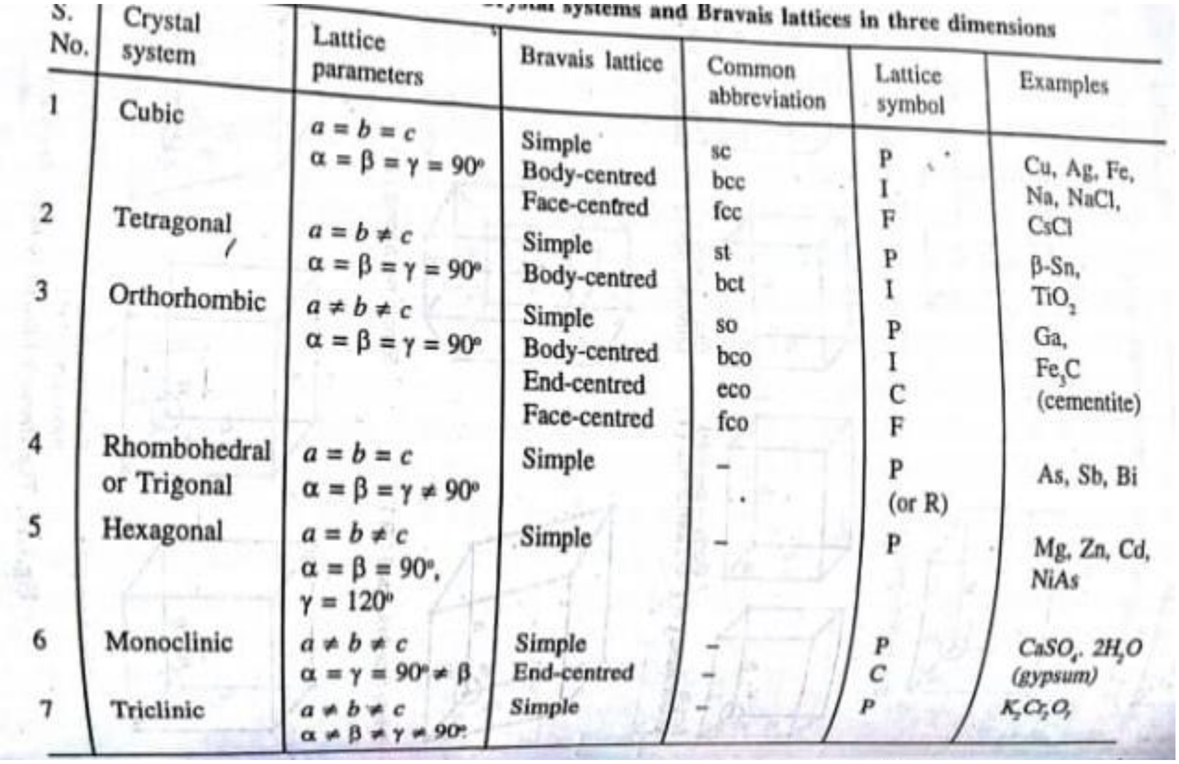


Figure 1.2 Bravis lattice in 3-dimension

Table 1.2 Crystal system and Bravis lattices in three dimensions



systems and Bravais lattices in three dimensions

S. No.	Crystal system	Lattice parameters	Bravais lattice	Common abbreviation	Lattice symbol	Examples
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred Face-centred	sc bcc fcc	P I F	Cu, Ag, Fe, Na, NaCl, CsCl
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred	st bct	P I	β-Sn, TiO_2
3	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred End-centred Face-centred	so bco eco fco	P I C F	Ga, Fe_3C (cementite)
4	Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Simple	–	P (or R)	As, Sb, Bi
5	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Simple	–	P	Mg, Zn, Cd, NiAs
6	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	Simple End-centred	– –	P C	$CaSO_4 \cdot 2H_2O$ (gypsum)
7	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	–	P	$K_2Cr_2O_7$

1.2 Miller indices:

After joining the crystal lattice points by straight lines, those straight lines were assumed to be the set of parallel crystal planes extending them in three-dimensional geometry.

The problem that arose was the explanation of the orientation and direction of these planes. Miller evolved a method to designate the orientation and direction of the set of parallel planes with respect to the coordinate system by numbers h, k, and l (integers) known as the Miller Indices.

The planes represented by the *hkl* Miller Indices are also known as the *hkl* planes. Therefore, the Miller Indices definition can be stated as the mathematical representation of the crystallographic planes in three dimensions.

Construction of Miller Planes:

Let us understand the steps involved in the construction of Miller Planes one by one. To construct the Miller Indices and the Miller Plane we follow the following method:

Step 1:

Consider a point or an atom as the origin, construct a three-coordinate axis and find the intercepts of the planes along the coordinate axis.

Step 2:

Measure the distance or the length of the intercepts from the origin in multiples of the lattice constant.

Step 3:

Consider the reciprocal of the intercepts. Reduce the reciprocals of the intercepts into the smallest set of integers in the same ratio by multiplying with their LCM.

Step 4:

Enclose the smallest set of integers in parentheses and hence we found the Miller indices that explain the crystal plane mathematically.

Rules for Miller Indices:

- Determine the intercepts (*a*,*b*,*c*) of the planes along the crystallographic axes, in terms of unit cell dimensions.
- Consider the reciprocal of the intercepts measured.
- Clear the fractions, and reduce them to the lowest terms in the same ratio by considering the LCM.
- If a *hkl* plane has a negative intercept, the negative number is denoted by a bar (¯) above the number.
- Never alter or change the negative numbers. For example, do not divide -3,-3, -3 by -1 to get 3,3,3.
- If the crystal plane is parallel to an axis, its intercept is zero and they will meet each other at infinity.
- The three indices are enclosed in parenthesis, *hkl* and known as the hkl indices. A family of planes is represented by *hkl* and this is the Miller index notation.

1.3 Simple crystal structures and atomic packing factor:

The basic crystal structures which are either monoatomic or contain simple basis. These include close-packed structure like hexagonal close-packed or face-centered cubic structures and loose-packed structure like body-centered cubic or simple cubic structure.

Close – packed structures:

Close – packed structures are mostly found in monoatomic crystals having non-directional bonding, such as metallic bonding. In these structures, the coordination number of each atom is 12. i.e., each atom is surrounded by twelve similar and equal size neighbours. Out of these twelve neighbors', six lie in one plane, three in an adjacent parallel plane above this plane and three in a similar plane below it. There are two types of close-packed structures:

(i) Hexagonal close-packed(hcp) structure
(ii) Face-centred cubic(fcc) structure.

These structures are described as follows:

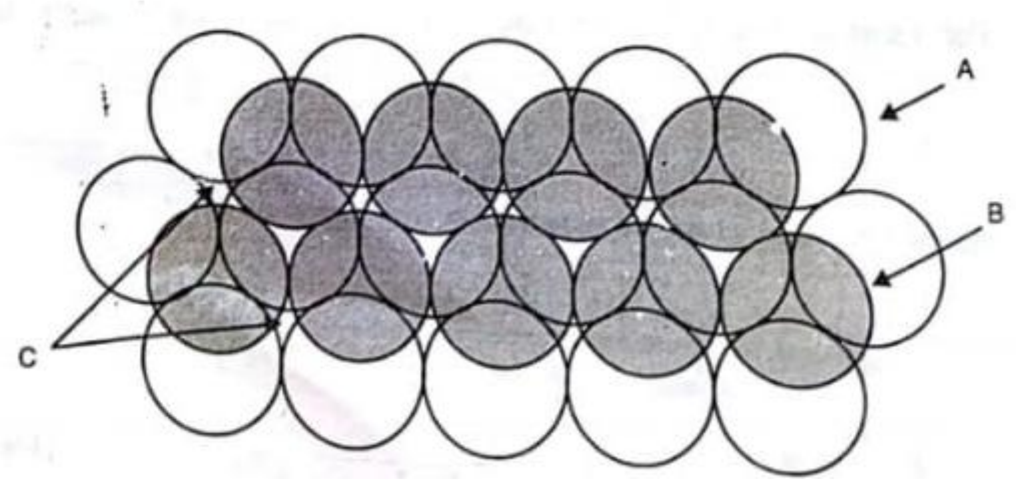


Figure1.3 Layered arrangement of close-packed structure

(i) Hexagonal close-packed (hcp) structure:

Consider a layer of similar atoms with each atom surrounded by six atoms in one plane as shown in figure. Another similar layer B can be placed on top of layer A such that the atoms of layer B occupy the alternate valleys formed by the atom of layer A.

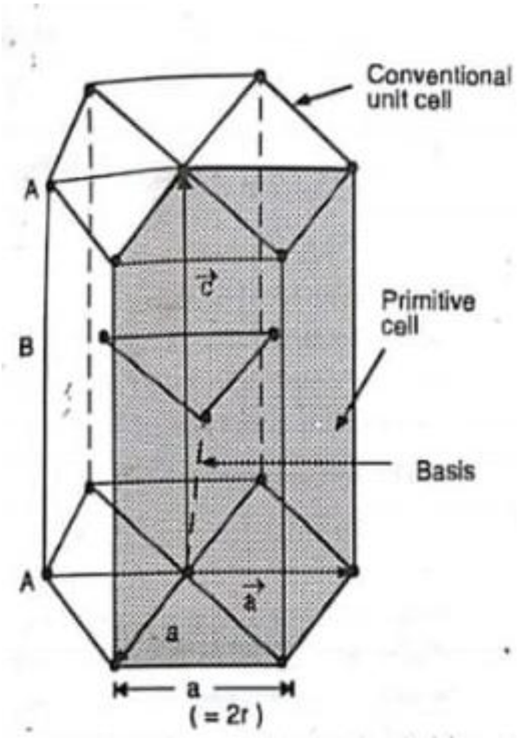


Figure 1.4 Conventional and primitive cells of hexagonal close-packed structure

If a third similar layer is placed on the top of the B layer in such a way that the atoms of B layer exactly overlap the atoms of A layer and this type of stacking is repeated successively, the following layered arrangement is obtained:

…………..ABABAB…………

This type of stacking is called hexagonal close-packed structure. There are twelve atoms located at the corners, two at the centres of the basal planes, and three completely inside the hexagon forming a part of the B layer.

The effective number of atoms in a unit cell is

$$12\left(\frac{1}{6}\right) + 2\left(\frac{1}{2}\right) + 3 = 6$$

The interatomic distance for the atoms withing a layer is a. the distance between the two adjacent layer is c/2. C – the height of the unit cell. For ideal hcp structure, c = 1.633a.

It may be noted that although the structure is hcp, the space lattice is simple hexagonal with basis consisting of two atoms placed in such a way that if one atom lies at the origin, the other atom lies at the point $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. the shaded portion of the figure represent the primitive cell of this structure. It contains 2 atoms instead of one which is due to the presence of the basis. Also the volume of the primitive cell is exactly one-third of the volume of the hexagonal cell.

The packing fraction f, is defined as the ration of the volume occupied by the atoms present in a unit cell to the total volume of the unit cell. It is also referred as the packing factor or packing efficiency of the unit cell.

From primitive cell, $$f = \frac{2\,(\frac{4}{3}\pi r^3)}{a\,(a \sin 60°)\,c}$$

Where r is the atomic radius.

Using c = 1.633a and a = 2r, r = a/2. Substitute the values in above equation we get,

$$f = 0.74$$

Thus in ideal hcp structure 74% of the total volume is occupied by atoms. Metals like Mg, Zn, Cd, Ti, etc, exhibit this type of structure.

(ii) Face-centred cubic (fcc) structure.

In this structure the stacking of first two layers A and B is similar to that of hcp structure. The difference arises in the third layer which, in the present case, does not overlap the first layer. The atoms of the third layer occupy the positions of those valleys of the A layer which are not occupied by the B layer atoms. The third layer is designated by the letter C, the fourth layer exactly overlaps the first layer and the sequence is repeated

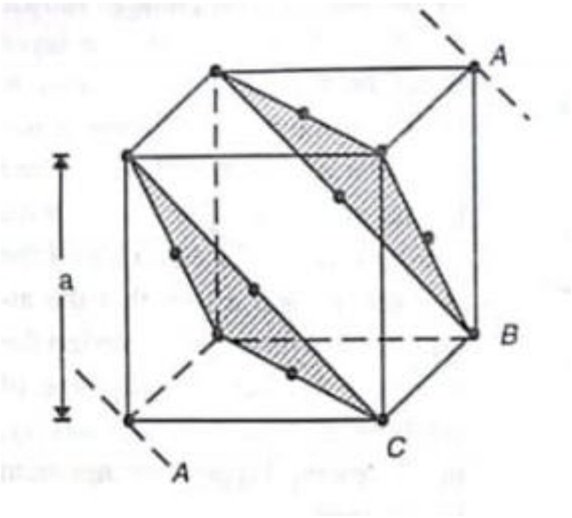


Figure 1.5 Conventional unit cell of fcc structure

.

Thus fcc structure is represented by the following stacking sequence:

………ABCABCABC……..

The conventional unit cell is face-centred cubic is shown in figure. It is a non-primitive cell having effective nuber of atoms equal to

$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$

The atoms touch one another along the face diagonals. The length of the cube edge a and atomic radius u are related to each other as

$$4\,r = \sqrt{2}\,a$$

The packing fraction f, is given by

$$f = \frac{4\left(\frac{4}{3}\pi\, r^3\right)}{a^3} = 0.74$$

Thus the packing fraction of fcc structure is exactly same as that of hcp structure which is expected because of close-packed nature of both the structures. Also, the coordination number of each atom is 12. Examples of materials having this type of structure are Cu, Ag, Au, Al, etc.

Loose-packed structure:

A loose-packed structure is that in which the coordination number of an atom is less than 12 or the packing fraction is less than 0.74. Among the various possible loose-packed structures, the most common and the simplest are,

(i) Body-centered cubic (bcc)
(ii) Simple cubic (sc)

(i) Body-centered cubic (bcc)

The conventional unit cell of bcc structure is non-primitive and is shown in figure. It has cubical shape with atoms located at the corners and the body centre.

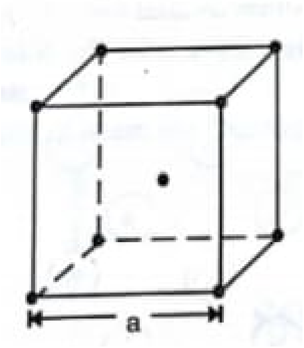


Figure 1.6 conventional unit cell of bcc structure

Thus the effective number of atoms per unit cell is

$$8\left(\frac{1}{8}\right) + 1 = 2$$

The coordination number of each atom is 8. The atoms touch one another along the body diagonal. Thus a is related to r as

$$4\,r = \sqrt{3}\,a$$

The packing fraction is given by

$$f = \frac{2(\frac{4}{3}\pi r^3)}{a^3} = 0.68$$

The examples of material exhibiting bcc structure are Na, K, Mo, W, etc.

(ii) Simple cubic (sc)

The conventional unit cell of sc structure is the same as its primitive cell and is shown in figure. The atoms are located at the corners only and touch one another along the cube edges.

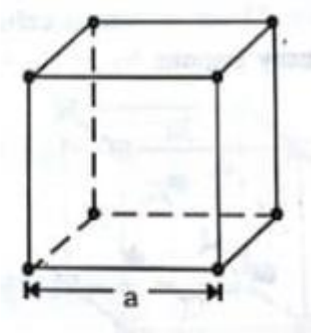


Figure 1.7 Unit cell of sc structure

Thus in sc structures, we have

$$a = 2r$$

the coordination number of each atom is 6. The packing fraction is given by

$$f = \frac{1(\frac{4}{3}\pi r^3)}{a^3} = 0.52$$

only polonium exhibits this type of structure at room temperature.

1.4 Crystal diffraction:

When an atomic electron is irradiated by a beam of monochromatic x-rays, it starts vibrating with a frequency equal to that of incident beam. Since an accelerating charge emits radiation, the vibrating electrons present inside a crystal become sources of secondary radiation having the same frequency as the incident x-rays.

These secondary x-rays spread out in all possible directions. The phenomenon may also be regarded as scattering of x-rays by atomic electrons. If the wavelength of incident radiation is quite large compared with the atomic dimensions, all the radiations emitted by electrons shall be in phase with one another.

The incident x-rays however, have the same order of wavelength as that of atomic dimensions; hence the radiations emitted by electrons are, in general, out of phase with one another.

These radiations may, therefore, undergo constructive or destructive interference producing maxima or minima in certain directions.

Consider a one-dimensional row of similar atoms having interatomic spacing equal to a. let a wave front of x-rays of wavelength λ be incident on the row of atoms such that the wave crests are parallel to the row.

The atoms emit secondary wavelets which travel in all possible directions. As shown in figure. The reinforcement of secondary wavelets takes place not only in a direction perpendicular to the row of atoms but also in other direction.

The zeroth, first and second order diffraction directions are shown in figure. It may be noted that reinforcement takes place in some particular directions only, whereas in other directions the wave fronts interfere destructively and the intensity is minimum. Such reinforcements produce Laue's pattern.

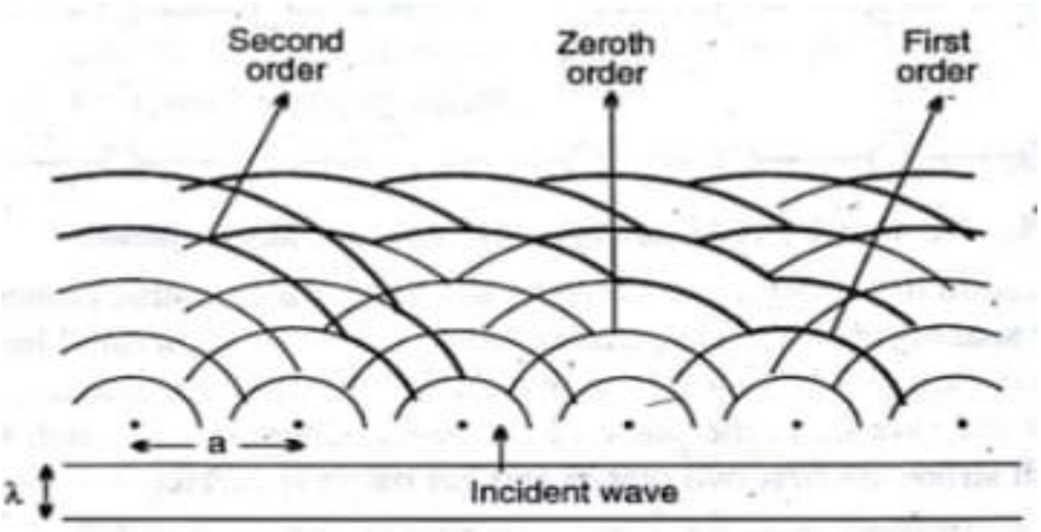


Figure 1.8 Reinforcement of scattered waves result in in diffracted beams of different orders.

In actual crystals, the problem is more complicated because of the presence of three-dimensional arrangement of atoms. The condition for a crystal to diffract x-rays can be determined by using either Bragg's treatment or Von Laue's treatment.

1.5 Bragg's law:

In 1912, W.H. Bragg and W.L. Bragg put forward a model which generates the conditions for diffraction in a very simple way. They pointed that a crystal may be divided into various sets of parallel planes.

The directions of diffraction lines can then be accounted for if x-rays are considered to be reflected by such a set of parallel atomic planes followed by the constructive interference of the resulting reflected rays.

Thus the problem of diffraction of x-rays by the atoms was converted into the problem of reflection of x-rays by the parallel atomic planes.

Bragg's derived a simple mathematical relationship which served as a condition for the Bragg reflection to occur. This condition is known as the Bragg's law.

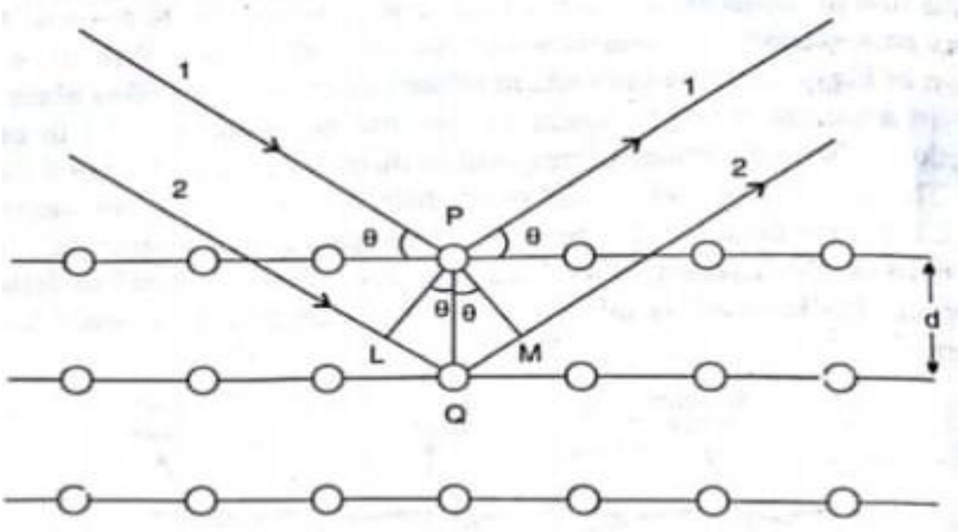


Figure 1.9 Bragg's reflection of x-rays from the atomic planes

To obtain the Bragg's law, consider a set of parallel atomic planes with interplanar spacing d and having Miller indices (hkl). Let a parallel bean of x-rays of wavelength λ be incident on these parallel planes at a glancing angle θ such that the rays lie in the planes of the paper.

Consider two such rays 1 and 2 which strike the first two planes and get partially reflected at the same angle θ in accordance with Bragg's treatment.

The diffraction is the consequence of constructive interference of these reflected rays. Let PL and PM be the perpendiculars drawn from the point P on the incident and reflected portions of ray 2 respectively.

The path difference between rays 1 and 2 is, therefore, given by (LQ + QM). Since

$$LQ = QM = d \sin \theta$$

$$\text{Path difference} = 2\, d \sin \theta$$

Where n is an integer. This equation is called the Bragg's law.

The diffraction lines appearing for n = 1, 2 and 3 are called first, second and third order diffraction lines respectively and so on.

The intensity of the reflected lines decreases with increase in the value of n or θ.

Reciprocal Lattice sc:

The primitive translation vectors of a simple cubic lattice may be written as

$$a = a\,\hat{\imath}\,,\ b = a\,\hat{\jmath},\ c = a\,\hat{k}$$

Volume of the simple cubic unit cell = a . b × c

$$= a^3\,(\,\hat{\imath}\,.\,\hat{\jmath}\ \times\ \hat{k})$$

$$= a^3$$

The reciprocal lattice vectors to the sc lattice are obtained as

$$a^* = 2\,\pi\,\frac{b\times c}{a\,.\,b\times c} = 2\,\pi\,\frac{a\,\hat{\imath}\ \times\ a\,\hat{k}}{a^3} = \frac{2\,\pi}{a}\,\hat{\imath}$$

similarly,

$$b^* = 2\,\pi\,\frac{c\times a}{a\,.\,b\times c} = \frac{2\,\pi}{a}\,\hat{\jmath}$$

$$a^* = 2\,\pi\,\frac{b\times c}{a\,.\,b\times c} = \frac{2\,\pi}{a}\,\hat{k}$$

The above equations indicates that all the three reciprocal lattice vectors are equal in magnitude which means that the reciprocal lattice to sc lattice is also simple cubic but with lattice constant equal to $\frac{2\pi}{a}$.

