M.Sc. Final Year
Physics, MP-08(B)

ADVANCED SOLID STATE PHYSICS

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल
MADHYA PRADESH BHOJ (OPEN) UNIVERSITY - BHOPAL

Reviewer Committee

1. Dr. S.K.Vijay
   Professor
   Govt. MLB College, Bhopal (M.P.)

2. Dr. Seema Hardikar
   Professor
   Sarojini Naidu Govt Girls PG (Autonomous) College, Bhopal (M.P.)

3. Dr. Ankit Goyana
   Asst Professor (Guest Faculty)
   Institute for Excellence in Higher Education, Bhopal (M.P.)

……

Advisory Committee

1. Dr. Jayant Sonwalkar
   Hon'ble Vice Chancellor
   Madhya Pradesh Bhoj (Open) University, Bhopal (M.P.)

2. Dr. L.S.Solanki
   Registrar
   Madhya Pradesh Bhoj (Open) University, Bhopal (M.P.)

3. Dr. Neelam Wasnik
   Dy Director Printing
   Madhya Pradesh Bhoj (Open) University, Bhopal (M.P.)

4. Dr. S.K.Vijay
   Professor
   Govt. MLB College, Bhopal (M.P.)

5. Dr. Seema Hardikar
   Professor
   Sarojini Naidu Govt Girls PG (Autonomous) College, Bhopal (M.P.)

6. Dr. Ankit Goyana
   Asst Professor (Guest Faculty)
   Institute for Excellence in Higher Education, Bhopal (M.P.)

……

COURSE WRITERS

G Vijayakumari, Assistant Professor of Physics, Government Arts College (Men), Krishnagiri

Units: (1.0-1.1, 1.2, 1.2.2, 4.0-4.2.1, 4.4-4.4.1, 4.4.3-4.4.4, 4.5.1, 5.2.1, 5.5.1)

Dr. G. Naveen Babu, Assistant Professor, Department of Electrical Engineering, Shiv Nadar University, Gautam Budh Nagar, UP

Units: (3.0-3.2.1, 3.3.2)

Dr Manika Khanuja, Assistant Professor, Centre of Nanoscience and Nanotechnology, Jamia Millia Islamia, Delhi

Mr Sachin Kumar, Research Scholar, Department of Physics and Astrophysics, University of Delhi, Delhi

Units: (1.2.1, 1.3-1.10, 2, 3.2.2, 3.3-3.3.1, 3.3.3-3.8, 4.2.2, 4.3-4.3.3, 4.4.2, 4.5, 4.6-4.14, 5.0-5.1, 5.2, 5.2.2-5.3, 5.4, 5.5, 5.6-5.11)

Copyright © Reserved, Madhya Pradesh Bhoj (Open) University, Bhopal

All rights reserved. No part of this publication which is material protected by this copyright notice may be reproduced or transmitted or utilized or stored in any form or by any means now known or hereinafter invented, electronic, digital or mechanical, including photocopying, scanning, recording or by any information storage or retrieval system, without prior written permission from the Registrar, Madhya Pradesh Bhoj (Open) University, Bhopal.

Information contained in this book has been published by VIKAS® Publishing House Pvt. Ltd. and has been obtained by its Authors from sources believed to be reliable and are correct to the best of their knowledge. However, the Madhya Pradesh Bhoj (Open) University, Bhopal, Publisher and its Authors shall in no event be liable for any errors, omissions or damages arising out of use of this information and specifically disclaim any implied warranties or merchantability or fitness for any particular use.

Published by Registrar, MP Bhoj (Open) University, Bhopal in 2020

VIKAS®

Vikas® is the registered trademark of Vikas® Publishing House Pvt. Ltd.

VIKAS® PUBLISHING HOUSE PVT. LTD.
E-28, Sector-8, Noida - 201301 (UP)
Phone: 0120-4078900 • Fax: 0120-4078999
Regd. Office: A-27, 2nd Floor, Mohan Co-operative Industrial Estate, New Delhi 1100 44
• Website: www.vikaspublishing.com • Email: helpline@vikaspublishing.com

SYLLABI-BOOK MAPPING TABLE

Advanced Solid State Physics

Syllabi	Mapping in Book
UNIT: 1 **Free Electron Gas:** Free Electron Model of Metals, Dielectric Response of Electrons, Transverse Optical Modes in a Plasma, Transparency of Alkali Metals in the Ultraviolet, Longitudinal Optical Modes in a Plasma Plasmon, Electrostatic Screening, Electron Collisions. **Band Theory:** Nearly Free Electron Model, Wave Equation of Electron in a Periodic Potential, Bloch Functions, Crystal Momentum of an Electron Reduced Zone Scheme, Periodic Zone Scheme, Approximate Solution and Near Zone Boundary, Number of Orbitals in Band Metals, Insulators and Semiconductors.	**Unit-1:** Free Electron Gas and Band Theory **(Pages 3-54);**
UNIT: 2 **Fermi Surfaces:** Construction of Fermi Surfaces, Electrons, Holes and Open Orbits, Physical Properties of Holes, Effective Mass Electrons in Crystals, Wave Functions for Zero Wave Vector, Lattice Effect on Cohesive Energy of Metals, Pseudo Potentials, Experimental Methods in Fermi Surface Studies, Cyclotron Resonance in Metals External Orbits, de Haas-Van Alphen Effect, Fermi Surfaces of Free Metals. **Transport Properties:** The Boltzmann Equation, Electrical Conductivity, Calculation of Relaxation Time, Impurity Scattering, Ideal Resistance, Carrier Mobility, General Transport Coefficients, Thermal Conductivity, Thermoelectric Effects, Lattice Conduction, Phonon Drag, The Hall Effect, The Two Band Model, Magneto Resistances.	**Unit-2:** Fermi Surfaces and Transport Properties **(Pages 55-115);**
UNIT: 3 **Semiconductors:** Intrinsic Conductivity, Band Gap, Law of Mass Action, Intrinsic Carrier Concentration, Impurity Conductivity, Impurity States, Thermal Ionization of Impurities, Energy Bands in Si and Ge, n-n Junctions, Rectification, Polarons, Semi Metals Mobility of Protons, Point Defects, Alloys and Dislocations, Lattice Vacancies, Schottky and Frenkel Defects, Diffusion, Colour Centres, Alloys, Magnetic Alloys and the Konde Effect, Order-Disorder Transformations, Dislocations, Dislocations and Crystal Growth Whiskers.	**Unit-3:** Semiconductors **(Pages 117-146);**
UNIT: 4 **Superconductivity:** Experimental Survey, Occurrence of Superconductivity, Destruction of Superconductivity by Magnetic Fields, Meissner Effect, Heat Capacity, Energy Gap, Microwave Gap, Microwave and Infra-Red Properties, Isotope Effect. Theoretical Survey, Thermodynamics of Superconducting Transition, London Equation, Coherence Length, BSC Theory of Superconductivity, BCS Ground State, Persistent Current, Single Particle Tunnelling, Josephson Effect and Flux Quantization, Type H Superconductors Vertex State.	**Unit-4:** Superconductivity: Optical Phenomenon, Experimental and Theoretical Surveys **(Pages 147-220);**

Optical Phenomena in Insulators: Colour Centres, Excitons, Weakly and Tightly Bound Excitons, Exciton Waves, Excitons in Molecular Crystals, Solid State Quantum Electronics, Principles of MASER Action, Three Level Maser, Ruby Laser, Semiconductor Junction Laser, Photoconductivity Traps, Space Charge Effect, Crystal Counters, Luminescence.

Study of Breakdown in Solid Dielectrics at Low, High and Intermediate Temperatures, Influence of Annealing, Temperature, Effect of Thickness of Electrode Edge Effects and Time Log.

UNIT: 5

Magnetism: Diamagnetism and Paramagnetism, Quantum Theory of Paramagnetism Ferromagnetic Order, Spin Waves and Magnons, Ferromagnetic Order, Antiferromagnetic Order, Ferromagnetic Domains.

Magnetic Resonance: Nuclear Magnetic Resonance, Line Width Hyperfine Splitting, Nuclear Quadrupole Resonance, Ferromagnetic Resonance, Antiferromagnetic.

Unit-5: Magnetism and Magnetic Resonance **(Pages 221-257);**

CONTENTS

INTRODUCTION

NOTES

Solid state physics is the study of rigid matter, or solids, through specific methods, such as quantum mechanics, crystallography, electromagnetism, and metallurgy. It is considered as the major branch of condensed matter physics. Solid state physics studies how the large-scale properties of solid materials result from their atomic scale properties. Consequently, the solid state physics forms a theoretical basis of materials science. It also has direct applications, for example in the technology of transistors and semiconductors.

Solid materials are formed from densely packed atoms, which interact intensely. These interactions produce the mechanical, for example hardness and elasticity, thermal, electrical, magnetic and optical properties of solids. Depending on the material involved and the conditions in which it was formed, the atoms may be arranged in a regular, geometric pattern, such as the crystalline solids, which include metals and ordinary water ice or irregularly shaped solids, an amorphous solid, such as common window glass.

Fundamentally, the solid state physics focuses on crystals. Primarily, this is because the periodicity of atoms in a crystal — its defining characteristic — facilitates mathematical modeling. Similarly, crystalline materials often have electrical, magnetic, optical, or mechanical properties that can be used for engineering purposes.

This book, *Advanced Solid State Physics*, is divided into five units which will help to understand the basic concepts of free electron gas, free electron model of metals, dielectric response of electrons, transverse optical modes in a plasma, electron collisions, band theory, nearly free electron model, Bloch functions, insulators and semiconductors, Fermi surfaces, construction of Fermi Surfaces, electrons, holes and open orbits, experimental methods in Fermi surface studies, cyclotron resonance, de Haas–Van Alphen effect, Boltzmann equation, electrical conductivity, thermal conductivity, thermoelectric effects, phonon drag, Hall effect, semiconductors, intrinsic conductivity, band gap, impurity states, Schottky and Frenkel defects, crystal growth whiskers, superconductivity, Meissner effect, isotope effect, London equation, coherence length, BSC theory of superconductivity, Josephson effect, optical phenomena in insulators, colour centres, excitons, solid state quantum electronics, principles of MASER, photoconductivity, luminescence, magnetism and magnetic resonance, and Nuclear Magnetic Resonance (NMR).

The book follows the Self-Instruction Mode or the SIM format wherein each unit begins with an 'Introduction' to the topic followed by an outline of the 'Objectives'. The content is presented in a simple and structured form interspersed with Answers to 'Check Your Progress' for better understanding. A list of 'Summary' along with a 'Key Terms' and a set of 'Self-Assessment Questions and Exercises' is provided at the end of each unit for effective recapitulation.

UNIT 1 FREE ELECTRON GAS AND BAND THEORY

NOTES

Structure

1.0 INTRODUCTION

In physics and specifically in the solid state physics, the theory of free electron model of metals typically represents or signifies a metallic solid as a container which is precisely filled with a gas that is composed or comprised of free electrons, i.e., which are solely responsible or accountable for high electrical and thermal conductivity. In solid state physics, the free electrons are precisely considered similar or identical to the outermost or the valence electrons of free metal atoms which are assumed to move independently, freely, precisely and autonomously to each other throughout the complete or entire crystal. The Dutch physicist Hendrik A. Lorentz has initially proposed the free electron model in the year 1900 which was refined by Arnold Sommerfeld of Germany in the year 1928. The free electron model was principally superseded and replaced by the band theory of solids approximately by the mid-1930s.

In electromagnetism, the term dielectric or dielectric material or dielectric medium is precisely referred as an electrical insulator which has the property to be polarised through an applied electric field. When we place the dielectric material in an electric field, then the electric charges do not flow or drift or move through the dielectric material as they uniquely flow or move in an electrical conductor, because the dielectric material do not have loosely bound or free electrons that may flow or drift or move through the material, but instead they only slightly or marginally shift or move from their average equilibrium positions and therefore cause dielectric polarisation. As a consequence of the dielectric polarisation, typically the positive charges are said to be displaced in the direction of the field while the negative charges typically shift or move in the direction that is opposite to the field, for example consider that the field is moving or shifting parallel to the positive X-axis, then the negative charges will precisely shift or move in the negative X direction. This specific shift or movement will create or produce an internal electric field that will reduce the overall field within the dielectric itself. In addition, if a dielectric material is composed or comprised of weakly bonded molecules, then uniquely those dielectric molecules will not only become polarised but will also reorient in such a manner that their symmetry axes will get aligned to the field.

Characteristically, a plasmon is precisely defined and characterised as a quantum of plasma oscillation. Basically, as the light, an optical oscillation, distinctively consists of photons similarly the plasma oscillation distinctively consists of the plasmons. In solid state physics, the plasmon is uniquely considered or characterised as a quasiparticle because it evolves or occurs after the quantization of the plasma oscillations, exactly like the phonons which are defined as the quantization's of mechanical vibrations. Consequently, the plasmons are referred as collective (a discrete number) oscillations of the free electron gas density. Subsequently, when an electron collides with an atom or an ion, then there is some or certain probability that the electron may hit and kick out another electron, by leaving behind the ion in the state of having the next highest charge, i.e., the charge 'q' increased by +1. This is termed as the electron-impact ionization and is considered as the dominant process by means of which the atoms and the ions become more highly charged.

Band theory of solids typically describe the quantum state of matter and theoretically explain the notion which an electron takes or holds inside a metal solid. Every single molecule is precisely comprised of several discrete energy levels. The specific manner in which the electrons typically behave inside a molecule is properly explained through the band theory. The concept and theoretical formulations of the 'Band Theory' was initially developed from the information and experience achieved during the quantum revolution in physics. In the year 1928, Felix Bloch, a Swiss-American physicist and Nobel physics laureate, applied the quantum theory to study the unique properties of the solids.

In atoms, the electrons are characteristically filled in respective energy orbits following Pauli's exclusion principle. Two atomic orbitals combine in order to form a molecular orbit with two distinct energy levels. Band theory helps to visualize the difference between conductor, semiconductor, and an insulator by plotting available energies for an electron in a material.

Bloch's theorem states that the solutions to the Schrödinger equation in a periodic potential uniquely and distinctively takes the form of a plane wave precisely modulated by a periodic function. Named after the Swiss physicist Felix Bloch, the description and notions of the electrons in the Bloch functions are termed as the 'Bloch Electrons', also sometimes as the 'Bloch Waves', characteristically defines the concept of electronic band structures.

In the Nearly Free Electron (NFE) approximation, the interactions between the electrons are ignored or disregarded completely. This approximation permits the use of Bloch's theorem which states that electrons in a periodic potential have wavefunctions and energies which are periodic in wavevector up to a constant phase shift between the neighbouring reciprocal lattice vectors.

NOTES

In this unit, you will study about the free electron gas, free electron model of metals, dielectric response of electrons, transverse optical modes in a plasma, transparency of alkali metals in the ultraviolet, longitudinal optical modes in a plasma plasmon, electrostatic screening, electron collisions, band theory, nearly free electron model, wave equation of electron in a periodic potential, Bloch functions, crystal momentum of an electron reduced zone scheme, periodic zone scheme, approximate solution and near zone boundary, number of orbitals in band metals, insulators and semiconductors.

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the theoretical basis of free electron gas
- Explain free electron model of metals
- Discuss the dielectric response of electrons
- Know about the transverse optical modes in a plasma
- Elaborate on the transparency of alkali metals in the ultraviolet
- Describe the longitudinal optical modes in a plasma plasmon
- State about electrostatic screening and electron collisions
- Discuss the characteristic features of band theory
- Explain the nearly free electron model
- Understand wave equation of electron in a periodic potential
- State the Bloch functions and crystal momentum of an electron reduced zone scheme
- Deacribe the number of orbitals in band metals, insulators and semiconductors.

1.2 FREE ELECTRON MODEL OF METALS

In physics and specifically in the solid state physics, the theory of free electron model of metals typically represents or signifies a metallic solid as a container which is precisely filled with a gas that is composed or comprised of free electrons, i.e., which are solely responsible or accountable for high electrical and thermal conductivity. In solid state physics, the free electrons are precisely considered similar or identical to the outermost or the valence electrons of free metal atoms which are assumed to move independently, freely, precisely and autonomously to each other throughout the complete or entire crystal.

In solid state physics, the representation of free electron model of metals of a metallic solid, such as a vessel filled with a gas containing free electrons, i.e., the electron responsible or accountable for high electrical and thermal conductivity.

Characteristically, as per the Encyclopaedia Britannica, "The free electrons, considered analogous or identical to the outermost or valence, electrons of free metal atoms are presumed to be moving independently of one another throughout the entire crystal".

The free electron model was originally proposed or recommended around 1900 by the Dutch physicist Hendrik A. Lorentz which was further revised and enhanced by Arnold Sommerfeld of Germany in 1928. The concepts of quantum mechanical were introduced by Sommerfeld, of which the most notable is the Pauli exclusion principle. Even though the model gives an adequate explanation for specific properties, for example the conductivity and electronic specific heat of simple metals, such as sodium, but it had significant shortcomings, because the interaction of free electrons with the metal ions was not considered. Several research were conducted to recognise a system that is capable of properly explaining the behaviour of complex metals and the semiconductors. The semiconductor is defined as any of the crystalline solids intermediate in electrical conductivity between a conductor and an insulator. Eventually, by the mid-1930s the free electron model was fundamentally superseded by the band theory of solids.

Following four key assumptions are considered in the free electron model:

Free Electron Approximation: The interaction between the ions and the valence electrons is mostly neglected, except in boundary conditions. The ions only keep the charge neutrality in the metal. Unlike in the Drude model, the ions are not necessarily the source of collisions.

Independent Electron Approximation: The interactions between electrons are ignored. The electrostatic fields in metals are weak because of the screening effect.

Relaxation-Time Approximation: There is some unknown scattering mechanism such that the electron probability of collision is inversely proportional to the relaxation time τ, which represents the average time between collisions. The collisions do not depend on the electronic configuration.

Pauli Exclusion Principle: Each quantum state of the system can only be occupied by a single electron. This restriction of available electron states is considered by Fermi–Dirac statistics. Main predictions of the free-electron model are derived by the Sommerfeld expansion of the Fermi–Dirac occupancy for energies around the Fermi level.

The name of the model comes from the first two assumptions, as each electron can be treated as free particle with a respective quadratic relation between energy and momentum.

Electron Theory of Metals

The study of valence electrons present in a band, which controls the various properties of metals is known as electron theory of metals.

The electron theory of metals is classified into the following three types.

1. Classical Free Electron Theory or Drude-Lorentz Theory.
2. Quantum Free Electron Theory or Sommerfeld Theory.
3. Zone Theory or Band Theory of Solids.

Classical Free Electron Theory of Metals

This theory was developed by Drude and Lorentz. Eventhough it is a macroscopic theory it successfully explained most of the properties of metals.

In this theory, the free electrons in a metal are treated like molecules in a gas and Maxwell-Boltzmann statistics is applied.

The main assumptions or postulates of this theory are:

1. A metal is composed of positive metal ion fixed in the lattice.
2. All the valence electrons are free to move among the ionic array. Such freely moving electrons contribute towards conduction (electrical and thermal) in metals.
3. There are a large number of free electrons in a metal and they move about the whole volume like the molecules of a gas.
4. The free electrons collide with the positive ions in the lattice and also among themselves. All the collisions are elastic, i.e., there is no loss of energy.
5. The electrostatic force of attraction between the free electrons and the metallic ions are neglected, i.e., the total energy of free electron is equal to its kinetic energy.
6. All the free electrons in metal have wide range of energies and velocities.
7. In the absence of electric field, the random motion of free electron is equally probable in all directions. So, the net current flow is zero.
8. When an electric field is applied as shown in Figure (1.1) the electrons gain a velocity called drift velocity V_d and moves in opposite direction to the field resulting in a current flow in the direction of field.

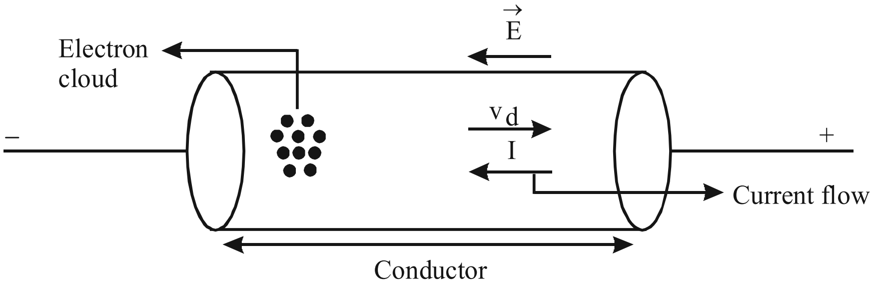


Fig. 1.1 *Conduction of Electrons in a Metal*

Thus, drift velocity is the average velocity acquired by an electron on applying an electric field.

