SOLID STATE PHYSICS

M.Sc. Physics

FIRST YEAR, SEMESTER-II, PAPER-II

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
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Semester 2
M.Sc. Physics
202PH24 SOLID STATE PHYSICS

Course Objectives:

- The present syllabus Sequence of articles in each unit enables the student to understand the gradual development of the subject regarding solid state matter.
- Solid-state physics is provided an understanding of structure concerned with their association and regular, periodic arrangement in crystals.
- Understand the physics of insulators, semiconductor and conductors with special emphasis on the elementary band theory of semiconductors.

UNIT I

CRYSTAL STRUCTURE: Periodic array of atoms—Lattice translation vectors and lattices, symmetry operations, The Basis and the Crystal Structure, Primitive Lattice cell, Fundamental types of lattices—Two-Dimensional lattice types, three-Dimensional lattice types, Index system for crystal planes, Packing density: SC, BCC and FCC, simple crystal structures-- sodium chloride, cesium chloride, diamond structures and Zinc Sulfide.

Learning Outcomes:

- To understand the arrangement of atoms and the possible arrangements in solid stale materials.
- To know about different parameters regarding the structure of the materials and crystal planes.
- Discussing structures of some familiar materials NaCl, CsCl, diamond and ZnS.

UNIT II

CRYSTAL DIFFRACTION AND RECIPROCAL LATTICE: Bragg's law, Experimental diffraction methods- Laue method and powder method, Derivation of scattered wave amplitude, Geometrical Structure Factor, Reciprocal lattice, Reciprocal lattice to SC lattice, BCC lattice and FCC Lattice, Propertiesof reciprocal lattice, Brillouin Zone, Neutron diffraction, Electron diffraction.

Learning Outcomes:

- Clear understanding of X-ray diffraction techniques like Laue, powder methods using Bragg's law.
- To know some useful parameters about cubic and non-cubic crystal systems.
- Understanding of positions of the atoms in a unit cell further useful to obtain knowledge on reciprocal lattice for different systems.

UNIT III

Lattice Vibrations and Thermal Properties: Elastic waves in one dimensional array of identical atoms. Vibrational modes of a diatomic linear lattice and dispersion relations. Acoustic and optical modes. Infrared absorption in ionic crystals. Phonons and verification of dispersion relation in crystal lattices. Lattice heat capacity– Einstein and Vibrational modes of continuous medium-Debye theory. Origin of thermal expansion and Gruneisen relation.

Learning Outcomes:

- To obtain expressions for one dimensional linear lattice and diatomic lattice.
- Distinguish between acoustical and optical modes.
- Understand the importance of Einstein's theory and Debye's theory.

UNIT IV

FREE ELECTRON FERMI GAS: Failures of free electron theory of metals (Qualitative only) Energy levels and density of orbits in one dimension, Free electron gas in 3 dimensions-Fermi-Dirac distribution function and variation of Fermi function with temperature (Qualitative only)-Density of states-Heat capacity of the electron gas, Experimental heat capacity of metals-Electrical conductivity and Ohm's law-Thermal conductivity of metals-Wiedemann-Franz law-Motion of magnetic field-Hall effect.

Learning Outcomes:

- Understanding the classical free electron theory - their failure and quantum free electron theory.
- Understanding about electrical and thermal conductivity.

UNIT V

THE BAND THEORY OF SOLIDS: Nearly free electron model, Origin of the energy gap, The Block Theorem, Kronig-Penny Model, wave equation of electron in a periodic potential, Approximate solution near a zone boundary, Effective mass of electron**,** The distinction between metals, insulators and semiconductors.

Learning Outcomes:

- Understanding the conduction, valance bands and reasons for energy band gap.
- Understanding about the band theory of solids and must be able to differentiate insulators, conductors and semiconductors.

Course Outcome:

- A brief idea about crystalline and amorphous substances, about lattice, unit cell, miller indices, reciprocal lattice, concept of Brillouin zones.
- The students should be able to clucidate the important features of solid state physics by covering structural aspects like lattice cell parameters which are studied by diffraction techniques.
- A detailed understanding on band theory of solids helps to distinguish metals, insulators and semiconductors.

Text and Reference books:

1. Introduction to Solid State Physics, C. Kittel, 5th Edition,
2. Solid State Physics, A.J. Dekker.
3. Solid State Physics, S.O. Pillai 7th Edition
4. Solid State Physics H.C. Gupta, Vikas Publisher, Noida, 2nd Edition
5. Fundamentals of quantum Mechanics, Statistical Mechanics & Solid State Physics by S.P.Kuila, Books and Allied, Kolkata
6. Solid State Physics, M.A. Wahab, Narosa publishing house.

(202PH24)

M.Sc. DEGREE EXAMINATION
Physics
Paper-II: SOLID STATE PHYSICS

Time: Three hours Maximum:70 marks.

All questions carry equal marks.

1 (a) What are Lattice translation vectors and lattices?
(b) What is Basis, Crystal structure and a Primitive cell?
OR
(c) Explain the structures SC and BCC.
(d) Explain the structures Caesium chloride and Dimond structures.

2 (a) Explain Laue method to determine crystal structure.
(b) Derive Bragg's Law.
OR
(c) What is Neutron diffraction? Explain.
(d) Explain Reciprocal lattice and Reciprocal Brillouin zone.

3 (a) What are vibrational modes and derive dispersion relations.
(b) Explain Infrared absorption in ionic crystals.
OR
(c) How do you verify dispersion relation in crystal lattices.
(d) Derive the expression for specific heat in Einstein model.

4 (a) Explain Fermi-Dirac distribution function.
(b) Derive the expression for density of states.
OR
(c) Explain the thermal conductivity of metals.
(d) What is Hall effect? Explain to determine Hall coefficient.

5 (a) What is the origin of energy gap? Explain
(b) Derive the expression for effective mass.
OR
(c) What is Bloch Theorem? Explain Kronig- Penny model to determine band structure in the crystals.

CONTENTS

LESSON-1

CRYSTAL STRUCTURE

Aim:

To study and understand the periodic arrangement (periodic array) of atoms in the modern periodic table and the basis on which elements are classified. A crystal structure is formed by the combination of a mathematical abstraction (the lattice) and a physical entity (the basis).To study symmetry operations in crystal lattices and understand how the basis combined with a lattice leads to the formation of different crystal structures.

Objectives:

- To understand the concept of the periodic array of atoms in crystalline solids.
- To study the arrangement of atoms in a regular and repeating lattice.
- To learn about lattice points and lattice translational vectors.
- To understand the concept of symmetry in crystals.
- To study different symmetry operations such as translation, rotation, reflection, and inversion.
- To understand the role of symmetry operations in classifying crystal structures.
- To learn the meaning of a basis and its importance in crystal formation.
- To understand how a lattice combined with a basis forms a crystal structure.
- To identify and study common crystal structures such as simple cubic, body-centered cubic, and face-centered cubic.
- To relate atomic arrangement and symmetry to the physical properties of solids.

STRUCTURE:

1.1 Crystal Structure:

A crystal structure is formed by the combination of a mathematical abstraction (the lattice) and a physical entity (the basis).

- Lattice: A regular, periodic arrangement of points in space. It is a purely mathematical concept where every point has an identical environment.

- Basis (or Motif): An atom or a group of atoms associated with each lattice point. The basis must be identical in composition, arrangement, and orientation for every point.

Crystal Structure = Lattice + Basis

Basic definitions:

The study of crystal physics aims to interpret the macroscopic properties in terms of properties of the microscopic particles of which the solid is composed. The geometric form & physical properties of crystalline solids can be determined by using X-rays, electron beams & neutron beams.

The main difference between the crystals & other solids is that there is a arrangement of atoms, ions (or) molecule in three dimensional periodic manner in crystals and this is absent in other solids. In order to explain this periodicity Bravais introduced the concept of space lattice in 1848. Space lattice is obtained by simply considering the translation of an object (J) to a finite distance (a) & when repeated systematically along the three crystallographic directions i.e. x, y & z. The one-dimensional periodic array of object is shown in below fig. 1.8a.

It is easy to represent this periodicity by replacing each object in the array with a point. It should be remembered that a point is an imaginary infinitesimal spot in space i.e. lattice points are imaginary i.e.Fig 1.8a represents real objects whereas Fig 1.8b shows the same array intermsof imaginary lattice points.

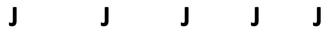


Fig 1.1(a)

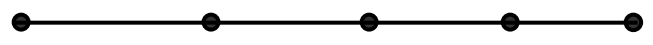
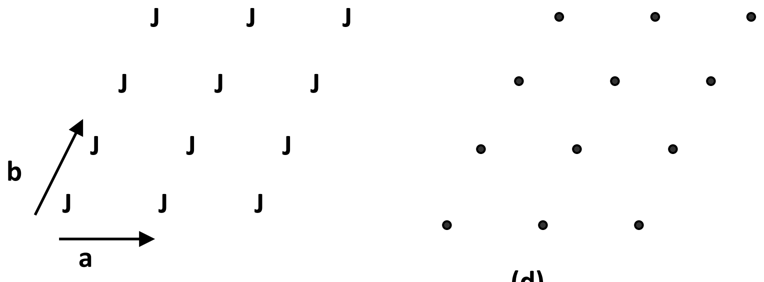


Fig 1.2(b)

If translation "a" is combined with another non collinear translation "b" then a two dimensional array is obtained as shown in 1.8 c and 1.8d



(c)

(d)

Fig 1.3 Two dimensional array of: (c) Objects, (d) Points; a plane lattice

Similarly if "a" & "b" is combined with a third non-coplanar translation c, then a three dimensional array is obtained, which is shown in fig1.4.

The characteristic feature of the space lattice is that the environment around any one point is identical. The location of any lattice point can be defined as, $T=n_1a+n_2b+n_3c$. Where n_1, n_2, n_3 are arbitrary integers.

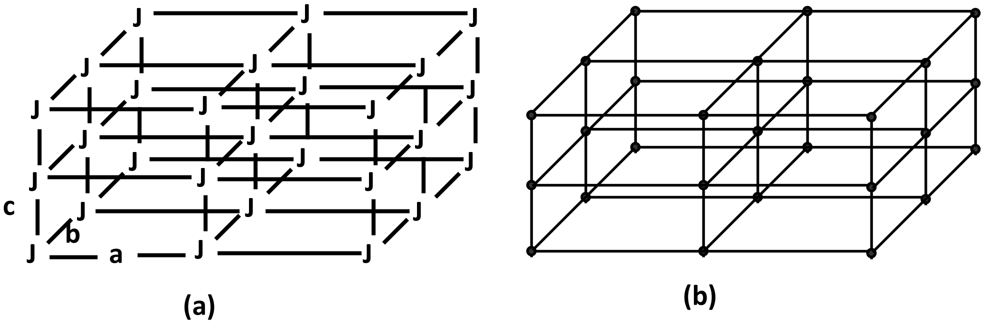


Fig 1.4 Three dimensional array of: (a) Objects, (b) Points; a space lattice

Basis:

In preceding section we studied the periodicity & lattice points. Now it is essential to distinguish a lattice from a crystal. A crystal structure is formed only when a group of atoms (or) molecules are attached identically to each lattice points. This group of atoms (or) molecules is called basis. Basis is identical in composition, arrangement and orientation, which is repeated periodically in space to form the crystal structure.

∴ Lattice + Basis = crystal structure

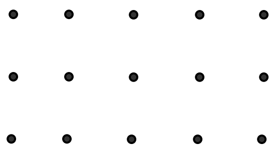


Fig 1.5(a) space lattice

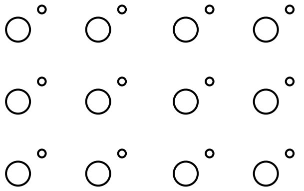


Fig 1.5 (b) Basis containing two different atoms

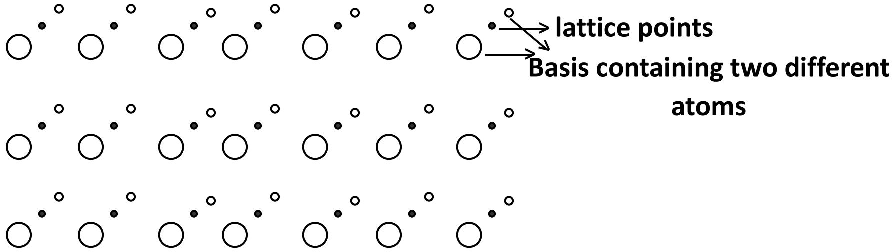


Fig 1.5 (c) Crystal structure (lattice + Basis)

Unit cell: -

The atomic order in crystalline solids indicates that the small groups of atoms form a repetitive pattern. Thus, in describing crystal structure, it is often convenient to subdivide the structure into small repeat entities called unit cells. i.e. in every crystal some fundamental grouping of particles is repeated. Such collection of particles is called a "Unit Cell". Unit cells for most crystals are parallelopiped (or) cubes having 3 set of parallel faces.

It can be used to represent the crystal symmetry. It is a "building block" of the crystal structure. The fig 1.6(a) shows a unit cell of a 3 dimensional crystal lattice. The lattice is made-up of a repetition of unit cells, and a unit cell can be completely described by the three vectors a, b, c & the angles between them (α, β, γ). If the values of these intercepts & interfacial angles are known, we can easily determine the form & actual size of the unit cell.

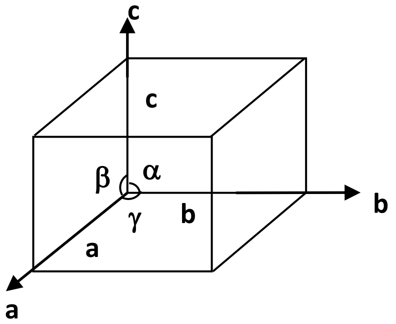


Fig 1.6 (a) Lattice parameter of

a unit cell

Table 1 Unit cell volume of different lattice types

Lattice type	Volume
Cubic	a^3
Orthorhombic	abc
Tetragonal	a^2c
Hexagonal	$\sqrt{3}\, a^2c/2$
Rhombohedra	$a^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha}$
Monoclinic	abc sinβ
Triclinic	$abc\sqrt{1-\cos\alpha-\cos\beta-\cos\gamma+2\cos\alpha\cos\beta\cos\gamma}$

1.2 Lattice Translation Vectors:

The defining feature of a lattice is its translational symmetry. This means that if you shift the entire lattice by a specific vector, the resulting arrangement is indistinguishable from the original.

Mathematical Definition

In three dimensions, any lattice point can be reached from an origin point by a Lattice Translation Vector T defined as:

$T = n_1 a_1 + n_2 a_2 + n_3 a_3$

- Vector a_1, a_2, a_3 These are the fundamental translation vectors (or primitive vectors) that define the axes of the crystal.
- n_1, n_2, n_3: These are any set of integers.

If a vector T satisfies the condition that the atomic environment at r is identical to the environment at r+T for all rit is a valid translation vector.

Types of Lattices

While there are infinite ways to arrange atoms, symmetry constraints limit the number of possible lattice types.

Primitive vs. Non-Primitive

- Primitive Lattice Vectors: The smallest possible vectors that can build the lattice. A unit cell formed by these vectors contains exactly one lattice point.
- Non-Primitive Vectors: These vectors may be easier to work with (e.g., they might be orthogonal) but result in a unit cell that contains more than one lattice point (like Body-Centered Cubic or Face-Centered Cubic).

Bravais Lattices

In 3D space, there are only 14 unique ways to arrange points such that each point has an identical environment. These are known as the Bravais Lattices, which are further categorized into 7 Crystal Systems:

1. Cubic (SC, BCC, FCC)
2. Tetragonal
3. Orthorhombic
4. Monoclinic
5. Triclinic
6. Trigonal (Rhombohedral)
7. Hexagonal

Seven Crystal Systems:

In 3 dimensional case by applying the restrictions on the lattice translations a, b, c and angles α, β, γ, one can verify that only 7 crystal groups (or) basic systems are possible. They are collectively known as Bravais lattices. In order to specify the given arrangement of points in a space lattice (or) of atoms in a crystal, it is customary to define its co-ordinates with reference to a set of axes chosen with its origin at a lattice point. The three axes & angles are defined as shown in fig 1.11(b). Each space lattice has a convenient set of axes, however only seven different systems of axes have been found to be sufficient for representing all Bravais lattices.

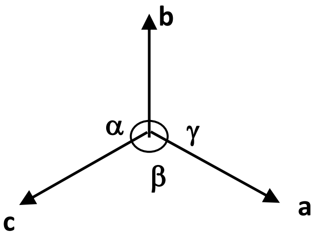


Fig 1.7 The crystallographic axes and the corresponding angles

They are

1.Triclinic

2. Monoclinic

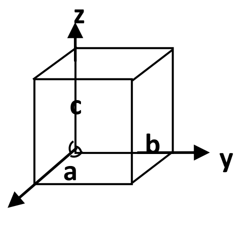
3. Orthorhombic

4. Tetragonal

5. Trigonal

6. Hexagonal

7. Cubic



Explanation of each crystal system is given below.

(1) Cubic crystal system: -

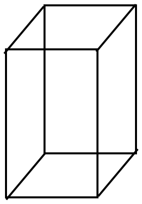
The crystal axes are perpendicular to one another & the repetitive interval is the same along all the 3 axes.

Cubic crystallites may be simple (or) body centered (or) face centered.

a = b = c; $\alpha = \beta = \gamma = 90^0$;

(2) **Tetragonal crystal system**:-

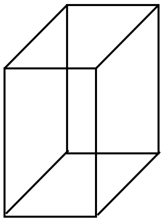
The crystal axes are perpendicular to one another. The repetitive intervals along two axes are the same, but the interval along the third axis is different. Tetragonal lattices may be simple (or) body centered.



$a=b \neq c$; $\alpha=\beta=\gamma=90^0$;

(3) **Orthorhombic crystal system**:-

The crystal axes are perpendicular to one another, but the repetitive intervals are different along all the three axes. Orthorhombic lattices may be simple, base centered, body centered (or) face centered.

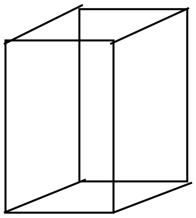


$a \neq b \neq c$; $\alpha=\beta=\gamma=90^0$;

(4) **Monoclinic Crystal system**:-

Two of the crystal axes are perpendicular to each other, but the third is obliquely inclined. The repetitive

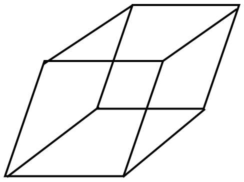
intervals are different along all the three axes. Monoclinic lattices may be simple (or) base centered.



$a \neq b \neq c$; $\alpha=\beta=90^0 \neq \gamma$

(5) **Triclinic crystal system**:-

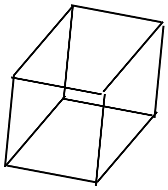
None of the crystal axes is perpendicular to any of the others, and the repetitive intervals are different along all the three axes.



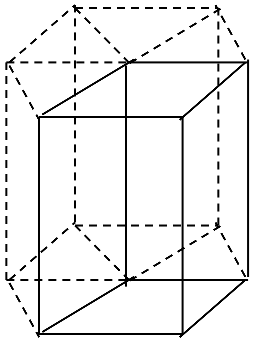
$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^0$

(6) **Trigonal (or) rhombohedral crystal system**:-

The three axes are equal in length and are equally inclined to each other at an angle other than 90^0.



(7) **Hexagonal crystal system**:-



Two of the crystal axes are 60^0 apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60^0 apart, but the interval along the third axis is different. The properties of seven are shown in table 1.

Table 1.4

S. No.	Crystal system	Axial length of unit cell (a,b&c)	Inter axial angles (α, β & γ)	Example
1	Cubic	a=b=c	$\alpha=\beta=\gamma=90^0$	Au, Cu, NaCl
2	Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^0$	TiO_2, SnO_2
3	Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^0$	KNO_3, $BaSO_4$
4	Monoclinic	$a\neq b\neq c$	$\alpha=\beta=90^0\neq\gamma$	$CaSO_4$, $2H_2O$,$FeSO_4$
5	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90^0$	$K_2Cr_2O_7$
6	Trigonal	a=b=c	$\alpha=\beta=\gamma\neq 90^0$	As, Sb, Bi, Calcite
7	Hexagonal	$a=b\neq c$	$\alpha=\beta=90^0$ & $\gamma=120^0$	SiO_2, Zn, Mg, Cd

1.3 SYMMETRY OPERATIONS:

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 crystal.

A crystal possesses different symmetries (or) symmetry elements. They are described by certain operations. A symmetry operation is one that leaves the crystal and its environment invariant, i.e. the body becomes indistinguishable from its initial configuration after symmetry operation. The geometrical locus about which a group of finite operations act is known as "symmetry element". A crystalline solid can have the following symmetry elements.

(i) Pure translation
(ii) Proper rotation
(iii) Reflection
(iv) Inversion

(i) **Pure translation**: -

A two dimensional space lattice is shown in fig1.6(a) The distance between any two nearest neighbours along the x direction is "a" and along the y direction is "b". A perfect crystal maintains this periodicity in both x and y directions from $-\propto$ to $\propto$ i.e. the periodicity of atoms A, B and C are equivalent. In other words, to an observer located at any of the atomic sites, the crystal appears exactly the same. From the above point we can say that a crystal possesses a translation symmetry. If the crystal is translated by any vector joining two atoms say R in fig.1.8, the crystal appears exactly the same as before the translation. Therefore crystal remains invariant under any translation. A translation operation is a displacement vector represented in terms of the basis vectors a, b and c as

$T = n_1a + n_2b + n_3c$

where n_1, n_2 and n_3 are integers.

(ii) Proper rotation (through an angle ϕ): -

The proper rotation is shown in fig1.9. Let us imagine a line (or) axis passing through the centre & normal to the fig.1.7, so that the J's are represented by a rotation through any angle $\phi = 2\pi/n$ about the axis of rotation, the axis is said to have n-fold symmetry.

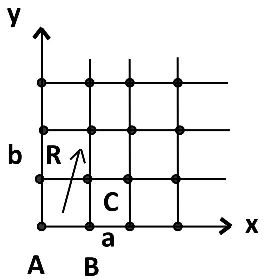


Fig 1.8 Translation in two dimensional lattice

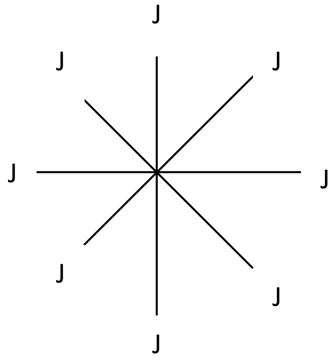


Fig 1.9 Rotation

Because of reticular structure of crystals, only 1-,2-,3-,4- & 6- fold rotational symmetries are possible. Crystalline solid cannot possess either 5-fold (or) any other rotational symmetry higher than 6-fold.

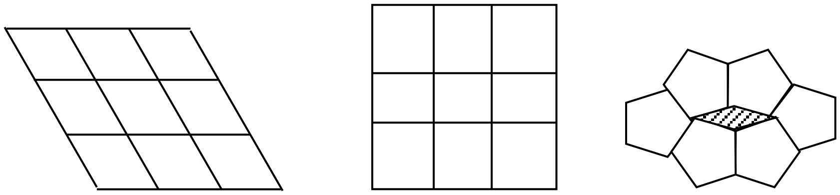


Fig 1.9(a) Some Possible and Non-existent Symmetry axes

(iii) Reflection: -

The proper reflection is shown in fig 1.8. In the fig, we find that a plane transforms left-handed object into a right-handed one and vice-versa. The element of symmetry in this case is known as a symmetry plane (or) a mirror plane and symbolically represented by the letter "m". i.e. A plane in a cell such that, when a mirror reflection in this plane is performed, the cell remains invariant.

iv) Inversion center (center of symmetry):

The proper inversion is shown in fig 1.9(a). A cell has an inversion center if there is a point at which the cell remains invariant when the mathematical transformation $\gamma \rightarrow -\gamma$ is performed on it. This is similar to reflection, with the difference that reflection occurs in a plane of mirror, while inversion is equivalent to reflection through point called inversion centre (or) centre of symmetry. The inversion centre has the property of inverting all space through points.

Ex: All bravoes lattices have inversion symmetry. A Non-bravais lattice may or may not have an inversion centre, depending on the symmetry of the basis.

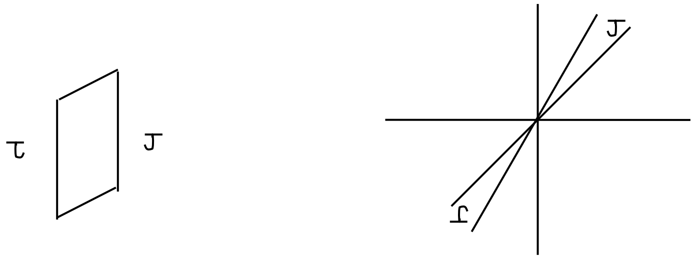


Fig 1.9(b) Inversion

1.4 Basis & Crystal Structures

In preceding section we studied the periodicity & lattice points. Now it is essential to distinguish a lattice from a crystal. A crystal structure is formed only when a group of atoms (or) molecules are attached identically to each lattice points. This group of atoms (or) molecules is called basis. Basis is identical in composition, arrangement and orientation, which is repeated periodically in space to form the crystal structure.

∴ Lattice + Basis = crystal structure

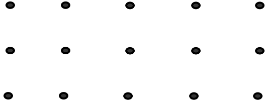


Fig 1.10(a) space lattice

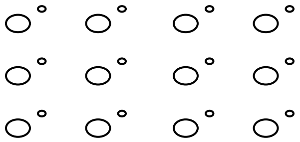
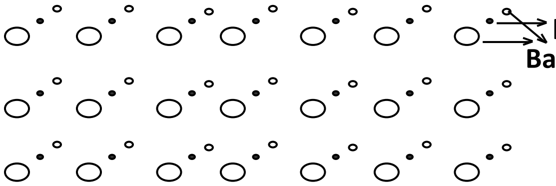


Fig 1.10 (b) Basis containing two



lattice points

Basis containing two different

Fig 1.10 (c) Crystal structure (lattice + Basis)

The Fourteen Bravais Lattices:-

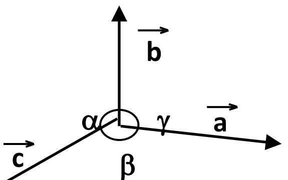
A three-dimensional unit cell is defined by vectors a, b, &c representing its edges (or) crystal axes and the angles $\alpha, \beta \& \gamma$ defined as shown in fig 1.11

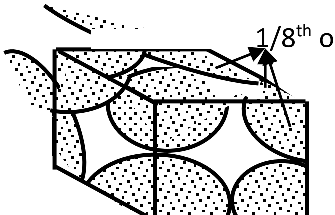
The number of bravais lattices is 14 with 32-point groups & 230 space groups. Based on the relationship between a, b &c in terms of magnitude and relative orientation $\alpha, \beta \& \gamma$. The 14 types are grouped into seven different classes of crystal lattices. A description of the 14 bravais lattices of 3 dimensions along with the axial relationship for the class of crystal lattices to which each belongs is entered in table 2.

The simple cube (SC):-

The unit cell is cube having one atom (or) molecule at each corner. So there are eight atoms (or) molecules at eight corners of the cube. Since each corner atom is shared by eight surrounding cubes, share of each cube comes to one eighth of an atom, shown in fig 1.13a.

∴Total No. of atoms = $\frac{1}{8} \times 8$ = 1 atom.





The Body Centered cube (BCC):-The unit cell of body centered cube structure is shown in fig 1.13(b). It has eight corner atoms & one center atom. The number of atoms belonging to this cube are (a) One center atom &

(b) $\frac{1}{8}\times 8$ = 1 corner atom

$\therefore$ Total No. of atoms per cube =1+1=2

The Face centered cube (FCC): -

The unit cell of face centered cube structure is shown in fig 1.13c. It has 6 face centered and eight corner atoms. The six face centered atoms at six faces of the cube are shared by their adjacent cubes. Hence, a total of 6/2=3 such atoms belong to the cube. As each corner atom is shared by eight surrounding cubes, the share of each cube comes to one eighth of an atom.

$\therefore$ Total no. of atoms per cube $=3+\frac{1}{8}\times 8=3+1=4$.

Similarly monoclinic lattice has two types simple and base centered. Orthorhombic has four types three as mentioned above for cubic and base centered, Tetragonal has two types of lattices.

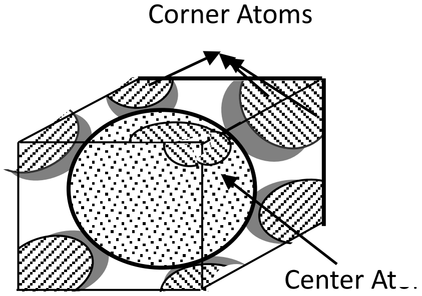


Fig 1.13(b) Body centered cube

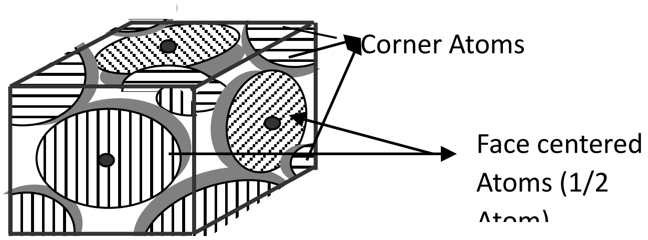
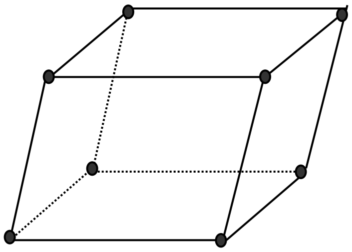


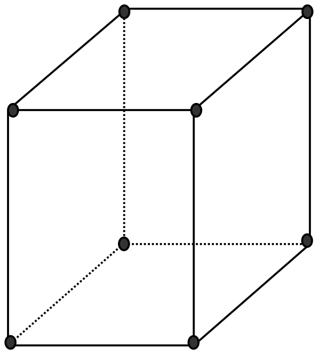
Fig 1.13(c) Face centered cube

Table 2

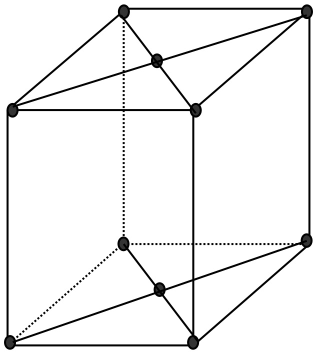
Class	Bravais lattice	No. of lattices	Unit cell Characteristics
Triclinic	Simple	1	$a \neq b \neq c$ & $\alpha \neq \beta \neq \gamma \neq 90^0$
Monoclinic	Simple Base centered	2	$a \neq b \neq c$ & $\alpha = \beta = 90^0 \neq \gamma$
Orthorhombic	Simple base-centered body-centered	4	$a \neq b \neq c$ & $\alpha = \beta = \gamma = 90^0$
Tetragonal	Simple Body centered	2	$a = b \neq c$ & $\alpha = \beta = \gamma = 90^0$
Cubic	Simple body-centered face-centered	3	$a = b = c$ & $\alpha = \beta = \gamma = 90^0$
Trigonal	Simple	1	$a = b = c$ & $\alpha = \beta = \gamma \neq 90^0$
Hexagonal	Simple	1	$a = b \neq c$ & $\alpha = \beta = 90^0$ $\gamma = 120^0$



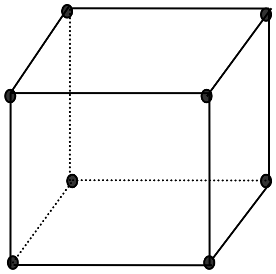
Triclinic



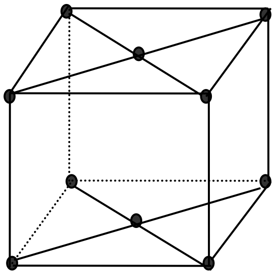
Simple monoclinic



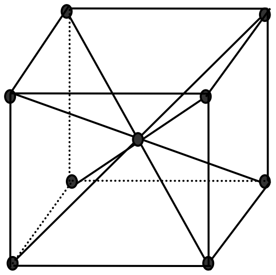
Base-centered monoclinic



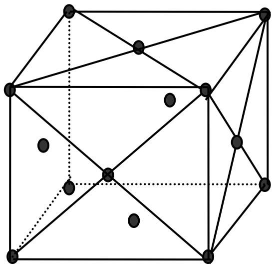
Simple orthorhombic



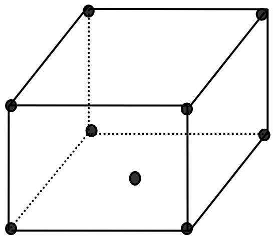
Base-centered orthorhombic



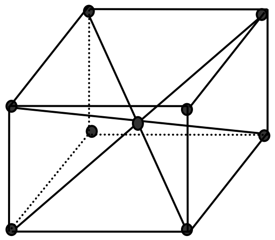
Body-centered orthorhombic



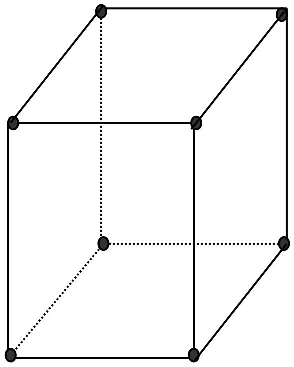
Face-centered orthorhombic



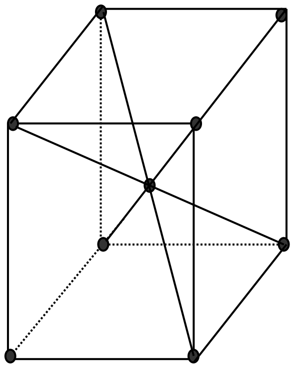
Simple tetragonal



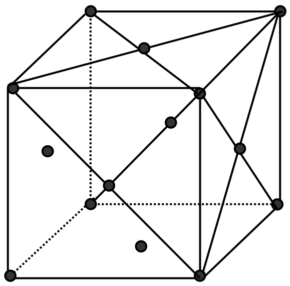
Body-centered tetragonal



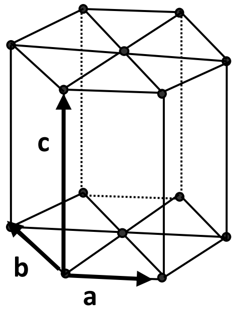
Simple cubic



Body-centered cubic



Face-centered cubic



Hexagonal

1.5 Summary:

The periodic array of atoms forms the foundation of crystalline solids, where atoms are arranged in a regular, repeating three-dimensional pattern known as a lattice. This ordered arrangement determines the physical and chemical properties of materials. The study of lattices, symmetry, and crystal structures helps in understanding the internal structure of solids.