1.6 Reciprocal Lattice bcc:

The primitive translation vectors of a body-centred cubic lattice is shown in Fig.1.10

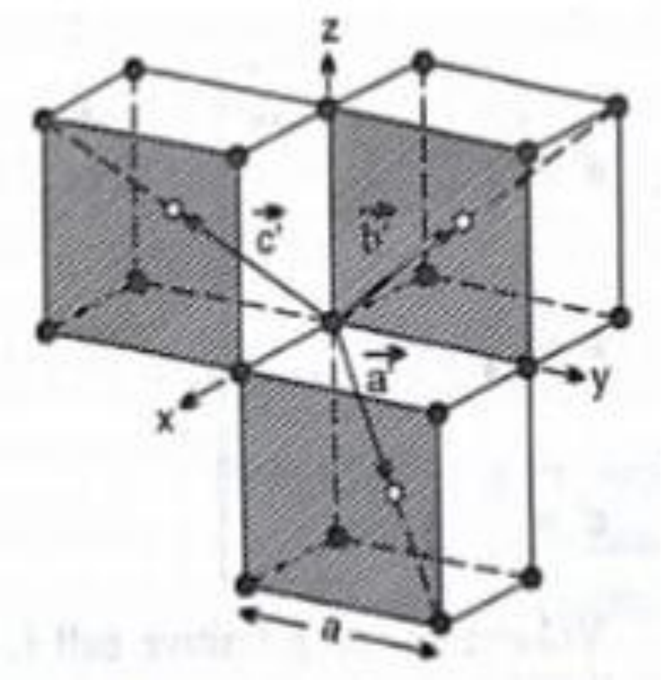


Figure 1.10 Primitive translation vectors of a bcc lattice

$$a' = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k})$$

$$b' = \frac{a}{2}(-\hat{i} + \hat{j} + \hat{k})$$

$$c' = \frac{a}{2}(\hat{i} - \hat{j} + \hat{k})$$

Where a is the length of the cube edge and $\hat{i}$, $\hat{j}$ *and* $\hat{k}$ are the orthogonal unit vectors along the cube edges. The volume of the primitive cell is given by

$$V = a' \cdot b' \times c'$$

$$= \frac{a}{2}(\hat{i} + \hat{j} - \hat{k}) \cdot \left[\frac{a^2}{4}(-\hat{i} + \hat{j} + \hat{k}) \times \left(\hat{i} - \hat{j} + \hat{k}\right)\right]$$

$$= \frac{a^3}{2}$$

The reciprocal lattice vectors are obtained as

$$a^* = 2\pi \frac{b' \times c'}{a' \cdot b' \times c'} = \frac{2\pi\,(\frac{a^2}{2})}{\frac{a^3}{2}}(\hat{\imath} + \hat{\jmath}) = \frac{2\pi}{a}(\hat{\imath} + \hat{\jmath})$$

similarly,

$$b^* = 2\pi \frac{c' \times a'}{a' \cdot b' \times c'} = \frac{2\pi\,(\frac{a^2}{2})}{\frac{a^3}{2}}(\hat{\jmath} + \hat{k}) = \frac{2\pi}{a}(\hat{\jmath} + \hat{k})$$

$$c^* = 2\pi \frac{a' \times b'}{a' \cdot b' \times c'} = \frac{2\pi\,(\frac{a^2}{2})}{\frac{a^3}{2}}(\hat{k} + \hat{\imath}) = \frac{2\pi}{a}(\hat{k} + \hat{\imath})$$

These are the primitive translation vectors of an fcc lattice. Thus the reciprocal lattice to bcc lattice is fcc lattice.

1.7 Reciprocal Lattice fcc:

The primitive translation vectors of an fcc lattice, as shown in figure.

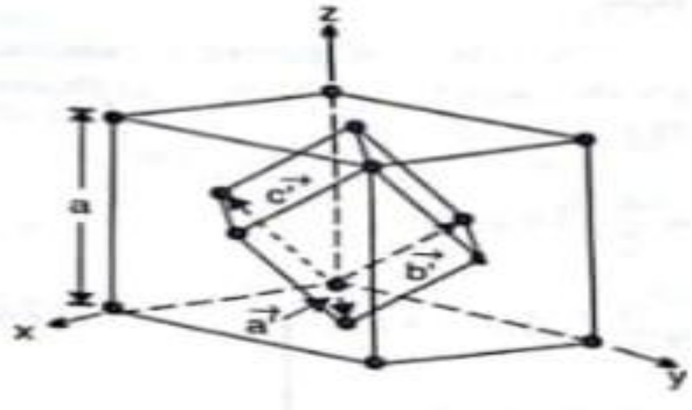


Figure 1.11 Primitive translation vectors of an fcc lattice

$$a' = \frac{a}{2}(\hat{\imath} + \hat{\jmath})$$

$$b' = \frac{a}{2}(\hat{\jmath} + \hat{k})$$

$$c' = \frac{a}{2}(\hat{k} + \hat{\imath})$$

Volume of the primitive cell is given by

$$V = a' \,.\, b' \times c'$$

$$= \frac{a}{2}(\hat{\imath} + \hat{\jmath}) \,.\, \left[\frac{a^2}{4}(\hat{\jmath} + \hat{k}) \times \left(\hat{k} + \hat{\imath}\right)\right]$$

$$= \frac{a}{2}(\hat{\imath} + \hat{\jmath}) \,.\, \frac{a^2}{4}(\hat{\imath} + \hat{\jmath} - \hat{k})$$

$$= \frac{a^3}{4}$$

The primitive translation vectors of the reciprocal lattice are obtained as

$$a^* = 2\pi \frac{b' \times c'}{a' \,.\, b' \times c'} = \frac{(\frac{a^2}{4})}{\frac{a^3}{4}}(\hat{\imath} + \hat{\jmath} - \hat{k}) = \frac{2\pi}{a}(\hat{\imath} + \hat{\jmath} - \hat{k})$$

$$b^* = 2\pi \frac{c' \times a'}{a' \,.\, b' \times c'} = \frac{(\frac{a^2}{4})}{\frac{a^3}{4}}(-\hat{\imath} + \hat{\jmath} + \hat{k}) = \frac{2\pi}{a}(-\hat{\imath} + \hat{\jmath} + \hat{k})$$

$$c^* = 2\pi \frac{a' \times b'}{a' \,.\, b' \times c'} = \frac{(\frac{a^2}{4})}{\frac{a^3}{4}}(\hat{\imath} - \hat{\jmath} + \hat{k}) = \frac{2\pi}{a}(\hat{\imath} - \hat{\jmath} + \hat{k})$$

The reciprocal lattice of a fcc lattice is a bcc lattice.

1.8 Structure and properties of liquid crystals:

When cooled, most liquids undergo a simple phase transition to an ordered crystalline solid, a relatively rigid substance that has a fixed shape and volume.

In the phase diagrams for these liquids, there are no regions between the liquid and solid phases. Thousands of substances are known, however, that exhibit one or more phases intermediate between the liquid state, in which the molecules are free to tumble and move past one another, and the solid state, in which the molecules or ions are rigidly locked into place.

In these intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid. Hence they are called ***liquid crystals***, and their unusual properties have found a wide range of commercial applications. They are used, for example, in the liquid crystal displays (LCDs) in digital watches, calculators, and computer and video displays.

The first documented example of a liquid crystal was reported by the Austrian Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholesteryl benzoate, and noticed that it behaved strangely as it melted.

The white solid first formed a cloudy white liquid phase at 145°C, which reproducibly transformed into a clear liquid at 179°C. The transitions were completely reversible: cooling molten cholesteryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C.

In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as isotropic, which means that it is equally disordered in all directions.

Liquid crystals, in contrast, are anisotropic: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.

1.9 Laue equations:

Laue treated the phenomenon of diffraction in a more general way by considering the scattering of x-rays from individual atoms in the crystal followed by their recombination to obtain the direction of diffraction maxima.

Diffraction maxima appear in some specific directions which obey certain conditions known as the Laue's equation.

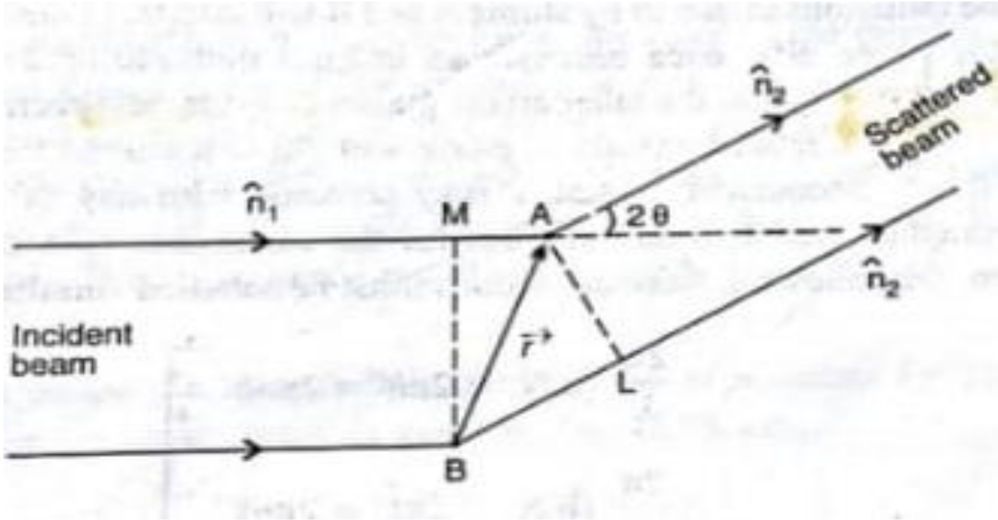


Figure 1.12 Scattering of x-rays from two identical scattering centres separated by a distance r

Consider the scattering of an incident beam from two identical scattering centres A and B placed at a distance r from each other in a crystal as shown in figure.

Let $\widehat{n_1}$ and $\widehat{n_2}$ be the unit vectors in the directions of the incident and scattered beam respectively and let the angle $\widehat{n_1}$ and $\widehat{n_2}$ be 2 θ.

Draw BM and AL perpendiculars to the directions of the incident and scattered beams respectively.

The path difference between the rays scattered from A and B is given by

$$\text{Path difference} = AM - BL$$

$$= r.\widehat{n_1} - r\,.\,\widehat{n_2} = r\,(\,\widehat{n_1}\,.\,\widehat{n_2}) = r\,.\,N \qquad \text{-------(1)}$$

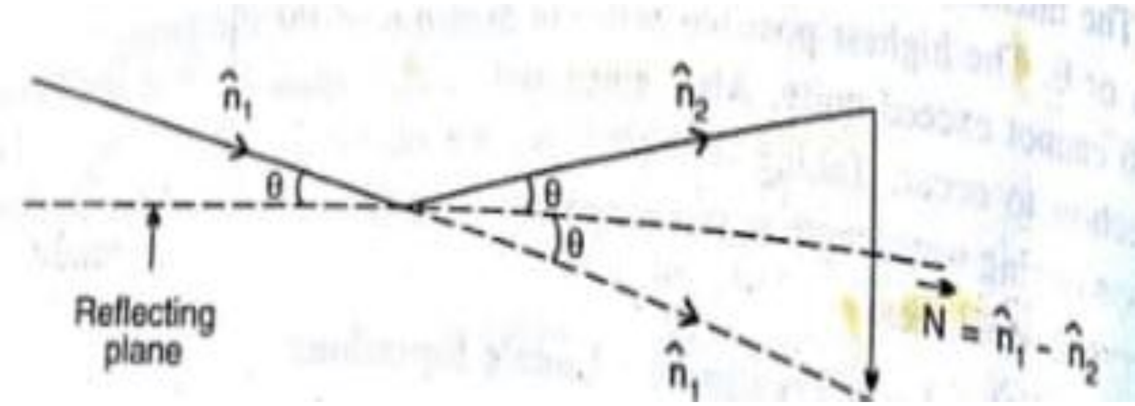


Figure 1.13 Geometrical relationship of incident beam. scattered beam, reflecting plane and the normal

The phase difference between the rays scattered from A and B is

$$\varphi = \frac{2\pi}{\lambda}(\mathrm{r} . \mathrm{N}) \qquad \text{--------(2)}$$

The radiation scattered by atoms A and B will interfere constructively only if the phase difference become an integral multiple of 2π. Due to periodicity of the crystal, the other atoms placed in the same direction would also scatter the radiations exactly in phase with those scattered from A and B.

In three-dimensional crystal, r may coincide with any of the three crystallographic axes a, b and c. thus for the occurrence of a diffraction maximum, the following three conditions must be satisfied simultaneously:

$$\frac{2\pi}{\lambda}(\mathrm{a} . \mathrm{N}) = 2\pi h' = 2\pi \mathrm{n\,h}$$

$$\frac{2\pi}{\lambda}(\mathrm{b} . \mathrm{N}) = 2\pi k' = 2\pi \mathrm{n\,k}$$

$$\frac{2\pi}{\lambda}(\mathrm{c} . \mathrm{N}) = 2\pi l' = 2\pi \mathrm{n\,l} \qquad \text{------(3)}$$

Where h', k' and l' represent any three integers.

Let α, β and γ be the angles between the scattering normal N and the crystallographic axes a, b and c respectively.

$$\mathrm{a} . \mathrm{N} = \mathrm{a\,N} \cos \alpha$$

$$= 2\,\mathrm{a} \sin\theta \cos\alpha$$

Equation (3) become

$$\mathrm{a} . \mathrm{N} = 2\,\mathrm{a} \sin\theta \cos\alpha = h'\lambda = \mathrm{n\,h}\,\lambda$$

$$\mathrm{b} . \mathrm{N} = 2\,\mathrm{a} \sin\theta \cos\beta = k'\lambda = \mathrm{n\,k}\,\lambda$$

$$\mathrm{c} . \mathrm{N} = 2\,\mathrm{a} \sin\theta \cos\gamma = l'\lambda = \mathrm{n\,h}\,l \qquad \text{-----------(4)}$$

the above equation known as Lau’s equation.

1.10 Diffraction Conditions:

In an orthogonal coordinate system, α, β and γ also satisfy the condition

$$cos^2\alpha + \ cos^2\beta + \ cos^2\gamma = 1 \qquad \text{--------(5)}$$

Where cos , cos β and cos γ represent the direction of cosine of the scattering normal.

Equation(4) and (5) yield the values of α, β , γ and θ for which diffraction takes place provided h, k, l and n are known. Thus, for a given reflecting plane, equation (4) serve to determine unique values of θ and N which define a scattering direction.

To obtain Bragg's law consider the expression for the interplanar spacing for the (hkl) planes is given by

$$d = \frac{a}{h}\cos\alpha = \frac{b}{k}\cos\beta = \frac{c}{l}\cos\gamma$$

in combination with equation (4), these yield

$$2\ d \sin\theta = n\ \lambda$$

Which is Bragg's law. Here n represents the order of reflection is the greatest common factor among the integers h', k' and l' in equation (4). Thus one may have the planes (hkl) and consider different orders of reflection from these; alternatively, one may have the plane (nh, nk nl) and always consider the first order reflection.

Thus putting n = 1, one can get rid of the factor n in the Bragg's equation provided the reflections from all the planes, real or imaginary, having Miller indices with or without a common factor be considered.

1.11 Brillouin zone:

The first **Brillouin zone** (named after Léon Brillouin) is a uniquely defined primitive cell in reciprocal space. In the same way the Bravais lattice is divided up into Wigner–Seitz cells in the real lattice, the reciprocal lattice is broken up into Brillouin zones. The boundaries of this cell are given by planes related to points on the reciprocal lattice. The importance of the Brillouin zone stems from the description of waves in a periodic medium given by Bloch's theorem, in which it is found that the solutions can be completely characterized by their behavior in a single Brillouin zone.

Structure factor:

The structure factor F_{hkl} is a mathematical function describing the amplitude and phase of a wave diffracted from crystal lattice planes characterized by Miller indices *h*,*k*,*l*.

The structure factor may be expressed as

$$F_{hkl} = F_{hkl} \exp(\, i\alpha_{hkl}\,)$$

$$= \sum_j f_i \exp[\,2\,\pi\, i\,(\,hx_j + ky_j + lz_j\,)] \qquad \text{-----(1)}$$

$$= \sum_j f_i \cos[\,2\,\pi\, i\,(\,hx_j + ky_j + lz_j\,)] + i\,\sum_j f_i \sin[\,2\,\pi\, i\,(\,hx_j + kyj + lzj\,)] \qquad \text{----(2)}$$

$$= A_{hkl} + i\,B_{hkl} \qquad \text{--------(3)}$$

where the sum is over all atoms in the unit cell, x_j, y_j, z_j are the positional coordinates of the j^{th} atom, f_j is the scattering factor of the j^{th} atom, and α_{hkl} is the phase of the diffracted beam.

The intensity of a diffracted beam is directly related to the amplitude of the structure factor, but the phase must normally be deduced by indirect means. In structure determination, phases are estimated and an initial description of the positions and anisotropic displacements of the scattering atoms is deduced. From this initial model, structure factors are calculated and compared with those experimentally observed. Iterative refinement procedures attempt to minimize the difference between calculation and experiment, until a satisfactory fit has been obtained.

Consider Bragg's law for an array of atom scatterers in a primitive lattice with just one atom at each lattice point. An incident X-ray wave of wavelength λ diffracts strongly through an angle 2θ2θ where the perpendicular distance between two lattice planes d_{hkl} satisfies the relation

$$2\, d_{hkl} \sin\theta = n\lambda$$

It is seen that the path difference between waves diffracted from the two planes shown differs by just one wave cycle.

Now consider a second atom added to the unit cell. Each original atom is now accompanied by a companion atom of the new type, offset by a displacement vector $\mathbf{r}_1$. The incident X-ray beam will also diffract from these new scatterers (since they occupy planes parallel to those originally drawn). But now there is a phase difference φ_1 between the waves scattered from the first and the new sets of atoms.

The amplitudes of the waves are proportional to the atomic scattering factors f_0 and f_1. The phases differ by the angle φ_1 . The resultant vector represents the two-atom structure factor with amplitude F_{hkl}. Note that there is a net phase φ arising from the phase difference due to the offset in position between the two sets of diffracting atoms.

As in the case of two atoms, the resultant diffracted wave is obtained from the linear superposition of the wave vectors scattered from each different atom.

1.12 Atomic form factor:

A measure of the scattering power of an isolated atom (also known as the ***atomic form factor)***. The scattering factor depends on the scattering amplitude of an individual atom and also the Bragg angle of scattering. It depends on the type of radiation involved.

The scattering from a crystal of an X-ray beam results from the interaction between the electric component of the incident electromagnetic radiation and the electrons in the crystal. Tightly bound electrons scatter coherently (***Rayleigh scattering***); free electrons scatter incoherently (***Compton scattering***). The scattering process from atomic electrons in a crystal lattice has both coherent and incoherent components, and is described as Thomson scattering.

The scattering amplitude from a neutral atom depends on the number of electrons (\Z\ ) = the atomic number) and also on the Bragg angle θ destructive interference among waves scattered from the individual electrons reduces the intensity at other than zero scattering angle.

For θ = 0 the scattering amplitude is normally equal to Z. However, the scattering factor is modified by anomalous scattering if the incident wavelength is near an absorption edge of the scattering element.

The X-ray scattering factor is evaluated as the Fourier transform of the electron density distribution of an atom or ion, which is calculated from theoretical wavefunctions for free atoms.

1.13 Inert gas crystals:

- Inert gases, also known as noble gases, are elements in the periodic table that do not readily react with other element.
- These gases include helium, neon, argon, krypton, xenon and radon
- At low temperature and high pressures, inert gases can for crystalline structures.
- These crystals are non-molecular and do not exhibit the typical characteristic of covalent or ionic bonding.
- The bonding in inert gas crystals is known as metallic bonding and is characterized by delocalized electron cloud shared among the atoms in the crystal.
- the strength of the metallic bond in inert gas crystals decreases with increasing atomic size. As a result, the melting and boiling points of these crystals also decrease with increasing atomic size.

1.14 Cohesive energy of ionic crystals:

There exist two types of interaction in ionic crystals, one is long range Coulomb’s electrostatic interaction which may be attractive or repulsive in nature, and the other is short range repulsive interaction which comes into play when the interionic distance becomes so small that the electronic clous of ions start overlapping.

The Coulomb's electrostatic interaction energy between two ions with charges $\pm q$ is given by $\pm \frac{q^2}{r}$ where the positive sign stands for electrostatic repulsive energy, i.e., the energy of ions with like charges and the negative sign stands for attractive energy.

Since each ion in an ionic crystal is surrounded by a large number of ions of the similar or opposite type, the total interaction energy or cohesive energy of i^th^ ion is given by,

$$U_i = \sum_j U_{ij} \qquad \text{--------(1)}$$

Where U_{ij} is the interaction energy between i^{th} and j^{th} ions and may be written as

$$U_{ij} = \lambda \exp\left(\frac{-r_{ij}}{\rho}\right) \pm \frac{q^2}{r} \qquad \text{--------(2)}$$

The constants ρ and λ can be empirically determined from the observed values of lattice constant and compressibility.

In an ionic crystal like NaCl, the value of U_i does not depend on the type of the reference ion i particularly when it is not present near the surface of the crystal.. the surface effects are ignored here.

If the crystal contains N molecules, i.e., N positive ions and N negative ions, the total lattice energy of the total binding energy of the lattice becomes

$$U_{tot} = N\, U_i \qquad \text{-------(3)}$$

For convenience, we introduce a dimensionless quantity p_{ij} such that

$$r_{ij} = p_{ij} R \qquad \text{--------(4)}$$

R is the nearest neighbor separation in the crystal. The factor p_{ij} thus defines the distance between any two ions in terms of the nearest neighbor distance.

If ions I and ja are the nearest neighbours, then

$$r_{ij} = R$$

$$p_{ij} = 1$$

from equation(2) and (4) we get

$$U_{ij} = \lambda \exp\left(\frac{-p_{ij} R}{\rho}\right) \pm \frac{q^2}{p_{ij} R}$$

Equation(1) becomes

$$U_i = \sum_j \exp\left(\frac{-p_{ij} R}{\rho}\right) \pm \frac{q^2}{p_{ij} R}$$

Assuming the repulsive interaction(first term) is effective for the nearest neighbours only and there are x nearest neighbours f ith ion, the expression (4) for the cohesive energy of the ith ion takes the form

$$U_{ij} = z\ \lambda \exp\left(\frac{-R}{\rho}\right) \pm \sum_j \frac{q^2}{p_{ij}\,R}$$

$$= z\ \lambda \exp\left(\frac{-R}{\rho}\right) - \frac{\alpha\, q^2}{R} \qquad \text{------(5)}$$

Equation (3) become

$$U_{tot} = N\, U_i$$

$$= N\left(z\ \lambda \exp\left(\frac{-R}{\rho}\right) - \frac{\alpha\, q^2}{R}\right) \qquad \text{-------(6)}$$

Here α is a constant called the Madelung constant and is given by

$$\alpha = \sum_j \mp \frac{1}{p_{ij}} \qquad \text{------(7)}$$

The choice of sign depends upon the type of the reference ions. If the reference ion is negative, the positive sign is used for a positive ion and the negative sign for a negative ion.

Thus the value of Medelung constant depends on the lattice structure.

At the nearest neighbour equilibrium distance R_0 we have

$$\frac{dU_{tot}}{dR} = 0$$

Therefore equation (5) becomes

$$N\,\frac{dU_i}{dR} = \frac{-N\, z\, \lambda}{\rho}\, e^{\frac{-R_0}{\rho}} + \frac{N\, \alpha\, q^2}{{R_0}^2} = 0$$

Or $$e^{\frac{-R_0}{\rho}} = \frac{\rho\, \alpha\, q^2}{z\, \lambda\, {R_0}^2} \qquad \text{------(8)}$$

The equation (3) written as

$$U_{tot} = N\left(z\, \lambda\, \frac{\rho\, \alpha\, q^2}{z\, \lambda\, {R_0}^2} - \frac{\alpha\, q^2}{R_0}\right)$$

$$= -\left(\frac{N\, \alpha\, q^2}{R_0}\right)\left[1 - \frac{\rho}{R_0}\right] \qquad \text{----(9)}$$

The first term within parentheses resemble the second term of equation (6). It represent the electrostatic interaction energy or the Madelung energy.

The similar expression for cohesive energy of ith ion is

$$U_i = \frac{U_{tot}}{N}$$

$$= -\left(\frac{\alpha\, q^2}{R_0}\right)\left[1 - \frac{\rho}{R_0}\right] \qquad \text{-------(10)}$$

For the range $\rho \sim 0.1\ R_0$, U_i is dominated by the Madelung contribution. It increases rapidly for low values of $\frac{\rho}{R_0}$ which indicates that the repulsive interaction has very short range.

1.15 Evaluation of the Madelung constant:

Considering the simplest case of a one-dimensional crystal consisting of alternate positive and negative ions with interionic distance R as shown in fig.1.14 The Madelung constant is represent as

$$\alpha = \sum_j \mp \frac{1}{p_{ij}}$$

$$= 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \ldots\right] \qquad \text{--------(11)}$$

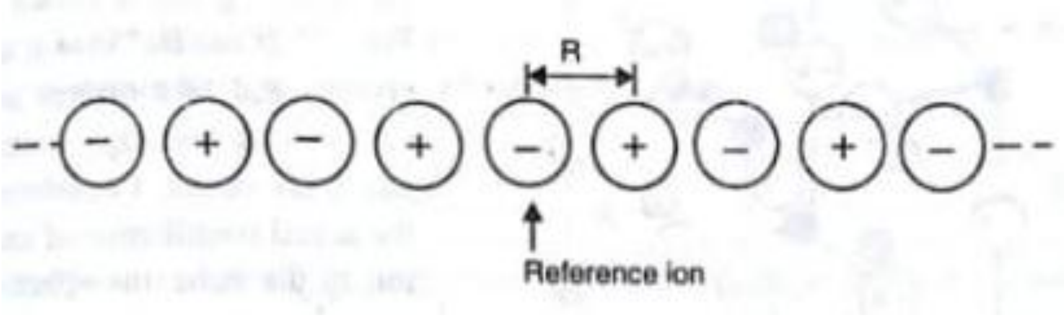


Figure 1.14 One-dimensional crystal consisting of alternate positive and negative ions with interionic distance R

This expression is written taking a negative ion as the reference ion. The factor of 2 appears because similar ions are present on both sides of the reference ion.

