



M.Sc. PHYSICS - I YEAR
DKP15 : SOLID STATE PHYSICS - I
SYLLABUS

UNIT I: CRYSTAL STRUCTURE AND DIFFRACTION

Recapitulation of basic concepts- crystal systems- Bravais Lattice- Miller indices-symmetry elements- symmetry groups- simple crystal structures (sodium chloride, cesium chloride, diamond and zinblende structures)

Bragg's law- Laue equations- reciprocal lattice- Brillouine zones- atomic scattering factor- geometrical structure factor- experimental methods of structure analysis (the laue, rotating crystal and powder methods)

UNIT II: CRYSTAL BINDING AND ELASTIC PROPERTIES OF SOLIDS

Crystal bindings: Ionic bond- covalent bond- molecular bond- Hydrogen bond- metallic bond- Vanderwaal's bond-Binding energy of crystals- polaron

Elastic properties: Stress components- displacement and strain components- elastic compliances and stiffness constants- relation between elastic compliances and stiffness constants -elastic constants for cubic isotropic crystals-elastic waves- experimental determination of elastic constants

UNIT III: LATTICE DYNAMICS AND THERMAL PROPERTIES

Lattice dynamics: Concept of phonons- momentum of phonons- normal and Umklapp process- vibrations of one dimensional monoatomic and diatomic linear lattices- inelastic scattering of neutrons by phonons

Thermal properties: Theories of specific heat- Dulong and Petit's law- Einstein theory and Debye's theory- Widemann Franz law

UNIT IV: ELECTRONIC PROPERTIES OF SOLIDS

Free electron gas model in three dimensions: Density of states- Fermi energy- Effect of temperature- heat capacity of electrons- experimental heat capacity of metals- thermal effective mass- electrical conductivity and ohm's law- Hall effect- failure of the free electron gas Band theory of solids- periodic potential and Bloch's theorem- Kronig-Penny model-wave equation of electron in a periodic potential- periodic, extended and reduced zone schemes of energy representation- number of orbitals in an energy band- classification of metals, semi conductors and insulators- tight binding method and its applications to FC and BCC structures.

UNIT V: SUPER CONDUCTIVITY

Experimental survey: Superconductivity and its occurrence- destruction of superconductivity by magnetic field- Meissner effect- Type I and II super conductors- entropy- free energy- heat capacity- energy gap- isotope effect

Theoretical survey: Thermodynamics of the superconducting transition- London equation- coherence length- salient features of the BCS theory of super conductivity- flux quantization in a superconductivity ring- DC and AC Josephson effects

Books for Study and Reference

1. Introduction to Solid State Physics - 7 The edition - by Charles Kittel
2. Solid State Physics by Neil W Ashroff and N.David Mermin
3. Solid State Physics by S.L. Kakani and C. Hemarajani
4. Elementary Solid State Physics by M. Ali Omar



UNIT – I

CRYSTAL STRUCTURE AND DIFFRACTION

Recapitulation of basic concepts – crystal systems – Bravais Lattice – Miller indices – symmetry elements – symmetry groups – simple crystal structures (sodium chloride, cesium chloride, diamond and zinc blende structures)

Bragg's law – Laue equations – reciprocal lattice – Brillouine zones – atomic scattering factor – geometrical structure factor – experimental methods of structure analysis (the laue, rotating crystal and powder methods).

Basic Concepts of Crystal

Solid state physics is largely concerned with crystals and electrons in crystals. The structure of all crystals can be described in terms of a lattice, with a group of atoms attached to every lattice point. This group of atoms is called the basis. That is the atomic arrangement in a crystal is called crystal structure.

A lattice is a regular periodic array of points in space. A space lattice is defined as an infinite array of points in three dimensions in which every point has surroundings identical to that of every other point in the array.

Each lattice point associated a group of atoms or molecules identical in composition, called the basis or the pattern. When the basis repeated in space it forms the crystal structure. The crystal structure is formed when a basis of atoms is attached identically to every lattice point.

ie., Lattice + basis \rightarrow crystal structure

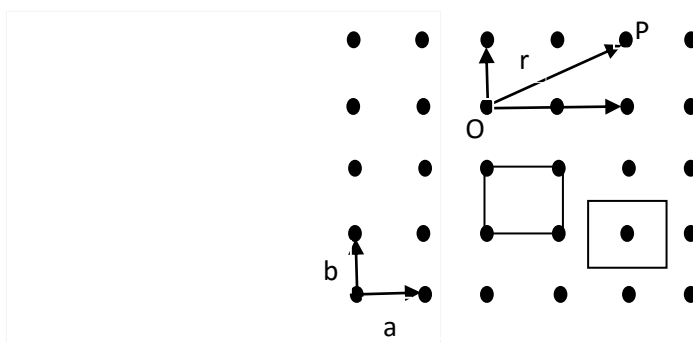


Figure 1: Lattice



Let 'a' and 'b' are having equal magnitude and be unity. The angle between them is 90° . Then a and b are called the fundamental translational vectors that generate the square array.

Let O be the origin and P be a lattice point with position vector r , then the translational vectors, $\vec{r} = la + mb$. l and m are integers, in Figure $l = 2$ and $m = 1$

In 3 dimensional lattice, translational vectors $\vec{r} = la + mb + nc$.

A three dimensional space lattice is generated by repeated translation of three non coplanar vectors a, b and c. The lattice translation vectors a, b, c are said to be primitive if any two points r, r' from which the atomic arrangements looks same as

$$r' = r + u_1a + u_2b + u_3c$$

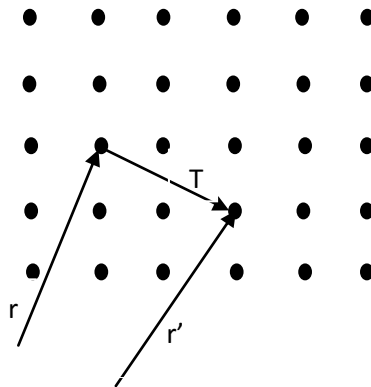


Figure1. 2: Translation Vector

The lattice translation operation is defined as $T = u_1a + u_2b + u_3c$, any two lattice points are connected by a vector of this form.

Unit cell and Lattice parameter of an unit cell

A unit cell is defined as a parallelepiped formed by the three basis vectors a, b and c along the three crystallographic axes x, y and z respectively. The unit cell is the smallest unit, which when repeated in space indefinitely, generates the space lattice. The square obtained by joining four neighbouring lattice points is a unit cell (fig.1). Each lattice point is common for four unit cells. \therefore The effective number of lattice points in the unit cell is $(\frac{1}{4} \times 4 = 1)$ one only. (or) the unit cell can be visualized by taking one lattice point at the centre of the square.



The volume of the cell is $V = (\vec{a} \times \vec{b}) \cdot \vec{c}$. If this volume contains only one lattice point, it is termed as primitive unit cell.

Crystallographic axes :

The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.

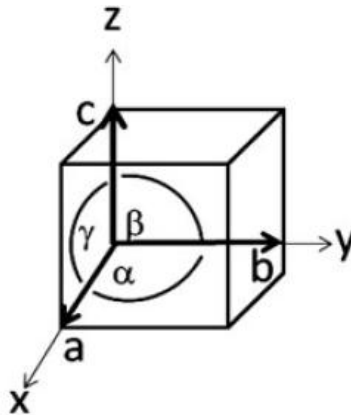


Fig. 1. 3 Crystal axes

Primitives

- The intercepts, a, b and c define the dimensions of a unit cell and are known as its primitives.
- The Angles between the three crystallographic axes are known as interfacial angles α , β and γ .
- The intercepts (primitives) a, b, c and interfacial angles α , β and γ are the basic lattice parameters. This determines the form and size of the unit cell.
- The unit cell formed by the primitives a, b and c are called primitive cell. (only one lattice point).
- It is not necessary that the unit cell should be a primitive cell (unit cell of various crystals contain two or more lattice point)

Wigner-Seitz Unit Cell:

The wigner-Seitz unit cell about a lattice point is the region of space that is closer to that particular point than to any other lattice point. The space is completely filled. The



construction of wigner-Seitz unit cell is same for both two and three dimensional lattices. The following procedure is adopted.

1. For a given lattice point, draw lines to connect this point to all nearby lattice points.
2. Draw new lines or planes at the midpoint of each of the previous lines.

The smallest area (in two dimensions) or volume(in three dimensions) enclosed in this way gives the the wigner-Seitz primitive unit cell.

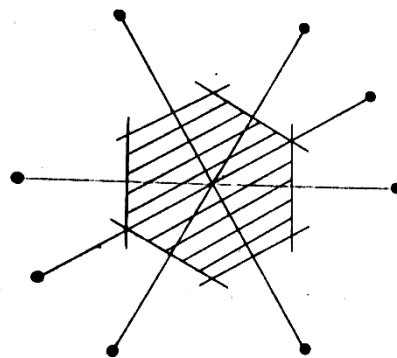


Fig. 1.4 Wigner-Seitz unit cell

Bravais lattice

There are only 14 distinguishable ways of arranging points in three dimensional space and these 14 arrangements are known as Bravais lattice. And the Bravais lattices belong to 7 crystal systems. They are tabulated as below

Crystal type	Bravais Lattice	Symbol
Cubic	Simple	P
	Body centred	I
	Face centred	F
Tetragonal	Simple	P
	Body centered	I
Orthorhombic	Simple	P
	Base-centred	C
	Body centred	I
	Face centred	F
Monoclinic	Simple	P



	Base – centred	C
Triclinic	Simple	P
Trigonal	Simple	P
Hexagonal	Simple	P

Crystal system	Unit vector	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

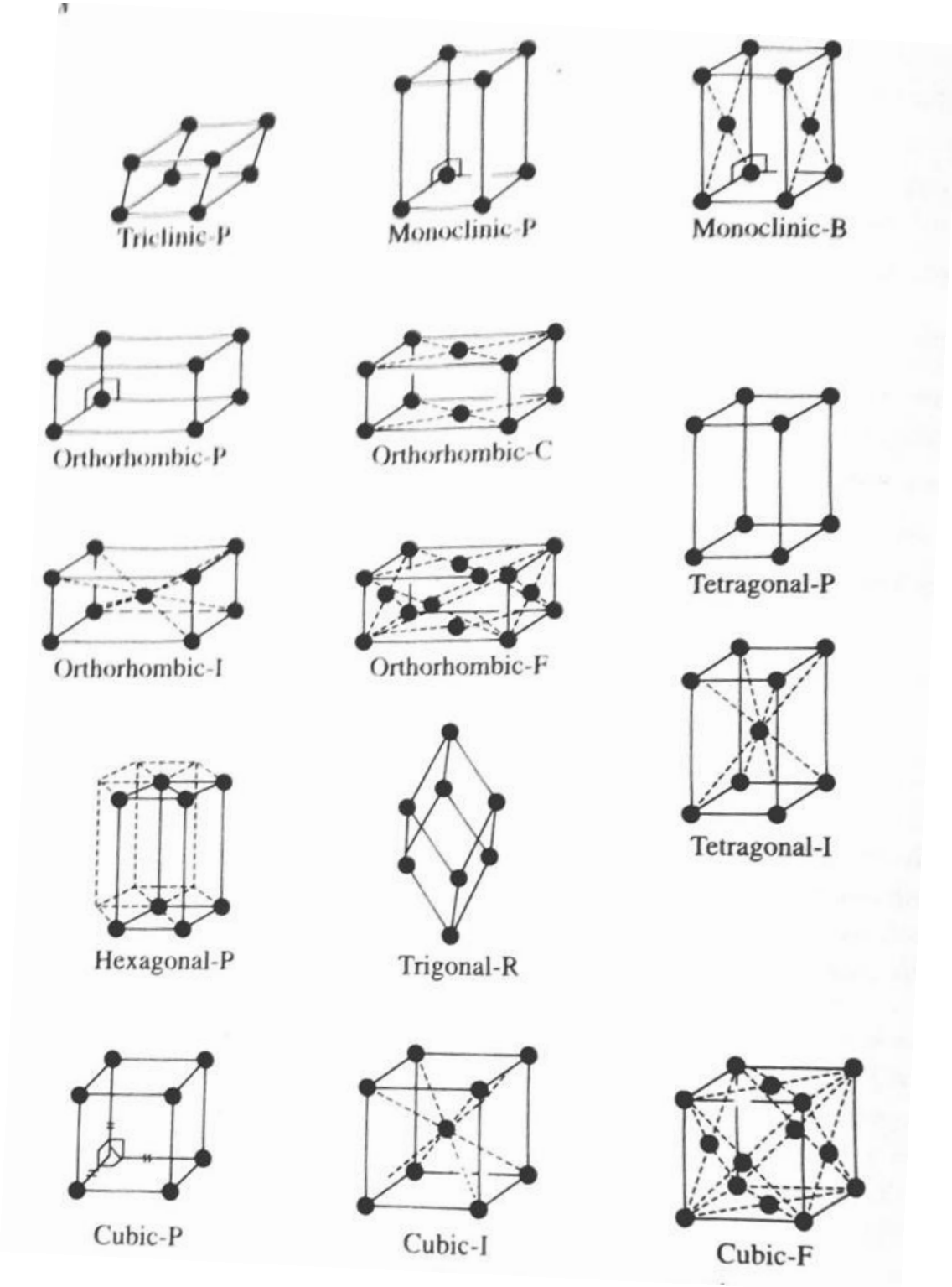


Fig. 1.5 The fourteen Bravais or space lattices



Miller Indices:

A crystal lattice may be considered as an assembly of a number of equidistant parallel planes passing through the lattice points and are called lattice planes. For a given lattice, these sets of planes can be selected in a number of ways. The inter-planar spacing for a set of parallel planes is fixed but for different sets of planes the inter-planar spacing varies as also the density of lattice points.

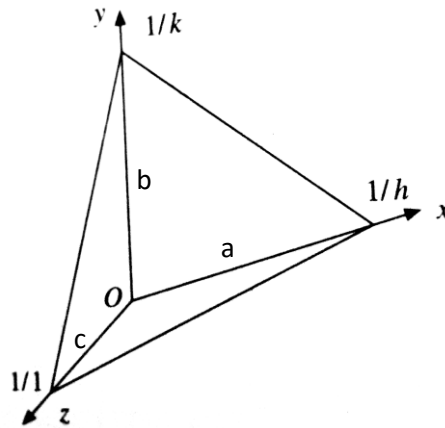


Fig. 1.6 Intercepts along x, y and z axes

The equation of plane in three dimensions having the intercepts a, b and c (Fig. 1.5) along the axes x, y, z respectively will be

$$\frac{x}{a} + \frac{y}{b} + \frac{z}{c} = 1$$

Let $h = \frac{1}{a}$, $k = \frac{1}{b}$, and $l = \frac{1}{c}$ then the above equation becomes

$hx + ky + lz = 1$ This equation describes the first lattice plane, nearest to the origin, in a set of parallel, identical and equally spaced planes. The set of three integers h, k and l are expressed as (h,k,l) called Miller indices .

Then the equation can be written as $\frac{x}{1/h} + \frac{y}{1/k} + \frac{z}{1/l} = 1$

Where $1/h$, $1/k$ and $1/l$ are intercepts along x, y and z axes respectively.

To obtain Miller indices of a plane the following procedure will be adopted:

1. Determine the intercepts of the plane along x, y, z axes in terms of lattice parameters.
2. Divide these intercepts by the proper unit translations.
3. Find their reciprocals.
4. If Fraction results, multiply each of them by the smallest common divisor.



5. Put the final integers in parenthesis (hkl) to get the required Miller Indices.

Example: In a crystal, a plane cuts intercepts of 2a, 3b and 6c along three crystallographic axes. Determine the miller indices

Solution:

1	Intercepts	2a	3b	6c
2	Division by unit translations	$\frac{2a}{a} = 2$	$\frac{3b}{b} = 3$	$\frac{6c}{c} = 6$
3	Reciprocals	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{6}$
4	After clearing fraction	3	2	1
5	The required Miller indices are (321)			

Crystal symmetry :

The definite ordered arrangement of the faces and edges of a crystal is known as crystal symmetry. It is a powerful tool for the study of the internal structure of crystals.

A symmetry operation is one that leaves the crystal and its environment invariant. It is an operation performed on an object or pattern which brings it to a position which is indistinguishable from the old position. The geometrical locus about which a group of finite operations act is known as 'Symmetry element'. There are translation, rotation, reflection and inversion operations, called point operations. The combined translation and point operations are known as compound operation.

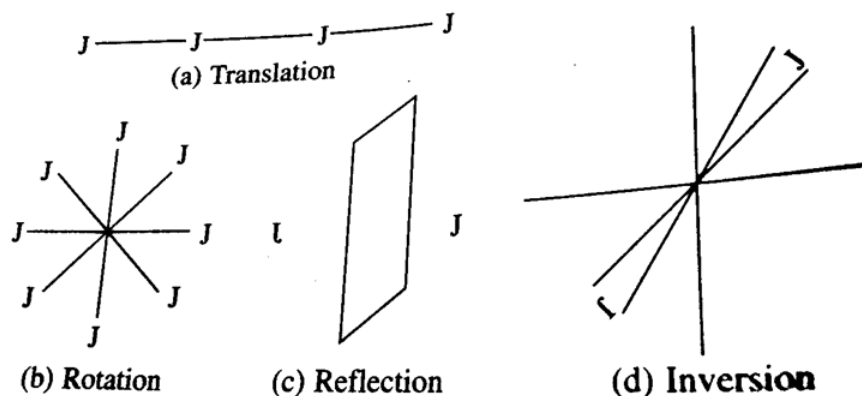


Fig. 1.7 Simple Symmetry Operations

A rotation about an axis that passes through a lattice point is a symmetry operation. Lattice can be found that one, two, three, four and six fold rotation axes carry the lattice into



itself corresponding to rotations by integral multiples of $2\pi, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4},$ and $\frac{2\pi}{6}$ radians.

Mirror reflection 'm' about a plane through a lattice point. The inversion is composed of a rotation of π followed by reflection.

There are three symmetry elements

1. The centre of symmetry
2. The planes of symmetry
3. The axes of symmetry

Centre of symmetry

In an unit cell of cubic lattice the point at the body centre represents the centre of symmetry (Fig.1.8). Any line passing through it meets the surface of the crystal at equal distance in both directions. Since the centre lies at equal distances from various symmetrical positions it is also named as centre of inversion. For every lattice point of position vector 'r' there will be a corresponding lattice point at the position '- r'. It is equivalent to reflection.

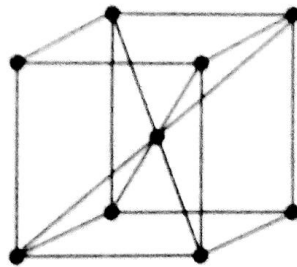
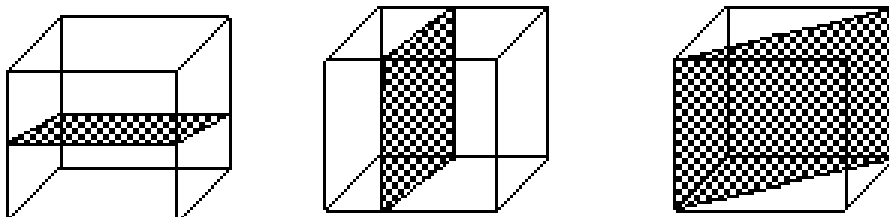


Fig. 1.8 Centre of Symmetry

Plane of symmetry :

An imaginary plane passing through a crystal, such that portions on the two sides of the plane are exactly alike, is known as plane of symmetry.

For cube, three planes of symmetry parallel to the faces and six diagonal planes of symmetry. \therefore Total planes of symmetry = 3+6=9. These planes divide the crystal into two halves.



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Fig. 1.9 Plane of Symmetry



Axis of symmetry

A body is said to possess rotational symmetry about an axis if after rotation of the body about this axis through some angle, it appears same as prior to rotation.

If a rotation through an angle $\frac{360^\circ}{n}$ about an axis brings the crystal into the congruent position, then the axis is called n-fold axis of symmetry.

If $n=1$, $\frac{360^\circ}{1} = 360^\circ$ ie., the crystal has to be rotated through an angle 360° about an axis to achieve self-coincidence. This axis is called identity axis.

$n=2$, $\frac{360^\circ}{2} = 180^\circ$, This axis of rotation is called diad axis.

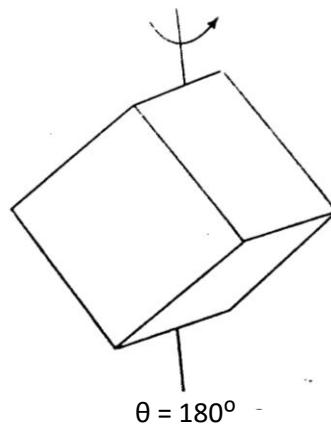


Fig.1.10 Diad axis

$n=3$, $\frac{360^\circ}{3} = 120^\circ$, This axis of rotation is called triad axis.

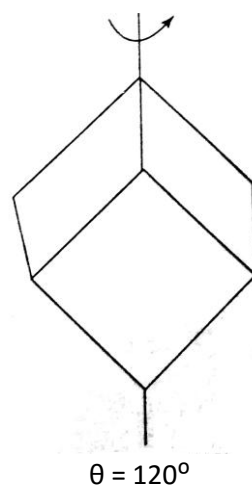


Fig.1.11 Triad axis



$n=4, \frac{360^\circ}{4}=90^\circ$, This axis of rotation is tetrad axis.

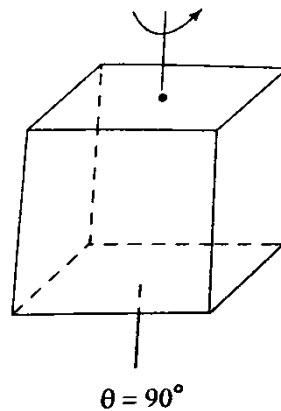


Fig.1.12 Tetrad axis

$n=6, \frac{360^\circ}{6}=60^\circ$, axis of rotation is hexad axis.

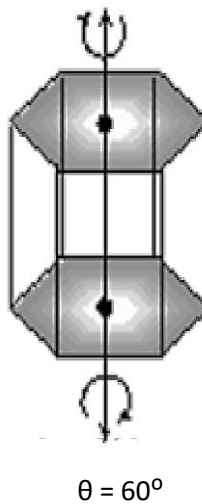


Fig.1.13 Hexad axis

Crystallographic symmetry elements of the cube :-

a)	centre of symmetry	-	1
b)	plane of symmetry	-	9
c)	Tetrad axes	-	3
d)	Triad axes	-	4
e)	Diad axes	-	6
Total number of symmetry elements			23



Combination of symmetry elements:

Different combinations of the basic symmetry elements give rise to different symmetry points in the crystal. There are 32 compatible combinations of these point group symmetry elements. These 32 combinations are called point groups. All the possible combinations of 32 point groups with 14 Bravais lattices are considered, 230 space groups.

RotoInversion axis:

Roto Inversion is a symmetry element. It is a hybrid operation of a proper rotation and an inversion. A crystal has a roto inversion axis if it is brought into self coincidence by rotation about that axis followed by inversion. It is found that when 90° rotation followed by inversion is giving four times original position is obtained. This is an example of four fold rotoinversion (fig.1.13).

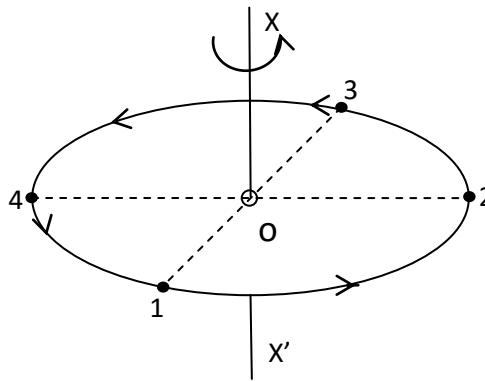


Fig. 1.13 Four fold Roto inversion symmetry

Screw axis:

This symmetry element screw axis has a hybrid operation of a proper rotation with a translation parallel to the rotation axis. Rotation through an angle θ from A to B about xy axis and translation from B to C by T is an example for screw axis (fig.)

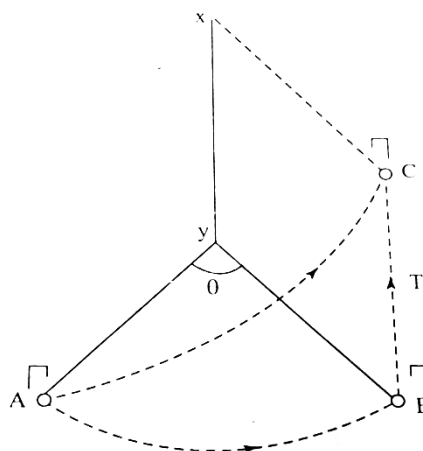


Fig. 1.14 Screw axis



Glide Plane:

This symmetry element has a hybrid operation of a reflection with a translation parallel to the reflection plane. If the upper layer of atoms is moved through a distance $a/2$ and then reflected in the plane mm' the lower plane of atoms is generated.

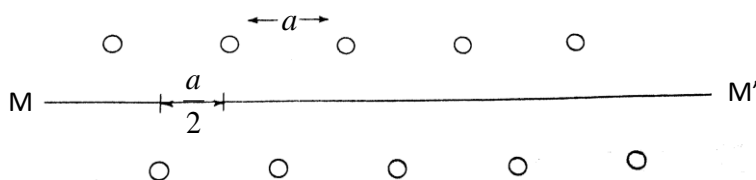


Fig.1.15 Glide Plane

Symmetry group:

A symmetry group is a set of symmetry operators that are combined together according to a particular set of rules:

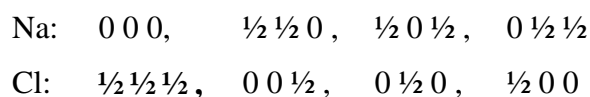
1. The resulting action from the combination of two symmetry operators must always be equivalent to the action of a single symmetry operator that belongs to the same group.
2. The group must always contain the identity symmetry operator.
3. Each symmetry operator in the group must have an inverse operator belonging to the group.
4. Beyond the scope of this course is the associative rule specifying the way in which symmetry operators are combined with each other.

Simple Crystal Structure:

Sodium Chloride Structure:

The Sodium Chloride Structure is shown in figure 1.16. It consists of equal number of sodium and chlorine ions placed at alternate points of a simple cubic lattice. Each ion has six of the other kind of ions as nearest neighbours. The lattice is face centred cubic. The basis consists of one Sodium (Na) ion and one Chlorine ion (Cl) separated by one half the body diagonal of a unit cube.

There are four units of NaCl in each cube, with ions in the positions:



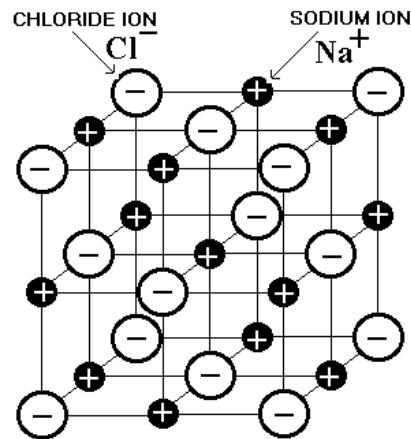


Fig.1.16 Sodium chloride Structure

In figure 1.16, the Sodium Chloride structure, Na^+ and Cl^- are shown by small and big circles respectively. Big and small circles form interpenetrating fcc lattice.

Cesium chloride Structure:

The Cesium chloride (CsCl) structure is shown in fig. 1.17. It consists of equal number of Cesium and Chlorine ions. This is described as simple cubic lattice with a basis consisting of a Cesium ion at the corners or origin (000) and a chlorine ion at the body centred position ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$). One type of ions is situated at the body centred positions so that each ion has eight other type of ions as nearest neighbour. The value of a is 4.11 \AA

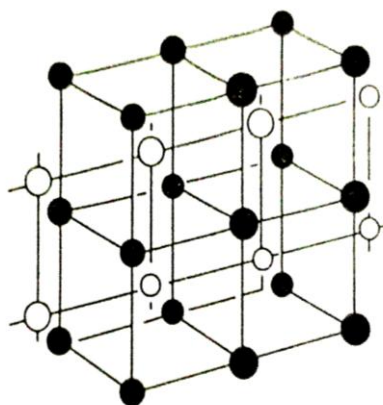


Fig.1.17. The Cesium Chloride Structure

In figure 1.17 the Cesium Chloride structure the filled circle ● and the hollow circle ○ represents two different ions which form interpenetrating simple cubic lattice



Diamond Structure:

The space lattice of Diamond is fcc. The primitive basis has two identical atoms at 000 , $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ associated with each lattice point. It is characterised by a tetrahedral bond arrangement as shown in fig.1.18. Each atom has four nearest neighbours and twelve next nearest neighbours. The diamond structure is relatively empty, ie the proportion of available volume filled by hard spheres is 0.34 (the atomic packing factor) only. It has 46% of filling factor for closest structure of fcc or hcp

Example: Carbon, Silicon, Germanium and Tin with lattice constant $a = 3.56, 5.43, 5.65$ and 6.46 \AA

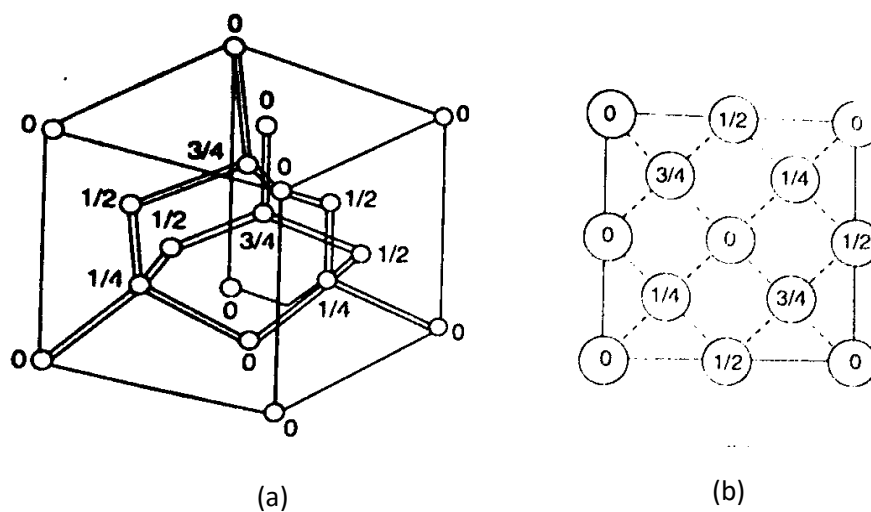


Fig.1.18 Diamond Structure

In figure 1.18, (a) denotes the crystal structure of diamond showing the tetrahedral bond arrangement and (b) shows the atomic positions in the cubic cell of diamond structure projected on a cube face.