Relaxation Time (τ)

Definition - 1 : *It is defined as the time required for the drift velocity to reduce to (1/e) times of its initial value, just when the field is switched off.*

Definition - 2 : *It is defined as the time taken by the free electron to reach its equilibrium position from its disturbed position just when the field is switched off.*

Mean Collision Time (τ_c)

The average time between two consecutive collisions of an electron with the lattice points is called collision time.

Mean Free Path (λ)

It is the average distance travelled by the conduction electron between successive collisions with the lattice ions.

In the following sections, based on classical free electron theory, expression for electrical conductivity, thermal conductivity and Wiedemann-Franz law is derived.

- **Bound Electrons –** All the valence electrons in an isolated atom bound to their parent nuclei are called as bound electrons.
- **Free Electrons –** In a solid, due to the boundaries of neighbouring atoms overlap each other, the valence electrons find continuity from atom to atom; and thus, can move easily throughout the solid. All such valence electrons of its constituent atoms in a solid are called as free electrons.

  The movements of the free electrons are confined to regions within the boundaries of the solid.
- **Difference between Ordinary Gas and the Free Electron Gas**

  The molecules of ordinary gas are neutral. But, the free electron gas is charged.

  The density of molecules is smaller than the density of free electrons.

Electrical Conductivity (S)

The electrical conductivity σ is defined as the rate of charge flow across a unit area in a conductor per unit potential (voltage) gradient.

i.e.,
$$\sigma = \frac{J}{E} \qquad ...(1.1)$$

Its unit is **mho–m^{-1} or Ω^{-1} m^{-1}.**

Expression for Electrical Conductivity

Electrical conductivity of a conductor is the property by which it allows the flow of electric current. *In a metal, the valence electrons are not attached to the individual atoms and are free to move about within the lattice. Hence, the valence electrons are also called free electrons or conduction electrons.*

In the absence of an electric field, the motion of the free electrons are completely random like those of the molecules of a gas in a container. But, when an electric field is applied to a metal, the electrons modify their random motion in such a way that, they drift slowly in the opposite direction to that of the applied field with an average velocity called the drift velocity v_d.

When an electric field E is applied, the free electrons in a metal experiences a force eE. Due to this force, the acceleration "*a*" gained by the electron is,

$$F = eE$$

$$ma = eE \qquad [\because F = ma]$$

or
$$a = \frac{eE}{m} \qquad ...(1.2)$$

Consider an electron that has just collided with an ion core. The collision momentarily destroys the tendency to drift and the electron will have truly random direction after this collision. In the next collision, the electrons velocity would have changed, to an average value v_d given by,

NOTES

$$v_d = a\tau \qquad ...(1.3)$$

Where τ is called the mean free time.

Substituting Equation (1.2) in Equation (1.3), we get

$$v_d = \frac{eE\tau}{m} \qquad ...(1.4)$$

The current density is given by,

$$J = nev_d \qquad ...(1.5)$$

where, n is the number of free electrons per unit volume.

Hence, substituting Equation (1.4) in Equation (1.5), we get

$$J = ne \times \frac{eE\tau}{m}$$

$$\therefore \qquad J = \frac{ne^2\tau}{m}.E \qquad ...(1.6)$$

But, J is also expressed as,

$$J = \sigma E \qquad ...(1.7)$$

Therefore, substituting for J in Equation (1.6) from Equation (1.7),

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

$$\text{or} \qquad \sigma = \frac{ne^2\tau}{m} \qquad ...(1.8)$$

Thus, the above expression relates the electrical conductivity to the number of free electrons per unit volume.

Expression for S in Terms of $k_B T$

The mean free time τ in terms of mean free path λ and average thermal velocity v is given by,

$$\tau = \frac{\lambda}{v} \qquad ...(1.9)$$

The kinetic energy of an electron based on kinetic theory is given by,

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

(where k_B is the Boltzmann constant)

$$\text{or} \qquad m = \frac{3k_B T}{v^2} \qquad ...(1.10)$$

Substituting Equation (1.10) for m and Equation (1.9) for τ in Equation (1.8), we have,

$$\sigma = \frac{ne^2\tau}{\frac{3k_B T}{v^2}} = \frac{ne^2\lambda}{3k_B T.v}.v^2$$

$$\therefore \qquad \sigma = \frac{ne^2 \lambda v}{3k_B T} \qquad \text{...(1.11)}$$

Thus, from the above expression of σ it is observed that, the electrical conductivity of a metal decreases with increase of temperature.

Note:
- For an isotropic material the mean collision time τ_c is equal to the relaxation time τ. i.e., $\tau_c = \tau$.
- **Determination of Density of Electrons**

  (Determination of Number of Electrons/Unit Volume in Terms of Avagadro's Number).

  The Density of Free Electrons or the Number of Free Electrons/ Unit Volume is *n* = Number of Free Electrons / Atom × Number of Atoms/Unit Volume

  To Evaluate Number of Atoms / Unit Volume

  In general, the volume occupied by 1 kg of a material is $= \frac{1}{D}$ **m^3**

  $$\left[\because \text{Volume} = \frac{\text{Mass}}{\text{Density}}\right]$$

  Where D, is the density of the material.

  Therefore, volume occupied by a material of mass, equal to its atomic weight in kg

  $$= \frac{\text{Atomic Weight}}{D}\ \mathbf{m^3} \qquad \text{...(1.12)}$$

  But we know, the number of atoms in a material of mass equal to its atomic weight in kg = N_A (The Avagadro number expressed per k mole).

  ...(1.13)

  Therefore, number of atoms in a volume of $\left[\frac{\text{Atomic Weight}}{D}\right] = N_A$

  Hence, number of atoms / unit volume of the material $= \frac{N_A \times D}{\text{Atomic Weight}}$

  ...(1.14)

  Hence, substituting Equation (1.14) in (1.12) we get,

  The density of electrons or the number of electrons / unit volume

  n = **Number of Free Electrons / Atom** × $\frac{\mathbf{N_A \times D}}{\textbf{Atomic Weight}}$ **m^{-3}.**

Example 1

A conductor has electron concentration of 5.9×10^{28} m^{-3}. What current density in the conductor corresponds to a drift velocity of 0.625 ms^{-1}? Calculate the mobility of the charge carriers. Given $\sigma = 6.22 \times 10^7\ \Omega^{-1}\ \text{m}^{-1}$.

Solution:

Given, $n = 5.9 \times 10^{28}$ m^{-3}; $v_d = 0.625$ ms^{-1}; $\sigma = 6.22 \times 10^7\ \Omega^{-1}\ \text{m}^{-1}$; J = ?; μ = ?

NOTES

Formula

$$J = nev_d$$

$$= 5.9 \times 10^{28} \times 1.6 \times 10^{-19} \times 0.625$$

$$\therefore \quad \mathbf{J = 5.9 \times 10^{9}\ Am^{-2}}$$

We know,

$$\sigma = ne\mu$$

$$\therefore \quad \mu = \frac{\sigma}{ne} = \frac{6.22 \times 10^{7}}{5.9 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$$\boldsymbol{\mu} \mathbf{= 6.588 \times 10^{-3}\ m^2\,V^{-1}s^{-1}.}$$

Example 2

Find the drift velocity of the free electrons in a copper wire whose cross-sectional area is A = 1.05 mm^2 when the wire carries a current of 1 A. Assume that, each copper atom contributes one electron to the electron gas. [Given density of free electrons in copper = 8.5 × 10^{28} m^{-3}].

Solution:

Given, $n = 8.5 \times 10^{28}\ m^{-3}$; $A = 1.05\ mm^2 = 1.05 \times 10^{-6}\ m^2$; $I = 1A$.

Formula

$$J = nev_d$$

$$\therefore \quad v_d = \frac{J}{ne} = \frac{I}{Ane}$$

$$\left[\because J = \frac{I}{A}\right]$$

$$v_d = \frac{1}{1.05 \times 10^{-6} \times 8.5 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$$\mathbf{v_d = 7.002 \times 10^{-5}\ ms^{-1}.}$$

Example 3

Calculate the drift velocity of the free electrons [with a mobility of 3.5 × 10^{-3} m^2 V^{-1} s^{-1}] in copper for an electric field strength of 0.5 V/m.

Solution:

Given, $\mu = 3.5 \times 10^{-3}\ m^2\,V^{-1}\,s^{-1}$; $E = 0.5\ Vm^{-1}$; $V_d = ?$;

Formula

$$v_d = \mu E$$

$$v_d = 3.5 \times 10^{-3} \times 0.5$$

$$\mathbf{v_d = 1.75 \times 10^{-3}\ ms^{-1}.}$$

Example 4

For a metal having 6.5 × 10^{28} conduction electrons per m^3, find the relaxation time of the conduction electrons if the metal resistivity is 1.435 × 10^{-8} Ω–m.

Solution:

Given, $n = 6.5 \times 10^{28}\ m^{-3}$; $\rho = 1.435 \times 10^{-8}\ \Omega - m$; $\tau = ?$

Formula

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

NOTES

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

$$\left[\because \sigma = \frac{1}{\rho}\right]$$

$$\therefore \quad \tau = \frac{9.11\times10^{-31}}{1.435\times10^{-8}\times6.5\times10^{28}\times(1.6\times10^{-19})^2}$$

$$\boldsymbol{\tau = 3.815 \times 10^{-14}\ \mathrm{s.}}$$

Example 5

Calculate the mean free path between collisions of the free electrons in copper at 20°C. The resistivity of copper at 20°C is 1.72×10^{-8} Ωm and density of free electrons is $8.48 \times 10^{+28}$ m^{-3}.

Solution:

Given, $\rho = 1.72 \times 10^{-8}$ Ωm; T = 20°C = 293 K; $n = 8.48 \times 10^{+28}$ m^{-3}; $\lambda = ?$

Formula

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

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

$$\tau = \frac{m}{\rho ne^2} = \frac{9.11\times10^{-31}}{1.72\times10^{-8}\times8.48\times10^{+28}\times(1.6\times10^{-19})^2}$$

$$\boldsymbol{\tau = 2.439 \times 10^{-14}\ \mathrm{sec.}}$$

$$\text{But,} \quad \tau = \frac{\lambda}{v}$$

To Calculate v (Thermal Velocity)

$$v = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\times1.38\times10^{-23}\times293}{9.11\times10^{-31}}}$$

$$= \sqrt{1.33\times10^{10}}$$

$$\boldsymbol{v = 115368.97\ \mathrm{ms^{-1}}.}$$

$$\therefore \quad \lambda = \tau v$$

$$= 2.439 \times 10^{-14} \times 115368.97$$

$$\therefore \quad \boldsymbol{\lambda = 2.8138 \times 10^{-9}\ \mathrm{m.}}$$

Example 6

Calculate the drift velocity of electrons in a metal of thickness 1mm across which a potential difference of 1 V is applied. Compare this value with the thermal velocity at temperature 300 K. Given the mobility 0.04 m^2 V^{-1}s^{-1}.

Solution:

Given, $t = 1\ \text{mm} = 1\times 10^{-3}\ \text{m}$; $V = 1\ \text{V}$; $T = 300\ \text{K}$; $\mu = 0.04\ \text{m}^2\ \text{V}^{-1}\text{s}^{-1}$;

$v = ?$; $v_d = ?$

Formula

Thermal Velocity

$$v = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\times 1.38\times 10^{-23}\times 300}{9.11\times 10^{-31}}}$$

$$= \sqrt{1.36333\times 10^{10}}$$

$$v = 116762.02\ \text{ms}^{-1}$$

or $$\mathbf{v = 116.76 \times 10^3\ ms^{-1}.}$$

Drift Velocity v_d

$$\mu = \frac{v_d}{E}$$

or $$v_d = E\mu$$

But, $$E = \frac{V}{t} = \frac{1}{1\times 10^{-3}} = \mathbf{1000\ Vm^{-1}.}$$

$\therefore$ $$v_d = 1000 \times 0.04$$

$$\mathbf{v_d = 40\ ms^{-1}.}$$

Thus, the thermal velocity is very high compared to the drift velocity.

Example 7

Calculate the electrical conductivity of copper. Given atomic weight, density and relaxation time as 63.5, $8.9 \times 10^3\ \text{kgm}^{-3}$ and 2.48×10^{-14} s, respectively.

Solution:

Given,

Atomic Weight = 63.5; Density $D = 8.93 \times 10^3\ \text{kgm}^{-3}$; $\tau = 2.48 \times 10^{-14}$ s;

$\sigma = ?$

Formula

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

To find n

$$n = \text{Number of Free Electrons / Atom} \times \frac{N_A \times D}{\text{Atomic weight}}\ \text{m}^{-3}$$

$$= \frac{1\times 6.023\times 10^{26}\times 8.93\times 10^{3}}{63.5}$$

$$\mathbf{n = 8.4701 \times 10^{28}\ m^{-3}.}$$

$\therefore$ $$\sigma = \frac{8.4701\times 10^{28}\times\left(1.6\times 10^{-19}\right)^2\times 2.48\times 10^{-14}}{9.11\times 10^{-31}}$$

$$\sigma = 5.87 \times 10^7\ \Omega^{-1}\text{m}^{-1}$$

or $$\frac{1}{10} = \mathbf{5.87 \times 10^7\ Sm^{-1}.} \qquad [\Omega^{-1} = \text{Siemens}]$$

NOTES

Example 8

Calculate the drift velocity of electrons in copper and current density in a wire of diameter 0.16×10^{-2} m which carries a current of 10 A. [Given $n = 8.48 \times 10^{28}\ m^{-3}$]

Solution:

Given, $I = 10$ A; Diameter of Wire $= 0.16 \times 10^{-2}$ m

$\therefore$ Radius $= 0.8 \times 10^{-2}$m; $n = 8.48 \times 10^{28}\ m^{-3}$; $J = ?$; $v_d = ?$

Formula

$$\text{The current density is } J = \frac{I}{A}$$

$$= \frac{10}{\pi r^2} = \frac{10}{3.14 \times (0.8 \times 10^{-2})^2}$$

$$\mathbf{J = 4.9761 \times 10^4\ Am^{-2}.}$$

The drift velocity is,

$$v_d = \frac{J}{ne} \qquad [\because J = nev_d]$$

$$= \frac{4.9761 \times 10^4}{8.48 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$$\mathbf{v_d = 3.6675 \times 10^{-6}\ ms^{-1}.}$$

Example 9

A uniform silver wire has a resistivity of $1.54 \times 10^{-8}\ \Omega$m at room temperature, for an electric field along the wire of 1V/cm. Compute the drift velocity of electron assuming that there are 5.8×10^{28} conduction electrons/m^3. Also calculate the mobility.

Solution:

Given, $\rho = 1.54 \times 10^{-8}\ \Omega m$; $E = 1$ V/cm $= 100$V/m; $n = 5.8 \times 10^{28}\ m^{-3}$; $v_d = ?$

Formula

$$v_d = \mu E$$

$$\text{But,} \quad \mu = \frac{\sigma}{ne} = \frac{1}{\rho ne} = \frac{1}{1.54 \times 10^{-8} \times 5.8 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$$\mathbf{\mu = 6.99 \times 10^{-3}\ m^2\ V^{-1}s^{-1}}$$

$$\therefore \quad v_d = \mu E$$

$$= 6.99 \times 10^{-3} \times 100$$

$$\text{or} \quad \mathbf{v_d = 0.6997\ ms^{-1}.}$$

Example 10

The following datas are given for copper:

(*i*) Density $= 8.92 \times 10^3$ kg/m^3 (*ii*) Resistivity $= 1.73 \times 10^{-8}\ \Omega$m

(*iii*) Atomic Weight = 63.5

Calculate the mobility and the average time collision of electrons in copper obeying classical laws.

Solution:

Given, $D = 8.92 \times 10^3$ kg / m^3; Atomic Weight = 63.5; $\rho = 1.73 \times 10^{-8}$ Ωm;

$N_A = 6.02 \times 10^{26}$ per kg mol μ = ?; τ = ?

Formula

$$n = \frac{D \times \text{Avagadro number}}{\text{Atomic weight}} = \frac{8.92 \times 10^3 \times 6.02 \times 10^{26}}{63.5}$$

$$\therefore \qquad \mathbf{n = 8.456 \times 10^{28}\ m^{-3}.}$$

$$\tau = \frac{m}{ne^2\rho} = \frac{9.1 \times 10^{-31}}{8.456 \times 10^{28} \times \left(1.6 \times 10^{-19}\right)^2 \times 1.73 \times 10^{-8}}$$

$$\therefore \qquad \frac{1}{100} \mathbf{= 2.43 \times 10^{-14}\ s.}$$

$$\mu = \frac{1}{\rho ne} = \frac{1}{1.73 \times 10^{-8} \times 8.456 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$$\therefore \qquad \boldsymbol{\mu} \mathbf{= 0.427 \times 10^{-2}\ m^2V^{-1}s^{-1}.}$$

Example 11

Sodium metal with a bcc structure has two atoms/unit cell. The radius of sodium atom is 1.85 Å. Calculate the electrical resistivity at 0°C if the classical value of mean free time at this temperature is 3×10^{-14} sec.

Solution:

Given, $r = 1.85 \times 10^{-10}$m; $\tau = 3 \times 10^{-14}$ sec

Number of atom per unit cell = 2; ρ = ?

Formula

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

n

$$= \frac{\text{Number of atoms per unit cell} \times \text{Number of electrons per unit cell}}{\text{Volume}}$$

$$= \frac{2 \times 1}{a^3} \qquad \left(\because \text{volume} = a^3\right)$$

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

$$\therefore \qquad a = \frac{4 \times 1.85 \times 10^{-10}}{\sqrt{3}}$$

$$\boldsymbol{a} \mathbf{= 4.27 \times 10^{-10}\ m.}$$

$$\therefore \qquad n = \frac{2}{\left(4.27 \times 10^{-10}\right)^3}$$

$$\mathbf{n = 2.57 \times 10^{28}\ m^{-3}.}$$

Electrical Resistivity $\rho = \frac{m}{ne^2\tau} = \frac{9.11 \times 10^{-31}}{2.57 \times 10^{28} \times \left(1.6 \times 10^{-19}\right)^2 \times 3 \times 10^{-14}}$

$\therefore \qquad \boldsymbol{\rho = 4.46 \times 10^{-8}\ \Omega m.}$

Note: The above problem with a different question. Compute electrical resistivity of sodium at 0°C, if the mean free time at this temperature is 3.1×10^{-14} sec. Futher more, sodium builds a bcc lattice with two atoms per unit cell, and the side of the unit cell is 0.429 nm.

Example 12

Calculate the free electron concentration, mobility and drift velocity of electrons in an aluminium wire of length 5m and resistance 60 mΩ if it carries a current of 15 A. Assuming that each aluminium atom contributes 3 free electrons for conduction. [Given for aluminium $\rho = 2.7 \times 10^{-8}$ Ωm, atomic weight = 26.98 and density = 2.7×10^{3} kg m^{-3}]

Solution:

Given, $\rho = 2.7 \times 10^{-8}$ Ωm; Atomic Weight = 26.98; D = 2.7×10^{3} kg m^{-3}

from problem $\qquad R = 60 \times 10^{-3}$ W

$l = 5$ m, I = 15 A

Number of Free Electron=3

$n = ?;\ v_d = ?;\ \mu = ?$

Formula $\quad$ n =

$$\frac{\text{Avogadro number} \times \text{Density} \times \text{Number of free electron per atom}}{\text{Atomic weight}}$$

$$= \frac{6.023 \times 10^{26} \times 3 \times 2.7 \times 10^{3}}{26.98}$$

$\therefore \qquad \boldsymbol{n = 1.81 \times 10^{29}}$ **electrons/m^3.**

$$\mu = \frac{1}{ne\rho} = \frac{1}{1.81 \times 10^{29} \times 1.6 \times 10^{-19} \times 2.7 \times 10^{-8}}$$

$\boldsymbol{\mu = 1.279 \times 10^{-3}\ m^2\ V^{-1}\ s^{-1}.}$

$$E = \frac{V}{l} = \frac{IR}{l} = \frac{15 \times 60 \times 10^{-3}}{5}$$

E = 0.18 V/m.