Using the series expansion,

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

and putting x = 1 in it, we get

$$\ln(2) = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots$$

equation (11) become

$$\alpha = 2\ \ln(2) = 1.38 \qquad \text{----- (12)}$$

For the actual three-dimensional crystals, the evaluation of the Madelung constant is not so simple. It is very difficult to write the successive terms by a casual inspection and the seirs converges quite slowly.

Consider for a example the unit cell of NaCl structure as shown in Fig 1.15. Each Cl^- ion has 6 nearest neighbour Na^+ ions, and so on. Since the distance of the first, second, third, fourth, etc. nearest neighbours from the central Cl^- ion is 1, $\sqrt{2}$, $\sqrt{3}, \sqrt{4}$, etc. respectively, the Madelung constant becomes

$$\alpha = \frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} \ldots\ldots$$

$$= 6.00 - 8.485 + 4.619 - 3.000 + 10.733 - \ldots\ldots$$

Clearly, the convergence of the series is poor. In fact, the series may never converge quickly unless the terms are so arranged that the contributions from the successive positive and negative terms nearly cancel.

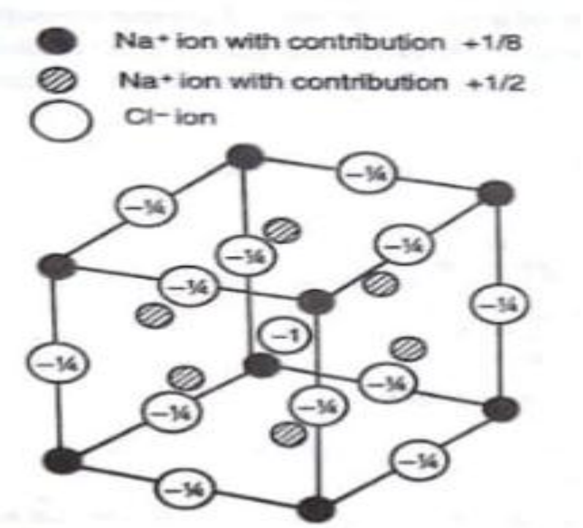


Figure 2.15 Unit cell of NaCl structure

One such cubical neutral group is shown in figure. It has Na^+ ions at the corners and face centres and Cl^- ions at the edge centres and body centre. Considering the actual contribution of each ion to be the cube, the effective charge carried by this group of ions is

$$-1\left(\frac{1}{2}\right)6 - 12\left(\frac{1}{4}\right) + 8\left(\frac{1}{8}\right) = 0$$

Taking Cl^- ions present at the body-centred position as the reference ion, the contribution of this neutral group to α is

$$\frac{\left(\frac{6}{2}\right)}{\sqrt{1}} - \frac{\left(\frac{12}{4}\right)}{\sqrt{2}} + \frac{\left(\frac{8}{8}\right)}{\sqrt{3}} = 1.46$$

The first term corresponds to the contribution of 6 nearest Na^+ ions occupying the face centres, the second term corresponds to the contribution of 12 next nearest neighbour Cl^- ions, and so on.

Similarly, taking into account the ions of the next larger cube surrounding the first cube, the value of α is calculated from the first two cubes comes out to be 1.75 which is close to the accurate value as given below. The values of the Madelung constant for CsCl and ZnS strucures are also given.

NaCl	;	1.747565
CsCl	;	1.762675
ZnS	;	1.6381

In general the higher values of the Madelung constant indicate the stronger Madelung contribution to the cohesive energy and hence greater stability of the structure.

1.16 Types of crystal binding (general ideas)

- A chemical bond is a lasting attraction between atoms, ions or molecules that enables the formation of chemical compounds.
- The bond may result from the electrostatic force of attraction between oppositely charged ions as in ionic bonds or through the sharing of electrons as in covalent bonds. The strength of chemical bonds varies considerably; there are "strong bonds" or "primary bonds" and "weak bonds" or "secondary bonds" such as Vander waals and Hydrogen bond.

The three primary bonds

- Covalent Bonds (Sharing of electrons)
- Metallic Bonds (free nature of valence electrons)
- Ionic Bonds (Transfer of electrons)

The two secondary bonds are

- Hydrogen
- Vander Waals Bond or Molecular bond

Ionic bonding

- An ionic bonding is the attractive force existing in between a positive ion and a negative ion.
- These ions are formed when the atoms of different elements involved in loss or gain of electrons in order to stabilize their outer shell electron configuration.
- Electro positive elements readily give up electrons and are usually group I or II elements.
- Eg. Na, K and Ba
- Electro negative elements readily take up electrons and are typically group VI or VII elements

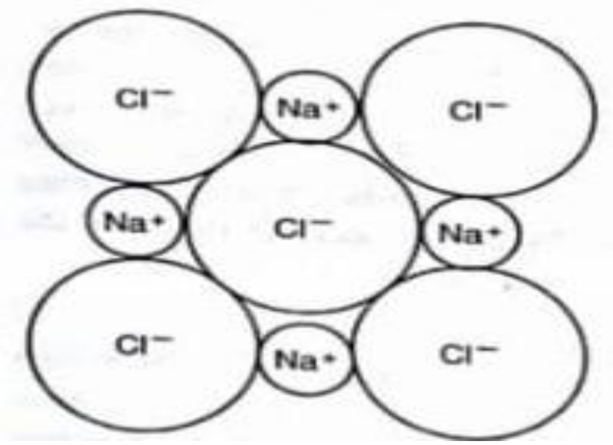


Figure 1.16 Ionic bonding

Let us consider a molecule of NaCl . When neutral atoms of Na and Cl are brought close together the outer valence electron of Na gets transformed to the chlorine atom to acquire a stable electronic configuration. Eg. NaCl, KCl, KBr etc.,

Properties of Ionic solids:

- ❖ Ionic solids are crystalline in nature
- ❖ They are hard and brittle
- ❖ They have high melting and boiling point
- ❖ Solids are good insulator of electricity
- ❖ They are soluble in polar solvents and insoluble in non polar solvents.

Covalent Bonding

- In covalent bonding the stable arrangement of electrons in an outer shell is achieved by a process of sharing of valence electrons rather than electron transfer and usually takes place in non metal elements.
- Such sharing results lowering of potential energy of the system

When two atoms are involved in the bond formation process and they share a single pair of electrons and they are known as single covalent bond.

- When two atoms are involved in the bond formation process and they share two or three pair of electrons results in double or triple bond.

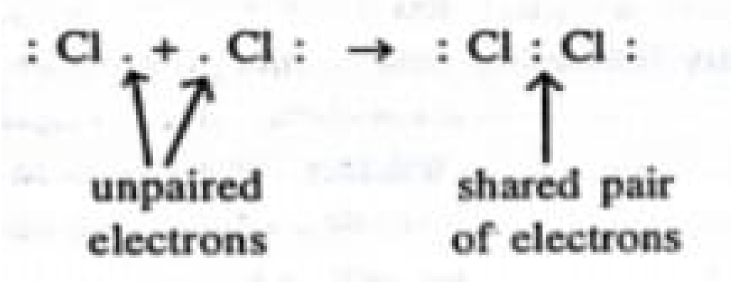


Figure 1.17 Covalent bonding

- A Covalent bond is formed not only due to overlap of either pure 's' orbital or 'p' orbital, but also due to overlap of 's' and 'p' orbital. such bonding is called hybrid bonding. Eg. Cl_2, H_2O, HCl, Carbon, NH_3

Properties of Covalent bond

- Covalent bonds are directional
- Covalent solids are hard and brittle ; crystalline in nature
- When compared to ionic solids they have low melting and boiling point. 9
- Pure covalent solids are insulators
- It will become semiconductor upon doping.

METALLIC BONDING

- The valence electrons from all the atoms belong to the crystal are free to move throughout the crystal.
- The crystal may consider as on array of positive metal ions embedded in a cloud or sea of free electrons. This type of bonding is called metallic bonding.
- Eg. Cu, Ag, Al etc.,

Formation of metallic bond:

In metallic bonds, the valence electrons from the s and p orbitals of the interacting metal atoms delocalize. That is to say, instead of orbiting their respective metal atoms, they form a “sea” of electrons that surrounds the positively charged atomic nuclei of the interacting metal ions. Metallic bonding is a type of chemical bonding that rises from the electrostatic attractive force between conduction electrons (in the form of an electron cloud of delocalized electrons) and positively charged metal ions

.

Properties of metallic bond / metallic solids

- The metallic bond is weaker than the ionic and the covalent bonds.
- Non directional
- Metals are good conductors of electricity when solid, or liquid. The de localized electrons are able to move under an electric field.
- Metals are good conductors of heat. The delocalized electrons disperse heat more quickly.

- Metals are malleable and ductile, not brittle. The cations are able to slide past each other and still retain their attraction to the electron sea.
- Metallic solids are not soluble in polar and non polar solvents

Hydrogen Bonding

- In a molecule, when a hydrogen atom is linked to a highly electronegative atom, it attracts the shared pair of electrons more and so this end of the molecules becomes slightly negative while the other end becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called the hydrogen bond.
- Hydrogen bonding is a special class of attractive intermolecular forces that arise due to the dipole-dipole interaction between a hydrogen atom that is bonded to a highly electronegative atom and another highly electronegative atom while lies in the vicinity of the hydrogen atom. For example, in water molecules (H2O), hydrogen is covalently bonded to the more electronegative oxygen atom. Therefore, hydrogen bonding arises in water molecules due to the dipole-dipole interactions between the hydrogen atom of one water molecule and the oxygen atom of another H2O molecule.

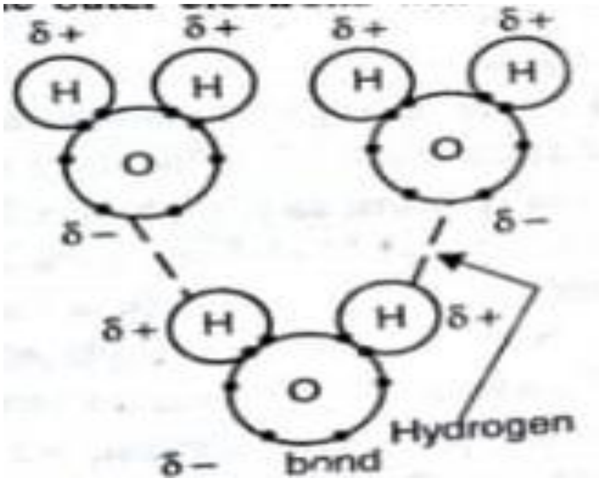


Figure 1.17 Hydrogen bonding

Here, the location of the bond pair of electrons in the O-H bond is very close to the oxygen nucleus (due to the large difference in the electronegativities of oxygen and hydrogen). Therefore, the oxygen atom develops a partial negative charge (-δ) and the hydrogen atom develops a partial positive charge (+δ). Now, hydrogen bonding can occur due to the electrostatic attraction between the hydrogen atom of one water molecule (with +δ charge) and the oxygen atom of another water molecule (with -δ charge). Thus, hydrogen bonds are a very special class of intermolecular attractive forces that arise only in compounds featuring hydrogen atoms bonded to a highly electronegative atom. Hydrogen bonds are mostly strong in comparison to normal dipole-dipole and dispersion forces. However, they are weak compared to true covalent or ionic bonds.

The conditions for hydrogen bonding are:

1. The molecule must contain a highly electronegative atom linked to the hydrogen atom. The higher the electronegativity more is the polarization of the molecule.

2. The size of the electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction. eg. HF, H_2O and carboxylic acid etc.,

Properties of Hydrogen Bonding

- Solubility: Lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecule.
- Volatility: As the compounds involving hydrogen bonding between different molecules have a higher boiling point, so they are less volatile.
- Viscosity and surface tension: The substances which contain hydrogen bonding exists as an associated molecule. So their flow becomes comparatively difficult. They have higher viscosity and high surface tension.
- The lower density of ice than water: In the case of solid ice, the hydrogen bonding gives rise to a cage-like structure of water molecules. As a matter of fact, each water molecule is linked tetrahedral to four water molecules. The molecules are not as closely packed as they are in a liquid state. When ice melts, this case like structure collapses and the molecules come closer to

each other. Thus for the same mass of water, the volume decreases and density increases. Therefore, ice has a lower density than water at 273 K. That is why ice floats.

Van Der Waals Bonding

Secondary bonds are weak in comparison to primary bonds. They are found in most materials, but their effects are often overshadowed by the strength of the primary bonding. Secondary bonds are not bonds with a valence electron being shared or donated. They are usually formed when an uneven charge distribution occurs, creating what is known as a dipole (the total charge is zero, but there is slightly more positive or negative charge on one end of the atom than on the other). These dipoles can be produced by a random fluctuation of the electrons around what is normally an electrically symmetric field in the atom. Once a random dipole is formed in one atom, an induced dipole is formed in the adjacent atom. This is the type of bonding present in N2 molecules, and is known as Van Der Waals Bonding.

Secondary bonding may also exist when there is a permanent dipole in a molecule due to an asymmetrical arrangement of positive and negative regions. Molecules with a permanent dipole can either induce a dipole in adjacent electrically symmetric molecules, and thus form a weak bond, or they can form bonds with other permanent dipole molecules.

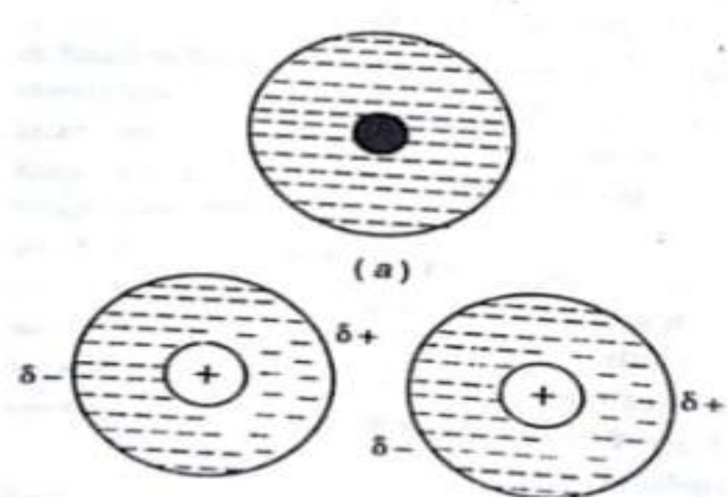


Figure 1.18 Van Der Waals Bonding

Properties:

- The main characteristics of van der Waals forces are: They are weaker than normal covalent and ionic bonds.
- Van der Waals forces are additive and cannot be saturated.
- They have no directional characteristic.

UNIT II

LATTICE DYNAMICS

Lattice with two atoms per primitive cell - First Brillouin zone - Group and phase velocities - Quantization of lattice vibrations - Phonon momentum - Inelastic scattering by phonons - Debye's theory of lattice heat capacity - Thermal Conductivity - Umkalapp processes.

2.1 Lattice with two atoms per primitive cell

When the lattice is at equilibrium each atom is positioned exactly at its lattice site. Now suppose that an atom displaced from its equilibrium site by a small amount. Due to force acting on this atom, it will tend to return to its equilibrium position. This results in lattice vibrations. Due to interactions between atoms, various atoms move simultaneously, so we have to consider the motion of the entire lattice

Consider a one-dimensional crystal lattice and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions.

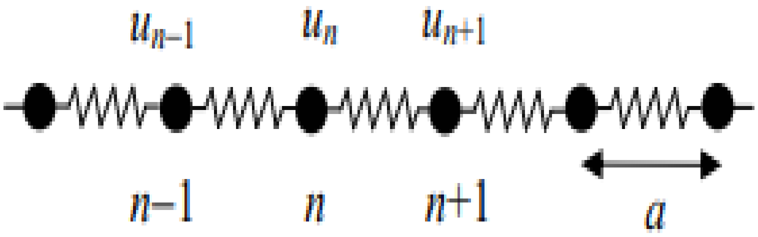


Figure 2.1 One-dimensional crystal lattice

This is known as the harmonic approximation, which holds well provided that the displacements are small. One might think about the atoms in the lattice as interconnected by elastic springs. Therefore, the force exerted on n-the atom in the lattice is given by

$$F_n = C\ (\ u_{n+1} - u_n\ ) + (\ u_{n-1} - u_n\ ) \qquad \text{-------(1)}$$

where C is the interatomic force (elastic) constant. Applying Newton's second law to the motion of the n^{th} atom we obtain

$$M\frac{d^2u_n}{dt^2} = F_n = C\,(u_{n+1} - u_n) + (u_{n-1} - u_n)$$

$$= -C\,(2u_n - u_{n+1} - u_{n-1}) \qquad \text{-------(2)}$$

where M is the mass of the atom. Note that we neglected here by the interaction of the n-th atom with all but its nearest neighbors. A similar equation should be written for each atom in the lattice, resulting in N coupled differential equations, which should be solved simultaneously (N is the total number of atoms in the lattice).

In addition the boundary conditions applied to the end atom in the lattice should be taken into account.

Now let us attempt a solution of the form

$$u_n = A\,e^{i(\,q\,x_n - a\,x)} \qquad \text{------(3)}$$

where x_n is the equilibrium position of the n-th atom so that x_n=na. This equation represents a traveling wave, in which all the atoms oscillate with the same frequency ω and the same amplitude A and have wavevector q.

Note that a solution of the form (3) is only possible because of the transnational symmetry of the lattice.

Now substituting Eq.(3) into Eq.(2) and canceling the common quantities (the amplitude and the time-dependent factor) we obtain

$$M\,(-\omega^2)\,e^{iqna} = -C\,[\,2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}] \qquad \text{-------(4)}$$

This equation can be further simplified by canceling the common factor e^{iqna} , which leads to

$$M\ \omega^2 = C\,(\,2e^{iqa} - e\text{-}^{iqa}\,)$$

$$= 2C\,(1 - \cos qa)$$

$$= 4C\,sin^2\frac{qa}{2} \qquad \text{---------(5)}$$

We find therefore the dispersion relation for the frequency

$$\omega = \sqrt{\frac{4C}{M}\sin\frac{qa}{2}} \qquad \text{--------(6)}$$

which is the relationship between the frequency of vibrations and the wavevector q. This dispersion relation has a number of important properties.

(i) ***Reducing to the first Brillouin zone***.

The frequency (6) and the displacement of the atoms (3) do not change when we change q by q + 2π/a.

This means that these solutions are physically identical. This allows us to set the range of independent values of q within the first Brillouin zone, i.e.

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a} \qquad \text{-------(7)}$$

Within this range of q the ω versus q is shown in Fig. 2.2

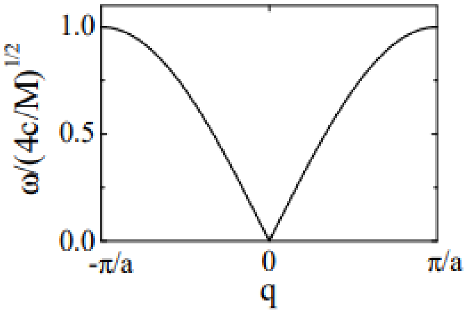


Figure .2.2 ω versus q

The maximum frequency is $\sqrt{\frac{4C}{M}}$. The frequency is symmetric with respect to the sign change in q, i.e. ω (q) = ω (-q).

This is not surprising because a mode with positive q corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative q corresponds to the wave traveling from the right to the left.

Since these two directions are equivalent in the lattice the frequency does not change with the sign change in q.

At the boundaries of the Brillouin zone q = ±π/a the solution represents a standing wave ($u_n = A(-1)^n e^{-iwt}$):

atoms oscillate in the opposite phases depending on whether n is even or odd. The wave moves neither right nor left

(ii)***Phase and group velocity***.

The phase velocity is defined by

$$V_P = \frac{\omega}{q} \qquad \text{-------(8)}$$

and the group velocity by

$$V_g = \frac{d\omega}{dq} \qquad \text{-------(9)}$$

The physical distinction between the two velocities is that v_p is the velocity of the propagation of the plane wave, whereas the vg is the velocity of the propagation of the wave packet. The latter is the velocity for the propagation of energy in the medium. For the particular dispersion relation (6) the group velocity is given by

$$V_g = \sqrt{\frac{C\,a^2}{M}} \cos\frac{qa}{2} \qquad \text{-----(10)}$$

As is seen from Eq.(10) the group velocity is zero at the edge of the zone where $q = \pm\pi/a$. Here the wave is standing and therefore the transmission velocity for the energy is zero.

(iii) Long wavelength limit.

The long wavelength limit implies that $\lambda >> a$. In this limit $qa << 1$

$$\omega = \sqrt{\frac{C}{M}}\, q\, a \qquad \text{---(11)}$$

We see that the frequency of vibration is proportional to the wavevector. This is equivalent to the statement that velocity is independent of frequency. In this case

$$V_P = \frac{\omega}{q}$$

$$= \sqrt{\frac{C}{M}}\; a \qquad \text{------(12)}$$

This is the velocity of sound for the one dimensional lattice which is consistent with the expression we obtained earlier for elastic waves.

2.2 First Brillouin zone

The first Brillouin zone is defined as the Wigner–Seitz primitive cell of the reciprocal lattice. Thus, it is the set of points in the reciprocal space that is closer to $K = 0$ than to any other reciprocal lattice point. It shown in Figure that the Bragg planes bisect the lines joining 0 (the origin) to the reciprocal lattice points. Thus, we can also define the first Brillouin zone as the set of points that can be reached from 0 without crossing any Bragg planes. Here, the points common to the surface of two or more zones have not been considered.

The region in *k*-space (here an imaginary plane whose rectangular coordinates are k_x and k_y) that low-k electrons can occupy without being diffracted is called first Brillouin Zone, shown in Figure. The second Brillouin zone is also shown; it contains electrons with kk values from π/aπ/a to 2π/a 2π/a for electrons moving in the ±x and ±y directions, with the possible range of *k* values narrowing as the diagonal directions are approached.

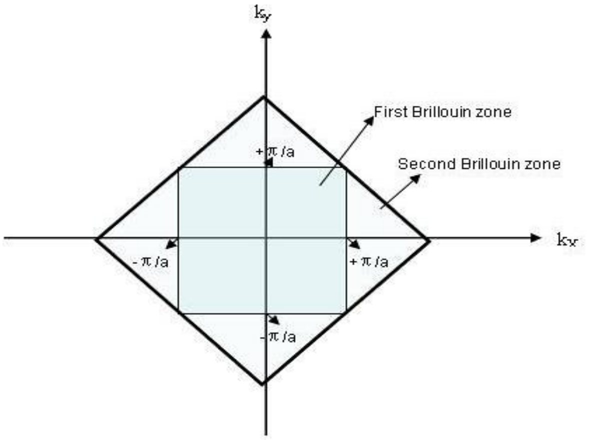


***Figure 2.3* Brillouin zone**

2.3 Phonons

The energy of electromagnetic wave is quantized and this quantum of energy is called a photon. Similarly, the energy of a lattice vibration or an elastic wave is also quantized and a quantum of this energy is known as phonon.

All types of lattice vibrations in crystals comprise phonons-thermal vibrations are thermally excited phonons, sound waves are acoustical phonons and excitations of the optical branch generate optical phonons.

Most of the concepts which apply to photons are also valid for phonons. For example, the concept of wave particle duality holds good for phonons. Also, the energy of a phonon is given by $\hbar\omega$, where ω is the angular frequency of a mode of vibration.

If n is the number of phonons in a particular mode of vibration, the total energy that mode is written as

$$\varepsilon = \mathrm{n}\,\hbar \qquad \text{-------(1)}$$

where n can be zero or a positive integer.

Since the number of phonons may change with temperature, the average number of phonons in a vibrational mode is given by

$$\bar{n} = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} \qquad \text{-------(2)}$$

Where K_B is the Boltzman's constant and T is the absolute temperature of the crystal.

2.4 Momentum of phonons

Physically lattice phonon does not carry any momentum, but it interacts with other particles and fields as if it has a momentum $\hbar K$, where K represent the wave vector of the phonon. Aso from the de Broglie relation

$$\mathrm{P} = \frac{h}{\lambda} = \hbar K \qquad \text{-----(3)}$$

It is apparent that a phonon of wavelength λ carries a momentum $\hbar K.$ The quantity $\hbar K$ is sometimes called the crystal momentum. The physical significance of $\hbar K$ is provided by the momentum conservation law in crystals.