Zinc Blende Structure:

The Zinc Blende (ZnS) has equal number of Zinc and Sulphur ions distributed on a Diamond lattice so that each has four of the opposite kind as nearest neighbours. Zinc atoms are placed on one fcc lattice and S atoms on the other fcc lattice.

The coordinates of Zn atoms are $000, 0 \frac{1}{2} \frac{1}{2}, \frac{1}{2} 0 \frac{1}{2}, \frac{1}{2} \frac{1}{2} 0$

The coordinates of S atoms are $\frac{1}{4} \frac{1}{4} \frac{1}{4}, \frac{1}{4} \frac{3}{4} \frac{3}{4}, \frac{3}{4} \frac{1}{4} \frac{3}{4}, \frac{3}{4} \frac{3}{4} \frac{1}{4}$

The Diamond structure allows centre of inversion symmetry but the Zinc Blende structure does not have inversion symmetry.

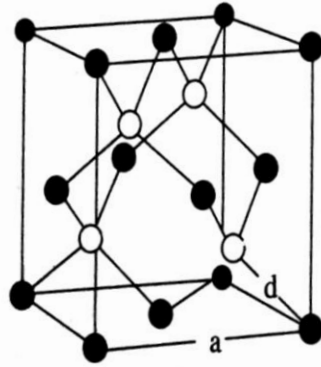


Fig.1.19 Crystal Structure of Cubic Zinc Sulphide

Example: CuF, CuCl, AgI, GaAs with $a = 4.26, 5.41, 6.47, 5.65 \text{ \AA}$

Bragg's law:

Bragg's law is the fundamental law of x-ray crystallography. Bragg's diffraction was first proposed by William Lawrence Bragg and William Henry Bragg, in the year 1913, during their experiments on crystalline solids. Bragg's diffraction occurs when electromagnetic radiation, or subatomic particle, waves have wavelengths that are comparable to atomic spacing in a crystal lattice.

The penetrating X-ray travels down the internal layer, gets reflected, and travels back through the same distance as the back of the surface. The distance traversed by the wave is dependent on the distance between the layers of the lattice and the angle of incidence of the X-ray

Bragg's law describes the angles for the coherent and incoherent scattering from a crystal lattice. As per Bragg's law, when X-rays are scattered from a crystal lattice, the peaks of scattered intensity correspond to the following conditions:

1. Angle of incidence is equal to the angle of scattering
2. Difference in path length is an integer value of the number of wavelengths

Bragg's law gives the condition for the maximum intensity, and the details about the crystal lattice. In conditions where the crystal structure is known, the wavelength of the X-rays incident on the crystal can be calculated using Bragg's law.

.Bragg's equation is given below:

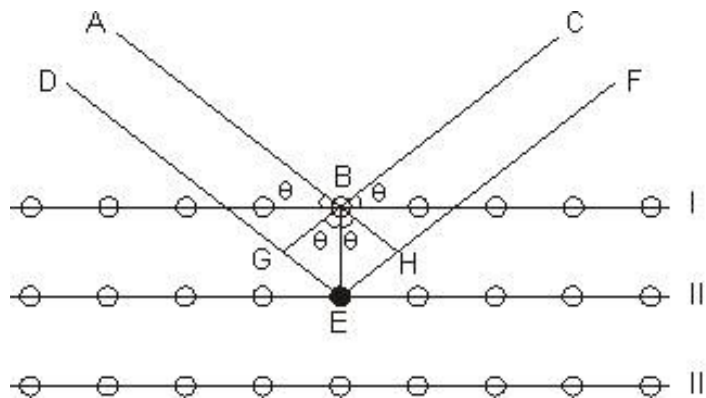
$$2 d \sin \theta = n \lambda$$



where n is an integer, λ is the wavelength of a beam of x-rays incident on a crystal with lattice planes separated by distance d , and θ is the angle of scattering known as Bragg angle.

Derivation of Bragg's Law:

Consider a crystal in which atoms are arranged in a periodic manner with interatomic spacing ' d '. A narrow beam of monochromatic X-Ray of wavelength λ is allowed to fall on a crystal at a glancing angle θ . The crystal acts as a diffracting grating with atoms as the opaque part and the spacing between them as the transparent part.



Let AB and DE be the incident rays and BC and EF be the corresponding reflected rays the path difference between the rays ABC and DEF is (GE+EH) therefore the path difference is given by

$$\Delta = GE + EH$$

$$\Delta = d \sin \theta + d \sin \theta$$

$$\Delta = 2d \sin \theta$$

Constructive interference takes place only when the path difference is equal to $n\lambda$ that is when the following condition satisfied

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



Laue Equations:

If an X-ray beam impinges on a row of atoms, each atom can serve as a source of scattered X-rays. The scattered X-rays will reinforce in certain directions to produce zero, first, and higher-order diffracted beams. Diffraction from a crystal can be obtained with the following assumptions:

- i. Let ' S_0 ' be a unit vector in the direction of the incident wave, and ' S ' be a unit vector in the direction of the scattered wave.
- ii. let R_1 and R_2 be the position vectors of a pair of atoms in a Bravais lattice, and let $r_{12} = R_1 - R_2$.

Let us consider the waves scattered by R_1 and by R_2 and traveling different path lengths as shown in Figure 1.18. The difference in path length is $|R_2A - BR_1|$. But this is clearly equal to $|r_{12} \cdot S - r_{12} \cdot S_0|$. We define S as $S = S - S_0$; then the difference in path length for the two rays is given by

$$\Delta = |r_{12} \cdot S| \quad (1.11)$$

For constructive interference, this must be equal to an integral number of wave length.

ie.,
$$r_{12} \cdot S = m \lambda \quad (1.12)$$

where m is an integer and λ is the wave length.

Constructive interference will occur only if

$$R_n \cdot S = \text{integer} \times \lambda \quad (1.13)$$

for every lattice vector R_n in the crystal. in general there will be different integers for different R_n . Therefore

$$R_n = n_1 a_1 + n_2 a_2 + n_3 a_3. \quad (1.14)$$

Equation (1.13) will be satisfied if
$$a_i \cdot S = p_i \lambda \quad (1.15)$$

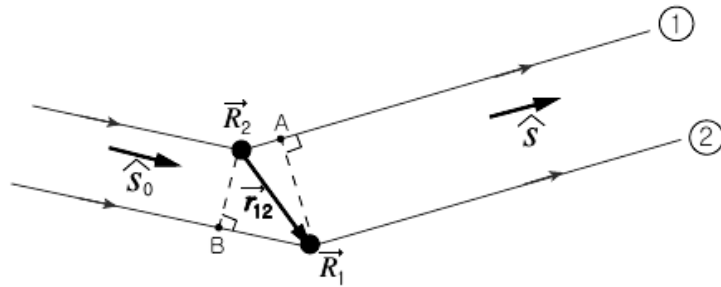


Fig. 1.18. Scattering of X-rays by a pair of atoms in a crystal

where h_i is the smallest set of integers and p is a common multiplier. Then \mathbf{S} can be expressed as

$$\mathbf{S} = (\mathbf{S} \cdot \mathbf{a}_1) \mathbf{b}_1 + (\mathbf{S} \cdot \mathbf{a}_2) \mathbf{b}_2 + (\mathbf{S} \cdot \mathbf{a}_3) \mathbf{b}_3 \quad (1.16)$$

Therefore condition Equation (1.13) is satisfied and constructive interference from every lattice site occurs if

$$\mathbf{S} = p (h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3) \lambda \quad (1.17)$$

or

$$\frac{\mathbf{S}}{\lambda} = p \mathbf{G}_h \quad (1.18)$$

where \mathbf{G}_h is a vector of the reciprocal lattice. Equation (1.18) is called the Laue equation.

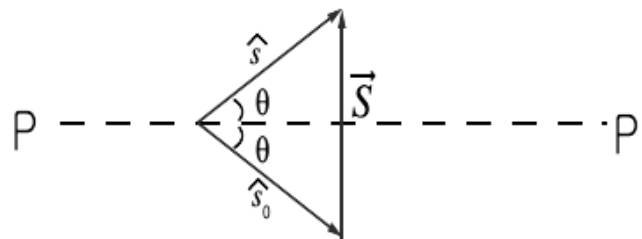


Fig. 1.19. Relation between the scattering vector $\mathbf{S} = \mathbf{s} - \mathbf{s}_0$ and the Bragg angle θ

Connection of Laue Equations and Bragg's Law

From Equation (1.18) \mathbf{S} must be perpendicular to the planes with Miller indices $(h_1 h_2 h_3)$.

The distance between two planes of this set is

$$d(h_1 h_2 h_3) = \frac{2\pi}{|\mathbf{G}_h|} = p \frac{\lambda}{|\mathbf{S}|} \quad (1.19)$$



We know that \mathbf{S} is normal to the reflection plane PP' with Miller indices $(h_1h_2h_3)$. From Figure 1.19, it is apparent that $|S| = 2\sin\theta$. Therefore, Equation (1.19) can be written by

$$2d(h_1h_2h_3)\sin\theta = p\lambda$$

where p is an integer. According to Laue's equation, associated with any reciprocal lattice vector, $G_h = h_1b_1 + h_2b_2 + h_3b_3$ there is an X-ray reflection satisfying the equation $\lambda^{-1}S = pG_h$ where p is an integer

Reciprocal Lattice:

The reciprocal lattice of a lattice (usually a Bravais lattice) is the lattice in which the Fourier transform of the spatial wave function of the original lattice (or direct lattice) is represented.

If a, b, c are primitive vectors of the crystal lattice, then a^*, b^* and c^* are primitive vectors of the reciprocal lattice and defined as

$$a^* = 2\pi \frac{b \times c}{a \cdot (b \times c)}, \quad b^* = 2\pi \frac{c \times a}{a \cdot (b \times c)}, \quad c^* = 2\pi \frac{a \times b}{a \cdot (b \times c)}$$

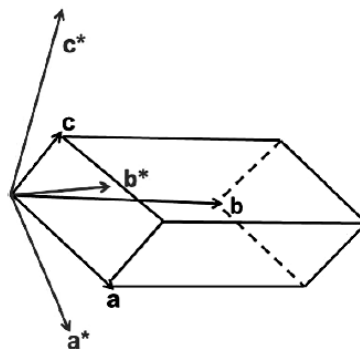


Fig. 1.20 Reciprocal basic vectors $a^*, b^*,$ and c^* and their relationship to the real-space basic vectors $a, b,$ and c

Where $a \cdot (b \times c)$ is the volume V of a unit cell in real space(Fig. 1.20). The previous relationships can be rewritten as

$$a^* = 2\pi \frac{b \times c}{V}, \quad b^* = 2\pi \frac{c \times a}{V}, \quad c^* = 2\pi \frac{a \times b}{V}$$



Each vector is orthogonal to two axis vectors of the crystal lattice. Vectors a , b , and c are related to a^* , b^* , and c^* as

$$a^* \cdot b = a^* \cdot c = b^* \cdot a = b^* \cdot c = c^* \cdot a = c^* \cdot b = 0$$

and $a^* \cdot a = b^* \cdot b = c^* \cdot c = 2\pi$

The magnitude of a^* is inversely proportional to the magnitude of a . The same relationship is true for b^* and c^* . This means the size of a reciprocal lattice unit cell is inversely proportional to the size of the real space unit cell. One can obtain the reciprocal unit vectors a^* , b^* , and c^* from a , b , and c in the previous relationships. A reciprocal lattice can be generated by

$$G(hkl) = ha^* + kb^* + lc^*$$

where h , k , and l are integers.

The relationship between the reciprocal unit vectors and the real space unit vectors in a two-dimensional lattice shown in Fig. 1.21.

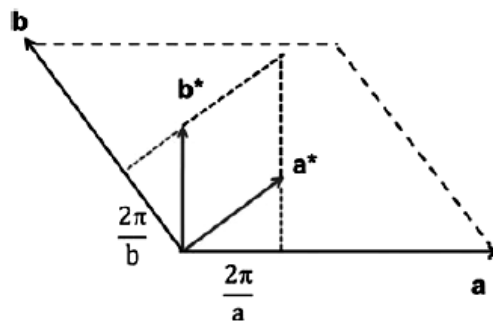


Fig. 1.21 Relationship between real-space basic vectors a and b and reciprocal-space basic vectors a^* and b^*

A two-dimensional real space unit mesh consists of unit vectors a and b that are parallel to the page. The a^* is perpendicular to b , and the b^* is perpendicular to a . Also, the length of a^* projected on a is $2\pi/a$ and is the inverse of the length of a . Also, b^* and b are related in a similar way.

For example, if one has the (001) plane in real space, the reciprocal lattice direction in the reciprocal space can be determined as $G(hkl) = G(001) = c^*$ since $h=0$, $k=0$, and $l=1$. This means $G(001)$ is perpendicular to a and b (because of the cross product of $a \times b$) and its magnitude is inversely proportional to the magnitude of c .



A Brillouin Zone:

A Brillouin Zone is the unit cell of the reciprocal lattice. It is defined as the Wigner-Seitz cell of the reciprocal lattice. Brillouin Zone formed by perpendicular bisectors of G vectors.

It is constructed as the set of points enclosed by the Bragg planes, the planes perpendicular to a connection line from the origin to each lattice point and passing through the midpoint. Alternatively, it is defined as the set of points closer to the origin than to any other reciprocal lattice point. The whole reciprocal space may be covered without overlap with copies of such a Brillouin Zone.

The first Brillouin zone is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin. The concept of Brillouin zone is particularly important in the consideration of the electronic structure of solids. There are also second, third, etc., As a result, the first Brillouin zone is often called simply the Brillouin zone. (In general, the n-th Brillouin zone consist of the set of points that can be reached from the origin by crossing $n - 1$ Bragg planes.)

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 Fig.1.22. The second Brillouin zone is also Shown; it contains electrons with k values from π/a to $2\pi/a$ for electrons moving in the $\pm x$ and $\pm y$ directions, with the possible range of k values narrowing as the diagonal directions are approached.

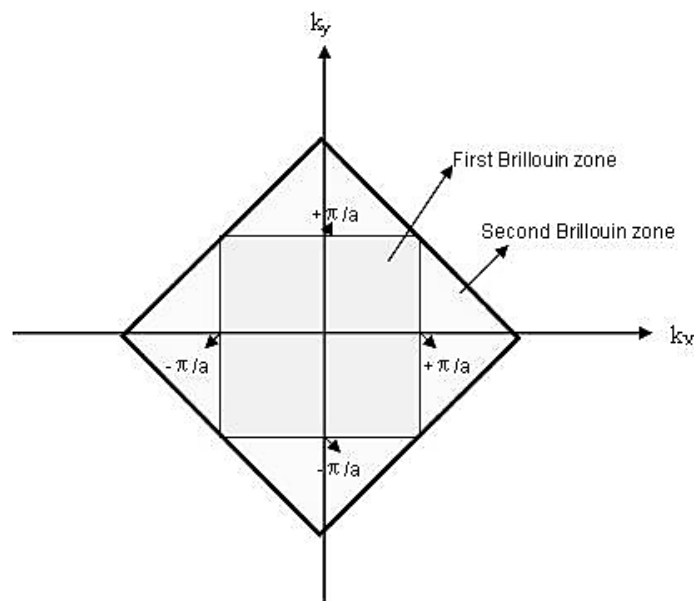


Fig.1.22 The first and second Brillouin zones of a two-dimensional square lattice



The atomic form factor:

The atomic form factor, or atomic scattering factor, is a measure of the scattering amplitude of a wave by an isolated atom. The atomic form factor depends on the type of scattering, which in turn depends on the nature of the incident radiation, typically X-ray, electron or neutron. The common feature of all form factors is that they involve a Fourier transform of a spatial density distribution of the scattering object from real space to momentum space (also known as reciprocal space). For an object that is spherically symmetric, the spatial density distribution can be expressed as a function of radius, $\rho(r)$ so that the form factor, $f(Q)$ is defined as

$$f(Q) = \int \rho(r) e^{iQ \cdot r} d^3r$$

where $\rho(r)$ is the spatial density of the scatterer about its center of mass ($r = 0$) and Q is the momentum transfer. As a result of the nature of the Fourier transform, the broader the distribution of the scatterer ρ in real space r , the narrower the distribution of f in Q ; i.e., the faster the decay of the form factor.

For crystals, atomic form factors are used to calculate the structure factor for a given Bragg peak of a crystal.

The structure factor:

The structure factor is a mathematical function describing the amplitude and phase of a wave diffracted from crystal lattice planes characterised by Miller indices hkl . And the structure factor is defined as the ratio of the amplitude of radiation scattered by the entire unit cell to the amplitude of radiation scattered by a single point-electron at the origin for the same wavelength.

The structure factor for a system with many atoms, each with its own form factor f_j and sitting within the unit cell at a site with the crystallographic coordinates (u_j, v_j, w_j) is described by:

$$F_{hkl} = \sum_{j=1}^N f_j \exp[2\pi i (h u_j + k v_j + l w_j)] \quad (1)$$

The square of the structure factor is an indication of the intensity of any spot/peak/intensity in the diffraction pattern corresponding to the Bragg conditions being satisfied for the particular hkl .



When the atoms are identical, all the f_j are equal and equal to f . Then

$$F_{hkl} = f S \quad (2)$$

Where $S = \exp[2\pi i(hu_j + kv_j + lw_j)]$ is called the geometrical structure factor.

Equation (2) defines the structure factor S as the ratio of the total scattering amplitude F to the atomic structure factor f

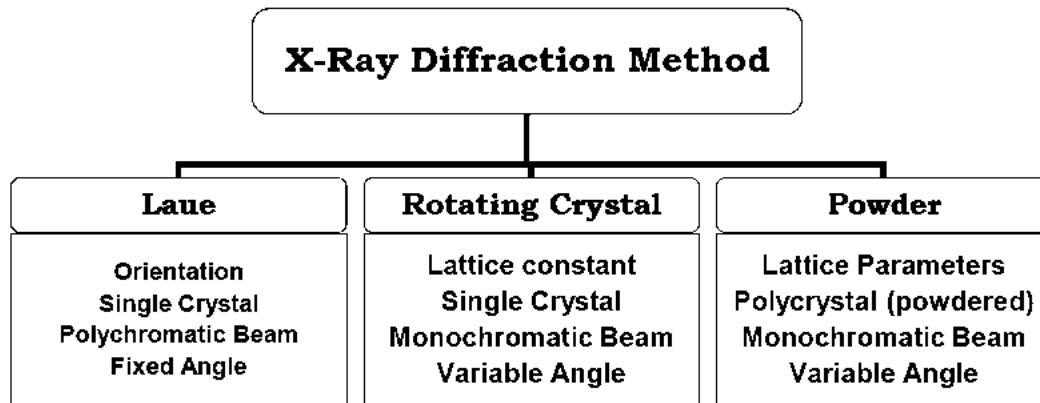
Since the intensity is proportional to the square of the amplitude, the intensity I of the diffracted beam is given by $I = |F|^2 = F^* F$ where F^* is the complex conjugate of F

X-ray diffraction

X-ray diffraction is a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law $n\lambda = 2d \sin \theta$. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice.

There are many types of X-ray camera to sort out reflections from different crystal planes. We will study only three types of X ray photograph that are widely used for the simple structures.

1. Laue photograph
2. Rotating crystal method
3. Powder photograph



The Laue method

The Laue method is mainly used to determine the orientation of large single crystals while radiation is reflected from, or transmitted through a fixed crystal. The diffracted beams form arrays of spots, which lie on curves on the film.

The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and θ involved.

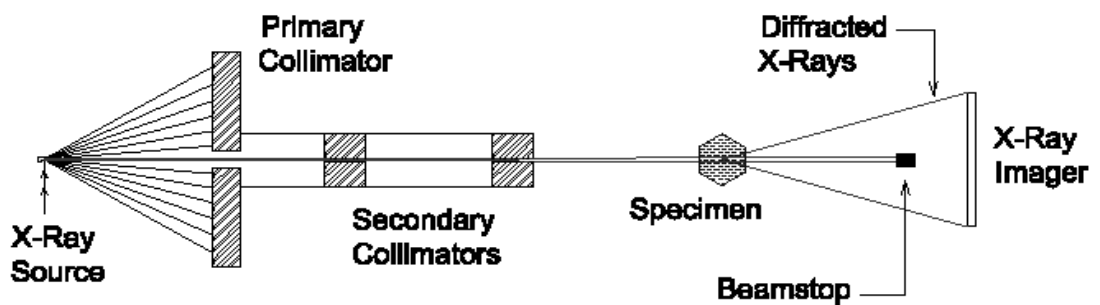


Fig.1.23 Schematic representation of Laue Technique

In the back-reflection method, the film is placed between the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded. One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.

In the transmission Laue method, the film is placed behind the crystal to record beams which are transmitted through the crystal. One side of the cone of Laue reflections is defined by the



transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.

The symmetry of the spot pattern reflects the symmetry of the crystal when viewed along the direction of the incident beam. Laue method is often used to determine the orientation of single crystals by means of illuminating the crystal with a continuous spectrum of X-rays;

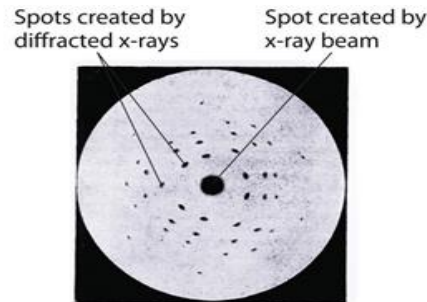


Fig. X-ray diffraction pattern captured on photographic film

Therefore, the Laue method is mainly used to determine the crystal orientation. Although the Laue method can also be used to determine the crystal structure, several wavelengths can reflect in different orders from the same set of planes, with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity difficult. Rotating crystal method overcomes this problem

Rotating crystal method

In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis.

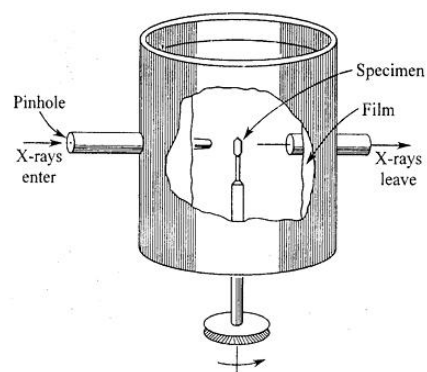


Fig.1.25 Schematic representation of Rotating Crystal Technique



As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed.

Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle θ at which a d_{hkl} reflection occurs is known, can be determined.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.

THE POWDER METHOD

If a powdered specimen is used, instead of a single crystal, then there is no need to rotate the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample. This method is useful for samples that are difficult to obtain in single crystal form.

The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors a , b and c which define the unit cell for the crystal. For every set of crystal planes, by chance, one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

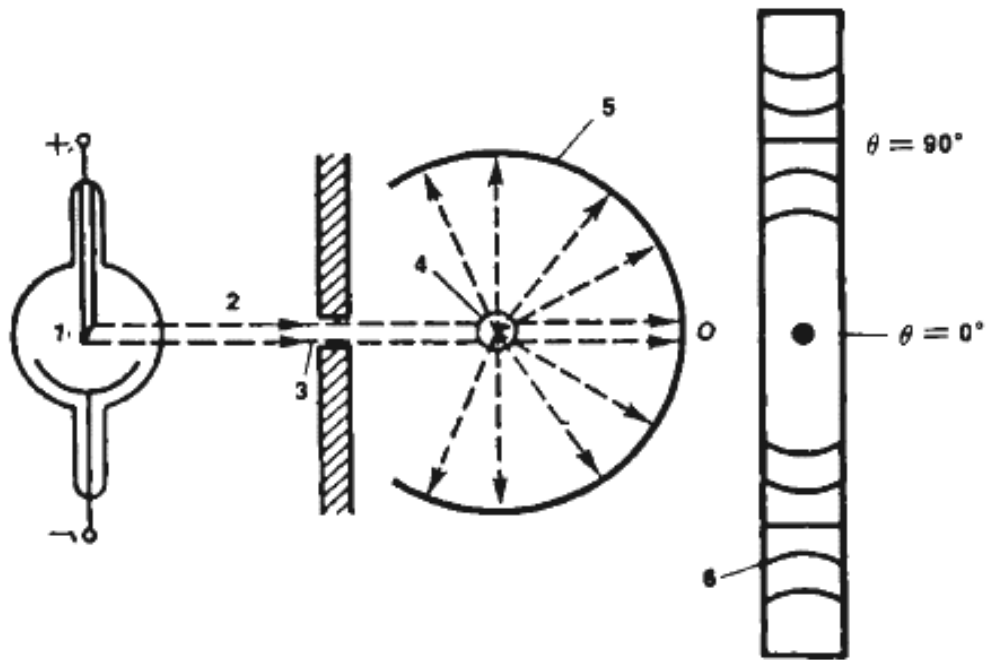


Fig.1.26 Experimental arrangement in powder method

A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.

A very small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract x-rays. The specimen is placed in the Debye Scherrer camera and is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator. The powder diffracts the x-rays in accordance with Bragg's law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.

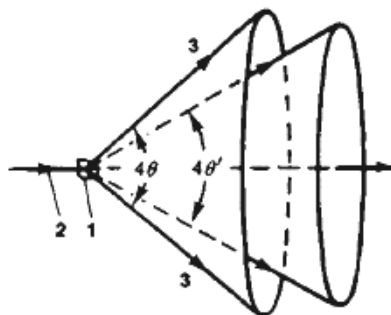


Fig.1.27 Cones of Diffracted Beams of X ray



When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.

Application of XRD

1. Differentiation between crystalline and amorphous materials;
2. Determination of the structure of crystalline materials;
3. Determination of electron distribution within the atoms, and throughout the unit cell;
4. Determination of the orientation of single crystals;
5. Determination of the texture of polygrained materials;
6. Measurement of strain and small grain size.....etc

Advantages

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward
- X-ray is the cheapest, the most convenient and widely used method.
- X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

Disadvantage

- Homogeneous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacings, *hkl*)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample



- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle reflections
- They do not interact very strongly with lighter elements.



Unit II

CRYSTAL BINDINGS AND ELASTIC PROPERTIES OF SOLIDS

Crystal bindings: Ionic bond – covalent bond – molecular bond – Hydrogen bond – metallic bond – Van der wall bond – Binding energy of crystals – Polarons

Elastic Properties: Stress components – displacement and strain components – elastic compliances and stiffness constants – relation between elastic compliances and stiffness constants – elastic constants for cubic isotropic crystals – elastic waves – experimental determination of elastic constants

Cohesive energy:

The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation with the same electronic configuration.

The term lattice energy is used in the discussion of ionic crystals and is defined as the energy that must be added to the crystal to separate its component ions into free ions at rest at infinite separation.

The inert gas crystals are weakly bound. The alkali metal crystals have intermediate values of the cohesive energy. The transition element metals are strongly bound. The melting temperature and bulk moduli vary as the cohesive energies.

Crystals of inert gases

The inert gases form the simplest crystal. The crystals are transparent insulators, weakly bound with low melting temperatures. The atoms have very high ionization energies. In the crystal, the inert gas atoms pack together as closely as possible. The crystal structures are all cubic close packed (fcc)

As the cohesive energy of an atom in the crystal is less, the electron distribution in the crystal cannot be distorted. No much energy is available to distort free atom charge distributions. Part of this distortion gives the Van der waals interaction.

Vander Waals London interaction

Consider two identical inert gas atoms at a separation R large in comparison with the radii of the atoms. As the atoms are neutral, there is no interaction between atoms. Therefore the inert gas atoms have no cohesion and could not condense. But the



atom induce dipole moments in each other and the induced moments cause an attractive interaction between the atoms.

Consider two identical linear harmonic oscillator separated by R . Each oscillator bears charges $\pm e$ with separations x_1 and x_2 (fig.2.1). The particle oscillates along x axis.