$v_d = \mu E = 1.279 \times 10^{-3} \times 0.18$

$\therefore \qquad \boldsymbol{v_d = 2.302 \times 10^{-4}}$ **m/sec.**

Example 13

Find the resistance of an intrinsic Ge rod of 1cm long 1mm wide and 1mm thick at 300 K. The intrinsic carrier density is 2.5×10^{19} /m^3 at 300 K and the mobility of electron and hole are 0.39 and 0.19 m^{2}V^{-1}s^{-1}.

Solution:

Given, l = 1 cm; b = 1 mm; t = 1 mm; T = 300 K; ρ = ?; R = ?

$$n_i = 2.5 \times 10^{19}/\text{m}^3;\ \mu_e = 0.39\ \text{m}^2\text{V}^{-1}\text{s}^{-1};\ \mu_n = 0.19\ \text{m}^2\text{V}^{-1}\text{s}^{-1}$$

Formula $$\sigma = n_i e\,(\mu_e + \mu_h) = 2.5 \times 10^{19} \times 1.6 \times 10^{-19}\ (0.39 + 0.19)$$

$$\boldsymbol{\sigma = 2.32\ \Omega^{-1}\text{m}^{-1}.}$$

$$\rho = \frac{1}{\sigma} = \frac{1}{2.32}$$

$$\boldsymbol{\rho = 0.431\ \Omega\text{m}.}$$

$$R = \frac{\rho l}{A} = \frac{0.431 \times 1 \times 10^{-2}}{1 \times 10^{-3} \times 1 \times 10^{-3}}$$

$$\mathbf{R = 4310\ \Omega.}$$

Thermal Conductivity K

The thermal conductivity is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.

i.e., $$K = -\frac{Q'}{A\left(\dfrac{dT}{dx}\right)}$$

Where, Q' is the rate of heat flow given by $\left(\dfrac{dQ}{dt}\right)$

A is the cross sectional area of the conductor.

$\dfrac{dT}{dx}$ is the temperature gradient.

The –ve (Negative) sign is optional, which indicates that, the heat flows from higher to lower temperature side.

The unit for thermal conductivity is **W m^{-1}K^{-1}.**

In solids, heat transfer takes place by conduction. In the process of heat transfer both electrons and phonons take part. Hence in general, the total thermal conductivity can be written as,

$$K_{\text{Total}} = K_{\text{Electron}} + K_{\text{Phonon}}$$

Since, thermal conductivity due to electrons is greater than the thermal conductivity due to phonons in the case of pure metals, the total thermal conductivity is given by $K_{\text{Total}} = K_{\text{Electron}}$.

Expression for Thermal Conductivity K

Consider a uniform metallic rod AB. Let the surface A be at a higher temperature T, and the surface B be at a lower temperature T-dT as shown in Figure (1.2). Let the distance of separation between the surface be λ (Mean Free Path). The electrons conduct heat from A to B. During collision, the electrons near A lose their kinetic energy while, the electrons near B gain the energy.

NOTES

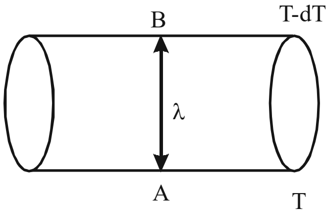


Fig. 1.2 *A Uniform Metallic Rod AB*

Let,

The density of electrons = n

The average thermal velocity = v.

Based on kinetic theory,

The average kinetic energy of an electron at A = $\frac{3}{2}$ k_BT ...(1.15)

Similarly, the average kinetic energy of an electron at B = $\frac{3}{2}$ $k_B(T–dT)$ ...(1.16)

Therefore, the excess kinetic energy carried by electrons from A to B,

$$= \frac{3}{2} k_BT - \frac{3}{2} k_B(T - dT)$$

$$= \frac{3}{2} k_BdT \quad ...(1.17)$$

Since, there is equal probability for the electrons to move in all the six directions (x, y, z) and (–x, –y, –z).

The number of electrons crossing unit area in unit time from A to B = $\frac{1}{6}nv$ ...(1.18)

Therefore, the excess energy transferred from A to B per unit area in unit time,

$$= \frac{1}{6}nv \times \frac{3}{2} k_BdT = \frac{1}{4}nv\ k_BdT \quad ...[1.19]$$

Similarly, the deficiency of energy carried from B to A per unit area in unit time,

$$= -\frac{1}{4} nv\ k_BdT \quad ...[1.20]$$

Since, the net energy transferred from A to B per unit area per unit time is the rate of heat flow Q. Then,

$$Q = \frac{1}{4} nv\ k_BdT - \left(-\frac{1}{4}nvk_BdT\right)$$

$$= \frac{1}{2} nv\ k_BdT. \quad ...[1.21]$$

But, from the definition of thermal conductivity,

$$K = \frac{Q}{\left(\frac{dT}{dx}\right)}$$

NOTES

In this case, $dx = \lambda$

$$\therefore \quad K = \frac{Q}{\frac{dT}{\lambda}} \qquad ...[1.22]$$

Hence, substituting for Q from Equation (1.21) in Equation (1.22), we get

$$K = \frac{\left(\frac{1}{2}\right) nvk_B dT}{\frac{dT}{\lambda}}$$

$$\therefore \quad \mathbf{K = \frac{nvk_B\lambda}{2}} \qquad ...[1.23]$$

The value of K obtained with the above expression is verified experimentally and the free electron theory is found to be successful in explaining the thermal conductivity.

Note: **Thermal Resistance:** $R_T = \frac{\Delta T}{Q'}$. It is defined as the temperature drop per unit heat flow. It depends on both, the geometry and material. In terms of thermal conductivity, $R_T = \frac{l}{KA}$ where l is the length of the sample and A is the cross sectional area.

Wiedemann-Franz Law

Statement: *This law states that, the ratio of thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature.*

i.e., $$\frac{K}{\sigma} \propto T$$

Or $$\frac{K}{\sigma} = LT$$

Where L is a constant called the Lorentz number. Its value is ***2.44 × 10⁻⁸ WΩK⁻²****.*

Derivation

The electrical conductivity is,

$$\sigma = \frac{ne^2\lambda v}{3k_BT}$$

The thermal conductivity from Equation (1.23) is,

$$K = \frac{nvk_B\lambda}{2}$$

$$\therefore \quad \frac{K}{\sigma} = \frac{nvk_B\lambda}{2\left(\frac{ne^2\lambda v}{3k_BT}\right)} = \frac{nvk_B\lambda.3k_BT}{2ne^2\lambda v} = \frac{3}{2}\,\frac{k_B^2}{e^2}\,T$$

$$\therefore \qquad \frac{K}{\sigma} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T = L\,T, \text{ where } L = \frac{3}{2}\left(\frac{k_B}{e}\right)^2.$$

Thus, Wiedemann-Franz law is obtained.

NOTES

$\boldsymbol{L = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1.12 \times 10^{-8}\ W\Omega K^{-2}}$ *is known as the Lorentz number.*

The above value of Lorentz number based on classical concept does not agree with the experimental value. Hence, the assumption that all the free electrons of a metal participate in thermal conductivity is not correct.

The actual experimental value of the Lorentz number is $\boldsymbol{2.44 \times 10^{-8}\ W\Omega K^{-2}}$**.**

Thus, there is a discrepancy in the value of L between classical theory and the experimental value. This discrepancy gets eliminated on applying quantum theory.

Success of Free Electron Theory

1. It verifies Ohm's law.
2. It explains the thermal and electrical conductivities of metals.
3. It is used to deduce Wiedemann-Franz law.
4. It explains the optical properties of metals.

1.2.1 Nearly Free Electron Model

In solid state physics, the Nearly Free Electron model or NFE model or quasi-free electron model is defined as a quantum mechanical model of physical properties of electrons that moves almost freely through the crystal lattice of a solid. The model is closely related to the theoretical empty lattice approximation and is typically used to calculate the electronic band structure, specifically the metals. In addition, this model is referred as an immediate enhancement of the free electron model, in which the metal was considered as a non-interacting electron gas and the ions were neglected completely.

Mathematical Formulation of Nearly Free Electron Model

The Nearly Free Electron or NFE model is defined as a modification or variation of the free-electron gas model which comprises of a weak periodic perturbation specifically designed for modeling the interaction between the conduction electrons and the ions in a crystalline solid. The NFE model, similar to the free-electron model, does not consider electron–electron interactions, i.e., the approximation of independent electron is yet in effect.

As demonstrated by the **Bloch's theorem**, when a periodic potential is introduced into the **Schrödinger equation** then it will result in the following form of a wave function,

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

Where the function u_k has the same periodicity as the lattice:

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T})$$

Here **T** is defined as a lattice translation vector.

Because it is a nearly free electron approximation, therefore, it can be assumed that,

$$u_{\mathbf{k}}(\mathbf{r}) \approx \frac{1}{\sqrt{\Omega_r}}$$

Here Ω_r denotes the volume of states of fixed radius r, as described in the Gibbs's paradox.

When this form of solution is plugged into the Schrödinger equation, then the resulting **central equation** is of the form:

$$(\lambda_{\mathbf{k}} - \epsilon)C_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0$$

Where the kinetic energy λ_k is given by,

$$\lambda_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2(u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}})$$

Which after dividing by $\psi_{\mathbf{k}}(\mathbf{r})$ reduces to,

$$\lambda_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

If it is assumed that $u_{\mathbf{k}}(\mathbf{r})$ is almost constant and $\nabla^2 u_{\mathbf{k}}(\mathbf{r}) << k^2$.

The reciprocal parameters C_k and $U_{\mathbf{G}}$ are the Fourier coefficients of the wave function $\psi(\mathbf{r})$ and the screened potential energy $U(\mathbf{r})$, respectively:

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$
$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

The vectors **G** are considered as the reciprocal lattice vectors and the discrete values of '**k**' are determined through the boundary conditions of the lattice under consideration.

In any perturbation analysis, the base case must be considered to which the perturbation is applied. In this instance, the base case is with U(x) = 0, and therefore all the Fourier coefficients of the potential are also zero. Consequently, the central equation reduces to the form,

$$(\lambda_{\mathbf{k}} - \epsilon)C_{\mathbf{k}} = 0$$

This identity implies that for each **k**, one of the two following cases must hold:

1. $C_{\mathbf{k}} = 0$
2. $\lambda_{\mathbf{k}} = \varepsilon$

If the values of $\lambda_{\mathbf{k}}$ are of non-degenerate form, then the second case occurs for only one value of **k**, while for the rest, the Fourier expansion coefficient $C_{\mathbf{k}}$ must be zero. In this non-degenerate case, the standard free electron gas result is retrieved:

$$\psi_{\mathbf{k}} \propto e^{i\mathbf{k}\cdot\mathbf{r}}$$

In the degenerate case, however, there will be a set of lattice vectors $\mathbf{k}_1, ..., \mathbf{k}_m$ with $\lambda_1 = ... = \lambda_m$. When the energy 'ε' is equal to this value of λ, there will be *m* independent plane wave solutions of which any linear combination is also a solution:

$$\psi \propto \sum_{j=1}^{m} A_j e^{i\mathbf{k}_j\cdot\mathbf{r}}$$

Non-degenerate and degenerate perturbation theory can be applied in these two cases for solving the Fourier coefficients $C_{\mathbf{k}}$ of the wavefunction (correct to first order in U) and the energy eigenvalue (correct to second order in U). An important result of this derivation is that there is no first order shift in the energy ε in the case of no degeneracy, while there is in the case of near degeneracy, implying that the latter case is more important in this analysis. Particularly, at the Brillouin zone boundary or equivalently at any point on a Bragg plane, one finds a twofold energy degeneracy that results in a shift in energy given by:

$$\epsilon = \lambda_{\mathbf{k}} \pm |U_{\mathbf{G}}|$$

This energy gap between Brillouin zones is known as the band gap, with a magnitude of $2|U_{\mathbf{G}}|$.

This weak perturbation when introduced has substantial effects on the solution to the Schrödinger equation and considerably results in a band gap between wave vectors in different Brillouin zones.

Difference Between Free Electron Model and Nearly Free Electron Model

The key difference between free electron model and nearly free electron model is that the free electron model does not consider the electron interactions and the potential, however the nearly free electron model considers the potential.

Free electron model is defined as a quantum mechanical model specifically used to describe the behaviour and action of the charge carriers in a metallic solid. Nearly free electron model is defined as a quantum mechanical model that typically explains the physical properties of those electrons which move nearly freely through a crystal lattice of a solid.

1.2.2 Dielectric Response of Electrons

A **dielectric** or dielectric material or dielectric medium is an electrical insulator that can be polarised by an applied electric field. When a dielectric material is placed in an electric field, electric charges do not flow through the material as they do in an electrical conductor, because they do not have loosely bound **electrons** or free electrons that may drift through the material, but as an alternative they slightly shift from their average equilibrium positions, causing **dielectric polarisation**. Because of dielectric polarisation, positive charges are displaced in the direction of the field and negative charges shift in the direction opposite to the field, for example if the field is moving parallel to the positive X axis, then the negative charges will shift in the negative X direction. This creates an internal electric field that reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules, those molecules not only become polarised, but also reorient so that their symmetry axes align to the field.

NOTES

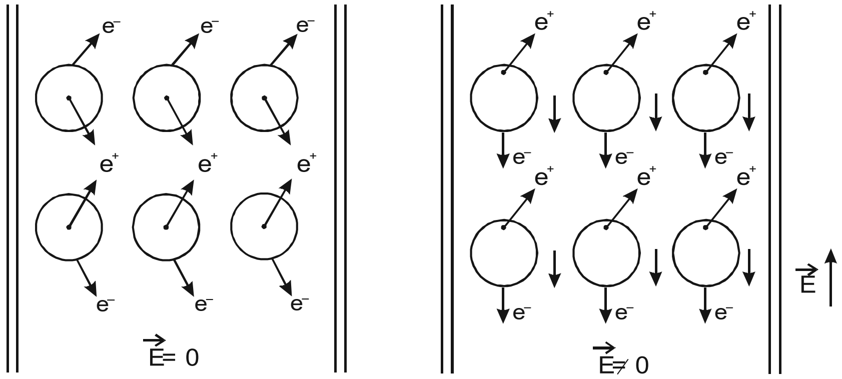
The term dielectric was coined by William Whewell, taken from **'Dia + Electric'** in response to a request from Michael Faraday. A perfect dielectric is a material with zero electrical conductivity, consequently exhibiting only a displacement current, hence it stores and returns electrical energy as if it were an ideal capacitor.

In electromagnetism, the term dielectric or dielectric material or dielectric medium is precisely referred as an electrical insulator which has the property to be polarised through an applied electric field. When we place the dielectric material in an electric field, then the electric charges do not flow or drift or move through the dielectric material as they uniquely flow or move in an electrical conductor, because the dielectric material do not have loosely bound or free electrons that may flow or drift or move through the material, but instead they only slightly or marginally shift or move from their average equilibrium positions and therefore cause dielectric polarisation. As a consequence of the dielectric polarisation, typically the positive charges are said to be displaced in the direction of the field while the negative charges typically shift or move in the direction that is opposite to the field, for example consider that the field is moving or shifting parallel to the positive X-axis, then the negative charges will precisely shift or move in the negative X direction. This specific shift or movement will create or produce an internal electric field that will reduce the overall field within the dielectric itself. In addition, if a dielectric material is composed or comprised of weakly bonded molecules, then uniquely those dielectric molecules will not only become polarised but will also reorient in such a manner that their symmetry axes will get aligned to the field.

The behaviour of a dielectric material can be changed by the application of an external electric field.

We know that, in an atom there is a positively charged nucleus at the centre surrounded by orbiting electrons (electron cloud) which are negatively charged. An isolated atom does not have any dipole moment; since, the centeroid of the negative charge distribution and the positive charge coincide.

But, when an external electric field is applied, it causes the electron cloud to move in opposite direction. Thus, the centeroids of the positive and negative charges now no longer coincide and as a result an electric dipole is induced in the atom. Thus, the atoms are said to be polarised. The Figure (1.3) illustrates the above process.



No Polarisation
Centroids of Positive and Negative
Charge Coincide

Polarisation
Non Coincidence of Centroids of
Positve and Negative Charge

Fig. 1.3 *Dielectric Polarisation*

Note: **Dipole:** A pair of equal and opposite charges separated by a small distance constitutes an electric dipole.
The product of magnitude of one of the charges q and the distance of their separation x is called the dipole moment μ, i.e., $\mu = q \times x$.

Therefore, polarisation is defined as the process of creating or inducing dipoles in a dielectric material by an external electric field. The polarisation increases with the field upto the critical value.

On the basis of polarisation concept, *the dielectrics are the materials that have either permanent dipoles or induced dipoles in the presence of an applied electric field.* They are classified into two categories, namely *polar and non-polar dielectrics.*

Non-Polar Dielectrics

A dielectric material in which, there is no permanent dipole existence in the absence of an external field is called non-polar dielectrics.

This is because, in these type of dielectrics, the centroid of the positive and negative charges of the molecules constituting the dielectric material coincide.

Examples *are* H_2, N_2, O_2, CO_2 and CH_4. These molecules are called *non-polar molecules.*

Polar Dielectrics

A dielectric material in which there is an existence of permanent dipole even in the absence of an external field is called a polar dielectric.

This is because, in these type of dielectrics, the center of the positive charges and negative charges of the molecules constituting the dielectric material do not coincide even in the absence of an external field.

Examples *are* H_2O, HCl and CO. These molecules are called *polar molecules.*

Polarization Field

1. *Relative Permittivity or Dielectric Constant* ε_r

The dielectric characteristics are determined by the dielectric constant.

The dielectric constant or relative permittivity ε_r is *defined as, the ratio between the permittivity of the medium* ε *and the permittivity of free space* ε_o.

i.e.,
$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o}$$

ε_r is a dimensionless quantity and varies widely from material to material. ε_r has a value of unity for vacuum and for all other dielectrics ε_r is always greater than 1. Since $\varepsilon_r > 1$, we can write $\varepsilon_r = 1 + \chi_e$, where χ_e is called electric susceptibility. Permittivity of a medium (material) indicates, the polarisable nature of a material.

Note:
- ε_r is a constant for a given isotropic material when the applied field is static (dc) and is referred to as static dielectric constant. But, when the material is subjected to an alternating field it becomes a frequency dependent complex quantity.
- ε_r value varies with direction in the case of anisotropic materials.

2. *Polarisation Vector P*

Polarisation vector measures the extent of polarisation in a unit volume of dielectric matter.

Definition - 1 : *It is defined as the induced dipole moment per unit volume of the dielectric.*

P is a vector quantity and, its direction is along the direction of the applied field. If μ is the average induced dipole moment per unit molecule and N is the number of molecules per unit volume then, the polarisation is given by,

$$P = N\mu$$

Definition 2 : *The polarisation P is also defined as the induced surface charge per unit area.*

The above definition is explained below.

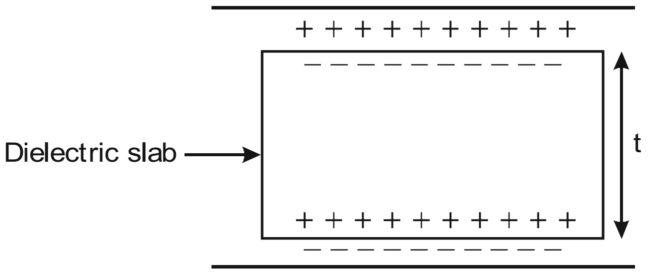


Fig. 1.4 *Dielectric Slab in a Capacitor*

Let, the polarisation of the dielectric slab as a whole give rise to +q and –q induced charges on the respective faces of a dielectric slab of thickness t and volume V kept between the two plates of a capacitor as shown in Figure (1.4). Therefore, the dipole moment of the slab is given by qt. Thus, the dipole moment per unit volume of the dielectric or the polarisation is given by

$$P = \frac{qt}{V}$$

$$P = \frac{qt}{At} \quad [\because V = At, \text{ where A is the area of the slab}]$$

$$\therefore \qquad P = \frac{q}{A}$$

Thus, the polarisation is also defined as the induced surface charge per unit area.

But, $\frac{q}{A}$ is the induced charge density. Therefore, magnitude of polarisation is equal to the induced charge density.