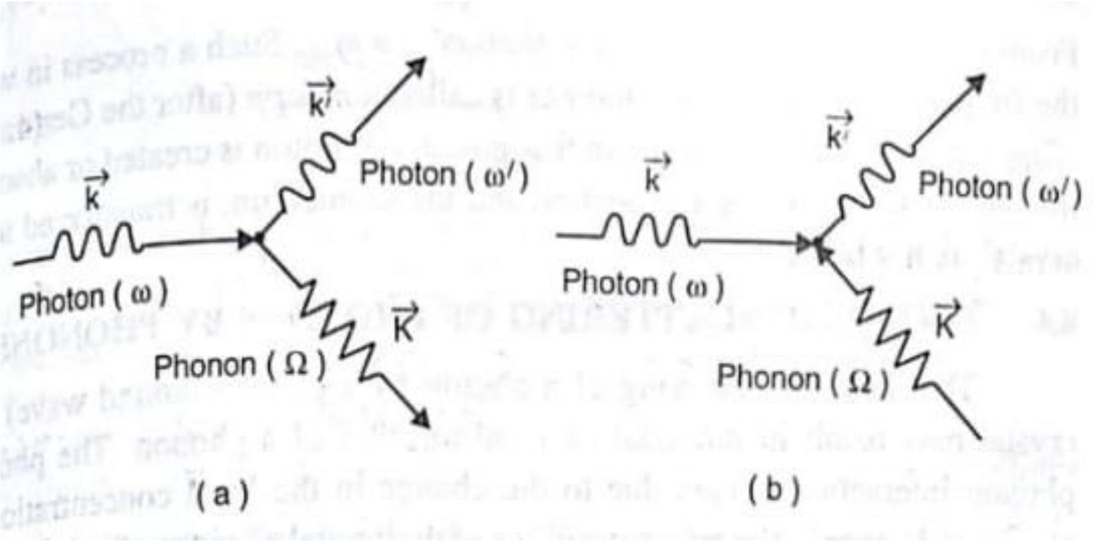


Figure 2.4 inelastic scattering of incident photon of wave vector k to produce scattered photon of wave vectork' along with the emission(a) or absorption(b) of a phonon of wave vector K.

The wave vector conservation law for elastic scattering or the Bragg's diffraction of X-ray photons from crystals is given by

$$K' = k + G \qquad \text{---------(4)}$$

Where k' and k represent the wave vectors for the scattered and incident photons respectively and G is the reciprocal lattice vector. The conservation of momentum and energy yields

$$\hbar K' = \hbar\, k + \hbar\, G \qquad \text{---------(5)}$$

and

$$\hbar\omega_{ph} = \hbar\, \omega'_{ph} \qquad \text{----------(6)}$$

ω_{ph} and ω'_{ph} are the frequencies of incident and scattered photons respectively.

In this process the crystal as a whole recoils with a momentum - $\hbar$ G and the frequency of the incident photons remains unchanged. Such the process in which the frequency of the incident photon is the same as that of the scattered photon is called normal or N – process.

Consider now the case of inelastic scattering of the photon which proceeds with the emission of a phonon of wave vector K as shown in figure. The wave vector conservation law then takes the form

$$k' + K = k + G \qquad \text{-----------(7)}$$

accordingly, the momentum and energy conservation laws can be written as

$$\hbar k' + \hbar K = \hbar k + \hbar G \qquad \text{-----------(8)}$$

$$\hbar\,\omega'_{ph} + \hbar\,\omega = \hbar\,\omega_{ph} \qquad \text{---------(9)}$$

where ω is the frequency of the phonon generated. In case a phonon is absorbed in the scattering process, as shown in figure(b), the wave vector conservation law gives

$$k' = k + K + G \qquad \text{--------(10)}$$

and the momentum and energy conservation laws become

$$\hbar K' = \hbar K + \hbar k + \hbar G \qquad \text{-----------(11)}$$

and

$$\hbar\,\omega'_{ph} = \hbar\,\omega_{ph} + \hbar\,\omega \qquad \text{--------(12)}$$

equations (9) and (12) we find that

$$\omega'_{ph} \neq \omega_{ph}$$

Such a process in which the frequency of the photon changes is called ***umcalap or U – process***. In this process a photon is created or absorbed in addition to the Bragg's reflection and the momentum transferred to the crystal as a whole.

2.5 Inelastic scattering by phonons.

The inelastic scattering of a photon by a phonon (sound wave) in a crystal may result in the creation or absorption of a phonon. The photon-phonon interaction occurs due to the change in the local concentration of atoms, and hence in the refractive index of the crystal.

Conversely, the electric field of the light wave induces mechanical vibrations in the medium and hence affects its elastic properties.

Consider a photon of frequency $\nu = \frac{\omega_{ph}}{2\pi}$ and wave vector k propagating through a crystal which is viewed as a continuum of refractive index n. then we have

$$\omega_{ph} = \frac{ck}{n}$$

$$\lambda\,\nu = \frac{c}{n} \qquad \text{----------(13)}$$

Where c is the velocity of light.

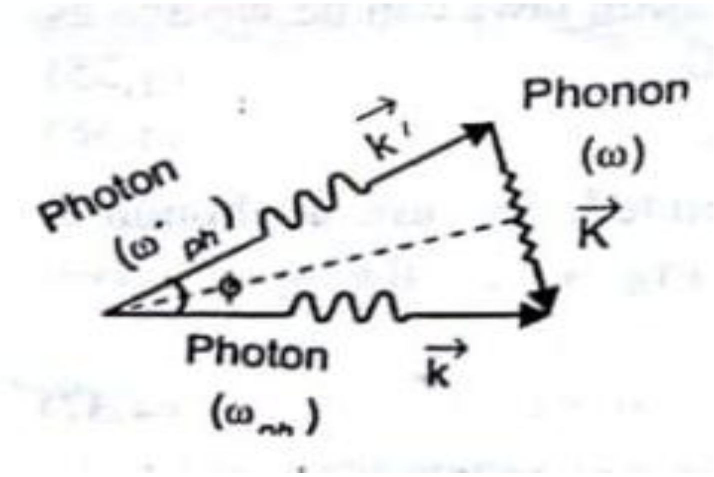


Figure 2.5 Selection rule diagram for the emission of phonon when k = k'

Let this photon interact with a phonon. As a result of this interaction, the wave vector and frequency of the photon change to k' to ν' respectively. If a phonon of wave vector K and angular frequency ω is created in this process. The conservation of energy and momentum gives,

$$\hbar\,\omega_{ph} = \hbar\,\omega'_{ph} + \hbar\,\omega \qquad \text{--------(14)}$$

$$\hbar\,k = \hbar\,k' + \hbar\,K \qquad \text{--------(15)}$$

Equation (15) has been written without taking into account the phenomenon of Bragg's diffraction along with that of scattering. Taking v_s as the velocity of sound(phonon) and assuming it to be constant, we can write

$$\omega = v_s\,k \qquad \text{-------------(16)}$$

The wavelength of the emitted phonon is comparable to the wavelength of the incident photon whereas its energy is only a small fraction of the incident photon energy. From equation (13) and (16) we find that $v_s \ll c$ or $\omega_{ph} \gg \omega$.

It therefore follows from equation (14) and (15) that

$$\omega_{ph} \approx \omega'_{ph}$$

And

$$K \approx k'$$

The wave vectors k,k' and K are related to each other as shown in figure. From the figure k = k' the triangle becomes isosceles and we have

$$K = 2\,k \sin\frac{\varphi}{2} \qquad \text{---------(17)}$$

Where φ is the angle between k and k'. thus a phonon is produced when a photon is scattered inelastically at an angle $\frac{\varphi}{2}$ from the direction of incidence.

The frequency of the phonon is given by

$$\omega = v_s\,k$$

$$= 2\,v_s\,k \quad \sin\frac{\varphi}{2}$$

$$= 2\,\frac{v_s\,n\,\omega_{ph}}{c}\sin\frac{\varphi}{2} \qquad \text{-----(18)}$$

The phonons have been generated in quartz and sapphire in the microwave frequency rang by scattering the visible light produced from an intense laser source.

The observed shift in frequency of the photon agrees well with the shift calculated form equation (18) using the value of the velocity of sound determined by ultrasonic methods at low frequencies.

2.6 Debye's theory of lattice heat capacity:

The vibrational motion of the crystal as a whole was considered to be the same as the vibrational motion of a single atom and therefore all the atomic vibrations of the crystal were assigned a common frequency ω_0 which is the natural frequency of vibration of a single atom.

Debye proposed that crystals can propagate elastic waves of wavelengths ranging from low frequencies to high frequencies corresponding to infrared absorption.

This means that the crystal can have a number of modes of vibration. The number of vibrational modes per unit frequency ranges is called density of modes, Z(v).

Now determine the density of vibrational modes of crystal treating it as a continuous medium.

2.7 Density of modes

Consider a one-dimensional continuous string of length L. let is vibrate in a longitudinal mode with both ends fixed. Let x be the position of a line element and u (x,t) its displacement from the mean position at any time t. therefore, the amount of strain e, is given by

$$\text{e} = \frac{du}{dx}$$

If this strain is produced by a force F and Y is the young's modulus of the string, then for a unit cross-section, we can write,

$$\frac{F}{e} = Y$$

Now consider an element of length Δx. If the strain at one of its ends in e(x), then its value at the other end is

$$\text{E (x)} + \frac{\partial e}{\partial x}\Delta x = \text{e (x)} + \frac{\partial^2 u}{\partial x^2}\Delta x$$

the force at the two end of the string is

$$\text{e (x) Y and [e(x)} + \frac{\partial^2 u}{\partial x^2}\Delta x\text{] Y}$$

therefore, the net force on the element is

$$[\ \frac{\partial^2 u}{\partial x^2}\ ]\ \Delta x\ \ \text{Y}$$

The force on the line element Δx can also be written as

$$\rho\ \ \Delta x\ [\ \frac{\partial^2 u}{\partial x^2}\ ]$$

Where ρ is the density of the string. Therefore, we have

$$[\ \frac{\partial^2 u}{\partial x^2}\ ]\ \Delta x\ \ \text{Y}\ = \ \rho\ \ \Delta x\ [\ \frac{\partial^2 u}{\partial x^2}\ ]$$

$$\frac{\partial^2 u}{\partial x^2} = \frac{\rho}{\gamma}\frac{\partial^2 u}{\partial t^2}$$

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{{v_s}^2}\frac{\partial^2 u}{\partial t^2} \qquad \text{-------(1)}$$

Where ${v_s}^2 = \frac{Y}{\rho}$ represent the velocity propagation of the wave along the string.

It is independent of frequency. The equation (1) is the known one-dimensional wave equation. Since the string is fixed at both the ends, the solution of equation (1) should correspond to standing waves. These type of solution are given by

u(x,t) = A sin ($\frac{n\pi}{L}$ x) cos 2 π v_2 t ---------(2)

where n is the positive integer. Using equation (2) in (1) we get

$$\lambda_n = \frac{2L}{n}$$

$$v_n = \frac{v_s}{\lambda_n} = \frac{n\, v_s}{2L} \qquad \text{--------(3)}$$

$$v_1 = \frac{v_s}{2L}\, , v_2 = \frac{v_s}{L}\, . v_3 = \frac{3v_s}{2L}\, , etc \qquad \text{-------(4)}$$

This shows that the frequency of the string can have discrete values only. From equation (3) we have

$$\text{n} = \frac{2L}{v_s} v_n$$

$$\text{dn} = \frac{2L}{v_s}\,\text{dv} \qquad \text{---------(5)}$$

this gives the number of possible modes of vibration in the frequency interval dv.

Considering the three-dimensional case the wave equation (1) can be written as,

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{{v_s}^2}\frac{\partial^2 u}{\partial t^2} \qquad \text{-------(6)}$$

The standing wave solution of the wave equation (2)

u(x, y, z, t) = A sin ($\frac{n_x\pi}{L}$ x) sin ($\frac{n_y\pi}{L}$ x) sin ($\frac{n_z\pi}{L}$ x) cos 2 π v t ---------(7)

where $n_x n_{y,} n_z$ are positive integers.

Substituting this solution into equation (6) and simplifying we get,

$$\frac{\pi^2}{L^2}\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right) = \frac{4\,\pi^2\,\nu^2}{v_s{}^2} \qquad \text{-------- ---(8)}$$

$$n_x{}^2 + n_y{}^2 + n_z{}^2 = \frac{4\,L^2\,\nu^2}{v_s{}^2} \qquad \text{---------(9)}$$

This equation gives the possible modes of vibration.

The radius vector R of any point from the origin is given by

$$R^2 = n_x{}^2 + n_y{}^2 + n_z{}^2 = \frac{4\,L^2\,\nu^2}{v_s{}^2} \qquad \text{---------(10)}$$

This is the equation of a sphere of volume

$$V' = \frac{4}{3}\pi R^3$$

Differentiating it we get

$$dV' = 4\,\pi\,R^2\,dR$$

the number of modes present in the frequency range ν + d ν should be the same as number of points lying in the volume interval V' and V'+dV' or in the range R and R+dR of the radius vector.

Since each point occupies on an average, a unit volume in the space of integers, number of points present in the volume dV' of the spherical shell is numerically equal to the volume of the shell

$$dn = 4\,\pi\,R^2\,dR$$

the number of possible modes of vibration is

$$z(\nu)\,d\,\nu = \frac{1}{8}\left(4\,\pi\,R^2\,dR\right)$$

$$= \frac{1}{8}\,4\,\pi\;\frac{4\,L^2\,\nu^2}{v_s{}^2}\,\frac{2L}{v_s}\,d\,\nu\,)$$

$$= \frac{4\,\pi\,L^3\,\nu^2}{v_s{}^3}\,d\,\nu$$

$$= \left(\frac{4\,\pi\,V}{v_s{}^3}\right)\nu^2\,d\,\nu \qquad \text{---------(11)}$$

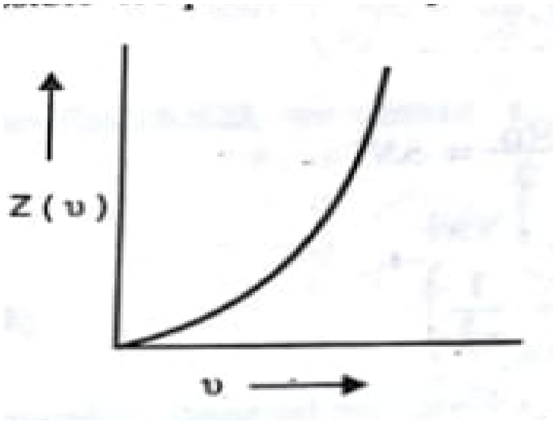


Figure 2.6 Frequency spectrum of a three-dimensional continuum

Where V = L^3 is the volume of the solid cube. For a perfect continuum, the possible frequencies vary between zero and infinity and the number of possible vibrational modes with square of the frequency as shown in figure.

In general, the elastic wave propagating in a solid are of two types- transverse waves and longitudinal waves. The velocity of propagation of transverse waves v_t in generally different from the velocity of propagating of longitudinal waves v_l.. also for each frequency or direction of propagation, the transverse waves have two vibrational modes perpendicular to the direction of propagation whereas the longitudinal waves have only one mode which lies along the direction of propagation.

For such a case, the total number if vibrational modes is expressed as

$$z(\nu)\, d\,\nu = 4\,\pi\, V\, \left(\frac{2}{{v_t}^3} + \frac{2}{{v_l}^3}\right) v^2\, dv \qquad \text{--------(12)}$$

2.8 The Debye approximation:

If the interatomic distance is small as compared to the wavelength of elastic waves, the crystal can be regarded as a continuum from the point of view of the wave. Based on this idea, Debye assumed that the continuum model is applicable to all possible vibrational modes of the crystal.

Further, the fact that the crystal consists of finite number (N) of atoms is taken into account by limiting the total number of vibrational modes to 3N. this puts an upper limit to the frequency of the elastic waves which can propagate through the crystal.

This highest frequency propagating through a crystal is called the Debye frequency v_D. it is common to transverse and longitudinal modes of vibrations.

Hence, the frequency spectrum of a continuous medium is cut off at the Debye frequency as shown in figure. For the total number of vibrational modes with frequencies ranging from zero to v_D, we can write

$$\int_0^{v_D} z(v)dv = 3N \qquad \text{---------(13)}$$

From equation(12) we obtain

$$\int_0^{v_D} 4\,\pi\,\mathrm{V}\left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right) v^2\,\mathrm{dv} = 3N$$

$$4\,\pi\,\mathrm{V}\left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right)\frac{{v_D}^3}{3} = 3\mathrm{N}$$

$${v_D}^3 = \frac{9N}{4\,\pi\,\mathrm{V}}\left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right)^{-1} \qquad \text{------(14)}$$

This equation can be used to determined v_D.

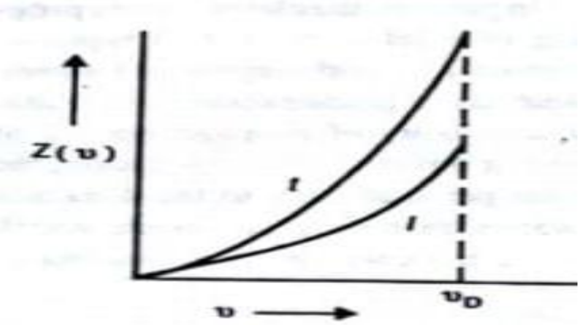


Figure 3.7 Frequency spectrum of transverse (t) and longitudinal (l) modes in continuum showing cut-off at the Debye frequency

The vibrational energy of a crystal is determined by using the Plank's theory. The average energy of an oscillator having frequency v at a temperature T is given by

$$\bar{\varepsilon} = \frac{hv}{e^{\frac{hv}{k_BT}} - 1} \qquad \text{------(15)}$$

We can associate a harmonic oscillator of the same frequency with each vibrational mode. Thus the vibrational energy of the crystal is given by

$$\mathrm{E} = \int_0^{v_D} \bar{\varepsilon}\; z(v)dv$$

Equation (12) and (15) we get

$$E = \int_0^{v_D} 4\ \pi V \left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right) \frac{hv^3}{e^{\frac{hv}{k_BT}} - 1}\, dv$$

$$= 4\ \pi V h \left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right) \int_0^{v_D} \frac{v^3}{e^{\frac{hv}{k_BT}} - 1}\, dv$$

From equation (14)

$$4\ \pi V \left(\frac{2}{{v_t}^3} + \frac{1}{{v_l}^3}\right) = \frac{9N}{{v_D}^3}$$

$$E = \frac{9Nh}{{v_D}^3} \int_0^{v_D} \frac{v^3}{e^{\frac{hv}{k_BT}} - 1}\, dv \qquad \text{--------(16)}$$

Putting $\frac{hv}{k_BT} = x$ and $\frac{hv_D}{k_BT} = x_m$ we get

$$v = \frac{x\, k_BT}{h}$$

$$dv = \frac{k_BT}{h}\, dx$$

Therefore equation (16) becomes

$$E = \frac{9Nh}{{v_D}^3} \left(\frac{k_BT}{h}\right)^4 \int_0^{x_m} \frac{x^3}{e^x - 1}\, dx$$

$$= 9N \left(\frac{k_BT}{h}\right)^3 \int_0^{x_m} \frac{x^3}{e^x - 1}\, dx$$

As in Einstein's theory, we introduce here a characteristic temperature, θ_D, called the debye temperature defined as

$$\theta_D = \frac{h\, v_D}{k_B} \qquad \text{-------(17)}$$

$$x_m = \frac{\theta_D}{T}$$

Equation (16) become,

$$E = 9\,N\,k_B T\,\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{e^x\ x^4}{(e^x - 1)^2}\,dx \qquad \text{---------(18)}$$

$$= 3\,R\,\left(\frac{\theta_D}{T}\right) F_D$$

The function F_D is called a Debye function and is expressed as

$$F_D = 3\,\left(\frac{T}{\theta_D}\right)^4 \int_0^{\frac{\theta_D}{T}} \frac{e^x\ x^4}{(e^x - 1)^2}\,dx \qquad \text{------(19)}$$

Consider the high and low temperature cases.

(i) High temperature case

For T $\gg \theta_D$, x is small compared with unity for the complete range of integration. Therefore, we can write,

$e^x - 1 \cong$ x

Equation (18) then become

$$E = 9\,N\,k_B T\,\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} x^2\,dx$$

$$= 3\,N\,k_B T \qquad \text{----------(20)}$$

$$C_v = \frac{\partial E}{\partial T}$$

$$= 3\,N\,k_B$$

$$= 3\,R$$

(ii) Low temperature case

For T $\ll \theta_D$, $x_m = \frac{\theta_D}{T} \rightarrow \infty$

Equation (17) become

$$E = 9\,N\,k_B T\,\left(\frac{T}{\theta_D}\right)^3 \int_0^{\infty} \frac{x^3}{(e^x - 1)^1}\,dx$$

$$\int_0^{\infty} \frac{x^3}{(e^x - 1)^1}\,dx = \frac{\pi^4}{15}$$

$$E = 9\,N\,k_BT\,\left(\frac{T}{\theta_D}\right)^3\frac{\pi^4}{15}$$

$$= \frac{3}{5}\pi^4\,N\,k_B\,\frac{T^4}{\theta^3{}_D} \qquad \text{---------(21)}$$

This is shows that the vibrational energy is proportional to T^4 which is analogous to the Stefen's law of black body radiation.

The expression for the specific heat is obtained as

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

$$= \frac{12}{5}\pi^4\,N\,k_B\,\left(\frac{T}{\theta_D}\right)^3$$

$$= \frac{12}{5}\pi^4\,R\,\left(\frac{T}{\theta_D}\right)^3$$

Thus, at very low temperatures, the specific heat is proportional to T^3. This is called Debye T^3 law.

UNIT III

THEORY OF METALS AND SEMICONDUCTORS

Free electron gas in three dimensions - Electronic heat capacity - Wiedemann- Franz law - Band theory of metals and semiconductors - Bloch theorem - Kronig-Penney model - Semiconductors - Intrinsic carrier concentration – Temperature Dependence - Mobility - Impurity conductivity – Impurity states - Hall effect - Fermi surfaces and construction - Experimental methods in Fermi surface studies - de Hass-van Alphe effect .

3.1 Free electron gas in three dimensions:

According to this model, the valence electrons of the constituent atoms of the crystal become conduction electrons and travel freely throughout the crystal. Therefore, within this model we neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons. In this sense we are talking about a ***free electron gas***. However, there is a principle difference between the free electron gas and ordinary gas of molecules.

The Schrödinger equation in the three dimensions takes the form

$$\mathrm{H}\,\Psi\,(\mathrm{r}) = \frac{p^2}{2\,m}\,\Psi\,(\mathrm{r})$$

$$= \frac{-\hbar^2}{2\,m}\,\nabla^2\,\Psi\,(\mathrm{r})$$

$$= \frac{-\hbar^2}{2\,m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi\,(\mathrm{r})$$

$$= \mathrm{E}\,\Psi\,(\mathrm{r}) \qquad \text{--------(1)}$$

The Schrödinger equation in the three dimensions takes the form

$$\Psi\,(\mathrm{r}) = \mathrm{A}\sin\left(\frac{\pi\,n_x}{L}\,x\right)\,\sin\left(\frac{\pi\,n_y}{L}\,y\right)\,\sin\left(\frac{\pi\,n_z}{L}\,z\right) \qquad \text{-------(2)}$$

where *nx*, *ny*, and *nz* are positive integers.

Assume that our crystal is infinite and disregard the influence of the outer boundaries of the crystal on the solution. We require then that our wavefunction is periodic in *x*, *y*, and *z* directions with period *L*, so that

$$\Psi\ (\mathrm{x} + \mathrm{L}, \mathrm{y}, \mathrm{z}) = \Psi\ (\mathrm{x}, \mathrm{y}, \mathrm{z}) \qquad \text{--------(3)}$$

and similarly for the *y* and *z* coordinates. The solution of the Schrödinger equation (1) which satisfies these boundary conditions has the form of the traveling plane wave:

$$\Psi_k(r) = A \exp(ik \,.\, r) \qquad \text{--------(4)}$$

provided that the component of the wavevector **k** are determined from

$$k_x = \frac{2\,\pi\, n_x}{L}$$

$$k_y = \frac{2\,\pi\, n_y}{L}$$

$$k_z = \frac{2\,\pi\, n_z}{L} \qquad \text{-------(5)}$$

where n_x, n_y, and n_z are positive or negative integers.