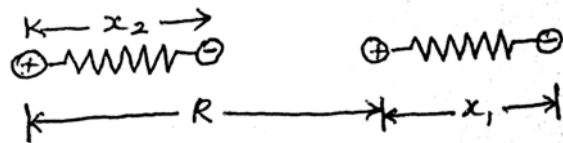


Figure 2.1

Let P_1 and P_2 be momenta, C be the force constant. Then the Hamiltonian of the unperturbed system is

$$H_0 = \frac{1}{2m} P_1^2 + \frac{1}{2} C x_1^2 + \frac{1}{2m} P_2^2 + \frac{1}{2} C x_2^2$$

where $C = m\omega_0^2$, ω_0 is the frequency of the strongest optical absorption line of the atom

Let H_1 be coulomb interaction energy of the two oscillators. The inter nuclear coordinate is R .

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2}$$

$|x_1|, |x_2| \ll R$, reduce to lowest order

$$\therefore H_1 \approx -\frac{2e^2 x_1 x_2}{R^3}$$

H_1 can be diagonalized by the normal mode transformation

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2); \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2)$$

On solving,

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a); \quad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a)$$

The subscripts s and a denote symmetric and antisymmetric modes of motion.

Further,

$$P_1 = \frac{1}{\sqrt{2}}(P_s + P_a); \quad P_2 = \frac{1}{\sqrt{2}}(P_s - P_a)$$

\therefore The total Hamiltonian H ($H_0 + H_1$) after transformation is



$$H = \left[\frac{1}{2m} P_s^2 + \frac{1}{2} \left(C - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{1}{2m} P_a^2 + \frac{1}{2} \left(C + \frac{2e^2}{R^3} \right) x_a^2 \right]$$

The two frequencies of the coupled oscillators are

$$\omega = \left[\left(C \pm \frac{2e^2}{R^3} \right) / m \right]^{1/2} \approx \omega_0 \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{CR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{CR^3} \right)^2 + \dots \right]$$

Where $\omega_0 = \left(\frac{C}{m} \right)^{1/2}$

The zero point energy of the system is $\frac{1}{2} \hbar (\omega_s + \omega_a)$

$$\Delta U = \frac{1}{2} \hbar (\Delta \omega_s + \Delta \omega_a) = -\hbar \omega_0 \frac{1}{8} \left(\frac{2e^2}{CR^3} \right)^2 = -\frac{A}{R^6}$$

This attraction varies as the minus sixth power of the separation of the two oscillators. This is known as Van der Waals interaction (or) London interaction (or) induced dipole-dipole interaction. The interaction is a quantum effect. An approximate value of A for identical atoms is given by $\hbar \omega_0 \alpha^2$ where $\hbar \omega_0$ is the energy of the strongest optical absorption line and α is the electronic polarizability.

Repulsive interaction

As the two atoms approach close, their charge distributions gradually overlap. At sufficiently close separations, the overlap energy is repulsive; because of Pauli Exclusion Principle (Two electrons cannot have all their quantum numbers equal).

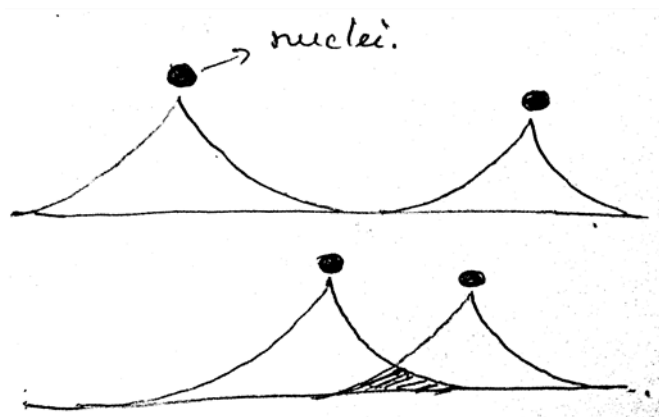


Figure 2.2



When the charge distributions of two atoms overlap, there is a tendency for electrons from atom B to occupy in part states of atom A already occupied by electrons of atom A and vice versa. Thus the electron overlap increases the total energy of system and gives a repulsive contribution to the interaction. The overlap energy depends on the radial distribution of charge about each atom.

The empirical repulsive potential is $\frac{B}{R^{12}}$ where B is a positive constant. When used together with a long range attractive potential, the total potential energy of two atoms at separation R as

$$U(R) = 4 \epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

where ϵ and σ are new parameters. $4 \epsilon \sigma^6 \equiv A$ and $4 \epsilon \sigma^{12} \equiv B$. U(R) is Lennard-Jones potential. The force between the two atoms is $-dU/dR$.

Equilibrium Lattice constant.

The cohesive energy of an inert gas is summing the Lennard Jones potential over all pairs of atoms in the crystal.

The total potential Energy is
$$U_{tot} = \frac{1}{2} N \left(4 \epsilon \left[\sum_j \left(\frac{\sigma}{P_{ij} R} \right)^{12} - \sum_j \left(\frac{\sigma}{P_{ij} R} \right)^6 \right] \right) \text{-----(I)}$$

Where N is the number of atoms in crystal, $P_{ij}R$ is the distance between reference atom i and any other atom j and $\frac{1}{2}$ to compensate for counting twice each pair of atoms.

For fcc structure,
$$\sum_j P_{ij}^{-12} = 12.13188 \quad \sum_j P_{ij}^{-6} = 14.45392 \text{-----(a)}$$

The nearest neighbours are 12 sites. U_{tot} be minimum with respect to R (nearest neighbour distance)

i.e.
$$\frac{dU_{tot}}{dR} = 0 = -2N \epsilon \left[12(12.13) \frac{\sigma^{12}}{R^{13}} - 6(14.45) \frac{\sigma^6}{R^7} \right]$$

whence
$$\frac{R_0}{\sigma} = 1.09 \text{-----(b)}$$

R_0 is the equilibrium value. From measurement on the gas phase, we have predicted the lattice constant of the crystal.

Cohesive energy : substituting a and b in I we get



$$U_{\text{tot}}(R) = 2N \epsilon \left[12.13 \left(\frac{\sigma}{R} \right)^{12} - 14.45 \left(\frac{\sigma}{R} \right)^6 \right]$$

At $R=R_0$, $U_{\text{tot}}(R_0) = - (2.15)4N\epsilon$

This is same for all inert gases. This cohesive energy is calculated for atoms at rest.

Ionic crystals

Ionic crystals are made up of positive (+) and negative (-)ve ions.

Example: Sodium chloride and Cesium chloride structure.

The electronic configurations of all ions of a simple ionic crystal correspond to closed electronic shells as in the inert atoms

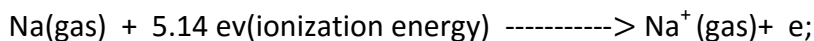
Example: Lithium fluoride

The configuration of neutral atom Li : $1s^2 2s$; F : $1s^2 2s^2 2p^5$

The configuration of singly charged ions Li^+ : $1s^2$; F^- : $1s^2 2s^2 2p^6$ as for Helium and Neon atoms.

Inert gas atoms have closed shells and the charge distributions are spherically symmetric. The charge distribution on each ion in an ionic crystal is approximately spherical symmetry.

The distance between a positive ion and nearest negative ion in crystalline sodium chloride is 2.81×10^{-8} cm and the attractive potential energy of the two ions is 5.1 eV. This energy is close When compared with the lattice energy of the crystalline NaCl (7.9 eV experimental values)



Electrostatic (or) madelung energy

The main contribution to the binding energy of ionic crystals is electrostatic and is called the Madelung energy..

Let the energy of all interaction involving the ion i, $U_i = \sum_j U_{ij}$

where U_{ij} is the interaction energy between ions i and j. The summation includes all ions except $j=i$



U_{ij} may be written as the sum of repulsive potential ($\lambda \exp(-r/\rho)$) and a coulomb potential $\pm q^2/r$

$$\therefore U_{ij} = \lambda \exp\left(-\frac{r_{ij}}{\rho}\right) \pm \frac{q^2}{r_{ij}} \quad \text{+for like charges and - for unlike charges}$$

ρ is a measure of the range of the repulsive interaction when $\rho = r$. the repulsive interaction is reduced to e^{-1} of the value at $r=0$.

The total lattice energy U_{tot} of a crystal composed of N molecules or $2N$ ions as $U_{\text{tot}} = NU_i$ (N , not $2N$ because each pair of interaction only once)

The total lattice energy is defined as the energy required separating the crystal into individual ions at infinite distances apart.

Let $r_{ij} \equiv P_{ij}R$, R is the nearest neighbor separation in the crystal

$$U_{ij} = \lambda \exp(-R/\rho) - \frac{q^2}{R} \quad (\text{nearest neighbours})$$

$$= \pm \frac{1}{P_{ij}} \frac{q^2}{R} \quad (\text{otherwise})$$

Then $U_{\text{tot}} = N U_i = N \left(z \lambda e^{-\frac{R}{\rho}} - \alpha \frac{q^2}{R} \right)$ where Z is the number of nearest neighbours

of any ion and $\alpha \equiv \sum_j \frac{\pm}{P_{ij}} \equiv \text{Madelung constant}$.

The value of Madelung constant is important in the theory of an ionic crystal.

$$\text{At equilibrium separation } \frac{dU_{\text{tot}}}{dR} = 0$$

$$\text{i.e., } N \frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho} \exp\left(-\frac{R}{\rho}\right) + \frac{N\alpha q^2}{R^2} = 0$$

$$\frac{N\alpha q^2}{R^2} = \frac{Nz\lambda}{\rho} \exp\left(-\frac{R}{\rho}\right)$$

$$R_0^2 \exp(-R/\rho) = \frac{\rho \alpha q^2}{z \lambda}$$

R_0 can be determined if ρ , λ of the repulsive interaction are known



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

$$= N \left(\frac{\rho\alpha q^2}{R_0^2} - \frac{\alpha q^2}{R_0} \right)$$

$$= -\frac{N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0} \right)$$

The $-\frac{N\alpha q^2}{R_0}$ is the Madelung energy

Evaluation of the Madelung constant:

$$\text{The Madelung constant } \alpha = \sum_j \frac{(\pm)}{P_{ij}}$$

If the reference ion is positive, + sign will apply; if the reference ion is negative, -ve sign will apply.

$$\frac{\alpha}{R} = \sum_j \frac{(\pm)}{r_j}$$

r_j is distance of the j^{th} ion from the reference ion . R is the nearest neighbor distance.

To find the Madelung constant ,consider the infinite line of ions of alternate sign



Let -ve ion as the reference ion, R be the distance between the adjacent ions.

$$\frac{\alpha}{R} = 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \dots \right]$$

2 represents r_j for both sides of reference ion

$$\alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \right]$$

2 because there are two ions.

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

\therefore The Madelung constant for the one dimensional chain is $\alpha = 2 \ln 2$

Example : Madelung constant for NaCl = 1.747565



$$\text{CaCl} = 1.762675$$

$$\text{Zns} = 1.6381$$

Covalent crystals

The covalent bond is formed from two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. The spins of the two electrons in the bond are anti parallel. e.g The binding of molecular Hydrogen(H_2).

The strongest binding occurs when the spins of the two electrons are anti parallel. The binding depends on the relative spin orientation. The spin dependent coulomb energy is called the exchange interaction.

The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the shells are not filled, electrons overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter.

The difference between Cl_2 and Ar_2 is that the Cl atom has five electrons in the 3p shell and the Ar atom has six electrons filling the shell so that the repulsive interaction is stronger in Ar than in Cl.

The elements C, Si and Ge lack four electrons with respect to filled shells and thus these elements can have an attractive interaction associated with charge overlap. The electron configuration of carbon is $1s^2 2s^2 2p^2$. To form a tetrahedral system of covalent bonds, the carbon atom must first be promoted to the electronic configuration $1s^2 2s^2 2p^3$. This promotion from the ground state requires 4 eV, an amount more than regained when the bonds are formed.

There is a continuous range of crystals between the ionic and the covalent limit.

Metals

Metals having high electrical conductivity with a large number of free electrons called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal.

In some metals, the interaction of the ion cores with the conduction electrons makes a large contribution to the binding energy. But the metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.



The binding energy of an alkali metal crystal is less than that of an alkali halide crystal, the bond formed by a conduction electron is not very strong. The interatomic distances are relatively large in alkali metals, Because the K.E of the conduction electrons is lower at large interatomic distances. This leads to weak binding.

Metals tends to crystallize in closed packed structure hcp, fcc, bcc and not in loosely packed structure such as diamond. In transition metals, there is additional binding energy from inner electrons and are having high binding energy.

Hydrogen bond

Neutral Hydrogen atom has only one electron , it can form a covalent bond with only one other atom.

Under certain conditions, an atom of Hydrogen is attracted by two atoms, thus forming hydrogen bond between them, with a bond energy of 0.1 eV. Hydrogen bond is largely ionic in character. It is formed only between the electro negative atoms like F, O and N. Hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond.

In the extreme ionic form of the hydrogen bond the hydrogen atom loses its electron to another atom in the molecule. The bare proton forms the hydrogen bond. The hydrogen bond connects only two atoms

The hydrogen bond is an important part of the interaction between water molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. It is important in certain ferroelectric crystals.

Polaron

A **polaron** is a quasi-particle used in condensed matter physics to understand the interactions between electrons and atoms in a solid material. The polaron concept was first proposed by Lev Landau in 1933 to describe an electron moving in a dielectric crystal where the atoms move from their equilibrium positions to effectively screen the charge of an electron, known as a phonon cloud. This lowers the electron mobility and increases the electron's effective mass.

The general concept of a polaron has been extended to describe other interactions between the electrons and ions in metals that result in a bound state, or a lowering of energy compared to the non-interacting system. Major theoretical work has focused on



solving Froehlich and Holstein Hamiltonians. This is still an active field of research to find exact numerical solutions to the case of one or two electrons in a large crystal lattice, and to study the case of many interacting electrons.

Experimentally, polarons are important to the understanding of a wide variety of materials. The electron mobility in semiconductors can be greatly decreased by the formation of polarons. Organic semiconductors are also sensitive to polaronic effects, which is particularly relevant in the design of organic solar cells that effectively transport charge. The electron phonon interaction that forms Cooper pairs in low- T_c superconductors (type-I superconductors) can also be modeled as a polaron, and two opposite spin electrons may form a bipolaron sharing a phonon cloud. This has been suggested as a mechanism for Cooper pair formation in high- T_c superconductors (type-II superconductors). Polarons are also important for interpreting the optical conductivity of these types of materials.

The polaron, a fermionic quasiparticle, a bosonic quasiparticle analogous to a hybridized state between a photon and an optical phonon.

Elastic Properties

An elastic modulus is just the ratio of stress to the associated strain. The basic elastic equations and its physical meaning are as follows:

For a stress, σ (hydrostatic, shear, axial...), resulting in an elastic deformation strain,

$$\epsilon : \sigma = M\epsilon$$

where M is an elastic modulus (bulk, shear, Young's...).

For a hydrostatic stress (i.e., equally applied forces in all directions), which is often assumed within planetary interiors, the stress is the hydrostatic pressure: $\sigma = \Delta P$

and the strain is the relative change in volume of the system: $\epsilon = -\Delta V/V$

therefore: $\Delta P = -M(\Delta V/V)$

and the elastic modulus in this case is the incompressibility or bulk modulus: $M = -V(\Delta P/\Delta V)$
 $= K$

Elastic strain

According to Hooke's law, the strain is directly proportional to the stress in an elastic solid. This law applies to small strain only. In nonlinear region, when the strain is large, Hooke's law is no longer satisfied.

We specify the strain in terms of components e_{xx} , e_{yy} , e_{zz} , e_{xy} , e_{yz} , e_{zx}



The strain components e_{xx}, e_{yy}, e_{zz} can be defined by the relations

$$e_{xx} = \frac{\partial u}{\partial x} \quad e_{yy} = \frac{\partial v}{\partial y} \quad e_{zz} = \frac{\partial w}{\partial z}$$

where the displacement R of the position vector after deformation is

$$R(r) = u(r)\hat{x} + v(r)\hat{y} + w(r)\hat{z}$$

$$e_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \quad e_{yz} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \quad e_{zx} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}$$

Dilation : The fractional increase of volume associated with a deformation is called the dilation. The dilation is negative for hydrostatic pressure.

Volume of cube after deformation is V' and original V

$$\therefore \text{The dilation } \delta \equiv \frac{V' - V}{V} = e_{xx} + e_{yy} + e_{zz}.$$

Stress components :The force acting on a unit area in the solid is defined as the stress. There are nine stress components $X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z$. The capital letter indicates the direction of the force, and subscript indicates the normal to the plane to which the force is applied.

The stress components have the dimensions of force per unit area or energy per unit volume. The stress components are ratios of lengths and are dimensionless.

Elastic Energy density: the elastic energy density U is a quadratic function of the strain i.e.,

$$U = \frac{1}{2} \sum_{\lambda=1}^6 \sum_{\mu=1}^6 C_{\lambda\mu} e_{\lambda} e_{\mu}$$

1=xx; 2=yy ; 3=zz; 4=yz; 5=zx; 6=xy

C 's are called the elastic stiffness constants Or moduli of elasticity.

The elastic stiffness constants are symmetrical

$$C_{\alpha\beta} = \frac{1}{2} (\bar{C}_{\alpha\beta} + \bar{C}_{\beta\alpha}) = C_{\beta\alpha}$$

The elastic energy density of a cubic crystal is

$$U = \frac{1}{2} C_{11} (e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \frac{1}{2} C_{44} (e_{yz}^2 + e_{zx}^2 + e_{xy}^2) + C_{12} (e_{yy} e_{zz} + e_{zz} e_{xx} + e_{xx} e_{yy})$$

Bulk Modulus and compressibility:

Consider the uniform dilation $e_{xx} = e_{yy} = e_{zz} = \frac{1}{3} \delta$



∴ For deformation the energy density of a cubic crystal

$$U = \frac{1}{6}(C_{11} + 2C_{12})\delta^2$$

There are a maximum of 21 elastic constants for a crystalline body, but for cubic crystals the elastic constants, C_{ij} , may be reduced to just three independent elastic constants:

$C_{11} = C_{22} = C_{33} \rightarrow$ modulus for axial compression, i.e., a stress σ_{11} results in a strain ϵ_{11} along an axis;

$C_{44} = C_{55} = C_{66} \rightarrow$ shear modulus, i.e., a shear stress σ_{23} results in a shear strain ϵ_{23} across a face;

$C_{12} = C_{13} = C_{23} \rightarrow$ modulus for dilation on compression, i.e., an axial stress σ_{11} results in a strain ϵ_{22} along a perpendicular axis.

All other $C_{ij} = 0$.

For single crystals, the elastic constants can be related to common elastic moduli such as:

We define the bulk modulus B by the relation $U = \frac{1}{2}B\delta^2$

This is equivalent to the definition $-V \frac{d\rho}{dv}$

$$\therefore B = \frac{1}{3}(C_{11} + 2C_{12})$$

The compressibility K is defined as $K \equiv \frac{1}{B}$

Shear modulus:

$$\mu = C_{44} \text{ and } \mu = \frac{1}{2}(C_{11} - C_{12})$$

Elastic Stiffness

The stiffness, k , of a body is a measure of the resistance offered by an elastic body to deformation. For an elastic body with a single degree of freedom (DOF) (for example, stretching or compression of a rod), the stiffness is defined as

$$k = \frac{F}{\delta}$$

where,

F is the force applied on the body



δ is the displacement produced by the force along the same degree of freedom (for instance, the change in length of a stretched spring)

In SI units, stiffness is measured in newtons per meter.

Generally, deflections (or motions) of an infinitesimal element (which is viewed as a point) in an elastic body can occur along multiple DOF (maximum of six DOF at a point).

For example, a point on a horizontal beam can undergo both a vertical displacement and a rotation relative to its undeformed axis. When there are M degrees of freedom a $M \times M$ matrix must be used to describe the stiffness at the point. The diagonal terms in the matrix are the direct-related stiffnesses (or simply stiffnesses) along the same degree of freedom and the off-diagonal terms are the coupling stiffnesses between two different degrees of freedom (either at the same or different points) or the same degree of freedom at two different points.

For a body with multiple DOF, the equation above generally does not apply since the applied force generates not only the deflection along its own direction (or degree of freedom), but also those along other directions.

. The ratios between the reaction forces (or moments) and the produced deflection are the coupling stiffnesses.

A description including all possible stretch and shear parameters is given by the elasticity tensor.

A body may also have a rotational stiffness, k , given by $k = \frac{M}{\theta}$

where

M is the applied moment

θ is the rotation

In the SI system, rotational stiffness is measured in newton-metres per radian.

- shear stiffness - ratio of applied shear force to shear deformation
- torsional stiffness - ratio of applied torsion moment to angle of twist

Elastic Compliance

The inverse of stiffness is *flexibility* or *compliance*, typically measured in units of metres per newton. It may be defined as the ratio of strain to stress, and so take the units of reciprocal stress, e.g. 1/Pa



Elastic compliance, s , is the strain produced in a piezoelectric material per unit of stress applied and, for the 11 and 33 directions, is the reciprocal of the modulus of elasticity (Young's modulus, Y). s^D is the compliance under a constant electric displacement; s^E is the compliance under a constant electric field. The first superscript indicates the direction of strain; the second is the direction of stress.

s_{11}^E elastic compliance for stress in direction 1 and accompanying strain in direction 1, under constant electric field

s_{33}^D elastic compliance for stress in direction 3 and accompanying strain in direction 3, under constant electric displacement

Elastic wave

Elastic wavemotion in a medium in which, when particles are displaced, a force proportional to the displacement acts on the particles to restore them to their original position. If a material has the property of elasticity and the particles in a certain region are set in vibratory motion, an elastic wave will be propagated. For example, a gas is an elastic medium (if it is compressed and the pressure is then released, it will regain its former volume), and sound is transmitted through a gas as an elastic wave.

Sound waves are an example of such elastic waves. Only two types of elastic waves—longitudinal and shear, or transverse, waves—can propagate in a homogeneous and isotropic solid medium of infinite extent.

Elastic constants for isotropic solids

Young's modulus and Poisson's ratio are the most common properties used to characterize elastic solids, but other measures are also used. For example, we define the shear modulus, bulk modulus and Lamé modulus of an elastic solid as follows:

$$\text{Bulk Modulus } K = \frac{E}{3(1-2\nu)}$$

$$\text{Shear Modulus } \mu = \frac{E}{2(1+\nu)}$$

$$\text{Lamé Modulus } \lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}$$

It is important for the physical significance of the two elastic constants E and ν

Young's modulus E is the slope of the stress-strain curve in uniaxial tension. It has dimensions of stress (N/m^2) and is usually large for steel ($E = 210 \times 10^9 N/m^2$), that is E as



a measure of the stiffness of the solid. The larger the value of E , the stiffer the solid. For a stable material, $E > 0$.

Poisson's ratio ν is the ratio of lateral to longitudinal strain in uniaxial tensile stress. It is dimensionless and typically ranges from 0.2 to 0.49, and is around 0.3 for most metals. For a stable material, $-1 < \nu < 0.5$. It is a measure of the compressibility of the solid. If $\nu = 0.5$, the solid is incompressible its volume remains constant, no matter how it is deformed. If $\nu = 0$, then stretching a specimen causes no lateral contraction. Some bizarre materials have $\nu < 0$ if you stretch a round bar of such a material, the bar increases in diameter.

Thermal expansion coefficient quantifies the change in volume of a material if it is heated in the absence of stress. It has dimensions of $(\text{degrees Kelvin})^{-1}$ and is usually very small. For steel, $\alpha \approx 6 - 10 \times 10^{-6} K^{-1}$

The bulk modulus quantifies the resistance of the solid to volume changes. It has a large value (usually bigger than E).

The shear modulus quantifies its resistance to volume preserving shear deformations. Its value is usually somewhat smaller than E

Strain Energy Density for Isotropic Solids

The strain energy density of a solid is defined as the work done per unit volume to deform a material from a stress free reference state to a loaded state. To write down an expression for the strain energy density, it is convenient to separate the strain into two parts

$$\epsilon_{ij} = \epsilon_{ij}^e + \epsilon_{ij}^T$$

where, for an isotropic solid,

$$\epsilon_{ij}^T = \alpha \Delta T \delta_{ij}$$

represents the strain due to thermal expansion (known as thermal strain), and

$$\epsilon_{ij}^e = \frac{1+\nu}{E} \sigma_{ij} - \frac{\nu}{E} \sigma_{kk} \delta_{ij}$$

is the strain due to mechanical loading (known as elastic strain).



Work is done on the specimen only during mechanical loading. It is straightforward to show that the strain energy density is

$$U = \frac{1}{2} \sigma_{ij} \varepsilon_{ij}^e$$

Therefore it is re-written as

$$U = \frac{1+\nu}{2E} \sigma_{ij} \sigma_{ij} - \frac{\nu}{2E} \sigma_{kk} \sigma_{jj}$$

$$U = \frac{E}{2(1+\nu)} \varepsilon_{ij}^e \varepsilon_{ij}^e + \frac{E\nu}{2(1+\nu)(1-2\nu)} \varepsilon_{jj}^e \varepsilon_{kk}^e$$

That is

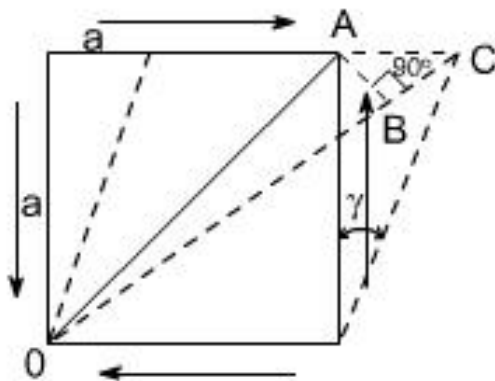
$$\varepsilon_{ij}^e = \frac{\partial U}{\partial \sigma_{ij}} \quad \sigma_{ij} = \frac{\partial U}{\partial \varepsilon_{ij}^e}$$

RELATION AMONG ELASTIC CONSTANTS

Relation between E, G and u :

Let us establish a relation among the elastic constants E,G and u. Consider a cube of material of side 'a' subjected to the action of the shear and complementary shear stresses as shown in the figure and producing the strained shape as shown in the figure below.

Assuming that the strains are small and the angle A C B may be taken as 45° .



Therefore strain on the diagonal OA= Change in length / original length



Since angle between OA and OB is very small hence $OA \approx OB$ therefore BC, is the change in the length of the diagonal OA

$$\begin{aligned} \text{Strain on diagonal OA} &= \frac{BC}{OA} \\ &= \frac{AC \cos 45^\circ}{OA} \end{aligned}$$

$$OA = \frac{a}{\sin 45^\circ} = a\sqrt{2}$$

$$\begin{aligned} \text{Hence } \text{strain} &= \frac{AC}{a\sqrt{2}} \frac{1}{\sqrt{2}} \\ &= \frac{AC}{2a} \end{aligned}$$

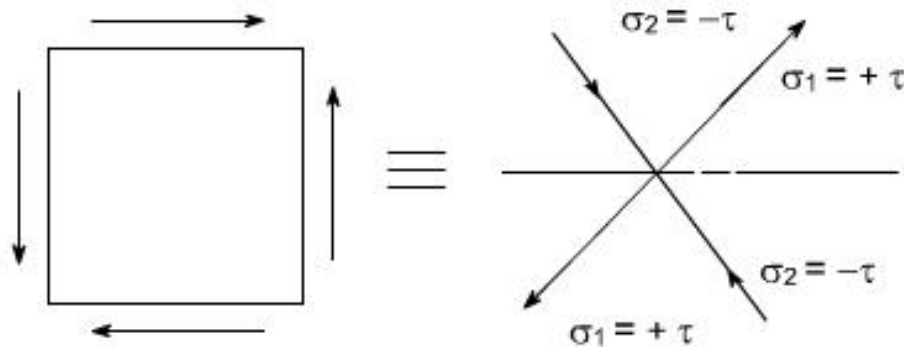
But $AC = a\gamma$, where γ is the shear strain

$$\text{Thus the strain on diagonal} = \frac{a\gamma}{2a} = \frac{\gamma}{2}$$

$$\text{From the definition } G = \frac{\tau}{\gamma} \text{ or } \gamma = \frac{\tau}{G}$$

$$\text{ie., the strain on diagonal} = \frac{\gamma}{2} = \frac{\tau}{2G}$$

Now this shear stress system is equivalent or can be replaced by a system of direct stresses at 45° as shown below. One set will be compressive, the other tensile, and both will be equal in value to the applied shear strain.



Thus, for the direct state of stress system which applies along the diagonals:



$$\begin{aligned}\text{strain on diagonal} &= \frac{\sigma_1}{E} - \mu \frac{\sigma_2}{E} \\ &= \frac{\tau}{E} - \mu \frac{(-\tau)}{E} \\ &= \frac{\tau}{E}(1 + \mu)\end{aligned}$$

equating the two strains one may get

$$\begin{aligned}\frac{\tau}{2G} &= \frac{\tau}{E}(1 + \mu) \\ \text{or } \quad &\boxed{E = 2G(1 + \mu)}\end{aligned}$$

We have introduced a total of four elastic constants, i.e E, G, K and ν . It turns out that not all of these are independent of the others. Infact given any two of them, the other two can be found.

$$\text{Again } E = 3K(1 - 2\nu)$$

$$\Rightarrow \frac{E}{3(1 - 2\nu)} = K$$

$$\text{if } \nu = 0.5 \quad K = \infty$$

$$\epsilon_v = \frac{(1 - 2\nu)}{E} (\epsilon_x + \epsilon_y + \epsilon_z) = 3 \frac{\sigma}{E} (1 - 2\nu)$$

(for $\epsilon_x = \epsilon_y = \epsilon_z$ hydro static state of stress)

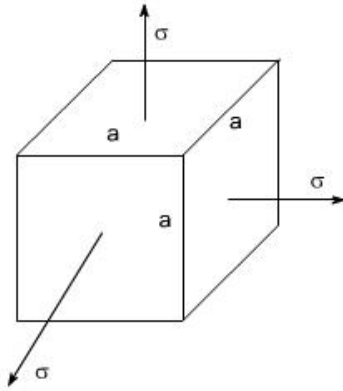
$$\epsilon_v = 0 \text{ if } \nu = 0.5$$

irrespective of the stresses i.e, the material is incompressible.