Lattice Translational Vectors and Lattices:

A lattice is an infinite, regular arrangement of points in space, each representing the position of an atom or a group of atoms. The entire lattice can be generated by translating a point through lattice translational vectors. These vectors define the periodicity of the crystal and ensure that the arrangement of atoms repeats uniformly throughout the solid.

Symmetry Operations:

Symmetry operations are movements that bring a lattice or crystal structure into a position indistinguishable from its original one. Common symmetry operations include translation, rotation, reflection, and inversion. These operations play a crucial role in classifying crystal structures and understanding their physical properties such as optical behavior and mechanical strength.

The Basis and Crystal Structures:

A crystal structure is formed when a basis (one atom or a group of atoms) is attached to each lattice point. While the lattice defines the geometric framework, the basis determines the actual atomic arrangement. Different combinations of lattices and bases lead to various crystal structures such as simple cubic, body-centered cubic, and face-centered cubic structures.

Primitive Lattice Cell:

The primitive lattice cell is the smallest volume of a crystal lattice that can be repeated through translational symmetry to generate the entire lattice. It contains exactly one lattice point and represents the fundamental building block of a crystal. Understanding the primitive cell is essential for analyzing crystal geometry and packing efficiency.

1.6 Technical terms

Crystal Structure, Lattice Translational vector and lattices, Symmetry Operations, Basis & Crystal Structure.

1.7 Self assessment questions

1. Explain about the Crystal structure
2. Briefly explain about Lattice Translational vector and lattices
3. Explain about the Basis & Crystal Structure.

1.8 Suggested readings

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

Prof. R.V.S.S.N. Ravi Kumar

LESSON - 2

TYPES OF LATTICES

Aim:

To study the concept of a primitive lattice, understand the fundamental types of two-dimensional and three-dimensional lattices, and learn the index system used to describe crystal lattices.To understand the primitive lattice and its unit cell, classify the fundamental types of two-dimensional and three-dimensional lattices, and study the index system of crystal lattices used to represent lattice planes and directions.

Objectives:

- To understand the concept of a lattice and a primitive lattice.
- To study the primitive unit cell and its significance in crystal structures.
- To learn about lattice points and translational symmetry.
- To classify and understand the fundamental types of two-dimensional lattices.
- To study the fundamental types of three-dimensional lattices (Bravais lattices).
- To compare two-dimensional and three-dimensional lattice structures.
- To understand the need for an index system in crystal lattices.
- To learn the Miller indices used to represent crystal planes.
- To understand how lattice directions and planes are identified using the index system.
- To appreciate the importance of lattice indexing in the study of crystal properties.

STRUCTURE:

2.1 PRIMITIVE LATTICE CELL:

A Primitive Lattice Cell is the smallest possible repeating unit of a crystal lattice that contains exactly one lattice point. While a "conventional" unit cell is often chosen to highlight the symmetry of the crystal (like the cube in Face-Centred Cubic), the primitive cell is the most fundamental mathematical building block.

Key Characteristics

- Minimum Volume: It is the smallest volume that can tile the entire space by simple translation without gaps or overlaps.
- Single Lattice Point: Although it may have points at its corners, the total contribution equals exactly one point (e.g., 8 corners X 1/8 per corner = 1).
- Defined by Primitive Vectors: It is spanned by the primitive translation vectors a_1,a_2,a_3
- Non-Unique: For any given lattice, there are infinite ways to choose a primitive cell, provided the volume remains the same.

Construction Methods

There are two primary ways to define or visualize a primitive cell:

A. The Parallelepiped Method

This is the standard geometric approach where you choose three primitive translation vectors a_1, a_2, a_3 that reach the nearest neighbours. The volume of this cell is given by the triple scalar product:

$Vp = |a_1.(a_2 \times a_3)|$

The Wigner-Seitz Cell

The Wigner-Seitz cell is a special type of primitive cell that displays the full symmetry of the lattice. It is defined as the region of space around a lattice point that is closer to that point than to any other.

How to construct it:

1. Draw lines connecting a central lattice point to all its nearest neighbors.
2. Draw planes (in 3D) or lines (in 2D) that perpendicularly bisect these connecting lines.
3. The smallest enclosed volume created by these intersecting planes is the Wigner-Seitz cell.

Comparison: Primitive vs. Conventional

It is often more convenient to use a Conventional Unit Cell (which may contain 2 or 4 lattice points) because it aligns with the x, y, z axes, making calculations easier.

Feature	Primitive Cell	Conventional Unit Cell
Lattice Points	Exactly 1	1 or more (often 2 or 4)
Volume	Smallest possible Vp	Integer multiple of Vp
Symmetry	May not show full symmetry	Always shows full crystal symmetry
Example (BCC)	Rhombic parallelepiped	Cube (contains 2 points)

Examples in Cubic Systems

- Simple Cubic (SC): The conventional cube is already primitive (1 point).
- Body-Centered Cubic (BCC): The conventional cube has 2 points. The primitive cell is a slanted parallelepiped with $V_p = a^{3/2}$.

- Face-Centered Cubic (FCC): The conventional cube has 4 points. The primitive cell is a parallelepiped with $V_p = a^{3/4}$.

2.2 FUNDAMENTAL TYPES OF LATTICES:

Lattice

A lattice is a regular, periodic arrangement of points in space. Each point represents the position of an atom or a group of atoms.

All lattice points are identical and equivalent.

Fundamental Types of Lattices (Based on Centring)

Lattices are classified according to the position of lattice points in the unit cell. There are four fundamental lattice types:

(a) Simple (Primitive) Lattice — P

- Lattice points only at the corners of the unit cell
- Each corner atom is shared by 8 unit cells

Lattice points per unit cell:

$$8 \times \frac{1}{8} = 1$$

Examples:

- Simple cubic (Polonium)

(b) Body-Centered Lattice — I

- Lattice points at:
    - All corners
    - One at the center of the unit cell

Lattice points per unit cell:

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

Examples:

- BCC structure: Iron (Fe), Chromium (Cr)

(c) Face-Centered Lattice — F

- Lattice points at:
    - All corners
    - Centers of all six faces

Lattice points per unit cell:

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

Examples:

- FCC structure: Copper (Cu), Aluminum (Al), Silver (Ag)

(d) Base-Centered (End-Centered) Lattice — C

- Lattice points at:
    - All corners

- Centers of two opposite faces (usually top and bottom)

Lattice points per unit cell:

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

Examples:

- Some orthorhombic and monoclinic crystals

Summary Table

Lattice Type	Symbol	Lattice Points per Unit Cell
Simple (Primitive)	P	1
Body-Centered	I	2
Face-Centered	F	4
Base-Centered	C	2

2.3 Two dimensional crystalline lattices:

Introduction to Space lattice

In general infinite number of lattices are possible because there is no restriction on the length a, b of the lattice translations and on angle ϕ between them. Such a lattice is known as oblique lattice and is shown in fig 2.1(a).

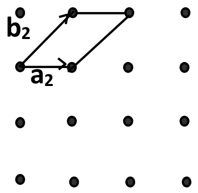


Fig 2.1 (a) Obliqe

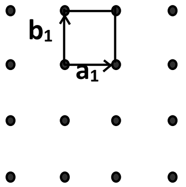


Fig 2.2 (b) square

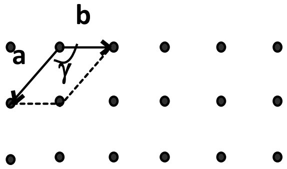


Fig2.1(c) Hexagonal lattice

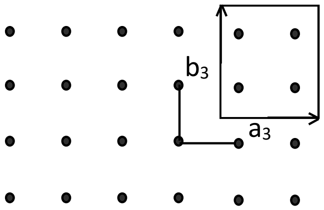


Fig 2.1(d) Rectangular lattice

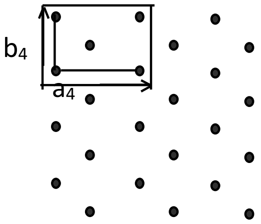


Fig 2.1(e) centred rectangle

Oblique lattice is invariant under the rotation 2π/n (n= 1 & 2) about any lattice point. However, this can also be invariant under the rotation 2π/n with n=3,4,6 (or) mirror reflection if some suitable restrictions are imposed on a, b & ϕ. These symmetry elements in turn put restrictions on the shape of the lattice. The resulting lattices are known as special lattices. They are

1. Square lattice $|a| = |b|$, ϕ (or) $\gamma = 90^0$

2. Hexagonal lattice $|a| = |b|$, $\gamma = 120^0$

3. Rectangular lattice $|a| \neq |b|,\ \gamma = 90^0$

4. Centred rectangular

Lattice axes are shown for both the primitive cell and the rectangular unit cell for which dimensions. Out of the five Bravais lattices, one is general and other four are obtained by exhausting the feasible axial relationships between a and b and the relative orientations of the two. The general lattice is termed as oblique lattice.

$|a| \neq |b|, \gamma = 90^0$

Table 1 Bravais lattice in two dimension

There are in all five Bravais lattices, ten point groups and seventeen space groups in two-

S.No.	Lattice type	Conventional unit cell	Axes & angles	Point group symmetry about lattice point
1.	Oblique	Parallelogram	a$\neq$ b; ϕ (or) $\gamma \neq 90^0$	2mm
2.	Square	Square	a = b; $\gamma = 90^0$	4mm
3.	Hexagonal	Rhombus	a = b; $\gamma = 120^0$	6mm
4.	Primitive Rectangular	Rectangle	a$\neq$ b; $\gamma = 90^0$	2mm
5.	Centred rectangular	Rectangle	a$\neq$ b; $\gamma = 90^0$	2mm

2.4 Three dimensional crystalline lattices:

In previous section, we observe that in two dimensions suitable restrictions on lattice translations & angles allow only five types of lattices. By extending the same idea to a 3-dimensional case and applying the similar restrictions on the lattice translations a, b &c and angles α, β and γ we obtain a Bravais lattice.

Crystal system	Restriction on conventional cell, axes & angles	Associate lattice		Characteristic symmetry element
		Number	Symbol	
Triclinic	a $\neq$ b $\neq$ c; $\alpha \neq \beta \neq \gamma \neq 90^0$	1	P	None
Monoclinic	a $\neq$ b $\neq$ c; $\gamma = \alpha = 90^0 \neq \beta$	2	P, C	One 2-fold-rotation axis.
Orthorhombic	a $\neq$ b $\neq$ c; $\alpha = \beta = \gamma = 90^0$;	4	P, C, F, I	Three 2-fold rotation axis
Tetragonal	a=b$\neq$ c; $\alpha = \beta = \gamma = 90^0$;	2	P, I	One 4-fold rotation axis
Cubic	a=b=c; $\alpha = \beta = \gamma = 90^0$;	3	P, I, F	Four 3-fold rotation axis
Trigonal	a=b=c; $\alpha = \beta = \gamma < 120^0 \neq 90^0$;	1	P	One 3-fold rotation axis
Hexagonal	a=b$\neq$ c; $\alpha = \beta = 90^0$; $\gamma = 120^0$;	1	P	One 6-fold-rotation axis.

A three-dimensional unit cell is defined by vectors a, b &c representing its edges (or) crystal axes and the angles α, β & γ. The numbers of Bravais lattices is14 with 32 points groups and 230 space groups. Based on relationships between a, b & c in terms of magnitude and relative orientations α, β & γ, the 14 types of unit cells are grouped into seven different classes of crystal lattices. They are Triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal & hexagonal. The table 2 gives the 7 classes of crystal lattices.

Table 2 Crystal classes

P stands for Primitive, C for Side centered (or) base centered, I for Body centered and
F for Face centered

Index System for Crystal planes

2.5 INDEX SYSTEM FOR CRYSTAL PLANES

It is difficult to designate the different planes in a crystal. To avoid this difficulty Miller evolved a method to designate a set of parallel planes in a crystal by three numbers (h, k, l) know as Miller indices.

The steps for the determination of Miller indices of a set of parallel planes are illustrated as follows

(1) Determine the intercepts made by the plane along the three crystallographic axes (x, y, z)

i.e	x	y	z
	2a	3b	c
	p	q	r

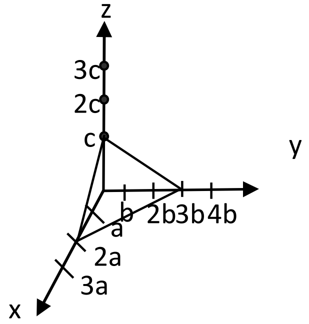


Fig 2.2(a)

where p = 2; q = 3; r = 1;

(2) Express the intercepts as multiples of the unit cell dimensions, (or) lattice parameters along the axes i.e.

$$\frac{2a}{a}\quad \frac{3b}{b}\quad \frac{c}{c} \Rightarrow 2\quad 3\quad 1$$

(3) Determine the reciprocals of these numbers i.e. $\rightarrow \frac{1}{2}\quad \frac{1}{3}\quad \frac{1}{1}$

(4) Reduce the reciprocals to the smallest set of integral number and enclose them in brackets $\Rightarrow \frac{6}{2}\quad \frac{6}{3}\quad \frac{6}{1} \Rightarrow (3\quad 2\quad 6)$

Thus Miller indices may be defined as the reciprocal of the intercepts made by the plane on the crystallographic axes when reduced to smallest number. Important features of Miller indices of crystal planes are,

a) All the parallel equidistant planes have the same Miller indices.
b) A plane parallel to one of the Co-ordinate axes has an intercept of infinity.
c) If the Miller indices of two planes have the same ratio i.e.(844) and (422) or (211) then the planes are parallel to each other.
d) If (h, k, l) are the Miller indices of a plane, then the plane cuts the axes into h, k & l equal segments respectively.

The Miller indices define a set of parallel planes or a set of parallel planes. If (h, k, l) are the Miller indices of a plane, then, the plane cuts the axes into h, k and l equal segments respectively. If a plane cuts an axis on the negative side of the origin, the corresponding index is negative and is indicated by placing a bar above the index; $(h\bar{k}l)$. The cube faces of a cubic crystal are (100);

(010); (001); $(\bar{1}00)$;$(0\bar{1}0)$ and $(00\bar{1})$. Planes equivalent by symmetry are denoted by curly brackets around miller indices; the cube faces are {100}. Regarding direction the x axis is the [100] direction; the –y axis is the $[0\bar{1}0]$ direction. A full set of equivalent directions is denoted this way: <uvw>. In cubic crystals a direction [uvw] is perpendicular to a plane (uvw) having the same indices, but this is not generally true in other crystal systems.

The positions of points in a unit cell are specified in terms of lattice coordinates, in which each coordinate is a fraction of the axial length, a, b or c, in the direction of the coordinate, with the origin taken at the corner of unit cell. Thus the coordinates of the central point of a cell are $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and the face center positions are $\frac{1}{2}\frac{1}{2}0$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$.

2.3 Spacing between planes of same Miller indices: -

It is necessary to know the inter planar distance between planes labeled by the same Miller indices for the x-ray diffraction from the crystal. Let us call this distance d_{hkl}.

Now, we shall derive a formula for the spacing between two parallel planes in a given cell with the help of figure shown in fig 2.3.

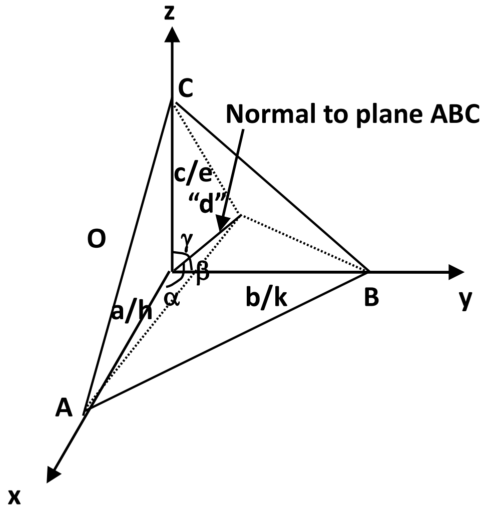


Fig 2.3

For convenience, we shall take a simple unit cell in which co-ordinate axes are orthogonal, therefore they are mutually perpendicular (cubic, tetragonal and orthorhombic cells), for the calculation of inter-planer spacing using cartesian co-ordinates.

In the fig ox, oy & oz are orthogonal axes the origin O is taken at any lattice point. Now we consider any set of crystal planes defined by the Miller indices, (h, k, l). Suppose the reference plane passes through the origin and the next plane makes intercepts a/h, b/k & c/l on x, y & z-axes respectively.

A normal is drawn on to the plane ABC from the origin. The length "d" of this normal planewill be the distance between the adjacent planes.

Now we have to find an expression for d in terms of a, b, c & h, k, l.

Since d is normal to the plane ABC, we write

$$\text{Cos}\,\alpha = \left(\frac{ON}{OA}\right); \quad \text{Cos}\beta = \left(\frac{ON}{OB}\right); \quad \text{Cos}\,\gamma = \left(\frac{ON}{OC}\right);$$

Where $\angle\alpha = \angle NOA$, $\angle\beta = \angle NOB$, $\&\angle\gamma = \angle NOC$

According to law of direction co-sines,

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

$$\Rightarrow \left(\frac{ON}{OA}\right)^2 + \left(\frac{ON}{OB}\right)^2 + \left(\frac{ON}{OC}\right)^2 = 1$$

$$\Rightarrow \left(\frac{d}{a/h}\right)^2 + \left(\frac{d}{b/k}\right)^2 + \left(\frac{d}{c/l}\right)^2 = 1$$

$$\Rightarrow d^2\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right] = 1$$

$$\Rightarrow d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

The above relation is applicable to the primitive lattice in cubic, orthorhombic & tetragonal systems. For tetragonal crystal a = b

$$\Rightarrow d = \left[\frac{h^2 k^2}{a^2} + \frac{l^2}{c^2}\right]^{-1/2}$$

For cubic system a = b = c

$$\Rightarrow d = \frac{1}{\sqrt{h^2 + k^2 + l^2}}$$

Note:- In non-orthogonal lattice, calculation of inter planer spacing is more complex.

2.6 Packing Density in Crystal Structures (SC, BCC and FCC)

Packing density (also called Atomic Packing Factor – APF) is the fraction of volume of a unit cell occupied by atoms.

$$\text{Packing Density} = \frac{\text{Volume occupied by atoms in a unit cell}}{\text{Total volume of the unit cell}}$$

Atoms are considered as hard spheres.

The simple cube (SC):-

The unit cell is cube having one atom (or) molecule at each corner. So there are eight atoms (or) molecules at eight corners of the cube. Since each corner atom is shared by eight surrounding cubes, share of each cube comes to one eighth of an atom, shown in fig 1.13a.

$\therefore$ Total No. of atoms = $\frac{1}{8} \times 8 = 1$ atom.

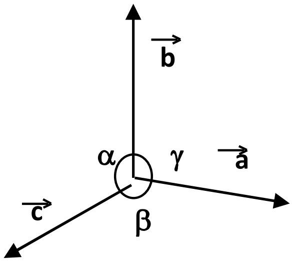


Fig 2.4 Notation for angles between the crystal axis

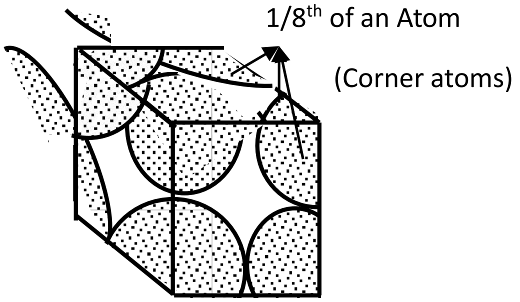


Fig 2.5 The simple cube

The Body Centered cube (BCC):-

The unit cell of body centered cube structure is shown in fig 2.6. It has eight corner atoms & one center atom. The number of atoms belonging to this cube are (a) One center atom &

(b) $\frac{1}{8} \times 8 = 1$ corner atoms

$\therefore$ Total No. of atoms per cube =1+1=2

The Face centred cube (FCC): -

The unit cell of face centred cube structure is shown in fig 2.7. It has 6 face centered and eight corner atoms. The six face centred atoms at six faces of the cube are shared by their adjacent cubes. Hence, a total of 6/2=3 such atoms belong to the cube. As each corner atom is shared by eight surrounding cubes, the share of each cube comes to one eighth of an atom.

$\therefore$ Total no. of atoms per cube $=3+\frac{1}{8}\times 8=3+1=4$.

Similarly monoclinic lattice has two types simple and base centred. Orthorhombic has four types three as mentioned above for cubic and base centred, Tetragonal has two types of lattices. These are shown in fig 2.7.

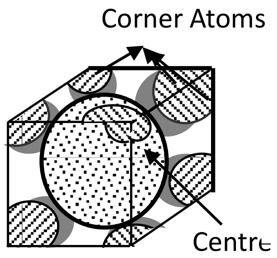


Fig 2.6 Body centred

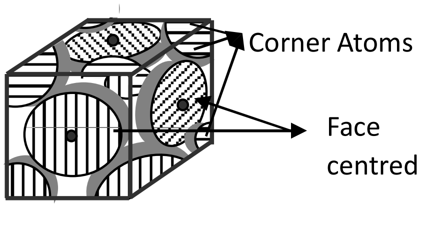


Fig 2.7 Face centred cube

2.7 Summary:

The structure of crystalline solids is based on the regular and periodic arrangement of atoms in space, known as a crystal lattice. Understanding primitive lattices, lattice types, indexing systems, and packing density helps explain the physical properties of materials.

Primitive Lattice:

A primitive lattice is the simplest lattice that represents the entire crystal structure through repetition. The primitive unit cell is the smallest volume that, when translated in space, can generate the whole lattice. It contains exactly one lattice point and reflects the fundamental symmetry of the crystal.

Fundamental Types of Lattice (Two-Dimensional):

Two-dimensional lattices represent periodic arrangements in a plane. There are five fundamental 2D lattice types: oblique, rectangular, centered rectangular, square, and hexagonal. These lattices are used to study surface structures and thin crystalline layers.

Fundamental Types of Lattice (Three-Dimensional):

Three-dimensional lattices describe the full spatial arrangement of atoms in crystals. There are fourteen fundamental 3D lattices known as Bravais lattices, grouped into seven crystal systems such as cubic, tetragonal, orthorhombic, and others. These lattices form the backbone of all crystal structures.

Index System of Crystal Lattice:

The index system, commonly known as Miller indices, is used to represent crystal planes and directions. Miller indices are a set of integers that define the orientation of planes within a crystal lattice. This system is essential for analyzing crystal geometry, diffraction patterns, and material properties.

Packing Density in Crystal Structures

Packing density (or packing fraction) is defined as the fraction of volume in a crystal structure that is actually occupied by atoms, assuming atoms to be hard spheres. It depends on the type of crystal structure:

- Simple cubic (SC): low packing density
- Body-centered cubic (BCC): intermediate packing density
- Face-centered cubic (FCC) and hexagonal close-packed (HCP): maximum packing density

Packing density plays a crucial role in determining mechanical strength, stability, and physical properties of crystalline materials.

2.8 Technical terms

Primitive Lattice Cell, Fundamental Types of Lattice, Two Dimensional Crystalline Lattice, Three Dimensional Crystalline Lattice, Index system for crystal planes, Packing Density in Crystal Structures.

2.9 Self assessment questions

1. Explain about the Primitive Lattice Cell
2. Write about the Fundamental Types of Lattice
3. Explain about the Two Dimensional Crystalline Lattice
4. Explain about the Three Dimensional Crystalline Lattice
5. Write about the Index system for crystal planes
6. Explain about the Packing Density in Crystal Structures.

2.10 Suggested readings

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

Prof. R.V.S.S.N. Ravi Kumar

LESSON- 3

SIMPLE CRYSTAL STRUCTURES

Aim:

To study and understand simple crystal structures such as Sodium Chloride, Cesium Chloride, Diamond, and Zinc Sulfide, and relate their atomic arrangements to their physical properties**.**

Objectives:

1. To understand the concept of crystal structures in solids.
2. To study the arrangement of atoms or ions in simple crystal structures.
3. To examine the structure of Sodium Chloride (NaCl) crystal.
4. To study the Cesium Chloride (CsCl) crystal structure.
5. To understand the Diamond crystal structure.
6. To study the Zinc Sulfide (ZnS) crystal structure.
7. To compare ionic and covalent crystal structures.
8. To determine coordination numbers in different crystal structures.
9. To understand the role of bonding and atomic arrangement in determining crystal properties.
10. To appreciate the importance of simple crystal structures in material science.

STRUCTURE:

3.1 SIMPLE CRYSTAL STRUCTURES

Common Crystal Structures:-

A large percentage of metallic structures crystallize in hcp, fcc, bcc. Simple cubic is very rare in metals.

Simple Cubic:-

The simplest crystal structure that we can think of is that of simple cubic symmetry with a basis of one atom. In this structure the atoms are situated at the corners of the cube touching each other along the edges, which can be shown in fig 3.1.

Each atom surrounded by 6 nearest neighbors. So, that the Co-ordination number is 6. The atomic radius is a/2 ($r = a/2$). Where a is the cube edge.

The number of atoms per unit cell is 1. Polonium is the lone known example of thisclass in nature.

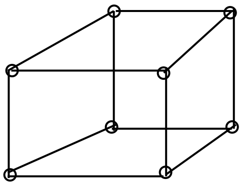


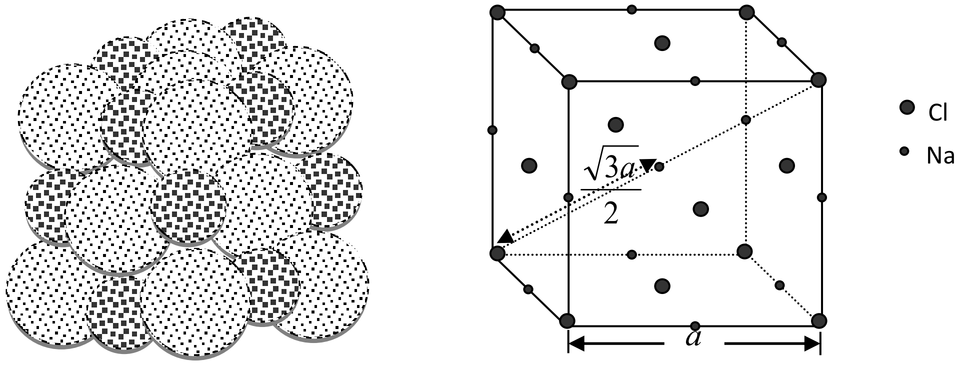
Fig 3.1

3.2 THE NACL STRUCTURE:-

Bravais lattice is fcc. An atom on the edge contributes 1/4th of the atom. Thus, the unit cell gets three sodium atom from those on the edges $\left(\frac{12}{4}=3\right)$ & one from that at the centre. The total cell consists of 4 Na atoms. Similarly the contribution of chlorine atoms to the unit cell comes to 4 [8/8 + 6/2 = 4]. A single unit cell accommodates four formula unit cells of NaCl. The positions of atoms in the unit cell are,

Na:	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$	$0\;0\;\frac{1}{2}$	$0\;\frac{1}{2}\;0$	$\frac{1}{2}\;0\;0$
Cl:	$0\;0\;0$	$\frac{1}{2}\,\frac{1}{2}\;0$	$\frac{1}{2}\;0\;\frac{1}{2}$	$0\;\frac{1}{2}\,\frac{1}{2}$.

The Sodium Chloride (NaCl) structure is shown in below fig 3.2.



(a) (b)

Fig 3.2: (a) The arrangement of Na and Cl (shown bigger) atoms on the unit cell of NaCl crystal. (b) Locations of Na and Cl (shown bigger) atoms in the cube representing the unit cell. The separation between the basis partners is half the length of the body diagonal $\frac{\sqrt{3}a}{2}$

Since each ion has six nearest neighbors of opposite kind, the co-ordination number is 6.Some of the crystals representative of NaCl arrangement, along with their lattice parameter are shown in table.

Crystal	Lattice parameter A^0
NaCl	5.63
LiH	4.08
KBr	6.50
RbI	7.33

3.3 THE CSCL STRUCTURE:-

The structure of Cesium Chloride is shown in fig 3.3. The space lattice is simple cube.

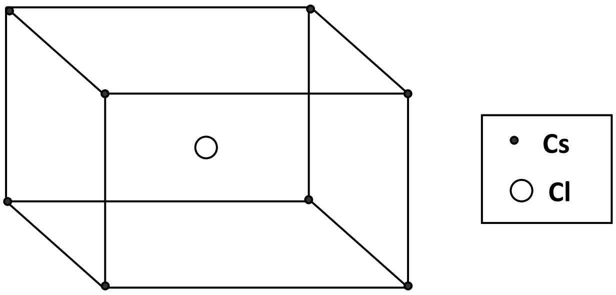


Fig 3.3(a) The unit cell structure of CsCl crystal

The basis has one Cs^+ ion of 000 and one Cl^- ion at ½ ½ ½. The central atom is surrounded by eight atoms of the other type at the corners, the co-ordination number is thus eight. It may be noticed that this structure cannot be interpreted as body centred cubic (BCC). The lattice points of CsCl are two interpenetrating simple cubic lattices,

Crystal	Lattice parameter A^0 ($A^0 = 10^{-10}$m)
CsCl	4.11
CsBr	4.29
CSI	4.56
TICl	3.84
TIBr	3.97
TII	4.18

The corner of one sub-lattice is the body centre of the other. One sub-lattice is occupied by Cs^+ ions and the other by Cl^- ions. The lattice parameter of some ionic crystal having this structure is given below.

Crystal of Alkali Metals:-

Crystals of alkali metals (Li, Na, K, Rb, Cs) are typical representatives of the body centered cubic (bcc) structure. The unit cell is non-primitive with 2 lattice points and the basis of one atom. The cell consist of one atom of each corner & one atom in the centre of the cube which is shown in fig 3.2(b). Each atom has only 8 nearest neighbors. Therefore e Co-ordination number is 8.

(1) Total No. of atoms = 1 + 1 = 2

(2) Atomic radius r = $\frac{\sqrt{3}a}{4}$

(3) Volume of atoms in unit cell u = $2\times\frac{4}{3}\pi r^3 = \frac{\pi\sqrt{3}a^3}{8}$

(4) Volume of a unit cell V = a^3.

(5) Packing factor $\simeq \frac{u}{V} = \frac{\pi\sqrt{3}a^3}{8\times a^3} \simeq 0.68.$

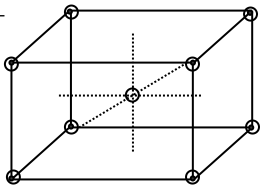


Fig 3.2(b)

Crystals of Noble Metals:-

The Noble metals Cu, As, Au, crystallize in another structure, the face centered cubic (fcc). The unit cell has four lattice points with the basis of one atom. The positions of the atoms in the unit cell are 000, ½ ½ 0, 0 ½ ½ , ½ 0 ½. The Co-ordination number is 12. The structure is also close packed. The lattice parameters are given below (in $\overset{0}{A}$).

Cu	3.61
Ag	4.08

3.4 DIAMOND STRUCTURE:-

The diamond lattice can be considered to be formed by inter penetrating two fcc lattice along the body diagonal by (1/4)th cube edge. One sub-lattice has its origin at the point 0, 0, 0 and the other at a point quarter of the way along the body diagonal $\left(\frac{a}{4},\frac{a}{4},\frac{a}{4}\right)$. The basic diamond lattice and the atomic positions in the cubic cell of diamond projected on a cube face are shown in fig 3.3.

The fractions denote height about the base in units of cube edge. The print at 0 and ½ are on the fcc lattice, those at ¼ and ¾ are on a similar lattice displace among the body diagonals by ¼ of the cube edge.

The packing factor is $(XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{8}+\frac{a^2}{16}=\frac{3a^2}{16}$

But, XZ = 2r

$\therefore\ (2r)^2 = \frac{3a^2}{16} \Rightarrow a = \frac{8r}{\sqrt{3}}.$

$$\text{Packing factor} = \frac{U}{V} = \frac{8\times\frac{4}{3}\pi r^3}{a^3} = \frac{\pi\sqrt{3}}{16} = 0.34\,(or)\,34\%$$

Thus it is a loosely packed structure. Carbon, Silicon and Germanium crystallize in thisstructure.