The unit of polarisation is **Cm^{-2}.**

3. *Electric Susceptibility χ_e*

In a large number of dielectrics it is found that the polarisation is directly proportional to the external field (applied) E. For such case,

$$P \propto E$$

Thus, the relation between P and E can be given as,

$$P = \varepsilon_o \chi_e E$$

or

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

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

Definition: *The ratio of polarisation to the net electric field $\varepsilon_o E$ as modified by the induced charges on the surface of the dielectric is called susceptibility.*

4. *Relation between Polarisation P, Susceptibility χ_e and the Dielectric Constant ε_r*

Let us consider a parallel plate capacitor as shown in the Figure (1.5) between which an electric field E_o exists.

If σ is the surface charge density (i.e., charge per unit area) then, from Gauss law,

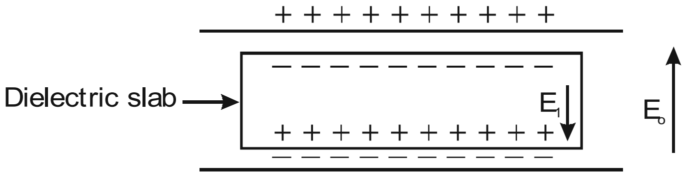


Fig. 1.5 *Fields in a Parallel Plate Capacitor with Dielectric in Between*

$$E_o = \frac{\sigma}{\varepsilon_o} \qquad \text{...(1.24)}$$

If a dielectric slab is placed between the plates of the capacitor; then, due to polarisation charges appear on the two faces of the slab and establish another field E_1 within the dielectric. This field will be in a direction opposite to that of E_o.

Therefore, the resultant field E can be given as,

$$E = E_o - E_1 \quad ...(1.25)$$

If σ_s is the surface charge density on the slab then, by following Equation (1.25), we can write,

$$E_1 = \frac{\sigma_s}{\varepsilon_o} \quad ...(1.26)$$

Therefore, from Equations (1.25), (1.26) and (1.27),

$$E = \frac{\sigma}{\varepsilon_o} - \frac{\sigma_s}{\varepsilon_o}$$

Or $$\varepsilon_o E = \sigma - \sigma_s \quad ...(1.27)$$

But, $$\sigma_s = P \quad (\because \text{ Polarisation is Charge/Unit Area})...(1.28)$$

Also, by gauss' law, the electric flux density or electric displacement density D is given by,

$$D = \sigma \ \text{ (D is charge/unit area)} \quad ...(1.29)$$

Therefore, Equation (1.28) can be written as,

$$\varepsilon_o E = D - P \quad ...(1.30)$$

Or $$D = \varepsilon_o E + P \quad ...(1.31)$$

But, from electrostatics we know,

$$D = \varepsilon E = \varepsilon_o \varepsilon_r E \quad ...(1.32)$$

Therefore, Equation (1.29) becomes,

$$\varepsilon_o \varepsilon_r E = \varepsilon_o E + P$$

Rearranging the above equation we can write,

$$\varepsilon_o E (\varepsilon_r - 1) = P \quad ...(1.33)$$

Or $$\frac{P}{\varepsilon_o E} = (\varepsilon_r - 1) \quad ...(1.34)$$

But, we know $\dfrac{P}{\varepsilon_o E} = \chi_e$

$$\therefore \quad \chi_e = \varepsilon_r - 1. \quad ...(1.35)$$

5. *Polarisability* α

Let us consider an individual atom in a dielectric material. Let, the material be subjected to an electric field E. It is found that, the induced dipolement μ acquired by the atom is proportional to the strength of the electric field E.

i.e., $\mu \propto E$

Or $\mu = \alpha E$

Where α is the proportionality constant *called polarisability.* Its unit is **$\mathbf{Fm^2}$.**

Note: Polarisability is not a bulk property of the material but, it is the property of an individual atom or molecule.

1.3 TRANSVERSE OPTICAL MODES IN A PLASMA

NOTES

In plasma physics, waves in plasmas are referred as an interconnected set of particles and fields which propagate in a periodically repeating fashion. A plasma is a quasineutral, electrically conductive fluid. In the simplest case, it is composed of electrons and a single species of positive ions, but it may also contain multiple ion species including negative ions as well as neutral particles. Due to its electrical conductivity, a plasma couples to electric and magnetic fields. This complex of particles and fields supports a wide variety of wave phenomena.

The word 'Plasma' is taken from Ancient Greek which means 'Moldable Substance'; it is one of the four fundamental states of matter after solid, liquid, and gas and is typically consists of a gas of ions – atoms or molecules which have at least one orbital electron stripped, or an extra electron attached and, thus, an electric charge. The plasma is the most abundant form of ordinary matter in the universe, primarily associated with stars, including the Sun.

In a plasma, however, the particles react in concert with any electromagnetic field, for example as in an electromagnetic wave, in addition to any pressure or velocity field, for example as in a sound wave. In fact, in a plasma sound wave the electrons and ions become slightly separated owing to their difference in mass, and an electric field builds up to bring them back together. The result is called an ion acoustic wave. This is just one of the many types of waves that can exist in a plasma.

Plasma parameters define various characteristics of a plasma, an electrically conductive collection of charged particles that responds collectively to electromagnetic forces. Plasma typically takes the form of neutral gas-like clouds or charged ion beams but may also include dust and grains.

A dusty plasma contains tiny charged particles of dust, typically found in space. The dust particles acquire high charges and interact with each other. A plasma that contains larger particles is called grain plasma. Under laboratory conditions, dusty plasmas are also called complex plasmas.

When the magnetic field is absent then the electromagnetic waves can propagate in plasma merely at the frequencies which are higher in comparison to the plasma frequency. Waves having frequencies lower than the plasma frequency are reflected from the plasma boundaries. When the magnetic field is present, then the waves polarised along with their electric fields that are typically parallel to the constant external magnetic field behaving in an analogous manner. Characteristically, the magnetic field has no impact on these waves. The plasma particles typically move in the direction of the electric field and the magnetic field which applies no influence on their motion.

The electromagnetic fields in a plasma are assumed to have two parts, one static/equilibrium part and one oscillating/perturbation part. Waves in plasmas can be classified as electromagnetic or electrostatic according to whether or not there is an oscillating magnetic field. Applying Faraday's law of induction to plane waves, we find,

$$\mathbf{k} \times \tilde{\mathbf{E}} = \omega \tilde{\mathbf{B}}$$

This implies that an electrostatic wave must be purely longitudinal. An electromagnetic wave, in contrast, must have a transverse component, but may also be partially longitudinal.

Transverse Optical Modes

A transverse mode of electromagnetic radiation is a particular electromagnetic field pattern of the radiation in the plane perpendicular, i.e., transverse to the radiation's propagation direction. Transverse modes occur in radio waves and microwaves confined to a waveguide, and also in light waves in an optical fiber and in a Laser's optical resonator.

Transverse modes occur because of boundary conditions imposed on the wave by the waveguide. For example, a radio wave in a hollow metal waveguide must have zero tangential electric field amplitude at the walls of the waveguide, so the transverse pattern of the electric field of waves is restricted to those that fit between the walls. For this reason, the modes supported by a waveguide are quantized. The allowed modes can be obtained by solving Maxwell's equations for the boundary conditions of a given waveguide.

Unguided electromagnetic waves in free space, or in a bulk isotropic dielectric, can be described as a superposition of plane waves. Typically, these electromagnetic waves can be described as TEM (Transverse ElectroMagnetic) modes.

However, in any sort of waveguide where boundary conditions are imposed by a physical structure, a wave of a particular frequency can be described in terms of a **transverse mode** or superposition of such modes. These modes generally follow different propagation constants. When two or more modes have an identical propagation constant along the waveguide, then there is more than one modal decomposition possible in order to describe a wave with that propagation constant, for instance a non-central Gaussian Laser mode can be equivalently described as a superposition of Hermite-Gaussian modes or Laguerre-Gaussian modes.

Waveguides

Following are the various modes in waveguides:

Transverse ElectroMagnetic (TEM) Modes: These are neither electric nor magnetic field in the direction of propagation.

Transverse Electric (TE) Modes: There is no electric field in the direction of propagation. These are sometimes called H modes because there is only a magnetic field along the direction of propagation. Here 'H' is the conventional symbol for magnetic field.

Transverse Magnetic (TM) Modes: There is no magnetic field in the direction of propagation. These are sometimes called E modes because there is only an electric field along the direction of propagation.

Hybrid Modes: These are non-zero electric and magnetic fields in the direction of propagation.

Following Figure (1.6) illustrates the field patterns of some commonly used waveguide modes.

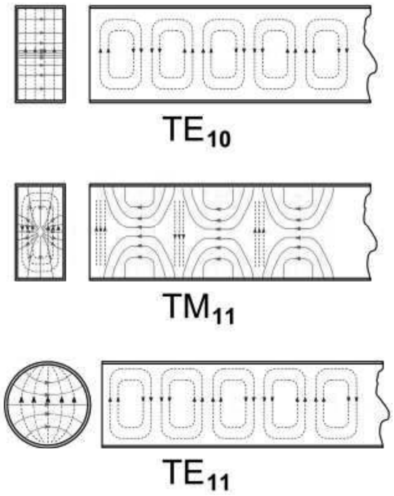


Fig. 1.6 *Field Patterns of Commonly used Waveguide Modes*

Hollow metallic waveguides filled with a homogeneous, isotropic material (usually air) support TE and TM modes but not the TEM mode. In coaxial cable, the energy is normally transported in the fundamental TEM mode. The TEM mode is also generally assumed for the majority of other electrical conductor line formats. This is usually an accurate assumption, but a key exception is microstrip which has a significant longitudinal component to the propagated wave due to the inhomogeneity at the boundary of the dielectric substrate below the conductor and the air above it. In an **optical fiber** or other **dielectric waveguide**, modes are generally of the hybrid type.

In rectangular waveguides, rectangular mode numbers are designated by two suffix numbers attached to the mode type, such as TE_{mn} or TM_{mn}, where 'm' is the number of half-wave patterns across the width of the waveguide and 'n' is the number of half-wave patterns across the height of the waveguide. In circular waveguides, circular modes exist and here 'm' is the number of full-wave patterns along the circumference and 'n' is the number of half-wave patterns along the diameter.

Optical Fibres

The number of modes in an optical fiber distinguishes multi-mode optical fiber from single-mode optical fiber. To determine the number of modes in a step-index fiber, the V number needs to be determined:

$$V = k_0 a \sqrt{n_1^2 - n_2^2}$$

Where k_0 is the wavenumber, a is the fibre's core radius, and n_1 and n_2 are the refractive indices of the core and cladding, respectively. Fiber with a V-parameter of less than 2.405 only supports the fundamental mode, a hybrid mode, and is therefore a single-mode fiber whereas fiber with a higher V-parameter has multiple modes.

Decomposition of field distributions into modes is useful because a large number of field amplitudes readings can be simplified into a much smaller number of mode amplitudes. Because these modes change over time according to a simple set of rules, it is also possible to anticipate future behaviour of the field distribution. These simplifications of complex field distributions ease the signal processing requirements of fiber-optic communication systems.

The modes in typical low refractive index contrast fibres are usually referred to as LP (Linear Polarization) modes, which refers to a scalar approximation for the field solution, treating it as if it contains only one transverse field component.

1.3.1 Transparency of Alkali Metals in the Ultraviolet

The **alkali metals** consist of the chemical elements Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs), and Francium (Fr). The alkali metals are so called because reaction with water forms alkalies, i.e., strong bases capable of neutralizing acids. Francium, a natural radioactive isotope. Together with hydrogen they constitute Group 1, which lies in the s-block of the periodic table. All alkali metals have their outermost electron in an s-orbital, this shared electron configuration results in their having very similar characteristic properties. Certainly, the alkali metals provide the best example of group trends in properties in the periodic table, with elements exhibiting well-characterised homologous behaviour. This family of elements is also known as the 'Lithium Family' after its leading element.

The alkali metals are all shiny, soft, highly reactive metals at Standard Temperature and Pressure (STP) and readily lose their outermost electron to form cations with charge +1. They can all be cut easily with a knife due to their softness, exposing a shiny surface that tarnishes rapidly in air due to oxidation by atmospheric moisture and oxygen. Because of their high reactivity, they must be stored under oil to prevent reaction with air and are found naturally only in salts and never as the free elements. Caesium, the fifth alkali metal, is the most reactive of all the metals. All the alkali metals react with water, with the heavier alkali metals reacting more vigorously than the lighter ones.

All of the discovered alkali metals occur in nature as their compounds; in order of abundance, sodium is the most abundant, followed by potassium, lithium, rubidium, caesium, and finally francium, which is very rare due to its extremely high radioactivity. Francium occurs only in minute traces in nature as an intermediate step in some obscure side branches of the natural decay chains.

The alkali metals have often been characterized as being **transparent** to optical radiation in the **UltraViolet (UV)**. The alkali metals become highly transparent in the ultraviolet region, there being for each metal a definite wavelength above which the metal becomes opaque. Kronig has used the quantum theory of the optical properties of metals previously developed by him to account qualitatively for the phenomenon and has suggested that it is due to the absorption bands caused by the periodicity of the lattice. If the electrons are treated as free (moving in no field), then only the qualitatively phenomenon can be accounted and also the approximate values of the critical wavelength can be predicted accurately. Subsequently, it can be deduced that the influence of the absorption bands is small.

1.3.2 Longitudinal Optical Modes in a Plasma Plasmon

Characteristically, a plasmon is precisely defined and characterised as a quantum of plasma oscillation. Basically, as the light, an optical oscillation, distinctively consists of photons similarly the plasma oscillation distinctively consists of the plasmons. In solid state physics, the plasmon is uniquely considered or characterised as a quasiparticle because it evolves or occurs after the quantization of the plasma oscillations, exactly like the phonons which are defined as the quantization's of mechanical vibrations. Consequently, the plasmons are referred as collective (a discrete number) oscillations of the free electron gas density. Subsequently, when an electron collides with an atom or an ion, then there is some or certain probability that the electron may hit and kick out another electron, by leaving behind the ion in the state of having the next highest charge, i.e., the charge 'q' increased by $+1$. This is termed as the electron-impact ionization and is considered as the dominant process by means of which the atoms and the ions become more highly charged.

The term plasmon was initially proposed in 1952 by David Pines and David Bohm and was shown to arise from a Hamiltonian for the long-range electron-electron correlations. Since plasmons are the quantization of classical plasma oscillations, most of their properties can be derived directly from Maxwell's equations.

A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, specifically in solids and some liquids. Often referred to as a quasiparticle, it is an excited state in the quantum mechanical quantization of the modes of vibrations for elastic structures of interacting particles. Phonons can be thought of as quantized sound waves, similar to photons as quantized light waves.

The concept of phonons was introduced in 1932 by Soviet physicist Igor Tamm. The name phonon comes from the Greek word 'Phonē' which translates to 'Sound or Voice', because long wavelength phonons give rise to sound. The name is analogous to the word photon.

Solids with more than one atom in the smallest unit cell exhibit two types of phonons, namely Acoustic Phonons and Optical Phonons.

Acoustic Phonons

Acoustic phonons are coherent movements of atoms of the lattice out of their equilibrium positions. If the displacement is in the direction of propagation, then in some areas the atoms will be closer, in others farther apart, as in a sound wave in air, hence the name acoustic. Displacement perpendicular to the propagation direction is comparable to waves on a string. If the wavelength of acoustic phonons goes to infinity, this corresponds to a simple displacement of the whole crystal, and this costs zero deformation energy. Acoustic phonons exhibit a linear relationship between frequency and phonon wave-vector for long wavelengths. The frequencies of acoustic phonons tend to zero with longer wavelength. Longitudinal Acoustic and Transverse Acoustic phonons are often abbreviated as LA and TA phonons, respectively.

Optical Phonons

Optical phonons are out-of-phase movements of the atoms in the lattice, one atom moving to the left, and its neighbour to the right. This occurs if the lattice basis consists of two or more atoms. They are called optical because in ionic crystals, such as sodium chloride, fluctuations in displacement create an electrical polarization that couples to the electromagnetic field. Hence, they can be excited by infrared radiation, the electric field of the light will move every positive sodium ion in the direction of the field, and every negative chloride ion in the other direction, causing the crystal to vibrate.

Optical phonons have a non-zero frequency at the Brillouin zone center and show no dispersion near that long wavelength limit. This is because they correspond to a mode of vibration where positive and negative ions at adjacent lattice sites swing against each other, creating a time-varying electrical dipole moment.

Optical phonons that interact in this way with light are called InfraRed (IR) active. Optical phonons that are Raman active can also interact indirectly with light, through Raman scattering.

Optical phonons are often abbreviated as LO and TO phonons, for the **Longitudinal Optical mode** and Transverse Optical mode, respectively. The splitting between LO and TO frequencies is often described accurately by the Lyddane–Sachs–Teller relation.

The Longitudinal Optical (LO) mode order in compounds can be explained with a plasmon or plasmon-like phonon mode and additional phonon modes. When the oscillator strength of the plasmon or plasmon-like mode is gradually increased, a reordering of the modes takes place. Since it is not possible in crystals with orthorhombic or higher symmetry that a LO mode crosses a Transverse Optical (TO) mode's position, this reordering takes place via mode hybridization. During this mode hybridization, the plasmon or plasmon-like LO mode gradually becomes the originally higher situated LO mode while the latter morphs into the former. As a consequence, an inner (LO-TO) and an outer (TO-LO) mode pair is formed. This process continues until the LO oscillator strength is so high that all other phonons are inverted and form LO-TO pairs within the outer TO-LO mode pair of the plasmon or plasmon-like mode. These insights can be readily transferred to other semiconductors or many mode materials with reststrahlen bands and allow simple mode assignments. These mode assignments will help to understand the nature of surface modes of structured layers of these materials for application of surface plasmon polariton and surface phonon polaritons based metamaterials.

The reststrahlen effect, German: "Residual Rays", is a reflectance phenomenon in which electromagnetic radiation within a narrow energy band cannot propagate within a given medium due to a change in refractive index concurrent with the specific absorbance band of the medium in question, this narrow energy band is termed the reststrahlen band. As a result of this inability to propagate, normally incident reststrahlen band radiation experiences strong reflection or total reflection from that medium. The energies at which reststrahlen bands occur vary and are particular to the individual compound.

Numerous physical attributes of a compound will have an effect on the appearance of the reststrahlen band. These include phonon band gap, particle/grain size, strongly absorbing compounds, compounds with optically opaque bands in the infrared.

When measuring optical phonon energy experimentally, optical phonon frequencies are sometimes given in spectroscopic wavenumber notation, where the symbol ω represents ordinary frequency (not angular frequency) and is expressed in units of cm^{-1}. The value is obtained by dividing the frequency by the speed of light in vacuum. In other words, the wave number in cm^{-1} units corresponds to the inverse of the wavelength of a photon in vacuum, that has the same frequency as the measured phonon.

Check Your Progress

1. What are free electrons?
2. Define the four key assumptions considered in the free electron model.
3. What is thermal conductivity?
4. State the Wiedemann-Franz law.
5. What is Nearly Free Electron (NFE) model?
6. What is dielectric material or dielectric medium?
7. Define the terms plasma and plasma parameters.
8. What are the various modes in waveguides?

1.4 ELECTROSTATIC SCREENING

In physics, **screening** is the damping of electric fields caused by the presence of mobile charge carriers. It is an important part of the behaviour of charge carrying fluids, such as ionized gases (classical plasmas), electrolytes, and charge carriers in electronic conductors (semiconductors, metals). In a fluid, with a given permittivity ε, composed of electrically charged constituent particles, each pair of particles (with charges q_1 and q_2) interact through the Coulomb force as,

$$\mathbf{F} = \frac{q_1 q_2}{4\pi\varepsilon|\mathbf{r}|^2}\hat{\mathbf{r}}$$

Where the vector **r** is the relative position between the charges. This interaction complicates the theoretical treatment of the fluid. For example, a naive quantum mechanical calculation of the ground-state energy density yields infinity, which is unreasonable. The difficulty lies in the fact that even though the Coulomb force diminishes with distance as $1/r^2$, the average number of particles at each distance r is proportional to r^2, assuming the fluid is fairly isotropic. As a result, a charge fluctuation at any one point has non-negligible effects at large distances.

In reality, these long-range effects are suppressed by the flow of particles in response to electric fields. This flow reduces the ***effective*** interaction between particles to a short-range **'Screened' Coulomb interaction**. This system corresponds to the simplest example of a renormalized interaction.