When $\nu = 0.5$ Value of k is infinite, rather than a zero value of E and volumetric strain is zero, or in other words, the material is incompressible.

Relation between E, K and ν :

Consider a cube subjected to three equal stresses s as shown in the figure below



The total strain in one direction or along one edge due to the application of hydrostatic stress or volumetric stress s is given as

$$= \frac{\sigma}{E} - \gamma \frac{\sigma}{E} - \gamma \frac{\sigma}{E}$$

$$= \frac{\sigma}{E} (1 - 2\gamma)$$

volumetric strain = 3.linear strain

$$\text{volumetric strain} = \epsilon_x + \epsilon_y + \epsilon_z$$

or thus, $\epsilon_x = \epsilon_y = \epsilon_z$

$$\text{volumetric strain} = 3 \frac{\sigma}{E} (1 - 2\gamma)$$

By definition

$$\text{Bulk Modulus of Elasticity (K)} = \frac{\text{Volumetric stress}(\sigma)}{\text{Volumetric strain}}$$

or

$$\text{Volumetric strain} = \frac{\sigma}{k}$$

Equating the two strains we get

$$\frac{\sigma}{k} = 3 \cdot \frac{\sigma}{E} (1 - 2\gamma)$$

$$\boxed{E = 3K(1 - 2\gamma)}$$

Relation between E, G and K :

The relationship between E, G and K can be easily determined by eliminating μ from the already derived relations



$$E = 2 G (1 + u) \text{ and } E = 3 K (1 - u)$$

Thus, the following relationship may be obtained

$$E = \frac{9 GK}{(3K + G)}$$

Relation between E, K and g :

From the already derived relations, E can be eliminated

$$E = 2G(1 + \gamma)$$

$$E = 3K(1 - 2\gamma)$$

Thus, we get

$$3k(1 - 2\gamma) = 2G(1 + \gamma)$$

therefore

$$\gamma = \frac{(3K - 2G)}{2(G + 3K)}$$

or

$$\gamma = 0.5(3K - 2G) (G + 3K)$$



UNIT III

LATTICE DYNAMICS AND THERMAL PROPERTIES

Lattice dynamics: Concepts of phonons – momentum of phonons – normal and Umklapp process – vibrations of one dimensional monoatomic and diatomic linear lattices – inelastic scattering of neutrons by phonons

Thermal Properties: Theories of specific heat – Dulong and Petit's law – Einstein theory and Debye's theory – Widemann Franz law

Concept of Phonons

The concept of phonons was introduced in 1932 by Soviet physicist Igor Tamm. The name phonon comes from the Greek word "phone," which translates into "sound" or "voice." The long-wavelength phonons give rise to sound at higher energy levels. Shorter-wavelength higher-frequency phonons are responsible for the majority of the thermal capacity of solids.

Phonons are quanta of lattice vibrations. Phonon is used to draw an analogy between photon representing a quantum of electromagnetic radiation and quanta of lattice vibration. Theory of phonons explains most solid state phenomena which cannot be explained with static lattice theory. Phonons don't exist as independent particles, but rather as a state of behavior within a system that can be thought of as a particle in its own right. For this reason, phonons as a "quasiparticle" or a "collective excitation."

Elastic waves in crystals are made up of phonons. The energy of an elastic mode of angular frequency ω is $\varepsilon = \left(n + \frac{1}{2}\right)\hbar\omega$. Where n is quantum number and $\frac{1}{2}\hbar\omega$ is the zero point energy of mode. An exact amount of energy $\hbar\omega$ must be supplied to the harmonic oscillator lattice to push it to the next energy level. In comparison to the photon case when the electromagnetic field is quantized, the quantum of vibrational energy is called a phonon.

Momentum of Phonon

By analogy to photons and matter waves, phonons have been treated with wavevector k as though it has a momentum $\hbar k$, however, this is not strictly correct, because $\hbar k$ is not actually a physical momentum; it is called the crystal momentum or pseudomomentum. This is because k is only determined up to addition of constant vectors.



This quantity is not unique as any quasi-momentum $\hbar k + \hbar b$, where b is a reciprocal lattice vector, is physically equivalent to $\hbar k$. The velocity of a phonon is determined as the group velocity of the corresponding classical waves $v_{gr} = \partial\omega/\partial k$ and has

the form:
$$v = \frac{\partial\varepsilon(p)}{\partial p}$$

The free wave motion is considered as the free motion of non-interacting phonons. Inclusion of the anharmonicity leads to scattering processes in the phonon gas. These scattering processes restore the thermal equilibrium of the phonon gas. The processes conserve the quasi-momentum. However, this is only valid within an addition of a reciprocal lattice vector $\hbar b$.

ie., The momentum conservation law as $k = k' + K + G$ where G is a reciprocal lattice vector and which, , corresponds to the $\hbar G$ recoil momentum of the whole lattice as a result of the collision.

Normal and Umklapp process

Umklapp scattering (also U-process or Umklapp process) is the transformation, like a reflection or a translation, of a wave vector to another Brillouin zone as a result of a scattering process, for example an electron-lattice potential scattering or an anharmonic phonon-phonon (or electron-phonon) scattering process, reflecting an electronic state or creating a phonon with a momentum k -vector outside the first Brillouin zone. Umklapp scattering is one process limiting the thermal conductivity in crystalline materials, the others being phonon scattering on crystal defects and at the surface of the

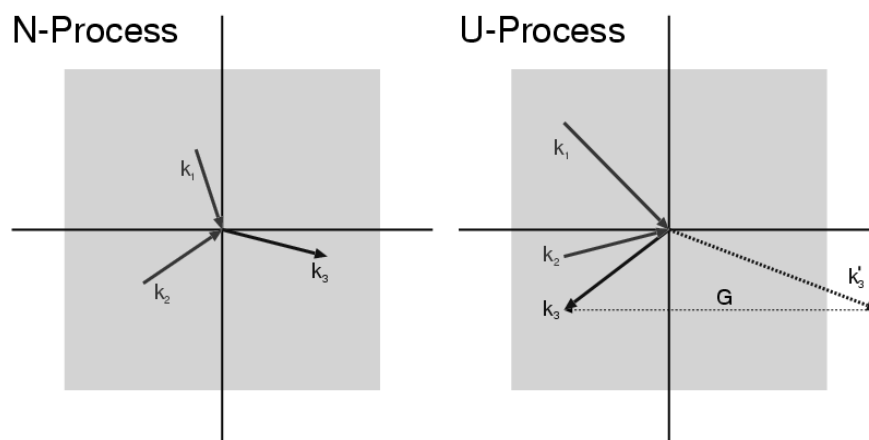


Figure 1.: Normal process (N-process) and Umklapp process (U-process). While the N-process conserves total phonon momentum, the U-process changes phonon momentum.



sample.

Figure 1 schematically shows the possible scattering processes of two incoming phonons with wave-vectors (k -vectors) k_1 and k_2 creating one outgoing phonon with a wave vector k_3 . As long as the sum of k_1 and k_2 stay inside the first Brillouin zone k_3 is the sum of the former two conserving phonon momentum. This process is called normal scattering (N-process).

With increasing phonon momentum and thus wave vector of k_1 and k_2 their sum might point outside the Brillouin zone (k'_3).

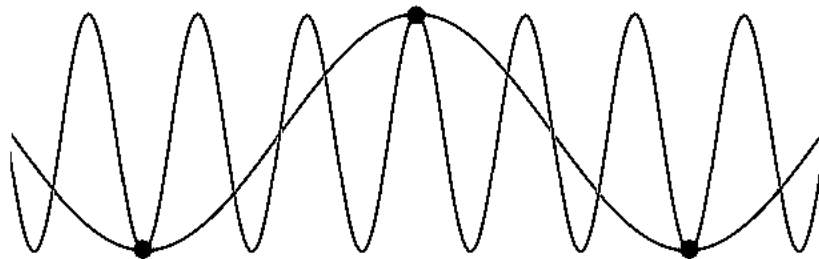


Figure 2.: k -vectors exceeding the first Brillouin zone do not carry more information than their counterparts in the first Brillouin zone.

As shown in Figure 2, k -vectors outside the first Brillouin zone are physically equivalent to vectors inside it and can be mathematically transformed into each other by the addition of a reciprocal lattice vector G . These processes are called Umklapp scattering and change the total phonon momentum.

Umklapp scattering is the dominant process for thermal resistivity at high temperatures for low defect crystals. The thermal conductivity for an insulating crystal where the U-processes are dominant has $1/T$ dependence.

The name derives from the German word *umklappen* (to turn over).

Lattice Vibrations(Mono atomic basis)

A lattice is usually regarded as an array of atoms connected with each other by elastic springs. That is the motion of every atom would be shared by all the atoms in the crystal and the crystal would thus vibrate as a whole.



Consider the elastic vibrations of a crystal with one atom in the primitive cell. The frequency of an elastic wave in terms of the wave vector that describes the wave and in terms of the elastic constant can be found.

And let the propagation direction in cubic crystal are [100],[110],[111].These are the directions of the cubic edge, face diagonal and body diagonal.

When a wave propagates along one of these directions, entire planes of atoms move in phase with displacements either parallel or perpendicular to the direction of the wave vector. It is considered as one dimensional.

For each wave vector, there are three modes, one of longitudinal polarization and two of transverse polarization.

Assume that the elastic response of the crystal is a linear function of the forces. The elastic energy is a quadratic function of the relative displacement of any two points in the crystal.

The force on the plane S caused by the displacement of the plane S + p is proportional to the difference $U_{s+p}-U_s$ of their displacement.

Consider only nearest –neighbour interaction Therefore $p=\pm 1$

Therefore, The total force on S comes from planes $S\pm 1$

$$\therefore F_s = C(U_{s+1} - U_s) + C(U_{s-1} - U_s) \text{-----(1)}$$

It is linear and the form of Hooke's law. C is the force constant and is defined for one atom the plane, F_s is the force on one atom in the plane S.

The equation of motion of the plane S is

$$M \frac{d^2 U_s}{dt^2} = C(U_{s+1} + U_{s-1} - 2U_s) \text{-----(2)}$$

Where M is the mass of an atom. The displacement with time dependence $\exp(-i\omega t)$.

Then
$$\frac{d^2 U_s}{dt^2} = -\omega^2 U_s$$

Therefore Equation 2 becomes

$$-M\omega^2 U_s = C(U_{s+1} + U_{s-1} - 2U_s) \text{-----(3)}$$

The travelling wave solutions of the form

$$U_{s\pm 1} = U \exp(iska) \exp(\pm ika) \text{-----(4)}$$

Where a is the spacing between planes and k is wave vector.

Using equation 4 in equation 3, we have



$$-\omega^2 MU \exp(iska) = C u \{ \exp[i(s+1)ka] + \exp[i(s-1)ka] - 2 \exp(iska) \} \text{-----(5)}$$

Cancelling $u \exp(iska)$ on both sides

$$\omega^2 M = -C [\exp(ika) + \exp(-ika) - 2] \text{-----(6)}$$

$$\omega^2 M = -C [2 \cos Ka - 2]$$

$$\therefore \omega^2 = \frac{2C}{M} [1 - \cos Ka] \text{-----(7)}$$

The first Brillouin zone lies at $k = \pm \pi/a$.

The slope of ω versus k is zero at the zone boundary

$$\frac{d\omega^2}{dk} = \frac{2Ca}{M} \sin ka = 0 \text{-----(8)}$$

At $K = \pm \pi/a$ $\sin Ka = \sin \pm \pi = 0$

Equation 7 can be written as

$$\omega^2 = \frac{4C}{M} \sin^2 \frac{1}{2} Ka$$

$$\omega = \left(\frac{4C}{M} \right)^{\frac{1}{2}} \left| \sin \frac{1}{2} ka \right| \text{-----(9)}$$

The ratio of the two successive planes is given by

$$\frac{U_{s+1}}{U_s} = \frac{U \exp[i(s+1)Ka]}{U \exp(iska)} = \exp(iKa) \text{-----(10)}$$

The range $-\pi$ to $+\pi$ for the phase Ka covers all independent values of the exponential.

The range of independent values of K is $-\pi < Ka \leq \pi$ (or) $-\pi/a < K \leq \pi/a$

This range is the first Brillouin zone of the linear lattice. The extreme values are $K_{\max} = \pm \pi/a$

In elastic continuum, $La \rightarrow 0$ and $k_{\max} \rightarrow \pm \infty$

At the boundaries, $K_{\max} = \pm \pi/a$ of the Brillouin zone, the solution $U_s = U \exp(iska)$ does not represent a travelling wave but a standing wave.

At the zero boundaries, $SK_{\max}a = \pm \pi$

Whence $U_s = U \exp(\pm is\pi) = U(-1)^s$

This is a standing wave, $U_s = \pm 1$ (for s is even or odd number)

The wave moves neither to the right nor to the left.

$$K_{\max} = \pm \pi/a \text{ satisfies the Bragg condition } 2d \sin \theta = n\lambda$$



Group velocity

The transmission velocity of a wave packet is the group velocity, the gradient of the frequency with respect to K

$$v_g = \frac{d\omega}{dk} = \text{grad}_k \omega(k)$$

This is the velocity of energy propagation in the medium. Substituting the value of ω from equation 9, we get

$$\text{That is } v_g = \frac{d}{dk} \left(\frac{4C}{M} \right)^{\frac{1}{2}} \left| \text{Sin} \frac{1}{2} Ka \right|$$

$$v_g = \left(\frac{Ca^2}{M} \right)^{\frac{1}{2}} \cos \frac{1}{2} Ka$$

This is zero at the edge of the zone $K = \pi/a$. That is the wave is standing wave.

Long wavelength limit

$$\text{When } Ka \ll 1, \quad \cos Ka = 1 - \frac{1}{2}(Ka)^2$$

$$\therefore \omega^2 = \left(\frac{C}{M} \right) K^2 a^2$$

That is frequency is directly proportional to the wave vector in the long wave length limit. It is equivalent to the velocity of sound. And it is independent of frequency in this limit i.e., $v = \omega / k$.

Force constant

In metals, the effective forces may be long range. The dispersion to the p nearest planes

$$\omega^2 = \left(\frac{2}{M} \right) \sum C_p (1 - \cos pKa)$$

to solve the inter planar force constant C_p , multiplying both sides by $\cos(rka)$ and

Integrating over a range of independent values of K . where r is an integer

$$\begin{aligned} M \int_{-\pi/a}^{\pi/a} dK \omega_k^2 \cos(rKa) &= 2 \sum_{p>0} C_p \int_{-\pi/a}^{\pi/a} dK (1 - \cos pKa) \cos rka \\ &= \frac{-2\pi C_r}{a} \end{aligned}$$



Integral vanishes except for $p = r$

$$\therefore C_p = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} dK \omega_k^2 \cos pka$$

This is the force constant at range pa for a structure with a monoatomic basis.

Two atoms per primitive cells

The phonon dispersion relation shows new features in crystals with two or more atoms per primitive cell.

Example: NaCl or diamond structure (two atoms in the primitive cell).

The dispersion relation ω Versus K develops two branches known as the acoustical and the optical branches.

We have longitudinal acoustical LA and transverse acoustical TA modes and longitudinal optical LO and transverse optical TO modes

If there are p atoms in the primitive cell, there are $3p$ branches to the dispersion relation: 3 acoustical branches and $3p-3$ optical branches

Example: Ge and KBr with two atoms have six branches one LA, one LO, two TA and two T

With P atoms in the primitive cell and for N primitive cells, there are PN atoms. Each atom has 3 degrees of freedom. Therefore in total there are $3PN$ degrees of freedom for the crystal. The number of allowed K values in a single branch is N for one Brillouin zone.

Therefore one LA and two TA branches have $3N$ modes, thereby they are $3N$ degrees of freedom.

The remaining $(3P-3)N$ degrees of freedom are accommodated by the optical branches.

Consider a cubic crystal where atoms of mass M_1 lie on one set of planes and atoms of M_2 lie on planes interleaved between those of the first set. Let 'a' denote the repeat distance of the lattice in the direction normal to the lattice plane. The wave directions are [111] in the NaCl structure and [100] in the CsCl structure.

Assume each plane interacts only with its nearest neighbour planes, and the force constants are identical in equation of motion.

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s) \quad \text{----- (a)}$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s)$$

Solution in the form of a traveling wave with different amplitude u and v



$$\begin{aligned} u_s &= u \exp(iska) \exp(-i\omega t) \\ v_s &= v \exp(iska) \exp(-i\omega t) \end{aligned} \quad \text{-----(b)}$$

Equation (b) in (a)

$$\begin{aligned} -\omega^2 M_1 u &= Cv[1 + \exp(-ika)] - 2Cu \\ -\omega^2 M_2 v &= Cu[\exp(ika) + 1] - 2Cv \end{aligned} \quad \text{-----(c)}$$

The homogeneous linear equations have solution only if determinant of the coefficient of u,v vanishes

$$\begin{vmatrix} 2C - M_1 \omega^2 & -C[1 + \exp(-ika)] \\ -C[1 + \exp(-ika)] & 2C - M_2 \omega^2 \end{vmatrix} = 0 \quad \text{-----(d)}$$

$$\text{i.e., } M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0 \quad \text{-----(e)}$$

solving this equation for ω^2 , for $Ka \ll 1$ and $Ka = \pm\pi$

For small Ka , $\cos Ka \approx 1 - \frac{1}{2} K^2 a^2$

$$\omega^2 = 2C \left[\frac{1}{M_1} + \frac{1}{M_2} \right] \quad \text{Optical branch} \quad \text{----- (f)}$$

$$\omega^2 = \frac{\frac{1}{2} C}{M_1 + M_2} K^2 a^2 \quad \text{Acoustical branch} \quad \text{-----(g)}$$

$$\text{At } K_{\max} = \pm \frac{\pi}{a}, \omega^2 = \frac{2C}{M_1}; \omega^2 = \frac{2C}{M_2} \quad \text{-----(h)}$$

The dependence of ω on K is shown in fig.(i)

The particle displacement in the transverse acoustical (TA) and transverse optical (TO) branches are shown in fig 5

For optical branch at $K=0$, equation(f) in (c) we get

$$\frac{u}{v} = -\frac{M_2}{M_1}$$

The atom vibrates against each other but their center of mass is fixed. If the two atoms carry opposite charges, a motion of this with the electric field forms a light wave. So this branch is called the optical branch.

Another solution at small k is $u=v$ ie ($K=0$). The atoms move together as long wavelength acoustical vibration. Therefore the term acoustical branch arises.



Between $\left(\frac{2C}{M_1}\right)^{1/2}$ and $\left(\frac{2C}{M_2}\right)^{1/2}$, no solution for certain frequencies so that the wave is damped in space.

Specific heats of solids

Consider a simple solid containing N atoms. Now, atoms in solids cannot translate (unlike those in gases), but are free to vibrate about their equilibrium positions. Such vibrations are called *lattice vibrations*, and can be thought of as sound waves propagating through the crystal lattice. Each atom is specified by three independent position coordinates, and three conjugate momentum coordinates. Let us only consider small amplitude vibrations. In this case, we can expand the potential energy of interaction between the atoms to give an expression which is quadratic in the atomic displacements from their equilibrium positions. It is always possible to perform a *normal mode analysis* of the oscillations. In effect, we can find $3N$ independent modes of oscillation of the solid. Each mode has its own particular oscillation frequency, and its own particular pattern of atomic displacements. Any general oscillation can be written as a linear combination of these *normal modes*. Let q_i be the (appropriately normalized) amplitude of the i^{th} normal mode, and p_i the momentum conjugate to this coordinate. In *normal mode coordinates*, the total energy of the lattice vibrations takes the particularly simple form

$$E = \frac{1}{2} \sum_{i=1}^{3N} (p_i^2 + \omega_i^2 q_i^2), \quad (11)$$

where ω_i is the (angular) oscillation frequency of the i^{th} normal mode. It is clear that in normal mode coordinates, the linearized lattice vibrations are equivalent to $3N$ independent harmonic oscillators (of course, each oscillator corresponds to a different normal mode).

The typical value of ω_i is the (angular) frequency of a sound wave propagating through the lattice. Sound wave frequencies are far lower than the typical vibration frequencies of gaseous molecules. In the latter case, the mass involved in the vibration is simply that of the molecule, whereas in the former case the mass involved is that of very many atoms (since lattice vibrations are non-localized). The strength of interatomic bonds in gaseous molecules



is similar to those in solids, so we can use the estimate $\omega \approx \sqrt{k/m}$ (k is the force constant which measures the strength of interatomic bonds, and m is the mass involved in the oscillation) as proof that the typical frequencies of lattice vibrations are very much less than the vibration frequencies of simple molecules. It follows from $\Delta E = \hbar\omega$ that the quantum energy levels of lattice vibrations are far more closely spaced than the vibrational energy levels of gaseous molecules. Thus, it is likely (and is, indeed, the case) that lattice vibrations are not frozen out at room temperature, but, instead, make their full classical contribution to the molar specific heat of the solid.

If the lattice vibrations behave classically then, according to the equipartition theorem, each normal mode of oscillation has an associated mean energy kT in equilibrium at temperature T { $(1/2)kT$ resides in the kinetic energy of the oscillation, and $(1/2)kT$ resides in the potential energy}. Thus, the mean internal energy per mole of the solid is

$$\bar{E} = 3NkT = 3\nu RT. \quad (12)$$

It follows that the molar heat capacity at constant volume is

$$c_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial T} \right)_V = 3R \quad (13)$$

for solids. This gives a value of 24.9 joules/mole/degree. In fact, at room temperature most solids (in particular, metals) have heat capacities which lie remarkably close to this value.

Dulong–Petit law

The Dulong–Petit law, a thermodynamic rule proposed in 1819 by French physicists Pierre Louis Dulong and Alexis Thérèse Petit, states the classical expression for the molar specific heat capacity of certain chemical elements. Experimentally the two scientists had found that the heat capacity per weight (the mass-specific heat capacity) for a number of elements was close to a constant value, *after* it had been multiplied by a number representing the presumed relative atomic weight of the element. These atomic weights had shortly before been suggested by Dalton.



The specific heat capacity c of a solid element (measured in joule per kelvin per kilogram) is equal to $3R/M$, where R is the gas constant (measured in joule per kelvin per mole) and M is the molar mass (measured in kilogram per mole). Thus, the heat capacity per mole of many elements is $3R$.

The initial form of the Dulong–Petit law was: $cM = K$

where c is the specific heat, M the atomic weights, and K is a new constant is about $3R$.

The mass m divided by atomic weight M gives the number of moles N .

$$m/M = N$$

Therefore, using uppercase C for the total heat capacity, and lowercase c for the specific heat capacity

$$(C/m)M = K$$

$$C(M/m) = C/N = K = 3R \quad \text{or} \quad C/N = 3R$$

Therefore the heat capacity of most solid crystalline substances is $3R$ per mole of substance.

Dulong and Petit did not state their law in terms of the gas constant R (which was not then known). Instead, they measured the values of heat capacities (per weight) of substances and found them smaller for substances of greater atomic weight as inferred by Dalton and other early atomists. Dulong and Petit then found that when multiplied by these atomic weights, the value for the heat capacity (which would now be the heat capacity *per mole* in modern terms) was nearly constant, and equal to a value which was later recognized to be $3R$.

The specific heat of copper is 0.093 cal/gm K ($.389 \text{ J/gm K}$) and that of lead is only 0.031 cal/gmK ($.13 \text{ J/gm K}$). The difference is mainly because it is expressed as energy per unit mass; if it is expressed as energy per mole, they are very similar. It is in fact that similarity of the molar specific heats of metals which is the subject of the Law of Dulong and Petit. The similarity can be accounted for by applying equi-partition of energy to the atoms of the solids.



From just the translational degrees of freedom we get $3kT/2$ of energy per atom. Energy added to solids takes the form of atomic vibrations and that contributes three additional degrees of freedom and a total energy per atom of $3kT$. The specific heat at constant volume should be just the rate of change with temperature (temperature derivative) of that energy.

Energy per mole = $3kTN_A$

Where k = Boltzmann's constant; T = Temperature in Kelvins; and N_A = Avagadro's number

The law of Dulong and Petit $C_V = \frac{\partial}{\partial T}(3kT N_A) = 3k N_A / \text{mole} = 24.94 \text{ J / mole K}$

When looked at on a molar basis, the specific heats of copper and lead are quite similar:

Copper $0.386 \text{ J / gm K} \times 63.6 \text{ gm / mole} = 24.6 \text{ J / mole K}$

Lead $0.128 \text{ J / gm K} \times 207 \text{ gm / mole} = 26.5 \text{ J / mole K}$

Einstein Theory

Dulong and Petite's law is essentially a high temperature limit. The molar heat capacity cannot remain a constant as the temperature approaches absolute zero, since, by

Equation $\nu \int_0^T \frac{c_V(T,V)}{T} dT$ this would imply $S \rightarrow \infty$, which violates the third law of

thermodynamics. We can make a crude model of the behaviour of c_V at low temperatures by assuming that all the normal modes oscillate at the same frequency, ω , say.. According

to Equation $E = \frac{1}{2} \sum_{i=1}^{3N} (p_i^2 + \omega_i^2 q_i^2)$ the solid acts like a set of $3N$ independent oscillators

which, making use of Einstein's approximation, all vibrate at the same frequency. We can

use the quantum mechanical result $\bar{E} = \hbar \omega \left[\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right]$ for a single oscillator to

write the mean energy of the solid in the form

$$\bar{E} = 3N \hbar \omega \left[\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right] \quad (14)$$



The molar heat capacity is defined

$$c_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{\nu k T^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V, \quad (15)$$

giving

$$c_V = -\frac{3 N_A \hbar \omega}{k T^2} \left[-\frac{\exp(\beta \hbar \omega) \hbar \omega}{[\exp(\beta \hbar \omega) - 1]^2} \right], \quad (16)$$

which reduces to

$$c_V = 3 R \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2}. \quad (17)$$

Here,

$$\theta_E = \frac{\hbar \omega}{k} \quad (18)$$

is called the *Einstein temperature*. If the temperature is sufficiently high that $T \gg \theta_E$ then $kT \gg \hbar \omega$, and the above expression reduces to $c_V = 3R$, after expansion of the exponential functions. Thus, the law of Dulong and Petite is recovered for temperatures significantly in excess of the Einstein temperature. On the other hand, if the temperature is sufficiently low that $T \ll \theta_E$ then the exponential factors in Equation

$c_V = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2}$ become very much larger than unity, giving

$$c_V \sim 3 R \left(\frac{\theta_E}{T} \right)^2 \exp(-\theta_E/T). \quad (19)$$

So, in this simple model the specific heat approaches zero exponentially as $T \rightarrow 0$.

The specific heats of solids do not approach zero quite as quickly as suggested by Einstein's model when $T \rightarrow 0$. The experimentally observed low temperature behaviour is more like $c_V \propto T^3$. The reason for this discrepancy is the crude approximation that all normal modes have the same frequency. In fact, long wavelength modes have lower



frequencies than short wavelength modes, so the former are much harder to freeze out than the latter (because the spacing between quantum energy levels, $\hbar\omega$, is smaller in the former case). The molar heat capacity does not decrease with temperature as rapidly as suggested by Einstein's model because these long wavelength modes are able to make a significant contribution to the heat capacity even at very low temperatures.

Debye Theory

A more realistic model of lattice vibrations was developed by the Dutch physicist Peter Debye in 1912. In the Debye model, the frequencies of the normal modes of vibration are estimated by treating the solid as an isotropic continuous medium. This approach is reasonable because the only modes which really matter at low temperatures are the long wavelength modes: *i.e.*, those whose wavelengths greatly exceed the interatomic spacing. It is reasonable that these modes are not particularly sensitive to the discrete nature of the solid: *i.e.*, the fact that it is made up of atoms rather than being continuous.