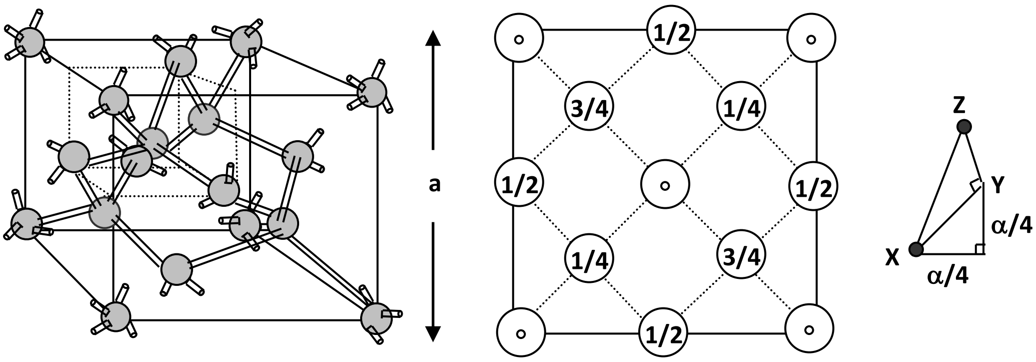


Fig 3.3 Diamond structure.

3.5 Zinc Sulfide structure:

In diamond structure consists of two fcc lattice displaced from each other by one-quarter of a body diagonal. The cubic zinc sulfide structure results from the diamond structure when Zn atoms are placed on one fcc lattice and S atoms on the other fcc lattice. The coordinates oZn atoms are 000; there are four atoms of ZnS per unit cell.

Each atom has about it four equally distant atoms of the opposite kind arranged at the corners of a regular tetrahedron. The diamond structure possesses a center of symmetry at the mid point of each line connecting neighbor atoms; the ZnS structure does not have inversion symmetry. Examples of the cubic zinc sulfide structure are CuF, CuCl, *ZnS,ZnSe, CdS, InAs, InSb,*

3.6 SUMMARY:

Simple Crystal Structures

Sodium Chloride (NaCl) Structure:

- Sodium Chloride has a **face-centered cubic (FCC)** lattice of chloride ions with sodium ions occupying all the octahedral voids.
- Each Na^+ ion is surrounded by **6 Cl^- ions**, and each Cl^- is surrounded by **6 Na^+ ions** (coordination number = 6:6).
- This is an **ionic crystal**, and its cubic arrangement gives NaCl its characteristic high melting point and hardness.

Cesium Chloride (CsCl) Structure:

- Cesium Chloride has a **simple cubic lattice** where Cl^- ions occupy the corners of the cube and Cs^+ ions sit at the **body center**.
- Each Cs^+ ion is surrounded by **8 Cl^- ions**, and each Cl^- is surrounded by **8 Cs^+ ions** (coordination number = 8:8).

- This structure is also ionic and results in a cubic crystal with relatively lower packing efficiency compared to NaCl.

Diamond Structure:

- Diamond is a **covalent crystal** where each carbon atom is tetrahedrally bonded to **4 other carbon atoms**.
- It has a **face-centered cubic (FCC) lattice** with a basis of 2 carbon atoms per lattice point.
- Diamond has **very high hardness**, high melting point, and excellent thermal conductivity due to strong covalent bonding and rigid 3D network.

Zinc Sulfide (ZnS) Structure:

- ZnS exists in two common forms: **zinc blende (cubic)** and **wurtzite (hexagonal)**.
- In the cubic (zinc blende) structure, Zn^{2+} ions occupy half the tetrahedral sites in an FCC lattice of S^{2-} ions.
- Each Zn^{2+} is surrounded by **4 S^{2-} ions**, and each S^{2-} is surrounded by **4 Zn^{2+} ions** (coordination number = 4:4).
- ZnS is a **covalent/ionic mixed crystal** used in optoelectronic applications due to its wide band gap.

Conclusion:

Simple crystal structures demonstrate how atoms or ions arrange themselves in 3D space based on bonding type and size. Coordination number, lattice type, and packing efficiency are key factors in determining their physical and chemical properties. Ionic crystals like NaCl and CsCl show high melting points, while covalent crystals like Diamond and ZnS have strong bonds and specific applications in technology and materials science.

3.7 TECHNICAL TERMS

Simple Crystal Structure, Sodium Chloride, Cesium Chlordie, Diamond Structure, Zinc Sulfide.

3.8 SELF ASSESSMENT QUESTIONS

1. Explain about the Simple Crystal Structure
2. Write about the Sodium Chloride crystal structure
3. Write about the Cesium Chlordie crystal structure
4. Write about the Diamond Structure
5. Write Zinc Sulfide crystal structure

3.9 SUGGESTED READINGS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
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6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

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LESSON -4

CRYSTAL DIFFRACTION

Aim:

To study the principles of X-ray diffraction in crystals, understand Bragg's law, explore experimental diffraction methods (Laue and powder techniques), derive the amplitude of scattered waves, and analyze the geometrical structure factor of crystal lattices.

Objectives:

1. To understand the phenomenon of X-ray diffraction by crystals.
2. To study and derive **Bragg's law** relating diffraction angle, wavelength, and interplanar spacing.
3. To learn about **experimental diffraction techniques**, including the Laue method and powder method.
4. To understand the concept of **scattered wave amplitude** and its derivation from crystal lattice planes.
5. To study the **geometrical structure factor** and its role in determining diffraction intensity.
6. To relate crystal symmetry and atomic arrangement to diffraction patterns.
7. To analyze how diffraction data can be used to determine **crystal structure** and **interatomic distances**.
8. To develop practical understanding of X-ray diffraction experiments and interpretation of results.

STRUCTURE:

4.1BRAGG'S LAW IN TERMS OF RECIPROCAL LATTICE VECTORS:-

We learn more about x ray diffraction in the forth coming lesson and for the present the Bragg's law derived for the X ray diffraction condition can be expressed suitably in the reciprocal lattice, We now see how to do this.

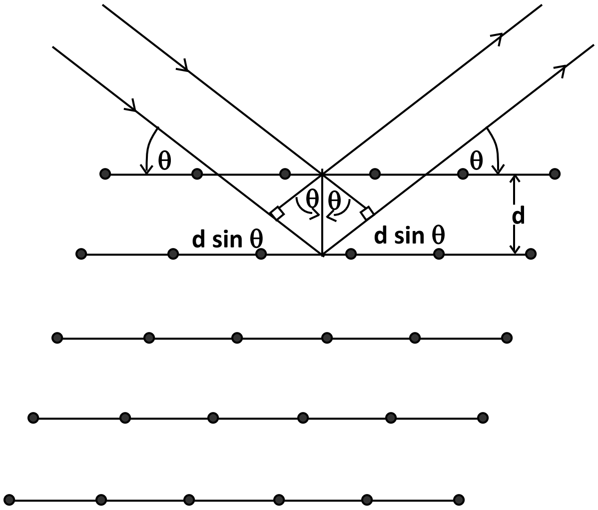


Fig 4.1 Bragg reflection from a family of planes with inter planar spacing d. Note that the incident beam is deflected by twice the Bragg angle θ.

In the X ray diffraction phenomenon, the crystal planes are believed to act like plane mirrors. Radiations reflected from two successive parallel planes under certain conditions may interfere constructively to produce a diffraction maximum. The Bragg diffraction shown in fig4.1. Occurs for secular reflections (angle of incidence = angle of reflection). The constructive interference occurs when the path difference (2d sinθ) between the interfering rays equals an integral multiple of the X-ray wavelength λ. That is,

$$2d \sin \theta = n\lambda \text{ ----------------- } (1)$$

where d is the inter planar spacing θ is the angle of the incident radiation with the plane n = 1, 2, 3 …… (order of diffraction)

The relation (1), which is a mathematical statement of the Bragg law, shows that the diffraction effects cannot be observed from a family of planes for any arbitrary angle of incidence.

Bragg's diffraction condition in terms of reciprocal lattice:

The Bragg condition can be expressed as a relation between vectors in the reciprocal lattice. The Bragg condition can be expressed as

$$\sin\theta_{hkl} = \frac{\lambda}{2d_{hkl}} \text{ --------------- } (2)$$

in which the order of reflection is already included. The equation (2) can also be written as

$$\sin\theta_{hkl} = \frac{1/d_{hkl}}{1/\lambda} \text{ -------------- } (3)$$

A geometrical interpretation of eqn.(3) is given in fig (1). ***SO*** is a vector whose length is 1/λ. This vector is drawn in the direction of incident X-ray beam and ending at the origin of reciprocal lattice. Now a sphere of radius 1/λ is constructed about a point ***S*** as centre. Let this sphere intersect some point (***h′, k′, l′***) of the reciprocal lattice at ***P***.

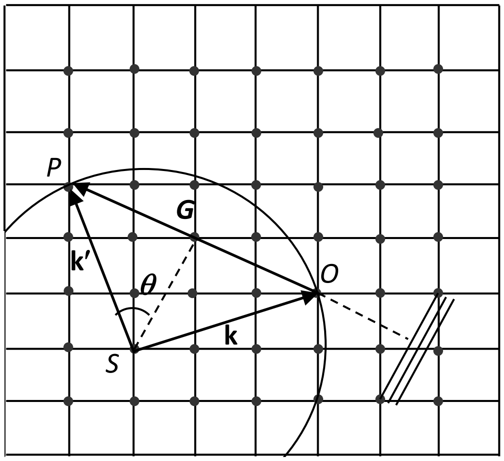


Fig: 4.1 Vector geometry of Bragg reflection in the reciprocal lattice.

The vector ***OP*** then represents a vector counting the origin of the reciprocal lattice and a point (***h′, k′, l′***) of that lattice. The vector is normal to ***h, k, l*** plane of direct lattice and its length is **1/*d*$_{hkl}$.** From the figure the length of the vector ***OP*** can be calculated from fig. which is 2 $\sin\theta/\lambda$.

Hence $2\sin\theta/\lambda = \frac{1}{d_{hkl}}$ ------------- (4)

i.e.$\lambda = 2d\sin\theta$

and the Bragg condition is satisfied. Thus the vector ***OP*** represents a normal to the reflecting planes **(*h, k, l*)** and the vector ***SP*** is in the direction of diffracted beam. The direction of the diffracted beam is shown in figure (2). For any experimental set up, the direction of X-ray beam is defined as ***AO***.

Diffraction occurs only when the orientation of the crystal is such that a reciprocal lattice point ***P*** comes to lie on the circumference of a circle ***S*** of radius $1/\lambda$. When this occurs, a diffracted beam is developed in the direction ***SP***.

It is customary to imagine all the vectors of fig (2) to be multiplied by a constant factor of **2π** as represented in figure (3). Here the vector **K** is **2π** times the vector ***SO*** and the vector **G** is **2π** times the vector ***OP***. Again the disposition of vector is such that vector ***SP*** must be vector sum of **K** and **G**.

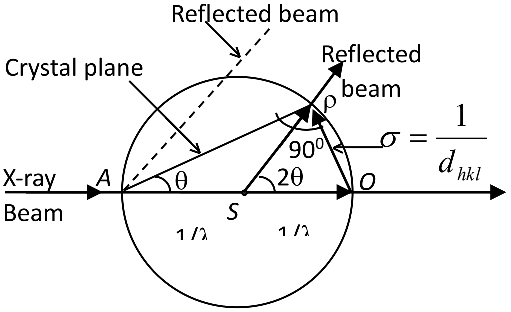


Fig: 4.1 Showing the direction of diffracted beam.

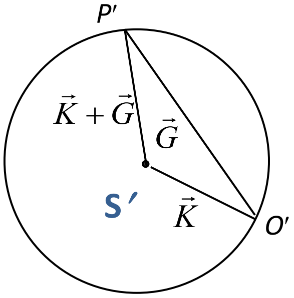


Fig :4.1 Vector diagram of the figure expanded by a scale factor 2π

Now the magnitude of the vector ***S′P′*** i.e., **K**+**G** and the magnitude of the incident beam vector ***S′O′*** i.e., **K** must be equal. Applying this condition the Bragg condition is satisfied ; the Bragg condition must imply that

$$(\mathbf{K}+\mathbf{G})^2 = (\mathbf{K}+\mathbf{G}).(\mathbf{K}+\mathbf{G}) = K^2$$

$$\text{i.e.,}\quad 2\mathbf{K}\,.\,\mathbf{G} + \mathbf{G}^2 = 0 \qquad \text{--------------} \quad (5)$$

Equation (3.17) represents the vector form of Bragg equation.

Here $G = h^*\mathbf{a} + k^*\mathbf{b} + l^*\mathbf{c}$ (h, k, l = integers)

4.2 Experimental method in X-ray Diffraction:

4.2.1 The Laue Method:

The experimental equipment here is relatively simple and is shown in figure 4.4. The crystal is held stationary in the beam of X– rays. The rays after passing through the crystal are diffracted and are recorded on the photographic plate place at a certain distance from the crystal. Before passing through the crystal, the X– rays are limited to a fine pencil by a slit system. The diameter of the pinhole is importance from the stand point of detail in diffraction pattern. The smaller is the diameter the sharper is the interference. The crystal is set on a holder to adjust its orientation. The Laue method employs white radiation (X– rays beam of continuous range of wavelength) which is usually obtained from a tungsten target at about 60,000 volts.

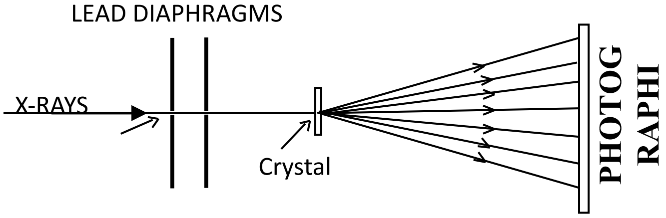


Fig: 4.5 Diffraction of white X-rays by a single stationary crystal

We have seen that if a beam of X– rays of a given wavelength λ is passed in a given direction through a crystal, the diffraction is not in general to be expected. This is because very few sets of planes would be in a favourable position to meet the requirements of the Bragg equation and reflections would of course be rare. But since there is a whole range of wavelengths in the continuous spectrum, there will be discrete values of λ which satisfy the Bragg condition-no matter what may be the orientation of the lattice planes. In another words, for any values of *d* and θ_0, there will be found in the beam some value of λ such that diffraction can occur. We know that atoms of crystal have an orderly arrangement in all the these dimensions in space, hence the diffraction of X-ray will occur from many families of atomic planes at once, each family picking out the wavelength which it can diffract at the angle at which it finds itself. The sort of diffraction pattern obtained is illustrated in figure 4.5.

Examination of the Laue photograph shows that the spots do actually occur at the positions to be expected from the reflection law. When the primary beam passes along the axis symmetry of the crystal, the Laue pattern consists of a series of spots whose loci are ellipses which pass through the *central image* made by primary beam. The spots on any one ellipse are produced by planes belonging to the same zone i.e. planes which are parallel to one common direction.

The Laue pattern can be used to orient crystal for solid state experiments. Let us consider the case of a crystal with four fold axial symmetry which is oriented with the axis parallel to the beam. Each reflecting plane then selects a wavelength satisfying the Bragg equation from the incident beam. The Laue pattern obtained in this case shows the four fold symmetry.

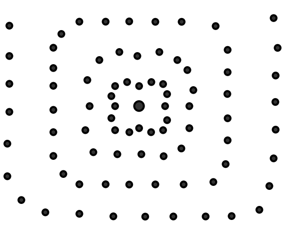


Fig: 4.6 The arrangement of the spots in a Laue photograph of simple cubic crystal

Practically this method is never used for crystal structure determination. In this case several wavelengths may be reflected in different orders from a single plane, so that different orders of reflection may superpose on a single spot. Due to this fact the determination of a reflected intensity is difficult and thus the determination of the basis.

4.2.2 The Powder-Photograph Method:

The powder method is the only method which can be used with that large class of substances which cannot be obtained easily in the form of perfect crystals of appreciable size. This class includes not only the most metals and their alloys but also a large number of compounds. The method was devised independently by Debye and Scherrer in Germany and by Hill in America. In this method a monochromatic X-rays beam is used and instead of using a single crystal, fine powders of crystalline aggregates of all kinds, having random of chaotic orientations are used. Such a powder requires no rotation because every atomic plane is present in every possible orientation and hence the diffraction depends upon the fact that in a fine powder the grains are arrange in an entirely chaotic manner. The entirely random orientations of the grains with respect to the beam means that some of them will be in a position to reflect the radiation from an important set of planes. Now diffracted rays go out from individual crystallites, which happen to be oriented with planes making an angle θ with the beam satisfying the Bragg equation. Any fragment in which the normal to the plane in questions makes an angle $(90 - \theta^0)$ with the incident beam will be in a position to reflect and since all orientations of the fragment are equally likely, the reflected rays will form a cone, concentric with the original beam and whose semi vertical angle is 2θ. There is such a cone of diffracted rays for each set of planes. The cones intercept the film in a series of concentric circular halves, from the radii of which the angle θ and hence the spacing of the planes can be deduced. The formation of powder photograph is shown in fig (4.7).

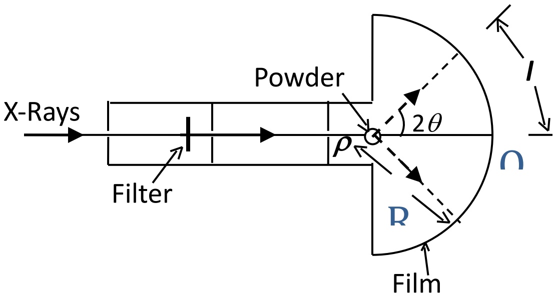


Fig 4.7 Design of an arrangement for taking powder photographs.

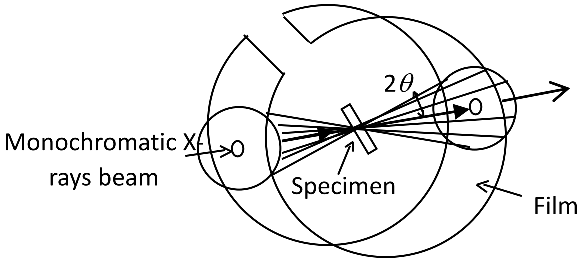


Fig 4.8 X-ray powder diffraction camera.

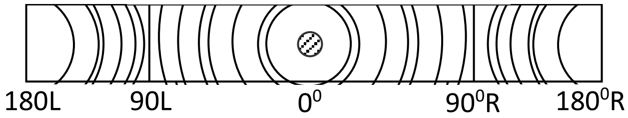


Fig 4.9 Arrangement of lines in a powder photograph

The radiation is made approximately monochromatic with the help of filter as shown in fig 4.8. *P* is the powder and *O* is the point where the direct beam would have struck the film. Point *A* on the film corresponds at which a spectrum with glancing angle $\theta$is formed. The diffracted maxima lie on cones coaxial with the direct beam, and if a photographic plate is mounted normal to the direct beam, and if a photographic plate is mounted normal to the direct beam, concentric circles are registered upon it as shown in fig 4.8(b). Usually a plate or film in the form of cylindrical shame is employed whose axis is perpendicular to the beam. There appear arcs of the circles as shown in fig 4.9.

From fig. 4.9 it is observed that when rays are different through small angles, they make arcs around the central spot on the film, when the rays are diffracted through 90^0, the cones become flat and the corresponding trace is a straight line. When the diffracted angle increases above 90^0, the curvature is reversed and when the angle approaches to 180^0, the traces are nearly circular. Thus the curvature of lines changes from the centre to the outside of the film.

Now considering fig 4.8, if l is the distance from *O* to *A*, measured on the film and R is the radius of camera, then $\theta = l/2R$. In this way by measuring l, the value of θ can be calculated.

This method is very useful in investigating the structures of simple crystals particularly belonging to cubic system of which spacings *a, b, c* of unit cell are all equal. In these crystals, there are certain definite relationship between the angles at which spectra can occur. The spacings of all planes parallel to faces of the same form {*h, k, l*} are equal and therefore produce spectra at the same–angle. In the most general case, in which all *h, k, l* are different, there are 48 faces in the form and 24 sets of planes all having the same spacing. These all co-operate to produce one line on the film. When the three axes of different length are at right angles to one another, the general form {*h, k, l*} corresponds to six different spacing and hence there are six different lines on the film.

4.3 DERIVATION OF AMPLITUDE OF SCATTERED WAVE:

Let us consider the case of a plane wave which is incident on a small crystal. Again let in the free space at point x the amplitude be F, then

$$F(x) = F_0 e^{i(\mathbf{K}\cdot\mathbf{x}-\omega t)} \text{ --------------- } (6)$$

Referred to an origin at x = 0. Equation (6) represents a traveling wave having wave vector K, angular frequency ω and the wavelength λ = 2π/K, Now we place the crystal in the beam with origin O chosen anywhere within the crystal. Here it is assumed that the incident beam is not greatly disturbed by crystal i.e., neither by the refractive index nor by the loss of energy through scattering. At a point $\vec{\rho}$, the amplitude of the incident wave is given by

$$F(\vec{\rho}) = F_0 e^{i(\mathbf{K}\cdot\vec{\rho})} \quad \text{[at instant of time } t = 0] \text{ ----------- } (7)$$

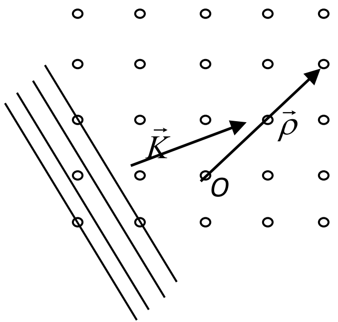


Fig: 4.10 Showing an electromagnetic wave incident upon a small crystal.

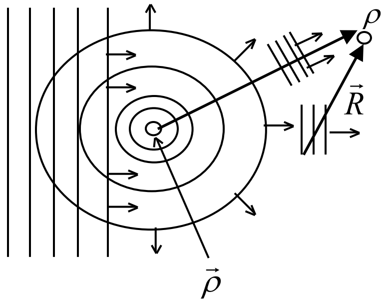


Fig: 4.11 Showing the radiation scattered $\vec{\rho}$

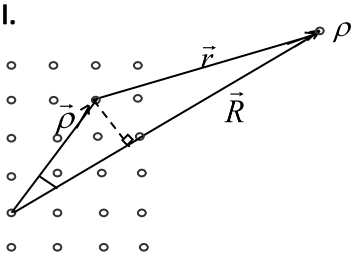


Fig: 4.12 Showing the wave scattered at *O* as received at R

The atom at $\vec{\rho}$ will scatter some of the radiation out of the incident beam. As in fig 4.10 (a) and (b), the amplitude of the scattered radiation as seen at point P is R = $\vec{\rho}$ + r i.e., at a point distant r from $\vec{\rho}$ outside the crystal will be proportional to

$$(F_0 e^{iK\vec{\rho}})\left(\frac{e^{iKr}}{r}\right) \text{-------------- } (8)$$

where the first parenthesis contains the amplitude and phase factor of the incident beam and the second parenthesis describes the spatial variation of the radiation scattered from a point atom at $\vec{\rho}$. The total phase factor at R is

$$e^{i\mathbf{K}\cdot\vec{\rho}} \cdot e^{i\mathbf{K}r} = e^{(i\mathbf{K}\cdot\vec{\rho} + i\mathbf{K}r)} \text{ ------------- } (9)$$

From fig 4.10(c), we have

$$r^2 = (R - \vec{\rho})^2 = R^2 + \rho^2 - 2\rho R \cos(\vec{\rho}, R) = R^2\left[1 + \frac{\rho^2}{R^2} - \frac{2\rho}{R^2}\cos(\vec{\rho}, R)\right]$$

when R is at a large distance so that $\rho/R << 1$, we have

$$\cong R^2\left[1 - \frac{2\rho}{R^2}\cos(\vec{\rho}, R)\right]$$

or $\qquad r \cong R[1 - (2\rho/R)\cos(\vec{\rho}, R)]^{1/2}$

$$\cong R - \rho\cos(\vec{\rho}, R)$$

now from equation (4.30), the total phase factor of the scattered wave on arriving at R is

$$e^{[i\mathbf{K}\rho + i\mathbf{K}R - i\mathbf{K}\rho\cos(\rho, R)]} \text{ ---------------- } (10)$$

Now it can be assumed that the amplitude of the wave scattered from an element of volume of the crystal is proportional to the electron concentration n($\vec{\rho}$) in the volume element. Hence the amplitude of the scattered radiation at R will be proportional to the integral

$$\int dV \,.\, n(\vec{\rho}) \,.\, e^{[i\mathbf{K}\cdot\rho - i\mathbf{K}\cdot\rho\cos(\rho R)]} \text{-------------- } (11)$$

The factor e^{iKR} is omitted, being constant over the volume. Equation (11) can be written in more compact form i.e.

$$\int dV \,.\, n(\vec{\rho}) \,.\, e^{-i\rho\cdot\Delta R} \text{ -------------- } (12)$$

where

$$iK \,.\, \vec{\rho} - iK\rho\cos(\vec{\rho}, R) \equiv i\vec{\rho}\,(K - K') \equiv -i\vec{\rho} \,.\, \Delta K,$$

K' is the wave vector in scattering direction R and

$\Delta K \equiv K' - K$.

Equation (4.33) gives the amplitude of the scattered wave.

Scattering from lattice of point atoms.

Consider a finite crystal and let all points be scattering centers. The lattice points are defined by

$$\vec{\rho} = ma + nb + pc \text{ ------------- } (13)$$

where m, n, p are integers. The amplitude a of radiation by entire crystal seen at R will be proportional to

$$a \equiv \sum_{\rho} e^{-i\vec{\rho}.\Delta K}$$

$$= \sum_{mnp} e^{[-i(ma+nb+pc).\Delta K]}$$

$$= (\sum_m e^{[-im(a.\Delta K)]})\ (\sum_n e^{[-in(b.\Delta K)]})\ (\sum_p e^{[-ip(c.\Delta K)]}) \text{ --------------- } (14)$$

We know that the intensity is the square of the amplitude, hence

$$\text{Intensity} = |\sum_m \exp.[-im\,(a\,.\,\Delta K)]\,|^2\ |\sum_n \exp.[-in\,(b\,.\,\Delta K)]\,|^2\ |\sum_p \exp.[-ip\,(c\,.\,\Delta K)]\,|^2$$

------------- (15)

Now we shall consider the value of one sum out of the three from equation (15). Let us consider the crystal of dimension Ma is the direction a where M is integer. We may let that m, n and p run from 0 to (M – 1), the crystal will have M^3 primitive cells because the total volume will be M^3abc; abc is the volume of one cell. Thus

$$|\sum_{m=0}^{M-1} \exp.[-im(a\,.\,\Delta K)]\,|^2$$

This is a geometric series and the summation therefore will be

$$\left[\frac{1-\exp.[-iM(a.\Delta K)]}{1-\exp.[-i(a.\Delta K)]}\right]^2 \text{ ------------- } (16)$$

Now using the series.

$$\sum_{m=0}^{M-1} x^m = \sum_{m=0}^{\infty} x^m - \sum_{m=M}^{\infty} x^m = \frac{1}{1-x} - \frac{x^M}{1-x} \text{ with } x \equiv \exp\,.\,[-i\,(a.\ \Delta K)] \text{ ----------- } (17)$$

Thus sum in equation (17) can be written as

$$\left[\frac{\exp.\left[-\tfrac{1}{2}iM(a.\Delta K)\right]}{\exp.\left[-\tfrac{1}{2}i(a.\Delta K)\right]} \cdot \frac{\exp.\left[\tfrac{1}{2}iM(a.\Delta K)\right]-\exp.\left[-\tfrac{1}{2}iM(a.\Delta K)\right]}{\exp.\left[\tfrac{1}{2}i(a.\Delta K)\right]\ -\ \exp.\left[-\tfrac{1}{2}i(a.\Delta K)\right]}\right]^2$$

Multiplying by its complex conjugate, we get

$$\frac{\sin^2 \frac{1}{2} M(a.\Delta \mathrm{K})}{\sin^2 \frac{1}{2}(a.\Delta \mathrm{K})}$$

$$\therefore \left| \sum_m \exp.[-im(a\,.\,\Delta \mathrm{K})] \right|^2 = \frac{\sin^2 \frac{1}{2} M(a.\Delta \mathrm{K})}{\sin^2 \frac{1}{2}(a.\Delta \mathrm{K})}, \text{-------------} \quad (18)$$

A plot of the function in equation (18) is shown in figure (4.13) for M = 20. The intensity will be maximum when each term in the sum on left hand side is unity i.e.

$a\,.\Delta K = 2\pi q$ ------------- (19)

where q is an integer. At these values equation (18) has a value M^2.,

Now we shall consider the width of the maxima as the value of $a\,.\Delta K$ is slightly changed. Let it be changed by $\in$ where $\in$ is the smallest non-zero number i.e.

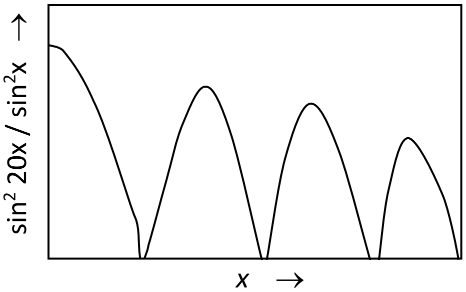


Fig : 4.13 Plot of function in equation 14 for M = 20

$a\,.\Delta K = 2\pi q + \in$.

When $\in = 2\pi/M$, we have

$\mathrm{Sin}\ \frac{1}{2} M\ (a\,.\Delta K) = \mathrm{Sin}\ \frac{1}{2} M\ (2\pi q + 2\pi/M) = \sin \phi\ (Mq + 1) = 0$

In this way if we choose $\in = 2\pi/M$, the width of maxima is proportional to $2\pi/M$ or 1/M. This shows that larger is the length of the crystal, smaller will be the width of maxima.

The area under the central maxima of equation (18) is given by the height ($\propto M^2$) times the width ($\propto$, 1/M), so the area is proportional to M, the number of atoms in the line. If the crystal in three dimensions has M^3 atoms, the scattered intensity will be directly proportional to M^3.

4.4 Geometrical structure factor

For a crystal with atoms at positions $\mathbf{r}_j$ inside the unit cell:

$$\boxed{F_{hkl} = \sum_j f_j \; e^{2\pi i(hx_j + ky_j + lz_j)}}$$

where:

- f_j= atomic scattering factor of atom j
- (x_j, y_j, z_j)= fractional coordinates of atom j
- h, k, l= reciprocal lattice indices

This is purely a **geometrical phase sum** when all f_j are equal.

Meaning in reciprocal space

- The **reciprocal lattice** determines **where diffraction spots occur**
- The **structure factor** determines **their intensity**
- If $F_{hkl} = 0$, that reciprocal lattice point is **systematically absent**

Examples of geometrical structure factors

(a) Simple cubic (SC)

One atom at $(0, 0, 0)$:

$$F_{hkl} = f$$

→ All reciprocal lattice points allowed.

(b) Body-centered cubic (BCC)

Atoms at:

- $(0, 0, 0)$
- $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

$$F_{hkl} = f\left[1+e^{\pi i(h+k+l)}\right]$$

$$F_{hkl} = \begin{cases} 2f & h+k+l = \text{even} \\ 0 & h+k+l = \text{odd} \end{cases}$$

➞**Only even** $h+k+l$ reciprocal lattice points exist.

(c) Face-centered cubic (FCC)

Atoms at:

- $(0, 0, 0)$
- $\left(0, \frac{1}{2}, \frac{1}{2}\right)$
- $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$
- $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$

$$F_{hkl} = f\left[1+e^{\pi i(k+l)}+e^{\pi i(h+l)}+e^{\pi i(h+k)}\right]$$

$$F_{hkl} = \begin{cases} 4f & h, k, l \text{ all even or all odd} \\ 0 & \text{otherwise} \end{cases}$$

Physical interpretation

- The structure factor is a **Fourier transform of the basis**
- Extinctions arise from **destructive interference** of waves scattered by atoms
- Reciprocal lattice = geometry of periodicity
- Structure factor = geometry of basis inside the unit cell

Compact statement

$$\boxed{\text{Diffraction pattern} = \text{Reciprocal lattice} \times \text{Structure factor}}$$

4.5 SUMMARY:

X-ray Diffraction and Crystal Structure Analysis

Bragg's Crystal Diffraction:

- X-rays incident on a crystal lattice are scattered by atoms in the lattice planes.
- Constructive interference of scattered X-rays occurs only at specific angles, producing a diffraction pattern.
- This diffraction provides information about **interplanar spacing** and **crystal structure**.

Bragg's Law:

- Bragg's Law gives the condition for constructive interference:

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

where:

- n= order of reflection
- λ= wavelength of incident X-rays
- d= distance between lattice planes
- θ= angle of incidence (Bragg angle)
- Bragg's law allows determination of lattice spacing from diffraction angles.

Experimental Diffraction Methods:

a) Laue Method:

- Uses a **single crystal** and a **continuous X-ray spectrum**.
- Produces a pattern of spots on a photographic plate.
- Useful for determining **crystal orientation** and symmetry.

b) Powder Method:

- Uses **finely powdered crystalline sample** with monochromatic X-rays.
- Diffraction occurs from many randomly oriented crystals, producing **concentric rings**.
- Used to determine **lattice parameters** and **identify unknown crystalline materials**.