If we now substitute this solution to Eq.(1) we obtain for the energies of the orbital with the wavevector **k**

$$\mathrm{E_k} = \frac{\hbar^2\ k^2}{2\,m}$$

$$= \frac{\hbar^2}{2\,m}\ (\ k_x{}^2 + k_y{}^2 + k_z{}^2) \qquad \text{----- (6)}$$

The wavefunctions (4) are the eigenfunctions of the momentum **p** = - i $\hbar$ ∇, which can be easily seen by differentiating (4) :

$$\mathrm{p}\ \Psi_k(r) = -\,\mathrm{i}\,\hbar\,\nabla\,\Psi_k(r)$$

$$= \hbar\ \mathrm{k}\ \Psi_k(r) \qquad \text{------- (7)}$$

The eigenvalue of the momentum is $\hbar$ **k** . The velocity of the electron is defined by

$$\mathrm{V} = \frac{p}{m}$$

$$= \frac{\hbar\ \mathrm{k}}{m}$$

In the ground state a system of N electrons occupies states with lowest possible energies. Therefore all the occupied states lie inside the sphere of radius k_F. The energy at the surface of this sphere is the Fermi energy E_F. The magnitude of the wavevector k_F and the Fermi energy are related by the following equation:

$$E_F = \frac{\hbar^2 \, k_F{}^2}{2\,m} \qquad \text{-------(8)}$$

The Fermi energy and the Fermi wavevector (momentum) are determined by the number of valence electrons in the system. In order to find the relationship between N and k_F, we need to count the total number of orbitals in a sphere of radius k_F which should be equal to N.

There are two available spin states for a given set of kx, ky, and kz. The volume in the **k** space which is occupies by this state is equal to $(2p / L)^3$. Thus in the sphere of ($\frac{4\,\pi\,k_F{}^3}{3}$) the total number of states is

$$2\ \left(\frac{4\,\pi\,k_F{}^3/3}{(\,2\,\pi/L\,)^3}\right)$$

$$= \frac{V}{3\,\pi^2}\,k_F{}^3$$

$$= \text{N} \qquad \text{--------(9)}$$

where the factor 2 comes from the spin degeneracy. Then

$$K_F = \left(\frac{3\,\pi^2\,N}{V}\right)^{1/3} \qquad \text{------ (10)}$$

which depends only of the electron concentration. We obtain then for the Fermi energy:

$$E_F = \frac{\hbar^2}{2\,m}\ \left(\frac{3\,\pi^2\,N}{V}\right)^{2/3} \qquad \text{-------(11)}$$

and the Fermi velocity

$$V_F = \frac{\hbar}{m}\ \left(\frac{3\,\pi^2\,N}{V}\right)^{1/3} \qquad \text{------(12)}$$

The total number of orbitals of energy < E :

$$N\,(E) = \frac{V}{3\,\pi^2}\ \left(\ \frac{2\,m\,E}{\hbar^2}\ \right)^{3/2} \qquad \text{----------(13)}$$

The density of states is the

$$D\,(E) = \frac{dN}{dE}$$

$$= \frac{V}{2\,\pi^2}\ \left(\ \frac{2\,m}{\hbar^2}\ \right)^{3/2}\ \ E^{1/2} \qquad \text{------(14)}$$

or equivalently

$$D\,(E) = \frac{3N}{2E} \qquad \text{--------(15)}$$

So within a factor of the order of unity, the number of states per unit energy interval at the Fermi energy (E_F) , is the total number of conduction electrons divided by the Fermi energy, just we would expect.

The density of states normalized in such a way that the integral

$$N = \int_0^{E_F} D(E)dE \qquad \text{--------(16)}$$

gives the total number of electrons in the system. At non-zero temperature we should take into account the Fermi distribution function so that

$$N = \int_0^{E_F} D(E)\, f(E)\, dE \qquad \text{------(17)}$$

This expression also determines the chemical potential.

3.2 Wiedemann- Franz law:

Franz Law is one of the important laws in physics. This law was discovered and termed after the German physicists, Gustav Wiedemann and Rudolph Franz, in 1835. Gustav Wiedemann revealed that thermal Conductivity (κ) and electrical Conductivity (σ) are roughly having an identical value at the same temperature for dissimilar metals.

This empirical law is named after Gustav Wiedemann and Rudolph Franz, who, in 1853, described that κ / σ has about the identical value for dissimilar metals at the precise temperature. In 1872, the proportionality of κ / σ with temperature was revealed by Ludvig Lorenz.
In Wiedemann Franz law

k = Thermal Conductivity. It is a degree of measurement of a material to conduct heat.

σ = Electrical Conductivity is noted as a degree of measurement of a material to conduct electricity (1/ρ).

The law formulates that the proportion of the electronic contribution of the thermal conductivity (κ) to the electrical conductivity (σ) of metal is slightly similar to the temperature (T).

$$\frac{\mathrm{k}}{\sigma} = \mathrm{L\,T}$$

Here,

L = proportionality constant, and it is named as the Lorenz number.

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

- The connection in the middle of the thermal and electrical conductivity is centered on the point that heat and the electrical movement contain freely roaming electrons in the metal.
- The thermal conductivity raises the velocity of the average particle and also surges in the frontward energy movement. Alternatively, electrical conductivity reduces the velocity of the particle.
-

3.3 Band theory of metals and semiconductors :

The failure of the free electron model is due to the oversimplified assumption that a conduction electron in a metal experiences a constant or zero potential due to the ion cores and hence is free to move about in a crystal; the motion being restrained only by the surface of the crystal.

In fact, the potential due to ion core is not constant and may change with position of the electron in the crystal. Some contribution to potential may also arise because of the other electrons present in the crystal.

Thus the actual nature of potential under which an electron moves in a crystal is very complicated.

To a reasonable approximation, the ion cores may be considered at rest and the potential experienced by an electron in a crystal is assumed to be periodic with equal to the lattice constant as shown in figure. For a one-dimensional case.

This assumption is based on the fact that the ion cores in a crystal are distributed periodically on the lattice sites. The potential contribution due to all other free electrons may be taken as constant. This type of periodic potential extends up to infinity in all directions except at the surface of the crystal where, due to interruption in periodicity of the lattice. This type of potential irregularity may however be ignored.

The periodic potential described above forms the basis of the band theory of solids. The behaviour of an electron in this potential is described using one-electron approximation. In this approximation, the total wave function for the system is obtained from a combination of wave functions each one of which involves the coordinates of one electron.

In other words, the field experienced by a particular electron is assumed to be the resultant of the field due to fixed nuclei and the average field due to the charge distribution of all other electrons.

The motion of an electron in a periodic potential yields the following results:

(a) There exist allowed energy bands separated by forbidden regions or band gaps.

(b) The electronic energy function E(K) are periodic in the wave vector k.

These results are in contrast with those obtained from the free electron theory in the sense that, in the free electron theory, E varies with k as

$$E = \frac{\hbar^2 k^2}{2m}$$

There is no upper limit to the energy and k can have discrete values, which means that the energy levels are discrete and may have any spacing depending on the dimensions of the box.

The existence of band gaps is the most important new property which emerges when the free electron model is extended to include the effect of periodic potential of the ion cores.

It will shown that these band gaps result from the interaction of the conduction electron waves with ion cores of the crystal and are of decisive significance to determine whether a solid is a conductor, semiconductor or an insulator.

3.4 Bloch theorem :

In free electron theory, the one-dimensional Schrodinger equation for an electron moving in a constant potential V_0 is

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\Psi = 0 \qquad \text{-------(1)}$$

The solution to this equation are plane waves of the type

$$\Psi(x) = e^{\pm ikx} \qquad \text{--------(2)}$$

Where

$$(E - V_0) = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = E_{kin}$$

For an electron moving in a one-dimensional periodic potential V(x), the schrodinger equation is written as

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\Psi = 0 \qquad \text{-------(3)}$$

Since the potential is periodic with period equal to the lattice constant a, we have

$$V(x) = V(x + a)$$

There is an important theorem known as the Bloch theorem or the Floquet's theorem concerned with the solution to equation (3). According to this theorem, the solution to equation(3) are plane waves of the type of equation(2) which are modulated by a function $u_k(x)$ having the same periodicity as that of the lattice.

Thus the solution is of the form

$$\Psi(x) = e^{\pm ikx}\, u_k(x) \qquad \text{---------(4)}$$

With

$$u_k(x) = u_k(x + a) \qquad \text{---------(5)}$$

the wave function of the type of equation(4) are called Block functions.

3.5 Kronig-Penney model:

This model illustrates the behaviour of electrons in a periodic potential by assuming a relatively simple one-dimensional model of periodic potential as shown in figure.

The potential energy of an electron in a linear array of positive nuclei is assumed to have the form of a periodic array of square wells with period of (a+b). at the bottom of a well for 0 <x<a, the electron is assumed to be in the vicinity of a nucleus and the potential energy is taken as zero, whereas outside a well -b < x < 0, the potential energy is assumed to be V_0. Although this model employs a very crude approximation to the type of periodic potential existing inside a lattice, yet its is vey useful to illustrate various important features of the quantum behaviour of electron in the periodic lattice.

The wave functions are obtained by writing the Schrodinger equations for the two regions as

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} E \ \Psi = 0 \qquad \text{for } 0 < x < a \qquad \text{-------(1)}$$

and

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0) \Psi = 0 \qquad \text{for } -b < x < 0 \qquad \text{-------(2)}$$

Assuming the energy E of the electrons is less than V_0 we define two real quantities α and β as

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

$$\beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \qquad \text{--------(3)}$$

Therefore, equation(1) and (2) become

$$\frac{d^2\Psi}{dx^2} + \alpha^2 \ \Psi = 0 \qquad \text{for } 0 < x < a \qquad \text{-------(4)}$$

and

$$\frac{d^2\Psi}{dx^2} - \beta^2 \ \Psi = 0 \qquad \text{for } -b < x < 0 \qquad \text{-------(5)}$$

Since the potential is periodic, the wave functions must be of the form of block function.

$$\Psi(x) = e^{\pm ikx} u_k(x) \qquad \text{---------(6)}$$

Where $u_k(x)$ is the periodic function in x with periodicity of (a + b),i.e,

$$u_k(x) = u_k(x + a + b) \qquad \text{-------(7)}$$

from equation(6) we have

$$\frac{d\psi}{dx} = i\,k\,e^{ikx}\,u_k(x) + e^{ikx}\,\frac{du_k}{dx}$$

$$\frac{d^2\Psi}{dx^2} = -\,k^2\,e^{ikx}\,u_k(x) + 2\,i\,k\,e^{ikx}\,\frac{du_k}{dx} + e^{ikx}\,\frac{d^2u_k}{dx^2} \qquad \text{---------(8)}$$

Substituting equation(6 and (8) in equations(4) and (5) we get

$$\frac{d^2u_1}{dx^2} + 2\,i\,k\,\frac{du_1}{dx} + (\alpha^2 - k^2)\,u_1 = 0; \quad 0 < x < a \qquad \text{------(9)}$$

And

$$\frac{d^2u_2}{dx^2} + 2\,i\,k\,\frac{du_2}{dx} - (\beta^2 + k^2)\,u_2 = 0; \quad -b < x < 0 \qquad \text{------(10)}$$

The general solution of this equations are

$$u_1 = A\,e^{i(\alpha-k)x} + B\,e^{-i(\beta+k)x}; \qquad \text{-----(11)}$$

And

$$u_2 = C\,e^{(\beta-ik)x} + D\,e^{-(\beta+ik)x}; \qquad \text{------(12)}$$

Where A, B, C, D are constants.

On solving the determinant, we obtain

$$\frac{\beta^2+\alpha^2}{2\alpha\beta}\sin h\beta b\; sin\alpha a + cosh\beta b\,\cos\alpha a = cosk(a+b) \qquad \text{-----(13)}$$

To simplify this equation, Kronig and Penney considered the case when V_0 tends to infinity and b approaches zero but the produce V_0 b remains finite. i.e, the potential barriers become delta function.

As b→0, sinh $\beta b \rightarrow \beta b$ and $cosh\beta b \rightarrow 1$.

$$\frac{\beta^2 + \alpha^2}{2\alpha\beta} = \frac{mV_0}{\alpha\beta\hbar^2}$$

$$(\frac{mV_0b}{\alpha\beta\hbar^2})\sin\alpha a + \cos\alpha a = \cos ka$$

We defined the quantity P as

$$\frac{mV_0ba}{\hbar^2} = P$$

Thus increasing P has the physical meaning of binding an electron more strongly to a particular potential well.

$$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka.$$

3.6 Semiconductors:

Semiconductors are materials which have electrical conductivities lying between those of good conductor and insulators. The resistivity of semiconductors varies from 10^{-5} to 10^{+4}ohm-m compared to the values ranging from 10^{-8} to 10^{-6} ohm-m for conductors and from 10^{7} to 10^{8} ohm the ohm-m for insulators. 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 to 1.5 X 10^{3} ohm -m respectively.

3.7 Intrinsic carrier concentration :

The concentration of electrons and holes in a semiconductor can be obtained from the densities of available states in the valence band and the conduction band as well as Fermi-Dirac distribution function. The expression for the Fermi energy is obtained from these carrier concentrations.

3.7.1 Electron concentration in the conduction band:

The number of free electrons per unit volume in an energy range E and E + dE can be written as

$$dn = D(E)\ f(E)\ dE \qquad \text{------(1)}$$

where D(E) is the density of states defined as the total number of allowed electronic state per unit volume in a semiconductor and f(E) is the Fermi distribution function representing the probability of occupation of a state with energy E.

the expression for f(E) is given by

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{K\,T}\right) + 1} \qquad \text{-----(2)}$$

whereas that for D(E), which is strictly valid for free electrons,

$$D(E) = \frac{4\pi}{h^3}\,(2m)^{3/2}\,E^{1/2} \qquad \text{------(3)}$$

Using equation(3) in (1)

$$dn = \frac{4\pi}{h^3}\,(2m)^{3/2}\,E^{1/2}\,f(E)\,dE \qquad \text{------(4)}$$

it is apparent from figure, that an electron occupying an energy state E in the conduction band, in fact. Possesses the kinetic energy (E - E_C). therefore, in equation (3) must be replaced by (E - E_C).

thus equation (4) becomes

$$dn = \frac{4\pi}{h^3}\,(2m_n^*)^{3/2}\,(E - E_C)^{1/2}\,\frac{1}{\exp\left(\frac{E - E_F}{K\,T}\right) + 1}\,dE \qquad \text{------(5)}$$

where m_n^* is the effective mass of the electron in the conduction band.

The concentration of electrons n, in the conduction band is obtained by integrating equation (5) from E = E_C and E = ∞, i.e.,

$$n = \frac{4\pi}{h^3}\,(2m_n^*)^{3/2}\int_{E_C}^{\infty}\frac{1}{\exp\left(\frac{E - E_F}{K\,T}\right) + 1}\,(E - E_C)^{1/2}\;dE \qquad \text{------(6)}$$

near room temperature K T ≅ 0.026 eV. Therefore, for energies greater than E_C we have

$$\exp\left(\frac{E - E_F}{K\,T}\right) + 1 = \exp\left(\frac{E - E_F}{K\,T}\right)$$

$$n \ = \frac{4\,\pi}{h^3}\,(\,2m_n{}^*\,)^{3/2}\ \int_{E_C}^{\infty} \exp\left(-\left(\frac{E-\ E_F}{K\,T}\right)\right)(\,E-\ E_C\,)^{1/2}\ \ dE$$

$$= \frac{4\,\pi}{h^3}\,(\,2m_n{}^*\,)^{3/2}\quad \exp\left(\frac{E_F-\ E_C}{K\,T}\right)\ \int_{E_C}^{\infty} \exp\left(-\left(\frac{E-\ E_C}{K\,T}\right)\right)(\,E-\ E_C\,)^{1/2}\ \ dE$$

Let $\frac{E-\ E_C}{K\,T} \ = \ x$

dE = K T dx

for $E = E_C$, $x = 0$

$$n \ = \frac{4\,\pi}{h^3}\,(\,2m_n{}^*\,)^{3/2}\ \exp\left(\frac{E_F-\ E_C}{K\,T}\right)\int_0^{\infty} x^{1/2}\,(\,KT\,)^{1/2}\ e^{-x}\ KT\ \ dx$$

$$= \ \frac{4\,\pi}{h^3}\,(\,2m_n{}^*\ KT)^{3/2}\ \exp\left(\frac{E_F-\ E_C}{K\,T}\right)\int_0^{\infty} x^{1/2}\ e^{-x}\ \ dx$$

Now

$$\int_0^{\infty} x^{1/2}\ e^{-x}\ \ dx \quad = \ \left(\ \frac{\pi}{4}\right)^{1/2}$$

$$n \ = 2\left(\frac{2\,\pi m_n{}^*\,KT}{h^2}\right)^{3/2}\ \exp\left(-\left(\frac{E_F-\ E_C}{K\,T}\right)\right) \qquad \text{------(7)}$$

equation(2) the probability of occupancy of level E_C is given by

$$f\,(E_C) \ = \ \frac{1}{\exp\left(\frac{E-\ E_F}{K\,T}\right)+\ 1}$$

$$\cong \exp\left(-\left(\frac{E_F-\ E_C}{K\,T}\right)\right)$$

Equation (7) becomes

$$n \ = 2\left(\frac{2\,\pi m_n{}^*\,KT}{h^2}\right)^{3/2} f(E_C)$$

The first term on the right hand side must represent the effective density of states of electrons at the conduction band edge. Denoting it by N_C,

$$n = N_C \exp\left(-\left(\frac{E_F - E_C}{K\,T}\right)\right) \qquad \text{-----(8)}$$

$$N_C = 2\left(\frac{2\,\pi m_n^{*}\,KT}{h^2}\right)^{3/2} \qquad \text{--------(9)}$$

For silicon,

$N_C = 2.8 \times 10^{25} \left(\frac{T}{300}\right)^{3/2}$ m^{-3}

3.7.2 Hole concentration in the valence band:

An expression similar to equation (1) for the number of holes per unit volume in the energy range E and E + dE can be written as

$dn = D(E)\ [1 - f(E)]\, dE$ ------(10)

where we have replaced f(E) by [1 - f(E)] which represents the probability of an energy state E not to be occupied by an elector, i.e., the probability of finding a hole in the energy state E. now

$$1 - f(E) = 1 - \frac{1}{\exp\left(\frac{E - E_F}{K\,T}\right) + 1}$$

$$= \frac{\exp\left(\frac{E - E_F}{K\,T}\right)}{\exp\left(\frac{E - E_F}{K\,T}\right) + 1}$$

In the valence band, since $E < E_F$ the exponential term in the denominator may be neglected in comparison to unity. Thus we get

$$1 - f(E) = \exp\left(\frac{E - E_F}{K\,T}\right) \qquad \text{-------(11)}$$

It follows that the probability of finding holes decreases exponentially with increase in depth into the valence band.

Also, the kinetic energy of a hole in the energy state E in the valence band is $(E_v - E)$. therefore, the density of states per unit volume in the valence band can be written as

$$D(E) = \frac{4\,\pi}{h^3}\left(2\,m_p^{*}\right)^{3/2}\left(E_v - E\right)^{1/2} \qquad \text{------(12)}$$

where $m_p{}^*$ is the effective mass of a hole in the valence band. Using equation (11) and (12) in (10) and integrating form E = E$_v$ and E = $-\infty$, we obtain the hole concentration in the valence band as

$$n \;=\; \frac{4\,\pi}{h^3}\,(\,2m_p{}^*\,)^{3/2}\;\int_{-\infty}^{E_v}\exp\left(-\left(\frac{E\,-\,E_F}{K\,T}\right)\right)(\,E_v-\;E\,)^{1/2}\;\;dE$$

$$=\;\frac{4\,\pi}{h^3}\,(\,2m_p{}^*\,)^{3/2}\quad\exp\left(\frac{E_V\,-\,E_F}{K\,T}\right)\;\int_{-\infty}^{E_v}\exp\left(-\left(\frac{E\,-\,E_v}{K\,T}\right)\right)(\,E_v-\;E\,)^{1/2}\;\;dE$$

Let $\quad\frac{E_v-\,E}{K\,T}\;=\;x$

dE = - K T dx

for E = E$_v$, x = 0

$$n\;=\;\frac{4\,\pi}{h^3}\,(\,2m_p{}^*\,)^{3/2}\;\exp\left(\frac{E_v\,-\,E_F}{K\,T}\right)\int_0^{\infty}x^{1/2}\,(\,KT\,)^{1/2}\,e^{-x}\,(-KT)\;\;dx$$

$$=\;\frac{4\,\pi}{h^3}\,(\,2m_p{}^*\,)^{3/2}\;\exp\left(\frac{E_v\,-\,E_F}{K\,T}\right)(KT)^{3/2}\int_0^{\infty}x^{1/2}\;\;e^{-x}\;\;dx$$

$$=\;\frac{4\,\pi}{h^3}\,(\,2m_p{}^*KT\,)^{\frac{3}{2}}\;\exp\left(\frac{E_v\,-\,E_F}{K\,T}\right)\;\left(\,\frac{\pi}{4}\right)^{\frac{1}{2}}$$

$$=2\left(\frac{2\,\pi m_p{}^*\,KT}{h^2}\right)^{3/2}\;\exp\left(-\left(\frac{E_F\,-\,E_v}{K\,T}\right)\right)\qquad\text{-----(13)}$$

$$p\;=\;N_v\;\exp\left(-\left(\frac{E_F\,-\,E_v}{K\,T}\right)\right.\qquad\text{-----(14)}$$

$$N_v\;=\;2\left(\frac{2\,\pi m_p{}^*\,KT}{h^2}\right)^{3/2}\qquad\text{--------(15)}$$

For silicon,

$$N_v\;=\;2.8\times10^{25}\left(\frac{T}{300}\right)^{3/2}\;m^{-3}$$

The electron and hole concentrations given by equation (9) and (15) respectively are valid for both intrinsic and extrinsic materials. For intrinsic materials, these equations can also be written as

$$n_i \;=\; N_C\ \exp\,(- \left(\frac{E_c - E_i}{K\,T}\right)$$

$$p_i \;=\; N_v\ \exp\,(- \left(\frac{i - E_v}{K\,T}\right)$$

where the fermi level E_F has been replaced by the intrinsic level $E_{i.}$

3.8 Temperature Dependence - Mobility - Impurity conductivity:

At finite temperature, due to thermal agitation and lattice vibrations, some of the valence band electrons are always present in the conduction band, i.e., at ordinary temperatures, an intrinsic semiconductor always contains some free electrons in the conduction band and equal number of holes in valence band.

In the absence of any applied electric field, these electrons and holes move in random directions and constitute no current.

When an electric field is applied, these electrons and holes get accelerated towards the opposite ends of the field and their velocity begins to increase. This increase in velocity, however, does not continue indefinitely because of the collisions of these carriers with the various type of obstacles, such as atomic nuclei, phonons, etc.

Depending on the mean free path, the carriers acquire an average increment in velocity which is lost during the subsequent collision. This extra velocity acquired by the carriers in the presence of an applied electric field is called the ***drift velocity*** and is denoted by v_d it is proportional to the strength ε of the applied electric field .

$$v_d \;\propto \varepsilon$$

$$v_d = \mu E \qquad\qquad \text{--------(1)}$$

where μ is called the ***mobility*** of the charge carrier and is defined as the drift velocity acquired by a carrier per unit electric field strength.

Let v_{dn} , μ_n and n denote the drift velocity, mobility and concentration of electrons respectively in the conduction band.

Then current density due to electrons is given by

$$J_n \;=\; n\ \ e\, v_{dn} \qquad\qquad \text{-------(2)}$$

Where e is the electronic charge. We can write equation (1) for the electrons as

$$v_{dn} = \mu_n\ \varepsilon$$

therefore, equation(2) we obtain,

$$J_n = n\ e\,\mu_n\ \varepsilon \qquad \text{---------(3)}$$

Comparing it with Ohm's law, i.e.,

$$J_n = \sigma_n\ \varepsilon$$

Where σ_n represents the electronic conductivity of the material, we get

$$\sigma_n = n\ e\,\mu_n \qquad \text{-------(4)}$$

Similarly, we can write the expression for the conductivity due to holes in the valence band as

$$\sigma_p = p\ e\,\mu_p \qquad \text{-------(4)}$$

Where p and μ_p represent the concentration and mobility of holes respectively. Thus the toal conductivity of the material is

$$\sigma = \sigma_n + \sigma_p$$
$$= e\,(n\ \mu_n + p\ \mu_p) \qquad \text{--------(5)}$$

For an intrinsic semiconductor,

$$n = p = n_i$$

therefore equation(5) becomes

$$\sigma = e\,n_i\,(\mu_n + \mu_p) \qquad \text{--------(6)}$$

In semiconductor, the movement of carriers or the flow of current is, in fact, the consequenceof th efollowing two process;

(i) Drift of carriers under the effect of an applied field; the resulting current is called the ***drift current***.

(ii) Diffusion of carriers under the effect of concentration gradient of dopants present inside the semiconductor; the corresponding current is called the ***diffusion current***.