Consider a sound wave propagating through an isotropic continuous medium. The disturbance varies with position vector \mathbf{r} and time t like $\exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$, where the wave vector \mathbf{k} and the frequency of oscillation ω satisfy the dispersion relation for sound waves in an isotropic medium:

$$\omega = k c_s. \quad (20)$$

Here, c_s is the speed of sound in the medium. Suppose, for the sake of argument, that the medium is periodic in the x , y and z directions with periodicity lengths L_x , L_y , and L_z respectively. In order to maintain periodicity we need

$$k_x (x + L_x) = k_x x + 2\pi n_x, \quad (21)$$

where n_x is an integer. There are analogous constraints on k_y and k_z . It follows that in a periodic medium the components of the wave-vector are quantized, and can only take the values

$$k_x = \frac{2\pi}{L_x} n_x, \quad (22)$$



$$k_y = \frac{2\pi}{L_y} n_y, \quad (23)$$

$$k_z = \frac{2\pi}{L_z} n_z, \quad (24)$$

Where n_x , n_y , and n_z , are all integers. It is assumed that L_x , L_y , and L_z are macroscopic lengths, so the allowed values of the components of the wave-vector are very closely spaced. For given values of k_y and k_z , the number of allowed values of k_x which lie in the range k_x to $k_x + dk_x$ is given by

$$\Delta n_x = \frac{L_x}{2\pi} dk_x. \quad (25)$$

It follows that the number of allowed values of \mathbf{k} (i.e., the number of allowed modes) when k_x lies in the range k_x to $k_x + dk_x$, k_y lies in the range k_y to $k_y + dk_y$, and k_z lies in the range k_z to $k_z + dk_z$ is

$$\rho d^3\mathbf{k} = \left(\frac{L_x}{2\pi} dk_x\right) \left(\frac{L_y}{2\pi} dk_y\right) \left(\frac{L_z}{2\pi} dk_z\right) = \frac{V}{(2\pi)^3} dk_x dk_y dk_z, \quad (26)$$

Where $V = L_x L_y L_z$ is the periodicity volume, and $d^3k \equiv dk_x dk_y dk_z$. The quantity ρ is called the density of modes. Note that this density is independent of k , and proportional to the periodicity volume. Thus, the density of modes *per unit volume* is a constant independent of the magnitude or shape of the periodicity volume. The density of modes per unit volume, when the *magnitude* of k lies in the range k to $k + dk$, is given by multiplying the density of modes per unit volume by the "volume" in k -space of the spherical shell lying between the radii k and $k + dk$. Thus,

$$\rho_k dk = \frac{4\pi k^2 dk}{(2\pi)^3} = \frac{k^2}{2\pi^2} dk. \quad (27)$$

Consider an isotropic continuous medium of volume V . According to the above relation, the number of normal modes whose frequencies lie between ω and $\omega + d\omega$ (which is equivalent to the number of modes whose values lie in the range to is



$$\sigma_c(\omega) d\omega = 3 \frac{k^2 V}{2\pi^2} dk = 3 \frac{V}{2\pi^2 c_s^3} \omega^2 d\omega. \quad (28)$$

The factor of 3 comes from the three possible polarizations of sound waves in solids. For every allowed wave number (or frequency) there are two independent torsional modes, where the displacement is perpendicular to the direction of propagation, and one longitudinal mode, where the displacement is parallel to the direction of propagation. Torsion waves are vaguely analogous to electromagnetic waves (these also have two independent polarizations). The longitudinal mode is very similar to the compressional sound wave in gases. Of course, torsion waves can not propagate in gases because gases have no resistance to deformation without change of volume.

The Debye approach consists in approximating the actual density of normal modes $\sigma(\omega)$ by the density in a continuous medium $\sigma_c(\omega)$, not only at low frequencies (long wavelengths) where these should be nearly the same, but also at higher frequencies where they may differ substantially. Suppose that we are dealing with a solid consisting of N atoms. We know that there are only $3N$ independent normal modes. It follows that we must cut off the density of states above some critical frequency, ω_D , say, otherwise we will have too many modes. Thus, in the Debye approximation the density of normal modes takes the form

$$\begin{aligned} \sigma_D(\omega) &= \sigma_c(\omega) && \text{for } \omega < \omega_D \\ \sigma_D(\omega) &= 0 && \text{for } \omega > \omega_D. \end{aligned} \quad (29)$$

Here, ω_D is the *Debye frequency*. This critical frequency is chosen such that the total number of normal modes is $3N$, so

$$\int_0^{\infty} \sigma_D(\omega) d\omega = \int_0^{\omega_D} \sigma_c(\omega) d\omega = 3N. \quad (30)$$

Substituting Equation $\sigma_c(\omega) d\omega = 3 \frac{k^2 V}{2\pi^2} dk = 3 \frac{V}{2\pi^2 c_s^3} \omega^2 d\omega$ into the previous formula yields

$$\frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} \omega^2 d\omega = \frac{V}{2\pi^2 c_s^3} \omega_D^3 = 3N. \quad (31)$$



This implies that

$$\omega_D = c_s \left(6\pi^2 \frac{N}{V} \right)^{1/3}. \quad (32)$$

Thus, the Debye frequency depends only on the sound velocity in the solid and the number of atoms per unit volume. The wavelength corresponding to the Debye frequency is $2\pi c_s / \omega_D$, which is clearly on the order of the inter atomic spacing $a \approx (V/N)^{1/3}$. It follows that the cut-off of normal modes whose frequencies exceed the Debye frequency is equivalent to a cut-off of normal modes whose wavelengths are less than the inter atomic spacing.

For example, when compare the curves of the actual density of normal modes in diamond with the density predicted by Debye theory, both curves exhibit sharp cut-offs at high frequencies, and coincide at low frequencies. Furthermore, the areas under both curves are the same. This is sufficient to allow Debye theory to correctly account for the temperature variation of the specific heat of solids at low temperatures.

The quantum mechanical expression can be used for the mean energy of a single oscillator, Equation $\bar{E} = \hbar \omega \left[\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right]$ to calculate the mean energy of lattice vibrations in the Debye approximation. We obtain

$$\bar{E} = \int_0^{\infty} \sigma_D(\omega) \hbar \omega \left(\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right) d\omega. \quad (33)$$

According to Equation $c_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial T} \right)_\nu = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_\nu \frac{\partial \beta}{\partial T} = -\frac{1}{\nu k T^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_\nu$ the molar heat capacity takes the form

$$c_V = \frac{1}{\nu k T^2} \int_0^{\infty} \sigma_D(\omega) \hbar \omega \left[\frac{\exp(\beta \hbar \omega) \hbar \omega}{[\exp(\beta \hbar \omega) - 1]^2} \right] d\omega. \quad (34)$$

Substituting in Equation ,

$$\begin{aligned} \sigma_D(\omega) &= \sigma_c(\omega) && \text{for } \omega < \omega_D \\ \sigma_D(\omega) &= 0 && \text{for } \omega > \omega_D. \end{aligned}$$



we find that

$$c_V = \frac{k}{\nu} \int_0^{\omega_D} \frac{\exp(\beta \hbar \omega) (\beta \hbar \omega)^2}{[\exp(\beta \hbar \omega) - 1]^2} \frac{3V}{2\pi^2 c_s^3} \omega^2 d\omega, \quad (35)$$

giving

$$c_V = \frac{3V k}{2\pi^2 \nu (c_s \beta \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{\exp x}{(\exp x - 1)^2} x^4 dx, \quad (36)$$

in terms of the dimensionless variable $x = \beta \hbar \omega$ According to Equation $\omega_D = c_s \left(6\pi^2 \frac{N}{V}\right)^{1/3}$, the volume can be written

$$V = 6\pi^2 N \left(\frac{c_s}{\omega_D}\right)^3, \quad (37)$$

so the heat capacity reduces to

$$c_V = 3R f_D(\beta \hbar \omega_D) = 3R f_D(\theta_D/T), \quad (38)$$

where the *Debye function* is defined

$$f_D(y) \equiv \frac{3}{y^3} \int_0^y \frac{\exp x}{(\exp x - 1)^2} x^4 dx. \quad (39)$$

We have also defined the *Debye temperature* θ_D as

$$k\theta_D = \hbar\omega_D. \quad (40)$$

Consider the asymptotic limit in which $T \gg \theta_D$. For small y , we can approximate $\exp x$ as $1 + x$ in the integrand of Equation, $f_D(y) \equiv \frac{3}{y^3} \int_0^y \frac{\exp x}{(\exp x - 1)^2} x^4 dx$ so that

$$f_D(y) \rightarrow \frac{3}{y^3} \int_0^y x^2 dx = 1. \quad (41)$$

Thus, if the temperature greatly exceeds the Debye temperature we recover the law of Dulong and Petite that $c_V = 3R$. Consider, now, the asymptotic limit in which $T \ll \theta_D$. For large y ,

$$\int_0^y \frac{\exp x}{(\exp x - 1)^2} x^4 dx \simeq \int_0^\infty \frac{\exp x}{(\exp x - 1)^2} x^4 dx = \frac{4\pi^4}{15}. \quad (42)$$

The latter integration is standard (if rather obscure), and can be looked up in any (large) reference book on integration. Thus, in the low temperature limit



$$f_D(y) \rightarrow \frac{4\pi^4}{5} \frac{1}{y^3}. \quad (43)$$

This yields

$$c_V \simeq \frac{12\pi^4}{5} R \left(\frac{T}{\theta_D} \right)^3 \quad (44)$$

in the limit $T \ll \theta_D$: i.e., c_V varies with temperature like T^3 .

The fact that c_V goes like T^3 at low temperatures is quite well verified experimentally, although it is sometimes necessary to go to temperatures as low as $0.02\theta_D$ to obtain this asymptotic behaviour. Theoretically, θ_D should be calculable from Equation $\omega_D = c_s \left(6\pi^2 \frac{N}{V} \right)^{1/3}$ in terms of the sound speed in the solid and the molar volume. It can be seen that there is fairly good agreement between the theoretical and empirical Debye temperatures. This suggests that the Debye theory affords a good, representation of the behaviour of c_V in solids over the entire temperature range

Thermal conductivity of metals

The expression for thermal conductivity $k = \frac{1}{3} c v l$

Where v – velocity of free electrons, c – heat capacity per unit vol.

l - mean free path.

$$C_{elec} = \frac{\pi^2}{2} \frac{NK_B T}{T_F} \dots T^F = \frac{E_F}{K_B}$$

$$C_{elec} = \frac{\pi^2}{2} \frac{NK_B^2 T}{E_F}$$

$$\therefore k = \frac{1}{3} \left(\frac{\pi^2}{2} \frac{NK_B^2 T}{E_F} \right) v_F l \dots E_F = \frac{1}{2} m v_F^2$$

$$= \frac{1}{3} \frac{\pi N K_B^2 T}{2 \cdot \frac{1}{2} m v_f^2} v_F l \dots l = v_F \tau$$



$$k = \frac{\pi^2}{3} \frac{N K_B^2 T \tau}{m}$$

Widemann-Franz Law:

The Widemann-Franz states that the ratio of the thermal conductivity 'K' to the electrical conductivity ' σ ' is directly proportional to temperature and independent of the particular metal.

$$\text{Thermal Conductivity, } K = \frac{\pi^2}{3} \frac{N K_B^2 T}{m} \tau(E_f)$$

Where $\tau(E_f)$ is the collision time or relaxation time and N is electron concentration.

$$\text{Electrical Conductivity, } \sigma = \frac{n e^2}{m} \tau(E_f) = n e \mu$$

M is mobility and is defined as $\mu = \left| \frac{\vec{v}_z}{E_0} \right|$

$$\frac{K}{\sigma} = \frac{\pi^2 K_B^2 T N \tau(E_f) / 3m}{N e^2 \tau(E_f) / m}$$

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

$$\frac{K}{\sigma} = L T$$

Where L is Lorentz number and is defined as $L = \frac{\pi^2}{3} \left(\frac{K_B}{e} \right)^2 = \frac{K}{\sigma T}$

The relaxation times are same for electrical and thermal process.

At low temperature ($T \ll \theta_D$) the value of Lorentz number tends to decrease.



UNIT IV

ELECTRONIC PROPERTIES OF SOLIDS

Free electron gas model in three dimensions : Density of states – Fermi energy – Effect of temperature – heat capacity of electrons – experimental heat capacity of metals – thermal effective mass – electrical conductivity and ohm's law – Hall effect – failure of the free electron gas Band theory of solids – periodic potential and Bloch's theorem – Kronig – Penny model – wave equation of electron in a periodic potential – periodic, extended and reduced zone schemes of energy representation – number of orbitals in an energy band – classification of metals, semi conductors and insulators – tight binding method and its applications of FC and BCC structures.

Free electron gas model in three dimensions

Consider an electron of mass m confined to a length L by infinite barriers. (Fig.4.1)

The wave function $\psi_n(x)$ of the electron is a solution of the Schrodinger equation.

$$H\psi = E\psi$$

Where $H = \text{Kinetic Energy} + \text{Potential Energy}$; E is a set of allowed energies (or) eigenvalues of the electron in the orbital.

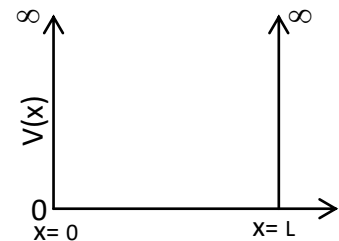


Figure 4.1

Since the total energy is Kinetic, $H = \frac{p^2}{2m}$ where p is moment, $i\hbar \frac{d}{dx}$ is its operator.

$$\therefore H\psi_n = -\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = E_n \psi_n$$

The boundary conditions are $\psi_n(0)=0$ and $\psi_n(L)=0$ by infinite potential barriers.

$$\therefore \text{The general solution is } \psi_n(x) = Ae^{ikx} + Be^{-ikx}$$

A and B are arbitrary constants $K^2 = \left(\frac{2m}{\hbar^2}\right) E_n$.

By its first boundary condition $\psi_n(0)$ gives $A = -B$

By 2nd boundary condition, $\sin kl = 0$



$$\therefore K_n = \frac{n\pi}{L} \text{ with } n = 1, 2, 3, \dots$$

and the allowed energy eigen values E_n are, $E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$

and the corresponding wave functions are $\psi_n = A \sin\left(\frac{n\pi x}{L}\right)$

n is Quantum number. The plot of energy E_n Vs n is in Figure 4.2.

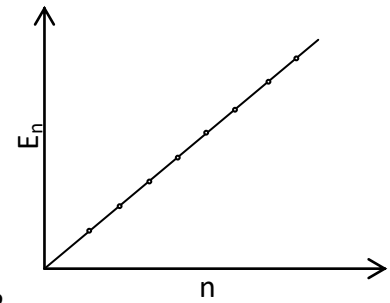


Figure 4.2

The energy spectrum consists of discrete energy levels, with their separation depending on

$$\left(\frac{n^2}{L^2} \right).$$

If L is large, the energy levels are spaced very closely together. (eg) if $L = 1\text{cm}$, $E_n - E_{n+1} = 3.5 \times 10^{-19} \text{ eV}$. 'A' can be chosen by the unit probability of finding the electron.

$$\int_0^L \psi_n^*(x) \psi_n(x) dx = 1.$$

$$\int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = 1$$

$$A^2 = \frac{2}{L} \text{ ie } A = \sqrt{\frac{2}{L}}$$

\therefore The normalized wave functions are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

The first few lower energy state wave functions are in Figure 4.3.

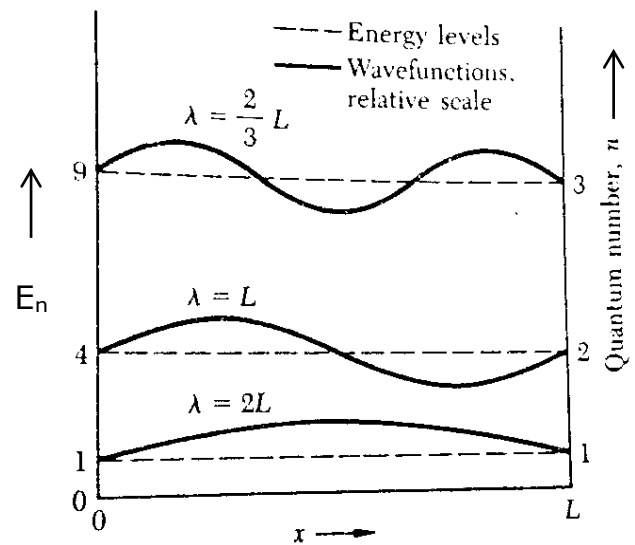


Figure 4.3

To accommodate N electrons :

By Pauli's exclusion principle, no two electrons can have all their Quantum numbers identical, ie each orbital can be occupied by one electron.

In a solid the Quantum numbers of an electron in conduction electron orbital are n

and m_s , where n is positive integer in equation $E = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$ and $m_s = \pm \frac{1}{2}$ Each



energy level with Quantum number n can accommodate 2 electrons in which one electron with spin up, another with spin down.

Let n_f be the top most filled energy level, filling from bottom ($n = 1$) to higher levels, N electrons can be accommodated. $2n_f = N$

n_f is the value of n of the uppermost filled level, Fermi level at 0°K (ground State)

$$n_f = \frac{N}{2}$$

The Fermi energy E_f is defined as the energy of the top-most filled level at 0K .

$$\therefore E_f = \frac{\hbar^2}{2m} \left(\frac{n_f \pi}{L} \right)^2 = \frac{\hbar^2}{2m} \left(\frac{n\pi}{2L} \right)^2$$

Energy of the top electron depends on the number of electrons in the box and on the size of the box just as an atom the ground state depends on the number of electrons and on the size of the central coulomb field strength (ie., number of Protons in nucleus). The ground state is the state of the system at absolute zero.

For N electrons in the lowest energy state of the system, the total energy E_0 is obtained by summing the individual energies E_n between $n=1$ and $n_f = \frac{1}{2}N$. The factor 2 due to spin.

$$\therefore E_0 = \sum_{n=1}^{N/2} 2 \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 \sum_{n=1}^{N/2} n^2$$

$$\sum n^2 = 1^2 + 2^2 + \dots \dots \dots S^2 \text{ where } S = N/2$$

$$\frac{1}{6} S (2S^2 + 3S + 1) \approx \frac{1}{3} S^3 \text{ for } S \gg 1$$

$$\approx \frac{1}{3} \left(\frac{N}{2} \right)^3$$

$$\therefore E_0 = \frac{2\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 \frac{1}{3} \left(\frac{N}{2} \right)^2 = \frac{1}{3} \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L} \right)^2$$

$$E_0 = \frac{1}{3} N E_f$$

ie in one dimension, the average K.E. in ground state is one third of Fermi Energy.



Density of states

The no. of orbitals per unit energy is called the density of states.

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$$

$$dE_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 2n \, dn.$$

$\frac{dn}{dE_n}$ denotes the energy level per unit energy corresponding to two spin states, there are

two quantum states.

$$\therefore \text{Density of states of free electron gas } D(E) = 2 \frac{dn}{dE_n}$$

$$= 2 \cdot \frac{2m}{\hbar^2} \left(\frac{L}{\pi} \right)^2 \cdot \frac{1}{2n}$$

$$D(E) = \frac{4L}{\hbar} \left(\frac{m}{2E_n} \right)^{1/2}$$

Density of States in 3D.

The Density of state $D(E)$ defined that all the energy state below $E_f(0)$ are occupied and is equal to the total no. of electrons

$$\int_0^{E_f(0)} D(E) dE = N$$

$$\int_0^{E_f(0)} D(E) dE = \frac{V}{3\pi^2} \left(\frac{2mE_f(0)}{\hbar^2} \right)^{3/2}$$

For infinitive integral,

$$\int D(E) dE = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot E^{3/2}$$

$$= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot E^{3/2}$$

$$D(E) = CE^{1/2}$$



It is also written as, $D(E_{f(o)}) = \frac{dN}{E_{f(o)}} = \frac{3}{2} \frac{N}{E_{f(o)}}$

The no. of orbital per unit energy range at the Fermi energy is the total no. of conduction electrons divided by Fermi energy.

Free electron gas in three Dimension:

Schrodinger equation in three dimensions is

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

E_k - total energy of the electron in K state.

If the electrons are confined to a cube of edge L , the wave function at a particular point x, y, z are so chosen so that it is periodic with L to satisfy the periodic boundary condition. ie., the wave function to be periodic with L , $\psi(x+L, y, z) = \psi(x, y, z)$; $\psi(x, y+L, z) = \psi(x, y, z)$; $\psi(x, y, z+L) = \psi(x, y, z)$

The wave function which satisfies the boundary condition and the free electron Schrodinger equation is of the form

$$\therefore \psi(x, y, z) = A e^{ik.r} = A e^{i(K_x x + K_y y + K_z z)}$$

provided that the wave vector satisfy $K_x = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots$ similarly K_y and K_z

$$\therefore K \text{ is of the form } \frac{2n\pi}{L}$$

$$\begin{aligned} \therefore E_k &= \frac{\hbar^2}{2m} (K_x^2 + K_y^2 + K_z^2) \\ &= \frac{\hbar^2}{2m} K^2 \end{aligned}$$

$$\psi_k(r) = \sqrt{\left(\frac{8}{L^3}\right)} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

n_x, n_y, n_z are positive integer $\sqrt{\left(\frac{8}{L^3}\right)}$ is normalising constant.

The energy spectrum consists of discrete levels which lie usually very close together ($\approx 10^{-15}$ eV a part) and may be taken as continuous. Such energy levels are quasi continuous.



The separation between the energy levels depends on the size of the box.

Using normalizing condition $\int \psi^*(r)\psi(r) d\tau = 1$.

$$\int_0^L \int_0^L \int_0^L A^2 e^{-ik \cdot r} e^{ik \cdot r} dx dy, dz = 1.$$

$$A = \left(\frac{1}{V}\right)^{1/2}$$

\therefore The normalized wave function is $\psi_k(r) = \left(\frac{1}{V}\right)^{1/2} e^{ik \cdot r}$

At absolute zero all the levels below a certain level will be filled with electrons and all the levels above it will be empty. The level which divides the filled and vacant level is called the Fermi level ($E_{f(0)}$).

At non zero temperature, Fermi shown that the probability that a particular Quantum state at energy E is filled is given by

$$f(E) = \frac{1}{\exp\{(E - E_f) / k_{BT}\} + 1}$$

At absolute zero,

$$f(E) = 1 \text{ for } E < E_f(0)$$

$$= 0 \text{ for } E > E_f(0)$$

Fermi Distribution function becomes step function. Temperature increases distribution function loses its step like character and varies much slowly with energy.

$$f(E) \text{ at } E = E_f \text{ is } \frac{1}{2} \therefore f(E_f) = \frac{1}{2}$$

ie E_f is a level lying half way between filled and empty states.

Fermi Energy

Fermi sphere

In the ground state of a system of N free electrons, the occupied orbitals may be represented as points inside a sphere in K space. It allows maximum values of K vectors. At absolute zero Fermi sphere separates filled and unfilled orbits. The energy at the surface of



the sphere is Fermi energy. The wave vector at the Fermi surface is K_f . K_f is independent of mass, but depends upon $\left(\frac{N}{V}\right)$ electron concentration.

Let the linear momentum P , $P = -i\hbar\nabla$

For the energy state $P\psi_k(r) = -i\hbar\nabla\psi_k(r) = \hbar k\psi_k(r)$

ψ_k is eigen function of linear moment with eigen value $\hbar k$.

The particle velocity is $V = \frac{\hbar k}{m}$

$$E_{f(0)} = \frac{\hbar^2 k_f^2}{2m}$$

The volume of Fermi sphere is $\frac{4}{3}\pi k_f^3$,

The total number of orbitals in k space is $N = 2 \times \frac{\frac{4}{3}\pi k_f^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{3\pi^2} k_f^3$.

Where 2 represents the two allowed values of m_s , and $k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$

This depends only on particle concentration $\frac{N}{V}$ and not on the mass.

$$\therefore \text{The Fermi energy } E_f(0) = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\text{The electron velocity } v_f = \frac{\hbar k_f}{m} = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Heat capacity of the electron gas: $\left(\frac{dE}{dT}\right)$

The energy absorbed by a unit mass when its temperature is raised by one degree is specific heat capacity. According to classical theory, heat capacity of free particle is $\frac{3}{2} K_B$. If there are N atoms, each give one valance electron to the electron gas, \therefore electronic contribution to heat capacity is $\frac{3}{2} NK_B$.



But the observed value of Specific heat capacity at room temperature is $\frac{1}{100}$ of the clinical value. This discrepancy is explained by using Pauli Exclusion Principle and Fermi distribution function. Fermi found the specific heat vanishes at absolute zero, and at low temperature, it is proportional to absolute temperature.

Qualitative expression for specific heat capacity

When the temp increases from absolute zero, the electron in orbitals within an energy range $K_B T$ of the Fermi level are excited thermally. These electrons gain an energy with an order of $K_B T$.

For N electrons, only a fraction of $\frac{T}{T_F}$ can be excited thermally at temperature T, because only these lie within the energy range $K_B T$.

$$\therefore \frac{NT}{T_F} \text{ electron as thermally excited}$$

$$\therefore \text{Thermal energy } \Delta E = \frac{NT}{T_F} K_B T$$

$$\begin{aligned} \therefore \text{The electronic specific heat capacity } C_{ele} &= \frac{\partial \Delta E}{\partial T} \\ &= \frac{NT}{T_F} K_B \\ C_{el} &= NK_B \frac{T}{T_F} \end{aligned}$$

$$\text{ie } C_{elec} \propto T$$

Quantitative expression for electronic Heat capacity

This is valid at low temp. in $K_B T \ll E_F$

For a system of N electrons, the increases in the total energy ΔE for a raise of temp from 0 to T is

$$\Delta E = \int_0^{\infty} d\varepsilon \varepsilon D(\varepsilon) f(\varepsilon) - \int_0^{E_F} d\varepsilon \varepsilon D(\varepsilon) \quad \dots(1)$$

$$\text{The total no. of particles, } N = \int_0^{\infty} d\varepsilon f(\varepsilon) D(\varepsilon) \quad \dots(2)$$



multiply equation (2) by ε_F , $\varepsilon_F N = \varepsilon_F \int_0^{\infty} d\varepsilon f(\varepsilon) D(\varepsilon)$... (3)

Differentiate equation (1) with respect to T , $\frac{\partial \Delta E}{\partial T} = \int_0^{\infty} d\varepsilon \varepsilon D(\varepsilon) \frac{df}{dT}$

ie., $C_{elec} = \int_0^{\infty} d\varepsilon \varepsilon_F D(\varepsilon) \frac{dF}{dT}$... (4)

Differentiate equation (3) with respect to T , $0 = \int_0^{\infty} d\varepsilon \varepsilon_F D(\varepsilon) \frac{df}{dT}$.. (5)

Subtracting equation (4) from (5) $C_{elec} = \int_0^{\infty} d\varepsilon (\varepsilon - \varepsilon_F) D(\varepsilon) \frac{df}{dT}$... (6)

At low temp. (ie $\frac{K_B T}{\varepsilon_F} < 0.01$), $\frac{\partial F}{\partial T}$ is large only at energy near ε_F .

$$\therefore D(\varepsilon) = D(\varepsilon_F)$$

$$\therefore C_{elec} = D(\varepsilon_F) \int_0^{\infty} d\varepsilon (\varepsilon - \varepsilon_F) \frac{df}{dT}$$

Where $f(E) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1}$

$$\therefore \frac{\partial f}{\partial T} = \frac{\varepsilon - \varepsilon_F}{K_B T^2} \frac{e^{(\varepsilon - \varepsilon_F)/K_B T}}{\{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1\}^2}$$

$$\therefore C_{elec} = D(\varepsilon_F) \int_0^{\infty} \frac{(\varepsilon - \varepsilon_F)^2}{K_B T^2} d\varepsilon \frac{e^{(\varepsilon - \varepsilon_F)/K_B T}}{\{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1\}^2}$$

Let $\frac{\varepsilon - \varepsilon_F}{K_B T} = x$. $\therefore (\varepsilon - \varepsilon_F)^2 = x^2 K_B^2 T^2$, $(\varepsilon - \varepsilon_F) = x K_B T$ $\therefore d\varepsilon = K_B T dx$

If $\varepsilon = 0$, $x = -\varepsilon_F / K_B T$; and if $\varepsilon = \alpha$, $x = \infty$

$$C_{elec} = D(\varepsilon_F) \int_{-\varepsilon_F/K_B T}^{\infty} \frac{K_B^2 T^2 x^2}{K_B T^2} K_B T dx \frac{e^x}{(e^x + 1)^2}$$



Since T is very small the lower limit $-\frac{\epsilon_F}{K_B T} \approx -\infty$

$$C_{elec} = D(\epsilon_F) \int_{-\infty}^{\infty} K_B^2 T x^2 \frac{e^x}{(e^x + 1)^2} dx$$

$$= D(\epsilon_F) K_B^2 T \int_{-\infty}^{\infty} x^2 \frac{e^x}{(e^x + 1)^2} dx$$

The integral $\int_{-\infty}^{\infty} x^2 \frac{e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}$

$$\therefore C_{elec} = \frac{\pi^2}{3} K_B^2 T D(\epsilon_F)$$

But $D(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2K_B T_F} \dots\dots\dots (\epsilon_F = K_B T_F)$

$$\therefore C_{elec} = \frac{\pi^2}{3} K_B^2 T \frac{3N}{2K_B T_F}$$

$$C_{elec} = \frac{\pi^2}{2} N K_B \frac{T}{T_F}$$

This is in agreement with the qualitative result.

Experimental heat capacity of metals:

At temperature much below the Debye temperature and very much below the Fermi temperature the heat capacity of metals at constant volume consists of two parts namely

$C_{electronic}$ and $C_{lattice}$

$$\therefore C = C_{elet} + C_{lattice}$$

This is given as

$$C = \gamma T + AT^3$$

Where γ and A are constants.

$$\frac{C}{T} = \gamma + AT^2$$



A graph is drawn taking $\frac{C}{T}$ along y axis and T^2 along x axis. We get a straight line. The intercept gives the value of γ and the slope gives the value of A .

For potassium, the values of $\gamma = 2.08$; $A = 2.58$ from graph

The value of γ corresponding to electronic contribution agrees with the value with 2% error.

Reasons for 2% error

The following interactions were neglected. The interaction of negative ion core. The interaction of conduction electrons with the periodic potential of the crystal lattice. The interaction of conduction electrons with phonons. The interaction of conduction electrons with themselves. These causes the small variations.