In solid state physics, especially for metals and semiconductors, the **screening effect** describes the electrostatic field and Coulomb potential of an ion inside the solid. Like the electric field of the nucleus is reduced inside an atom or ion due to the shielding effect, the electric fields of ions in conducting solids are further reduced by the cloud of conduction electrons.

NOTES

Consider a fluid composed of electrons moving in a uniform background of positive charge, one-component plasma. Each electron possesses a negative charge. According to Coulomb's interaction, negative charges repel each other. Consequently, this electron will repel other electrons creating a small region around itself in which there are fewer electrons. This region can be treated as a positively charged 'Screening Hole'. Viewed from a large distance, this screening hole has the effect of an overlaid positive charge which cancels the electric field produced by the electron. Only at short distances, inside the hole region, can the electron's field be detected. For a plasma, this effect can be made explicit by an N-body calculation. If the background is made up of positive ions, their attraction by the electron of interest reinforces the above screening mechanism. In atomic physics, a germane effect exists for atoms with more than one electron shell, the shielding effect. In plasma physics, electric-field screening is also called Debye screening or shielding. It manifests itself on macroscopic scales by a sheath (Debye sheath) next to a material with which the plasma is in contact.

The screened potential determines the inter atomic force and the phonon dispersion relation in metals. The screened potential is used to calculate the electronic band structure of a large variety of materials, often in combination with pseudopotential models. The screening effect leads to the independent electron approximation, which explains the predictive power of introductory models of solids like the Drude model, the free electron model and the nearly free electron model.

Theory and Models

The first theoretical treatment of electrostatic screening, due to Peter Debye and Erich Hückel, dealt with a stationary point charge embedded in a fluid.

Consider a fluid of electrons in a background of heavy, positively charged ions. For simplicity, the motion and spatial distribution of the ions are ignored, approximating them as a uniform background charge. This simplification is permissible since the electrons are lighter and more mobile than the ions, provided the distances much larger than the ionic separation are considered. In condensed matter physics, this model is referred to as 'Jellium'.

Screened Coulomb Interactions

Let ρ denote the number density of electrons, and ϕ the electric potential. At first, the electrons are evenly distributed so that there is zero net charge at every point. Therefore, ϕ is initially a constant as well.

We now introduce a fixed point charge Q at the origin. The associated charge density is $Q\delta(r)$, where $\delta(r)$ is the Dirac delta function. After the system has returned to equilibrium, let the change in the electron density and electric potential be $\Delta\rho(r)$ and $\Delta\phi(r)$, respectively. The charge density and electric potential are related by Poisson's equation, which gives,

NOTES

$$-\nabla^2[\Delta\phi(r)] = \frac{1}{\varepsilon_0}[Q\delta(r) - e\Delta\rho(r)],$$

Where ε_0 is the vacuum permittivity.

To proceed, we must find a second independent equation relating $\Delta\rho$ and $\Delta\phi$. We consider two possible approximations, under which the two quantities are proportional, namely the Debye–Hückel approximation, valid at high temperatures, for example classical plasmas, and the Thomas–Fermi approximation, valid at low temperatures, for example electrons in metals.

In a region free of charge, the electrostatic potential $V(x)$ is a harmonic function. If a bounded region $\mathcal{R}$ of space is surrounded by boundaries kept at the same potential, the potential satisfies,

$$\Delta V = 0 \quad \text{in} \quad \mathcal{R}, \qquad V\big|_{\partial\mathcal{R}} = C \qquad \text{…..(1.36)}$$

Theorem 1. The static electric field vanishes in the enclosed domain.

The presences of static electric charges and currents outside cannot create an electric field on the inside, therefore, it is perfectly shielded.

Proof. The function $V = C$ is one solution of Equation (1.36). Uniqueness of solutions follows from the maximum and minimum principals for harmonic functions. The field equal to grad V vanishes. If the domain $\mathcal{R}$ is the annular region $r_1 \leq |z| \leq r_2$, the unique harmonic function on $\mathcal{R}$ that has constant potential V_1 on the inner boundary and V_2 on the outer boundary is of the form $A \ln r + B$.

1.4.1 Electron Collisions

Electron collisions with atoms, ions, and molecules have represented an important area of 'Applied Quantum Mechanics' for more than a century.

When **electrons** pass through the conductor, the positive field of the ions attract the electrons, and this causes **collisions**. The greater the nuclear charge, the stronger the positive electric field of the ion will be and will attract electrons more, causing more collisions. Due to the high kinetic energy of the particle, when a positive ion attracts it towards itself, a collision can occur between the drifting charge and electrons in orbitals around the ion. The rate of collisions depends on the electronegativity of the atom.

When an electron collides with an atom or ion, there is a small probability that the electron kicks out another electron, leaving the ion in the next highest charge state, charge q increased by +1. This is called electron-impact ionization and is the dominant process by which atoms and ions become more highly charged. The rate equation is given by,

$$\mathbf{e^- + A(q) \rightarrow e^- + e^- + A(q+1)}$$

From energy conservation, it is clear that the initial energy of the incident electron must be larger than the ionization potential of the electron being removed.

1.5 BAND THEORY: NEARLY FREE ELECTRON MODEL

In solid state physics, the electronic band structure or simply band structure of a solid describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have called band gaps or forbidden bands.

Band theory of solids typically describe the quantum state of matter and theoretically explain the notion which an electron takes or holds inside a metal solid. Every single molecule is precisely comprised of several discrete energy levels. The specific manner in which the electrons typically behave inside a molecule is properly explained through the band theory. The concept and theoretical formulations of the 'Band Theory' was initially developed from the information and experience achieved during the quantum revolution in physics. In the year 1928, Felix Bloch, a Swiss-American physicist and Nobel physics laureate, applied the quantum theory to study the unique properties of the solids.

Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids, such as electrical resistivity and optical absorption, and forms the foundation of the understanding of all solid state devices, such as transistors, solar cells, etc.

The electrons of a single, isolated atom occupy atomic orbitals each of which has a discrete energy level. When two or more atoms join together to form a molecule, their atomic orbitals overlap and hybridize. Therefore, if two identical atoms combine to form a diatomic molecule, each atomic orbital splits into two molecular orbitals of different energy.

Similarly, if a large number N of identical atoms come together to form a solid, such as a crystal lattice, the atoms' atomic orbitals overlap with the nearby orbitals. Each discrete energy level splits into N levels, each with a different energy. Since the number of atoms in a macroscopic piece of solid is a very large number ($N \sim 10^{22}$) the number of orbitals is very large and thus they are very closely spaced in energy (of the order of 10^{-22} eV). The energy of the adjacent levels is so close together that they can be considered as a continuum, an **energy band**.

This formation of bands is mostly a feature of the outermost electrons (valence electrons) in the atom, which are the ones involved in chemical bonding and electrical conductivity. The inner electron orbitals do not overlap to a significant degree, so their bands are very narrow.

Band gaps are essentially leftover ranges of energy not covered by any band, a result of the finite widths of the energy bands. The bands have different widths, with the widths depending upon the degree of overlap in the atomic orbitals from which they arise. Two adjacent bands may simply not be wide enough to fully cover the range of energy. For example, the bands associated with core orbitals, such as 1s electrons are extremely narrow due to the small overlap between adjacent atoms. As a result, there tend to be large band gaps between the core bands. Higher bands involve comparatively larger orbitals with more overlap, becoming progressively wider at higher energies so that there are no band gaps at higher energies.

Band theory is only an approximation to the quantum state of a solid, which applies to solids consisting of many identical atoms or molecules bonded together.

Nearly Free Electron Model

In the Nearly Free Electron (NFE) approximation, interactions between electrons are completely ignored. This approximation allows use of Bloch's Theorem which states that electrons in a periodic potential have wavefunctions and energies which are periodic in wavevector up to a constant phase shift between neighbouring reciprocal lattice vectors. The consequences of periodicity are described mathematically by the Bloch's theorem.

The NFE model works particularly well in materials like metals where distances between neighbouring atoms are small. In such materials, the overlap of atomic orbitals and potentials on neighbouring atoms is relatively large. In that case the wave function of the electron can be approximated by a (modified) plane wave. The band structure of a metal like aluminium even gets close to the empty lattice approximation.

1.5.1 Wave Equation of Electron in a Periodic Potential and Bloch Function

A wave function is a function that attempts to describe the total energy of an electron. This includes all of the possible energy states of the electron and the amount of time that the electron stays in each state.

Wave equation of electron in a periodic potential is explained with reference to Bloch's theorem.

Bloch's theorem states that solutions to the Schrödinger equation in a periodic potential take the form of a plane wave modulated by a periodic function. Mathematically, the **Bloch Function** is written as,

$$\psi(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u(\mathbf{r})$$

Where **r** is position, ψ is the wave function, u is a periodic function with the same periodicity as the crystal, the wave vector **k** is the crystal momentum vector, 'e' is Euler's number, and 'i' is the imaginary unit.

Functions of this form are known as **Bloch functions** or **Bloch states**, and serve as a suitable basis for the wave functions or states of electrons in crystalline solids.

NOTES

Named after Swiss physicist Felix Bloch, the description of electrons in terms of Bloch functions, termed **Bloch electrons** (or less often **Bloch Waves**), underlies the concept of electronic band structures.

These eigenstates are written with subscripts as $\psi_{n\mathbf{k}}$, where n is a discrete index, called the band index, which is present because there are many different wave functions with the same **k** (each has a different periodic component u). Within a band (i.e., for fixed n), $\psi_{n\mathbf{k}}$ varies continuously with **k**, as does its energy. Also,$\psi_{\mathrm{n}\mathbf{k}}$ is unique only up to a constant reciprocal lattice vector **K**, or,

$$\psi_{n\mathbf{k}} = \psi_{n(\mathbf{k}+\mathbf{K})}.$$

Therefore, the wave vector **k** can be restricted to the first Brillouin zone of the reciprocal lattice without loss of generality.

The most common example of Bloch's theorem is describing electrons in a crystal, especially in characterizing the crystal's electronic properties, such as electronic band structure. However, a Bloch wave description applies more generally to any wave like phenomenon in a periodic medium. For example, a periodic dielectric structure in electromagnetism leads to photonic crystals, and a periodic acoustic medium leads to phononic crystals. It is generally treated in the various forms of the dynamical theory of diffraction.

Wave Vector and Bloch Wave Function

Suppose an electron is in a Bloch state,

$$\psi\,(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}}\,u(\mathbf{r})$$

Where u is periodic with the same periodicity as the crystal lattice. The actual quantum state of the electron is entirely determined by ψ, not **k** or u directly. This is important because **k** and u are **not unique**. Specifically, if ψ can be written as above using **k**, it can **also** be written using ($\mathbf{k} + \mathbf{K}$), where **K** is any reciprocal lattice vector (Refer Figure 1.7). Therefore, wave vectors that differ by a reciprocal lattice vector are equivalent, in the sense that they characterize the same set of Bloch states.

The first Brillouin zone is a restricted set of values of **k** with the property that no two of them are equivalent, yet every possible **k** is equivalent to one (and only one) vector in the first Brillouin zone. Therefore, if we restrict **k** to the first Brillouin zone, then every Bloch state has a unique **k**. Therefore, the first Brillouin zone is often used to depict all of the Bloch states without redundancy, for example in a band structure, and it is used for the same reason in many calculations.

When **k** is multiplied by the reduced Planck's constant, it equals the electron's crystal momentum. Related to this, the group velocity of an electron can be calculated based on how the energy of a Bloch state varies with **k**.

NOTES

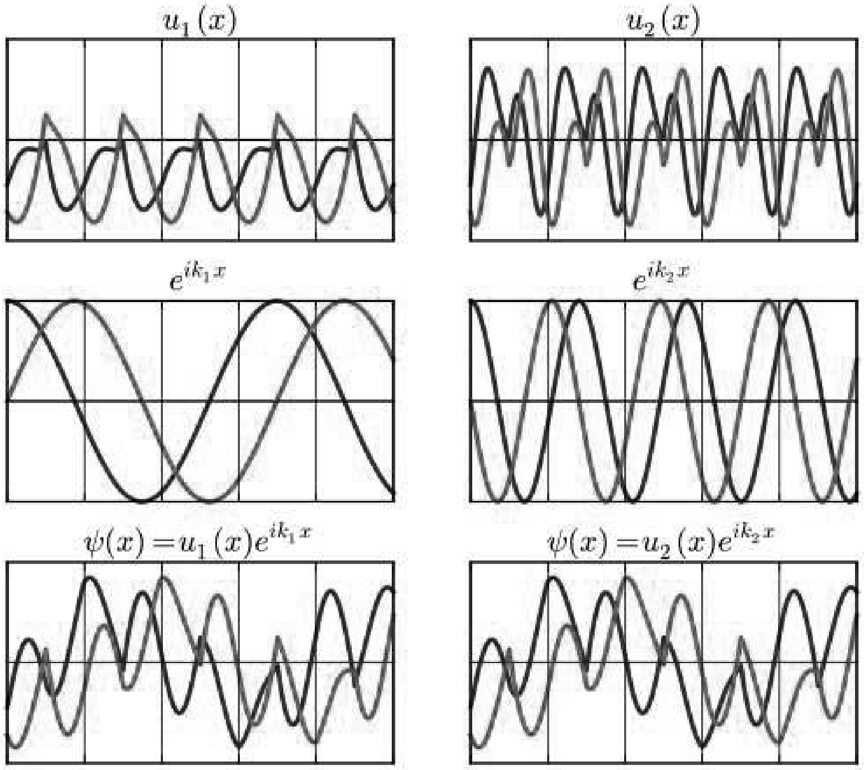


Fig. 1.*7 Bloch Wave Function*

Figure (1.7) illustrates a Bloch wave function (bottom), which can be broken up into the product of a periodic function (top) and a plane wave (center). The left side and right side represent the same Bloch state broken up in two different ways, involving the wave vector k_1 (left) or k_2 (right). The difference $(k_1 - k_2)$ is a reciprocal lattice vector.

1.5.2 Crystal Momentum of an Electron Reduced Zone Scheme

In solid state physics, **crystal momentum** or quasimomentum is a momentum like vector associated with electrons in a crystal lattice. It is defined by the associated wave vectors **k** of this lattice, according to,

$$\mathbf{p}_{\text{crystal}} \equiv \hbar\mathbf{k}$$

Where $\hbar$ is the reduced Planck's constant. Normally, crystal momentum is conserved like mechanical momentum, making it useful to physicists and materials scientists as an analytical tool.

Reduced Zone Schemes

The reduced zone scheme is where all the bands have been translated into the first Brillouin zone. Consider the consequences of the fact that,

$$\psi_{\mathbf{k+g}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$$

For the energy value(s) associated with that wavefunction; with **g** = Arbitrary Reciprocal Lattice Vector. Writing this as $\psi(\mathbf{k} + \mathbf{g}, \mathbf{r}) = \psi(\mathbf{k}, \mathbf{r})$ and taking **k** as a continuous variable, this means that $\psi(\mathbf{k}, \mathbf{r})$ is periodic in **k**-space. As a solution of the Schrödinger equation for the system, associated with $\psi(\mathbf{k}, \mathbf{r})$ there is a specific energy $E(\mathbf{k})$ which necessarily is also periodic:

$$\mathbf{E(k + g) = E(k)}$$

It means that any reciprocal lattice point can serve as the origin of the $E(\mathbf{k})$ function. It is possible to select the wavevector index **k** of any Bloch function to lie within the first Brillouin zone. The procedure is known as mapping the band in the reduced zone scheme.

Electrons in Crystals

A study of semiconductors define how electrons move through solids. The free electron gas model simply assumes that the electrons move through an empty periodic box. But of course, to describe a real solid the box should really be filled with the countless atoms around which the conduction electrons move.

The solid is crystalline, which means that the atoms are arranged in a periodic pattern. The atomic period should be as sumed to be many orders of magnitude shorter than the size of the periodic box. There must be many atoms in each direction in the box. Figure (1.8) illustrates the potential energy of an electron along a line of nuclei.

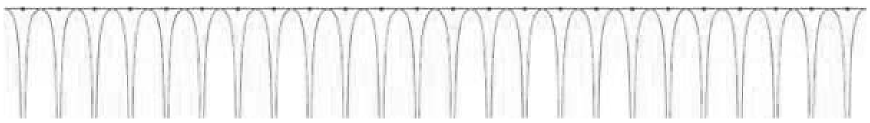


Fig. 1.8 *Potential Energy of an Electron along a Line of Nuclei*

The effect of the crystal is to introduce a periodic potential energy for the electrons. For example, Figure (1.8) gives a sketch of the potential energy of an electron along a line of nuclei. Whenever the electron is right on top of a nucleus, its potential energy falls or drops. Close enough to a nucleus, a very strong attractive Coulomb potential is seen. Of course, on a line that does not pass exactly through nuclei, the potential will not drop that low.

Figure (1.9) illustrates the potential energy of an electron in the one-dimensional simplified model stated by Kronig & Penney.

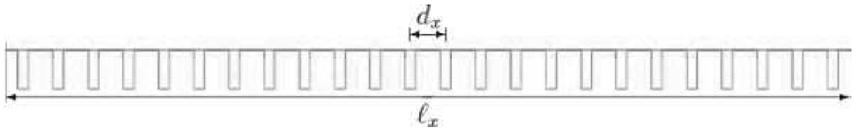


Fig. 1.9 *Potential Energy of an Electron in the One-Dimensional Simplified Model given by Kronig & Penney*

Kronig & Penney developed a very simple onedimensional model that explains much of the motion of electrons through crystals. It assumes that the potential energy seen by the electrons is periodic on some atomic scale period d_x. It also assumes that this potential consists of square dips, as illustrated in Figure (1.9). The regions of lowered potential energy are defined as the immediate vicinity of the nuclei. This is the model that will be examined. The atomic period

d_x is assumed to be much smaller than the periodic box size l_x, i.e. the size of the complete crystal. In particular, the box should contain a large and whole number of atomic periods. Three dimensional Kronig & Penney quantum states can be formed as products of one-dimensional ones. How-ever, such states are limited to potentials that are sums of one-dimensional ones.

1.5.3 Periodic Zone Scheme

The Kronig-Penney model is a simplified model for an electron in a one-dimensional periodic potential. The possible states that the electron can occupy are determined by the Schrödinger equation of the form,

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

In the case of the Kroning & Penney model, the potential $V(x)$ is a periodic square wave as shown in Figure (1.10).

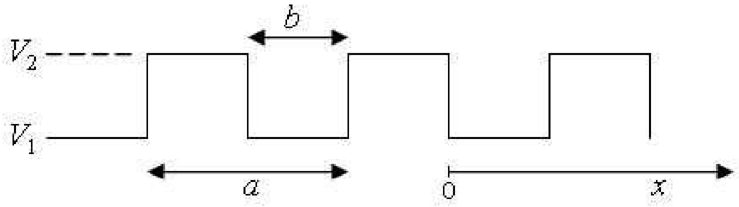


Fig. 1.10 *Kroning & Penney: Potential V(x) in a Periodic Square Wave*

A virtue of this model is that it is possible to analytically determine the energy eigenvalues and eigenfunctions. It is also possible to find analytic expressions for the dispersion relation (E vs. k) and the electron density of states.

1.5.4 Number of Orbitals in Metals, Band Insulators and Semiconductors

Although there are an infinite number of bands and thus an infinite number of states, there are only a finite number of electrons to place in these bands. The preferred value for the number of electrons is a consequence of electrostatics, even though the surface of a material can be charged, the internal bulk of a material prefers to be charge neutral. The condition of charge neutrality means that N/V must match the density of protons in the material. For this to occur, the material electrostatically adjusts itself, shifting its band structure up or down in energy (thereby shifting **g**(E)), until it is at the correct equilibrium with respect to the Fermi level.

A solid has an infinite number of allowed bands, just as an atom has infinitely many energy levels. However, most of the bands simply have too high energy, and are usually disregarded under ordinary circumstances. Conversely, there are very low energy bands associated with the **core orbitals**, such as **1s electrons**. These low-energy core bands are also usually disregarded since they remain filled with electrons at all times and are therefore inert. Likewise, materials have several band gaps throughout their band structure.

Bonding in metals and semiconductors can be described using **band theory**, in which a set of molecular orbitals is generated that extends throughout the solid. Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence ns, (n – 1)d, and np orbitals (with a total capacity of 18 electrons per metal atom) or their ns and (n – 1)d orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators: In contrast to metals, electrical insulators are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible, thermal energy cannot excite an electron from a filled level to an empty one. Consider the valence-band structure of diamond, because diamond has only 4 bonded neighbours rather than the 6 to 12 typical of metals, therefore the carbon **2s orbitals** and **2p orbitals** combine to form **two bands** in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus, there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

Semiconductors: The difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators. This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller. Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction band.