3.9 Hall effect:

The Hall effect is observed in a conductor whenever it is falling in a region where both magnetic and electric fields are present. Scientist Hendrick Lorentz proposed the concept of Lorentz force, which states that the charges in a conductor experience forces due to both electric and magnetic fields. Edwin Hall, in 1879, observed that a potential difference is developed between the ends of a current carrying conductor that is falling in a magnetic field. It is also applicable for semiconductors.

Definition of Hall effect:

When a solid material, carrying an electric current, is placed in a magnetic field, then an electric field is set up in a transverse direction inside the material. The principle of Hall effect is that when a semiconductor or a conductor is placed perpendicular to the magnetic field, then an appreciable voltage or potential difference is established between the ends of the material, which is in turn called the Hall effect. When no magnetic field is applied, the charge carriers travel in a straight path without being deflected. This straight line is called the "line of sight path". On the other hand, when a magnetic field is applied, the path of the charge carries becomes curved. Due to this curved trajectory, the charges accumulate on either side of the conductor - the positive charges towards one side, and the negative charges towards the other. Hence, the charge gets distributed symmetrically across the conductor

Theory of Hall effect

When a conductive plate is placed between the ends of a battery, then the circuit gets completed, and the current starts flowing. The charge flows in a linear path from one end of the plate to the other end. This motion of charge carriers causes the production of a magnetic field. When a magnet is brought near the plate, it distorts the existing magnetic field. The force exerted on the charge carries is nothing but the Lorentz force.

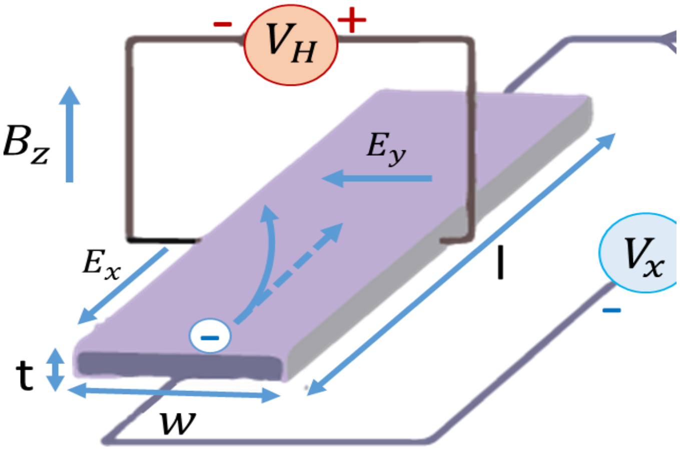


Figure. 3.1 Hall effect

As a result of the distortion, the negatively charged electrons get thrown towards one side of the plate, and the positive holes towards the other. The Hall voltage thus established can be written as ,

$$V_H = I_x B_z \; / \; n \, t \, e$$

n- number density of charge carriers per unit volume
B_z- magnetic field strength
e- value of electronic charge

Also,

$V_H = V_x B_z w$
V_x-Voltage across the conductor
B_z- Magnetic field
w- width of the conductor

The charge carriers could be ions, electrons, holes or maybe even a combination of the three.

Hall coefficient

The Hall coefficient RH can be written as,

$$R_H = E_y \; / \; J_x \, B_z$$

J_x- current density
E_y- Electric field established due to Hall Effect
B_z- Magnetic field

The Hall coefficient is positive if the number of positive charges is greater than the number of negative charges.

$$M_e = \sigma R_H,$$

σ, being the conductivity. e is mobility.

3.10 Fermi surfaces and construction:

The **Fermi surface** is the surface in reciprocal space which separates occupied from unoccupied electron states at zero temperature. The shape of the Fermi surface is derived from the periodicity and symmetry of the crystalline lattice and from the occupation of electronic energy bands. The existence of a Fermi surface is a direct consequence of the Pauli exclusion principle, which allows a maximum of one electron per quantum state.

Area of the Brilouin zone corresponding to a square lattice of periodicity is a

$$A = \frac{4\pi^2}{a^2} \qquad \text{------(1)}$$

$$\pi \; {K_F}^2 = n\frac{4\pi^2}{a^2} \qquad \text{-----(2)}$$

where n is the occupied area of the brilouin zone for monovalent(1/2), divalent(1) and tetravalent(2) . π/a is the distance of the zone boundary from the centre of the zone

construction:

(a) Monovalent

for monovalent n= ½

$$\pi \quad {K_F}^2 \; = \frac{1}{2}\frac{4\,\pi^2}{a^2}$$

$$K_F = \sqrt{\frac{2}{\pi}}\,(\frac{\pi}{a})$$

$$K_F = \sqrt{0.6369}\,(\frac{\pi}{a})$$

$$K_F = 0.798 \;\; (\frac{\pi}{a})$$

A circle of radius K_F is not completely filled in the first brilioun zone.

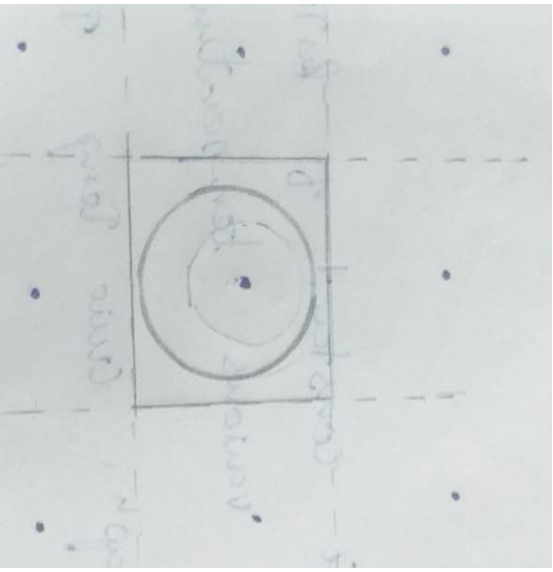


Figure 3.2 Monovalent

(b) Divalent

for divalent n= 1

$$\pi \quad {K_F}^2 \ = \frac{4}{\pi}\frac{\pi^2}{a^2}$$

$$K_F \ = \sqrt{\frac{2}{\pi}}\,(\frac{\pi}{a})$$

$$K_F \ = \ \frac{2}{1.772}\,(\frac{\pi}{a})$$

$$K_F = 1.128 \ (\frac{\pi}{a})$$

The first brilion zone of the metal is not completely filled with electron while the second zone is partially filled.

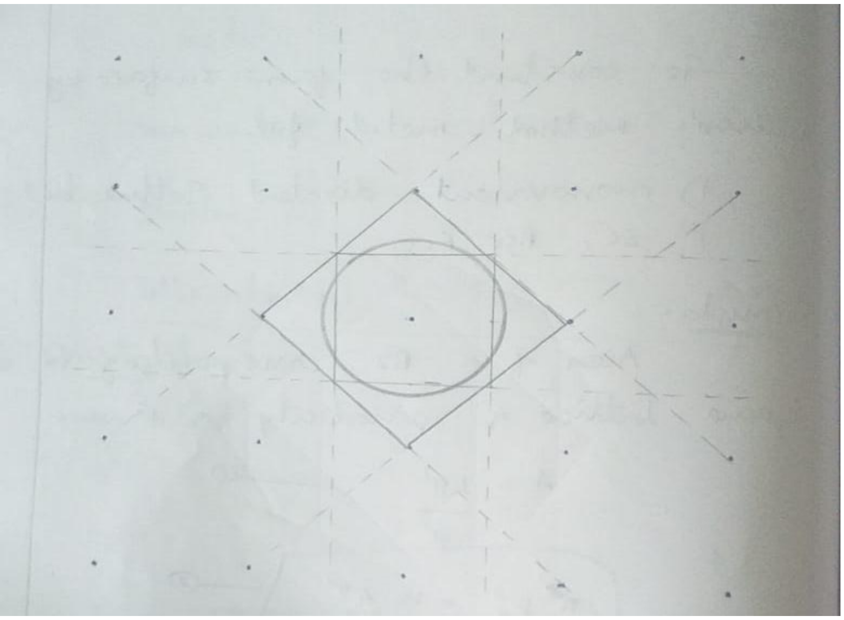


Figure 3.3 divalent

(c) Tetravalent

for tetravalent n= 2

$$\pi \quad {K_F}^2 \; = \; 2 \; \frac{4\,\pi^2}{a^2}$$

$$K_F \; = \sqrt{\frac{2}{\pi}}\,(\frac{\pi}{a}\,)$$

$$K_F \; = 2.5477\;(\frac{\pi}{a}\,)^2$$

$$K_F \; = 1.596\;(\frac{\pi}{a}\,)$$

Fermi circle is completely enclose the first brilion zone and through the first, second, third, and fourth zone

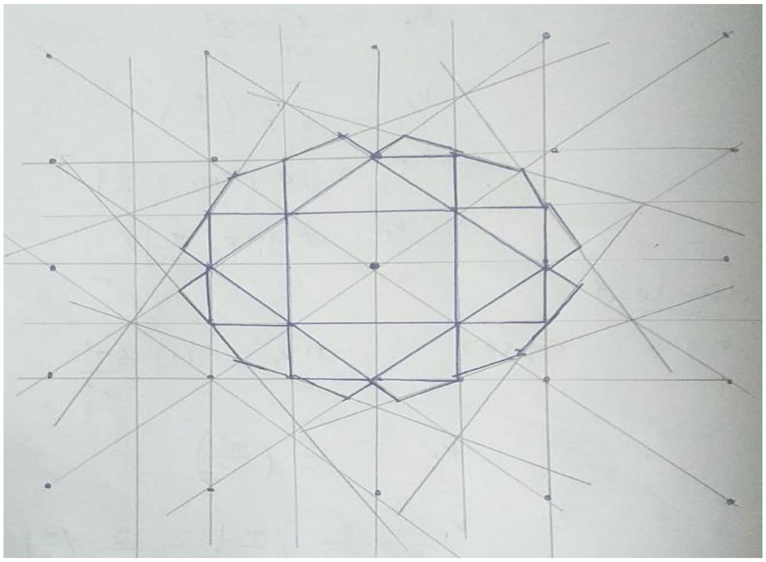


Figure 3.4Ttetravalent

3.11 de Hass-van Alphen effect:

The **De Haas–Van Alphen effect**, often abbreviated to **DHVA**, is a quantum mechanical effect in which the magnetic susceptibility of a pure metal crystal oscillates as the intensity of the magnetic field *B* is increased. It can be used to determine the Fermi surface of a material. Other quantities also oscillate, such as the electrical resistivity (Shubnikov–de Haas effect), specific heat, and sound attenuation and speed.

The differential magnetic susceptibility of a material is defined as

$$x = \frac{\partial M}{\partial H}$$

where H is the applied external magnetic field and M the magnetization of the material. Such that

$$B = \mu_0 (H + M)$$

where μ_0 is the vacuum permeability. For practical purposes, the applied and the measured field are approximately the same $B \approx \mu_0 H$ (if the material is not ferromagnetic).

The oscillations of the differential susceptibility when plotted against 1/B, have a period P (in teslas^{-1}) that is inversely proportional to the area S of the extremal orbit of the Fermi surface (m^{-2}), in the direction of the applied field, that is

$$P(B^{-1}) = \frac{2\pi e}{\hbar S}$$

where $\hbar$ is Planck constant and e is the elementary charge. The existence of more than one extremal orbit leads to multiple periods becoming superimposed. A more precise formula, known as Lifshitz–Kosevich formula, can be obtained using semiclassical approximations.

The modern formulation allows the experimental determination of the Fermi surface of a metal from measurements performed with different orientations of the magnetic field around the sample.

UNIT IV

MAGNETISM

Diamagnetism - Quantum theory of paramagnetism - Rare earth ion - Hund's rule - Quenching of orbital angular momentum - Adiabatic demagnetization - Quantum theory of ferromagnetism - Curie point - Exchange integral - Heisenberg's interpretation of Weiss field - Ferromagnetic domains – Bloch wall - Spin waves - Quantization - Magnons - Thermal excitation of magnons - Curie temperature and susceptibility of ferrimagnets - Theory of anti ferromagnetism - Neel temperature.

4.1 Diamagnetism:

Diamagnetism is an material arises due to changes in the atomic orbital state induced by applied magnetic field.

An electron revolving in an orbit constitutes an electric current. When a magnetic flux linked with such an electric circuit is changes, an induced current is set up in such a direction as to oppose the change in flux in accordance with the Lenz’s law.

The magnetic field of the induced current is opposite to the applied field and produces the diamagnetic effect. The occurrence of diamagnetism is manifested by the very small and negative value of the magnetic susceptibility.

Diamagnetism exist in all materials but is usually suppressed due to the presence of stronger effects such as para magnetism., ferro magnetism etc. the diamagnetism has been described quantitatively by applying the classical and quantum theories.

4.2 Paramagnetism:

Paramagnetism occurs in those atoms, ions and molecules which have permanent magnetic moments. In the absence of magnetic field, these magnetic moments are oriented randomly and no net magnetization is produced. When a magnetic field is applied, these moments orient themselves in the direction of the field which results in some net magnetization parallel to the applied field. The paramagnetic materials have small, positive and temperatute-dependent susceptibility.

4.3 Quantum theory of paramagnetism:

The classical theory assumes that the permanent magnetic moment of a given atom or ion rotates freely and can possess any orientation with respect to the applied magnetic field.

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

The direct relationship between the magnetic dipole moment μ of an atom or ion in free space and its angular momentum J as

$$\mu = -\, g\, \mu_B\, J \qquad \text{--------(1)}$$

the quantity μ_B is called Bohr magneton and is equal to $\frac{e\hbar}{2m}$ in SI system and $\frac{e\hbar}{2mc}$ in CGS system of units; g is known as Lande's g-factor and is equal to 2 if the net angular momentum of the dipole is due to electron spin and 1 if it is due to orbital motion only.

In general, it has mixed origin and obtained from the equation;

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

where S and L represent the spin and orbital quantum umbers of the dipole respectively.

The orientations of the magnetic moment μ with respect to the direction of the applied magnetic field are specified by the rule that the possible components of μ along the field direction are given by

$$\mu_z = - g\,\mu_B\, m_J \qquad \text{--------(3)}$$

where $m_J = -J, -J+1, \ldots\ldots, J-1, J$ is the magnetic quantum number associated with J

the potential energy of a magnetic dipole in the presence of magnetic field B is,

$$E = m_J \;\; g\,\mu_B\;\; B \qquad \text{--------(4)}$$

According to Maxwell-Boltzmann distribution, the number of atoms having a particular value of m_j is thus proportional to

$$e^{\frac{-m_J \;\; g\,\mu_B \;\; \mathrm{B}}{KT}}$$

Considering a unit volume of a paramagnetic material containing a total of N atoms, the magnetization in the direction of the field is given by

M = N × (statistical average of the magnetic moment component per atom along B)

$$= \;\; N \;\sum_{m_J=-J}^{m_J=+J} \frac{-m_J\, g\,\mu_B\, e^{\frac{-m_J \;\; g\,\mu_B \;\; \mathrm{B}}{KT}}}{e^{\frac{-m_J \;\; g\,\mu_B \;\; \mathrm{B}}{KT}}} \qquad \text{---------(5)}$$

Consider the two cases:

(i) At normal flux densities and ordinary temperatures,

$$\frac{-m_J \;\; g\,\mu_B \;\; \mathrm{B}}{KT} \ll 1$$

Therefore, the equation (5) can be approximated as

$$M \qquad N\, \frac{N\, g\,\mu_B \sum_{m_J=-J}^{m_J=+J} \; -m_J \left(1 - \frac{m_J \;\; g\,\mu_B \;\; \mathrm{B}}{KT}\right)}{\sum_{m_J=-J}^{m_J=+J} \;\left(1 - \frac{m_J \;\; g\,\mu_B \;\; \mathrm{B}}{KT}\right)}$$

Now, $\sum_{m_J=-J}^{m_J=+J} \;\; m_J \;=\; 0$

And $\qquad \sum_{m_J=-J}^{m_J=+J} \;\; {m_J}^2 \;=\; 2 \;\; \sum_{m_J=0}^{m_J=+J} \;\; {m_J}^2$

$$= \frac{J(J+1)(2J+1)}{3}$$

$$M = N \frac{\frac{g^2 \mu_B{}^2}{KT} \frac{J(J+1)(2J+1)}{3}}{(2J+1)}$$

$$= N \frac{g^2 \mu_B{}^2}{3KT} J(J+1) \quad \text{-----------(6)}$$

$$x_{para} = \frac{\mu_0 M}{B}$$

$$= \frac{\mu_0 N \mu_B{}^2}{3KT} g^2 J(J+1) \quad \text{--------(7)}$$

$$= \frac{\mu_0 N P_{eff}{}^2 \mu_B{}^2}{3KT} \quad \text{----(8)}$$

Where P_{ff} is the effective number of Bohr magnetons and is given by

$$P_{ff} = g\sqrt{J(J+1)} \quad \text{-------(9)}$$

The equation(8) is identical to the classical express with

$$\mu^2 = P_{eff}{}^2 \mu_B{}^2 \quad \text{--------(10)}$$

(ii) At low temperatures and strong magnetic field $\frac{m_J \; g\mu_B \; B}{KT}$ is not smaller than unity and it is not possible to make a series expansion of the exponential term in the equation(5) . after some alegebraic manipulation equation(5) yields

$$M = N_g J \mu_B B_J(x) \quad \text{--------(11)}$$

Where $x = \frac{g J \mu_B \; B}{KT}$ and $B_J(x)$ is the Brillouin function defined as

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\right) x - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \quad \text{--------(12)}$$

For x ≪ $1, we\ have$

$$\text{Cot hx} = \frac{1}{x} + \frac{x}{3}$$

$$B_J(x) = \frac{x(J+1)}{3J}$$

Thus the susceptibility becomes

$$x_{para} = \frac{\mu_0\, M}{B}$$

$$= \frac{\mu_0\, N\, J\, (J+1)\, g^2 {\mu_B}^2}{3KT}$$

$$= \frac{\mu_0\, N\, {P_{eff}}^2 {\mu_B}^2}{3KT} \qquad \text{--------(13)}$$

For x ≫ 1 i.e, at low temperature and strong fields,

$$\text{Cot hx} = 1$$

$$B_J(x) \approx 1$$

And equation(11) become

$$M = Ng\, J\, \mu_B \qquad \text{---------(14)}$$

This results implies the state of magnetic saturation.

For a large number of allowed orientations of a magnetic dipole,

$$\cot h\, \frac{x}{2J} \rightarrow \frac{2J}{x} \qquad \text{and}$$

$$\cot h\, \left(1 + \frac{1}{2J}\right) x \rightarrow \cot hx$$

$$B_J(x) \rightarrow \cot hx - \frac{1}{x} \qquad \text{or} \qquad L(x)$$

4.4 Rare earth ion and Quenching of orbital angular momentum:

The order of magnitude of paramagnetic susceptibility of a solid as estimated from equation(13) at room temperature is about 10^{-7} which is quite small.

It increases by more than hundred times at 1 K. equation (13) is successfully employed to predict the values of susceptibility for various paramagnetic crystals particularly rare earth ions.

The value of j is determined by applying the Hund's rule. However equation (13) is unable to account for the experimental observations of susceptibility for the ions of the iron group. This is because of presence of crystal field due to other ions which cannot be neglected in comparison with the externally applied field.

In paramagnetic materials where the crystal field is negligible equation (13) holds good. But when it is strong, it may break the rotational symmetry of the dipole and affect its total angular momentum. Also, the average value of L_z may reduce to zero which is known as quenchin of the orbital angular momentum.

In such a case

$$E = 2 m_s \mu_B B \quad (\text{as } g = 2)$$

$$= (\frac{e\hbar}{m}) m_s B \qquad \text{----------(15)}$$

for $(\frac{e\hbar}{m}) m_s B \ll K T$, it yields

$$x = \frac{\mu_0 N}{3KT} (\frac{e\hbar}{m})^2 S(S+1) \qquad \text{-------(16)}$$

For example, Mn^{3+} ions, the value of x as obtained from the above expression with S = 2 is in conformity with the experimental observations where equation (13) predicts a zero susceptibility.

4.5 Hund's rule:

Hund's rule state that, for the ground state of atoms with incompletely filled shells,

(i) The electron spins add up to give the maximum possible S consistent with the Pauli's exclusion principle.

(ii) The orbital momenta combine to give the maximum value for L that is consistent with(i)

(iii) The value of J is given by

J = L – S, if a shell is less than half-filled

J = L + S, if a shell is more than half-filled

If the shell is just half-filled, L = 0 and therefore J = S

4.6 Ferromagnetism:

Like paramagnetism, ferromagnetism is also associated with the presence of permanent magnetic dipoles, but unlike paramagnetism, the magnetic moments of adjacent atoms in this case are aligned in a particular direction even in the absence of the applied magnetic field.

Thus a ferromagnetic material exhibits a magnetic moment in the absence of a magnetic field. The magnetization existing in a ferromagnetic material n the absence of an applied magnetic field is called the spontaneous magnetization. It exists below a certain temperature called the curie temperature T_C.

The alignment of magnetic moments below the Curie temperature is due to the exchange interaction between the magnetic ions.

Above the curie temperature, the thermal effects offset the spin alignment and ferromagnetic substance become paramagnetic.

4.7 Quantum theory of ferromagnetism:

Consider the ferromagnetic solid containing N atoms per unit volume each having a total angular momentum quantum number J. the expression for magnetization as

$$M = N_g J \mu_B B_J(x) \qquad \text{--------(1)}$$

where

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\right) x - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \qquad \text{-----(2)}$$

And

$$x = \frac{g\,J\,\mu_B\,B_{eff}}{KT}$$

$$= \frac{g\,J\,\mu_B}{KT}\ (B + \lambda M) \qquad \text{------(3)}$$

In case of spontaneous magnetization B = 0 and equation (3) becomes

$$x = \frac{g\,J\,\mu_B \lambda\, M}{KT} \qquad \text{------(4)}$$

$$M(T) = \frac{x\,K\,T}{J\,\mu_B \lambda\, g} \qquad \text{-------(5)}$$

The magnetic moments align themselves parallel to the field and the magnetization M becomes the saturation magnetization, $M_s(0)$. Therefore

$$M_s(0) = N\,g\,J\,\mu_B \qquad \text{----------(6)}$$

From equation (5) and (6)

$$\frac{M(T)}{M_S(0)} = \frac{x\,K\,T}{\mu_B{}^2 \lambda N\,g^2\;J^2} \qquad \text{-------(7)}$$

Also equation (1) and (5) give

$$\frac{M(T)}{M_S(0)} = B_J(x) \qquad \text{--------(8)}$$

At temperature equal to the critical temperature T_C this line is tangent to the Brillouin function at the origin. The intersection of the two plots at the point O represents a positive solution, but the magnetization corresponding to this point is unstable.

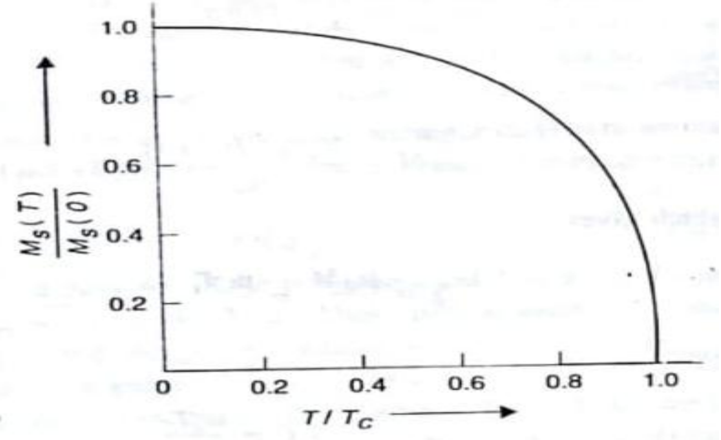


Figure 4.1 Spontaneous magnetization versus temperature for $T<T_C$

Another point of intersection appears for $T < T_C$ which indicates a non-zero value of m even for zero external field and hence corresponds to spontaneous magnetization. It also follows that the spontaneous magnetization decreases with increase in temperature and vanishes beyond the temperature T_C which is known as the ferromagnetic curie temperature.

4.8 Exchange integral - Heisenberg's interpretation of Weiss field:

The Weiss theory of ferromagnetism is based on the concept of ferromagnetic domains which are spontaneously magnetized due to the presence of internal molecular field called Weiss field or exchange field B_E. the theory however does not explain the origin and nature of this field.

The Weiss field cannot be simply due to magnetic dipole-dipole interaction between the neighbouring dipoles as this would generate fields of the order of 10^3 G only whereas the actual field strength is observed to be quite high.

For example, the Weiss field for iron is order of 10^7 G.

The interaction arises due to the pauli's exculsion principle according to which any change in the relative orientation of the two spins would disturb the spatial distribution of charge, thus producing interaction between the two atoms.