Fermi liquid :

A Fermi gas is a system of non-interacting identical particles subject to the Pauli exclusion principle. The same system with interaction is called a Fermi liquid.

(eg) i) conduction electrons in a metal

(ii) liquid Helium He^3

Effective mass concept in Band theory :

The effective mass is a new concept and arises due to the interaction of the electron wave packet with the periodic lattice. If the binding force between the electron and lattice is strong, the electron acquires a large effective mass.

the energy of the free electron in terms of k is given as, $E = \frac{h^2}{8\pi^2 m} K^2$

where m is the mass of the electron.

Differentiate the expression we get,

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

So that

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



For a free electron model E versus k has a parabolic relation. The mass and d^2E/dk^2 are taken as constant.

When the electron move in a periodic potential of the crystal lattice, the parabolic relation no longer exists, there is a break up in the curve at various zone boundaries leading to the origin of allowed and forbidden bands. Near the forbidden band the curvature of curve changes, since as k approaches the zone boundary d^2E/dk^2 first reduces to zero and then becomes negative. The mass and d^2E/dk^2 are not constant and both of them are a

function of k . Thus under periodic potential, the mass of electron $m = \frac{h^2}{4\pi^2} \left(\frac{d^2E}{dk^2} \right)^{-1}$ is known as effective mass and is represented as m^* and is represented as

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

The effective mass is positive in the lower part of the band (lower k value) and negative close to the boundary (near $k \approx \frac{\pi}{a}$).

For example, considering the energy of the electron, orbital of the bottom of 2nd zone.

$$\begin{aligned} E_1 &= E^1 + \left(1 + \frac{2\lambda}{v_1}\right) \frac{\hbar^2 \delta^2}{2m} \\ &= E^1 + \frac{\hbar^2 \delta^2}{2m^*} \text{ where } m^* = \frac{m}{\left(\frac{1+2\lambda}{v}\right)} \end{aligned}$$

$$m^* < m$$

If we consider the position of the electron in the crystal, for away from the Brillouin zone boundary, the effective mass is very nearly equal to electron mass. But very near to the Brillouin zone boundary the mass of free electron is some time negative also. The negative nature of effective mass can be explained as follows. Due to electric or magnetic field, the momentum associated with the electron, increases. Momentum is considered as forward momentum when it approaches the boundary whereas the lattice gives the momentum in the backward direction. The backward momentum is greater than the forward momentum possessed by the electrons. Hence mass of the electron is considered to be negative in this region.



Electrical conductivity and ohm's law :-

The momentum of a free electron $p = mv = \hbar k$.

The force acting of a particle (Newtons 2d law) $F = m \frac{dv}{dt}$

$$= m \frac{d}{dt} \left(\frac{\hbar k}{m} \right)$$

$$F = \hbar \frac{dk}{dt}$$

In an electric and magnetic field, the force on an electron is

$$F = -e \left[E + \frac{1}{C} (v \times B) \right]$$

$$\text{ie } \hbar \frac{dk}{dt} = -e \left[E + \frac{1}{C} (v \times B) \right]$$

$$\text{if } B=0, \hbar \frac{dk}{dt} = -eE$$

$$dk = -\frac{eE}{\hbar} dt$$

$$\left[\int_0^t dk \right] = \frac{eE}{\hbar} \int_0^t dt$$

$$k(t) - k(0) = \frac{-eE}{\hbar} t \quad \left] \right.$$

At $t = 0$, centre of the Fermi sphere at the origin of k space after t time the centre of the sphere displaced to a new centre at

$$\partial k = \frac{-eEt}{\hbar}$$

Because of the collisions of electrons with impurities, lattice imperfections and phonons, the displaced sphere may be maintained in a steady state in an electric field.

If the collision time is τ the displacement of Fermi sphere in the steady state is

$$\partial k = \frac{-eE\tau}{\hbar}$$



The change in velocity of a free electron due to electric field is $dv = +\hbar \frac{dk}{m}$

$$= -\frac{\hbar}{m} \frac{eE\tau}{\hbar}$$

$$dv = -\frac{eE\tau}{m}$$

If there are n free electrons in unit volume of specimen then the current density $j = nqdv$

Where q is the charge of electron = $-e$

$$\therefore j = n(-e) \left(\frac{-eE\tau}{m} \right)$$

$$j = \left(\frac{ne^2E\tau}{m} \right)$$

This is in the form of ohm's law $j = \sigma E$

Compaing these two equs. We get $\sigma = \frac{ne^2\tau}{m}$

Where σ is the electrical conductivity

\therefore The electrical conductivity $\sigma = \frac{ne^2\tau}{m}$

The electrical resistivity (ρ) is the reciprocal of the conductivity

$$\therefore \rho = \frac{m}{ne^2\tau}$$

(σ) conductivity is proportional to the charge density (ne)

$$\sigma \propto \frac{e}{m}$$

$\sigma \propto \tau$ the free time during which the field acts on the carrier.

The mean free path of a conduction electron is defined as $l = v_F \tau$ Where V_F is the velocity at Fermi surface.

Matthiessen's rule :-

The resistivity of a metal consists two parts.



- (i) resistivity caused by the thermal motion of the lattice ρ_L
- (ii) resistivity caused by the scattering of the electron waves by impurity atoms ρ_i

$$\therefore \rho = \rho_L + \rho_i$$

This statement is known as Matthiessen's rule.

If the concentration of impurity atoms is small, ρ_i is independent of temperature.

A graph is drawn between the relative resistance and temperature. The extrapolated resistivity at $0^\circ K$ is residual resistivity. It is ρ_i because ρ_L vanishes as $T \rightarrow 0$.

The resistivity ratio is defined as the ratio of its resistivity at room temperature to its resistivity at liquid helium temperature.

Hall effect

When a piece of conductor (metal or Semiconductor) carrying a current is placed in a transverse magnetic field, an electric field is produced inside the conductor in a direction normal to both the current and magnetic field. This phenomenon is known as the Hall effect and the generated voltage is known as Hall Voltage.

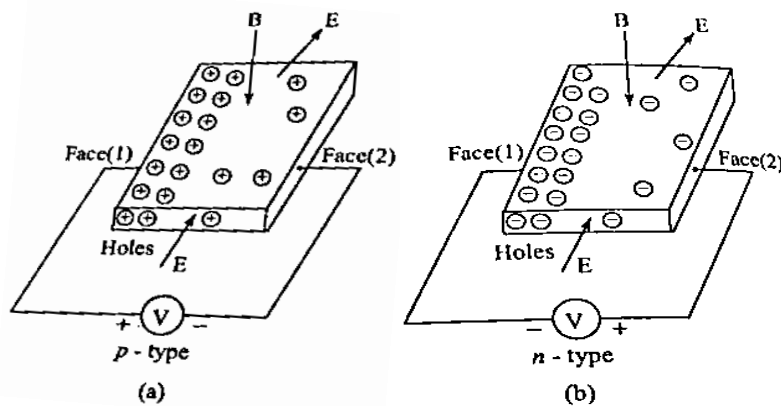


Figure 4.4

Consider a P-type semiconductor specimen (fig. b). Electric and magnetic fields are applied at right angle to each other. Holes of the semiconductor experiences a mutually perpendicular force from right to left and they accumulated near the face1 of the slab and measures a voltage between the two faces known as Hall voltage. In case of N-type semiconductor, electrons accumulated on face 1 (fig. 4.4a).



Let B be the transverse magnetic field and E be the longitudinal electric field applied on a slab of N type semiconductor, and v be the velocity of electrons. Then the electrons experiences a force Bev . A potential difference is established across the faces 1 and 2 of the slab causing a field E_H . This field generates a force eE_H on electrons in the opposite direction.

At equilibrium, $Bev = eE_H$

ie., $E_H = Bv$

The current density $J = nev$ where n is the concentration of current carriers

Therefore $v = \frac{J}{ne}$,

Then $E_H = \frac{BJ}{ne}$

Now the Hall coefficient $R_H = \frac{1}{ne}$, Hence $E_H = BJR_H$

ie., $R_H = \frac{E_H}{BJ} = \frac{1}{ne}$

Since all the three quantities E_H , B , and J are measurable, the Hall coefficient R_H and hence the carrier density n can be found out.

For P-type semiconductor, negative sign is used to denote R_H

ie., $R_H = -\frac{E_H}{BJ} = -\frac{1}{ne}$

and the current is developed by holes concentration p , p is used instead of n

Therefore $R_H = \frac{E_H}{BJ} = \frac{1}{pe}$

$$k = \frac{\pi^2}{2} \frac{NK_B^2 T \tau}{m}$$



Wave equation of electron in a periodic potential : (General theory of band theory of a crystal)

Consider a crystal of length 'L' with lattice constant a; Let $U(x)$ be the Potential Energy of an electron in a linear lattice. It is invariant under a crystal lattice translation.

ie.,
$$U(x) = U(x + a)$$

When any function in a crystal is invariant, it may be represented as a Fourier series in the reciprocal lattice vectors G.

ie.,
$$U(x) = \sum_G U_G e^{iGx}$$

$U_G \propto \frac{1}{G^2}$, ie., U_G coefficient of crystal potential decreases with the increasing the reciprocal lattice vector G, and $U(x)$ is real and even function. Then the wave equation of an electron in the crystal is

$$H\psi = E\psi$$

Where H – Hamiltonian; E – Energy eigen value; and ψ - eigen function (or) orbital $\psi \rightarrow$ the wave function may be expressed as a Fourier series.

$$\psi(x) = \sum_k c(k) e^{ikx} \quad \text{where } k \text{ is real } \frac{-2n\pi}{L}$$

\therefore The wave equation,

$$\left[\frac{P^2}{2m} + U(x) \right] \psi(x) = E\psi(x)$$

$$\left[\frac{P^2}{2m} + \sum_G U_G e^{iGx} \right] \sum_k c(k) e^{ikx} = E \sum_k c(k) e^{ikx}$$

where $p = -i\hbar \frac{\partial}{\partial x}$, $p^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \sum_G U_G e^{iGx} \right] \sum_k c(k) e^{ikx} = E \sum_k c(k) e^{ikx}$$

$$\sum \frac{\hbar^2}{2m} k^2 c(k) e^{ikx} + \sum_G \sum_k U_G c(k) e^{i(k+G)x} = E \sum_k c(k) e^{ikx} .$$

...(A)



Using orthogonality properly of different Fourier components

$$\int_0^L dx e^{-ik^1x} e^{ikx} = \begin{cases} \frac{1}{i(k-k^1)} [e^{i(k-k^1)L} - 1] = 0 & \text{if } k^1 \neq k \\ L & \text{if } k^1 = k \end{cases}$$

$$k = \frac{2n\pi}{L}, \quad k^1 = \frac{2\pi n^1}{L} \quad n, n^1 \text{ are integers}$$

$$\therefore \exp [i(k - k^1)L] = \exp [2\pi i(n - n^1)] = 1.$$

Multiply equation (A) by e^{-ik^1x} and integrate over dx ,

$$\frac{\hbar^2}{2m} k^2 c(k^1) + \sum_G U_G c(k^1 - G) = E c(k^1)$$

$$\text{i.e., } K + G = K^1 \quad \therefore K = K^1 - G$$

For our convenience, in the above equation K^1 is replaced by K and put $\frac{\hbar^2}{2m} k^2 = \lambda_k$

Then the equation becomes

$$\lambda_k C(K) + \sum_G U_G C(K - G) = E C(K)$$

$$(\lambda_k - E) C(K) + \sum_G U_G C(K - G) = 0 \quad (I)$$

This is the most important equation in the band theory of solids.

$$\therefore C(K) = - \frac{\sum_G U_G C(K - G)}{\lambda_k - E}$$

$$C(K) = - \frac{\sum_G U_G C(K - G)}{E - \frac{\hbar^2}{2m} K^2}$$

$$\text{The wave function } \psi_K(x) = \sum_G C(K - G) e^{i(K-G)x}$$

The equation (I) is for a given Fourier coefficient $C(K)$. For the infinite number of the other Fourier coefficients, the wave vector differs from K by a reciprocal lattice vector G^1 .

To form an infinite set of independent equations by subtracting successive reciprocal lattice vector from K we get,



$$(\lambda_{K-G^1} - E)C(K - G^1) + \sum_G U_G C(K - G^1 - G) = 0.$$

$$C(K - G^1) = \sum_G \frac{U_G C(K - G^1 - G)}{E - \frac{\hbar^2}{2m}(K - G^1)^2} = 0.$$

$(K - G^1)$ in the place of K . $\therefore (K - G^1)^2 = K^2$

Both $\exp(ikx)$ and $\exp[i(K - G^1)x]$ are important components of the orbital $\psi_k(x)$.

(i) Wave function on the zone boundary :-

At the Brillouin zone boundary the wave vector $K = \frac{1}{2}G$.

$$\therefore (K - G) = \left(\frac{1}{2}G - G\right) = -\frac{1}{2}G.$$

\therefore The equation I contains both coefficients $C\left(\frac{1}{2}G\right)$ and $C\left(-\frac{1}{2}G\right)$

Then the equ (I) becomes, $U_1 = U_G = U_{-G}$; and $\lambda_1 = \lambda_{-1} = \lambda$

$$(\lambda - E)C\left(\frac{1}{2}G\right) + U_1 C\left(-\frac{1}{2}G\right) = 0 \quad \dots(i)$$

$$(\lambda - E)C\left(-\frac{1}{2}G\right) + U_1 C\left(\frac{1}{2}G\right) = 0 \quad \dots(ii)$$

These two equations have nontrivial solutions for the two coefficients

$C\left(\frac{1}{2}G\right)$ and $C\left(-\frac{1}{2}G\right)$ if the energy E satisfies

$$\begin{vmatrix} \lambda - E & U_1 \\ U_1 & \lambda - E \end{vmatrix} = 0$$

$$(\lambda - E)^2 - U_1^2 = 0$$

$$(\lambda - E)^2 = U_1^2$$

$$\lambda - E = \pm U_1$$

$$E = \lambda \mp U_1$$

ie $E_1 = \lambda + U_1$ and $E_2 = \lambda - U_1$



At the first Brillouin zone boundary we have two energies with a differences

$$E_1 - E_2 = \lambda + U_1 - (\lambda - U_1) = 2U_1$$

$2U_1$ is called band gap.

From equation (ii), we get

$$\frac{C(-G/2)}{C(G/2)} = -\frac{U_1}{\lambda - E} = \frac{U_1}{E - \lambda}$$

but $E - \lambda = U_1$

$$\therefore \frac{C(-G/2)}{C(G/2)} = \pm 1$$

\therefore The Fourier expansion of $\psi(x)$ has the two solution.

$$\psi(x) = e^{iG/2 x} \pm e^{-iG/2 x}$$

These orbitals are identical to standing waves. One solution gives the wave function at the bottom of the energy gap, and the other gives the wave function at the top of the energy gap.

(iii) Wave function near the Brillouin zone Boundary :

Consider the wave k very near to Brillouin Zone boundary, $k = \frac{G}{2} - \delta$ where δ is very small.

The general expression is

$$(\lambda_k - E)C(K) + U_1 C(K - G) = 0$$

Put $K = K - G$

$$(\lambda_{k-G} - E)C(K - G) + U_1 C(K) = 0$$

These equations have a solution if the energy E satisfies

$$\begin{vmatrix} \lambda_K - E & U_1 \\ U_1 & \lambda_{K-G} - E \end{vmatrix} = 0$$

$$(\lambda_K - E)(\lambda_{K-G} - E) - U_1^2 = 0$$



$$\epsilon^2 - \epsilon(\lambda_{K-G} + \lambda_K) + \lambda_{K-G}\lambda_K - U_1^2 = 0$$

$$\therefore \epsilon = \frac{(\lambda_{K-G} + \lambda_K) \pm \sqrt{(\lambda_{K-G} + \lambda_K)^2 - 4(\lambda_{K-G}\lambda_K - U_1^2)}}{2}$$

$$= \frac{1}{2}(\lambda_{K-G} + \lambda_K) \pm \frac{1}{2} \sqrt{(\lambda_{K-G} + \lambda_K)^2 - 4\lambda_{K-G}\lambda_K - 4U_1^2}$$

$$= \frac{1}{2}(\lambda_{K-G} + \lambda_K) \pm \frac{1}{2} \sqrt{(\lambda_{K-G} - \lambda_K)^2 - 4U_1^2}$$

$$\epsilon = \frac{1}{2}(\lambda_{K-G} + \lambda_K) \pm \sqrt{\frac{1}{4}(\lambda_{K-G} - \lambda_K)^2 - U_1^2}$$

$$K - G = \frac{G}{2} - \delta - G = -\frac{G}{2} - \delta$$

$$\therefore \lambda_K = \frac{\hbar^2}{2m} \left(\frac{G}{2} - \delta \right)^2$$

$$\lambda_{K-G} = \frac{\hbar^2}{2m} \left(-\frac{G}{2} - \delta \right)^2$$

$$\lambda_{K-G} + \lambda_K = \frac{\hbar^2}{2m} \left(-\frac{G}{2} - \delta \right)^2 + \frac{\hbar^2}{2m} \left(\frac{G}{2} - \delta \right)^2$$

$$= \frac{\hbar^2}{2m} \left[\frac{G^2}{4} + \delta^2 + GS + \frac{G^2}{4} + \delta^2 - GS \right]$$

$$\lambda_{K-G} - \lambda_K = \frac{\hbar^2}{2m} \left[\frac{G^2}{4} + \delta^2 + GS - \frac{G^2}{4} - \delta^2 + G\delta \right]$$

$$\therefore \frac{1}{2}(\lambda_{K-G} + \lambda_K) = \frac{\hbar^2}{2m} \cdot \frac{1}{2} \left[\frac{2G^2}{4} + 2\delta^2 \right] = \frac{\hbar^2}{2m} \left[\frac{G^2}{4} + \delta^2 \right]$$

$$(\lambda_{K-G} - \lambda_K)^2 = \frac{\hbar^2}{2m} \cdot \frac{\hbar^2}{2m} \cdot 4 \cdot G^2 \delta^2$$

$$\therefore \epsilon = \frac{\hbar^2}{2m} \left(\frac{G^2}{4} + \delta^2 \right) \pm \sqrt{\frac{1}{4} \cdot \frac{\hbar^2}{2m} \cdot \frac{\hbar^2}{2m} \cdot 4\delta^2 G^2 + U_1^2}$$

$$\epsilon = \frac{\hbar^2}{2m} \left(\frac{G^2}{4} + \delta^2 \right) \pm \left(\frac{\hbar^2}{2m} \cdot \frac{\hbar^2}{2m} \cdot \delta^2 G^2 + U_1^2 \right)^{\frac{1}{2}}$$



$$\text{But } \lambda = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} \frac{G^2}{4}, \quad \therefore \frac{\hbar^2}{2m} G^2 = 4\lambda$$

$$\begin{aligned} \epsilon &= \frac{\hbar^2}{2m} \left(\frac{G^2}{4} + \delta^2 \right) \pm \left(4\lambda \frac{\hbar^2}{2m} \cdot \delta^2 + U_1^2 \right)^{\frac{1}{2}} \\ \epsilon &= \frac{\hbar^2}{2m} \left(\frac{G^2}{4} + \delta^2 \right) \pm U_1 \left(1 + \frac{2\lambda}{U_1^2} \frac{\hbar^2 \delta^2}{m} \right)^{\frac{1}{2}} \end{aligned} \quad (X)$$

On the zone boundary we get,

$$\epsilon = \frac{\hbar^2}{2m} \left(\frac{1}{2} G \right)^2 \pm U_1$$

$$\text{From this} \quad \epsilon_1 (+) = \frac{\hbar^2}{2m} \frac{G^2}{4} + U_1$$

$$\epsilon_1 (-) = \frac{\hbar^2}{2m} \frac{G^2}{4} - U_1$$

The equation (X) can be written as

$$\epsilon = \frac{\hbar^2}{2m} \frac{G^2}{4} \pm \frac{\hbar^2}{2m} \delta^2 \pm U_1 \left(1 + \frac{1}{2} \cdot \frac{2\lambda}{U_1^2} \cdot \frac{\hbar^2 \delta^2}{m} \right)$$

$$\epsilon = \frac{\hbar^2}{2m} \frac{G^2}{4} + \frac{\hbar^2 \delta^2}{2m} \pm U_1 \pm \frac{\lambda}{U_1} \cdot \frac{\hbar^2 \delta^2}{2m}$$

$$= \frac{\hbar^2}{2m} \frac{G^2}{4} \pm U_1 + \frac{\hbar^2 \delta^2}{2m} \left(1 \pm \frac{2\lambda}{U_1} \right)$$

They we may write as,

$$\epsilon_K (+) = \epsilon_1 (+) + \frac{\hbar^2 \delta^2}{2m} \left(1 + \frac{2\lambda}{U_1} \right)$$

$$\epsilon_K (-) = \epsilon_1 (-) + \frac{\hbar^2 \delta^2}{2m} \left(1 - \frac{2\lambda}{U_1} \right)$$

These are the roots for the energy when the wave vector is very close to the zone boundary at $\frac{1}{2}G$. For $U_1(-)ve$, $\epsilon_K (-)$ corresponds to the upper band and $\epsilon_K (+)$ corresponds to the lower band.



Block theorem

Block theorem is a mathematical form of one electron wave function for a perfectly periodic potential. The wave function $\psi_K(x) = U_K(x)e^{ikx}$ is the statement of Block theorem. Orbital of this form is Block function.

Block theorem states that the eigen function of the wave equation for a periodic potential are of the form of the product of a plane wave $e^{ik \cdot r}$ times a function $U_K(r)$ which is periodic in the crystal lattice.

Proof

Let the P.E of an electron satisfy the equation $V(x) = V(x + a)$ (where a is period)

The Schrodinger wave equation is

$$\frac{\partial \psi}{\partial x^2} + \frac{2m}{\hbar} [E - V(x)] \psi = 0$$

Block theorem states that the solutions are plane waves modulated by the function $U_K(x)$ which has the same periodicity as the lattice.

Let us consider the wave function associated with electron in a periodic potential and of the form,

$$\psi_K(x) = \sum_G C(K - G) e^{i(K-G)x}$$

$$\psi_K(x) = \left(\sum_G C(K - G) e^{-iGx} \right) e^{ikx}$$

$$\psi_K(x) = U_K(x) e^{ikx}$$

$$\text{Where } U_K(x) = \sum_G C(K - G) e^{-iGx}$$

$U_K(x)$ is a Fourier series over the reciprocal lattice vector, \therefore it is invariant under a crystal translation.

$$\text{ie } U_K(x) = U_K(x + a)$$

$$\text{ie } U_K(x + a) = \sum_G C(K - G) e^{-iG(x+a)}$$



$$= \sum_G C(K-G) e^{-iGx} e^{-iGa}$$

$$e^{-iGa} = e^{-i \frac{2\pi}{a} \cdot a} \quad \text{Since } G = \frac{2\pi}{a}$$

$$e^{-i2\pi} = \cos 2\pi - i \sin 2\pi = 1$$

$$\therefore U_K(x+a) = \sum_G C(K-G) e^{-iGx}$$

$$= U_K(x)$$

$\therefore U_K(x)$ is periodic with crystal lattice.

Properties :-

(i) In the crystal lattice translation, ie., r to $r+T$

$$\begin{aligned} \psi_K(r+T) &= e^{iK \cdot T} e^{iK \cdot r} U_K(r+T) \\ &= e^{iKT} \cdot \psi_k(r) \quad \text{since } U_K(r) = U_K(r+T) \end{aligned}$$

$\therefore e^{iKT}$ is the phase factor.

(ii) If the lattice potential = 0, the general equation becomes

$(\lambda_K - \epsilon)C(K) = 0$, so that $C(K-G)$ are zero except $C(K)$ and $U_k(r)$ is constant.

$$\psi_K(r) = e^{ik \cdot r}$$

(iii) $\hbar k$ is crystal momentum. When an electron of wave vector K collided with a phonon of wave vector K , it scattered.

$$k + K = k^1 + G \quad (\text{Selection rule})$$

k is scattered wave vector, G is reciprocal lattice vector.

Extended, Reduced and Periodic zone scheme:

The wave vector representation of a plane wave eigen state is simple and definite while the representation of Bloch states are not so because the Bloch functions is not a simple plane wave but a modulated plane wave. To represent these states three different schemes are commonly used. They are called the extended zone scheme (or the Brillouin zone scheme), the Reduced zone scheme and Periodic zone scheme. All the three schemes represent the identical physical behavior.



Periodic zone scheme :-

A Brillouin zone can be periodically repeated in wave vector space by a reciprocal lattice vector. If translation of a band from other zones into the first zone is possible the translation of a band in the first zone to any or every other zone also possible. This construction is periodic or repeated zone scheme.

The energy ϵ_K of a band is periodic function with the reciprocal lattice ie., $\epsilon_K = \epsilon_{K+G} \dots$

Let the energy band of Simple Cubic lattice.

$$\epsilon_K = E_0 - \alpha - 2\gamma(\cos K_x a + \cos K_y a + \cos K_z a)$$

E_0, α, γ are constants.

Reciprocal lattice vector of Simple Cubic is $G = \frac{2\pi}{a} \hat{x}$

$\therefore \cos(k_x a)$ only changes

$$\cos(k_x a) = \cos\left(k_x + \frac{2\pi}{a}\right)a = \cos(k_x a + 2\pi) = \cos k_x a$$

\therefore There is no change in energy

\therefore In the periodic zone scheme energy is periodic function and in which every band is drawn in every zone.

Extended Zone Scheme:

Consider one dimensional lattice in which the energy of electron increases slowly with increase of k value. When k becomes large the wavelength becomes small ($k = \frac{2\pi}{\lambda}$), the electron will suffer a Bragg reflection. The Bragg reflections occur at $k = \frac{n\pi}{\lambda}$ where $n = \pm 1, \pm 2, \dots$ and energy gaps are developed as shown in fig. This representation of energy as a function of k is known as extended zone scheme. The extended zone scheme represents various Brillouin zones in k space, that is in which different bands are drawn in differ zones in wavevector space..



Reduced Zone Scheme :-

The process to bring a wave vector of Bloch function from outside the 1st Brillouin zone to inside the zone using a suitable reciprocal lattice vector G is known as reduced zone scheme.

$$\psi_{K^1}(r) = e^{iK^1 \cdot r} U_{K^1}(r) \quad \dots(1)$$

K^1 lies outside the 1st Brillouin zone

$K = K^1 - G$ lies within the zone.

Equation (1) becomes $\psi_{K+G}(r) = e^{i(K+G) \cdot r} U_{K+G}(r)$

$$= e^{iK \cdot r} [e^{iG \cdot r} U_{K+G}(r)]$$

We know that $e^{iG \cdot r} U_{K+G}(r) = U_K(r)$

$$\psi_{K^1}(r) = e^{iK \cdot r} U_K(r)$$

Both $e^{iG \cdot r}$ and $U_{K^1}(r)$ are periodic in the crystal lattice.

In reduced zone scheme all bands are drawn in the first Brillouin zone.

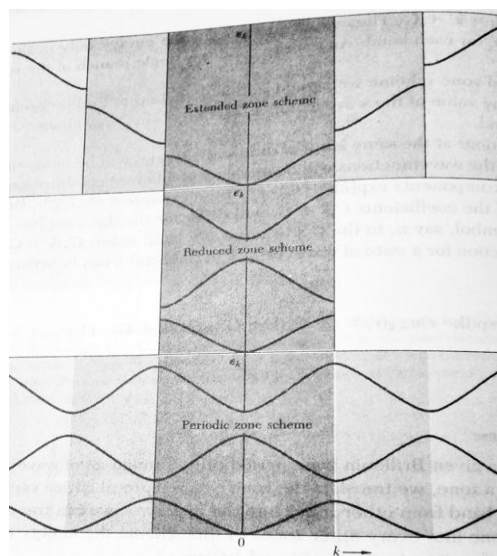


Figure 4.4 Three energy bands of a linear lattice



Kronig Penny model

Consider a simple crystal in one dimension with periodic potential. The period of the potential is $(a+b)$.