Derivation of Scattered Wave Amplitude:

- The amplitude of X-rays scattered by a crystal is the **sum of waves scattered by all atoms** in the lattice:

$$A = \sum_j f_j \, e^{i\mathbf{k}\cdot\mathbf{r}_j}$$

where f_j= scattering factor of the j-th atom, $\mathbf{r}_j$= position vector, and **k**= scattering vector.

- Constructive interference occurs when the **phase difference** between waves from successive planes is $2\pi n$, leading to Bragg's law.

Geometrical Structure Factor:

- The **structure factor (F)** accounts for the relative positions of atoms in a unit cell and determines the **intensity of diffracted beams**:

$$F_{hkl} = \sum_j f_j \;\; e^{2\pi i(hx_j+ky_j+lz_j)}$$

- hkl= Miller indices of the reflecting plane
- f_j= atomic scattering factor
- (x_j, y_j, z_j)= fractional coordinates of atoms in the unit cell
- The magnitude of F_{hkl}determines the intensity of each diffraction spot; some reflections may vanish if F = 0.

Conclusion:

X-ray diffraction provides a powerful tool to **determine crystal structure, interatomic distances, and symmetry**. Bragg's law, combined with Laue and powder diffraction methods, allows analysis of both single crystals and polycrystalline materials. The structure factor is essential for predicting the intensity of diffracted X-rays and understanding the arrangement of atoms within the unit cell.

4.6 TECHNICAL TERMS

Braggs Law in terms of Reciprocal Lattice Vectors, Experimental Methods on X-Ray Diffractions, The Laue Method, The Powder Method, Derivation of Amplitude of Scattered Wave, Geometrical Structure Factor

4.7 SELF ASSESSMENT QUESTIONS

1. Explain about the Braggs Law in terms of Reciprocal Lattice Vectors
2. Write about the Experimental Methods on X-Ray Diffractions,
3. Write about the Laue Method
4. Write about the Powder Method
5. Explain bout the Derivation of Amplitude of Scattered Wave
6. Explain about the Geometrical Structure Factor

4.8 Suggested Readings

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.

2. Solid State Physics, A. J. Dekker.

3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

Prof. M. Rami Reddy

LESSON -5

RECIPROCAL LATTICE

Aim:

To study the concept of reciprocal lattices, construct reciprocal lattices for simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) crystals, understand the properties of reciprocal lattices and Brillouin zones, and explore experimental diffraction methods using neutrons and electrons.

Objectives:

1. To understand the concept and definition of a reciprocal lattice.
2. To construct reciprocal lattices for simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) structures.
3. To study the properties of reciprocal lattices, including their relation to the direct lattice.
4. To understand Brillouin zones and their significance in solid-state physics.
5. To explore neutron diffraction as a method to study crystal structures.
6. To explore electron diffraction and its applications in determining lattice spacing and crystal symmetry..

STRUCTURE:

5.1 RECIPROCAL LATTICE:-

It is necessary to consider sets of planes in a crystal. This can be done in terms of their normal. Geometrically we have an advantage, that is, the planes are of 2-dimensions while normal lines are of one-dimensional nature. But it is not enough if we consider the orientation of planes alone to study the diffraction of x-rays by crystals but it is also necessary to know the inter-planar spacing d since they only determine the reflection angles θ. These inter-planar spacing may also be represented in the normal to the planes by appropriately limiting their lengths.

From the above discussion it is clear that one can indicate the orientation of a set of parallel planes by their common normal and the inter planar spacing by restricting the lengths of the normal proportionately.

Consider any given space lattice and apply the following.

1. From a common origin draw a normal to each crystal plane.
2. Set the length of each normal equal to (or) 2π times the reciprocal of the inter planar spacing d_{hkl}.
3. Mark a point at the end of each normal, which represents the crystal plane.

A collection of points obtained in this way corresponding to various crystal planes form a lattice array and is known as "reciprocal lattice". The points in the reciprocal lattice are called reciprocal lattice points. These points in 3 dimensional space form the reciprocal lattice space. This is also called k-space. From the concept of reciprocal lattice it may be understood that the "Co-ordinates of Points" in the reciprocal lattice space are defined by (h k l), the Miller indices. The concept of reciprocal lattice plays a very important role in the field of x-ray crystallography.

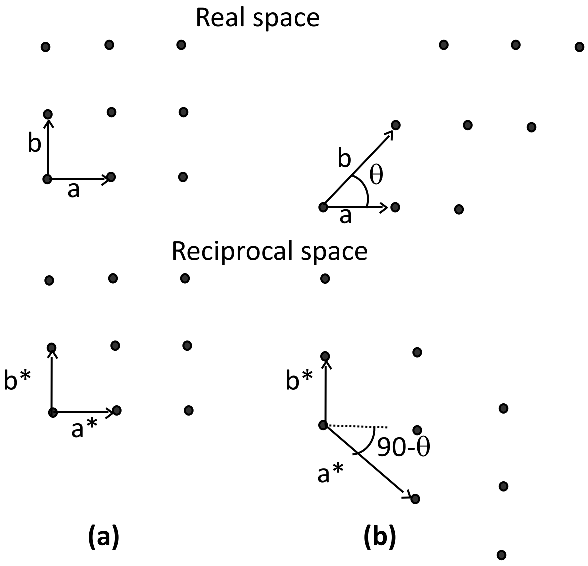


Fig 5.1 Direct and reciprocal lattice for a rectangular system

5.1.1Reciprocal lattice to (sc) simple cubic lattice:-

The primitive translation vectors of a sc lattice may be written as,

$\mathbf{a} = a\hat{i}$; $\mathbf{b} = b\hat{j}$; $\mathbf{c} = c\hat{k}$; where the volume of the unit cell is $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = a^3$. The Primitive translation vectors of the reciprocal lattice of the sclattice will be,

$$\mathbf{a}^* = 2\pi \cdot \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})} = \frac{2\pi}{a}\hat{i}(or)\frac{2\pi}{a}\hat{x}$$

$$\mathbf{b}^* = 2\pi \cdot \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})} = \frac{2\pi}{a}\hat{j}(or)\frac{2\pi}{a}\hat{y}$$

and $$\mathbf{c}^* = 2\pi \cdot \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})} = \frac{2\pi}{a}\hat{k}(or)\frac{2\pi}{a}\hat{z}$$

From these equations, it is evident that the reciprocal lattice to sc lattice is itself a sc lattice with a lattice const $2\pi/a$. The boundaries of the resulting primitive unit cell are the planes normal to the six reciprocal lattice vectors ±$\mathbf{a}^*$, ±$\mathbf{b}^*$, ±$\mathbf{c}^*$ at their mid points,

$$\therefore \pm\frac{\mathbf{a}^*}{2} = \pm\frac{\pi}{a}\hat{i}\ ;\quad \pm\frac{\mathbf{b}^*}{2} = \pm\frac{\pi}{b}\hat{j}\ ;\quad \pm\frac{\mathbf{c}^*}{2} = \pm\frac{\pi}{c}\hat{k}\,.$$

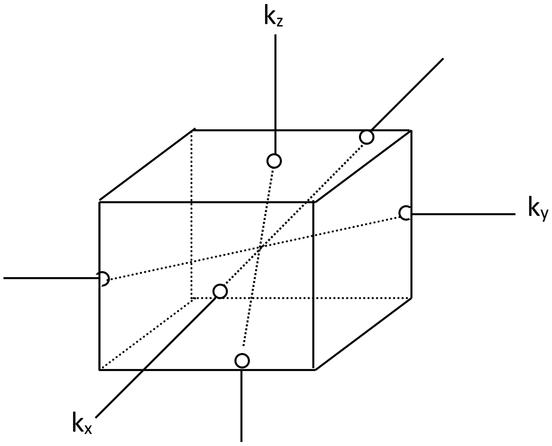


Fig 5.1 The first Brillouin zone of a simple cubic lattice

The space bounded by these Six planes is a cube of side $2\pi/a$ and volume $(2\pi/a)^3$. This cube is known as the first Brillouin Zone of the sc lattice is shown in fig 5.2.

5.1.2Reciprocal lattice to bcc lattice:-

The primitive translation vectors or the bcc lattice shown in fig 5.3 are given by,

$$\mathbf{a}^1 = \frac{a}{2}\,(\mathbf{i}+\mathbf{j}-\mathbf{k})$$

$$\mathbf{b}^1 = \frac{a}{2}\,(-\mathbf{i}+\mathbf{j}+\mathbf{k})$$

$$\mathbf{c}^1 = \frac{a}{2}\,(\mathbf{i}-\mathbf{j}+\mathbf{k})$$

Volume of the unit cell is $\frac{a^3}{2}$.

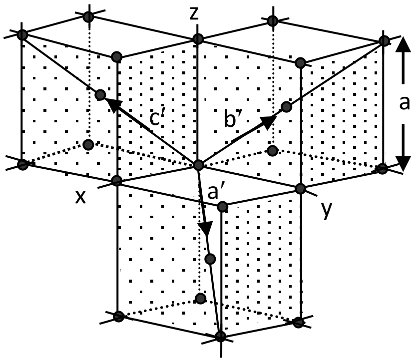


Fig 5.1.2 Primitive translation vectors of the bcc lattice

The primitive translation vectors $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$of the reciprocal lattice are defined by

$$\mathbf{a}^* = \frac{2\pi}{a}\,(\mathbf{i}+\mathbf{j})$$

$$\mathbf{b}^* = \frac{2\pi}{a}\,(\mathbf{j}+\mathbf{k}) \qquad \text{-------------} \quad (1)$$

$$\mathbf{c}^* = \frac{2\pi}{a}\,(\mathbf{k}+\mathbf{i})$$

We observe that, these reciprocal lattice vectors are just the primitive vectors of the fcc lattice, showing that an fcc lattice is the reciprocal lattice of the bcc lattice. The rhombohedron formed by $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ represents the primitive cell of volume V expressed as

$$\mathbf{V} = \mathbf{a}^*\cdot(\mathbf{b}^*\times\mathbf{c}^*) = \frac{16\pi^3}{a^3}$$

Similarly, it can be shown that the reciprocal lattice of the fcc lattice is a bcc lattice. There are in all 12 shortest vectors for the lattice described by (1):

$$\frac{2\pi}{a}\,(\pm\mathbf{x}\ \pm\mathbf{y})\,; \quad \frac{2\pi}{a}\,(\pm\mathbf{y}\pm\mathbf{z})\,; \quad \frac{2\pi}{a}\,(\pm\mathbf{z}\pm\mathbf{x})$$

with the choices of signs being independent.

Planes perpendicular to these vectors at their mid-points enclose the volume of the first Brillouin zone which turns out to be a rhombododecahedron (Fig.5.4).

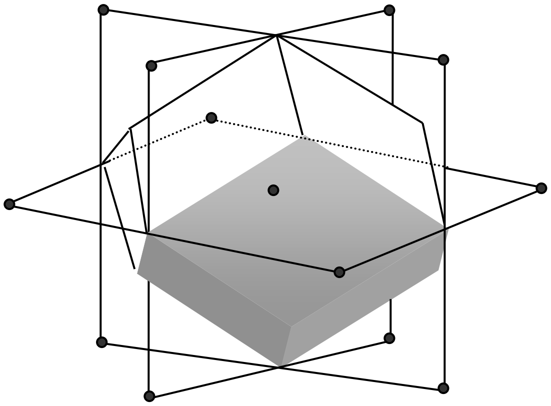


Fig 5.1.2 The first Brillouin zone of a bcc crystal. It is rhombododecahedral in shape.

5.1.3 Face-Centered Cubic Lattice:

The primitive translation vectors of the fcc lattice as shown in fig.5.5 may be taken as

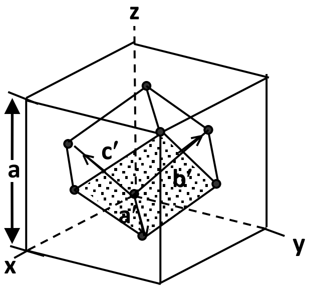


Fig 5.1.3 Primitive translation vectors of the FCC lattice.

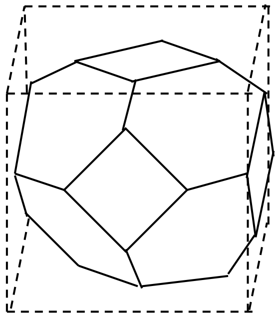


Fig 5.1.3 The first Brillouin zone in the FCC lattice.

$$\mathbf{a} = \frac{a}{2}\,(\mathbf{i} + \mathbf{j});$$

$$\mathbf{b} = \frac{a}{2}\,(\mathbf{i} + \mathbf{k}); \quad \text{--------------} \quad (2)$$

$$\mathbf{c} = \frac{a}{2}(\mathbf{j} + \mathbf{k}).$$

The volume of the primitive cell is **a .b**×**c** = $\frac{1}{4}a^3$. Using the primitive translations of the reciprocal lattice are found to be

$$\mathbf{a}^* = \frac{2\pi}{a}\ (\mathbf{i} + \mathbf{j} - \mathbf{k})$$

$$\mathbf{b}^* = \frac{2\pi}{a}\ (-\mathbf{i} + \mathbf{j} + \mathbf{k})\ ; \quad \text{-----------------}\ (3)$$

$$\mathbf{c}^* = \frac{2\pi}{a}\ (\mathbf{i} - \mathbf{j} + \mathbf{k})$$

These are the primitive translations of a bcc lattice. We have now

$$\mathbf{G} = (2\pi/a)\ [(h - k + l)\ \mathbf{i} + (h + k - l)\ \mathbf{j} + (-h + k + l)\ \mathbf{k}] \text{----------------}\ (4)$$

The shortest non-zero G's are the eight vectors

$$(2\pi/a)\ (\pm\mathbf{i}\pm\mathbf{j}\ \pm\mathbf{k}). \ \text{---------------}\ (5)$$

The zone boundaries are determined for the most part by the eight planes normal to these vectors at their midpoints, but it may be seen that the corners of the octahedron thus formed are truncated by the planes which are the perpendicular bisectors of the six vectors.

$$(2\pi/a)\ (\pm 2\mathbf{i});\ (2\pi/a)\ (\pm 2\mathbf{j});\ (2\pi/a)\ (\pm 2\mathbf{k}). \ \text{---------------}\ (6)$$

The first zone is then the truncated octahedron shown in fig 5.6.

5.2 PROPERTIES OF RECIPROCAL LATTICE:

General Properties The reciprocal lattice of a reciprocal lattice is the (original) direct lattice. The length of the reciprocal lattice vectors is proportional to the reciprocal of the length of the direct lattice vectors. This is where the term reciprocal lattice arises from. In real space, there are lattice vectors a and b. And in reciprocal space, there are lattice vectors a_2 and b_2 , which are perpendicular to their real counterpart. As you can see here, a change in real space produces an inverse result in reciprocal space. The reciprocal lattice plays a very fundamental role in most analytic studies of periodic structures, particularly in the theory of diffraction. In neutron and X-ray diffraction, due to the Laue conditions, the momentum difference between incoming and diffracted X-rays of a crystal is a reciprocal lattice vector. Reciprocal Lattice which represents the scattering possibilities of a given crystal (planes, then lines, then points for 1D-, 2D- and 3D-crystals respectively). There are rules about the precise dimensions of the reciprocal lattice for the different types of crystal systems but we do not need to get involved in them here; however, you will have noted that reciprocal parameters keep occurring (we have seen planes 1/a, 1/b and 1/c apart, and finally the parameter 1/d) hence "reciprocal lattice" is a good name in both senses (in the just-mentioned algebraic sense, and that it is an alternative "view" of crystal structure). 1 Suffice to say that many crystallographers think of the reciprocal lattice almost as though it were real; which, of course, it is not; its just an abstract property of the crystal whereas it is the crystal which possesses the "real lattice". The reciprocal lattice basically consists of points on a regular grid which represent diffraction possibilities. Each point can be labelled with a Miller index (h,k,l) which corresponds to the planes from which diffraction would occur (if it did). ith a bar above the number and pronounced "bar n").

5.3BRILLOUIN ZONES:

If we consider a parallelepiped formed by reciprocal lattices $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$, then this may be taken as the primitive cell of the reciprocal lattice. It can be observed that the eight corner points are shared among eight parallelepiped or we can say that one parallelepiped contains one-eighth of each of eight corner points. In this way the parallelepiped contains one reciprocal lattice point. But in solid state physics, a primitive cell of a reciprocal lattice is taken as the smallest volume bounded by planes normal to each of (shorter) **G**'s at its midpoint.

Each of the new cell contains on lattice point and the point is at the centre of the cell as shown in fig 5.6. The primitive cell formed in this way in the reciprocal lattice is called the first Brillouin zone. The same procedure adopted for real crystal lattice results in a real primitive cell called Wigner-Seitz cell.

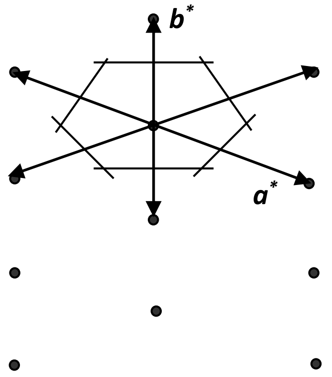


Fig 5.3 Construction of first Brillouin zone.

5.4 Neutrons Diffraction:

As neutrons are associated with wave and hence they can be diffracted from crystals like electrons. Here we shall consider the neutron diffraction by crystal in connection with the exploration the crystal structure, of course, the discussion will be confined to a comparison between X-ray, electron and neutron diffraction.

First of all we shall calculate the wavelength of suitable neutrons. We know that the wavelength in case of neutrons can be expressed as

$$\lambda = \frac{h}{p} = \frac{h}{M_n v} \text{------------} \quad (6)$$

$$E = \frac{p^2}{2m} = \frac{\hbar^2 K^2}{2m} \qquad (\because p = \hbar K)$$

$$= \frac{10^{-68} \times 10^{21}}{3 \times 10^{-27}} Jouls$$

$$= 3 \times 10^{-21} jouls$$

= 200K = 0.02 Ev

where M_n is the mass of the neutrons. The mass of a neutron is 2000 times large in comparison to an electron i.e., the wavelength associated with a neutron is about 1/2000 times that for an electron of the same velocity. The energy ∈ of the suitable neutrons may be calculated by the following expression

$$\lambda = \frac{h}{\sqrt{(2M_n v)}} \text{------------} \quad (7)$$

By equation (4.26), the energy ∈ of neutrons is approximately 0.1 e.V. for λ = 1Å which is required for diffraction work. It is important to note that for X-rays of 1Å the energy required is 10^4e.V. while for electron it is about 10^2e.V. In case of neutrons, the diffraction patterns are formed in a similar manner a in case of X-rays.

Some special features of the neutrons diffraction are :

1. Neutrons are scattered chiefly by the nuclei of the atoms.
2. As the wavelength of the neutrons is much greater than the dimensions of the scattering nucleus ($\cong 10^{-13}$ cm), the atomic scattering factor is nearly independent of the scattering angle.
3. The scattering power does not vary in a regular manner with atomic number. Due to this fact the light elements such as hydrogen and carbon produce relatively strong scattering than X-rays scattering because the X-rays scattering is done by electrons. This feature of the neutron diffraction enable us to deduce the positions of hydrogen and carbon atoms in a number of organic crystals.

4. The scattering from neighboring elements in the periodic system may differ appreciably. Hence neutron diffraction allows to detect with relative ease, ordered phases of an alloy, such as FeCo, where as their detection by X-rays is difficult.
5. The neutrons possess magnetic moments and these moments interact with the magnetic moments of the scattering atoms of the solid. This gives an additional scattering mechanism for neutrons, which often out-weights the nuclear scattering. Thus neutron diffraction methods are exceedingly valuable in structural studies of magnetic crystals.

In paramagnetic substances in which the atomic moments are randomly oriented, the magnetically scattered neutrons are incoherent in phase resulting in a diffuse background. This diffuse background of magnetic scattering is then superimposed on the lines produced by the nuclear scattering.

In ferromagnetic substances in which the magnetic moments within a domain are linked up in parallel, the diffuse background is absent.

In an antiferromagnetic solid the magnetic moments are aligned antiparallel and hence from the point of view of the neutron such atoms would appear to be different.

Figure (5.8) shows neutron diffraction patterns for Mno (Mn ion has a permanent moment), which is known to be an anti-ferromagnetic solid below and above its curie temperature (120^0).

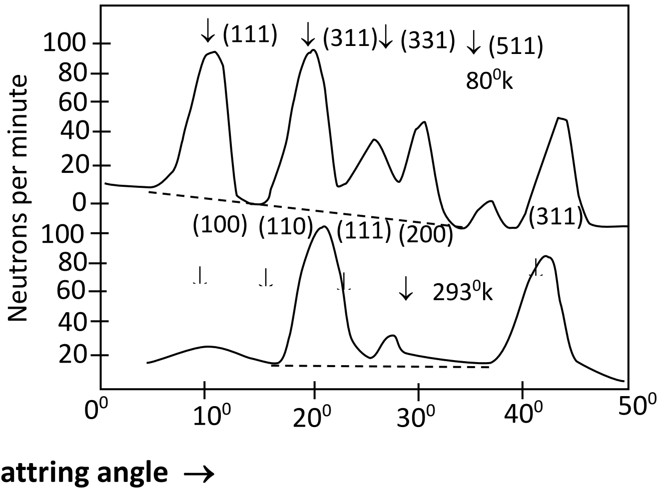


Fig: 5.4 The neutron diffraction patterns of MnO at 80^0K and 293^0K (below & above the curie temperature).

At room temperature (293^0K) the pattern shows coherent diffraction peaks, like those of X-ray diffraction, and in the positions expected from a lattice of NaCl structure. The diffuse background of magnetic scattering is also a visible, which is inductive of no magnetic order at all. At low temperatures, in a addition to these peaks certain other peaks are located at positions which one cannot expect on the basis of chemical structure of a unit cell.

5.5 Electrons Diffraction:

In 1924 de Broglie suggested that a material particle like electron in motion is always associated with a wave whose wavelength is given by $\lambda = h/mv = h/p$, where h be the Plank's constant and p, the momentum of the particle. The experimental evidence of this fact was provided by Davisson and Germer and G.P. Thomson. Since the material particle (electron) can be described by wave, it can be diffracted by crystals like *X*-rays. The amount of matter required to produce electron diffraction is small as compared with *X*-rays diffraction and the time of exposure required for a photographic record is measured in a fraction of a second. Thus we here introduce the diffraction of electrons in connection with the exploration of the crystal structure. The discussion would be confined to comparison between the electron diffraction and *X*-rays diffraction.

First of all we shall calculate the wavelength of an electron beam appropriate to the crystal diffraction work. According to de Broglie idea, the wavelength λ associated withthe particle is given by

$$\lambda = \frac{h}{mv} \text{ ------------ } (8)$$

If the electrons are accelerated by an applied electric potential V, then the kinetic energy $\frac{1}{2}.mv^2$of the electron is given by

$$\frac{1}{2} mv^2 = eV \text{ ----------- } (9)$$

where e is the electronic charge.

From equation (4.22) and (4.23) we have

$$\lambda = \frac{h}{\sqrt{(2meV)}} = \sqrt{\left(\frac{150}{V}\right)} \text{-----------} \quad (10)$$

where λ is in Å and V in volts.

It is evident from equation (4.24) that only 150 volts are required to produce electrons of a wavelength of one Å suitable for diffraction work. The X-rays suitable for diffraction work require approximately 12000 volts for the same wavelength.

The diffraction of electrons takes place in a similar way as in case of X-rays and the diffraction pattern obtained can be interpreted exactly in the same way as X-rays diffraction pattern.

Some special features of electron diffraction are:

1. In contrast with X-rays, electrons are scattered by the nucleus as well as by the electrons in atoms.
2. The scattering factor for electrons decreases with increasing value of Bragg's angle θ as in X-rays. However, the scattering efficiency of atoms is considerably greater for electrons than X-rays. Due to this reason the diffraction of electrons by gases requires much shorter exposure times than does X-rays diffraction.
3. Electrons are charged and interact strongly with matter as compare with X-rays.
4. Electrons penetrate a relatively short distance into a crystal. At normal incidence, an electron of about 50keV has a penetration depth of only about 500Å, whilest for small angles of incidence this may be only about 50 Å measured perpendicular to the surface. Thus the electron diffraction is particularly useful in investigating the structure of thin surface layers such as oxide layers on metals. These layers are not detected by X-rays diffraction because they penetrate deep into the solids and produce a pattern, which is the characteristic of the interior of the solid.
5. Electron diffraction can be used for the studies of orientation, lattice parameter and perfection of evaporated thin films.
6. By electron diffraction, the dislocation patterns in thin metallic foils can be seen.

5.6 SUMMARY:

Reciprocal Lattice:

- A reciprocal lattice is a mathematical construct used in crystallography to represent diffraction conditions in momentum space.
- It is defined such that wave vectors of diffracted waves correspond to points in the reciprocal lattice.
- If $\mathrm{a}, \mathrm{b}, \mathrm{c}$ are primitive vectors of the direct lattice, the reciprocal lattice vectors are:

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

Reciprocal Lattices for Common Structures:

- Simple Cubic (SC): Reciprocal lattice is also simple cubic, with lattice constant $a^* = \frac{2\pi}{a}$.
- Body-Centered Cubic (BCC): Reciprocal lattice is face-centered cubic (FCC).

- Face-Centered Cubic (FCC): Reciprocal lattice is body-centered cubic (BCC).
- This duality is fundamental in analyzing diffraction patterns.

Properties of Reciprocal Lattice:

- Each point represents a set of lattice planes in real space.
- Diffraction occurs when the difference in wavevectors of incident and scattered waves equals a reciprocal lattice vector ($\Delta k = G$).
- Reciprocal lattice simplifies Bragg diffraction conditions and helps define Brillouin zones.

Brillouin Zones:

- A Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice.
- It defines the unique region of wavevectors that represents all possible electron or wave states in the crystal.
- The first Brillouin zone contains all distinct diffraction conditions without redundancy.

Neutron Diffraction:

- Neutrons, being uncharged, penetrate deeply into materials and interact with atomic nuclei.
- Neutron diffraction provides structural information, especially for light atoms and magnetic structures.
- Diffraction patterns correspond to points in the reciprocal lattice.

Electron Diffraction:

- Fast electrons act as matter waves and undergo diffraction by crystal lattices.
- Electron diffraction is used for thin films, nanomaterials, and surface structures.
- It is sensitive to small lattice spacings and allows determination of crystal symmetry and interplanar distances.

Conclusion:

The reciprocal lattice provides a powerful framework to understand diffraction from crystals. Constructing reciprocal lattices for SC, BCC, and FCC structures helps predict diffraction patterns. Brillouin zones define the fundamental wavevector space of the crystal. Neutron and electron diffraction techniques utilize the reciprocal lattice concept to extract detailed structural information about materials.

5.7 TECHNICAL TERMS

Reciprocal Lattice, Reciprocal Lattice to Simple Cubic Lattice, Reciprocal Lattice to BCC lattice, Reciprocal Lattice to FCC Lattice, Properties of Reciprocal Lattice, Brillouin, Zones, Neutron Diffraction, Electron Diffraction

5.8 SELF ASSESSMENT QUESTIONS

1. Explain about the Reciprocal Lattice
2. Write about the Reciprocal Lattice to Simple Cubic Lattice
3. Write about the Reciprocal Lattice to BCC lattice,
4. Write about to Reciprocal Lattice to FCC Lattice
5. Write about the Properties of Reciprocal Lattice
6. Explain about the Brillouin, Zones
7. Write about the Neutron Diffraction and Electron Diffraction

5.9 SUGGESTED READING

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Solid State Physics, M. A. Wahab, Narosa Publishing House.

Prof. M. Rami Reddy

LESSON -6

LATTICE VIBRATION & THERMAL PROPERTIES

Aim:

To study elastic waves in a one-dimensional array of identical atoms, understand vibrational modes of diatomic linear lattices, derive dispersion relations for acoustic and optical modes, and explore infrared absorption in ionic crystals.\

Objectives:

1. To understand the concept of **elastic waves** in a one-dimensional chain of identical atoms.
2. To study **vibrational motion** in a diatomic linear lattice.
3. To derive the **dispersion relation** for diatomic chains and understand the relationship between frequency and wavevector.
4. To distinguish between **acoustic modes** (atoms oscillate in phase) and **optical modes** (atoms oscillate out of phase).
5. To understand the **physical origin of optical modes** and their role in crystal dynamics.
6. To study **infrared absorption** in ionic crystals due to optical vibrations.
7. To relate vibrational modes to **thermal and optical properties** of solids.
8. To develop a conceptual understanding of **phonons** and their significance in solid-state physics.

STRUCTURE:

6.1 ELASTIC WAVE IN A ONE-DIMENSIONAL ARRAY OF IDENTICAL ATOMS:

An **elastic wave in a one-dimensional array of identical atoms** is the standard model for **lattice vibrations (phonons)** in a crystal. Below is a **clear, step-by-step explanation**, suitable for exams and understanding.

Physical model

Consider:

- Identical atoms of mass **m**
- Arranged in a straight line with **equal spacing** a
- Nearest neighbours connected by identical springs with **force constant** C
- Motion allowed only along the line (longitudinal waves)

Let $u_n(t)$be the displacement of the n^{th}atom from equilibrium.

Equation of motion

The force on atom $n$comes from its neighbors:

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

Using Newton's second law:

$$\boxed{m\frac{d^2u_n}{dt^2} = C(u_{n+1} + u_{n-1} - 2u_n)}$$

This is the **lattice wave equation**.

Trial wave solution (plane wave)

Assume a traveling wave solution:

$$\boxed{u_n(t) = Ae^{i(nka-\omega t)}}$$

where:

- k= wave number
- ω= angular frequency
- A= amplitude

Dispersion relation

Substitute the trial solution into the equation of motion:

$$\boxed{\omega^2 = \frac{4C}{m}\sin^2\left(\frac{ka}{2}\right)}$$

or

$$\boxed{\omega = 2\sqrt{\frac{C}{m}}\,|\sin\left(\frac{ka}{2}\right)|}$$

This relation links **frequency** and **wave vector**.

Important features of the elastic wave

(a) Long-wavelength limit ($ka \ll 1$)

$$\sin\left(\frac{ka}{2}\right) \approx \frac{ka}{2}$$

$$\boxed{\omega \approx vk} \text{with} v = a\sqrt{\frac{C}{m}}$$

➞ Behaves like a **classical sound wave**.

(b) Maximum frequency

At the Brillouin zone boundary $k = \frac{\pi}{a}$:

$$\boxed{\omega_{\text{max}} = 2\sqrt{\frac{C}{m}}}$$

(c) Group velocity

$$v_g = \frac{d\omega}{dk} = a\sqrt{\frac{C}{m}}\cos\left(\frac{ka}{2}\right)$$

- Maximum at $k = 0$
- Zero at zone boundary

6.2 VIBRATIONAL MODES OF A DIATOMIC LINEAR LATTICE:

A diatomic linear lattice refers to a one-dimensional lattice structure composed of two different types of atoms. In this lattice, the atoms alternate along the linear array.

The vibrational modes of a diatomic linear lattice can be described by considering the motion of the atoms within the lattice. There are two primary types of vibrational modes:

1. Longitudinal modes: In a longitudinal mode, the atoms oscillate back and forth along the direction of the lattice. Both atoms in the unit cell move in the same direction at the same time. This mode is similar to a compression and expansion of the lattice.
2. Transverse modes: In a transverse mode, the atoms oscillate perpendicular to the direction of the lattice. The atoms move in opposite directions, with one atom moving to the right while the other moves to the left. This mode is similar to a shearing or bending of the lattice.

The vibrational modes of a diatomic linear lattice depend on factors such as the masses and bond strengths of the atoms involved. The frequency and energy of these modes can be calculated using mathematical models, such as the harmonic approximation, which assumes simple harmonic motion for the atoms around their equilibrium positions.

The study of vibrational modes in diatomic linear lattices is important for understanding the thermal and mechanical properties of materials, as well as their behavior in different phases, such as solids or liquids. It provides insights into phenomena like thermal conductivity, phonons (quantized lattice vibrations), and the lattice-specific heat capacity.