The total energy of a system of two atoms contains an exchange energy term is given by

$$U_{ij} = - 2 J_e \ S_i \cdot S_J$$

Where S_i and S_J represent the spins of the two atoms and J_e is the exchange integral which is assumed to be the same for any pair of atoms.

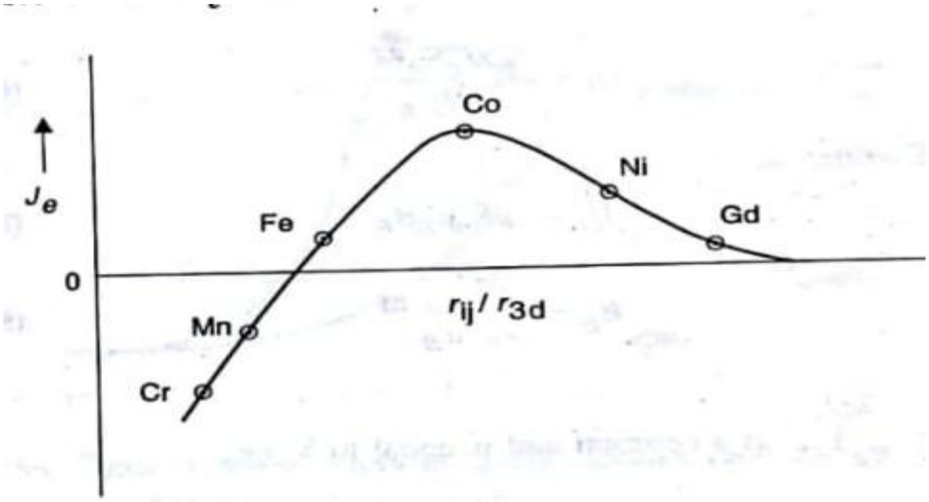


Figure 4.2 Plot of exchange integral J_e versus ratio of interatomic separation to the radius of 3d orbit

Its value depends on the overlap of the charge distributions of the two atoms i.e, o the interatomic distance. In general J_e is positive for large interatomic distance and negative for smaller ones.

The above expression is known as the Heisenberg model of exchange energy. It also follows from the above equation that hence is more stable as compared to the antiparallel arrangement, thereby producing magnetization.

In a similar way, it can be concluded that the negative value of J_e does not favour magnetism.

4.9 Ferromagnetic domains -Bloch wall:

According to the Weiss theory the exchange interaction between the neighbouring dipoles in a ferromagnetic material generate and internal exchange field B_E which aligns them in particular direction.

It is however observed that a ferromagnetic material such as iron does not exhibit a net magnetization unless it is placed in an external field.

Weiss explained this by introducing the concept of ferromagnetic domains. According to this concept, a single crystal of a ferromagnetic solid is divided into a number of small region is called domains each one of which is spontaneously magnetized by the exchange field.

The magnetization vectors of different domains are, however, randomly oriented so that no net magnetization is produced in the material as a whole.

In the presence of an external magnetic field, the domains pointing in the direction of field grow at the expense of those pointing in other directions, thereby result in in some non-zero magnetization in the material.

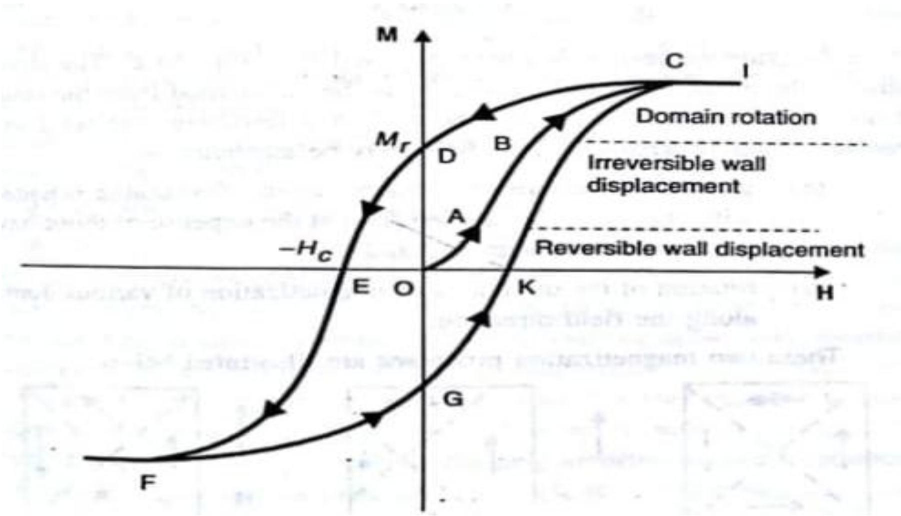


Figure 4.3 Typical hysteresis curve for a ferromagnetic materials

All ferromagnetic materials exhibit the well known hysteresis curves: the typical one is shown in figure. It is apparent that for $T < T_C$ there are two solutions for M which trace the boundary of the hysteresis curve.

$$M = \left(\frac{KT}{\mu_B\, g\, J\, \lambda}\right) x - \frac{1}{\lambda} B$$

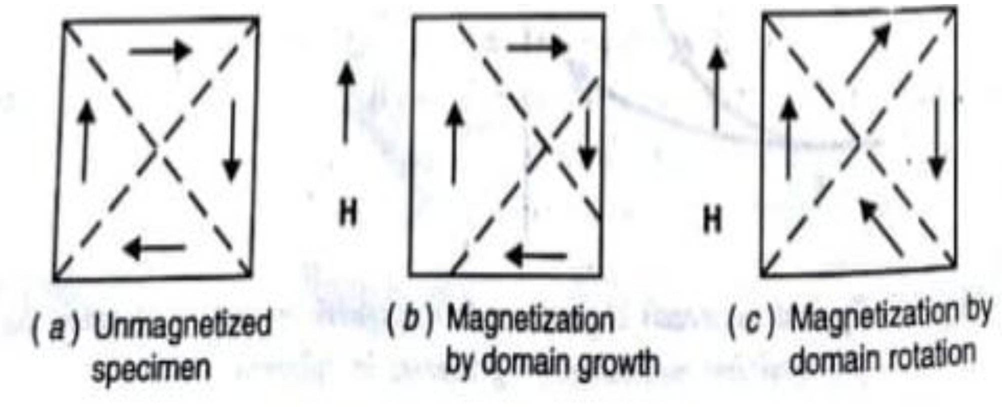


Figure 4.4 The two fundamental processes of magnetization

The magnetization produced in a ferromagnetic solid in the presence of an external magntic field may be attributed to

(i) Growth in the size of domains having favourable orientation with respect to the applied field at the expense of those having unfavourable orientation

(ii) Rotation of the directions of magnetization of various domains along the field directions.

4.10 Magnons:

A **magnon** is a quasiparticle, a collective excitation of the spin structure of an electron in a crystal lattice. In the equivalent wave picture of quantum mechanics, a magnon can be viewed as a quantized spin wave. Magnons carry a fixed amount of energy and lattice momentum, and are spin-1, indicating they obey boson behavior.

4.11 Thermal excitation of magnons:

When temperature T is applied, the total number of magnons excited be

- $\sum nk=\int d\omega\ D\ \omega\langle n(\omega)\rangle$

- where Dω is the number of magnon modes per unit frequency.
- At sufficiently low temperature, the integral ranges from 0 to ∞.

4.12 Curie temperature and susceptibility of ferrimagnets:

Above the critical temperature T_C, **ferromagnetic** compounds become paramagnetic and obey the **Curie-Weiss law:**

$$x = \frac{C}{T_C - T}$$

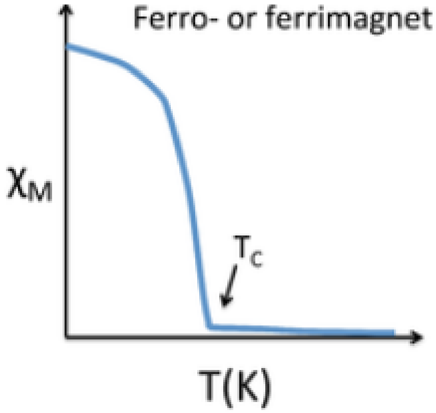


Figure 4.5 Curie temperature

4.13 Theory of anti feromagnetism - Neel temperature:

Antiferromagnetism originates when the spin moments of the neighbouring atoms are ordered in an antiparallel arrangement as shown in figure. When the exchange integral is negative.

A crystal exhibiting antiferromagnetism may be considered to be consisting of two interpenetrating sublattices A and B, one of which is spontaneously magnetized in one direction and the other is spontaneously magnetized in the opposite direction.

This type of magnetism was first observed in the crystals of MnO. In the absence of an external magnetic field, the neighbouring magnetic moments cancel out each other and the material as whole exhibits no magnetization.

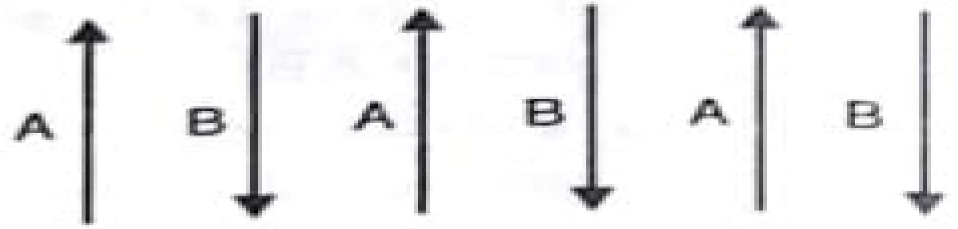


Figure 4.6 Neighboring antiparallel spin moments of A and B sublattices producing antiferromagnetism

When a field is applies, a small magnetization appears in the direction of the field which increases further with temperature. Such a behavior is typical of antiferromagnetic material.

The magnetization becomes the maximum at a critical temperature T_N called the Neel temperature, which is analogous to the Curie temperature in the paramagnetic or ferromagnetic substance.

Above this temperature, the magnetization decreases continuously which is indicative of the paramagnetic state of the material. The variation of susceptibility with temperature is shown in Fig.4.7 And is compared with the corresponding variations for the paramagnetic and ferromagnetic substances.

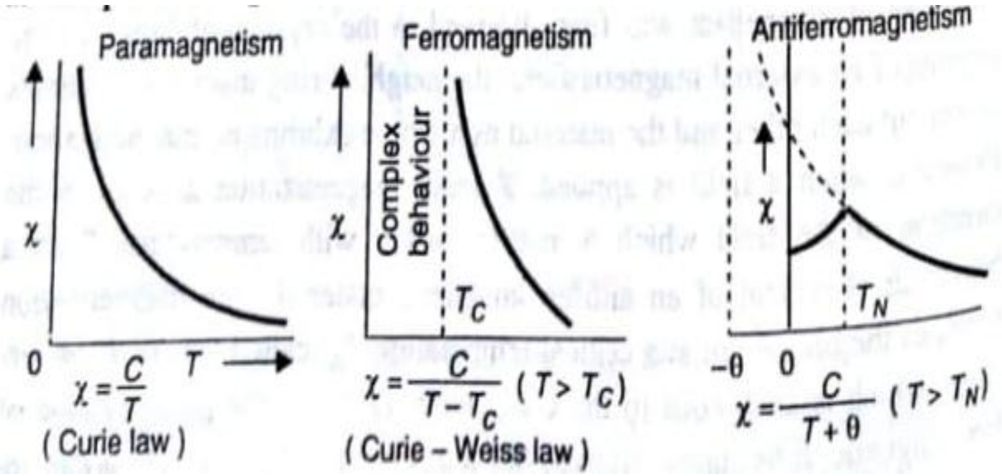


Figure 4.7 Variation of susceptibility with temperature

Unlike the ferromagnetic cases, the susceptibility of an antiferromagnetic substance is not infinite for T equal to T_N but has a weak cusp. The antiferromagnetic behaviour can be explained with the help of the molecular field theory.

UNIT V

Superconductivity

Experimental facts: Occurrence - Effect of magnetic fields - Meissner effect – Critical field – Critical current - Entropy and heat capacity - Energy gap - Microwave and infrared properties - Type I and II Superconductors.

Theoretical Explanation: Thermodynamics of super conducting transition - London equation - Coherence length – Isotope effect - Cooper pairs – Bardeen Cooper Schrieffer (BCS) Theory – BCS to Bose – Einstein Condensation (BEC) regime- Nature of paring and condensation of

Fermions. Single particle tunneling - Josephson tunneling - DC and AC Josephson effects - High temperature Superconductors – SQUIDS.

Experimental facts:

5.1 Occurrence:

The field of superconductivity has emerged as one of the most exciting fields of solid state physics and solid state chemistry during the last decade. The phenomenon was first discovered in 1911 by Kameringh Onnes in Leiden while observing the electrical resistance of mercury at very low temperatures close to 4.2 K, the melting point of helium.

It was observed that the electrical resistance of mercury decreased continuously from its melting point(233K) to 4.2 K and then within some hundredths of a degree, dropped suddenly to about a millionth of its original value at the melting point as shown in figure.

Similar results were obtained by using various other metals such as Pb, Sn, and In. the phenomenon of disappearance of electrical resistance of material below a certain temperature was called superconductivity by Onnes and material in this state was called superconductor.

5.2 Meissner effect:

Meissner and ochsenfeld discovered in 1933 that a superconductor expelled the magnetic flux as the former was cooled belot T_C in an external magnetic field.i.e., it behaved as a perfect diamagnet. This phenomenon is known as the Meissner effect.

Such a flux exclusion is also observed if the superconductor is first cooled below T_C and then placed in the magnetic field. It thus follows that the diamagnetic behavious of superconductor is indee\pendent of its history as illustrated in figure. It also follows from this figure that Meissner effect is a reversible phenomenon. Since B = 0 inside the superconductor, we can write

$$B = \mu_0 (H + M) = 0$$

$$H = - M$$

Therefore, the susceptibility is given by

$$x = \frac{M}{H} = -1 \qquad \text{--------(1)}$$

Which is true for a perfect diamagnet.

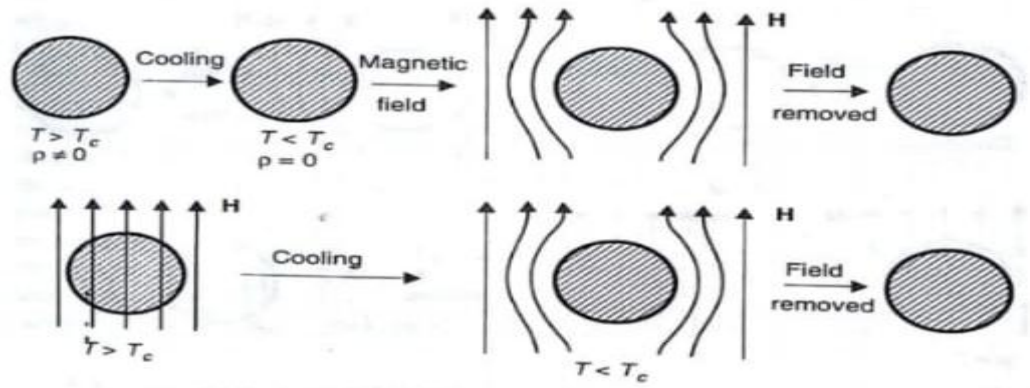


Figure 5.1 A superconductor showing a perfect diamagnetism independent of its history.

The perfect diamagnetic behaviour of a superconductor cannot be explained simply by considering its zero resistivity. Such a perfect conductor would behave differenty under different condition as illustrated in figure. Since the resistivity ρ is zero for a perfect conductor, the application of Ohm's law ($E = \rho J$) indicated that no electric field can exist inside the perfect conductor

Using one the Maxwell's equations, i.e.,

$$\nabla \times E = \frac{-\partial B}{\partial t}$$

B = constant

5.3 Effect of magnetic fields:

Thus the magnetic flux density passing through a perfect conductor becomes constant. This means that when a perfect conductor is cooled in the magnetic field until its resistance becomes zero, the magnetic field in the material gets frozen in and cannot change subsequently irrespective of the applied field. This is in contradiction to the Meissner effect.

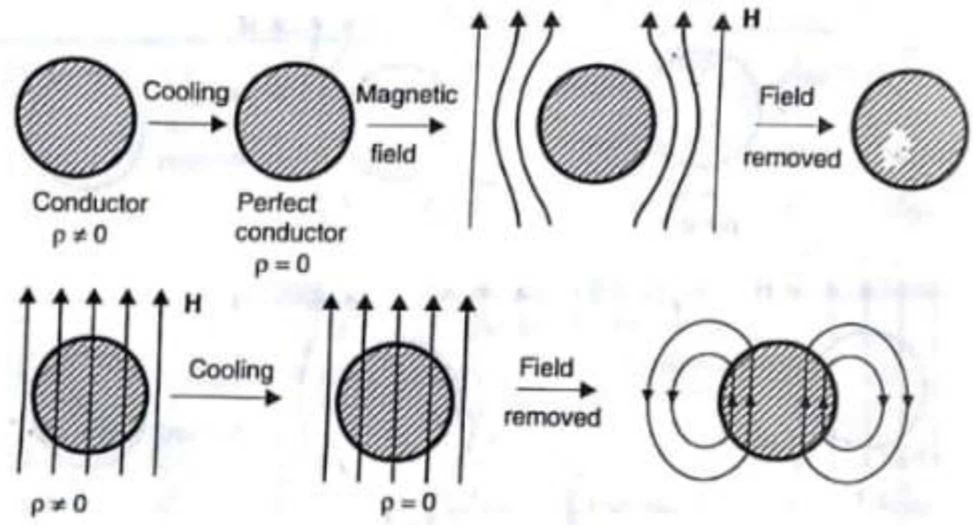


Figure 5.2 Magnetic behaviours of a perfect conductor

The behaviour of the superconductor is different from that of a perfect conductor and the superconducting state may be considered as a characteristic thermodynamic phase of a substance in which the substance cannot sustain steady electric and magnetic fields.

Hence the two mutualy independent properties defining the superconducting state are the zero resistivity and perfect diamagnetism. i.e.,

$$E = 0 \text{ and } B = 0$$

5.4 Critical field – Critical current:

In 1913, Kamerlingh Onnes bserved that a superconductor regains int0 normal state below the critical temperature if it is placed in a sufficiently strong magnetic field. The value of the magnetic field at which the superconductivity vanishes is called the threshold or the critical field H_C and is of the order of a few hundred oersteds for most of the pure superconductors.

This field changes with temperature. Thus the superconducting state is stable only in some definite ranges of magnetic fields and temperature.

For higher fields and temperatures, the normal state is more stable. A typical plot of critical magnetic field temperature for lead is shown in figure.

Such a plot is also referred the magnetic phase diagram.

These type of curved are almost parabolic and can be express by the relation

$$H_C = H_C(0)\left(1 - \frac{T^2}{{T_C}^2}\right)$$

Where $H_C(0)$ is the critical field at 0 K.

Thus, the critical temperature, the critical field becomes zero.

$$H_C(T_C) = 0.$$

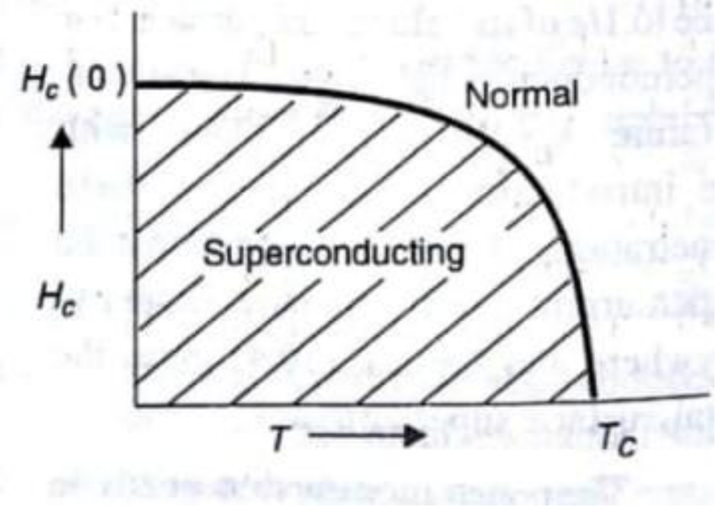


Figure 5.3 Variation of H_C with T for Pb

5.5 Entropy and heat capacity:

A decreased in entropy is observed during normal to superconducting transition near the critical temperature which indicates that the superconducting state is more ordered than the normal state.

The plots of entropy versus temperature for aluminium in the normal and superconducting state are shown in figure. It has been established that it is the electronic structure of a solid which is mainly affected during the superconducting transition.

Some or all the thermally excited electrons in the normal state are ordered in the superconducting state. Such an order may extend up to a distance of the order of 10^{-6} m in type I superconductors.

This range is called the ***coherence length.***

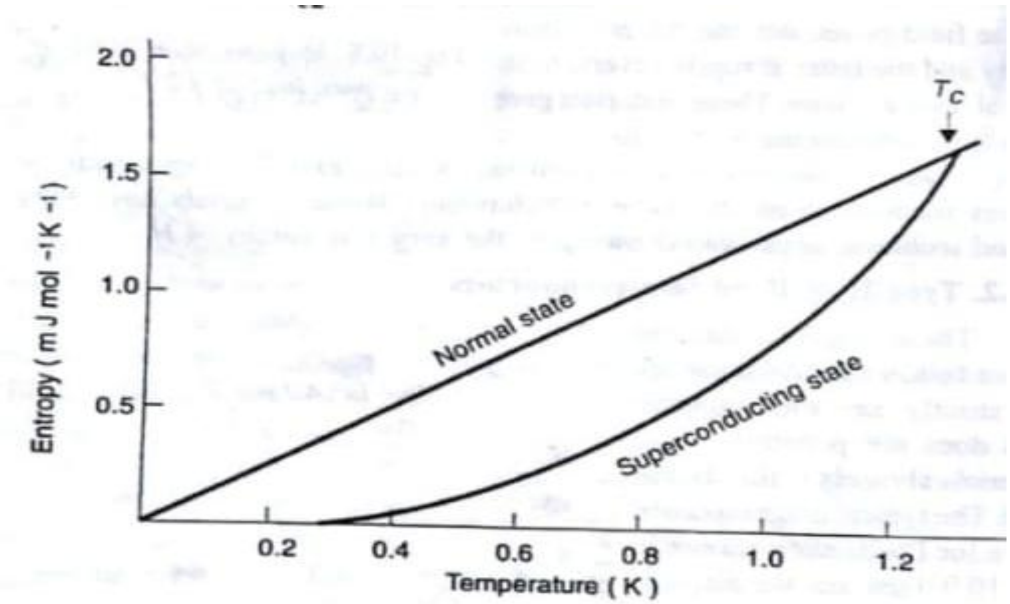


Figure 5.4 Entropy versus temperature for aluminium

5.6 Energy gap:

The temperature dependence of electronic specific heat indicates the existence of an energy gap E_g in a superconductor. This energy gap is of entirely different nature compared with the energy gap in insulators.

The gap is tied to the lattice in an insulator whereas it is tied to the Fermi gas in a superconductor. The gap separates the lowest excited state in a superconductor from the ground state is related to Δ as

$$E_g = 2\Delta$$

For gallium

$$E_g = 2 \times 1.4\, K_B T_C$$

$$= 2.8\, K_B T_C$$

$$\sim 10^{-4}\ \text{eV}$$

The electrons present in the excited states behave as normal electrons and create resistance whereas those present below it behave as superconducting electrons.

The energy gap varies with temperature. It is maximum at 0 K and decreases continuously to zero as the temperature is increased to the critical temperature shown in figure.

Thus at 0 K there are no electrons above the gap and at $T = T_C$, all the superconducting electrons become normal electrons. Due to the presence of an energy gap, the superconductors respond to high frequency electromagnetic radiations of a particular frequency.

Thus energy gap is a characteristic feature of all superconductors which determines their thermal properties as well as their response to high frequency electromagnetic fields.

The existence of an energy gap is accounted for in the ***BCS theory***.