The most important bands and band gaps—those relevant for electronics and optoelectronics—are those with energies near the Fermi level. The bands and band gaps near the Fermi level are given special names, depending on the material:

Semiconductor or Band Insulator: In a semiconductor or band insulator, the Fermi level is surrounded by a band gap, referred to as the band gap, to distinguish it from the other band gaps in the band structure. The closest band above the band gap is called the **conduction band**, and the closest band beneath the band gap is called the **valence band**. The name 'Valence Band' was coined by analogy to chemistry, since in semiconductors and insulators the valence band is built out of the **valence orbitals**.

NOTES

Metal or Semimetal: In a metal or semimetal, the Fermi level is inside of one or more allowed bands. In semimetals the bands are usually referred to as 'Conduction Band' or 'Valence Band' depending on whether the charge transport is more electron-like or hole-like, by analogy to semiconductors. In many metals, however, the bands are neither electron-like nor hole-like, and often just called 'Valence Band' as they are made of 'Valence Orbitals'.

Check Your Progress

9. What does screened potential determine?
10. How electron collision occurs?
11. What is Nearly Free Electron (NFE) approximation?
12. Define the term wave function.
13. What does Bloch's theorem state?
14. Why is crystal momentum studied?
15. Give the significant properties of semiconductor or band insulator and metal or semimetal.

1.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The free electrons, considered analogous or identical to the outermost or valence, electrons of free metal atoms are presumed to be moving independently of one another throughout the entire crystal.
2. Following four key assumptions are considered in the free electron model:

   Free Electron Approximation: The interaction between the ions and the valence electrons is mostly neglected, except in boundary conditions. The ions only keep the charge neutrality in the metal. Unlike in the Drude model, the ions are not necessarily the source of collisions.

   Independent Electron Approximation: The interactions between electrons are ignored. The electrostatic fields in metals are weak because of the screening effect.

   Relaxation-Time Approximation: There is some unknown scattering mechanism such that the electron probability of collision is inversely proportional to the relaxation time , which represents the average time between collisions. The collisions do not depend on the electronic configuration.

   Pauli Exclusion Principle: Each quantum state of the system can only be occupied by a single electron. This restriction of available electron states is considered by Fermi-Dirac statistics. Main predictions of the free-electron model are derived by the Sommerfeld expansion of the Fermi-Dirac occupancy for energies around the Fermi level.
3. The thermal conductivity is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.

4. Wiedemann-Franz law states that, the ratio of thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature.
5. The Nearly Free Electron model or NFE model or quasi-free electron model is defined as a quantum mechanical model of physical properties of electrons that moves almost freely through the crystal lattice of a solid. The model is closely related to the theoretical empty lattice approximation and is typically used to calculate the electronic band structure, specifically the metals.
6. A dielectric or dielectric material or dielectric medium is an electrical insulator that can be polarised by an applied electric field. When a dielectric material is placed in an electric field, electric charges do not flow through the material as they do in an electrical conductor, because they do not have loosely bound electrons or free electrons that may drift through the material, but as an alternative they slightly shift from their average equilibrium positions, causing dielectric polarisation.
7. The word 'Plasma' is taken from Ancient Greek which means 'Moldable Substance'; it is one of the four fundamental states of matter after solid, liquid, and gas and is typically consists of a gas of ions - atoms or molecules which have at least one orbital electron stripped, or an extra electron attached and, thus, an electric charge.

   Plasma parameters define various characteristics of a plasma, an electrically conductive collection of charged particles that responds collectively to electromagnetic forces.
8. Following are the various modes in waveguides:
   - Transverse ElectroMagnetic (TEM) Modes: These are neither electric nor magnetic field in the direction of propagation.
   - Transverse Electric (TE) Modes: There is no electric field in the direction of propagation. These are sometimes called H modes because there is only a magnetic field along the direction of propagation. Here 'H' is the conventional symbol for magnetic field.
   - Transverse Magnetic (TM) Modes: There is no magnetic field in the direction of propagation. These are sometimes called E modes because there is only an electric field along the direction of propagation.
   - Hybrid Modes: These are non-zero electric and magnetic fields in the direction of propagation.
9. The screened potential determines the inter atomic force and the phonon dispersion relation in metals. The screened potential is used to calculate the electronic band structure of a large variety of materials, often in combination with pseudopotential models. The screening effect leads to the independent electron approximation, which explains the predictive power of introductory models of solids like the Drude model, the free electron model and the nearly free electron model.
10. When electrons pass through the conductor, the positive field of the ions attract the electrons, and this causes collisions. The greater the nuclear charge, the stronger the positive electric field of the ion will be and will

attract electrons more, causing more collisions. Due to the high kinetic energy of the particle, when a positive ion attracts it towards itself, a collision can occur between the drifting charge and electrons in orbitals around the ion. The rate of collisions depends on the electronegativity of the atom.

11. In the Nearly Free Electron (NFE) approximation, interactions between electrons are completely ignored. This approximation allows use of Bloch's Theorem which states that electrons in a periodic potential have wavefunctions and energies which are periodic in wavevector up to a constant phase shift between neighbouring reciprocal lattice vectors. The consequences of periodicity are described mathematically by the Bloch's theorem.
12. A wave function is a function that attempts to describe the total energy of an electron. This includes all of the possible energy states of the electron and the amount of time that the electron stays in each state. Wave equation of electron in a periodic potential is explained with reference to Bloch's theorem.
13. Bloch's theorem states that solutions to the Schrödinger equation in a periodic potential take the form of a plane wave modulated by a periodic function. Mathematically, the Bloch Function is written as,

    $\Psi(\boldsymbol{r}) = e^{ik.r}\, u(\boldsymbol{r})$

    Where **r** is position, Ψ is the wave function, *u* is a periodic function with the same periodicity as the crystal, the wave vector **k** is the crystal momentum vector, ‘e’ is Euler's number, and ‘i’ is the imaginary unit.
14. The crystal momentum or quasimomentum is a momentum like vector associated with electrons in a crystal lattice. It is defined by the associated wave vectors **k** of this lattice, according to,

    $$\mathbf{p}_{\text{crystal}} \equiv \hbar\mathbf{k}$$

    Where $\hbar$ is the reduced Planck's constant. Normally, crystal momentum is conserved like mechanical momentum, making it useful to physicists and materials scientists as an analytical tool.
15. Semiconductor or Band Insulator: In a semiconductor or band insulator, the Fermi level is surrounded by a band gap, referred to as the band gap, to distinguish it from the other band gaps in the band structure. The closest band above the band gap is called the conduction band, and the closest band beneath the band gap is called the valence band. The name 'Valence Band' was coined by analogy to chemistry, since in semiconductors and insulators the valence band is built out of the valence orbitals.

    Metal or Semimetal: In a metal or semimetal, the Fermi level is inside of one or more allowed bands. In semimetals the bands are usually referred to as 'Conduction Band' or 'Valence Band' depending on whether the charge transport is more electron-like or hole-like, by analogy to semiconductors. In many metals, however, the bands are neither electron-like nor hole-like, and often just called 'Valence Band' as they are made of 'Valence Orbitals'.

1.7 SUMMARY

- In solid state physics, the representation of free electron model of metals of a metallic solid, such as a vessel filled with a gas containing free electrons, i.e., the electron responsible or accountable for high electrical and thermal conductivity.
- Characteristically, as per the Encyclopaedia Britannica, "The free electrons, considered analogous or identical to the outermost or valence, electrons of free metal atoms are presumed to be moving independently of one another throughout the entire crystal".
- The free electron model was originally proposed or recommended around 1900 by the Dutch physicist Hendrik A. Lorentz which was further revised and enhanced by Arnold Sommerfeld of Germany in 1928. The concepts of quantum mechanical were introduced by Sommerfeld, of which the most notable is the Pauli exclusion principle.
- Free Electron Approximation: The interaction between the ions and the valence electrons is mostly neglected, except in boundary conditions. The ions only keep the charge neutrality in the metal. Unlike in the Drude model, the ions are not necessarily the source of collisions.
- Independent Electron Approximation: The interactions between electrons are ignored. The electrostatic fields in metals are weak because of the screening effect.
- Relaxation-Time Approximation: There is some unknown scattering mechanism such that the electron probability of collision is inversely proportional to the relaxation time , which represents the average time between collisions. The collisions do not depend on the electronic configuration.
- Pauli Exclusion Principle: Each quantum state of the system can only be occupied by a single electron. This restriction of available electron states is considered by Fermi-Dirac statistics. Main predictions of the free-electron model are derived by the Sommerfeld expansion of the Fermi-Dirac occupancy for energies around the Fermi level.
- The study of valence electrons present in a band, which controls the various properties of metals is known as electron theory of metals.
- Classical free electron theory of metals was developed by Drude and Lorentz. Even though it is a macroscopic theory it successfully explained most of the properties of metals.
- The free electrons collide with the positive ions in the lattice and also among themselves. All the collisions are elastic, i.e., there is no loss of energy.
- The electrostatic force of attraction between the free electrons and the metallic ions are neglected, i.e., the total energy of free electron is equal to its kinetic energy.
- The average time between two consecutive collisions of an electron with the lattice points is called collision time.

NOTES

- Mean free path is the average distance travelled by the conduction electron between successive collisions with the lattice ions.
- Electrical conductivity of a conductor is the property by which it allows the flow of electric current. In a metal, the valence electrons are not attached to the individual atoms and are free to move about within the lattice. Hence, the valence electrons are also called free electrons or conduction electrons.
- The thermal conductivity is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.
- Wiedemann-Franz Law states that, the ratio of thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature.
- The Nearly Free Electron model or NFE model or quasi-free electron model is defined as a quantum mechanical model of physical properties of electrons that moves almost freely through the crystal lattice of a solid.
- The NFE model is closely related to the theoretical empty lattice approximation and is typically used to calculate the electronic band structure, specifically the metals.
- The Nearly Free Electron or NFE model is defined as a modification or variation of the free-electron gas model which comprises of a weak periodic perturbation specifically designed for modeling the interaction between the conduction electrons and the ions in a crystalline solid.
- The NFE model, similar to the free-electron model, does not consider electron-electron interactions, i.e., the approximation of independent electron is yet in effect.
- A dielectric or dielectric material or dielectric medium is an electrical insulator that can be polarised by an applied electric field.
- When a dielectric material is placed in an electric field, electric charges do not flow through the material as they do in an electrical conductor, because they do not have loosely bound electrons or free electrons that may drift through the material, but as an alternative they slightly shift from their average equilibrium positions, causing dielectric polarisation.
- Because of dielectric polarisation, positive charges are displaced in the direction of the field and negative charges shift in the direction opposite to the field, for example if the field is moving parallel to the positive X axis, then the negative charges will shift in the negative X direction. This creates an internal electric field that reduces the overall field within the dielectric itself.
- If a dielectric is composed of weakly bonded molecules, those molecules not only become polarised, but also reorient so that their symmetry axes align to the field.
- The term dielectric was coined by William Whewell, taken from 'Dia + Electric' in response to a request from Michael Faraday.
- A perfect dielectric is a material with zero electrical conductivity, consequently exhibiting only a displacement current, hence it stores and returns electrical energy as if it were an ideal capacitor.

NOTES

- The behaviour of a dielectric material can be changed by the application of an external electric field.
- But, when an external electric field is applied, it causes the electron cloud to move in opposite direction. Thus, the centeroids of the positive and negative charges now no longer coincide and as a result an electric dipole is induced in the atom. Thus, the atoms are said to be polarised.
- A pair of equal and opposite charges separated by a small distance constitutes an electric dipole.
- A dielectric material in which, there is no permanent dipole existence in the absence of an external field is called non-polar dielectrics.
- A dielectric material in which there is an existence of permanent dipole even in the absence of an external field is called a polar dielectric.
- In plasma physics, waves in plasmas are referred as an interconnected set of particles and fields which propagate in a periodically repeating fashion.
- A plasma is a quasineutral, electrically conductive fluid. In the simplest case, it is composed of electrons and a single species of positive ions, but it may also contain multiple ion species including negative ions as well as neutral particles. Due to its electrical conductivity, a plasma couples to electric and magnetic fields.
- The word 'Plasma' is taken from Ancient Greek which means 'Moldable Substance'; it is one of the four fundamental states of matter after solid, liquid, and gas and is typically consists of a gas of ions - atoms or molecules which have at least one orbital electron stripped, or an extra electron attached and, thus, an electric charge.
- The plasma is the most abundant form of ordinary matter in the universe, primarily associated with stars, including the Sun.
- In a plasma, however, the particles react in concert with any electromagnetic field, for example as in an electromagnetic wave, in addition to any pressure or velocity field, for example as in a sound wave.
- In fact, in a plasma sound wave the electrons and ions become slightly separated owing to their difference in mass, and an electric field builds up to bring them back together. The result is called an ion acoustic wave.
- Plasma parameters define various characteristics of a plasma, an electrically conductive collection of charged particles that responds collectively to electromagnetic forces. Plasma typically takes the form of neutral gas-like clouds or charged ion beams but may also include dust and grains.
- A transverse mode of electromagnetic radiation is a particular electromagnetic field pattern of the radiation in the plane perpendicular, i.e., transverse to the radiation's propagation direction. Transverse modes occur in radio waves and microwaves confined to a waveguide, and also in light waves in an optical fiber and in a Laser's optical resonator.
- Transverse ElectroMagnetic (TEM) modes are neither electric nor magnetic field in the direction of propagation.

- Transverse Electric (TE) Modes: There is no electric field in the direction of propagation. These are sometimes called H modes because there is only a magnetic field along the direction of propagation. Here 'H' is the conventional symbol for magnetic field.
- Transverse Magnetic (TM) Modes: There is no magnetic field in the direction of propagation. These are sometimes called E modes because there is only an electric field along the direction of propagation.
- Hybrid Modes: These are non-zero electric and magnetic fields in the direction of propagation.
- The alkali metals have often been characterized as being transparent to optical radiation in the UltraViolet (UV). The alkali metals become highly transparent in the ultraviolet region, there being for each metal a definite wavelength above which the metal becomes opaque.
- A plasmon is a quantum of plasma oscillation. Just as light, an optical oscillation, consists of photons, the plasma oscillation consists of plasmons.
- The plasmon can be considered as a quasiparticle since it arises from the quantization of plasma oscillations, just like phonons are quantisation's of mechanical vibrations. Thus, plasmons are collective, a discrete number, oscillations of the free electron gas density.
- The term plasmon was initially proposed in 1952 by David Pines and David Bohm and was shown to arise from a Hamiltonian for the long-range electron-electron correlations. Since plasmons are the quantization of classical plasma oscillations, most of their properties can be derived directly from Maxwell's equations.
- A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, specifically in solids and some liquids. Often referred to as a quasiparticle, it is an excited state in the quantum mechanical quantization of the modes of vibrations for elastic structures of interacting particles.
- The concept of phonons was introduced in 1932 by Soviet physicist Igor Tamm. The name phonon comes from the Greek word 'Phon?' which translates to 'Sound or Voice', because long wavelength phonons give rise to sound. The name is analogous to the word photon.
- Optical phonons have a non-zero frequency at the Brillouin zone center and show no dispersion near that long wavelength limit. This is because they correspond to a mode of vibration where positive and negative ions at adjacent lattice sites swing against each other, creating a time-varying electrical dipole moment.
- Optical phonons that interact in this way with light are called InfraRed (IR) active. Optical phonons that are Raman active can also interact indirectly with light, through Raman scattering.
- Optical phonons are often abbreviated as LO and TO phonons, for the Longitudinal Optical mode and Transverse Optical mode, respectively. The

splitting between LO and TO frequencies is often described accurately by the Lyddane-Sachs-Teller relation.

- The screened potential determines the inter atomic force and the phonon dispersion relation in metals.
- The screened potential is used to calculate the electronic band structure of a large variety of materials, often in combination with pseudopotential models.
- The screening effect leads to the independent electron approximation, which explains the predictive power of introductory models of solids like the Drude model, the free electron model and the nearly free electron model.
- When electrons pass through the conductor, the positive field of the ions attract the electrons, and this causes collisions. The greater the nuclear charge, the stronger the positive electric field of the ion will be and will attract electrons more, causing more collisions.
- Due to the high kinetic energy of the particle, when a positive ion attracts it towards itself, a collision can occur between the drifting charge and electrons in orbitals around the ion.
- The rate of collisions depends on the electronegativity of the atom.
- The electronic band structure or simply band structure of a solid describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have called band gaps or forbidden bands.
- Band theory has been successfully used to explain many physical properties of solids, such as electrical resistivity and optical absorption, and forms the foundation of the understanding of all solid state devices, such as transistors, solar cells, etc.
- In the Nearly Free Electron (NFE) approximation, interactions between electrons are completely ignored. This approximation allows use of Bloch's Theorem which states that electrons in a periodic potential have wavefunctions and energies which are periodic in wavevector up to a constant phase shift between neighbouring reciprocal lattice vectors. The consequences of periodicity are described mathematically by the Bloch's theorem.
- A wave function is a function that attempts to describe the total energy of an electron. This includes all of the possible energy states of the electron and the amount of time that the electron stays in each state.
- Wave equation of electron in a periodic potential is explained with reference to Bloch's theorem.
- Bloch's theorem states that solutions to the Schrödinger equation in a periodic potential take the form of a plane wave modulated by a periodic function. Mathematically, the Bloch Function is written as,

  $\Psi(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}}\, u(\boldsymbol{r})$

  Where **r** is position, Ψ is the wave function, u is a periodic function with the same periodicity as the crystal, the wave vector **k** is the crystal momentum vector, 'e' is Euler's number, and 'i' is the imaginary unit.

- Functions of this form are known as Bloch functions or Bloch states, and serve as a suitable basis for the wave functions or states of electrons in crystalline solids.
- Named after Swiss physicist Felix Bloch, the description of electrons in terms of Bloch functions, termed Bloch electrons (or less often Bloch Waves), underlies the concept of electronic band structures.
- The crystal momentum or quasimomentum is a momentum like vector associated with electrons in a crystal lattice. It is defined by the associated wave vectors k of this lattice, according to,

  $$\mathbf{p}_{\text{crystal}} \equiv \hbar\mathbf{k}$$

  Where $\hbar$ is the reduced Planck's constant. Normally, crystal momentum is conserved like mechanical momentum, making it useful to physicists and materials scientists as an analytical tool.
- In a semiconductor or band insulator, the Fermi level is surrounded by a band gap, referred to as the band gap, to distinguish it from the other band gaps in the band structure.
- The closest band above the band gap is called the conduction band, and the closest band beneath the band gap is called the valence band.
- The name 'Valence Band' was coined by analogy to chemistry, since in semiconductors and insulators the valence band is built out of the valence orbitals.
- In a metal or semimetal, the Fermi level is inside of one or more allowed bands. In semimetals the bands are usually referred to as 'Conduction Band' or 'Valence Band' depending on whether the charge transport is more electron-like or hole-like, by analogy to semiconductors.
- In many metals, however, the bands are neither electron-like nor hole-like, and often just called 'Valence Band' as they are made of 'Valence Orbitals'.

1.8 KEY TERMS

- **Free electron:** The free electrons, considered analogous or identical to the outermost or valence, electrons of free metal atoms are presumed to be moving independently of one another throughout the entire crystal
- **Electron theory of metals:** The study of valence electrons present in a band, which controls the various properties of metals is known as electron theory of metals.
- **Collision time:** The average time between two consecutive collisions of an electron with the lattice points is called collision time.
- **Mean free path:** Mean free path is the average distance travelled by the conduction electron between successive collisions with the lattice ions.
- **Thermal conductivity:** The thermal conductivity is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.

- **Wiedemann-Franz law:** This law states that, the ratio of thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature.
- **Dipole:** A pair of equal and opposite charges separated by a small distance constitutes an electric dipole.
- **Non-polar dielectrics:** A dielectric material in which, there is no permanent dipole existence in the absence of an external field is called non-polar dielectrics.
- **Polar dielectrics:** A dielectric material in which there is an existence of permanent dipole even in the absence of an external field is called a polar dielectric.