The potential $V=0$ for the region $0 < x < a$

The potential $V = V_0$ for $-b < x < 0$

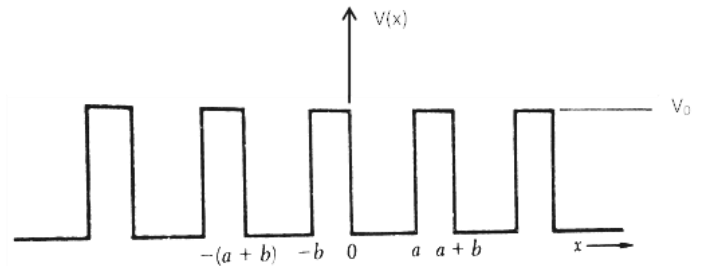


Figure 4.5

The wave equations for these regions are

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \text{..(1)}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \text{..(2)}$$

Let $\frac{2m}{\hbar^2} E = \alpha^2$ and $\frac{2m}{\hbar^2} (V - E) = \beta^2$

\therefore equation (1) and (2) becomes,

$$\frac{\partial^2 \psi}{\partial x^2} + \alpha^2 \psi = 0 \quad \text{..(3)}$$

$$\frac{\partial^2 \psi}{\partial x^2} - \beta^2 \psi = 0 \quad \text{..(4)}$$

Using Bloch theorem,

$$\psi(x) = e^{iKx} U_K(x)$$

$$\therefore \frac{\partial \psi}{\partial x} = ik e^{iKx} U_K(x) + e^{iKx} \frac{\partial U}{\partial x}$$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 e^{iKx} U_K(x) + ik e^{iKx} \frac{\partial U}{\partial x} + ik e^{iKx} \frac{\partial U}{\partial x} + e^{iKx} \frac{\partial^2 U}{\partial x^2}$$

$$= e^{iKx} \left[\frac{\partial^2 U}{\partial x^2} + 2ik \frac{\partial U}{\partial x} + K^2 U \right]$$

\therefore equation (3) becomes



$$e^{ikx} \left[\frac{\partial^2 U}{\partial x^2} + 2ik \frac{\partial U}{\partial x} - K^2 U \right] + \alpha^2 e^{ikx} U = 0$$

$$e^{ikx} \left[\frac{\partial^2 U}{\partial x^2} + 2ik \frac{\partial U}{\partial x} + (\alpha^2 - K^2) U \right] = 0$$

$$\frac{\partial^2 U}{\partial x^2} + 2ik \frac{\partial U}{\partial x} + (\alpha^2 - K^2) U = 0 \quad \text{..(5)}$$

Similarly equation (4) becomes $\frac{\partial^2 U}{\partial x^2} + 2ik \frac{\partial U}{\partial x} - (\beta^2 + K^2) U = 0$
 ..(6)

The solution of the periodic function is of the form $U = e^{mx}$

$$\therefore \frac{\partial U}{\partial x} = m e^{mx}, \quad \frac{\partial^2 U}{\partial x^2} = m^2 e^{mx}$$

$$\therefore \text{equ (5) becomes } e^{mx} [m^2 + 2ikm + (\alpha^2 - k^2)] = 0$$

$$\therefore m = \frac{-2ik \pm \sqrt{-4k^2 - (\alpha^2 - k^2)}}{2}$$

$$m = -ik \pm i\alpha,$$

$$i\alpha - ik = i(\alpha - k)$$

$$-i\alpha - ik = -i(\alpha + k)$$

$$\therefore U_1 = A e^{i(\alpha-k)x} + B e^{-i(\alpha+k)x} \quad \text{..(7)}$$

From equation (6), $e^{mx} [m^2 + 2ikm - (\beta^2 + k^2)] = 0$

$$\therefore m = \frac{-2ik \pm \sqrt{-4k^2 + 4(\beta^2 + k^2)}}{2}$$

$$= \frac{-2ik \pm \sqrt{4\beta^2}}{2} = -ik \pm \beta$$

ie $(\beta - ik), \quad -(\beta + ik)$

Therefore $U_2 = C e^{(\beta-ik)x} - D e^{-(\beta+ik)x}$

Boundary conditions are,



$$(i) \quad U_1(0) = U_2(0)$$

$$(ii) \quad \left. \frac{dU_1}{dx} \right|_{x=0} = \left. \frac{dU_2}{dx} \right|_{x=0}$$

$$(iii) \quad U_1(x=a) = U_2(x=-b)$$

$$(iv) \quad \left. \frac{dU_1}{dx} \right|_{x=a} = \left. \frac{dU_2}{dx} \right|_{x=-b}$$

By (i), $A + \beta = C + D \dots\dots(a)$

$$i(\alpha - k)Ae^{i(\alpha - k)x} - i(\alpha + k)\beta e^{-i(\alpha + k)x} = C(\beta - ik)e^{(\beta - ik)x} - D(\beta + ik)e^{-(\beta + ik)x}$$

at $x=0$,

$$i(\alpha - k)A - i(\alpha + k)\beta = C(\beta - ik) - D(\beta + ik) \dots\dots(b)$$

$$Ae^{i(\alpha - k)a} + \beta e^{-i(\alpha + k)a} = Ce^{-(\beta - ik)b} + De^{(\beta + ik)b} \dots\dots(c)$$

at $x = a, x = -b$,

$$i(\alpha - k)Ae^{i(\alpha - k)a} - i(\alpha + k)\beta e^{-i(\alpha + k)a} = C(\beta - ik)e^{-(\beta - ik)b} - D(\beta + ik)e^{(\beta + ik)b} \dots\dots(d)$$

For nontrivial solution the determinate of equation a, b, c & d must vanishes

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - k) & -(\alpha + k)i & \beta - ik & -(\beta + ik) \\ e^{i(\alpha - k)a} & e^{-i(\alpha + k)a} & e^{(\beta - ik)b} & e^{(\beta + ik)b} \\ (\alpha - k)e^{i(\alpha - k)a} & -(\alpha + k)e^{-i(\alpha + k)a} & (\beta - ik)e^{-(\beta - ik)b} & -(\beta + ik)e^{(\beta + ik)b} \end{vmatrix} = 0$$

On expanding the determinant we get,

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin h \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a + b)$$

$$\beta^2 - \alpha^2 = \frac{2m}{\hbar^2} (V - E) - \frac{2m}{\hbar^2} E$$

$$\beta^2 - \alpha^2 = \frac{2m}{\hbar^2} V$$

Let $b \rightarrow 0$, $\sin h \beta b = \beta b$ $\cosh \beta b = 1$

$$\therefore \frac{2m}{\hbar^2} V \cdot \frac{1}{2\alpha\beta} \cdot \beta b \sin \alpha a + \cos \alpha a = \cos k(a + 1)$$



$$\left(\frac{mV_0 b}{\hbar^2}\right) \sin \alpha a + \cos \alpha a = \cos ka$$

Since $V_0 \rightarrow \infty$, neglecting E in β in comparison to V_0

$$P = \beta^2 \frac{ab}{2} = \frac{2m}{\hbar^2} V_0 \cdot \frac{ab}{2} = \frac{mV_0 ab}{\hbar^2}$$

$$\therefore \frac{mV_0 b}{\hbar^2} = P/a$$

$$\therefore \text{the equation becomes } P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

The Quantity P is scattering power.

$$f(\alpha a) = \left\{ P \cdot \frac{\sin \alpha a}{\alpha a} + \cos \alpha a \right\} \quad \text{Vs } \alpha a \text{ Graph is shown in figure}$$

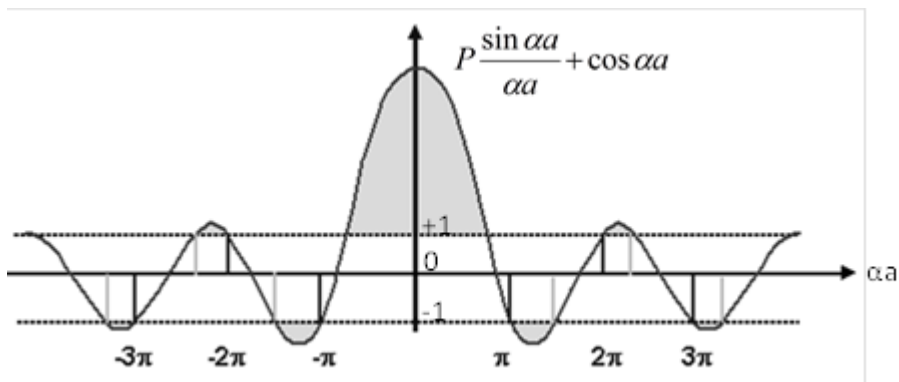


Figure 4.6

$|f(\alpha a)| < 1$, for k to be real. The value of E for which $|f(\alpha a)| > 1$, will be forbidden.

These are represented by shaded portions. $|f(\alpha a)| \leq 1$, will correspond to allowed values of energy.

Number of orbitals in a band

Consider a linear crystal constructed of an even number N of primitive cells of lattice constant a . To count the states, apply periodic boundary conditions to the wave functions over the length of the crystal.

The allowed values of the electron wave vector k in the first Brillouin zone are



$$k = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots; \pm \frac{N\pi}{L}$$

The zone boundary is $N\pi/L = \pi/a$. And the point $-N\pi/L = -\pi/a$ is not counted as an independent point because it is connected by a reciprocal lattice vector with π/a . The total number of points is N, the number of primitive cells.

Each primitive cell contributes one independent value of k to each energy band. With two independent orientation of spin, there are 2N independent orbitals in each energy band. If there is a single atom of valence one in each primitive cell, the band can be half filled with electrons. If each atom contributes two valence electrons to the band, the band can be exactly filled. Two atoms of valence one in each primitive cell, the band can be exactly filled.

Metals and Insulators

If the valance electrons exactly fill one or more bands, leaving others empty, the crystal will be an insulator. An external electric field will not cause current flow in an insulator, provided that a filled band is separated by an energy gap from the next higher band. A crystal can be an insulator only if the number of valence electrons in a primitive cell of the crystal is an even integer. If the bands overlap in energy, then two partly filled bands giving a metal (fig.)

The alkali metals and the nobel metals have one valence electron per primitive cell.

The alkaline earth metals have two valence electrons per primitive cell; they could be insulators, but the bands overlap in energy to give metals.

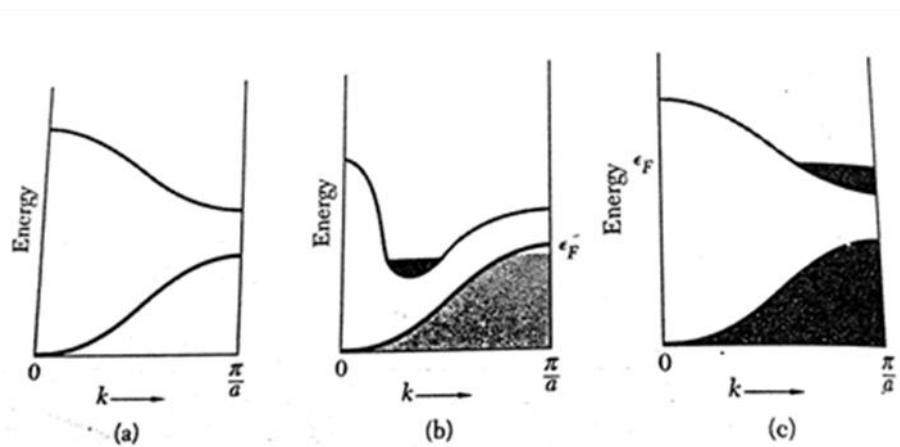


Figure 4.7 Occupied States and band stricture : (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration.



Diamond, Silicon and Germanium each have two atoms of valence four, so that there are eight valence electrons per primitive cell; the bands do not overlap, and the pure crystals are insulators at absolute zero.

Tight Binding Method

The tight-binding model (or TB model) is an approach to the calculation of electronic band structure using an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site. The method is closely related to the LCAO method (linear combination of atomic orbitals method). Though the tight-binding model is a one-electron model, the model also provides a basis for more advanced calculations like the calculation of surface states and application to various kinds of many-body problem and quasi-particle calculations.

The name "tight binding" of this electronic band structure model describes the properties of tightly bound electrons in solids. The electrons in this model should be tightly bound to the atom to which they belong and they should have limited interaction with states and potentials on surrounding atoms of the solid. As a result the wave function of the electron will be rather similar to the atomic orbital of the free atom to which it belongs. The energy of the electron will also be rather close to the ionization energy of the electron in the free atom or ion.

The most important element in the model is the interatomic matrix element, which would simply be called the bond energy. There are a number of atomic energy levels and atomic orbitals involved in the model.

Consider a solid which is composed of identical atoms which are characterized by an atomic orbitals $\varphi_\alpha(r)$. Here index α denotes the orbital state of the atom. Assume that one atom per unit cell. Then the solution of the Schrodinger wave equation

$$H\psi(r) = E\psi(r). \quad (1)$$

in terms of linear combination of the atomic orbitals, so that the Bloch wave function has a form of

$$\psi_k(r) = \sum_m \sum_\alpha e^{ikT_m} C_\alpha(k) \varphi_\alpha(r - T_m) \quad (2)$$



where The index m describing the lattice vector T_m

The orbital located at site m is $\varphi_\alpha(r - T_m)$.

And $C_\alpha(k)$ is the coefficients.

Equation (2) is the Bloch function which satisfies the requirement $\psi_k(r + T) = e^{ikT} \psi_k(r)$

$$\begin{aligned} \psi_k(r + T) &= \sum_{\alpha m} e^{ikT_m} C_\alpha(k) \varphi_\alpha(r - T_m + T) \\ &= e^{ikT} \sum_{\alpha m} e^{ik(T_m - T)} C_\alpha(k) \varphi_\alpha[r - (T_m - T)] \\ &= e^{ikT} \psi(r) \end{aligned} \quad (3)$$

Now we denote $\varphi_\alpha(r - T_m)$ by, $\varphi_{\alpha m}$. substitute (2) in (1) to have

$$\sum_{\alpha m} e^{ikT_m} C_\alpha(k) H \varphi_{\alpha m} = E \sum_{\alpha m} e^{ikT_m} C_\alpha(k) \varphi_{\alpha m} \quad (4)$$

Now multiply this equation by $\varphi_{\alpha' m'}^*$ and take an integral over the entire volume of a solid and denote in terms of the Dirac ket and bra vectors, so that

$$\sum_{\alpha m} e^{ikT_m} C_\alpha(k) \langle \varphi_{\alpha' m'} | H | \varphi_{\alpha m} \rangle = E \sum_{\alpha m} e^{ikT_m} C_\alpha(k) \langle \varphi_{\alpha' m'} | \varphi_{\alpha m} \rangle \quad (5)$$

We assume that the basis set is orthogonal, i.e.

$$\langle \varphi_{\alpha' m'} | \varphi_{\alpha m} \rangle = \delta_{m' m} \delta_{\alpha' \alpha} \quad (6)$$

This leads to the following equation for the coefficients

$$\sum_{\alpha} H_{\alpha' \alpha}(k) C_\alpha(k) = E C_{\alpha'}(k) \quad (7)$$

Where

$$H_{\alpha' \alpha}(k) = \sum_m e^{ik(T_m - T_{m'})} \langle \varphi_{\alpha' m'} | H | \varphi_{\alpha m} \rangle = \sum_m e^{ikT_m} \langle \varphi_{\alpha' 0} | H | \varphi_{\alpha m} \rangle \quad (8)$$



The last equation came from the fact that the sum does not depend on index m' .

Eq.(7) represents a set of linear equations with respect to coefficients $C_\alpha(k)$. The number of equations is equal to the number of orbitals in an atom, N_{orb} . Therefore we obtain N_{orb} solutions. The eigenvalues and the eigen functions will be the functions of the wavevector \mathbf{k} . Therefore, the solution will represent N_{orb} bands. In general these bands will represent mixed atomic states and cannot be characterized by a particular angular momentum.

The matrix elements of the Hamiltonian is used to solve the equation (8) . In some cases matrix elements are calculated from atomic wave functions. In many cases these matrix elements are considered as fitting parameters. These parameters can be fitted to obtain accurate electronic band structure. Now we consider two simple examples.

Example 1: linear chain of single-orbital atoms of lattice constant a with nearest-neighbor interactions. In this case we have just one equation (8)

$$\left[\langle \varphi_0 | H | \varphi_0 \rangle + \langle \varphi_0 | H | \varphi_{-1} \rangle e^{-ika} + \langle \varphi_0 | H | \varphi_1 \rangle e^{ika} \right] C(k) = EC(k) \quad (9)$$

and obtain for the energies:

$$E(k) = E_0 - 2\gamma \cos ka \quad (10)$$

where $E_0 = \langle \varphi_0 | H | \varphi_0 \rangle$ is the on-site atomic energy and $\gamma = -\langle \varphi_0 | H | \varphi_{-1} \rangle = -\langle \varphi_0 | H | \varphi_1 \rangle$ is the hopping or bond integral which depends on the overlap of the wave functions of the two nearest neighbor atoms

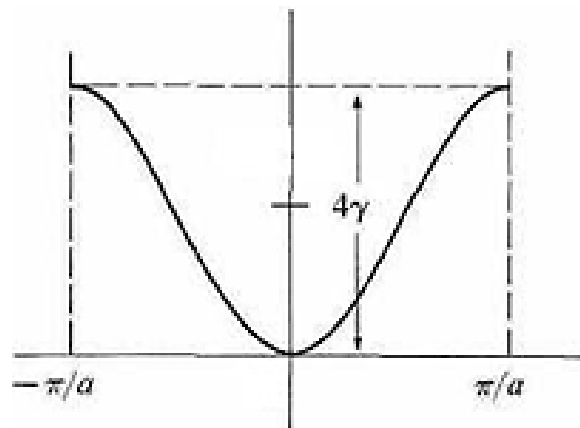


Fig.4. 8 The dispersion curve in the tight-binding model



The tight-binding band is shown in Fig.4.8. The bandwidth, 4γ , is proportional to the overlap integral. This is reasonable, because the greater the overlap the stronger the interaction, and consequently the wider the band.

When the electron is near the bottom of the band, where k is small, we find that

$$E(k) - (E_0 - 2\gamma) = \gamma k^2 a^2 \quad (11)$$

which has the same form as the dispersion relation of a free electron. An electron in that region of k -space behaves like a free electron with an effective mass

$$m^* = \frac{\hbar^2}{2\gamma a^2} \quad (12)$$

It is seen that the effective mass is inversely proportional to the bond integral. This is intuitively reasonable, since the greater the overlap the easier it is for the electron to hop from one atomic site to another, and hence the smaller is the inertia (or mass) of the electron. Conversely, a small overlap leads to a large mass, and vice versa.

Example 2: The above treatment can be extended to three dimensions in a straightforward manner. Thus for a sc lattice, the band energy is given by

$$E(k) = E_0 - 2\gamma[\cos k_x a + \cos k_y a + \cos k_z a] \quad (13)$$

The energy contours for this band, in the $k_x - k_y$ plane, are shown in Fig.4.9a, and the dispersion curves along the [100] and [111] directions are shown in Fig.4.9b. The bottom of the band is at the origin $k = 0$, and the electron there behaves as a free particle with an effective mass given by Eq.(12). The top of the band is located at the corner of the zone along the [111] direction, that is, at $[\pi/a, \pi/a, \pi/a]$. The width of the band is equal to 12γ .

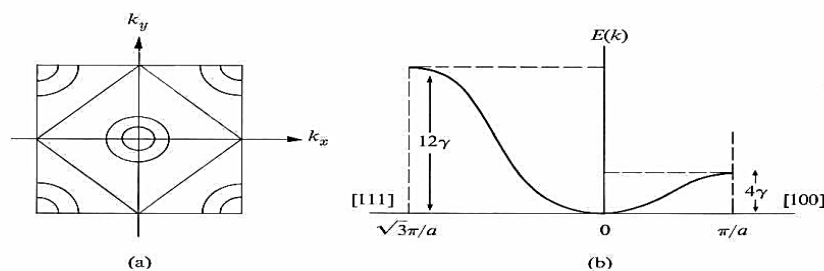


Fig. 4.9 (a) Energy contours for an sc lattice in the tight-binding model,



UNIT – V SUPER CONDUCTIVITY

Experimental survey : Superconductivity and its occurrence – destruction of Superconductivity by magnetic field – Meissner effect – Type I and II super conductors – entropy – free energy – heat capacity – energy gap – isotope effect

Theoretical survey : Thermodynamics of the superconducting transition – London equation – coherence length – salient features of the BCS theory of super conductivity – flux quantization in a superconductivity ring – DC and AC Josephson effects.

Introduction

Certain Metals and alloys exhibit almost Zero electric resistivity when they are cooled to sufficiently low temperature. This phenomenon is called Superconductivity and the material in this state is called superconductor.

This Phenomenon was first observed by H. K. Onnes in 1911. He found that when pure mercury was cooled down to below the temperature of 4 degree Kelvin (at 4.2K) a sudden decrease in the resistivity (dropped to zero Fig.5.1). This property is also observed in the metals such as Pb, Sn etc..

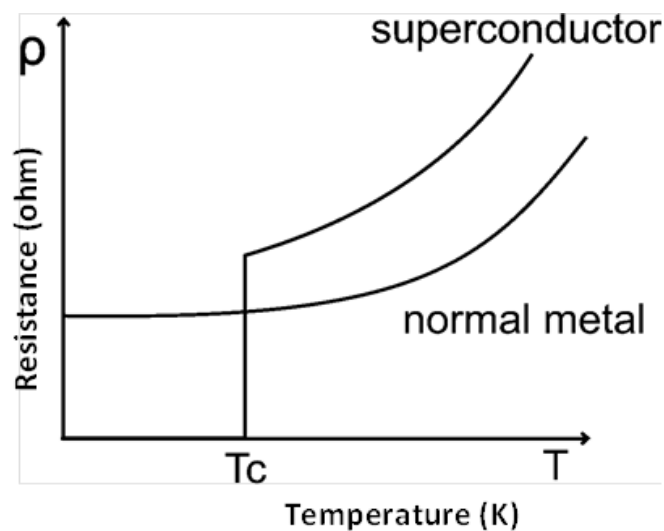


Fig. 5.1 Resistance versus absolute temperature curve



Critical Temperature:

The temperature at which the transition from normal state to superconducting state takes place on cooling in the absence of magnetic field is called the critical temperature (T_c) or the transition temperature.

General features of Super Conductors

- 1) The transition temperature is different for different materials. Materials having high normal resistivity exhibit superconductivity.
- 2) For chemically pure and structurally perfect specimen, the superconducting transition is very sharp. For impure and structurally imperfect the transition range is broad.
- 3) Superconductivity is found in metallic elements of valence electron lies between 2 and 8. ie., Superconducting elements lie in the inner columns of the periodic table
- 4) For elements in a given row in the periodic table T_c versus Z^2 gives straight line.
- 5) Metals having odd number of valence electrons are exhibiting superconductivity. But metals having even number of valence electrons are unfavourable.
- 6) Materials for which $Z \rho > 10^6$ show superconductivity. Where Z is number of valence electrons and ρ is resistivity of the material.
- 7) Superconductivity is favoured by small atomic volume, accompanied by a small atomic mass.
- 8) Ferromagnetic and antiferromagnetic materials are not superconductors.
- 9) When transition to Super conduction,
 - i. Magnetic flux lines are rejected out of the superconductor.
 - ii. There is a discontinuous change in specific heat.
 - iii. Small changes in thermal conductivity and the volume of the material.



Effect of Magnetic field

Superconducting state of a metal depends on temperature and strength of the magnetic field in which the metal is placed. The magnetic field and the superconductivity are found to be mutually exclusive.

Superconductivity disappears if the temperature of the specimen raised above T_c or a strong enough magnetic field is applied.

At temperature below T_c , in the absence of magnetic field, the material is in superconducting state. When the strength of the magnetic field applied is gradually increased to reach a critical value H_c the superconductivity disappears.

The dependence of the critical field upon the temperature is given by

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

Where $H_c(0)$ is the critical field at $T = 0K$ and $H_c(T_c) = 0$ at $T = T_c$

$H_c(0)$ and T_c , are constants and characteristics of the material.

Meissner effect :

When a weak magnetic field is applied to a superconducting specimen at a temperature below the transition temperature T_c , the magnetic flux lines are expelled out of the specimen as shown in figure 5.2. Now the specimen acts as an ideal diamagnetic material. This effect is called Meissner effect. This effect is reversible.

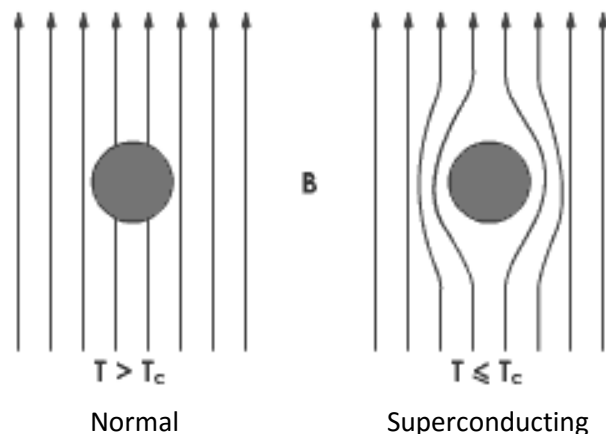


Fig. 5.2 Meissner effect



When the temperature is raised to T_c , i.e., at $T = T_c$ the flux lines penetrating and the specimen returns back to the normal state. Under this conduction, the magnetic induction inside the specimen is

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

H – is the external applied magnetic field

M – is the magnetisation produced inside the specimen.

According to Messiner effect, inside the superconductor

$$B = 0, \quad \therefore \mu_0 (H + M) = 0$$

$$M = -H$$

i.e., the magnetic Susceptibility will be $\chi = \frac{M}{H} = -1$

For superconducting material under normal state, By ohm's law $E = J\rho$

J – Current density panning through the material.

ρ – resistivity.

On cooling to its transition temperature ρ tends to 0, $\therefore E = 0$

From maxwell's equation

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

As $E = 0$, $\frac{\partial B}{\partial t} = 0 \quad \therefore B$ is a constant.

This means that the magnetic flux passing through the specimen should not change on cooling to the transition temperature. The Meissner effect contradicts this result and suggests that

perfect diamagnetism is an essential property of defining the superconducting state.

\therefore There are two independent properties require to define the superconducting state.

They are

- a) Zero resistivity, $\rho = 0 \Rightarrow E = 0$ and
- b) Perfect diamagnetism, $B = 0$ (from Meissner effect).



Effect of Current :

The critical field which destroys superconductivity, need not be an external magnetic field. An electric current flowing through a superconducting material itself may give rise to the necessary magnetic field to disappear superconductivity (Critical field H_c).

Example:

When a current flows through a superconducting ring, it gives rise to its own magnetic field. As the current is increased to a critical value I_c , the associated magnetic field also increases and become the critical field H_c , and the superconductivity disappears.

$$I_c = 2\pi r H_c$$

Where r is radius of the superconducting ring.

This limits the maximum possible current that flows through a superconductor.

∴ It is not possible to produce a high field superconducting magnets.

Type I and Type II Superconductors

Based on diamagnetic response, superconductors are classified as type I and type II superconductors. The identifying characteristics are zero electrical resistivity below a critical temperature, zero internal magnetic field (Meissner effect), and a critical magnetic field above which superconductivity ceases

Type –I

There are thirty pure metals which exhibit zero resistivity at low temperatures and have the property of excluding magnetic fields from the interior of the superconductor (Meissner effect). They are called Type I superconductors (soft Super conductors). The superconductivity exists only below their critical temperatures and below a critical magnetic field strength. The superconductivity in Type I superconductors is modelled well by the BCS theory which relies upon electron pairs coupled by lattice vibration interactions.

Remarkably, the best conductors at room temperature (gold, silver, and copper) do not become superconducting at all. They have the smallest lattice vibrations, so their behaviour correlates well with the BCS Theory. The Type I superconductors have been of limited practical usefulness because the critical magnetic fields are so small and the superconducting state disappears suddenly at that temperature.



Example:

Mat.	T _c (K)
Rh	0
W	0.015
Be**	0.026
Ir	0.1
Lu	0.1
Hf	0.1
Ru	0.5
Os	0.7
Mo	0.92
Zr	0.546
Cd	0.56
U	0.2
Ti	0.39
Zn	0.85
Ga	1.083

Mat.	T _c (K)
Gd*	1.1
Al	1.2
Pa	1.4
Th	1.4
Re	1.4
Tl	2.39
In	3.408
Sn	3.722
Hg	4.153
Ta	4.47
La	6.00
Pb	7.193

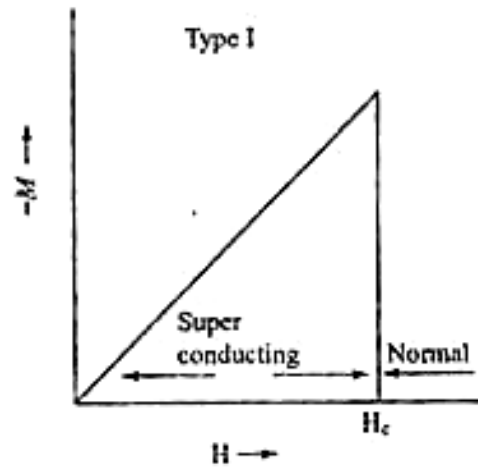


Fig. 5.3 Magnetization Curve for Type I Semiconductor

At H_c , the diamagnetic property disappears and the transition from superconducting state to normal state is sharp.

Type – II

Starting in 1930 with lead-bismuth alloys, a number of alloys were found which exhibited superconductivity. Superconductors made from alloys are called Type II superconductors. Besides being mechanically harder than Type I superconductors, they exhibit much higher critical magnetic fields and therefore could carry much higher current



densities while remaining in the superconducting state. Type II superconductors such as niobium-titanium (NbTi) are used in the construction of high field superconducting magnets.

Type-II superconductors usually exist in a mixed state of normal and superconducting regions. This is sometimes called a vortex state, because vortices of superconducting currents surround filaments or cores of normal material.