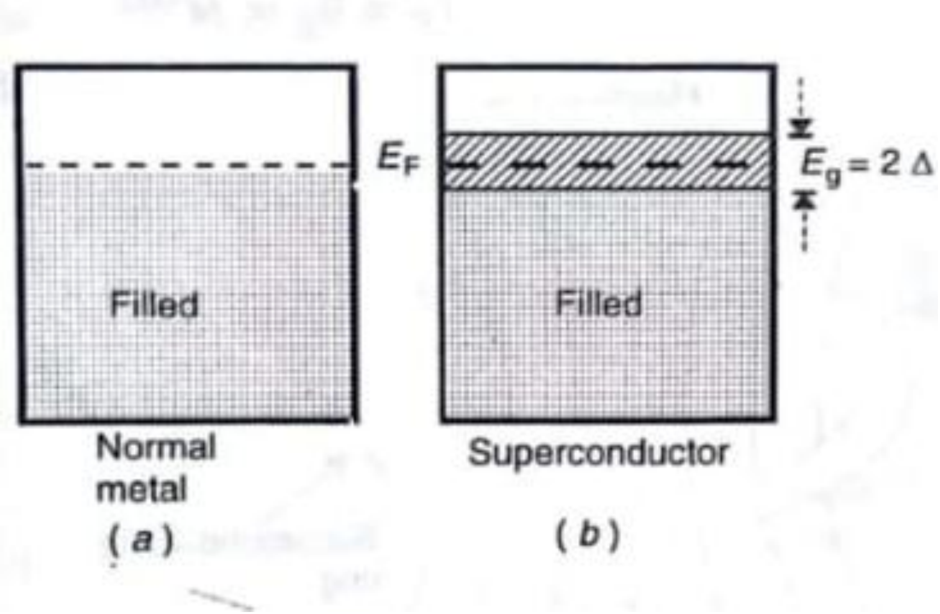


Figure 5.5 (a) Conduction band in the normal metal (b) Energy gap at the fermi level in the superconducting state

5.7 Microwave:

Microwaves are electromagnetic radiations, also known as microwave radiation. Microwaves have a frequency ranging between 300 MHz and 300 GHz. The wavelength of microwaves ranges from 1 mm to around 30 cm. Microwave radiations lie in between the radio waves and infrared radiations. Microwaves are short-wavelength radio waves having frequencies in the gigahertz (GHz) range. These microwaves are produced by dedicated vacuum tubes, known as klystrons, magnetrons, and Gunn diodes.

Microwave properties:

- They are the radiations capable of radiating electromagnetic energy with shorter wavelengths.
- Microwaves are reflected by metal surfaces.
- The transmission of microwaves is affected by phenomena like refraction, diffraction, reflection, and interference.
- They can easily pass through glass and plastics, and hence are used in heating and cooking in an oven.
- They are easily attenuated within shorter distances.
- These radiations are not reflected by the Ionosphere.
- Microwave radiation can pass through the atmosphere. Hence, microwaves are used in the satellite communication sector to transmit information back and forth to the satellite. We can know why satellite dishes are made of metal since they reflect microwave radiation.
- Microwaves travel in a straight line and are reflected by the conducting surfaces.
- Microwave currents have the capacity to flow through a thin layer of a cable.

5.8 Infrared:

Infrared waves are also called heat or thermal waves. This phenomenon occurs because they have a particular heat-inducing property. These waves have a wavelength range between

710 mm to 1mm. Sometimes infrared rays themselves are categorized into near-infrared and far-infrared rays. Near-infrared rays are profoundly used in electronic applications like TV remote sensors and photography.

Infrared properties:

1. Infrared Radiation characteristics are:
2. Infrared Radiation has its Origin from the Alteration in the movement of electrons.
3. Infrared Radiation has its Wavelength Range from 710 mm to 1mm
4. Infrared Radiation has its Frequency from:430 THz – 300 GHz
5. The infrared Radiation Wave type is, Transverse Wave
6. Infrared Radiation has its Speed of 3×10^8 m/s
7. Infrared Radiation, Exhibits the property of refraction.
8. Thermal Properties of Infrared Radiation include. Exhibiting of heat-inducing properties.

Absorption and Reflection characteristics of Infrared Radiation is that they can be absorbed or reflected depending on the nature of the surface that it strikes.

5.9 Type I and II Superconductors:

Superconductors have been classified as type I and type II depending upon their behaviours in external magnetic field, i.e., how strictly they follow the Meissner effect.

Type I or soft superconductor:

The superconductor which strictly follow the Meissner effect are called type I superconductors. The typical magnetic beaviour of lead, a type I superconductor is shown in figure.

These superconductors exhibit perfect diamagnetism below a critical field H_C which, for most of the cases, is of the order of 0.1 tesla.

As the applied magnetic field is increased beyond H_C the field penetrates the material completely and the latter abruptly reverts to its normal resistive state.

Theste materials give away their superconductivity at lower field strength and are referred to as the soft superconductors. Pure specimens of various metals exhibit this type of behavious. These materials have very limited technical applications owing to the very low value of H_C.

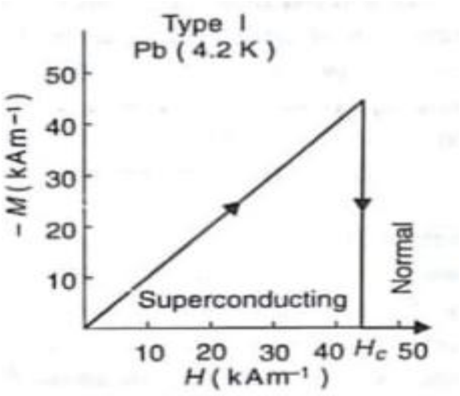


Figure 5.6 Magnetization curve of pure lead at 4.2 K

Type II or Hard superconductors:

These superconductors are do not follow the Messiner effect, the magnetic field does not penetrate these materials abruptly at the critical field. The typical magnetization curve for Pb-Bi alloy shown in figure.

If follows from this curve that for fields less than H_{C1} the material exhibits perfect diamagnetism and no flux penetration takes place.

Thus for $H < H_{C1}$ the material exists in the superconducting state.

As the field exceeds H_{C1} the flux begins to penetrate the specimen and for $H = H_{C2}$ the complete penetration occurs and the material becomes a normal conductor.

The fields H_{C1} and H_{C2} are called the lower and upper critical fields respectively.

In the region between the fields H_{C1} and H_{C2} the diamagnetic behaviours of the material vanishes gradually and the flux density B inside the specimen remains non-zero. The Meissner effect is not strictly followed.

The specimen in this region is said to be existing in the vortex or intermediate sate which has a complicated distribution of superconducting and non-superconducting regions and may be regarded as the mixture of superconducting and normal state.

Type II superconductors are also called the hard superconductors because relatively large fields are needed to bring them back to the normal state.

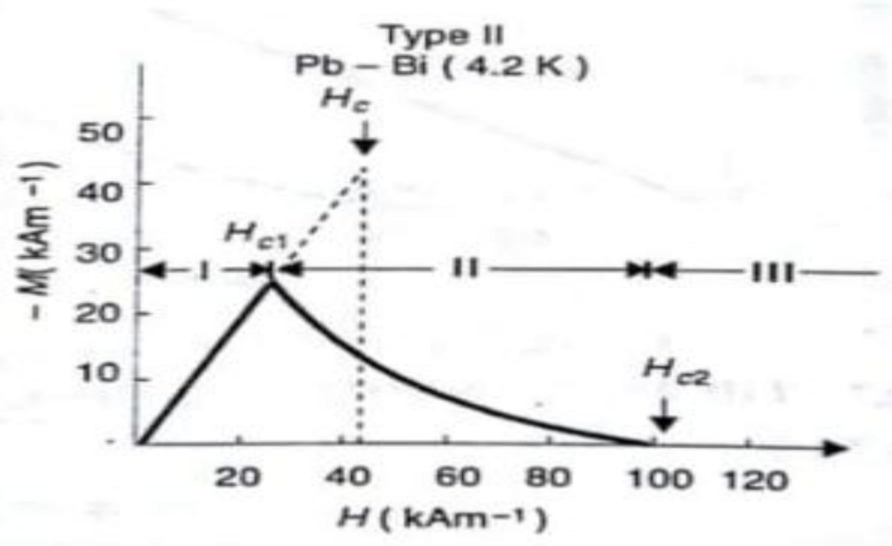


Figure 5.7 Magnetization curve of a lead-bismuth alloy at 4.2 K

Theoretical Explanation:

5.10 London equation:

There are two London equations when expressed in terms of measurable fields:

$$\frac{\partial j_s}{\partial t} = \frac{n_s e^2}{m} E,$$

$$\nabla \times j_s = -\frac{n_s e^2}{m} B$$

Here j_s is the (superconducting) current density, **E** and **B** are respectively the electric and magnetic fields within the superconductor, e is the charge of an electron or proton, m is electron mass, and n_s is a phenomenological constant loosely associated with a number density of superconducting carriers.

The two equations can be combined into a single "London Equation" in terms of a specific vector potential A_s which has been gauge fixed to the "London gauge", giving:

$$j_s = -\frac{n_s\, e^2}{m} A_s$$

In the London gauge, the vector potential obeys the following requirements, ensuring that it can be interpreted as a current density:

The first requirement, also known as Coulomb gauge condition, leads to the constant superconducting electron density $\dot{\rho}_s$ as expected from the continuity equation. The second requirement is consistent with the fact that supercurrent flows near the surface. The third requirement ensures no accumulation of superconducting electrons on the surface. These requirements do away with all gauge freedom and uniquely determine the vector potential. One can also write the London equation in terms of an arbitrary gauge A by simply defining

$$A_s = (A + \nabla \varphi),$$

where φ is a scalar function and $\nabla \varphi$ is the change in gauge which shifts the arbitrary gauge to the London gauge. The vector potential expression holds for magnetic fields that vary slowly in space.

London penetration depth

If the second of London's equations is manipulated by applying Ampere's law

$$\nabla \times B = \mu_0\, j$$

then it can be turned into the Helmholtz equation for magnetic field:

$$\nabla^2 B = \frac{1}{{\lambda_s}^2} B$$

where the inverse of the Laplacian eigenvalue

$$\lambda_s = \sqrt{\frac{m}{\mu_0\; n_s\, e^2}}$$

is the characteristic length scale, λ_s, over which external magnetic fields are exponentially suppressed: it is called the London penetration depth: typical values are from 50 to 500 nm.

For example, consider a superconductor within free space where the magnetic field outside the superconductor is a constant value pointed parallel to the superconducting boundary plane in the *z* direction. If *x* leads perpendicular to the boundary then the solution inside the superconductor may be shown to be

$$B_z(x) = B_0 e^{-x/\lambda_s}$$

From here the physical meaning of the London penetration depth can perhaps most easily be discerned.

5.11 Isotope effect :

It was observed in the year 1950 that the transition temperature of a superconductor varies with its isotopic mass M as

$$T_C \propto M^{-1/2}$$

$$T_C \; M^{1/2} = \text{constant} \qquad \text{--------(1)}$$

Thus larger the isotopic mass, lower is the transition temperature. For example the transition temperature of mercury changes from 4.185 K to 4.146 K when its isotopic mass changes from 199.5 to 203.4 amu.

The mean square amplitude of atomic or lattice vibrations at low temperatures in proportional to $M^{1/2}$ and Debye temperature, θ_D of the phonon spectrum is related to M as

$$\theta_D \, M^{1/2} = \text{constant} \qquad \text{-------(2)}$$

From equation(1) and (2)

$$\frac{T_C}{\theta_D} = \text{constant} \qquad \text{-----(3)}$$

It can be written as

$$T_C \propto \theta_D \propto M^{-1/2} \qquad \text{-----(4)}$$

The equation(3) and (4) indicate that the lattice vibrations are likely to be involved in causing superconductivity, i.e., the electron-phonon interaction might be playing an important role for the occurrence of superconductivity.

This led Frohlich to show that two electrons in a metal can effectively attract each other, the attraction being mediated by lattice vibrations. Later, in 1957 Bardeen, Cooper and Schrieffer developed a complete atomic theory of superconductivity which was based on the formation of such electron pairs known as ***cooper pairs*** and the coherent superposition of the pars into a single quantum state.

5.12 Bardeen Cooper Schrieffer (BCS) Theory:

The superconducting state of a metal may be considered to be resulting from a cooperative behaviour of conduction electrons. Such a cooperation or coherence of electrons takes place when a number of electrons occupy the same quantum state.

This however appears to be impossible for both statistical and dynamic reasons.

Statistically, electrons are fermions and hence occupy the quantum state singly. Secondly, the repulsive force among electrons tends to take them away from one another.

In metals, the repulsive forces are not very strong owing to screening. According to the BCS theory, both these difficulties can be overcome under certain circumstance. In such a case, the electrons attract each other in a certain energy range and form pairs.

Some physical arguments and ideas underlying this theory.

(i) Electron-phonon interaction

Electrons could attract each other via distortion of the lattice. When an electron moves through a crystal, it produces lattice distortion and sets the heavier ions into slow forced oscillations. Since the electron moves very fast it leaves this region much before the oscillations can die off.

Meanwhile, if another electron happens to pass through this distorted region, it experiences a force which is one of the attraction and is of the type of polarization force. This attractive force lowers the energy of the second electron.

The repulsive force between the electrons is small since the Coulomb's repulsion is instantaneous while the attraction mediated by the lattice distortion is highly retarded in time.

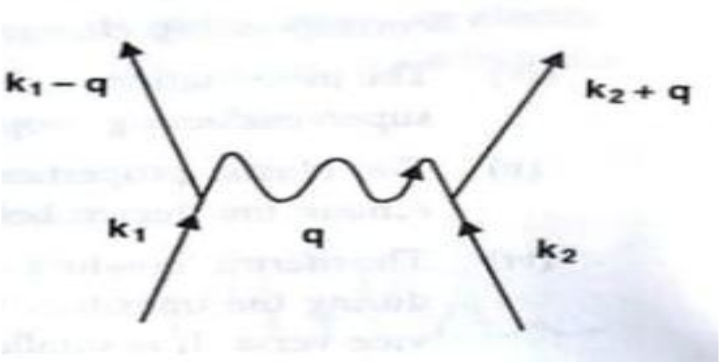


Figure 4 electron - phonon - electron interaction

In quantum-mechanical terms, the first electron of wave vector k_1 creates a virtual phonon q and loses momentum while the second electron of wave vector k_2 acquires this momentum during its collision with the virtual phonon so that the overall momentum remains conserved. This is depicted in figure. The phonons involved are called ***virtual phonons*** due to their very short life time which renders it unnecessary to conserve energy during interaction in accordance with the uncertainty principle.

Infact, the nature of the resulting electron-electron interaction depends on the relative magnitudes of the electronic energy change and the phonon energy.

If the phonon energy exceeds the electronic energy change, the interaction is attractive. Also the interaction is the strongest when the two electrons have equal and opposite momenta and spin.

$$k_1 = -k_2$$

$$S_1 = -S_2$$

Such a pair of electrons is called the Cooper pair as L.N. Cooper first discovered that it was energetically favourable for such electrons to entire into an attractive interaction of this type.

(ii) Cooper pair

A cooper pair is formed when the phonon mediated attractive interaction between two electrons dominates the usual repulsive Coulombic interaction. The energy of such a pair of electrons in the bound state is less than the energy of two unbound or free electrons.

The difference in energy is the binding energy E_B, of the electron pair and is basically the same as the energy gap parameter. Its typical value is of the order of 10^{-3} eV or about 10 K in temperature units.

The binding is the strongest when the total momentum of the pair is zero and the pairs are in a singlet state with symmetrical spatial wave function. Cooper calculated the size of the cooper pair as

$$r_0 = \frac{\hbar v_f}{E_B}$$

where v_f is the characteristic velocity of an electron in an metal and is called a ***fermi velocity***.

(iii) Existence of energy gap

The Cooper pairs are bound together by a very small energy Δ and form a new ground state which is super conducting and is separated by an energy gap 2Δ from the next lowest excited state above it.

The fermi level lies at the middle of the gap. The normal electron states lie above the energy gap and the superconducting electron states lie below the gap at the fermi surface.

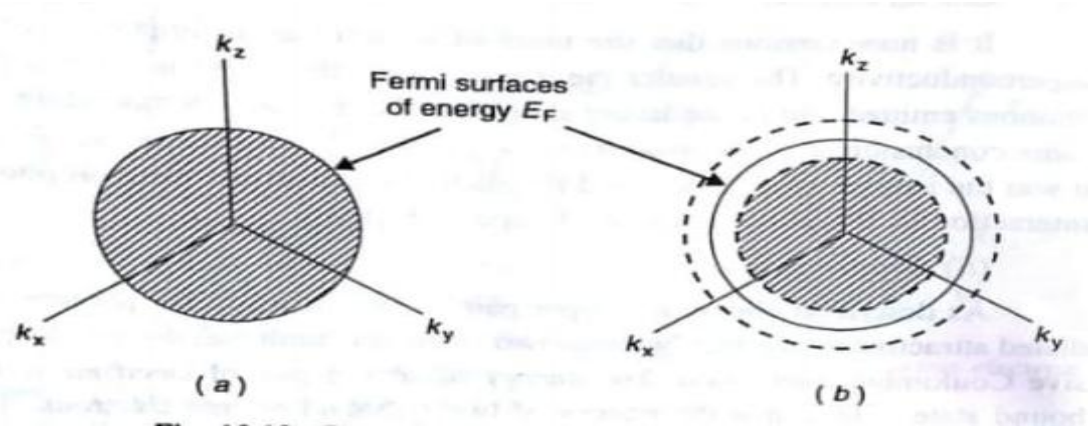


Figure 5.9 Ground state of non-interacting fermi gas (a), and BCS ground state (b) in three dimensions

5.13 Einstein Condensation (BEC):

A Bose–Einstein condensate (**BEC**) is a state of matter that is typically formed when a gas of bosons at very low densities is cooled to temperatures very close to absolute zero (−273.15 °C or −459.67 °F or 0 K).

Under such conditions, a large fraction of bosons occupy the lowest quantum state, at which microscopic quantum-mechanical phenomena, particularly wavefunction interference, become apparent macroscopically.

More generally, condensation refers to the appearance of macroscopic occupation of one or several states: for example, in BCS theory, a superconductor is a condensate of Cooper pairs.[1] As such, condensation can be associated with phase transition, and the macroscopic occupation of the state is the order parameter.

In order to fix the chemical potential μ we should choose it so that

$$\bar{N} = \sum_j \bar{n_j} = \int_0^\infty f(\varepsilon, \mu)\, g(\varepsilon) d\varepsilon \qquad \text{-------(1)}$$

where f is the Bose-Einstein distribution and $g(\varepsilon)$ is the density of states. Using the Bose-Einstein function

$$f = \frac{1}{\exp \beta(\varepsilon_j - \mu) - 1}$$

$$g(\varepsilon) = A\, V\, \varepsilon^{1/2}$$

Where $A = \frac{(\frac{2m}{\hbar^2})^{3/2}}{4\,\pi^2}$

we obtain from (1) an equation for the density ρ, defined as

$$\rho = \frac{\bar{N}}{V} \qquad \text{--------(2)}$$

which we think of as giving ρ as a function of μ:

$$\rho(\mu) = A \int_0^\infty \frac{(\varepsilon)^{3/2}}{\exp \beta(\varepsilon_j - \mu) - 1} \qquad \text{-------(3)}$$

We note that:

- ρ is an increasing function of μ. This can be seen directly from (3).
- The maximum allowed value is μ = 0. To see this we can go back to section 4 where we evaluated

$$Z_j = \sum_j \exp \beta n \left(\mu - \varepsilon_j \right)$$

as a geometric series which to converge requires

$$\exp \beta \left(\mu - \varepsilon_j \right) < 1$$

In the following we take the ground state energy as

$$\varepsilon_0 = 0$$

therefore we must have

$$\mu < 0$$

Suppose we hold T constant, and increase the density ρ by adding particles to the system from a particle reservoir. For the density to increase, we must correspondingly raise the value of μ.

However, we now find a paradox. If we choose the maximum possible value of μ (zero) in Eq.3, we obtain

$$\rho = A(kT)^{\frac{3}{2}} \int \frac{x^{1/2}}{e^x - 1} \mathrm{dx} \qquad \text{---(4)}$$

Note how we have changed integration variable to $x = \beta\varepsilon$ thus rendering the integral over x dimensionless. Then condition (4) becomes

$$\rho = \frac{(2\, m\, k\, T/\hbar^2)^{3/2}}{4\, \pi^2} \times 2.61$$

Apparently then, our attempt to pack more particles into the system fails at this point: the chemical potential is the maximum possible, but the density ρ = N/V of particles is finite, and stuck at ρ_C.

5.14 Nature of paring and condensation of Fermions:

A fermionic condensate is a superfluid phase formed by fermionic particles at low temperatures.

It is closely related to the Bose-Einstein condensate. Unlike the Bose- Einstein condensates, fermionic condensates are formed using fermions instead of bosons. The first atomic fermionic condensate was created by Deborah S. Jin in 2003.

A chiral condensate is an example of a fermionic condensate that appears in theories of massless fermions with chiral symmetry breaking. Fermionic condensates are a type of superfluid.

As the name suggests, a superfluid possesses fluid properties similar to those possessed by ordinary liquids and gases, such as the lack of a definite shape and the ability to flow in response to applied forces. However, super fluids possess some properties that do not appear in ordinary matter. For instance, they can flow at low velocities without dissipating any energy-i.e. zero viscosity.

5.15 Single particle tunneling - Josephson tunneling:

Josephson observed some remarkable effects associated with the tunnelling of superconducting electrons through a very thin insulator (1 – 5 nm) sandwiched between two superconductors. Such an insulating later forms a weak link between the superconductors which referred to as the Josephson junction. The effect observed by Josephson is given as follow:

(i) DC Josephson effects :

According to this effect, a dc current flow across the junction even when no voltage is applied across it.

(ii) AC Josephson effect

If a dc voltage is applied across the junction rf current oscillation of frequency

$$f = \frac{2\,eV}{h}$$

are set up across it. For example, a dc voltage of 1μV produces a frequency of 483.7 MHz. by measuring the frequency and the voltage, the value of e/h can be determined. Hence this effect has been utilized to measure e/h very precisely and may be used as a means of establishing a voltage standard.

Furthermore, an application of rf voltage along with the dc voltage can result in the flow of direct current through the junction.

5.16 SQUIDS:

Consider the arrange shown in figure which is known as the ***superconducting quantum interference device*** (SQUIDS). It consists of a ring of superconducting material having two side arms A and B which act as an entrance and exit for the supercurrent respectively.

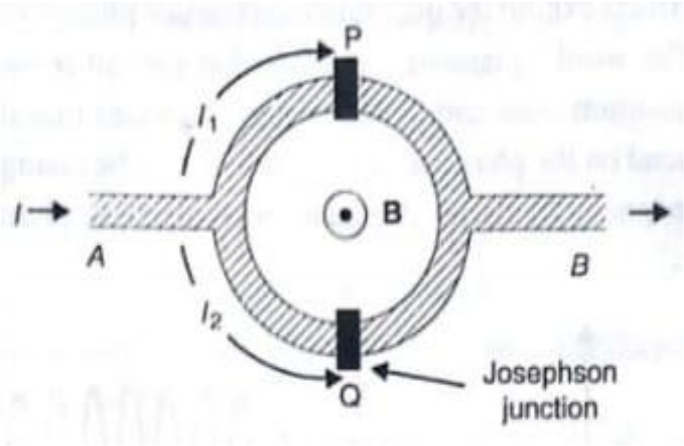


Figure 5.10 SQUIDS

The insulating layers P and Q may, in general, have different thickness and let the currents through these layers be I_1 and I_2 respectively. The variation I_1 and I_2 versus the magnetic field as obtained by Joklevic, Lambe, Mercerean and Silver are shown in figure. Both I_1 and I_2 very periodically with the magnetic field, the periodicity of I_1 being greater than that of I_2.

The variations of I_2 is an interference effect of the two junctions while that of I_1 is a diffraction effect that arises from the finite dimension of each junction. Since the current is very sensitive to very small changes in the magnetic field, the SQIDS can be used as a very sensitive galvanometer.

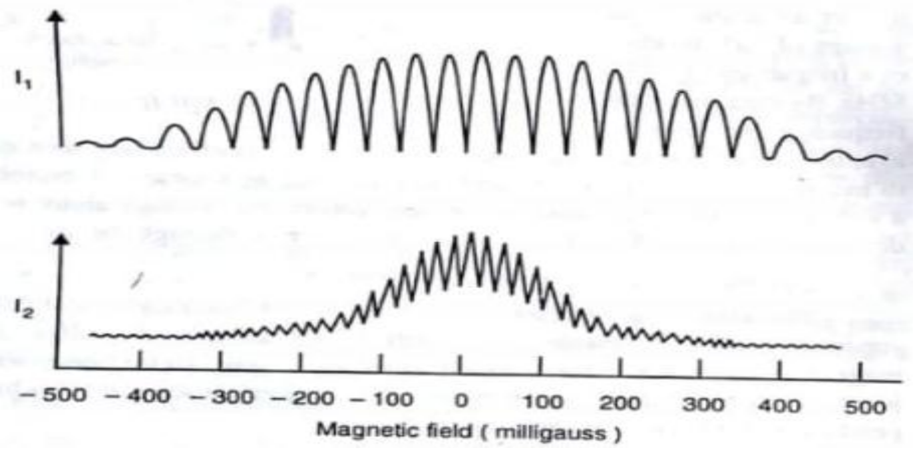


Figure 5.11 Dependence of super currents on the magnetic flux through the SQUID arrangement