Let's consider a linear chain of atoms having mass m and M such that M>m. Let 2_n-2, 2_n-1, 2n, 2_n+1 ....are positions of atoms having mass m and M respectively in alternate position. Two atoms are connected by an ideal spring having force constant c. Let U_2n-1, U2n, ...U2n+2 are displacement of atoms 2n-1 .....2n+1 respectively from their equilibrium position. We are considering the elastic response of crystal, the force applied on 2nth atom is linear function of displacement and we are considering the nearesr neighbour interaction.

$$F_{2n} = C\,(U_{2n+1} - U_{2n}) + C\,(U_{2n-1} - U_{2n}) = C\,(U_{2n+1} + U_{2n-1} - 2U_{2n}) \text{ ....i}$$

$$F_{2n+1} = C\,(U_{2n+1} + U_{2n} - 2U_{2n+1}) \text{ ....ii}$$

From Newton's 2nd law of motion,

$$F_{2n} = m\,\frac{d^2u_{2n}}{dt^2} \quad \text{........iii}$$

$$F_{2n+1} = M\,\frac{d^2u_{2n+1}}{dt^2} \quad \text{........iv}$$

On equating i and iii, ii and iv

$$m\,\frac{d^2u_{2n}}{dt^2} = C\,(U_{2n+1} + U_{2n-1} - 2U_{2n}) \text{ ....v}$$

$$M\,\frac{d^2u_{2n+1}}{dt^2} = C\,(U_{2n+2} + U_{2n} - 2U_{2n+1}) \text{ ....vi}$$

we seek the solution of eq v and vi

$$U_{2n} = A\,e^{i(k\,2na - wt)} \text{ ....vii}$$

$$U_{2n+1} = B\,e^{i(k\,(2n+1)a - wt)} \quad \text{......viii}$$

Substituting eq vii and viii in vand vi we have

$$-m\,w^2 A\,e^{i(k\,2na - wt)} = C\left[\,B\,e^{i(k\,(2n+1)a - wt)} + B\,e^{i(k\,(2n-1)a - wt)} - 2A\,e^{i(k\,2na - wt)}\right]$$

$$or,\ -mw^2\,Ae^{\,i2nka} = C\,Be^{i2nka}\left(e^{ika} + e^{-ika}\right) - 2CA\,e^{i\,2nka}$$

$$or,\ -\ mw^2 A = 2BC\ \cos ka - 2\,CA$$

$$or,\ \left(2C - mw^2\right)A = 2BC\cos kA$$

$$or,\ \left(2C - mw^2\right)A - 2BC\cos kA = 0$$

$$Again,\ -Mw^2Be^{i\,(2n+1)\,ka} = CAe^{i(2n+1)}\left[\,e^{ika} + e^{ika}\,\right] - 2\,CBe^{\,i(2n+1)ka}$$

$$or,\ -Mw^2B = 2CA\cos ka - 2\,CB$$

$$or,\ (2c\cos ka)\,A - \left(2C - Mw^2\right)B = 0 \text{ ......} x$$

Eq ix and x are homogeneous equation with two unknowns so eq ix and x is possible only if determinant of coefficient vanishes.

$$\begin{vmatrix} 2c - mw^2 & -2c \cos ka \\ 2c \cos kA & -(2c - Mw^2) \end{vmatrix} = 0$$

$$\text{or, } 4c^2 - 2c\,(m + M)\, w^2 + mMw^4 - 4c^2 \cos^2 ka = 0$$

$$\text{or, } mMw^4 - 2c\,(m + M)\, w^2 + 4c^2 \cos^2 ka = 0$$

$$\text{or, } w^4 - 2c\left(\frac{1}{M} + \frac{1}{m}\right) w^2 + \frac{4c^2}{mM} \sin^2 ka = 0$$

$$\text{or, } w^2 = \frac{2c\left(\frac{1}{m} + \frac{1}{M}\right) \pm \left[4c^2\left(\frac{1}{m} + \frac{1}{M}\right)^2 - 4.4\,\frac{c^2 \sin^2 ka}{mM}\right]^{1/2}}{2}$$

$$= c\left(\frac{1}{m} + \frac{1}{M}\right) \pm \left[c^2\left(\frac{1}{m} + \frac{1}{M}\right)^2 - 4\,\frac{c^2 \sin^2 ka}{mM}\right]^{1/2}$$

For higher frequency

$$w_f^2 = C\left(\frac{1}{m} + \frac{1}{M}\right) + C\left[\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4 \sin^2 ka}{mM}\right]^{1/2}$$

At k-> 0, sin ka -> 0

$$w_+^2 = C\left(\frac{1}{m} + \frac{1}{M}\right) + C\left(\frac{1}{m} + \frac{1}{M}\right) = 2C\left(\frac{1}{m} + \frac{1}{M}\right)$$

$$w_+ = \sqrt{2C\left(\frac{1}{m} + \frac{1}{M}\right)}$$

At k ->π/ 2a

$$w^2{}_f = C\left(\frac{1}{m} + \frac{1}{M}\right) + C\left[\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4}{mM}\right]^{1/2}$$

$$= C\left(\frac{1}{m} + \frac{1}{M}\right) + C\left(\frac{1}{m} - \frac{1}{M}\right) = \frac{2c}{m}$$

$$w_+ = \sqrt{\frac{2c}{m}}$$

For lower frequency,

$$w_-^2 = C\ (\frac{1}{m} + \frac{1}{M}) - C\ \left[(\frac{1}{m} + \frac{1}{M})^2 - \frac{4sin^2ka}{mM} \right]^{1/2}$$

$$\text{At } k \to 0,\ w_-^2 = C\ (\frac{1}{m} + \frac{1}{M}) - C\ [\ (\frac{1}{m} + \frac{1}{M})^2 - 4\frac{k^2a^2}{mM}\ ]^{1/2}$$

$$= C\ (\frac{1}{m} + \frac{1}{M}) - C\ (\frac{1}{m} + \frac{1}{M})[\ 1 - 4\frac{k^2a^2}{mM}\ (\frac{mM}{m+M})^2]^{1/2}$$

$$= C\ (\frac{1}{m} + \frac{1}{M})\ [\ 1 - \{\ 1 - \frac{1}{2}\frac{4\,k^2a^2}{mM}\ (\frac{mM}{m+M})^2\ \}]$$

$$= C\ (\frac{1}{m} + \frac{1}{M})\left[\frac{2k^2a^2nM}{(m+M)^2}\right]$$

$$= 2C\left(\frac{m+M}{mM}\right)\frac{2k^2a^2nM}{(m+M)^2}$$

$$w_-^2 = \frac{2Ck^2a^2}{m+M}$$

$$\text{At } k \to 0,\ \ w_- = \sqrt{\frac{2Ck^2a^2}{m+M}}$$

$$\text{At } k \to \frac{\pi}{2a},\ w_-^2 = C\ (\frac{1}{m} + \frac{1}{M}) - C\ \left[(\frac{1}{m} + \frac{1}{M})^2 - \frac{4}{mM} \right]^{1/2}$$

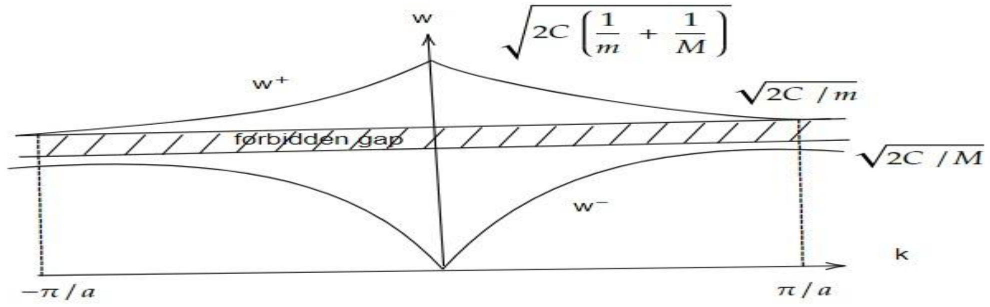
$$= C\ (\frac{1}{m} + \frac{1}{M}) - C\ (\frac{1}{m} - \frac{1}{M})$$

$$= \frac{2C}{M}$$

$$\therefore\ w_- = \sqrt{\frac{2C}{M}}$$

Upper branch is called optical branch and lower branch w- is called acoustic branch.

At the region π/ 2a, the value of w+ is √ 2C / m and w- is √ 2C / M. In between frequency √ 2C / m and √ 2C / M, there are no wave like solution i.e e^i(kx -wt). The region in which wave like solution is absent in forbidden band gap. The width of band gap depends upon the ratio of masses of two types of atoms i.e band gap depends on ratio M/m. The larger is the ratio, the width the frequency gap. If two masses are equal, the two branches join at k = π/ 2a and frequency disappear.



6.3 DISPERSION RELATION:

Substituting into the equations of motion and solving gives:

$$\boxed{\omega^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\sin^2\left(\frac{ka}{2}\right)}}$$

This yields **two branches** of solutions.

Vibrational modes

(a) Acoustic mode (lower branch, “–” sign)

- Atoms move **in phase**
- Frequency → 0 as $k \to 0$

$$\boxed{\omega \approx vk(k \to 0)}$$

➞ Corresponds to **sound waves**

(b) Optical mode (upper branch, “+” sign)

- Atoms move **out of phase**
- Non-zero frequency at $k = 0$

$$\boxed{\omega(0) = \sqrt{2C\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}}$$

6.4 Acoustic and Optical Modes (Lattice Vibrations):

In a crystal, atoms vibrate collectively. When there is **more than one atom per unit cell** (e.g., a diatomic lattice), these vibrations split into **acoustic** and **optical** modes.

Acoustic modes

Definition

Acoustic modes are lattice vibrations in which atoms in the unit cell move **in phase** with each other.

Key characteristics

- Frequency **goes to zero** as wave vector $k \to 0$
- Correspond to **sound waves** in the crystal
- Restore force arises from stretching of interatomic bonds between cells

Motion

At small k:

- All atoms move together
- Whole lattice oscillates as a rigid body

Dispersion behavior

$$\boxed{\omega \propto k (k \to 0)}$$

Energy transport

- Carry heat and sound
- Always present in any crystal

Optical modes

Definition

Optical modes are lattice vibrations in which atoms in the unit cell move **out of phase** with each other.

Key characteristics

- Have **finite frequency** at $k = 0$
- Do **not** correspond to rigid translation
- Common in crystals with **two or more atoms per unit cell**

Motion

At $k = 0$:

- Atoms oscillate against each other
- Center of mass remains fixed

Dispersion behavior

$$\boxed{\omega \neq 0 \text{at } k = 0}$$

Interaction with light

- In ionic crystals, optical modes interact with **infrared radiation**
- Hence the name *optical*

Comparison table

Feature	**Acoustic mode**	**Optical mode**
Phase relation	In phase	Out of phase

Feature	**Acoustic mode**	**Optical mode**
Frequency at $k = 0$	0	Finite
Physical meaning	Sound waves	Internal vibrations
Present in monoatomic lattice	Yes	No
Present in diatomic lattice	Yes	Yes

Number of modes (1D example)

For a **diatomic linear lattice**:

- **1 acoustic branch**
- **1 optical branch**

In 3D:

- 3 acoustic modes
- $3N - 3$optical modes (for Natoms per unit cell)

Simple physical picture

- **Acoustic mode**: atoms move together → wave travels like sound
- **Optical mode**: atoms vibrate oppositely → creates oscillating dipolesss

6.5 Infrared Absorption in an Ionic Crystal:

Infrared (IR) absorption in an ionic crystal arises from the interaction of **infrared radiation** with **optical lattice vibrations (optical phonons)**.

Basic idea

- Ionic crystals contain **positive and negative ions**
- In **optical modes**, these ions vibrate **out of phase**
- This creates a **time-varying electric dipole moment**
- The oscillating electric field of IR radiation couples to this dipole

$$\boxed{\text{Energy of IR light} \rightarrow \text{lattice vibrations}}$$

Role of optical phonons

Optical modes

- Positive and negative ions move in opposite directions
- Net dipole moment oscillates
- These modes are **IR active**

Acoustic modes

- Ions move in phase
- No dipole moment
- **No IR absorption**

Only optical phonons cause IR absorption

Condition for absorption

Infrared absorption occurs when:

$$\boxed{\hbar\omega_{\mathrm{IR}} = \hbar\omega_{\mathrm{opt}} \text{at } k \approx 0}$$

Reason:

- Photon momentum is very small
- Only **zone-center optical phonons** are excited

Physical explanation (simple picture)

- The electric field of IR radiation exerts opposite forces on $+$and $-$ions
- This excites optical vibrations
- Energy is absorbed from the radiation

Reststrahlen band

- Strong IR absorption occurs in a specific frequency range
- Called the **Reststrahlen band**
- Lies between **transverse optical (TO)** and **longitudinal optical (LO)** phonon frequencies

Mathematical viewpoint (brief)

The dielectric constant depends on frequency:

$$\boxed{\epsilon(\omega) = \epsilon_\infty \frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2}}$$

- Absorption is strong when $\omega \approx \omega_{TO}$

Examples

- NaCl, KBr, LiF show strong IR absorption

- Covalent crystals (e.g., Si, Ge) show weak or no IR absorption

6.6 SUMMARY:

Elastic Waves in a 1D Array of Identical Atoms:

- Consider a **one-dimensional chain of identical atoms** connected by springs representing interatomic forces.
- Small vibrations propagate as **elastic waves**, with frequency ωdepending on the **wavevector** $k$and force constant C.
- The **dispersion relation** for a monoatomic chain is:

$$\omega = 2\sqrt{\frac{C}{M}}\ |\sin\frac{ka}{2}|$$

where M= atomic mass, a= lattice spacing, k= wavevector.

Vibrational Modes of Diatomic Linear Lattice:

- In a **diatomic lattice** (alternating masses $M_1$and M_2), each unit cell has **two atoms**.
- Two types of vibrations occur:
    1. **Acoustic Mode:** Atoms move **in phase**, long-wavelength vibrations, frequency approaches zero as $k \to 0$.
    2. **Optical Mode:** Atoms move **out of phase**, higher frequency even at $k = 0$.
- The **dispersion relation** for a diatomic chain is:

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2(ka/2)}{M_1M_2}}$$

Acoustic and Optical Modes:

- **Acoustic Modes:** Responsible for **sound propagation**, low frequencies at small k.
- **Optical Modes:** Arise in **ionic or diatomic crystals**, involve opposite motion of ions, interact with **electromagnetic radiation**.

Infrared Absorption in Ionic Crystals:

- Optical vibrations in **ionic crystals** (e.g., NaCl, KBr) can couple with infrared light.
- The **frequency of IR absorption** corresponds to the **optical mode frequency**.
- This property is used to study lattice vibrations, crystal structure, and **phonon-related optical properties**.

Conclusion:

Vibrations in 1D lattices provide fundamental insight into crystal dynamics. Acoustic and optical modes explain how **phonons propagate** and interact with light. Infrared absorption in ionic crystals arises due to **optical vibrations**, linking lattice dynamics to observable physical properties.

6.7 TECHNICAL TERMS

- Elastic Wave in One Dimension Array of identical Atoms
- Vibrational Modes of Diatomic Linear Lattice
- Dispersion Relation
- Acoustic and Optical modes
- Infrared Absorption in Ionic Crystal

6.8 SELF ASSESSMENT QUESTIONS

1. Explain about the Elastic Wave in One Dimension Array of identical Atoms
2. Explain about the Vibrational Modes of Diatomic Linear Lattice
3. Write about the Dispersion Relation
4. Explain about the Acoustic and Optical modes
5. Explain bout the Infrared Absorption in Ionic Crystal

6.9 SUGGESTED READINGS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

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LESSON 7

DEBYE THEORY OF SPECIFIC HEAT

Aim:

To study phonons in crystal lattices, verify the dispersion relation for lattice vibrations, understand lattice heat capacity using Einstein and Debye theories, explore vibrational modes in continuous media, and investigate the origin of thermal expansion and its relation to the Grüneisen parameter.

Objectives:

1. To understand the concept of phonons as quantized lattice vibrations in solids.
2. To study vibrational waves in crystal lattices and their energy quantization.
3. To verify the dispersion relation for monoatomic and diatomic crystal lattices.
4. To distinguish between acoustic and optical modes in lattice vibrations.
5. To study lattice heat capacity and its temperature dependence using:
    - Einstein model (assuming identical independent oscillators)
    - Debye model (considering a continuous spectrum of vibrational modes)
6. To understand vibrational modes in a continuous medium and their contribution to thermal properties.
7. To investigate the origin of thermal expansion in solids due to anharmonicity of atomic vibrations.
8. To study the Grüneisen relation, linking thermal expansion, heat capacity, and elastic properties.
9. To relate experimental and theoretical results to the thermal and mechanical behavior of solids.

STRUCTURE:

7.1 Phonon:

A phonon is the quantized unit of lattice vibration in a crystal.

- Atoms in a crystal vibrate about their equilibrium positions

- These collective vibrations behave like waves
- In quantum mechanics, the vibrational energy is quantized → phonons

Energy and momentum of a phonon

$$\boxed{\boldsymbol{E = \hbar\omega, p = \hbar k}}$$

where:

- $\boldsymbol{\omega}$= angular frequency
- $\boldsymbol{k}$= wave vector (crystal momentum)

Types of phonons

(a) Acoustic phonons

- Atoms vibrate in phase
- $\boldsymbol{\omega \to 0}$as $\boldsymbol{k \to 0}$
- Responsible for sound propagation and heat conduction

(b) Optical phonons

- Atoms vibrate out of phase
- Finite $\boldsymbol{\omega}$at $\boldsymbol{k = 0}$
- Interact with infrared radiation (ionic crystals)

7.2 Dispersion relation:

The dispersion relation gives the relationship between frequency and wave vector:

$$\boxed{\boldsymbol{\omega = \omega(k)}}$$

Examples:

- Monoatomic lattice → single acoustic branch
- Diatomic lattice → one acoustic + one optical branch

Need for experimental verification

Theoretical dispersion relations are derived using:

- Harmonic approximation
- Interatomic force constants

They must be verified experimentally to:

- Confirm lattice dynamics
- Determine phonon frequencies and velocities

Experimental verification methods

(a) Inelastic neutron scattering (primary method)

Why neutrons?

- Wavelength comparable to lattice spacing
- Energy comparable to phonon energies
- No electric charge → deep penetration

Principle

- Neutrons exchange energy and momentum with phonons

$$\boxed{\begin{aligned}\boldsymbol{\Delta E} &= \hbar\boldsymbol{\omega}\\ \boldsymbol{\Delta k} &= \boldsymbol{G} \pm \boldsymbol{k}\end{aligned}}$$

By measuring:

- Energy change of scattered neutrons
- Change in momentum

➞ Full phonon dispersion curves are obtained

(b) Raman scattering

- Inelastic scattering of light by phonons
- Measures optical phonons near $\boldsymbol{k} \approx \boldsymbol{0}$
- Useful for symmetry studies

Infrared absorption

- Optical phonons absorb IR radiation
- Confirms phonon frequencies at zone center

X-ray scattering (limited)

- Thermal diffuse scattering gives indirect information

Experimental confirmation

Experiments show:

- Linear $\boldsymbol{\omega} \propto \boldsymbol{k}$at small $\boldsymbol{k}$(acoustic phonons)
- Existence of optical phonon branches
- Good agreement with theoretical predictions

Importance of phonons

- Explain specific heat of solids
- Govern thermal conductivity
- Affect electrical resistivity
- Play a role in superconductivity

7.3 Einstein quantum theory of specific heat

1. Lattice Heat Capacity

In a crystalline solid, atoms vibrate about their equilibrium positions. These vibrations (phonons) store thermal energy and give rise to the **lattice (phonon) heat capacity**.

Classical physics (Dulong–Petit law) predicts:

$$C_V = 3Nk_B$$

which agrees with experiments only at **high temperatures**, but fails at **low temperatures**.

Quantum theories:

- **Einstein Theory**
- **Debye Theory**

2. Einstein Theory of Lattice Heat Capacity

Assumptions

1. Each atom vibrates **independently**.
2. All atoms vibrate with the **same frequency** ν_E.
3. Vibrations are **quantized** (quantum harmonic oscillators).

Energy of an Einstein Oscillator

For one oscillator:

$$\langle E\rangle = \frac{h\nu_E}{e^{h\nu_E/k_B T} - 1}$$

For a solid with Natoms (3N oscillators):

$$U = 3N\frac{h\nu_E}{e^{\theta_E/T} - 1}$$

where

$$\theta_E = \frac{h\nu_E}{k_B}\text{(Einstein temperature)}$$

Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\boxed{C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}}$$

Limits of Einstein Model

High Temperature ($T \gg \theta_E$)

$$C_V \to 3Nk_B$$

✓ Correct (Dulong–Petit law)

Low Temperature ($T \ll \theta_E$)

$$C_V \propto e^{-\theta_E/T}$$

✗ Experimental result: $C_V \propto T^3$

Limitations

- Assumes **single frequency** → unrealistic
- Fails at **low temperatures**

7.4 Debye Theory (Vibrational Modes of a Continuous Medium)

Debye improved Einstein's model by treating the crystal as a **continuous elastic medium**.

Assumptions

1. Solid behaves like a **continuous elastic medium**.
2. Vibrations are **elastic waves** (phonons).
3. Frequencies range from **0 to a maximum** ν_D.
4. Total number of modes = **3N**.

Density of Vibrational States

$$g(\nu)\,d\nu = \frac{9N}{\nu_D^3}\nu^2 d\nu$$

Internal Energy

$$U = \int_0^{\nu_D} \frac{h\nu}{e^{h\nu/k_B T} - 1} g(\nu)\,d\nu$$

Introduce:

$$\theta_D = \frac{h\nu_D}{k_B} \text{(Debye temperature)}$$

Debye Heat Capacity

$$\boxed{C_V = 9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx}$$

Temperature Limits

Low Temperature ($T \ll \theta_D$)

$$\boxed{C_V = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\theta_D}\right)^3}$$

✓ **Debye T^3law** (matches experiment)

High Temperature ($T \gg \theta_D$)

$$C_V \to 3Nk_B$$

✓ Dulong–Petit law

Comparison: Einstein vs Debye

Feature	**Einstein Theory**	**Debye Theory**
Frequency	Single frequency	Continuous spectrum
Low-T behavior	Exponential	T^3law
High-T limit	Correct	Correct
Physical realism	Limited	Excellent
Agreement with experiment	Partial	Very good

Conclusion

- **Einstein model** introduces quantization but oversimplifies vibrations.
- **Debye theory** treats lattice vibrations realistically as **phonons in a continuous medium**.
- Debye theory successfully explains:
  - Low-temperature T^3behavior
  - High-temperature Dulong–Petit law

7.5 Origin of Thermal Expansion and Grüneisen Relation

Thermal expansion arises from the anharmonicity of atomic vibrations in solids. Let's go step by step.

Origin of Thermal Expansion

- Atoms in a solid vibrate about their equilibrium positions.
- The interatomic potential $U(r)$is not perfectly symmetric; it is anharmonic.
- At low vibrations, it can be approximated as:

$$U(r) = U_0 + \frac{1}{2}k(r - r_0)^2 - \frac{1}{3}\alpha(r - r_0)^3 + \cdots$$

where:

- r_0= equilibrium separation
- k= harmonic force constant
- α= measure of anharmonicity

Mechanism

- If the potential is anharmonic, the average atomic position shifts as temperature increases.
- This increases the average interatomic separation, leading to expansion of the solid.

Coefficient of Thermal Expansion

For a linear solid, the linear thermal expansion coefficient is:

$$\boxed{\alpha_L = \frac{1}{L}\frac{dL}{dT}}$$

where $L$is the length.

For volume:

$$\boxed{\alpha_V = \frac{1}{V}\frac{dV}{dT} \approx 3\alpha_L}$$

Grüneisen Parameter:

The Grüneisen parameter γlinks thermal expansion to vibrational properties of the lattice.

$$\gamma = -\frac{V}{\omega}\frac{\partial\omega}{\partial V}$$

where:

- ω= phonon frequency
- V= volume
- $\partial\omega/\,\partial V < 0$(frequency decreases as volume increases)

Interpretation:

- γmeasures the sensitivity of phonon frequencies to volume changes.

Grüneisen Relation:

The linear thermal expansion coefficient can be expressed as:

$$\boxed{\alpha = \frac{\gamma C_V}{3BV}}$$

where:

- α= linear thermal expansion coefficient
- C_V= specific heat at constant volume

- B= bulk modulus
- V= volume
- γ= Grüneisen parameter

Significance

- Explains why materials expand when heated
- Thermal expansion is proportional to specific heat and inversely proportional to stiffness
- At low temperatures ($C_V \sim T^3$), $\alpha \sim T^3$

7.6 SUMMARY:

Phonons and Lattice Vibrations:

- Phonons are quantized modes of lattice vibrations in a crystal, behaving as quasi-particles that carry energy.
- In a crystal lattice, atoms vibrate about their equilibrium positions, leading to elastic waves.
- Acoustic modes: Atoms move in phase; responsible for sound propagation.
- Optical modes: Atoms move out of phase; occur in diatomic or ionic lattices.

Dispersion Relation in Crystal Lattice:

- The dispersion relation $\omega(k)$describes how the frequency of lattice vibrations depends on the wavevector k.
- For a monoatomic chain:

$$\omega = 2\sqrt{\frac{C}{M}}\ |\sin\frac{ka}{2}|$$

For a diatomic chain, acoustic and optical branches arise.

- Verification of dispersion relation can be done experimentally via X-ray, neutron, or electron scattering.

Lattice Heat Capacity:

- Einstein Model:
    - Assumes each atom vibrates independently with the same frequency ω_E.
    - Heat capacity:

$$C_V = 3Nk_B\left(\frac{\hbar\omega_E}{k_BT}\right)^2\frac{e^{\hbar\omega_E/k_BT}}{\left(e^{\hbar\omega_E/k_BT}-1\right)^2}$$

    - Works well at high temperatures; fails at low temperatures (T^3 dependence not captured).

- Debye Model:
    - Considers a continuous spectrum of vibrational modes up to a maximum frequency (Debye frequency ω_D).
    - Heat capacity:

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4e^x}{(e^x-1)^2}dx$$

Accurately predicts $C_V \propto T^3$at low temperatures and approaches Dulong-Petit limit at high temperatures.

Vibrational Modes of Continuous Medium:

- Treats the solid as a continuous elastic medium.
- Phonons correspond to normal modes of vibration, forming a phonon spectrum that determines thermal properties.

Thermal Expansion and Grüneisen Relation:

- Origin of Thermal Expansion: Due to anharmonicity in interatomic potential; the average atomic separation increases with temperature.
- Grüneisen Parameter (γ) links volume change to lattice vibrations:

$$\gamma = -\frac{V}{\omega}\frac{\partial\omega}{\partial V}$$

- The Grüneisen relation connects thermal expansion coefficient (α), heat capacity (C_V), and bulk modulus (B):
-

$$\alpha = \frac{\gamma C_V}{BV}$$

- Explains how lattice vibrations lead to expansion and influence thermodynamic properties.

Conclusion:

Phonons and their dispersion relations govern the vibrational and thermal behavior of solids. Lattice heat capacity can be explained using Einstein and Debye models, while thermal expansion originates from anharmonic vibrations and is quantified via the Grüneisen parameter. Understanding these concepts is fundamental in solid-state physics, materials science, and thermal engineering.

7.7 TECHNICAL TERMS

Phonon, Dispersion Relation, Einstein Quantum theory of Specific heat, Debye Theory of Specific Heat,
Origin of Thermal Expansion & Gruneisen Relation

7.8 SELF ASSESSMENT QUESTIONS

1. Explain about the Phonons
2. Explain about the verification of dispersion relation in crystal lattice
3. Explain about the Einstein Quantum theory of Specific heat
4. Explain about the Debye Theory of Specific Heat
5. Explain about the Origin of Thermal Expansion & Gruneisen Relation

7.9 Suggested Readings

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

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LESSON - 8

FREE ELECTRON FERMI GAS

Aim and Objective of the lesson

This lesson aims to bridge the gap between classical and quantum physics by evaluating the limitations of the Classical Free Electron Theory and introducing the Quantum Free Electron Model. Students will qualitatively examine why classical models fail to explain phenomena like specific heat, subsequently transitioning to a wave-mechanical approach.

The objectives are to derive quantized energy levels and the density of orbits in a one-dimensional system, before generalising these concepts to a three-dimensional free electron gas. Ultimately, students will synthesize how the Pauli Exclusion Principle and Fermi-Dirac statistics define the electronic properties and energy distribution within metallic solids.

STRUCTURE

8.1 Introduction

8.2 Definitions

8.3 Failures of free electron theory of metals (Qualitative only)

8.4Energy levels and density of orbits in one dimension

8.5 Free electron gas in 3 dimensions

8.6 Summary

8.7 Technical terms

8.8 Self-assessment

8.9 Suggested books

8.1 INTRODUCTION

For decades, the **Classical Free Electron Theory**, pioneered by Drude and Lorentz, served as the bedrock for understanding metals. By treating valence electrons as a "gas" of classical particles bouncing off stationary ions, physicists successfully explained **Ohm's Law**and the relationship between electrical and thermal conductivity. However, as experimental precision grew, the classical model began to falter. It predicted a specific heat for electrons that was nearly a hundred times larger than observed values and failed to explain why some metals with more free electrons were poorer conductors than those with fewer.

The fundamental flaw lay in treating electrons like classical billiard balls. This lesson explores the **Quantum Free Electron Model**, a revolutionary shift that applies the principles of wave mechanics to the metallic interior. We begin by examining the qualitative failures of the classical approach—specifically its inability to account for the electronic heat capacity and the temperature dependence of conductivity.

To resolve these discrepancies, we move into the quantum realm, treating electrons as waves confined within the boundaries of the metal. We will analyze the **one-dimensional (1D)** model to derive discrete energy levels and the "density of orbits," which tells us how many states are available at a given energy. Finally, we expand this into **three dimensions (3D)**, visualizing the "Fermi Sphere" in momentum space. This transition from a classical gas to a quantum **Fermi Gas** provides the necessary framework to understand why only a small fraction of electrons contribute to a metal's thermal and electrical properties.

8.2 DEFINITIONS

1. Drude Model (Classical Free Electron Theory): A classical model that treats valence electrons in a metal as a gas of non-interacting classical particles (like a billiard ball gas) to explain electrical and thermal conductivity.

2. Mean Free Path: The average distance an electron travels between successive collisions with lattice ions or impurities.

3. Schrödinger Equation: The fundamental equation of quantum mechanics used here to determine the allowed wavefunctions and energy levels of an electron in a potential well.

8.3 FAILURES OF FREE ELECTRON THEORY OF METALS (QUALITATIVE ONLY)

The classical free electron theory, primarily the Drude model, was a significant milestone in solid-state physics. It successfully explained Ohm’s law and the Wiedemann-Franz law, which relates electrical and thermal conductivity. However, it encountered several "conspicuous failures" because it relied on classical Maxwell-Boltzmann statistics, treating electrons like a classical gas of "billiard balls."

1. The Specific Heat Capacity Paradox

The most striking failure involves the electronic heat capacity. According to classical equipartition of energy, every free electron should contribute $3/2k_B$to the heat capacity. In reality, the measured electronic heat capacity at room temperature is roughly 100 times smaller than this prediction. The classical theory failed because it assumed all electrons could absorb thermal energy, whereas quantum mechanics reveals that only a tiny fraction of electrons near the Fermi level can change their energy states.

2. Magnetic Susceptibility

Classical theory predicted a large paramagnetic contribution from electron spins (Langevin paramagnetism). However, experimental observations showed that the actual magnetic susceptibility of conduction electrons is much smaller and nearly independent of temperature.

3. The Mean Free Path Problem

In the classical model, electrons were expected to collide frequently with ion cores, limiting their mean free path to roughly the interatomic spacing (a few Angstroms). Yet, experiments on pure metals at low temperatures showed that electrons could travel distances of millions of atomic spacings (centimeters) without being deflected.

4. Dependence of Conductivity

The classical theory could not adequately explain why some materials are excellent conductors while others are insulators or semiconductors, nor could it precisely account for the temperature dependence of resistivity in complex alloys.

Note: These were not necessarily failures of the "free electron" concept itself, but failures of the classical distribution function. These issues were resolved by adopting Fermi-Dirac statistics and the Pauli Exclusion Principle, which dictate that electrons occupy states in a "Fermi sea" where only the most energetic electrons participate in thermal and transport processes.

8.4 Energy levels in one dimension

Consider a free electron gas in one dimension, taking account of quantum theory and of the Pauli principle. An electron of mass m is confined to a length L by infinite barriers (Fig. 1).

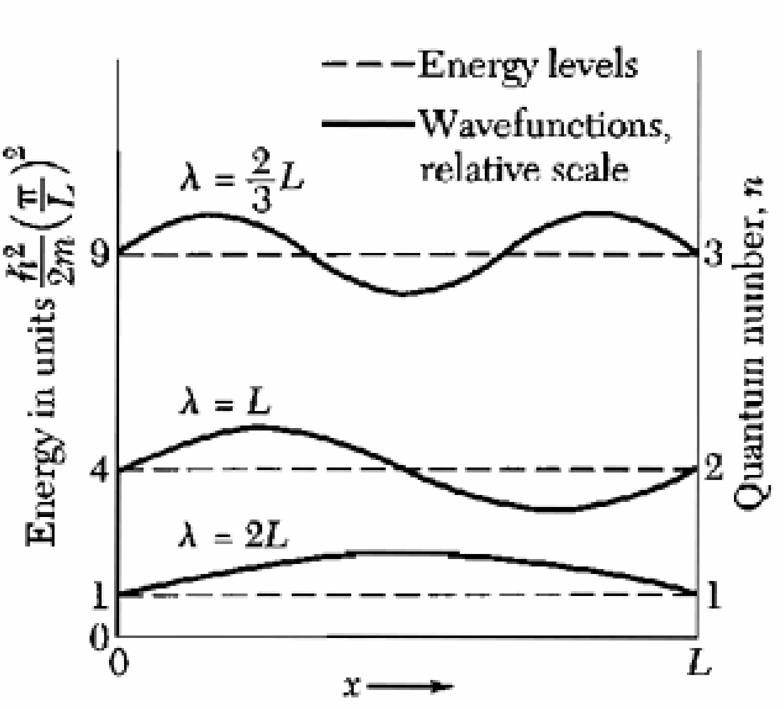


Fig. 1 First three energy levels and wave functions of a free electron of mass m confined to a line of length L. The energy levels are labelled according to the quantum number n which gives the number of half-wavelengths in the wavefunction. The wavelengths are indicated on the wavefunctions. The energy ϵ_n of the level of quantum number n is equal to $(h^2/2m)(n/2L)^2$.

The wavefunction ψ_n $(x)$of the electron is a solution of the Schrodinger equation$\mathcal{H}\psi = \epsilon\psi$; with the neglect of potential cnergy we have $\mathcal{H} = p^2/2m$, where p is the momentum. In quantum theory p may be represented by the operator $-i\hbar\, d/dx$, so that

$$\mathcal{H}\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n\psi_n \qquad (1)$$

where ϵ_n is the encra of the electron in the orbital.