1.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What is free electron?
2. State about the free electron model of metals.
3. Define dielectric response of electrons.
4. What does transverse optical modes in a plasma refer to?
5. State the transparency concept of alkali metals in the ultraviolet.
6. What do you mean by longitudinal optical modes in a plasma plasmon?
7. Define the terms electrostatic screening and electron collisions.
8. What does band theory state?
9. Define the Nearly Free Electron (NFE) model.
10. State about the wave equation of electron in a periodic potential.
11. Why are Bloch functions used?
12. What does crystal momentum of an electron reduced zone scheme state?
13. What is periodic zone scheme?
14. Define the number of orbitals in band metals, insulators and semiconductors.

Long-Answer Questions

1. Briefly discuss the concept of free electron for gas and free electron model of metals giving appropriate examples.
2. Explain the dielectric response of electrons with the help of examples.
3. Elaborate on the characteristic properties of transverse optical modes in a plasma.
4. Discuss the transparency of alkali metals in the ultraviolet giving relevant examples.
5. What is the significance of longitudinal optical modes in a plasma plasmon? Explain giving appropriate examples.

6. Explain briefly about electrostatic screening and electron collisions giving significant examples.
7. Discuss the importance of band theory.
8. Briefly explain the characteristic features of nearly free electron model.
9. Explain wave equation of electron in a periodic potential giving relevant examples.
10. Explain the applications and significance of Bloch functions and Bloch theory.
11. Analyse the principle of crystal momentum of an electron reduced zone scheme and periodic zone scheme.
12. Discuss the concept of orbitals in band metals, insulators and semiconductors giving relevant examples.

1.10 FURTHER READING

Wahab, M. A. 2005. *Solid State Physics: Structure and Properties of Materials*. New Delhi: Narosa Publishing House.

Kittel, Charles. 1971. *Introduction to Solid State Physics*. New Jersey (US): John Wiley & Sons, Inc.

Pillai, S. O. 2005. *Solid State Physics*. Noida (UP): Wiley India Private Ltd.

Saxena, B. S., P. N. Saxena and R. C. Gupta. 2019. *Fundamentals of Solid State Physics*. Meerut (UP): Pragati Prakashan.

Dekker, A. J. 2008. *Solid State Physics*. Noida (UP): Macmillan Publishers India Pvt. Ltd.

Kakani, S. L. and C. Hemarajani. 2005. *Solid State Physics*. New Delhi: Sultan Chand & Sons Pvt. Ltd.

UNIT 2 FERMI SURFACES AND TRANSPORT PROPERTIES

NOTES

Structure

2.0 INTRODUCTION

In condensed matter physics, the Fermi surface is the surface in reciprocal space which separates occupied from unoccupied electron states at zero temperature. Fermi surface are abstract interface that defines the allowable energies of electrons in a solid. It was named for Italian physicist Enrico Fermi, who along with English physicist P.A.M. Dirac developed the statistical theory of electrons. Fermi surfaces are important for characterizing and predicting the thermal, electrical, magnetic, and optical properties of crystalline metals and semiconductors. They are closely related to the atomic lattice, which is the underlying feature of all crystalline solids, and to energy band theory, which describes how electrons are distributed in such materials.

The shape of the Fermi surface is derived from the periodicity and symmetry of the crystalline lattice and from the occupation of electronic energy bands. The existence of a Fermi surface is a direct consequence of the Pauli exclusion principle, which allows a maximum of one electron per quantum state. The study of the Fermi surfaces of materials is called fermiology. Fermi level falls in a gap between bands is an insulator or semiconductor depending on the size of the bandgap. When a material's Fermi level falls in a bandgap, there is no Fermi surface. Solids with a large density of states at the Fermi level become unstable at low temperatures and tend to form ground states where the condensation energy comes from opening a gap at the Fermi surface. Examples of such ground states are superconductors, ferromagnets, Jahn–Teller distortions and spin density waves.

Materials with complex crystal structures can have quite intricate Fermi surfaces. The state occupancy of fermions like electrons is governed by Fermi–Dirac statistics so at finite temperatures the Fermi surface is accordingly broadened. In principle, all fermion energy level populations are bound by a Fermi surface although the term is not generally used outside of condensed matter physics.

The de Haas–Van Alphen effect, often abbreviated to DHVA, is a quantum mechanical effect in which the magnetic susceptibility of a pure metal crystal oscillates as the intensity of the magnetic field is increased. It can be used to determine the Fermi surface of a material. Other quantities also oscillate, such as the electrical resistivity (Shubnikov–de Haas effect), specific heat, and sound attenuation and speed. It is named after Wander Johannes de Haas and his student Pieter M. van Alphen. The DHVA effect comes from the orbital motion of itinerant electrons in the material.

The transport properties for metals and semiconductors can be explained on the basis of an intrinsic semiconductor. Basically, an intrinsic semiconductor has no carriers at T = 0 and therefore there is no transport of carriers under the influence of external fields. However, at finite temperatures there are thermally generated carriers. Impurities also can serve to generate carriers and transport properties. For insulators, there is very little charge transport and consequently the defects and the ions themselves can participate in charge transport under the influence of external applied fields. Metals make use of the Fermi-Dirac distribution function but are otherwise similar to semiconductors, for which the Maxwell–Boltzmann distribution function is usually applicable.

The thermal conductivity of a material is a measure of its ability to conduct heat. Heat transfer occurs at a lower rate in materials of low thermal conductivity than in materials of high thermal conductivity. The reciprocal of thermal conductivity is called thermal resistivity.

The Hall effect is the production of a voltage difference (the Hall voltage) across an electrical conductor that is transverse to an electric current in the conductor and to an applied magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879. A Hall effect can also occur across a void or hole in a semiconductor or metal plate, when current is injected via contacts that lie on the boundary or edge of the void or hole, and the charge flows outside the void or hole, in the metal or semiconductor.

In this unit, you will study about the Fermi surfaces, construction of Fermi surfaces, electrons, holes and open orbits, physical properties of holes, effective mass electrons in crystals, wave functions for zero wave vector, lattice effect on cohesive energy of metals, pseudo potentials, experimental methods in Fermi surface studies, cyclotron resonance in metals external orbits, de Haas–Van Alphen effect, Fermi surfaces of free metals, transport properties, the Boltzmann equation, electrical conductivity, calculation of relaxation time, impurity scattering, general transport coefficients, thermal conductivity, thermoelectric effects, lattice conduction, phonon drag, the Hall effect, the two band model, and magnetoresistances.

2.1 OBJECTIVES

After going through his unit, you will be able to:

- Discuss the characteristic properties of Fermi surfaces
- Construct Fermi surfaces
- Explain the electrons, holes and open orbits of Fermi surfaces
- Understand the physical properties of holes
- Describe the effective mass electrons in crystals
- Elaborate on the wave functions for zero wave vector
- Understand lattice effect on cohesive energy of metals and pseudo potentials
- Define the experimental methods in Fermi surface studies
- Know about the cyclotron resonance in metals external orbits
- Explain the de Haas–Van Alphen effect and Fermi surfaces of free metals
- Discuss the transport properties of electrons
- Understand the Boltzmann equation and electrical conductivity
- Calculate relaxation time
- Know about the impurity scattering
- Define the general transport coefficients, thermal conductivity and thermoelectric effects
- Recognise the lattice conduction and phonon drag
- Discuss the Hall effect, the two band model and magnetoresistances

2.2 FERMI SURFACES

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

As per the Encyclopaedia Britannica, "The Fermi surface, in condensed matter physics, is abstract interface that defines the allowable energies of electrons in a solid. It was named for Italian physicist Enrico Fermi, who along with English physicist P.A.M. Dirac developed the statistical theory of electrons. Fermi surfaces are essential and significant for characterizing and predicting the thermal, electrical, magnetic, and optical properties of crystalline metals and semiconductors. They are closely related to the atomic lattice, which is the underlying feature of all crystalline solids, and to energy band theory, which describes how electrons are distributed in such materials".

Theory

Consider a spinless ideal Fermi gas of N particles. According to Fermi–Dirac statistics, the mean occupation number of a state with energy ε_i is given by,

$$\langle n_i \rangle = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$$

Where,

- $\langle n_i \rangle$ = Mean Occupation Number of the ith State
- ε_i = Kinetic Energy of the ith State
- μ = Chemical Potential at Zero Temperature, this is defined as the Maximum Kinetic Energy (KE) the Particle can have, i.e., Fermi Energy E_F
- T = Absolute Temperature
- k_B = Boltzmann Constant

Suppose if we consider the limit $T \rightarrow 0$, then we have,

$$\langle n_i \rangle \rightarrow \begin{cases} 1 & (\epsilon_i < \mu) \\ 0 & (\epsilon_i > \mu) \end{cases}$$

By the Pauli exclusion principle, no two Fermions can be in the same state. Therefore, in the state of lowest energy, the particles fill up all energy levels below the Fermi energy E_F, which is equivalently stated as E_F, typically, referred as the energy level below which there are exactly N states.

In momentum space, these particles fill up a ball of radius k_F, uniquely this surface is called the Fermi surface.

The linear response of a metal to an electric, magnetic or thermal gradient is determined through the shape of the Fermi surface, because currents are produced because of the changes in the occupancy of states near the Fermi energy. In reciprocal space, the Fermi surface of an ideal Fermi gas is a sphere of radius,

$$k_F = \frac{p_F}{\hbar} = \frac{\sqrt{2mE_F}}{\hbar}$$

This determined by the valence electron concentration where $\hbar$ is the reduced Planck's constant. A material whose Fermi level falls in a gap between bands is an insulator or semiconductor depending on the size of the bandgap. When a material's Fermi level falls in a bandgap, there is no Fermi surface.

2.2.1 Construction of Fermi Surfaces, Electrons and Holes

NOTES

Materials with complex crystal structures can have quite intricate Fermi surfaces. The Figure (2.1) illustrates the anisotropic Fermi surface of graphite, which has both electron and hole pockets in its Fermi surface due to multiple bands crossing the Fermi energy along the $\mathbf{k}_z$ direction. Often in a metal the Fermi surface radius k_F is larger than the size of the first Brillouin zone which results in a portion of the Fermi surface lying in the second (or higher) zones. As with the band structure itself, the Fermi surface can be displayed in an extended-zone scheme where **k** is allowed to have arbitrarily large values or a reduced-zone scheme where wavevectors are shown modulo $\frac{2\pi}{a}$ (in the one-dimensional case) where a is the lattice constant. In the three-dimensional case the reduced zone scheme specifies that from any wavevector **k** there is an appropriate number of reciprocal lattice vectors **K** subtracted that the new **k** now is closer to the origin in **k**-space than to any **K**. Solids with a large density of states at the Fermi level become unstable at low temperatures and tend to form ground states where the condensation energy comes from opening a gap at the Fermi surface. Examples of such ground states are superconductors, ferromagnets, Jahn–Teller distortions and spin density waves.

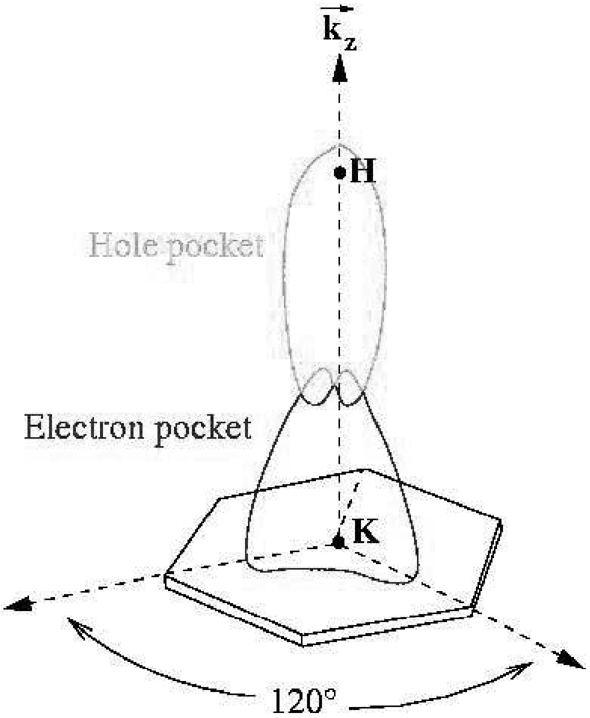


Fig. 2.1 *A View of the Graphite Fermi Surface at the Corner H Points of the Brillouin Zone Showing the Trigonal Symmetry of the Electron and Hole Pockets*

The state occupancy of Fermions like electrons is governed by Fermi–Dirac statistics therefore at finite temperatures the Fermi surface is accordingly broadened. In principle all Fermion energy level populations are bound by a Fermi surface although the term is not generally used outside of condensed matter physics.

Construction of Free Electron Fermi Surfaces

The free electron Fermi surface for an arbitrary electron concentration is shown in Figure (2.2).

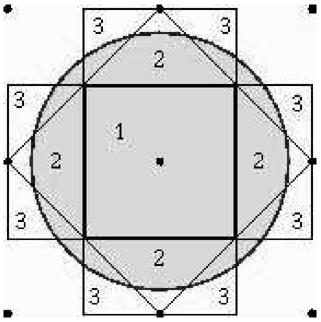


Fig. 2.2 *Fermi Surface for an Arbitrary Electron Concentration*

The free electron Fermi surfaces are defined as the Brillouin zones of a square lattice in two dimensions. The circle shown in Figure 2.2 is a surface of constant energy for free electrons; it will be the Fermi surface for some particular value of the electron concentration.

It is difficult to have sections of the Fermi surface that belong to the same Brillouin zone which appear detached one from another. The detachment can be repaired by a transformation to the first Brillouin zone. The procedure is known as mapping the Fermi surface in the reduced zone scheme.

There is also another way to represent the Fermi surface in the reduced and periodic zone scheme. Fermi surfaces for free electrons are constructed by a procedure credited to Harrison, as shown in Figure (2.3).

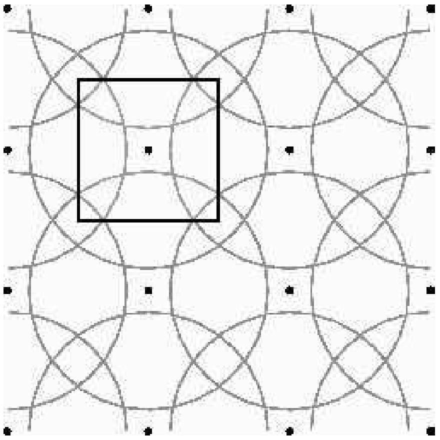


Fig. 2.3 *Fermi Surface in the Reduced and Periodic Zone Scheme*

The reciprocal lattice points of a square lattice are determined, and free-electron sphere of radius appropriate to the electron concentration is drawn around each point. Any point in **k** space that lies within at least one sphere corresponds to an occupied state in the first zone. Points within at least two spheres correspond to occupied states in the second zone, and similarly for points in three or more spheres.

In Figure (2.4), the black square shown is the first Brillouin zone, the circle is the surface of constant energy for free electrons, and the shaded area represents occupied electron states. The first zone is entirely occupied.

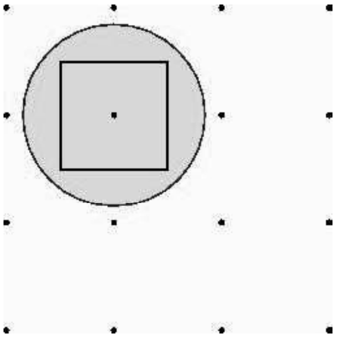


Fig. 2.4 *Shaded Area Represents Occupied Electron States*

In Figure (2.5), the black square shown is the first Brillouin zone, the lines are the Fermi surfaces for free electrons on the second zone, and the shaded area represents occupied electron states.

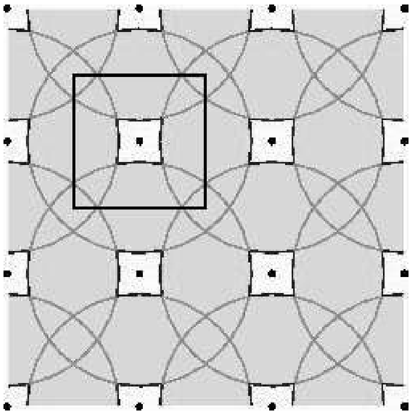


Fig. 2.5

In Figure (2.6), the black square shown is the first Brillouin zone, the lines are the Fermi surfaces for free electrons on the third zone, and the shaded area represents occupied electron states.

NOTES

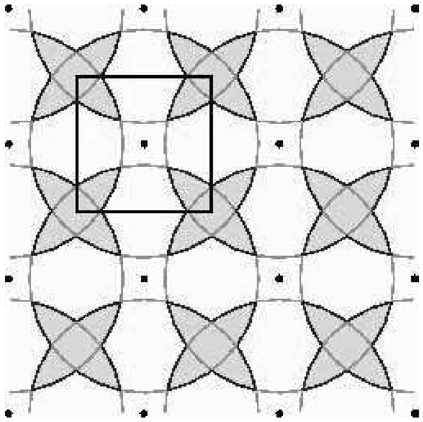


Fig. 2.6

In Figure (2.7), the black square shown is the first Brillouin zone, the blue lines are the Fermi surfaces for free electrons on the fourth zone, and the shaded area represents occupied electron states.

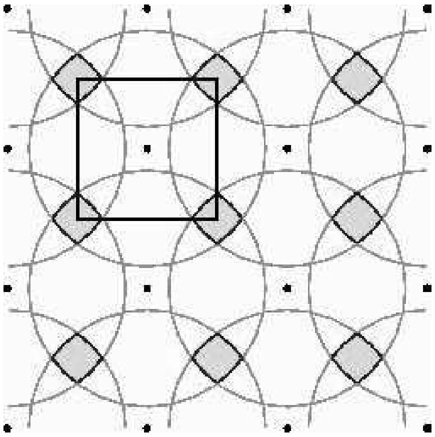


Fig. 2.7

Consequently, in Figure (2.8), the free electron Fermi surface is shown, as viewed in the reduced zone scheme. The shaded areas represent occupied electron states. Parts of Fermi surface (lines) fall in the second, third, and fourth zones. The first zone is entirely occupied.

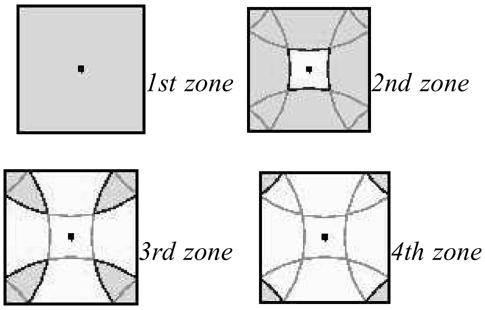


***Fig. 2.8** Fermi Surface (Lines) Fall in the Second, Third and Fourth Zones*

In Figure (2.9), the Fermi surface for free electrons is shown in the second zone as drawn in the periodic scheme. The figure can be constructed by repeating the second zone of Figure (2.8) or directly from Harrison construction.

NOTES

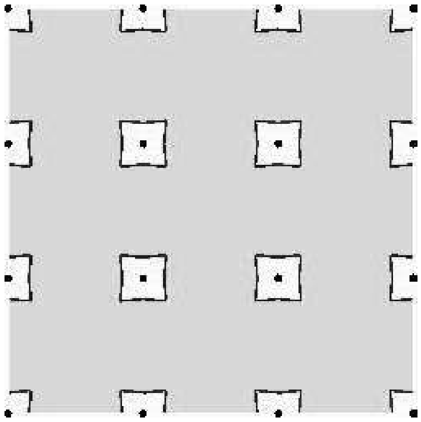


Fig. 2.9 Fermi Surface for Free Electrons in the Second Zone as the Periodic Scheme

In Figure (2.10), the Fermi surface for free electrons is shown in the third zone as drawn in the periodic scheme. The figure can be constructed by repeating the third zone of Figure (2.8) or directly from Harrison construction.

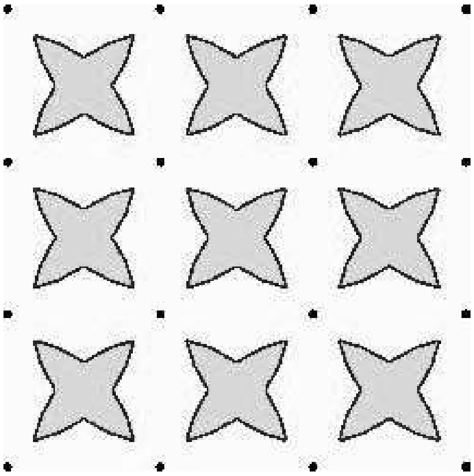


Fig. 2.10 Fermi Surface for Free Electrons in the Third Zone as the Periodic Scheme

In Figure (2.11), the Fermi surface for free electrons is shown in the fourth zone as drawn in the periodic scheme. The figure can be constructed by repeating the fourth zone of Figure (2.8) or directly from the Harrison construction.