Example:

Material	Transition Temp (K)	Critical Field (T)
NbTi	10	15
PbMoS	14.4	6.0
V ₃ Ga	14.8	2.1
NbN	15.7	1.5
V ₃ Si	16.9	2.35
Nb ₃ Sn	18.0	24.5
Nb ₃ Al	18.7	32.4
Nb ₃ (AlGe)	20.7	44
Nb ₃ Ge	23.2	38

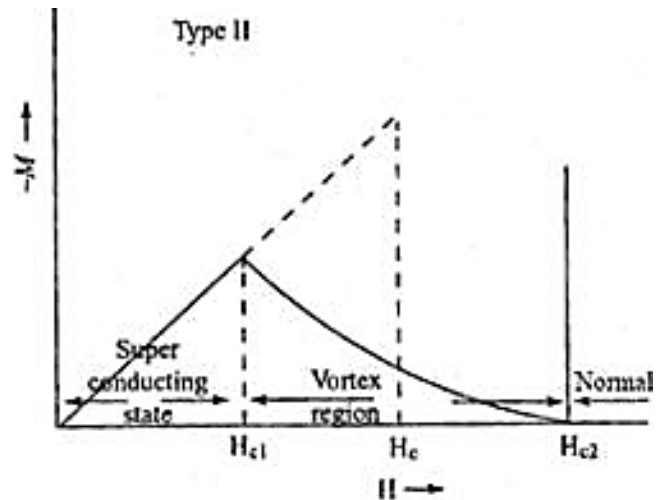


Fig. 5.4 Magnetization Curve For Type II Semiconductor

In Figure up to H_{c1} , field the specimen is pure superconducting state the magnetic flux lines are rejected. When the field is increased beyond H_{c1} , the magnetic flux lines start penetrating. The specimen is in a mixed state between H_{c1} , and H_{c2} and above H_{c2} , the specimen is in a normal state. This means that the Meissner effect is incomplete in the region bet H_{c1} , and H_{c2} . This region is vortex – region.

Type – II superconductors are hard superconductors. Type II superconductors are of great practical interest because of the high current densities that they can carry.

Thermal properties

In Superconducting state, the thermal properties such as entropy and electronic specific heat change abruptly.

Entropy :-

Entropy is a measure of the disorder of a system. In normal metals with decrease of temperature, entropy decreases linearly as shown in figure 5.5. In superconducting metal like Aluminium, the entropy decreases linearly upto critical temperature T_c , below this temperature the entropy decreases markedly. i.e., the superconducting state is more ordered



than the normal state. This means that the electrons thermally excited are more ordered in superconducting state.

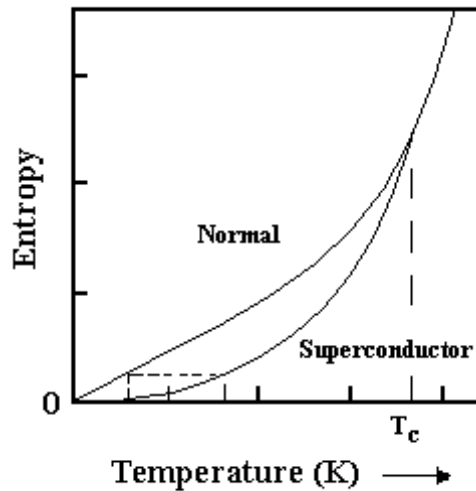


Fig. 5.5 Entropy S versus Temperature of Aluminium

In type I superconductors there is a special order which extends over a distance of the order of 10^{-6} m. This range is called coherence length.

Entropy is related to q , the heat flowing into the system from its surroundings, and to T , the absolute temperature of the system. The important properties for this discussion are:

1. $dS > q/T$ for a natural change.

$dS = q/T$ for a reversible change.

2. The entropy of the system S is made up of the sum of all the parts of the system.

The entropy of a solid is in terms of Gibbs free energy G is $S = -\left(\frac{\partial G}{\partial T}\right)_H$

$$\therefore S_N - S_S = -H_C \frac{dH_C}{dT}$$

Where dH_C/dT is always negative so that $S_N > S_S$. This means that the superconducting state is a more orderly state than the normal state.

At $T = T_c$, $H_c = 0$, $\Rightarrow S_N - S_S = 0$.

At $T = 0$ K, $\frac{dH_C}{dT} \rightarrow 0$ and hence $S_N - S_S = 0$.

Thus between the temperature $T = 0$ K and $T = T_c$ the value of $S_N - S_S$ is positive, i.e., $S_N > S_S$

These are explained in figure 5.5



The latent heat of the system is related to the entropy difference as

$$Q = T (S_N - S_S) = -T H_c \frac{dH_c}{dT}$$

At $T = T_c$, $H_c = 0$, and $S_N - S_S = 0$. This implies that $Q = 0$. i.e., when the transition occurs at T_c ($H_c = 0$), the latent heat is absent. At $H_c \neq 0$ i.e., in the presence of a magnetic field, the transition occurs at some lower temperature $T < T_c$. Between the temperatures 0K and T_c , the entropy $S_N > S_S$ and Q provides the amount of latent heat to occur transition at a constant temperature.

Free Energy:

The Transition between the normal and superconducting state is thermodynamically reversible. The meissner effect also suggests the same. Thus we may apply thermodynamics to this phase change and thereby get expression for the difference in entropy and specific heat between normal and superconducting states near absolute zero in terms of the critical field curve H_c versus T . For type I superconductor, $B=0$ inside the superconductor the critical field H_c is a quantitative measure of the free energy difference between the superconducting and normal states at constant temperature and H_c refers to a bulk specimen only. For type II superconductor, H_c is related to the stabilization free energy.

The stabilization free energy is obtained from the value of applied magnetic field that will destroy the superconducting state at constant temperature.

The work done on a superconductor when it is brought reversibly at constant temperature from a position at infinity (zero field) to a position r in the field of a permanent magnet

$$W = - \int_0^{B_a} M \cdot dB_a$$

Where M is the magnetization, and we have $B = B_a + \mu_0 M$, But $B=0$, $\therefore M = -\frac{B_a}{\mu_0}$

$$\therefore W = - \int_0^{B_a} -\frac{B_a}{\mu_0} \cdot dB_a$$

$$W = -\frac{B_a^2}{2\mu_0}$$

From second law of thermodynamics, $dQ = du + P dv$



$$\therefore du = dQ - P dv$$

$$\text{where } dQ = T ds, \text{ and } P dv = w = -\frac{B_a^2}{2\mu_0}$$

$$\therefore du = T ds + \frac{B_a^2}{2\mu_0}$$

$$\text{At absolute zero, } T ds = 0, \text{ then } du = \frac{B_a^2}{2\mu_0}$$

$$\text{ie., The increase in the energy density of the superconductor } du = U_s(B_a) - U_s(0) = \frac{B_a^2}{2\mu_0}$$

$$\text{ie., } U_s(B_a) - U_s(0) = \frac{B_a^2}{2\mu_0}$$

For normal nonmagnetic metal, the susceptibility is small, $M = 0$, the energy of normal metal is independent of field.

At critical field, $U_N(B_{ac}) = U_N(0)$ where (B_{ac}) is applied critical field. At (B_{ac}) the energies are equal in the normal and superconducting states.

$$\therefore U_N(B_{ac}) = U_s(B_{ac}) = U_s(0) + \frac{B_{ac}^2}{2\mu_0}$$

$$\text{The critical field } H_c = \frac{B_{ac}}{\mu_0}$$

The specimen is stable in either state when the applied field is equal to the critical field.

$$\Delta U = U_N(0) - U_s(0) = \frac{B_a^2}{2\mu_0}$$

Where ΔU is the stabilization free energy density of the superconducting state

Example: for aluminium, B_{ac} at absolute zero is 105 gauss, $\Delta U = 430 \text{ erg cm}^{-3}$ (CGS unit)

Specific heat :

The Specific Heat of a solid is given as

$$C_N = T \frac{dH}{dT}$$

The special heat differences between the normal and superconducting state is



$$C_N - C_S = - \left[T H_c \frac{d^2 H_c}{dT^2} + T \left(\frac{dH_c}{dT} \right)^2 \right]$$

At $T = T_c$, $H_c = 0$

$$C_N - C_S = -T_c \left(\frac{dH_c}{dT} \right)^2 = -ve$$

ie., near T_c , $C_N < C_S$

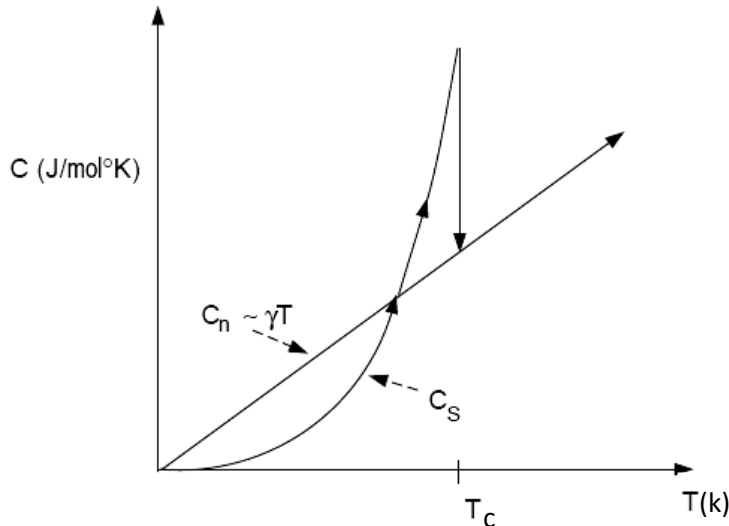


Fig.5.6 Electric contribution of specific heat of a conductor versus temperature in the normal and superconducting state

At low temperature, $C_N > C_S$ as shown in figure 5.6.

At T_c and in the absence of magnetic field, there is discontinuity in the specific heat curve.

But we know that both lattice and electron sources contribute the total specific heat

$$\therefore \text{Total specific heat is } C = C_{\text{lattice}} + C_{\text{ele}}$$

Specific heat in the normal and superconducting states are

$$C_N = (C_{\text{lattice}})_N + (C_{\text{ele}})_N$$

$$C_S = (C_{\text{lattice}})_S + (C_{\text{ele}})_S$$

When a material becomes superconductor, there is no change in the properties of lattice structure.

$$(C_{\text{lattice}})_N = (C_{\text{lattice}})_S$$

$$\therefore C_N - C_S = (C_{\text{ele}})_N - (C_{\text{ele}})_S$$

From figure, well below T_c , the electronic specific heat of a metal in the Superconducting state varies with temperature in an exponential manner



$$\text{ie. } (C_{ele})_S = a \exp\left(-\frac{\Delta}{KT}\right)$$

Where a is a constant and Δ is the energy gap.

Energy gap :

The exponential behaviour of the electronic specific heat in the superconducting state implies the presence of an energy gap in the energy spectrum of the electrons (Fig 5.7) or in the distribution of density of states (Fig. 5.8). The energy gap is situated at the Fermi level. In an insulator, the gap is associated with the lattice while in the superconductors the gap is associated with the Fermi gas or super electrons.

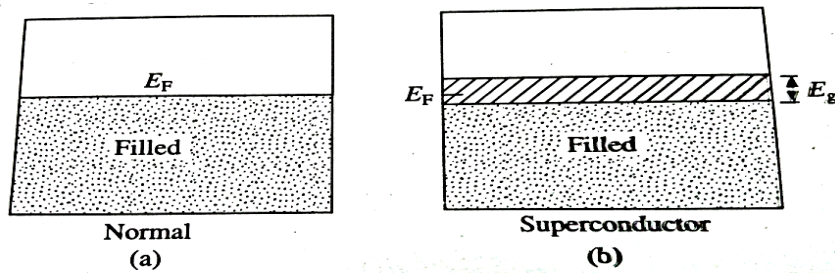


Fig. 5.7 (a) Conduction band in the normal state (b) energy gap at the Fermi level in

... re completely filled and above are completely empty.

But in super conductor, above T_C , super electrons behave like normal electrons and get excited. Below T_C these electrons are paired and their total energy is less than $2E_F$. Hence an energy gap is created at the Fermi level in the superconducting state.

The width of the gap 2Δ is of the order of kT_C . Figure 5.7 shows the presence of an energy gap in the energy spectrum of electron.

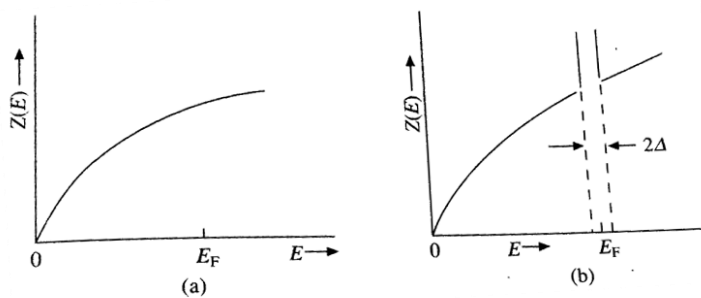


Fig. 5.8 Density of states as a function of energy (a) normal state (b) superconducting state



Figure 5.8 shows gap in the distribution of density of states. This energy gap is very small as compared to the gaps in Semiconductors and insulators. The variation of energy gap with temperature is shown in Figure 5.9.

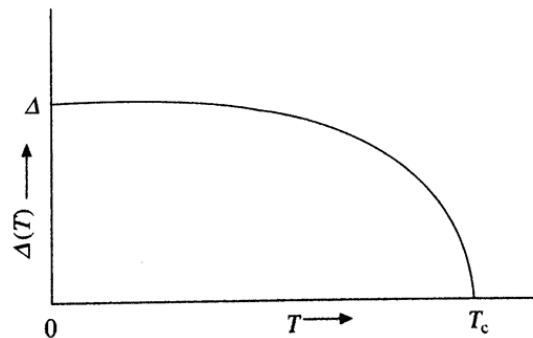


Fig. 5.9 Energy gap as a function of temperature

BCS explains the existence and temperature dependence of the energy gap in superconductors. According to this theory the ratio of the energy gap 2Δ , to the thermal energy at T_c (kT_c) is same for all superconductors and is equal to 3.53.

Isotope Effect

In superconducting materials, the transition temperature varies with the average isotopic mass, M of their constituents and is given as

$$T_c \propto M^{-\alpha}$$

$$M^\alpha T_c = \text{constant}$$

Where α is called isotope effect coefficient and is defined as

$$\alpha = \frac{\partial \ln T_c}{\partial \ln M} = 0.5 \left[1 - 0.01 \{N(0)V\}^{-2} \right]$$

where $N(0)$ is the density of single particle states for one spin at the Fermi level and V is the potential between the electrons.

Since the Debye temperature θ_D and the velocity of sound v is proportional to $M^{-1/2}$, the transition temperature of superconducting material is closely related to the corresponding Debye

temperature as $T_c \propto \theta_D$ or $\frac{T_c}{\theta_D} = \text{constant}$

Example: Mercury, isotopic mass varies from 199.5 to 203.4 atomic mass unit and its T_c varies from 4.185 K to 4.146K.



London Equations

London Brothers (F.London and H.London) proposed addition of two more equations to Maxwell's equation to explain Meissner effect.

Super conductor is composed of two distinct types of electrons, normal electrons and super electrons. Normal electrons behave in usual manner, Super electrons behave in different way, they experience, No Scattering

Above T_C , all the electrons are normal.

Below T_C , with decrease of temperature increasing electrons become super electrons.

At $T = 0K$, all are super electrons.

∴ The conduction electron density n ,

$$n = n_n + n_s$$

n_n → density of normal electrons.

n_s → density of super electrons.

The Normal current and the super current are assumed to flow parallel.

As the super current flows with no resistance, it carries the entire current induced by any small transitory electric field E . While current due to normal electrons is negligible.

If V_s is average velocity of super electrons, m is its mass, and e is its charge, then the equation of motion.

$$m \frac{dv_s}{dt} = -eE \quad \text{ie.,} \quad \frac{dv_s}{dt} = -\frac{eE}{m}$$

Current density of super electrons in

$$\begin{aligned} J_s &= -en_s v_s \\ \therefore \frac{dJ_s}{dt} &= -en_s \frac{dv_s}{dt} = -en_s \left(\frac{-eE}{m} \right) \\ \frac{dJ_s}{dt} &= \frac{n_s e^2}{m} E. \quad \dots(5.1) \end{aligned}$$

This is called First London equation,

For $E=0$, $\frac{dJ_s}{dt} = 0$ ie., J_s is constant or vice – versa.

The corresponding normal current density is

$$J_n = \sigma E \quad E=0, \text{ leads to another important result when combined with}$$

the maxwell's equation,



$$\Delta \times E = - \left(\frac{dB}{dt} \right) \quad \dots(2)$$

$$\text{ie } \frac{dB}{dt} = 0 \text{ or } B = \text{const}$$

Since this contradicts with the Meissner effect, London proposed some modification to remove this discrepancy

Taking curl on equation (1) we get

$$\Delta \times \frac{dJ_s}{dt} = \frac{n_s e^2}{m} (\Delta \times E)$$

Substituting equation (2) we get

$$\Delta \times \frac{dJ_s}{dt} = - \frac{n_s e^2}{m} \cdot \frac{dB}{dt}$$

Integrating w. r. to time and put zero for constant of integration, we get

$$\Delta \times J_s = - \frac{n_s e^2}{m} B. \quad \dots(3)$$

This is called Second London equation. This is in agreement with the experiment.

Penetration Depth

According to London equation the magnetic flux decreases exponentially (ie., the flux does not drops to zero at the surface of Type I superconductors).

To calculate to what depth the flux penetrates.

Maxwell's equation, $\Delta \times B = \mu_0 J_s$

Taking curl on both sides, $\Delta \times \Delta \times B = \mu_0 (\Delta \times J_s)$

$$\Delta (\Delta \cdot B) - \Delta^2 B = \mu_0 (\Delta \times J_s)$$

$$\Delta \cdot B = 0, \quad \therefore -\Delta^2 B = \mu_0 (\Delta \times J_s)$$

We have $\Delta \times J_s = - \frac{n_s e^2}{m} B$

$$\therefore \Delta^2 B = \mu_0 \frac{n_s e^2}{m} B$$

$$\Delta^2 B = \frac{B}{\lambda^2} \quad \dots(4)$$

Where $\lambda = \left(\frac{m}{\mu_0 n_s e^2} \right)^{1/2}$ is called London Penetration depth.



The solution of the equation (4) is

$$H = H(0) \exp\left(\frac{-x}{\lambda}\right) \quad \dots(5)$$

Graphical representation of equation (5) is shown in Figure

Ie., The flux density decreases exponentially inside the Superconductor.

To define penetration depth λ ,

$$\text{Let } x = \lambda, \quad \therefore \frac{H}{H(0)} = e^{-1}$$

$$H = \frac{H(0)}{e^{-1}} \quad \dots(6)$$

\therefore The penetration depth λ can be defined as the depth from the surface at which the magnetic flux density falls to $\frac{1}{e}$ of its initial value at the surface.

The penetration depth is about 500 \AA

With respect to temperature

$$\lambda(T) = \lambda(0) \left[1 - \frac{T^4}{T_c^4} \right]^{-1/2}$$

$\lambda(0)$ is the penetration depth at $T = 0\text{K}$.

λ increases with temperature T and at $T = T_c$, $\lambda = \infty$

BCS Theory

BCS theory of Superconductivity was introduced by Bardeen, cooper and Schrieffer in 1957. This theory helps to explain zero resistivity, Meissner effect, isotope effect etc.,

(i) Electron – Electron interaction via lattice Deformation:

When an electron passing through the packing of positive ions, the electron is attracted by the neighbouring positive ions, form a positive ion core as shown in Figure 5.10 and get screened by them. This screening reduces the effective charge of this electron and the ion core may produce a net positive charge on this assembly. Due to the attraction between the electron and the ion core the lattice gets deformed. This deformation is greater for smaller mass of positive ion core.

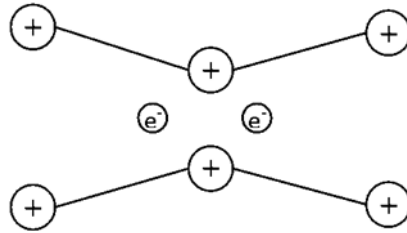


Fig. 5.10 Cooper pair of electrons.

If another electron passes by the side of the assembly of the electron and the ion core, it gets attracted towards the assembly (Fig. 5.10). By this way the second electron interacts with the first electron via lattice deformation. This interaction is due to the exchange of a virtual phonon q , between the two electrons. This interaction process can be written in terms of wave vector K ,

$$K_1 - q = K_1' \quad \text{and} \quad K_2 + q = K_2' \quad \text{ie., } K_1 + K_2 = K_1' + K_2'$$

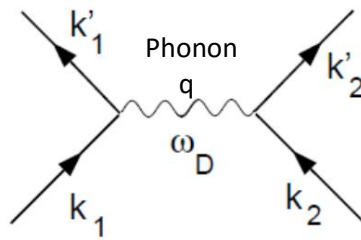


Fig. 5.11 Exchange of virtual Phonon between the two electrons

\therefore The net wave vector of the pair is conserved. The momentum is transferred between the electrons. These two electrons together form a Cooper pair and is known as Cooper electron. This process leaves the lattice invariant.

Cooper pair:

To study the mechanism of Cooper pair formation, consider the Fermi – Dirac distribution function of electrons in metals at absolute zero

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}$$

At $T = 0K$ all the quantum states below the Fermi level E_F are completely filled and all the quantum states above E_F are completely empty (fig.)



Since all the quantum states with energies $E \leq E_F$ are filled, by Pauli's exclusion principle they are forced to occupy states having energies $E > E_F$. Cooper showed that if there is an attraction between the two electrons, they are able to form a bound state so that their total energy is less than $2E_F$.

These electrons are paired to form a single system and their motions are correlated. These two electrons together form a Cooper pair and is known as Cooper electron.

The binding is strongest when the electrons forming the pair have opposite momenta and opposite spins, $K \uparrow, -K \downarrow$.

If there is an attraction between any two electrons lying in the neighbourhood of the Fermi surface then all other electrons lying in that region will form Cooper pairs. These pairs of electrons are superconducting electrons which are responsible for the superconductivity.

BCS Ground State:

In normal metals, the excited states lie just above the Fermi surface. Small excitation energy is sufficient to excite an electron from Fermi surface to excited state.

In superconducting materials, when a pair of electron lying just below the Fermi surface is taken just above it, they form a Cooper pair. This continues until the system can gain no additional energy by pair formation and hence the total energy is reduced.

Important features of BCS ground state:

1. Even At absolute zero, the energy distribution of electrons does not show any abrupt discontinuity as in normal metals
2. The states are occupied in pairs, i.e., A Cooper pair is imagined to be an electron pair in which the two electrons always occupy states and so on with opposite k - vectors and spins.

Flux Quantization :

Ginzburg and Landau developed a macroscopic theory for superconducting phase transition based on thermodynamics in 1950.

To describe superconducting state, Ginzburg and Landau introduced a complex wave function ψ . It is an order parameter, and is a function of position in the material, i.e., it is not constant and vanishes above T_c .

The density of the superconducting electrons $n_s \propto |\psi|^2$



ψ can be written in terms of magnitude and phase as $\psi = |\psi| \exp(i\phi)$.

Then the current density $J = - \left[\frac{2e^2}{mc} A + \frac{e\hbar}{m} \nabla\phi \right] |\psi|^2$

$A \rightarrow$ is vector potential.

Consider a ring shaped super conducting material and take a closed path (Fig. 5.12)

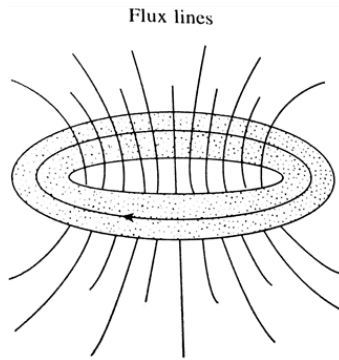


Fig. 5.12 A ring shaped superconducting material showing the path of integration C through its interior

$$\oint J \cdot dl = |\psi|^2 \oint \left(\frac{2e^2}{mc} A + \frac{e\hbar}{m} \nabla\phi \right) \cdot dl = 0 \quad \dots(1)$$

According to stokes theorem

$$\oint J \cdot dl = \int \nabla \times A \cdot ds = \int_{\epsilon} B \cdot ds = \phi \quad \dots(2)$$

ϕ -is the flux enclosed by the ring.

Since the order parameter is single valued, the phase change around the closed path must be zero or integral multiple of 2π .

$$\text{ie } \oint \nabla\phi \cdot dl = 2\pi n, \quad n = 0,1,2,\dots \quad (3)$$

Substituting (2) & (3) in (1) and solving for ϕ

We get

$$\phi = \frac{n\hbar c}{2e} = n \phi_0$$

Where $\phi_0 = \frac{\hbar c}{2e} = 2.07 \times 10^{-5}$ weber is known as fluxoid or flux quantum. Thus the magnetic

flux enclosed by the ring is quantized.

The flux through the ring is the sum of the flux due to the external source and the flux due to the super current flowing through the ring.



$$ie \quad \phi = \phi_{ext} + \phi_{sc}$$

The flux ϕ is quantized. As ϕ_{ext} is not quantized, ϕ_{sc} adjusts itself such that ϕ assumes a quantised value

Josephson Effect :

When a thin insulating layer is sandwiched between two metals, it acts as a potential barrier for the flow of electrons from one metal to another. Quantum mechanically electrons can tunnel across a thin potential barrier and in thermal equilibrium this continues until the chemical potential of electrons in both metals become equal.

When a potential difference is applied across the metals, more electrons tunnel through the insulating layer. The current-voltage relation across the junction is observed. (fig).

If one of the metals is a superconductor (Figure), no current flows across the junction until the potential reaches a threshold value. Threshold potential is half the energy gap in the superconducting state. Threshold potential helps to calculate the energy gap of superconductor.

As the temperature increases to T_c , more excited electrons are generated. Since they required less energy to tunnel, the threshold voltage decreases. \therefore the energy gap decreases.

The current voltage relation is shown in Figure.

If both the metals are superconductors in addition to normal electrons, the super electrons (cooper pair) not only can tunnel through the insulating layer from one to another without dissociation, even at zero potential difference across the junction, also their wave functions on both sides are highly correlated. This is known as Josephson Effect.

The current voltage relation is shown in Figure. The tunnelling current across the junction is very less.

D.C. Josephson Effect :

The effect of the insulating layer is introduce a phase different $\Delta\phi$ between the two parts of the wave function on opposite sides of the junction.

The tunnelling current is

$$I = I_0 \sin(\phi_0)$$



Where I_0 is the maximum Current that can flow through the junction without any potential difference across it. And it depends on the temperature and the structure of the junction.

With no applied voltage, a dc current flows across the junction with the magnitude between I_0 and $-I_0$. And the phase different $\phi_0 = (\phi_2 - \phi_1)$. This is called d.c. Josephson effect.

A.C. Josephson effect :

If a state potential V_0 is applied across the junction, an additional phase different $\Delta\phi$ is introduced by the cooper pair during tunnelling across the junction.

$$\text{ie } \Delta\phi = \frac{Et}{\hbar}$$

Where E is total energy of the system, $E = (2e)V_0$

$$\begin{aligned}\Delta\phi &= \frac{2eV_0 t}{\hbar} \\ \therefore I &= I_0 \sin(\phi_0 + \Delta\phi) \\ &= I_0 \sin\left(\phi_0 + \frac{2eV_0 t}{\hbar}\right) \\ &= I_0 \sin(\phi_0 + \omega t) \\ \therefore \omega &= \frac{2eV_0}{\hbar}\end{aligned}$$

This represent an alternating current with angular frequency ω . This is called a.c. Josephson effect.

When an electron pair crosses the junction a photon of energy $h\omega = 2eV_0$ is emitted or absorbed. By measuring the voltage and frequency, the fundamental constant $\frac{e}{h}$ can be obtained.

- (i) When $V_0 = 0$, a constant d.c. current i_c flows through the junction. This current is superconducting current and the effect is the d.c Josephson effect.
- (ii) So long $V_0 < V_c$ a constant d.c current i_c flows.



- (iii) When $V_o > V_c$, the junction has a finite resistance and the current oscillates with a frequency $\omega = \frac{2eV_o}{\hbar}$. This is a.c Josephson effect.

Applications of Josephson effect :

- (i) Josephson effect is used to generate microwaves with frequency $\omega = \frac{2eV_o}{\hbar}$
- (ii) A.C Josephson effect is used to define standard Volt.
- (iii) A.C. Josephson effect is used to measure very low temperature based on the variation of frequency of the emitted radiation with temperature.
- (iv) A Josephson junction is used for switching of signals from one circuit to another.

Application of Superconductors :-

1. Electric generator :

Using Superconducting coil, Motors with high powers could be constructed at very low voltage.

2. Low loss transmission lines and transformers :

Since the resistance of superconducting phase is zero, the power loss during transmission is negligible. If super conductors are used for winding of a transformer the power loss will be small.

3. Magnetic levitation

The rejection of magnetic flux property of Superconductor is used for high speed transportation.

4. Generation of high magnetic fields

Super conducting materials are used for producing very high magnetic fields of the order of 50 Tesla.



5. Fast Electrical switching

Application of magnetic field changes Superconducting to normal and removal of field reverses the process. This principle is used to develop switching element cryotron.

6. Logic and storage function in computers

Current Voltage characteristic of Josephson Junction are suitable for memory elements. Superconductors are used to perform logic and storage function in computers.

7. SQUIDS (Superconducting Quantum Interference Devices)

SQUIDS is a double junction quantum interferometer. It is based on flux quantization in Superconducting ring. Very minute magnetic signals are detected by SQUIDS sensors.

It is used to study tiny magnetic signals from the brain and heart. SQUIDS magnetometers are used to detect paramagnetic response in the liver. It gives the amount of iron content of liver accurately.

New oxide superconductors like thallium cuprates exhibit, Superconductivity with transition temperature about 125 K or above. These high temperature Superconductivity devices have very widespread commercial applications, such as energy technology, telecommunication, computing, super-fast transportation, medicine etc.

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