We use the term orbital to denote a solution of the wave equation for a system of only one electron. The term allows us to distinguish between an exact quantum state of the wave equation of a system of N interacting electrons and an approximate quantum state which we construct by assigning the N electrons to N different orbitals, where each orbital is a solution of a wave equation for one electron. The orbital model is exact only if there are no interactions between electrons. The boundary conditions are$\psi_n(0) = 0$; $\psi_n(L) = 0$,as imposed by the infinite potential energy barriers. They are satisfied if the wavefunction is sinelike with an integral number n of half-wavelengths between 0 and L:

$$\psi_n = A\sin\left(\frac{2\pi}{\lambda_n}x\right); \quad \frac{1}{2}n\lambda_n = L \tag{2}$$

where A is a constant. \Ve see that (2) is a solution of (1), because

$$\frac{d\psi_n}{dx} = A\left(\frac{n\pi}{L}\right)\cos\left(\frac{n\pi}{L}x\right); \quad \frac{d^2\psi_n}{dx^2} = -A\left(\frac{n\pi}{L}\right)^2\sin\left(\frac{n\pi}{L}x\right)$$

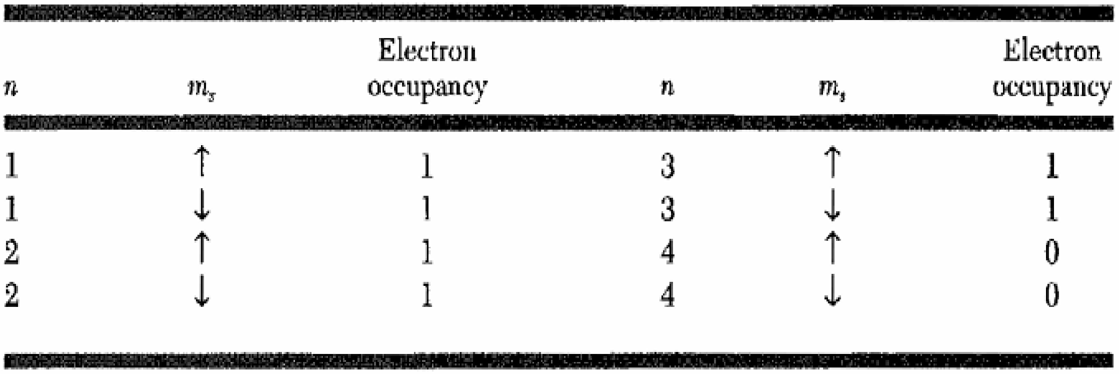
whence the energy ϵ_n is given by

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \tag{3}$$

We want to accommodate N electrons on the linc. According to the Pauli exclusion principle, no two electrons can have all their quantum numbersidentical. That is, each orbital can be occupied by at most one electron. This applies to electrons in atoms, molecules, or solids.

In a linear solid the quantum numbers of a conduction electron orbital are n and m_s, where n is any positive integer and the magnetic qnantum number m_s = ±½, according to spin orientation. A pair of orbitals labeled by the quantum number n can accommodate two electrons, one with spin up and one with spin down.

If there are six electrons, then in the ground state of the system the filled orbitals are those given in the table:



n	m_s	Electron occupancy	n	m_s	Electron occupancy
1	↑	1	3	↑	1
1	↓	1	3	↓	1
2	↑	1	4	↑	0
2	↓	1	4	↓	0

More than one orbital may have the same energy. The number of orbitals with the same energy is called the degeneracy.

Let n_F denote the topmost filled energy level, where we start filling the levels from the bottom (n = 1) and continue filling higher levels with electrons until all N electrons are accommodated. It is convenient to suppose that N is an even number. The condition $2n_F = N$ determines n_F, the value of n for the uppermost filled level.

The Fermi energy ϵ_F is defined as the energy of the topmost filled level in the ground state of the N electron system. By (3) with $n = n_F$, we have in one dimension:

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 \tag{4}$$

8.5 Free electron gas in 3 dimensions

The free-particle Schrodinger equation in three dimensions is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_k(r) = \epsilon_k\psi_k(r) \tag{5}$$

If the electrons are confined to a cube of edge L, the wavefunction is the standing wave

$$\psi(r) = A\sin(\pi n_x x/L)\sin(\pi n_y y/L)\sin(\pi n_z z/L) \tag{6}$$

where n_x, n_y, $n_z$are positive integers. The origin is at one corner of the cube.

It is convenient to introduce wave functions that satisfy periodic boundary conditions. We now require the wavefunctions to be periodic in x, y, z with period L. Thus

$$\psi(x+L,y,z) = \psi(x,y,z) \tag{7}$$

and similarly for the y and z coordinates. Wavefunctions satisfying the free-particle Schrodinger equation and the periodicity condition are of the form of a travelling plane wave:

$$\psi_k(r) = \exp(ik\cdot r) \tag{8}$$

provided that the components of the wavevector k satisfy

$$k_x = 0; \pm\frac{2\pi}{L}; \pm\frac{4\pi}{L}; \ldots \tag{9}$$

and similarly fork_y, and k_z.

Any component of k of the form 2nπ/L will satisfy the periodicity condition over a length L, where n is a positive or negative integer. The components of k are the quantum numbers of the problem, along with the quantum number m, for the spin direction. We confirm that these values of k_x, satisfy (7), for

$$\begin{aligned}\exp[ik_x(x+L)] &= \exp[i2n\pi(x+L)/L] \\ &= \exp(i2n\pi x/L)\exp(i2n\pi) = \exp(i2n\pi x/L) = \exp(ik_x x)\end{aligned} \quad (10)$$

On substituting (8) in (5) we have the energyϵ_k of the orbital with wavevector k:

$$\epsilon_k = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \quad (11)$$

The magnitude k of the wavevector is related to the wavelength λ by k = 2π/λ. The linear momentum p may be represented by the operator p = -iħ∇, whence for the orbital (8):

$$p\psi_k(r) = -i\hbar\nabla\psi_k(r) = \hbar k\psi_k(r) \quad (12)$$

so that the plane wave ψ_k is an eigenfunction of the linear momentum with the eigenvalue ħk. The particle velocity in the orbital k is given by v = ħk/m.

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. The energy at the surface of the sphere is the Fermi energy; the wavevectors at the Fermi surface have a magnitude k, such that (Fig. 2):

$$\epsilon_F = \frac{\hbar^2}{2m}k_F^2 \quad (13)$$

From (9) we see that there is one allowed wavevector - that is one distinct triplet of quantum numbers k_x, k_y, k_z,-for the volume element $(2\pi/L)^3$of k space. Thus in the sphere of volume $4\pi k_F^3/3$ the total number of orbitals is

$$2\cdot\frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2}k_F^3 = N \quad , \quad (14)$$

where the factor 2 on the left comes from the two allowed values of the spin quantum number for each allowed value of k. Then (14) gives

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad (15)$$

which depends only on the particle concentration.

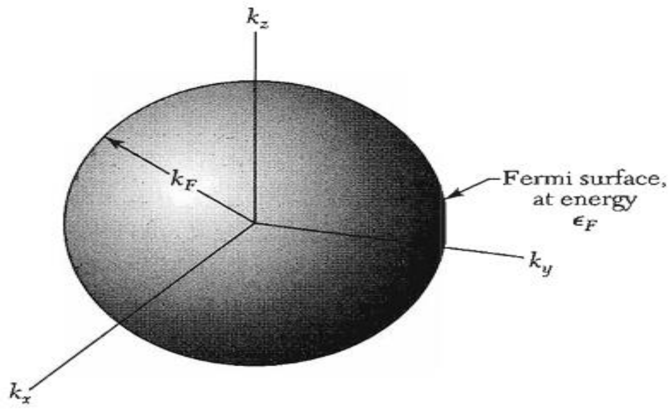


Fig. 2 In the ground state of a system of N free electrons the occupied orbitals of the system fill a sphere of radius k_F where $\epsilon_n = \hbar^2 k_F^3/2\mathrm{m}$ is the energy of an electron having a wavevector k_F.

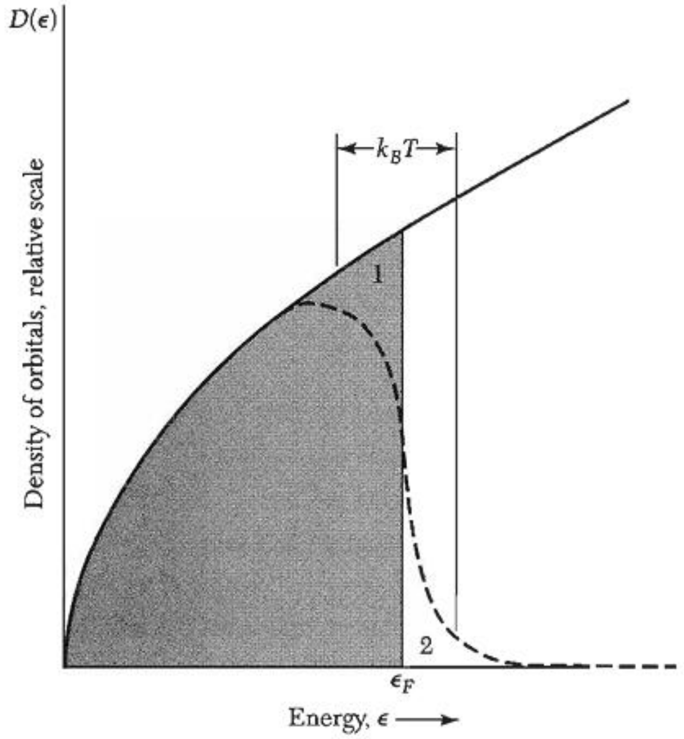


Fig. 3 Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density $f(\epsilon, T)D(\epsilon)$ of filled orbitals at a finite temperature, but such that $k_B\mathbf{T}$ is small in comparison with ϵ_F. The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to T, for electrons are thermally excited from region 1 to region 2.

Using equations (13) and (15),

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \tag{16}$$

This relates the Fermi energy to the electron concentration N/V. The electron velocity $v_F$at the Fermi surface is

$$v_F = \left(\frac{\hbar k_F}{m}\right) = \left(\frac{\hbar}{m}\right)\left(\frac{3\pi^2 N}{V}\right)^{1/3} \tag{17}$$

Calculated values of k_F, v_F, and ϵ_F, are given in Table 1 for selected metals; also given are values of the quantity T_F which is defined as ϵ_F/k_B. (The quantity T_F has nothing to do with the temperature of the electron gas!)

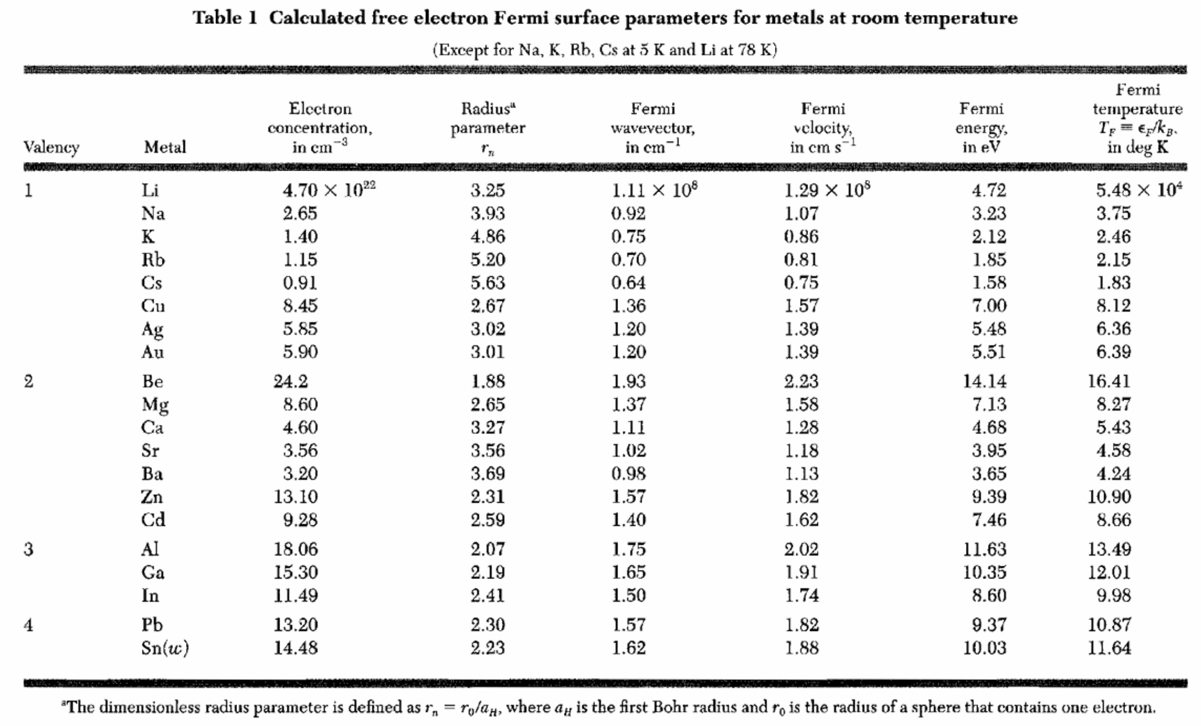


Table 1 Calculated free electron Fermi surface parameters for metals at room temperature

(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm^{-3}	Radius[a] parameter r_n	Fermi wavevector, in cm^{-1}	Fermi velocity, in $cm\ s^{-1}$	Fermi energy, in eV	Fermi temperature $T_F \equiv \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^{8}	1.29×10^{8}	4.72	5.48×10^{4}
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Be	24.2	1.88	1.93	2.23	14.14	16.41
	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(*w*)	14.48	2.23	1.62	1.88	10.03	11.64

[a] The dimensionless radius parameter is defined as $r_n = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

8.6 SUMMARY

The transition from classical to quantum physics in metallic conduction is the core focus of this lesson. It begins by evaluating the qualitative failures of the **Classical Free Electron Theory**, specifically its inability to explain why the experimental electronic specific heat is much lower than predicted and why the mean free path of electrons varies so significantly with temperature. These failures stem from the incorrect application of Maxwell-Boltzmann statistics to subatomic particles.

The lesson then introduces the **Quantum Free Electron Model**, where electrons are treated as waves confined in a potential well. In a one-dimensional system, we observe that energy levels are quantized, and the "density of orbits" describes how many states exist at each energy level.

By extending this logic to a **three-dimensional free electron gas**, the model accounts for the Pauli Exclusion Principle, which prevents electrons from crowding into the lowest energy state. Instead, they fill states up to a maximum level known as the **Fermi Energy**, forming a "Fermi Sphere" in momentum space.

This quantum framework successfully resolves classical discrepancies by showing that only electrons near the Fermi surface contribute to thermal and electrical processes, providing a precise summary of metallic behaviour.

8.7 TECHNICAL TERMS

Free electron gas
Mean free path
Schrödinger Equation

8.8 SELF-ASSESSMENT

1. Write a note on failures of the Classical Free Electron theory.
2. Define Fermi energy.
3. Derive an equation for the free electron gas in 3 dimensions.

8.9 SUGGESTED BOOKS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A.J. Dekker.
3. Solid State Physics, S.O. Pillai 7th Edition.
4. Solid State Physics, H.C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics by S.P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M.A. Wahab, Narosa publishing house.

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LESSON - 9

FERMI-DIRAC DISTRIBUTION FUNCTION

Aim and Objective of the lesson

The aim of this lesson is to provide a comprehensive understanding of the quantum statistical behavior of electrons in metals, moving beyond classical approximations to explain thermodynamic properties. By exploring the **Fermi-Dirac distribution function**, the lesson seeks to demonstrate how the Pauli Exclusion Principle governs electron occupancy and how the Fermi function evolves from a sharp step-function at absolute zero to a smoother distribution as temperature increases.

A primary objective is for students to define and calculate the **density of states**, which is critical for determining how many quantum states are available for electrons at specific energy levels. Furthermore, the lesson aims to derive the **heat capacity of the electron gas** using quantum mechanics, allowing students to resolve the long-standing discrepancy between classical predictions ($3/2k_B$ per electron) and the much smaller values observed in **experimental heat capacity** measurements. By the conclusion, students should be able to qualitatively and quantitatively explain why only electrons near the Fermi level contribute to a metal's thermal properties, thereby synthesizing a modern view of electronic transport and energy storage in solid-state systems.

STRUCTURE

9.1 INTRODUCTION

The transition from the classical Drude model to a modern quantum understanding of solids requires a deep dive into the statistical mechanics of particles that obey the Pauli Exclusion Principle. This lesson introduces the **Fermi-Dirac distribution function**, the fundamental mathematical tool used to describe the probability of an electron occupying a specific energy state at a given temperature.[1] Unlike classical particles that follow Maxwell-Boltzmann statistics—where any number of particles can crowd into the lowest energy state—electrons are fermions, meaning they fill energy levels from the bottom up, much like water filling a container. This "filling" process creates a sharp boundary at absolute zero known as the **Fermi Level**, and understanding how this boundary "blurs" as thermal energy is added is essential for predicting the physical properties of metals.

Central to this discussion is the **density of states**, which provides the geometric and quantum-mechanical framework for calculating how many electronic states exist within a specific energy range. By combining the Fermi-Dirac distribution with the density of states, we can finally address the "specific heat catastrophe" of classical physics. Classical theory erroneously predicted that every free electron should contribute 3/2 k_B to the heat capacity; however, experimental data consistently showed values nearly a hundred times smaller. Through this lesson, we will demonstrate that because of the exclusion principle, only the tiny fraction of electrons within a small thermal energy range k_BT of the Fermi surface are capable of being excited. This quantum refinement not only aligns theory with **experimental heat capacity** measurements but also clarifies the underlying physics of how energy is stored and transferred within the "electron sea" of a metallic crystal.

9.2 DEFINITIONS

1. Fermi-Dirac Distribution Function: A quantum statistical distribution used to describe the probability of an electron occupying a specific energy state at a given temperature, accounting for the Pauli Exclusion Principle.

2. Fermi Energy (E_F): The maximum energy level occupied by electrons in a metal at absolute zero temperature (0 K).

3. Fermi Temperature (T_F): The temperature at which the thermal energy (k_BT) is equal to the Fermi energy.

4. Density of States: The number of electronic energy states available per unit volume per unit energy interval at a specific energy level.

9.3 FERMI-DIRAC DISTRIBUTION FUNCTION AND VARIATION OF FERMI FUNCTION WITH TEMPERATURE (QUALITATIVE ONLY)

The Fermi Dirac distribution function describes the probability that a fermion, such as an electron, will occupy a particular energy level at a given temperature.

Variation of Fermi function with temperature:

The kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at absolute zero, and some levels are vacant which were occupied at absolute zero (Fig. 1). The Fermi-Dirac distribution gives the probability that an orbital at energy E will be occupied in art ideal electron gas in thermal equilibrium:

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_BT] + 1} \tag{1}$$

The quantity μ is a function of the temperature; μ is to be chosen for the particular problem in such a way that the total number of comes out correctly-that is, equal to N. At absolute zero $\mu = \epsilon_F$, in the system because in the limit T → 0 the function $f(\epsilon)$ changes discontinuously from the value 1 (filled) to the value 0 (empty) at $\epsilon = \epsilon_F = \mu$. At all temperatures $f(\epsilon)$is equal to ½ when $\epsilon = \mu$, for then the denominator of (1) has the value 2.

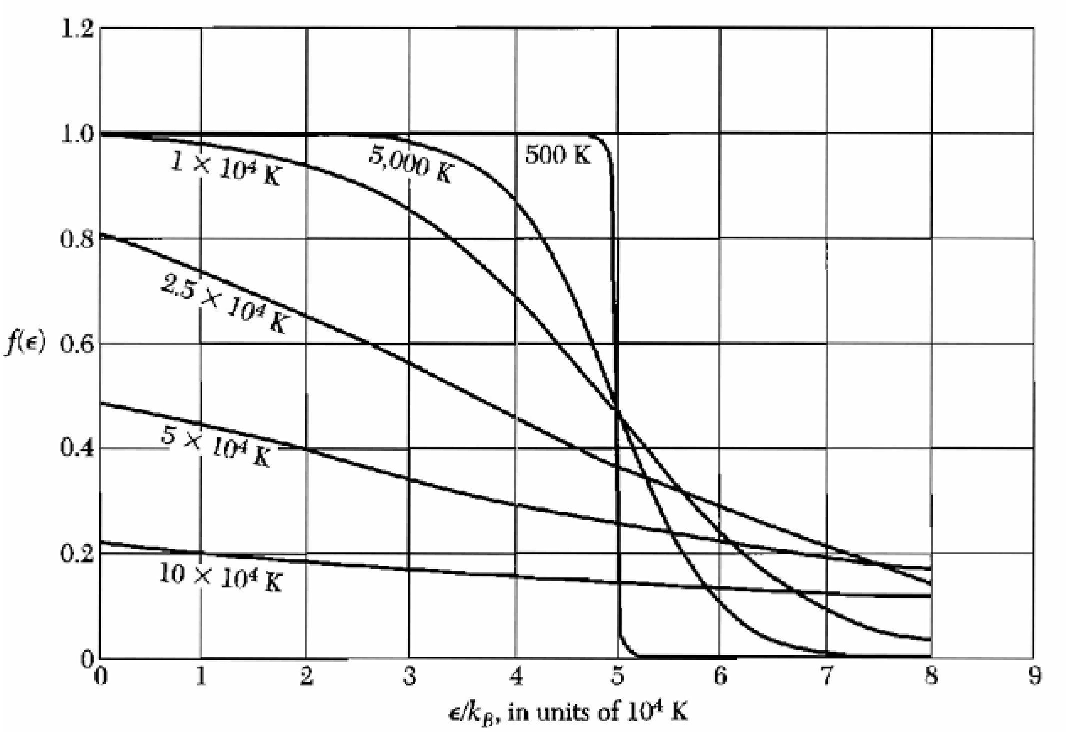

Fig. 1 Fermi-Dirac distribution function (5) at the various labelled temperatures, for ϵ_F/k_B = 50,000. The results apply to a gas in three dimensions. The total number of particles is constant, independent of temperature. The chemical potential p at each temperature may be read off the graph as the energy at which f = 0.5.

The quantity μ is the chemical potential (TP), and we see that at absolute zero the chemical potential is equal to the Fermi energy, defined as the energy of the topmost filled orbital at absolute zero.

The high energy tail of the distribution is that part for which $\epsilon - \mu \gg k_BT$; here the exponential term is dominant in the denominator of (1), so that $f(\epsilon) \cong \exp[(\epsilon - \mu)/k_BT]$. This limit is called the Boltzmann or Maxwell distribution.

9.4 DENSITY OF STATES

We now find an expression for the number of orbitals per unit energy range, D(ϵ), called the density of states[1]. We use

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

to obtain the total number of orbitals of energy $\leq \epsilon$:

$$N = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2} \qquad (2)$$

so that the density of states (Fig. 2) is

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \epsilon^{1/2} \tag{3}$$

[1] Strictly, D(ϵ) is the density of one-particle states, or density of orbitals.

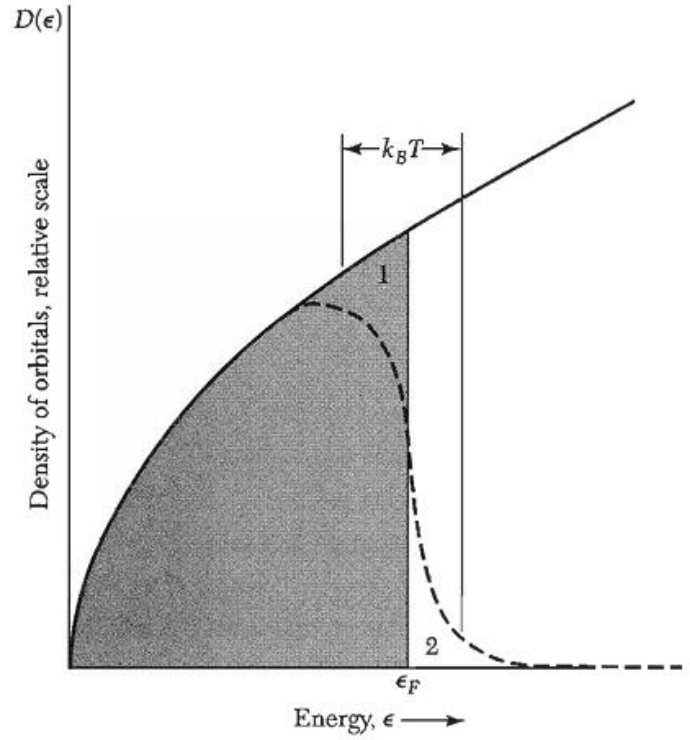

Fig. 3 Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density $f(\epsilon, T)D(\epsilon)$ of filled orbitals at a finite temperature, but such that **k_BT** is small in comparison with ϵ_F. The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to T, for electrons are thermally excited from region 1 to region 2.

This result may be expressed more simply by comparing (2) and (3) to obtain atϵ

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon} \tag{4}$$

Within a factor of the order of unity, the number of orbitals per unit energy range at the Fermi energy is the total number of conduction electrons divided by the Fermi energy, just as we would expect.

9.5 HEAT CAPACITY OF THE ELECTRON GAS

1. The Classical Discrepancy

- **Classical Prediction:** According to classical statistical mechanics, a free particle should have a heat capacity of 3/2 k_B. If each atom in a metal contributes one valence electron, the electronic contribution should be 3/2 Nk_B.
- **The Problem:** Observed values at room temperature are typically less than **1%** of this prediction. This discrepancy exists because electrons, as fermions, obey the **Pauli Exclusion Principle**.

2. Qualitative Quantum Explanation

The exclusion principle dictates that at absolute zero, electrons fill orbitals up to the **Fermi energy (ϵ_F)**.

- When a metal is heated, only electrons in orbitals within an energy range ~k_BT of the Fermi level can be excited thermally.
- Electrons deep within the Fermi sphere cannot gain energy because the states above them are already occupied.
- If N is the total number of electrons, only a fraction of roughly T/T_F is thermally excited (where $T_F = \epsilon_F/k_B$).
- Since each of these electrons gains thermal energy ~k_BT, the total internal energy $U_{el} \approx (NT/T_F)k_BT$.
- Differentiating with respect to temperature gives $C_{el} \approx Nk_B(T/T_F)$, showing a **linear dependence on T**.

3. Quantitative Derivation

At low temperatures where $k_BT \ll \epsilon_F$, the electronic heat capacity is derived by differentiating the internal energy ΔU:

$$C_{el} = \frac{dU}{dT} = \int_0^\infty d\epsilon(\epsilon - \epsilon_F)\frac{df}{dT}D(\epsilon)$$

Where:

- **$D(\epsilon)$** is the density of states.
- **$f(\epsilon, T)$** is the Fermi-Dirac distribution function.

By evaluating **$D(\epsilon)$** at the Fermi level and solving the integral, we obtain the standard result:

$$C_{el} = \frac{\pi^2}{3}D(\epsilon_F)k_B^2T$$

For a free electron gas where **$D(\epsilon_F)$**$= 3N/2\epsilon_F$, this simplifies to:

$$C_{el} = \frac{1}{2}\pi^2Nk_B\frac{T}{T_F}$$

9.6 EXPERIMENTAL HEAT CAPACITY OF METALS

The experimental heat capacity of metals is characterized by the coexistence of electronic and lattice contributions, often analyzed through the Sommerfeld parameter.

1. Theoretical Framework for Experimental Analysis

At temperatures much lower than both the **Debye temperature** and the **Fermi temperature (T_F)**, the total heat capacity (C) of a metal is expressed as the sum of its electronic and phonon contributions:

$$C = C_{el} + C_{ph} = \gamma T + AT^3$$

- **Electronic term (γT):** This term is linear in temperature and becomes the dominant factor at sufficiently low temperatures.
- **Phonon term (AT^3):** This represents the lattice contribution, following the Debye T^3 law.

2. Experimental Methodology: The C/T vs. T^2 Plot

To separate these two contributions experimentally, physicists plot the total heat capacity in a modified linear form:

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

- **Interpretation:** When experimental data is plotted this way, the points should fall on a straight line.
- **The Intercept (γ):** The y-axis intercept gives the **Sommerfeld parameter** (γ), which is characteristic of the material's electronic properties.
- **The Slope (A):** The slope of the line provides the constant A, which is related to the lattice vibrations (phonons).

3. The Sommerfeld Parameter (γ)

The observed Sommerfeld parameter (γ) is of the expected magnitude but often deviates from the theoretical value calculated for perfectly free electrons of mass m.

Calculated Free Electron Value: For a free electron gas, γ is proportional to the density of states at the Fermi level.

Experimental Discrepancy: The ratio between the observed γand the free electron value is used to define a thermal effective mass (m_{th}):

$$\frac{m_{th}}{m} = \frac{\gamma(\text{observed})}{\gamma(\text{free})}$$

4. Factors Influencing Experimental Values

The departure of the m_{th}/m ratio from unity (as seen in metals like Lithium with a ratio of ~1.63 or Beryllium at ~0.17) is attributed to three primary physical effects:

- **Band Effective Mass:** Interaction of conduction electrons with the rigid periodic potential of the crystal lattice.
- **Electron-Phonon Interaction:** A moving electron distorts the nearby lattice, "dragging" ions along and increasing its effective mass.
- **Electron-Electron Interaction:** Moving electrons cause inertial reactions in the surrounding electron gas, further increasing effective mass.

5. Notable Exceptions: Heavy Fermions

Some metallic compounds, such as UBe_{13} and $CeCu_2Si_2$, exhibit **Heavy Fermion** behaviour. These materials have enormousγ values—two to three orders of magnitude higher than standard metals—suggesting inertial masses as high as 1000m due to weak overlap of f-electron wavefunctions.

9.7 SUMMARY

This lesson provides an in-depth exploration of the quantum mechanical framework required to understand the thermodynamic behaviour of electrons in solids, specifically focusing on the transition from classical to quantum statistics. It begins by introducing the **Fermi-Dirac distribution function**, which is the fundamental probability function describing how fermions, such as electrons, occupy available energy states. Unlike classical particles, electrons are governed by the Pauli Exclusion Principle, which dictates that no two electrons can occupy the same quantum state. At absolute zero, this leads to a step-like distribution where all states are filled up to a specific level known as the **Fermi Energy**, while all states above remain empty. As the temperature increases, the lesson qualitatively explores how this

"Fermi sea" becomes thermally excited, with only those electrons near the Fermi surface gaining enough energy to move into higher, unoccupied states.

To bridge the gap between statistical probability and physical reality, the lesson defines the **density of states**, which represents the number of quantum states available per unit energy interval. This concept is vital for calculating the total internal energy of the system. A major highlight of the lesson is the resolution of the "specific heat catastrophe" found in classical Drude theory. While classical physics incorrectly predicted that every free electron should contribute 3/2 k_B to the heat capacity, leading to a constant molar value of 3/2 R, **experimental heat capacity** data reveals a much smaller, linear temperature dependence.

By synthesizing the Fermi-Dirac distribution with the density of states, the lesson demonstrates that only a tiny fraction of electrons—those within a thermal energy range of approximately k_B T from the Fermi energy—can actually absorb heat. This quantum refinement perfectly matches experimental observations and explains why the electronic contribution to heat capacity is negligible at room temperature compared to lattice vibrations. Ultimately, the lesson summarizes how these quantum constraints are essential for accurately modelling the thermal and electrical properties of modern metallic materials, providing a definitive correction to classical misconceptions.

9.8 TECHNICAL TERMS

Fermi-Dirac Distribution Function
Fermi Energy (E_F)
Fermi Temperature (T_F)
Density of States

9.9 SELF-ASSESSMENT

1. Explain the variation of Fermi function with temperature.
2. Define Fermi energy and Fermi temperature.
3. Explain the density of states.

9.10 SUGGESTED BOOKS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A.J. Dekker.
3. Solid State Physics, S.O. Pillai 7th Edition.
4. Solid State Physics, H.C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics &Solid State Physics by S.P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M.A. Wahab, Narosa publishing house.

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LESSON - 10

ELECTRICAL AND THERMAL CONDUCTIVITY OF METALS

Aim and Objective of the lesson

The aim of this lesson is to establish a comprehensive understanding of the transport properties of metals through the lens of the classical free electron model. Students will explore how the "electron gas" concept provides a physical basis for **electrical conductivity** and the derivation of **Ohm's law**, while also examining the mechanisms of **thermal conductivity**.

A primary objective is for students to analyze the relationship between these two transport phenomena by deriving and validating the **Wiedemann-Franz law**, which relates electrical and thermal conductivities via the Lorenz number. Furthermore, the lesson aims to broaden the scope of electron dynamics by investigating the **motion of electrons in a magnetic field**, specifically focusing on the **Hall effect**. Through this, students will learn to determine crucial material parameters, such as the charge carrier concentration and the Hall coefficient. By the end of the lesson, learners will be able to define key technical terms, perform self-assessments on transport equations, and evaluate the successes and limitations of classical transport theory in predicting the behavior of real metallic conductors.

STRUCTURE

10.1 INTRODUCTION

The study of solid-state physics is fundamentally a quest to understand how the microscopic arrangement of atoms and electrons dictates the macroscopic properties of the materials we use every day. Among all classes of solids, metals stand out due to their exceptional ability to conduct both electricity and heat. This lesson provides a comprehensive exploration of the electronic properties of metals, focusing on how electrons move and interact within a crystalline lattice to produce the phenomena of conductivity. By examining the underlying principles of transport theory, we can bridge the gap between quantum mechanical descriptions of individual particles and the observable laws of classical physics, such as Ohm's Law.

The journey begins with the foundational definitions required to describe a system of many particles. Central to this is the **Fermi-Dirac distribution function**, which describes how electrons—being fermions—occupy various energy states at a given temperature. Unlike classical particles, electrons are governed by the Pauli Exclusion Principle, meaning they cannot all settle into the lowest energy state. This quantum "stacking" leads to the concept of the **Fermi level**, a critical energy threshold that determines which electrons are available to participate in conduction. Understanding the **density of states**, or the number of available "seats" for electrons at specific energy levels, is the first step in predicting a metal's behavior. As we move into the dynamics of these electrons, we address **electrical conductivity and Ohm's law**. Here, we treat the metal as a lattice of positive ions through which a "gas" of free electrons flows. When an external electric field is applied, these electrons experience a force that causes them to drift. However, their motion is not unimpeded; they constantly collide with impurities, defects, and lattice vibrations (phonons). These collisions give rise to electrical resistance. By analyzing the average time between these collisions, known as the relaxation time, we can derive the microscopic basis for conductivity and demonstrate why some materials are better conductors than others.

Beyond electricity, metals are also renowned for their **thermal conductivity**. In a metal, heat is carried primarily by the same free electrons that carry charge. This dual role leads to one of the most elegant relationships in physics: the **Wiedemann-Franz law**. This law reveals that the ratio of thermal conductivity to electrical conductivity is directly proportional to the temperature, with the proportionality constant known as the Lorenz number. This relationship underscores the deep physical connection between the transport of energy and the transport of charge in metallic systems.

The lesson further expands into the behavior of electrons under the influence of **magnetic fields**. When a magnetic field is applied to a moving charge, it experiences the Lorentz force, which deflects its path. This leads to the **Hall effect**, a phenomenon where a transverse voltage is generated across a conductor. The Hall effect is a powerful diagnostic tool in material science, as it allows us to determine the sign and density of charge carriers, proving that in metals, the primary carriers are indeed negatively charged electrons. Through a structured progression from basic definitions to complex interactions in electromagnetic fields, this lesson equips students with the theoretical toolkit necessary to master the fundamental physics of metallic conduction.

10.2 DEFINITIONS:

1. **Free Electron Gas:** A model that treats the valence electrons in a metal as a gas of particles that are free to move throughout the volume of the solid, restricted only by the surface boundaries.

2. **Electrical Conductivity:** A measure of a material's ability to allow the flow of electric current, defined as the ratio of current density to the applied electric field.

3. **Ohm's Law:** The principle stating that the current through a conductor between two points is directly proportional to the voltage across those two points ($V = IR$).

4. **Mean Free Time (Relaxation Time):** The average time interval between two successive collisions of an electron with the lattice ions.
5. **Drift Velocity (v_d):** The average velocity that an electron attains in a conductor due to an applied electric field.
6. **Thermal Conductivity (K):** The property of a material that indicates its ability to conduct heat, primarily driven in metals by the movement of free electrons.
7. **Wiedemann-Franz Law:** An empirical law stating that the ratio of the thermal conductivity to the electrical conductivity of a metal is proportional to its absolute temperature.
8. **Lorenz Number (L):** The proportionality constant in the Wiedemann-Franz Law, theoretically calculated in classical models as $L = 3/2\ (k_B/e)^2$.
9. **Lorentz Force:** The force exerted on a charged particle (electron) moving through a magnetic field, given by $F = q(v \times B)$.
10. **Hall Effect:** The production of a voltage difference (the Hall voltage) across an electrical conductor, transverse to an electric current in the conductor and to an applied magnetic field perpendicular to the current.
11. **Hall Coefficient (R_H):** A constant that characterizes a material's Hall effect, defined as the ratio of the induced electric field to the product of the current density and the applied magnetic field; its sign indicates whether charge carriers are positive or negative.

10.3 ELECTRICAL CONDUCTIVITY AND OHM'S LAW

1. Local Form of Ohm's Law

While the circuit form is $V = IR$, the microscopic (vector) form is more relevant for solids:

$J = \sigma E$

- **J**: Current density (Amperes per unit area).
- **E**: Applied electric field.
- **σ**: Electrical conductivity.

In an isotropic solid, σ is a scalar; in an anisotropic crystal (like graphite), σ is a **rank-2 tensor**, meaning the current J might not be parallel to the applied field E.

2. The Drude Model (Classical Derivation)

The simplest explanation for Ohm's Law comes from Paul Drude (1900), who treated electrons as a classical gas.

The Equation of Motion

An electron with mass m and charge -e in an electric field E experiences a force F = -eE. In a solid, it also experiences "friction" due to collisions with ion cores, characterized by a **relaxation time (τ)**.

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

Steady-State Solution

At steady state (dv/dt = 0), the **drift velocity (v_d)** is:

$$v_d = -\frac{e\tau}{m}E$$

Since J = -nev_d (where n is electron density):

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

Thus, the **Drude Conductivity** is:

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

10.4 Thermal conductivity of metals

1. Microscopic Theory of Thermal Conduction

According to kinetic theory, the thermal conductivity (κ) of a gas of particles is given by:

$$\kappa = \frac{1}{3}Cv\lambda$$

Where:

- **C**: Heat capacity per unit volume.
- **v**: Average particle velocity.
- **λ**: Mean free path (distance between collisions).

In a metallic solid, the total thermal conductivity is the sum of two components:

$\kappa_{total} = \kappa_e + \kappa_{ph}$

- **κ_e (Electronic):** Transport of energy by delocalized conduction electrons.
- **κ_{ph}(Phononic/Lattice):** Transport by quantized lattice vibrations (phonons).

2. Electronic Thermal Conductivity (κ_e)

To derive κ_e, we use the **Sommerfeld Model** (Quantum Free Electron Theory).

A. The Derivation

1. **Electronic Specific Heat (C_{el}):** In the quantum model,

$$C_{el} = \frac{\pi^2}{2} n k_B \left(\frac{T}{T_F}\right).$$

2. **Velocity:** The electrons participating in transport are those near the Fermi surface, so $v \approx v_F$.
3. **Substitution:**

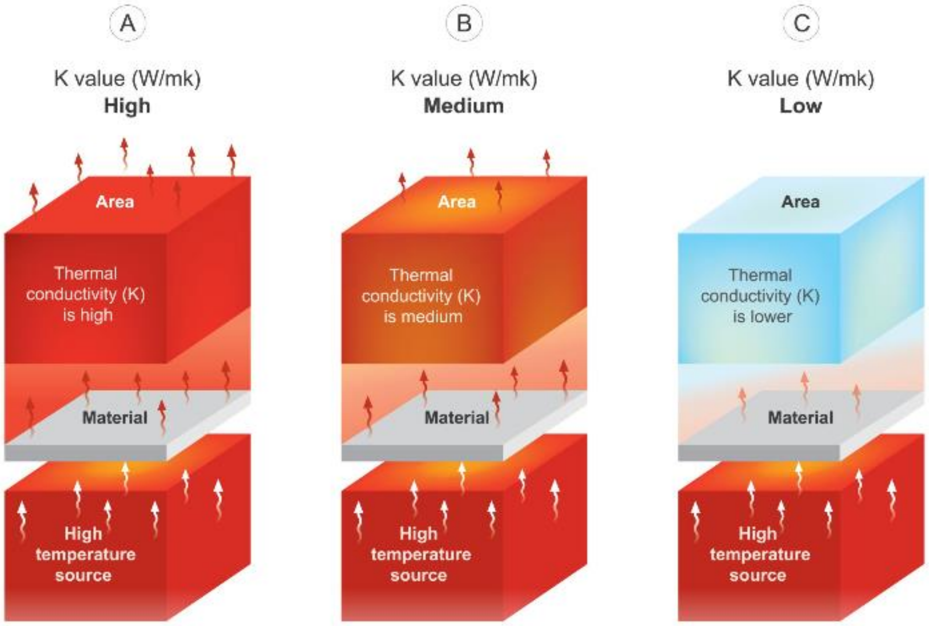
$$\kappa_e = \frac{1}{3}\left(\frac{\pi^2 n k_B^2 T}{m v_F^2}\right) v_F (v_F \tau) = \frac{\pi^2 n k_B^2 T \tau}{3m}$$

(Since $E_F = \frac{1}{2} m v_F^2$).

B. Temperature Dependence of κ_e

The behavior of κ_e depends on the scattering relaxation time (τ):

- **At High T ($T > \Theta_D$):** Scattering is dominated by phonons. Since the number of phonons $\propto T$, then $\tau \propto 1/T$. Because $\kappa_e \propto T\tau$, the T and 1/T terms cancel out, making **κ_e approximately constant**.
- **At Low T ($T \ll \Theta_D$):** Scattering is dominated by impurities/defects. Here τ is constant, so $\kappa_e \propto T$.



Thermal conductivity

3. Lattice Thermal Conductivity (κ_{ph})

While secondary in metals, the lattice contribution follows the Debye model:

- **HighT:** Phonon-phonon scattering (Umklapp processes) dominates. $\kappa_{ph} \propto 1/T$.
- **Low T:** Boundary scattering dominates. Since $C_{ph} \propto T^3$, then $\kappa_{ph} \propto T^3$.

4. Comparison for Pure Metals

Regime	**Scattering Mechanism**	**Electrical Resistivity (ρ)**	**Thermal Conductivity (κ)**
High T	Electron-Phonon	$\propto T$	Constant
Intermediate T	Inelastic scattering	Complex	Decreases
Low T	Impurity/Defects	Constant (Residual)	$\propto T$

10.5 WIEDEMANN-FRANZ LAW

The **Wiedemann-Franz Law** is a cornerstone of the free electron theory of metals. It quantifies the empirical observation that good electrical conductors are also good thermal conductors.

1. Statement of the Law

The law states that the ratio of the electronic contribution to the **thermal conductivity (κ)** to the **electrical conductivity (σ)** of a metal is directly proportional to its absolute **temperature (T)**.

Mathematically:

$$\frac{\kappa}{\sigma} = LT$$

where **L** is a proportionality constant known as the **Lorenz number**.

2. Theoretical Derivations

Classical Drude Model (1900)

Drude treated electrons as a classical "ideal gas".

Electrical Conductivity:

$$\frac{\kappa}{\sigma} = LT$$

Thermal Conductivity:

$\kappa = \frac{1}{2} n v^2 k_B \tau$

By substituting the classical kinetic energy

$\frac{1}{2} m v^2 = \frac{3}{2} k_B T,$

the ratio becomes:

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

Result: This yielded a Lorenz number

$L_{classical} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 \approx 1.11 \times 10^{-8}\,\mathrm{W\Omega K^{-2}}.$

This was about half of the experimental value.

10.6 Motion of the magnetic field

In solid-state physics and plasma physics, the "motion" of a magnetic field usually refers to **Magnetic Convection** or the **Frozen-in Flux Theorem**. This concept explains how a magnetic field behaves when it is embedded in a moving, highly conductive medium (like a metal or plasma).

1. The Induction Equation

To understand the motion of the field, we start with Maxwell's equations and Ohm's Law. In a moving conductor with velocity v, the current density is:

$J = \sigma(E + v \times B)$

By combining this with Faraday's Law

$(\nabla \times E = -\frac{\partial B}{\partial t})$

and Ampere's Law

$(\nabla \times B = \mu_0 J),$

we derive the **Induction Equation**:

$$\frac{\partial B}{\partial t} = \nabla \times (v \times B) + \eta \nabla^2 B$$

Where $\eta = \frac{1}{\mu_0 \sigma}$ is the **magnetic diffusivity**.

2. Two Regimes of Motion

The behavior of the magnetic field depends on the **Magnetic Reynolds Number** (R_m):

$$R_m = \frac{\text{Convection Term}}{\text{Diffusion Term}} \approx \frac{vL}{\eta}$$

A. The Diffusion Limit ($R_m \ll 1$)

In poorly conducting materials (low σ), the magnetic field "slips" through the matter. If the motion of the material stops, the magnetic field simply decays away. The field does not follow the motion of the atoms.[4]

B. The Frozen-in Limit ($R_m \gg 1$)

In perfect conductors (σ→∞) or very large-scale systems (like stellar interiors), the diffusion term vanishes.6 The equation becomes:

$$\frac{\partial B}{\partial t} = \nabla \times (v \times B)$$

This is known as **Alfvén's Theorem**.[7] It implies that the magnetic field lines are "frozen" into the material.[8] If the material moves, the field lines are carried along with it, stretching and twisting as the material deforms.

3. Physical Implications in Solids

While the "frozen-in" concept is most famous in astrophysics, it has critical applications in solid-state physics:

- **Eddy Currents:** When a bulk metal moves through a magnetic field, the field "resists" being left behind. This relative motion creates loops of current (Eddy currents) that exert a dragging force, essentially trying to keep the field and matter together.
- **Flux Pinning in Superconductors:** In Type-II superconductors, magnetic field lines (vortices) can become "pinned" to defects in the crystal lattice. If you move the superconductor, the magnetic field lines move with it perfectly. This is a literal "motion of the field" used in maglev technology.
- **Magnetic Domain Wall Motion:** In ferromagnetic solids, the "motion" of the field is observed as the movement of domain walls under an external force. This is not the movement of individual field lines, but the collective reconfiguration of electron spins.

10.7 Hall effect

The **Hall Effect** is a fundamental phenomenon in solid-state physics that provides a direct method for determining the sign and concentration of charge carriers in a material. Discovered by Edwin Hall in 1879, it remains one of the most powerful diagnostic tools for characterizing semiconductors and metals.

1. Physical Principle

When a magnetic field is applied perpendicular to a current-carrying conductor, a transverse electric field (the **Hall field**) is generated. This happens because the magnetic field exerts a **Lorentz force** on the moving charge carriers, pushing them toward one side of the material.

As charges accumulate on one surface, an internal electric field E_H is established. This field opposes the Lorentz force. Equilibrium is reached when these two forces balance each other out.

Mathematical Derivation

For a steady state, the net transverse force on the charge carriers is zero:

$$F = q(E_H + v \times B) = 0$$

In a simplified 1D geometry where the current I is in the x-direction and the magnetic field B is in the z-direction:

$$qE_y = qv_x B_z$$

$$E_H = v_x B_z$$

Using the relation for current density $J_x = nqv_x$ (where n is carrier density and q is the charge):

$$E_H = \frac{J_x B_z}{nq}$$

2. Key Parameters

The Hall Coefficient (R_H)

The Hall coefficient is defined as the ratio of the induced electric field to the product of the current density and the applied magnetic field:

$$R_H = \frac{E_H}{J_x B_z} = \frac{1}{nq}$$

- **Sign of R_H:** If the carriers are electrons ($q = -e$), R_H is negative. If the carriers are holes ($q = +e$), R_H is positive.
- **Magnitude:** R_H is inversely proportional to the carrier concentration n.

Hall Voltage (V_H)

For a sample of thickness t and width w, the measured Hall voltage is:

$$V_H = E_H \cdot w = \frac{IB}{nqt}$$

10.8 SUMMARY

This lesson provides a comprehensive analysis of how electrons behave within a metallic solid, transitioning from static quantum distributions to dynamic transport phenomena. The core of the lesson focuses on the "Free Electron Model," which treats conduction electrons as a gas that can move throughout the volume of the metal, restricted only by the boundaries of the material and the laws of quantum mechanics.

The foundation is built upon the **Fermi-Dirac Distribution** and the **Density of States**. These concepts explain that electrons do not behave like a classical gas; instead, they fill energy levels from the bottom up due to the Pauli Exclusion Principle. The **Fermi energy** acts as a crucial boundary, as only the electrons near this energy level have the mobility to respond to external electric or magnetic fields. By establishing these definitions, the lesson provides the necessary framework to calculate how many electrons are actually available to participate in conduction.

The discussion then moves to **Electrical Conductivity and Ohm’s Law**. By applying a classical approach to a quantum system (the Drude Model), we see that an electric field causes electrons to drift with a specific velocity. This motion is punctuated by collisions with the lattice, creating electrical resistance. This leads naturally into **Thermal Conductivity**, where we discover that in metals, electrons are the primary carriers of heat as well as charge. This dual responsibility is quantified by the **Wiedemann-Franz Law**, which proves that the ratio of thermal to electrical conductivity is a constant (the Lorenz number) multiplied by the absolute temperature. This law is a triumph of solid-state physics, as it links two seemingly different physical properties through a single carrier: the electron.

Finally, the lesson explores the **Motion in a Magnetic Field** and the **Hall Effect**. When a magnetic field is introduced, the Lorentz force acts on the moving electrons, pushing them to one side of the conductor. The resulting "Hall voltage" is a critical experimental tool, as it allows for the direct measurement of the carrier concentration and the sign of the charge carriers. This confirms that the current in metals is carried by negative electrons rather than positive charges.

In conclusion, the lesson synthesizes these topics to show that the macroscopic properties of metals—their shine, their heat, and their electricity—are all direct consequences of the quantum behavior of the electron gas.

10.9 TECHNICAL TERMS

Electrical conductivity and Ohm’s law
Thermal conductivity of metals
Wiedemann-Franz law
Motion of the magnetic field
Hall Effect

10.10 SELF-ASSESSMENT

1. Write about the Wiedemann-Franz field.
2. Discuss the thermal conductivity of metals.
3. What is the Hall effect?

10.11 SUGGESTED BOOKS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A.J. Dekker.
3. Solid State Physics, S.O. Pillai 7th Edition.
4. Solid State Physics, H.C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics &Solid State Physics by S.P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M.A. Wahab, Narosa publishing house.

Prof. Ch. Linga Raju

LESSON-11

THE BLOCH THEOREM

AIM:

To study the behavior of electrons in a **periodic crystal lattice** and to understand the form of the electron wavefunction using **Bloch's theorem**.

Objectives

- To analyze the motion of electrons in a **periodic potential** of a crystalline solid.
- To apply the **translational symmetry** of the lattice to the Schrödinger equation.
- To state and explain **Bloch's theorem** and its physical significance.
- To obtain the general form of the electron wavefunction known as a **Bloch function**.

STRUCTURE

11.1 Nearly free electron model

11.2 Origin of the energy potential

11.3 The Bloch theorem

11.4 Summary

11.5 Technical terms

11.6 Self assessment questions

11.7 Suggested readings

11.1 Nearly free electron model

The electronic properties of crystalline solids are governed by the behavior of electrons moving in a periodic potential created by the lattice of ions. Early attempts to understand electron motion in solids led to two limiting models: the **free electron model**, in which electrons move freely without any interaction with the lattice, and the **tight-binding model**, in which electrons are strongly bound to atoms. Real solids, however, lie between these two extremes.

The **nearly free electron (NFE) model** provides an improved and more realistic description by considering electrons that are almost free but experience a **weak periodic potential** due to the crystal lattice. This model successfully explains fundamental phenomena such as **energy band formation, band gaps at Brillouin zone boundaries, and the distinction between metals and insulators**.

Basic Assumptions of the Nearly Free Electron Model

The nearly free electron model is based on the following assumptions:

1. Electrons move in a **periodic potential** V(r) due to the regular arrangement of ions.
2. The periodic potential is **weak** compared to the kinetic energy of electrons.
3. Electron–electron interactions are neglected or treated approximately.
4. The crystal is infinite and perfectly periodic.

Under these assumptions, the behavior of electrons can be treated as a **small perturbation** of the free electron motion.

Schrödinger Equation in a Periodic Potential

The motion of an electron in a crystal is governed by the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Here, $V(r)$ is a periodic function satisfying:
$V(r+R)=V(r)$
where R is a lattice translation vector.
Because of this periodicity, the solutions of the Schrödinger equation are given by Bloch's theorem.

Effect of a Weak Periodic Potential

In the nearly free electron model, the periodic potential is treated as a **small perturbation** to the free electron states. The potential can be expanded as a Fourier series:

$$V(r) = \sum_{G} V_G e^{iG.r}$$

where G are reciprocal lattice vectors.
The weak periodic potential couples free electron states whose wave vectors differ by a reciprocal lattice vector. This coupling has significant effects near the Brillouin zone boundaries.

Free Electron Limit

If the periodic potential is neglected ($V=0$), the electron behaves as a free particle with energy:

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

This results in a parabolic energy–wave vector relation. However, this simple model fails to explain why real solids exhibit band gaps and why some materials are insulators rather than metals.

Physical Interpretation and Importance

The nearly free electron model provides a clear physical picture of how the crystal lattice modifies electron motion:

- Electrons propagate almost freely through the lattice.
- Periodic scattering by the lattice leads to standing waves at zone boundaries.
- These standing waves result in forbidden energy regions.

The model explains why:

- Metals have partially filled bands.
- Insulators and semiconductors have filled valence bands separated by band gaps.
- Electrical conductivity depends on band structure.

Applications of the Nearly Free Electron Model

The NFE model is particularly useful for:

- Alkali and noble metals
- Simple metals with weak ionic potentials
- Understanding Fermi surfaces
- Explaining electronic band structures in weakly bound solids

It forms the conceptual foundation for more sophisticated band structure methods.

Limitations of the Model

Despite its success, the nearly free electron model has limitations:

- Not suitable for strongly bound or covalent solids
- Neglects strong electron–electron interactions
- Cannot accurately predict band widths and gap sizes for complex materials

Nevertheless, it remains invaluable for building intuition about electronic structure.

Comparison with Other Models

- **Free electron model**: Ignores lattice effects completely.
- **Nearly free electron model**: Includes weak periodic potential.
- **Tight-binding model**: Assumes strong atomic binding.

The nearly free electron model occupies a central position between these two extremes.

Conclusion

The nearly free electron model represents a major step forward in understanding the electronic structure of crystalline solids. By incorporating the weak periodic potential of the lattice into the free electron picture, it successfully explains the formation of energy bands and band gaps, which are essential for distinguishing metals, semiconductors, and insulators.

For M.Sc. solid state physics, the nearly free electron model provides a clear and physically transparent framework that links quantum mechanics, crystal symmetry, and electronic properties of solids.

11.2 ORIGIN OF THE ENERGY POTENTIAL

In solid state physics, the concept of **energy potential** plays a central role in determining the electronic properties of crystalline solids. When atoms come together to form a solid, electrons no longer experience the potential of isolated atoms. Instead, they move under the influence of a **periodic potential** created by the regular arrangement of positively charged ion cores in a crystal lattice.

This periodic energy potential is responsible for the formation of **energy bands and forbidden energy gaps**, which ultimately determine whether a material behaves as a **metal, semiconductor, or insulator**.

Physical Origin of the Energy Potential

The total potential energy experienced by an electron in a crystal originates from several microscopic interactions:

(a) Coulomb Attraction due to Ion Cores

Each atom in a solid loses one or more valence electrons, becoming a **positively charged ion**. The remaining electrons move in the electrostatic (Coulomb) field of these ion cores.

Since the ions are arranged periodically in space, the electrostatic potential also becomes **periodic**.
Mathematically, this potential satisfies:
V(r+R)=V(r)
where R is a lattice translation vector.

(b) Electron–Electron Interaction (Screened Potential)

Electrons repel each other due to Coulomb repulsion. However, in solids, this interaction is **screened** by the presence of other electrons. As a result, the effective potential experienced by a single electron is weaker than the bare Coulomb potential.
In most band theory models, electron–electron interactions are either neglected or incorporated approximately into an **effective periodic potential**.

(c) Exchange and Correlation Effects

Due to the Pauli exclusion principle and quantum mechanical exchange effects, electrons with parallel spins avoid each other. These effects slightly modify the potential energy landscape but are generally included implicitly in advanced theories.

3. Periodic Nature of the Potential

The defining feature of the energy potential in a crystal is its **periodicity**, which arises directly from the periodic arrangement of atoms. Unlike isolated atoms where the potential is spherically symmetric, the potential in a solid varies periodically along each crystallographic direction.
This periodicity allows the potential to be expressed as a **Fourier series**:

$$V(r) = \sum_{G} V_G e^{iG.r}$$

where G are reciprocal lattice vectors.
This form is fundamental to the development of **Bloch's theorem** and modern band theory.

Importance in Solid State Physics

The origin of the energy potential explains several key phenomena:

- Electrical conductivity of solids
- Distinction between metals, semiconductors, and insulators
- Effective mass of electrons
- Optical and thermal properties

Hence, understanding the origin of the energy potential is fundamental to electronic band theory.

Conclusion

The energy potential in solids originates primarily from the **Coulomb attraction between electrons and periodically arranged ion cores**, modified by electron–electron interactions and quantum mechanical effects. Its periodic nature reflects the symmetry of the crystal lattice and forms the foundation of modern solid state physics. The periodic energy potential is the key factor responsible for the formation of energy bands and gaps, making it central to the understanding of electronic properties of crystalline materials.

11.3 THE BLOCH THEOREM

Suppose V(x) denotes the potential energy of an electron in a linear lattice of lattice constant a and that V(x) = V(x+a). i.e., the period of the potential is also a . The wave functions of the electron in this potential are then obtained from Schrodinger wave equation.

$\frac{\partial^2\Psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\Psi_0 = 0$

It has solutions of the form

$$\Psi(x) = e^{\pm ikx} u_k(x)$$

$u_k(x) = u_k(x+a)$

The solutions are plane waves $\Psi(x) = e^{\pm ikx}$ modulated by a function $u_k(x)$ which depends in general on the wave vector k and have periodicity of potential. This theorem is known as Bloch theorem . The function $u_k(x)$ is said to be bloch function.

$$\left.\begin{array}{ll} V(x) = 0 & 0 < x < a \text{ ----I region} \\ V(x) = V & -b < x < 0 \text{ --- II region} \end{array}\right\} \text{-------(1)}$$

$\frac{\partial^2\Psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E)\Psi_0 = 0$ --- I region ---(2)

$\frac{\partial^2\Psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\Psi_0 = 0$ ---- II region ---(3)

Let us define real quantities α and β by

$\alpha^2 = \frac{2mE}{\hbar^2}$ and $\beta^2 = \frac{2m(V-E)}{\hbar^2}$ (E <V)-----(4)

The equations are after substitution these constants

$\frac{\partial^2\Psi_0}{\partial x^2} + \alpha^2\Psi_0 = 0$ -------- (5)

$\frac{\partial^2\Psi_0}{\partial x^2} + \beta^2\Psi_0 = 0$ -------- (6)

Since the solution must have Bloch form. We may expect that

$$\Psi(x) = e^{-ikx} u_k(x) \quad \text{-------(7)}$$

Substituting (7) in (5) and (6) equations we get

$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} + (\alpha^2 - k^2)u_1 = 0$ ---------(8)

$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (\beta^2 + k^2)u_2 = 0$ ---------(9)

The solutions of these equations may be written as

$u_1 = A\,e^{i(\alpha-k)x} + B\,e^{-i(\alpha+k)x}$ ……..(10)

$u_2 = Ce^{(\beta-ik)x} + D\,e^{-(\beta+ik)x}$

Where A,B,C, and D are constants. These constants will be calculated by applying boundary conditions.

(1) $(u_1)_{x=0} = (u_2)_{x=0}$:

(2) $(\frac{du_1}{dx})_{x=0} = (\frac{du_2}{dx})_{x=0}$: -------(11)

(3) $(u_1)_{x=a} = (u_2)_{x=-b}$:

(4) $(\frac{du_1}{dx})_{x=a} = (\frac{du_2}{dx})_{x=-b}$:

Applying the boundary equations to the equations (10) it gives.

$$A + B = C + D \qquad \text{----------------(12)}$$

$$A\, i(\alpha-k) - B\, i(\alpha+k) = C(\beta - ik) - D(\beta + ik) \qquad \text{---------------(13)}$$

$$A\, e^{i(\alpha-k)a} + B e^{-i(\alpha+k)a} = C\, e^{-(\beta - ik)b} + D\, e^{(\beta + ik)b} \quad \text{-----(14)}$$

$$A\, i(\alpha-k) e^{i(\alpha-k)a} \_\_ B\, i(\alpha+k)\, e^{-i(\alpha+k)a} = C(\beta - ik)\, e^{-(\beta - ik)b} \_\_ D(\beta + ik) e^{(\beta + ik)b} \text{----(15)}$$

These equations will have no zero solution only if the determinant of the coefficient of A,B,C,D vanishes. This leads to the following equations.

$$\frac{(\beta^2-\alpha^2)}{2\alpha\beta} \sin h\beta b \sin \alpha a + \cos h\beta b \cos \alpha a = \cos k(a+b)$$

V → ∞ b→ 0 $\sin h\beta b$ = βb, and $\cos h\beta b = 1$

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

Since $\beta^2 = \frac{2m(V-E)}{\hbar^2}$ and $\alpha^2 = \frac{2mE}{\hbar^2}$

$\beta^2 \text{--}\ \alpha^2 = \frac{2m(V-2E)}{\hbar^2}$ since V>>2E

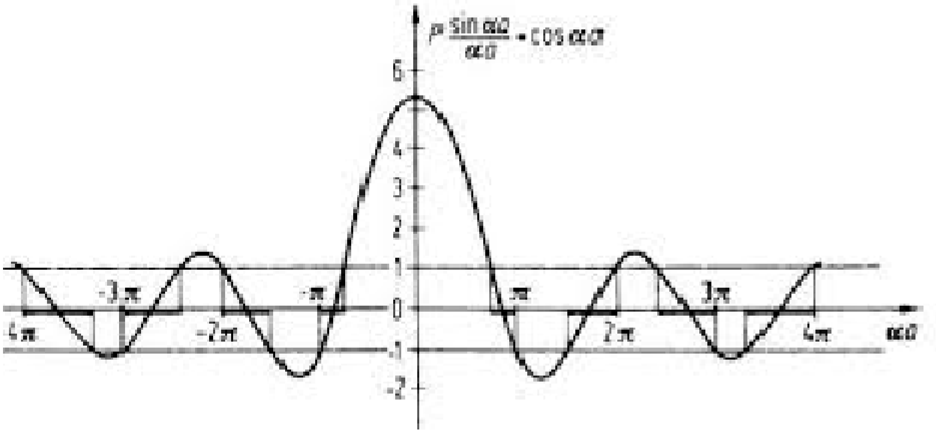
$\beta^2 \text{--}\ \alpha^2 \approx \frac{2mV}{\hbar^2}$

Multiplying numerator and denominator with a we get

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

Let $P = \frac{mVab}{\hbar^2}$ is called scattering power

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



The left side of the equation imposes a limitation on the values that the right side function can have, namely, a maximum value of +1 and a minimum value of -1. Hence only certain range of values of α are allowed.

Conclusions of the results:

1) Allowed bands are shown in figure . There are allowed bands and in between there are forbidden bands.
2) As the value of α increases the width of the allowed energy bands also increases and the width of the forbidden band decreases.
3) If the potential barrier strength P is large, the function described by the right hand side of the equation crosses +1 and -1 region at a steeper angle. Thus the allowed bands become narrower and forbidden bands become wider.

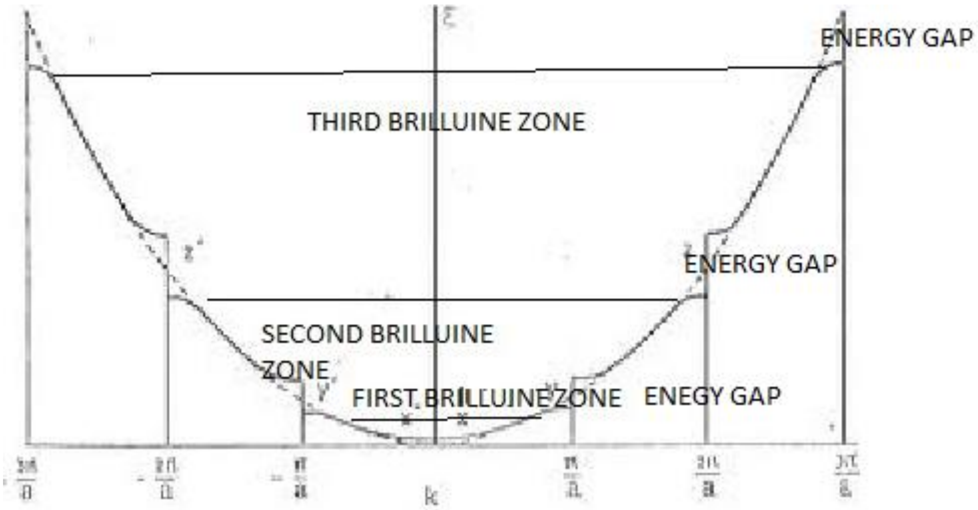
4) In the limit P → ∞ the allowed band reduces to onle single energy level corresponding to the discrete energy level of an isolated atom.
5) In the other extreme case when P→0

$\cos ka = \cos \alpha a$

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

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

This indicates that the particle is completely free and no energy levels exist.



$$K = \frac{+n\pi}{-a}$$

When n =1 First Brillouin zone extends from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ Similarly for n=2 second brilluin zone.

11.4 SUMMARY

The nearly free electron (NFE) model describes electrons in a crystalline solid as **almost free particles** moving under the influence of a **weak periodic potential** due to the lattice ions. It is an improvement over the free electron model and provides a realistic picture of electron behavior in simple metals.

In this model, the Schrödinger equation includes a weak periodic potential V(r). The periodicity of the lattice causes coupling between electron states whose wave vectors differ by a reciprocal lattice vector. This interaction becomes significant near **Brillouin zone boundaries**, where free electron energy levels are degenerate.

The **energy (periodic) potential** in a solid originates primarily from the **Coulomb attraction between electrons and the positively charged ion cores** arranged periodically in a crystal lattice. When isolated atoms come together to form a solid, their individual atomic potentials overlap, producing a **periodic potential field**.

Bloch's theorem is a fundamental result in solid state physics that describes the form of electron wavefunctions in a periodic potential. It states that the solutions of the Schrödinger equation for an electron in a crystal can be written as:

$$\Psi(x) = e^{-ikx} u_k(x)$$

where $u_k(x)$ has the same periodicity as the lattice.

11.5 TECHNICAL TERMS

Nearly free electron
Origin of the energy potential
The Bloch theorem

11.6 SELF ASSESSMENT QUESTIONS

1. Write about the nearly free electron
2. Explain about the Origin of the energy potential
3. Briefly explain about the the Bloch theorem

11.7 SUGGESTED READINGS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
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5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
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LESSON-12

KRONIG-PENNY MODEL

Aim:

To study the motion of an electron in a **one-dimensional periodic potential** and to understand the **origin of allowed energy bands and forbidden energy gaps** in crystalline solids using the Kronig–Penney model.

To formulate and analyze the **Schrödinger wave equation** for an electron moving in a **periodic lattice potential** and to understand how lattice periodicity modifies free-electron behavior in crystalline solids.

Objectives:

- To represent the crystal lattice potential by a **simplified periodic potential**.
- To apply the **time-independent Schrödinger equation** to an electron moving in a periodic field.
- To use **Bloch's theorem** to obtain permissible solutions of the wavefunction.
- To derive the **dispersion relation** between energy and crystal wave vector.
- To explain the formation of **energy bands and forbidden gaps** at Brillouin zone boundaries.
- To establish the theoretical basis of **electronic band structure** in solids.
- To incorporate the **periodic potential of the crystal lattice** into the Schrödinger equation.
- To study the consequences of **translational symmetry** in crystalline solids.
- To apply **Bloch's theorem** to obtain the general form of the electron wavefunction.
- To understand the concept of **Bloch waves** and crystal wave vector k.
- To explain the formation of **energy bands and forbidden energy gaps**.
- To distinguish between **free electron motion** and electron motion in a periodic potential.
- To provide a theoretical foundation for **nearly free electron, Kronig–Penney, and tight-binding models**.

STRUCTURE

12.1 KRONIG-PENNY MODEL

One of the most important problems in solid state physics is understanding how the **periodic arrangement of atoms in a crystal** affects the motion and energy of electrons.

While free electrons have a continuous energy spectrum, electrons in a crystal exhibit **allowed energy bands and forbidden energy gaps**. The **Kronig–Penney model** is a simplified but powerful theoretical model that demonstrates how a **periodic potential** leads naturally to the formation of energy bands.

Proposed by **R. de L. Kronig and W. G. Penney (1931)**, this model provides a clear mathematical foundation for **energy band theory** and serves as a bridge between the **nearly free electron model** and more realistic band-structure calculations.

2. Physical Basis of the Kronig–Penney Model

In a crystalline solid, positively charged ion cores are arranged periodically. An electron moving through the crystal experiences an **effective periodic potential** due to these ions. The Kronig–Penney model replaces the complicated real potential by a **one-dimensional periodic array of rectangular potential wells or barriers**, which retains the essential physics while remaining mathematically tractable.

The model assumes:

- Motion of electrons in **one dimension**
- A **periodic potential** with period aaa
- Non-interacting electrons
- Perfect crystal without defects

Despite its simplicity, the model captures the essential feature of **band formation**.

Form of the Periodic Potential

The Kronig–Penney potential consists of a repeating sequence of potential wells and barriers:

- Potential height: V_0
- Barrier width: b
- Well width: a–b
- Period of the lattice: a

Mathematically, the potential satisfies:

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

This periodicity allows the use of **Bloch's theorem** to solve the Schrödinger equation.

Schrödinger Equation for the Model

The time-independent Schrödinger equation for an electron of mass m is:

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

Since the potential is piecewise constant, the equation is solved separately in the **well region** and the **barrier region**.

5. Solutions in Different Regions

(a) Region I: Inside the Potential Well

Here, $V(x) = V_0$ and the Schrödinger equation becomes:

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

The general solution is:

$$\psi_I(x) = Ae^{ikx} + Be^{-ikx}$$

(b) Region II: Inside the Potential Barrier
Here, V(x)=V0V(x) = V_0V(x)=V0 and for E<V0E < V_0E<V0:
d2ψdx2−κ2ψ=0\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0dx2d2ψ−κ2ψ=0
where

$$\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

The solution is:

$$\psi_{II}(x) = Ce^{\kappa x} + De^{-\kappa x}$$

Boundary Conditions
To obtain a physically acceptable solution, the wavefunction and its first derivative must be **continuous** at the boundaries between regions. Applying these boundary conditions leads to a set of linear equations for the constants A,B,C,A, B, C,A,B,C, and DDD.
However, the most important constraint arises from **Bloch's theorem**.
Using Bloch's condition along with boundary conditions, one obtains the **Kronig–Penney dispersion relation**, which relates the electron energy to the crystal wave vector.

Kronig–Penney Dispersion Relation
After applying continuity and Bloch conditions, the final result is:

$$\cos(ka) = \cos[k(a-b)]\cosh(\kappa b) + \frac{\kappa^2 - k^2}{2k\kappa}\sin[k(a-b)]\sinh(\kappa b)$$

This transcendental equation determines the **allowed and forbidden energy regions**.

1. physical interpretation

The Kronig–Penney model provides a clear physical explanation for band formation:

- At Brillouin zone boundaries, electron waves are **Bragg reflected**
- Standing waves are formed
- Degeneracy of energy levels is lifted
- Energy gaps appear

The stronger the periodic potential, the wider the energy gaps.

2. Limiting Cases

(a) Free Electron Limit

If V0→0, the dispersion relation reduces to that of free electrons:

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

(b) Strong Potential Limit

For very large V_0, electrons become localized near ions, and the band width decreases, approaching the **tight-binding limit**.

Significance of the Kronig–Penney Model

The model is significant because it:

- Provides the **first rigorous proof** of energy band formation
- Explains the origin of **band gaps**
- Validates Bloch's theorem
- Forms the foundation of modern electronic band theory

It is extensively used as a pedagogical model in M.Sc. solid state physics.

1. Limitations of the Model

Despite its importance, the Kronig–Penney model has limitations:

- One-dimensional approximation
- Oversimplified potential
- Neglects electron–electron interaction
- Not quantitatively accurate for real solids

Nevertheless, it remains invaluable for conceptual understanding.

Conclusion

The Kronig–Penney model is a cornerstone of solid state physics. By introducing a simple periodic potential and applying Bloch's theorem, it clearly demonstrates how **energy bands and forbidden gaps** arise in crystalline solids. Although idealized, the model provides deep physical insight and forms the conceptual basis for understanding the electronic structure of materials

12.2 WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL

In solid state physics, the behavior of electrons in a crystalline solid is fundamentally different from that of free electrons. Unlike free space, a crystal consists of atoms arranged in a **regular periodic lattice**, and an electron moving through such a lattice experiences a **periodic potential** due to the positively charged ion cores. The study of the **wave equation of an electron in a periodic potential** is therefore central to understanding the **electronic properties of solids**, such as electrical conductivity, band structure, optical properties, and thermal behavior.

The mathematical description of electron motion in a crystal begins with the **Schrödinger wave equation** modified to include a periodic potential. The solutions of this equation lead to the concept of **Bloch waves**, energy bands, and forbidden energy gaps, which are the foundation of modern band theory.

Periodic Potential in a Crystal

When isolated atoms combine to form a solid, their individual atomic potentials overlap. The resulting potential experienced by an electron reflects the **periodicity of the crystal lattice**. If R\mathbf{R}R denotes a lattice translation vector, the potential energy function satisfies:

V(r+R)=V(r)

This periodicity is the defining feature of crystalline solids and distinguishes them from amorphous materials. The periodic potential arises mainly from:

- Coulomb attraction between electrons and ion cores
- Screened electron–electron interactions
- Exchange and correlation effects

For theoretical treatment, these contributions are combined into an **effective periodic potential**.

Schrödinger Wave Equation in a Periodic Potential

The time-independent Schrödinger equation for an electron of mass m moving in a periodic potential V(r) is given by:

$$-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

This equation is known as the **wave equation of an electron in a periodic potential**. Unlike the free electron case (V=0), this equation cannot be solved exactly for arbitrary V(r). However, the periodicity of the potential allows powerful symmetry-based methods to be used.

Fourier Expansion of the Periodic Potential

The periodic potential can be expressed as a Fourier series:

$$V(r) = \sum_G V_G e^{iG.r}$$

Similarly, the periodic part of the wavefunction can also be expanded:

$$u_k(r) = \sum_G C_G e^{iG.r}$$

Substituting these expansions into the Schrödinger equation transforms the wave equation into a set of **coupled algebraic equations**.

Free Electron and Weak Potential Limits

(a) Free Electron Case

If V(r)=0 the wave equation reduces to:

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

This corresponds to free electrons with a continuous energy spectrum.

(b) Weak Periodic Potential

For weak potentials, the energy deviates slightly from the free electron value except near **Brillouin zone boundaries**, where strong coupling occurs and energy gaps appear.

Physical Consequences of the Wave Equation

The wave equation of an electron in a periodic potential explains several important phenomena:

- Formation of energy bands and gaps
- Effective mass of electrons

- Electrical conductivity of solids
- Distinction between metals, semiconductors, and insulators

These properties cannot be explained by free electron theory alone.

Applications in Solid State Physics

The wave equation in a periodic potential forms the basis of:

- Nearly free electron model
- Kronig–Penney model
- Tight-binding approximation
- Semiconductor physics
- Modern band structure calculations

It is fundamental to understanding electronic transport and optical processes in solids.

Limitations of the Approach

Despite its importance, this treatment has limitations:

- Exact solutions are not possible for real crystals
- Electron–electron interactions are treated approximately
- Lattice imperfections are neglected

Advanced theories such as density functional theory build upon this basic framework.

Conclusion

The wave equation of an electron in a periodic potential is the cornerstone of solid state physics. By incorporating the periodicity of the crystal lattice into the Schrödinger equation and applying Bloch's theorem, it provides a unified framework for understanding the electronic structure of solids. The resulting concepts of **Bloch waves, energy bands, and forbidden gaps** are essential for explaining the electrical, thermal, and optical properties of materials.

12.3 SUMMARY

The **Kronig–Penney model** is a simplified one-dimensional model used to explain the **origin of energy bands and forbidden energy gaps** in crystalline solids. In this model, the complex periodic potential of a real crystal is approximated by a **periodic array of rectangular potential wells or barriers**. Despite its simplicity, the model captures the essential physics of electron motion in a periodic lattice.

An electron moving in this periodic potential obeys the **time-independent Schrödinger equation**. Since the potential is periodic with lattice constant a, **Bloch's theorem** is applied to the wave function:

$$\psi(x+a) = e^{ika}\psi(x)$$

Solving the Schrödinger equation in the well and barrier regions and applying boundary and Bloch conditions leads to the **Kronig–Penney dispersion relation**, which relates electron energy E to the crystal wave vector k.

In a crystalline solid, an electron experiences a **periodic potential** arising from the regular arrangement of ion cores. The motion of such an electron is described by the **Schrödinger wave equation**:

$$-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where the potential satisfies:
$V(r+R)=V(r)$
The periodicity of the potential leads to **translational symmetry**, allowing the application of **Bloch's theorem**. According to this theorem, the electron wavefunction can be written as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

where $u_k(r)$ has the same periodicity as the lattice.
This form of the wavefunction implies that electron states are characterized by a **crystal wave vector** k, and their energies form **continuous bands** rather than discrete levels. By expanding the periodic potential and wavefunction in Fourier series, the Schrödinger equation reduces to a set of coupled equations whose solutions yield the **energy band structure**.

12.4 TECHNICAL TERMS

Kronig-Penny Model
Wave equation of electron in a periodic potential

12.5 SELF ASSESSMENT QUESTIONS

1. Briefly explain about the Kronig-Penny Model
2. Write about the Wave equation of electron in a periodic potential

12.6 SUGGESTED READINGS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

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LESSON-13

EFFECTIVE MASS OF ELECTRON

Aim:

To introduce the concept of **effective mass** and to understand how the motion of an electron in a crystal lattice differs from that of a free electron.
To classify solids into **metals, insulators, and semiconductors** on the basis of **energy band theory** and to understand their electrical behavior.

Objectives:

- To study the influence of the **periodic lattice potential** on electron dynamics.
- To define effective mass in terms of the **curvature of the energy band**.
- To understand the significance of **positive and negative effective mass**.
- To explain the concept of **holes** in the valence band.
- To apply the effective mass concept to explain **electrical conduction and transport phenomena** in solids.
- To treat electrons in crystals as **quasi-particles** for simplified analysis.
- To study the **energy band structure** of solids.
- To analyze the role of the **valence band, conduction band, and forbidden energy gap**.
- To understand the significance of the **Fermi level** in determining electrical properties.
- To distinguish between metals, insulators, and semiconductors based on **band gap and band occupancy**.
- To explain the **temperature dependence of electrical conductivity**.
- To understand the importance of **semiconductors in electronic devices**.

STRUCTURE

13.1 APPROXIMATION SOLUTION NEAR ZONE BOUNDARY

In solid state physics, the behavior of electrons in a crystal is governed by the Schrödinger equation in the presence of a **periodic lattice potential**. Exact solutions of this equation are generally not possible for real crystals. However, important physical insight can be obtained by studying **approximate solutions** in specific regions of reciprocal space. One such crucial region is the **Brillouin zone boundary**, where the effects of the periodic potential are most pronounced.

Near the zone boundary, free-electron energy levels become **degenerate**, and even a weak periodic potential causes a significant modification of the electron energy spectrum. The approximate solution near the zone boundary explains the **opening of energy gaps**, which is a central result of band theory. This treatment forms the theoretical basis of the **nearly free electron model**.

Electron in a Periodic Potential

The motion of an electron in a crystal is described by the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where V(r) is the periodic potential satisfying:

$V(r+R)=V(r)$

Using Bloch's theorem, the electron wavefunction can be written as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

Free Electron Approximation and Its Breakdown

If the periodic potential is neglected, the electron behaves as a free particle with energy:

$$E_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

In this **free-electron approximation**, the energy spectrum is continuous and parabolic. However, this approximation fails near certain values of k, specifically at the **Brillouin zone boundaries**, where the Bragg condition is satisfied:

$k = \frac{G}{2}$

At these points, two or more free-electron states become degenerate, and the periodic potential can no longer be treated as a small perturbation.

Physical Meaning of the Zone Boundary

The Brillouin zone boundary corresponds to the condition where the electron wavelength is comparable to the lattice spacing. Under this condition, the electron wave undergoes **Bragg reflection** from the crystal planes.

As a result:

- Electron waves traveling in opposite directions interfere strongly
- Standing waves are formed
- Degenerate energy levels split

This splitting gives rise to **forbidden energy gaps**, which are absent in the free-electron model.

Approximation Near the Zone Boundary

To obtain an approximate solution near the zone boundary, we consider a **weak periodic potential** and focus only on the most important Fourier component V_G. Other components are neglected since their contribution is small.

Let the electron wave vector be close to the zone boundary:

$$\mathbf{k} \approx \frac{\mathbf{G}}{2}$$

Two-Wave Approximation

In the **two-wave approximation**, the Bloch wavefunction is written as a linear combination of two plane waves:

$$\psi(\mathbf{r}) = C_1 e^{i\mathbf{k}\cdot\mathbf{r}} + C_2 e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}$$

Substituting this form into the Schrödinger equation and using the Fourier expansion of the potential, one obtains a pair of coupled linear equations for the coefficients C_1 and C_2.

Coupled Equations and Energy Eigenvalues

The coupled equations can be written as:

$$(E_0(\mathbf{k}) - E)\, C_1 + V_{\mathbf{G}} C_2 = 0$$

$$V_{\mathbf{G}}^* C_1 + (E_0(\mathbf{k} - \mathbf{G}) - E)\, C_2 = 0$$

For non-trivial solutions, the determinant of the coefficients must vanish:

$$\begin{vmatrix} E_0(\mathbf{k}) - E & V_{\mathbf{G}} \\ V_{\mathbf{G}}^* & E_0(\mathbf{k} - \mathbf{G}) - E \end{vmatrix} = 0$$

Solving this determinant yields the approximate energy eigenvalues.

Energy Splitting at the Zone Boundary

At the exact zone boundary:

$k = \frac{G}{2}$

we have:

$$E_0(\mathbf{k}) = E_0(\mathbf{k} - \mathbf{G})$$

The energy eigenvalues then become:

$$E = E_0 \pm |V_{\mathbf{G}}|$$

Thus, the degeneracy of the free-electron states is lifted, and an **energy gap** of magnitude:

$$\Delta E = 2|V_{\mathbf{G}}|$$

appears at the Brillouin zone boundary.

Dispersion Relation Near the Zone Boundary

Away from the exact zone boundary, the energy eigenvalues are given approximately by:

$$E(\mathbf{k}) = \frac{1}{2}\left[E_0(\mathbf{k}) + E_0(\mathbf{k} - \mathbf{G})\right] \pm \sqrt{\frac{E_0(\mathbf{k}) - E_0(\mathbf{k} - \mathbf{G})}{2}^{2} + |V_{\mathbf{G}}|^2}$$

This expression shows how the free-electron parabolic energy curve is modified near the zone boundary, resulting in two branches separated by an energy gap.

Effective Mass Near Band Edges

Near the edges of the energy bands, the curvature of the E−k relation changes. This leads to the concept of **effective mass**:

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$

The effective mass may differ significantly from the free-electron mass and can even become negative near the top of a band, which is essential for understanding **hole conduction**.

Significance of the Approximate Solution

The approximate solution near the zone boundary explains several fundamental features of solids:

- Formation of forbidden energy gaps
- Origin of energy bands
- Difference between metals, semiconductors, and insulators
- Role of weak periodic potential in modifying free-electron motion

This approach forms the core of the **nearly free electron model**.

Limitations of the Approximation

Although highly instructive, the approximation has limitations:

- Valid only for weak periodic potentials
- Considers only a small number of plane waves
- Not suitable for strongly bound electrons

Nevertheless, it provides deep physical insight into band structure formation.
Together, these models give a comprehensive understanding of electron behavior in solids.

Conclusion

The approximate solution of the electron wave equation near the Brillouin zone boundary is a cornerstone of solid state physics. By considering the interaction between nearly degenerate free-electron states and a weak periodic potential, it clearly explains the **splitting of energy levels and the formation of forbidden energy gaps**. This treatment provides a powerful and physically transparent explanation of band structure and underpins the modern theory of electronic properties of crystalline solids.

13.2 EFFECTIVE MASS OF ELECTRON

In free space, an electron behaves as a particle with a constant mass mmm, and its motion under an external force is well described by Newton’s laws and quantum mechanics. However, in a **crystalline solid**, electrons do not move freely; instead, they move through a **periodic potential** created by the regular arrangement of atoms in the lattice. As a result, their response to external forces such as electric and magnetic fields differs significantly from that of free electrons.

To account for this modified behavior, the concept of **effective mass** is introduced. The effective mass allows electrons in a crystal to be treated as if they were free particles, but with a modified mass that incorporates the influence of the lattice potential. This concept is central to understanding **electrical conduction, carrier dynamics, optical properties, and semiconductor physics**.

Origin of the Concept of Effective Mass

The need for effective mass arises from the **band structure** of solids. When electrons move in a periodic potential, their allowed energies form **energy bands** rather than discrete levels. The relation between energy E and crystal wave vector k, known as the **dispersion relation**, deviates from the simple free-electron parabolic form:

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

In a crystal, the dispersion relation is generally more complex. However, near the extrema (minima or maxima) of energy bands, the E−k relation can often be approximated by a parabola. In this region, electron motion can still be described in a free-particle-like manner by introducing an **effective mass**.

Semi classical Motion of Electrons in a Crystal

The effective mass concept emerges naturally from the **semi classical theory of electro dynamics**. In this approach:

- Electrons are described by wave packets of Bloch waves
- Their motion in real space follows classical equations of motion
- Their energy and momentum are governed by quantum mechanics

The velocity of an electron in a band is given by:

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k})$$

When an external force F acts on the electron, the crystal momentum changes according to:

$$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F}$$

These equations form the basis for defining the effective mass.

Derivation of Effective Mass

Differentiating the velocity with respect to time:

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \frac{1}{\hbar} \frac{d}{dt} (\nabla_{\mathbf{k}} E)$$

Using the chain rule and the force equation:

$$\mathbf{a} = \frac{1}{\hbar^2} (\nabla_{\mathbf{k}} \nabla_{\mathbf{k}} E)\, \mathbf{F}$$

In one dimension, this simplifies to:

$$a = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F$$

Comparing this with Newton's second law F=m*a, the **effective mass m*** is defined as:

$$\boxed{\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}}$$

This expression shows that the effective mass depends on the **curvature of the energy band**.

Physical Interpretation of Effective Mass

The effective mass reflects how strongly the periodic lattice potential modifies electron motion:

- **Large curvature** of the E−k curve → small effective mass
- **Small curvature** → large effective mass

Thus, electrons near the bottom of a conduction band, where the curvature is large, behave as light particles and respond easily to external fields. Conversely, electrons in flatter bands have large effective masses and move more sluggishly.

Effective Mass in Free Electron Case

For a free electron:

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

Differentiating twice with respect to k:

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

Substituting into the effective mass expression:

$m^* = m$

Thus, the effective mass reduces to the actual electron mass in the absence of a periodic potential.

Effective Mass in Nearly Free Electron Model

In the nearly free electron model, the periodic potential slightly perturbs the free-electron dispersion. Near **Brillouin zone boundaries**, the curvature of the energy bands changes significantly due to band splitting.

As a result:

- Effective mass near band edges can differ greatly from m
- Effective mass may increase or decrease depending on the strength of the periodic potential

This explains why electrons in simple metals and semiconductors exhibit different transport properties.

Role of Effective Mass in Electrical Conductivity

The electrical conductivity σ of a material is given by:

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

where:

- n is the carrier concentration

- e is the electronic charge
- τ is the relaxation time

A smaller effective mass leads to higher conductivity, highlighting the importance of band curvature in determining material properties.

Effective Mass and Optical Properties

Effective mass also influences optical phenomena such as:

- Absorption edge in semiconductors
- Cyclotron resonance frequency
- Plasma frequency

The cyclotron frequency is given by:

$$\omega_c = \frac{eB}{m^*}$$

Thus, experimental measurement of ω provides a direct method for determining effective mass.

Experimental Determination of Effective Mass

Effective mass can be measured using:

- Cyclotron resonance
- Shubnikov–de Haas oscillations
- Optical absorption experiments

These methods confirm that effective mass varies widely between materials and even between different bands in the same material.

Limitations of the Effective Mass Approximation

Although extremely useful, the effective mass approximation has limitations:

- Valid mainly near band extrema
- Fails for strongly non-parabolic bands
- Does not include many-body interactions explicitly

Advanced theories extend this concept using energy-dependent effective mass.

Conclusion

The effective mass of an electron is a fundamental concept in solid state physics that encapsulates the influence of the crystal lattice on electron motion. By relating electron dynamics to the curvature of the energy band structure, the effective mass provides a powerful and intuitive way to understand electrical, optical, and transport properties of solids. It allows complex quantum mechanical behavior to be treated using classical equations of motion with modified parameters.

13.3 THE DISTINCTION BETWEEN METALS, INSULATORS AND SEMICONDUCTORS

One of the central problems in solid state physics is to understand why different solids exhibit vastly different **electrical conductivities**. Some materials such as copper and silver conduct electricity extremely well, while others like glass and rubber are excellent insulators. Between these two extremes lie **semiconductors**, whose conductivity can be controlled by temperature, impurities, and external fields.

The fundamental distinction between **metals, insulators, and semiconductors** arises from the **quantum mechanical energy band structure** of electrons in a crystalline solid. According to band theory, electrons in a solid can occupy only certain allowed energy ranges called **energy bands**, separated by forbidden regions known as **band gaps**. The way these bands are filled with electrons determines the electrical behavior of the material.

When isolated atoms come together to form a crystal, the discrete atomic energy levels broaden into bands due to the interaction between neighboring atoms. The most important bands for electrical conduction are:

- **Valence band (VB):** The highest occupied energy band at absolute zero
- **Conduction band (CB):** The lowest unoccupied or partially occupied band above the valence band
- **Forbidden energy gap (band gap, E_g)**: The energy separation between VB and CB where no allowed electron states exist

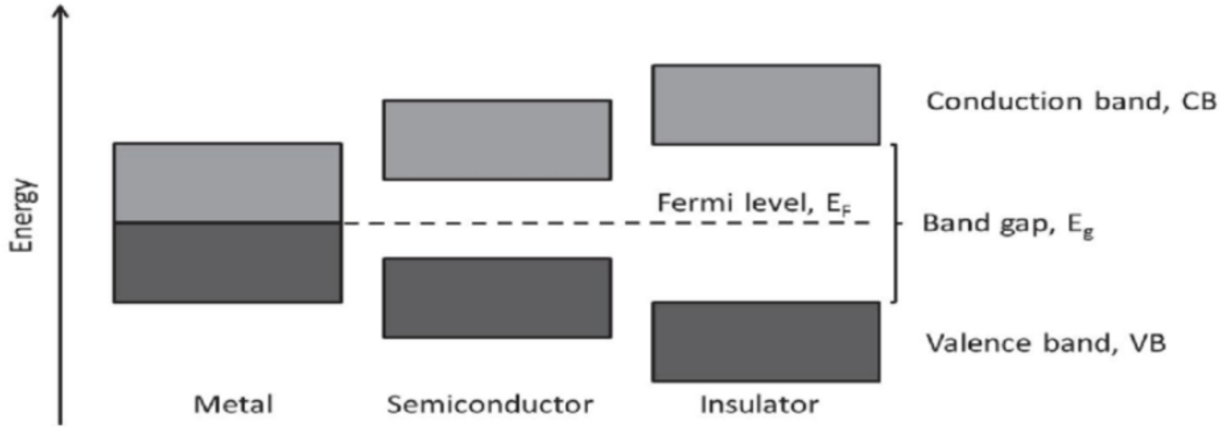
Electrical conduction depends on:

1. The availability of free charge carriers
2. The ease with which electrons can be excited to higher energy states

Metals

Band Structure of Metals

In metals, the valence band is either **partially filled** or **overlaps with the conduction band**. As a result, electrons can move freely under the influence of even a small applied electric field.



Key Features

- No forbidden energy gap at the Fermi level
- Large number of free electrons available for conduction
- High electrical conductivity even at low temperatures

In many metals, such as sodium and copper, the conduction band overlaps with the valence band. In others, the highest occupied band is only partially filled, allowing electrons to gain energy and move to nearby empty states without crossing a band gap.

Temperature Dependence

The conductivity of metals **decreases with increasing temperature** due to enhanced electron–phonon scattering, even though the number of charge carriers remains nearly constant.

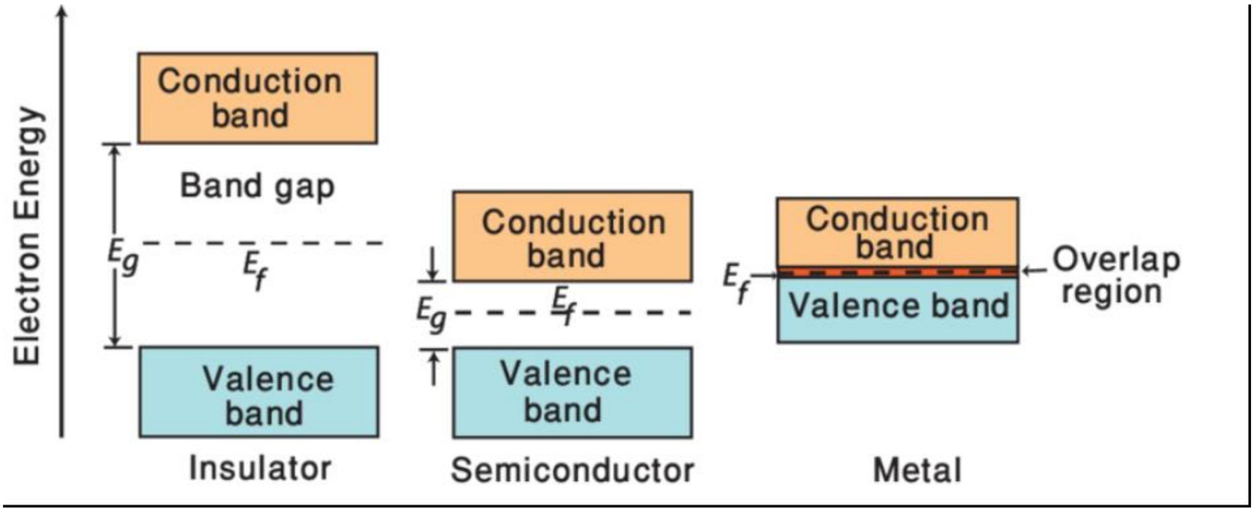
EXAMPLES

Copper, silver, gold, aluminum, iron

Insulators

Band Structure of Insulators

In insulators, the valence band is completely filled and the conduction band is completely empty, separated by a **large energy gap**.



Key Features

- Large band gap (E_g>3 eV)
- Negligible number of free charge carriers at room temperature
- Extremely low electrical conductivity

Because the band gap is very large, thermal energy at room temperature is insufficient to excite electrons from the valence band to the conduction band.

Temperature Dependence

Even at high temperatures, very few electrons can cross the large band gap. Hence, insulators remain poor conductors under normal conditions.

Examples

Diamond, glass, mica, rubber, ceramics

Semiconductors

Band Structure of Semiconductors

Semiconductors have a **moderate energy gap** between the valence and conduction bands.

- Small band gap (Eg≈0.1–3 eV)
- At absolute zero: valence band full, conduction band empty
- At room temperature: some electrons are thermally excited to the conduction band

The electrons excited into the conduction band contribute to electrical conduction, while the vacancies left behind in the valence band behave as **holes**, which also act as charge carriers.

Intrinsic Semiconductors

In a pure semiconductor:

- Number of electrons = number of holes
- Conductivity increases rapidly with temperature

Extrinsic Semiconductors

By adding small amounts of impurities (doping):

- **n-type:** extra electrons

- **p-type:** extra holes

This controllable conductivity is the key reason semiconductors are used in electronic devices.

Examples

Silicon, germanium, gallium arsenide

Fermi Level and Its Role

The **Fermi level** is the energy level at which the probability of electron occupation is 50% at thermal equilibrium.

- **Metals:** Fermi level lies inside a band
- **Insulators:** Fermi level lies in the middle of a large band gap
- **Semiconductors:** Fermi level lies within a small band gap

The position of the Fermi level plays a decisive role in determining the electrical properties of solids.

Electrical Conductivity Comparison

Property	**Metals**	**Semiconductors**	**Insulators**
Band gap	Zero / overlap	Small	Large
Charge carriers	Many electrons	Electrons + holes	Almost none
Conductivity	Very high	Moderate, controllable	Very low
Temperature effect	Conductivity decreases	Conductivity increases	Slight increase

Physical Explanation Using Band Theory

The distinction among metals, semiconductors, and insulators can be fully explained using **quantum mechanics and band theory**, without invoking classical free-electron ideas alone. The presence or absence of available energy states near the Fermi level determines whether electrons can respond to an external electric field.

Importance in Solid State Physics

Understanding this distinction is fundamental for:

- Electronic materials design
- Semiconductor device fabrication
- Solid-state electronics
- Modern technologies such as transistors, solar cells, LEDs, and integrated circuits

Exam-Oriented Summary

- **Metals:** No band gap → high conductivity
- **Insulators:** Large band gap → negligible conductivity
- **Semiconductors:** Small band gap → temperature and doping dependent conductivity
- Electrical properties are governed by **band structure and Fermi level position**

Conclusion

The distinction between metals, insulators, and semiconductors is one of the most important outcomes of band theory in solid state physics. By examining the arrangement and occupancy of energy bands, we gain a unified and powerful explanation for the electrical behavior of solids. This classification not only enhances our theoretical understanding but also forms the foundation of modern electronic and semiconductor technology.

13.4 SUMMARY

The approximation solution near a zone boundary explains the formation of **energy band gaps** due to Bragg reflection in a periodic lattice. The concept of **effective mass** describes how electrons respond to external forces within a crystal. Together with **band theory**, these ideas provide a complete explanation for the distinction between **metals, semiconductors, and insulators**, forming the foundation of modern solid state physics.

13.5 TECHNICAL TERMS

Approximation solution near a zone boundary
Effective mass of electron
metals, insulators and semiconductors

13.6 SELF ASSESSMENT QUESTIONS

1. Write about the Approximation solution near a zone boundary.
2. Explain about the Effective mass of electron.
3. Briefly explain about the distinguish between the metals, insulators and semiconductors

13.7 SUGGESTED READINGS

1. Introduction to Solid State Physics, C. Kittel, 5th Edition.
2. Solid State Physics, A. J. Dekker.
3. Solid State Physics, S. O. Pillai, 7th Edition.
4. Solid State Physics, H. C. Gupta, Vikas Publisher, Noida, 2nd Edition.
5. Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics, by S. P. Kuila, Books and Allied, Kolkata.
6. Solid State Physics, M. A. Wahab, Narosa Publishing House.

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