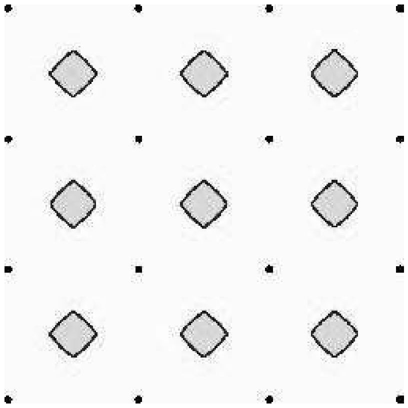


Fig. 2.11 Fermi Surface for Free Electrons in the Fourth Zone as the Periodic Scheme

2.2.2 Fermi Level in Semiconductors

In an extrinsic semiconductor, the number of electrons in the conduction and the number of holes in the valence band are not equal. Consequently, the chances of the occupation of the energy levels in valance and conduction bands are not equal. Therefore, in the case of extrinsic semiconductors, the Fermi level lies close to any of the valance or conduction band.

In semiconductors, the Fermi level is inside a band gap; however, in semiconductors the bands are near enough to the Fermi level to be thermally populated with electrons or holes. As we know that electrical conductivity arises due to the presence of electrons in states that are delocalized (extending through the material), however in order to transport electrons a state must be partially filled, containing an electron only part of the time. If the state is always occupied with an electron, then it is inert, blocking the passage of other electrons via that state. The energies of these quantum states are critical since a state is partially filled only if its energy is near the Fermi level.

High conductivity in material comes from it having many partially filled states and much state delocalization. Metals are good electrical conductors and have many partially filled states with energies near their Fermi level. Insulators, by contrast, have few partially filled states, their Fermi levels sit within band gaps with few energy states to occupy. Importantly, an insulator can be made to conduct by increasing its temperature: heating provides energy to promote some electrons across the band gap, inducing partially filled states in both the band of states beneath the band gap (valence band) and the band of states above the band gap (conduction band). An (intrinsic) semiconductor has a band gap that is smaller than that of an insulator and at room temperature, significant numbers of electrons can be excited to cross the band gap.

Some wider-band gap semiconductor materials are sometimes referred to as semi-insulators. When undoped, these have electrical conductivity nearer to that of electrical insulators, however they can be doped (making them as useful as semiconductors). Semi-insulators find niche applications in micro-electronics, such as substrates for HEMT (High-Electron-Mobility Transistor). An example of a common semi-insulator is gallium arsenide. Some materials, such as titanium dioxide, can even be used as insulating materials for some applications, while being treated as wide-gap semiconductors for other applications.

In an *n*-type semiconductor, the Fermi level is greater than that of the intrinsic semiconductor and lies closer to the conduction band than the valence band whereas for *p*-type semiconductors, the Fermi level is below the intrinsic semiconductor and lies closer to the valence band than the conduction band.

Extrinsic semiconductors are formed by adding suitable **impurities** to the intrinsic semiconductor. The added impurity is very small, of the order of one atom per million atoms of the pure semiconductor. The added impurity may be pentavalent or trivalent. Depending on the type of impurity added, the extrinsic semiconductors can be divided into two classes: *n*-type and *p*-type.

Fermi Level in *n*-Type Semiconductor

When pentavalent impurity is added to pure semiconductor, it results in *n*-type semiconductor. The fifth electron of donor atom is loosely bounded. By small thermal energy or by applying electric field, this electron can be easily excited from the valence band to the conduction band. So donor donates free electrons. Since current carriers are negatively charged particles, this type of semiconductor is called *n*-type semiconductor.

A pentavalent impurity is substituted in order to obtain an *n*-type semiconductor. Each pentavalent impurity contributes an extra electron. In this way, the presence of pentavalent impurity leaves free electrons in the conduction band.

In such a case, the number of electrons present in the conduction band is more than the number of holes present in the valence band, at room temperature. Henceforth, the chances of occupation of energy levels in the conduction band by the electrons are more than the chances of occupation of energy levels by the holes in the valence band. This probability of occupation of energy levels is represented in terms of Fermi energy level. Therefore, the Fermi level in the *n*-type semiconductor lies close to the conduction band.

An *n*-type semiconductor is a category of an extrinsic semiconductor. In the case of *n*-type semiconductors, the electron donor atoms play very significant role, as these types of semiconductors are doped with the electron donor atoms. Figure (2.12) illustrates the Fermi energy level diagram of a *n*-type semiconductor.

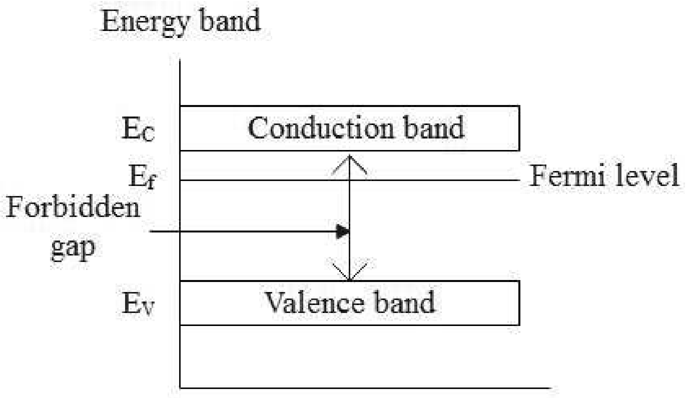


Fig. 2.12 *The Fermi Energy Level Diagram of a n-Type Semiconductor*

The donor atoms contribute the free electrons to the semiconductors; therefore, the *n*-type semiconductors have free electrons in plenty when compared to the holes. Basically, the pentavalent atoms are introduced into the semiconductors. Here, the pentavalent atoms refer to the atoms having 5 valence electrons.

The terms used in the Figure (2.12) can be described as follows.

- **Conduction Band:** An energy band filled with the free electrons.
- **Valence Band:** An energy band filled with the holes.
- **The Forbidden Gap:** The gap between the conduction and the valence band.

- **Fermi Level:** The highest energy level that an electron can occupy at absolute 0 (Zero) temperature.

From the energy level diagram of the n-type semiconductor, it is evident that the Fermi level is present near the conduction band and far away from the valence band. Typically, in the case of *n*-type semiconductor, the Fermi level is present just below the conduction band.

The Fermi level for *n*-type semiconductor is given as,

$$E_F = E_C - K_B T \log \frac{N_C}{N_D}$$

Where,

E_F = The Fermi Level.

E_C = The Conduction Band.

K_B = The Boltzmann Constant.

T = The Absolute Temperature.

N_C = The Effective Density of States in the Conduction Band.

N_D = The Concentration of Donor Atoms.

Fermi Level in *p*-Type Semiconductor

When **trivalent impurity** is added to pure semiconductor, it results in *p*-type semiconductor. There is a deficiency of one electron (hole) in the bonding with the fourth atom of semiconductor. Due to this, a hole is created in the adjacent atom. Since current carriers are positively charged particles, this type of semiconductor is called *p*-type semiconductor.

Additionally, in the *p*-type semiconductor, the trivalent impurities are added to the intrinsic semiconductor. Each trivalent impurity generates a hole in the valence band. The hole is receptive towards an electron. Consequently, the trivalent impurities create a proportional number of holes in the valence band.

In this situation, at room temperature, the counting of holes in the valence band is greater than the count of electrons available in the conduction band. Therefore, the chances of position occupied by the energy levels in the valence band by the holes are more than the chances of the conduction band to be occupied by the electrons. The probability of the position occupied by the energy levels is characterized in terms of Fermi level. Henceforth, in the *p*-type semiconductors, the Fermi level lies close to the valence band.

Because, in *p*-type semiconductor trivalent impurity is added, therefore each trivalent impurity creates a hole in the valence band and is ready to accept an electron. The addition of trivalent impurity creates large number of holes in the valence band. Figure (2.13) illustrates the Fermi energy level diagram of a *p*-type semiconductor.

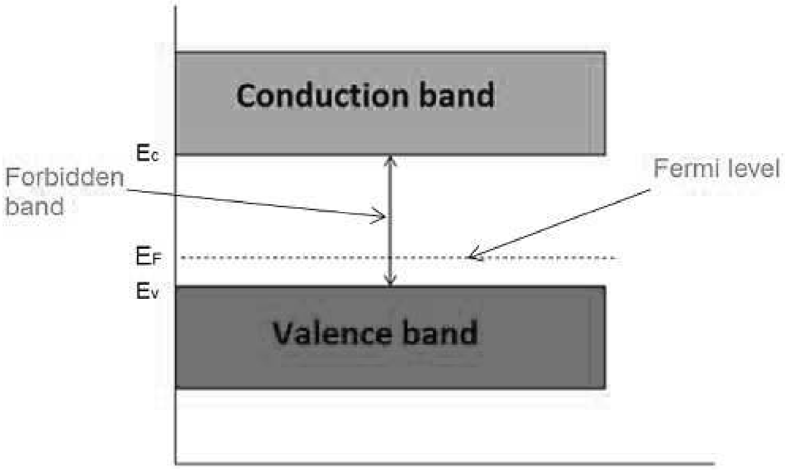


Fig. 2.13 *The Fermi Energy Level Diagram of a p-Type Semiconductor*

The Fermi level for *p*-type semiconductor is given as,

$$E_F = E_V + K_B T \log \frac{N_V}{N_A}$$

Where,

E_F = The Fermi Level.

E_V = The Valence Band.

K_B = The Boltzmann Constant.

T = The Absolute Temperature.

N_V = The Effective Density of States in the Valence Band.

N_A = The Concentration of Acceptor Atoms.

2.2.3 Fermi Energy

Characteristically, in an intrinsic semiconductor,

$$n_e = n_h$$

i.e.,

{Density of Electrons in the Conduction Band} = {Density of Holes in the Valence Band}

Therefore,

$$2\left(\frac{2\pi m_e^* k_B T}{h^2}\right)^{3/2} e^{\left(\frac{E_F - E_c}{k_B T}\right)} = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2} e^{\left(\frac{E_v - E_F}{k_B T}\right)}$$

Or $$\left(m_e^*\right)^{3/2} e^{\left(\frac{E_F - E_c}{k_B T}\right)} = \left(m_h^*\right)^{3/2} e^{\frac{E_v - E_F}{k_B T}}$$

Rearranging the above equation we get,

$$e^{\left(\frac{2E_F}{k_B T}\right)} = \left(\frac{m_h^*}{m_e^*}\right)^{3/2} e^{\left(\frac{E_v + E_c}{k_B T}\right)} \qquad ...(2.1)$$

Taking logarithm on both sides,

$$\frac{2E_F}{k_BT} = \frac{3}{2}\ln\left(\frac{m_h^*}{m_e^*}\right) + \frac{E_v + E_c}{k_BT}$$

[The RHS of Equation (2.1) has been precisely written using the formula ln (*a*b) = ln*a* + lnb].

Note: In is natural base of logarithm $\ln N = \log_e^N = 2.302 \log_{10}^N$.

$$\therefore \quad ME_F = \frac{3k_BT}{4}\ln\left(\frac{m_h^*}{m_e^*}\right) + \frac{E_v + E_c}{2} \qquad \text{...(2.2)}$$

When $m_e^* = m_h^*$, the above Equation gets reduced to,

$$E_F = \frac{E_v + E_c}{2}\text{, Since} \quad \ln(1) = 0 \qquad \text{...(2.3)}$$

Thus, the Fermi level is in the middle of the band gap, i.e., $E_F = \frac{E_g}{2}$. ...(2.4)

As shown in Figure 2.14(*a*) E_g lies half way between the top of valence band and bottom of conduction band.

Dependence of E_F on Temperature

The variation of Fermi level with temperature for an intrinsic semiconductor is shown in Figure (2.14). At T = 0 K, the Fermi level lies exactly in the middle of forbidden gap as shown in Figure (2.14(*a*)).

At low temperature region, E_F is practically independent of temperature. But, there is a slight variation in E_F in the high temperature region. The reason is that in the real condition $m_e^* > m_h^*$. Thus, the term $\ln\left(\frac{m_h^*}{m_e^*}\right)$ begins to contribute slightly. This results in a small increase in the magnitude of E_F. Subsequently, the Fermi level gets raised slightly as shown in Figure (2.14(*b*)) as T increases.

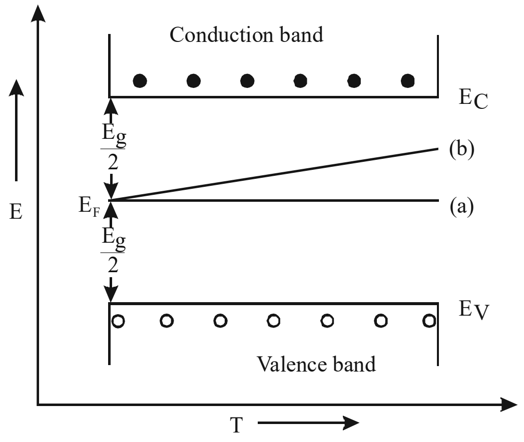


Fig. 2.14 *Position of Fermi Level in an Intrinsic Semiconductor at Various Temperatures*

2.2.4 Electron Orbits, Hole Orbits and Open Orbits in Fermi Surface

The electrons in a static magnetic field move on a curve of constant energy on a plane normal to B. An electron on the Fermi surface will move in a curve on the Fermi surface, because this is a surface of constant energy. Three types of orbits in a magnetic field are shown in Figure (2.15). The closed orbits of Figure (2.15 (a)) and (2.15 (b)) are traversed in opposite senses. Because particles of opposite charge circulate in a magnetic field in opposite senses, therefore one orbit is **electron like** and the other orbit is **hole like**. Electrons in hole like orbits move in a magnetic field as if endowed with a positive charge. In Figure (2.15 (c)) the orbit is not closed, the particle on reaching the zone boundary at A is instantly folded back to B, where B is equivalent to B' because they are connected by a reciprocal lattice vector. Such an orbit is called an **open orbit**. Open orbits have an important effect on the magnetoresistance. Vacant orbitals near the top of an otherwise filled band give rise to hole like orbits.

Therefore, the orbits that enclose filled states are **electron orbits**. Orbits that enclose empty states are **hole orbits**. Orbits that move from zone to zone without closing are **open orbits**.

Figure (2.15) illustrates the motion in a magnetic field of the wavevector of an electron on the Fermi surface. In Figure (2.15 (a)) the wavevector moves around the orbit in a clockwise direction; in Figure (2.15 (b)) the wavevector moves around the orbit in a counterclockwise direction. The direction in Figure (2.15 (b)) is what we expect for a free electron of charge '-e'; the smaller k values have the lower energy, so that the filled electron states lie inside the Fermi surface. The orbit in Figure (2.15 (b)) is called electron like. The sense of the motion in a magnetic field is opposite in Figure (2.15 (a)) to that in Figure (2.15 (b)), so that we refer to the orbit in Figure (2.15 (a)) as hole like. A hole moves as a particle of positive charge 'e'. In Figure (2.15 (c)) for a rectangular zone we show the motion on an open orbit in the periodic zone scheme. An open orbit is topologically intermediate between a hole orbit and an electron orbit.

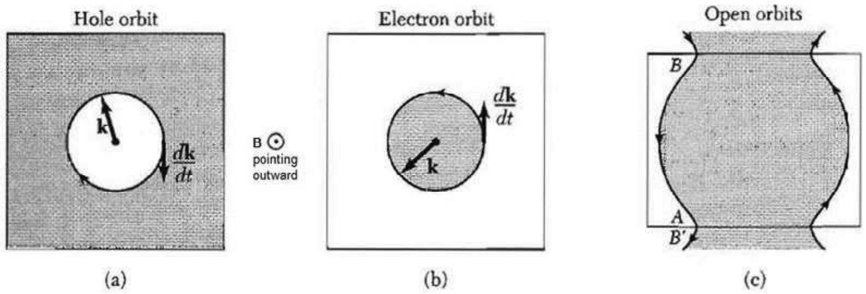


Fig. 2.15 *Electron Orbits, Hole Orbits and Open Orbits in Fermi Surface*

2.2.5 Physical Properties of Holes

In condensed matter physics, the name **hole** is given to a missing electron in certain solids, especially semiconductors. Holes affect the electrical, optical, and thermal properties of the solid. Along with electrons, the holes are considered very significant in the field of digital technology, because when they are introduced into semiconductors, they produce electronic and optical devices.

According to the band theory of solids as stated in the Encyclopaedia Britannica, "The electrons within a solid have energies only at certain discrete levels that combine into groups or bands. The valence band contains electrons that are bound into the atomic structure of the material, whereas the conduction band contains electrons at higher energies that are free to move".

Together with the significant applications of thermal energy, an electron can be uniquely motivated from the valence band across or throughout a forbidden region termed as the band gap and also into the conduction band, which precisely leaves behind a hole. Because a missing electron is considered identical as an added positive electric charge, therefore the holes can characteristically carry a current, similar to that of electrons but in the opposite direction, precisely under an electric field. Generally, the 'Holes' moves more slowly as compared to the electrons, even though, since they normally function within the tightly bound valence band instead of the conduction band.

Characteristically, an **electron hole** or a **hole** is precisely defined as the lack of an electron at a specified position where one electron could have existed in an atom or atomic lattice. Because in a normal atom or a crystal lattice the negative charge of the electrons is precisely balanced by means of the positive charge of the atomic nuclei, therefore the absence of an electron leaves a net positive charge at the location of the hole.

Fundamentally, in a metal or semiconductor crystal lattice the holes also move through the lattice as the electrons move and behave in the similar manner as the positively charged particles do. The holes have significant role in the operation of semiconductor devices, such as transistors, diodes and integrated circuits. When an electron is excited into a higher state, then it normally leaves a hole in its old or earlier state. This specification is distinctively used in Auger electron spectroscopy and other X-ray techniques, in computational chemistry, and in explaining the concept that how the low electron-electron scattering rate in crystals (metals, semiconductors). Even though they act or behave like elementary particles, but the fact that the holes are not essentially particles and are rather defined as the quasiparticles, the holes are considered different from the positron, which is the antiparticle of the electron.

A hole is essentially a method to conceptualize the interactions of the electrons within a nearly full valence band of a crystal lattice, which is missing a small fraction of its electrons. Following are some significant properties of hole:

1. The dispersion relation determines how electrons respond to forces through the concept of effective mass.
2. Electrons near the top of the valence band behave as if they hold the negative mass.
3. Positively charged holes as a shortcut for calculating the total current of approximately, full band.

4. A hole near the top of the valence band moves in the similar manner as an electron near the top of the valence band would move, which is in the opposite direction compared to conduction band electrons experiencing the same force.
5. Hole is defined as a positive charge, positive mass quasiparticle.
6. In most semiconductors, the effective mass of a hole is much larger than that of an electron. This results in lower mobility for holes under the influence of an electric field and this may slow down the speed of the electronic device made of that semiconductor. This is one major reason for adopting electrons as the primary charge carriers, whenever possible in semiconductor devices, rather than holes.
7. An alternate meaning for the term electron hole is used in computational chemistry. In coupled cluster methods, the ground or lowest energy state of a molecule is interpreted as the 'Vacuum State'—conceptually, in this state, there are no electrons. In this notion, the absence of an electron from a normally filled state is called a 'Hole' and is treated as a particle, while the presence of an electron in a normally empty state is simply called an 'Electron'.

2.2.6 Effective Mass Electrons in Crystals and Pseudopotentials

In solid state physics, a particle's **effective mass** (often denoted m^*) is the mass that it seems to have when responding to forces, or the mass that it seems to have when interacting with other identical particles in a thermal distribution. One of the results from the band theory of solids is that the movement of particles in a periodic potential, over long distances larger than the lattice spacing, can be very different from their motion in a vacuum. The effective mass is a quantity that is used to simplify band structures by modeling the behaviour of a free particle with that mass. For some materials, the effective mass can be considered to be a simple constant of a material. In general, however, the value of effective mass depends on the purpose for which it is used and can vary depending on a number of factors.

For electrons or electron holes in a solid, the effective mass is usually stated in units of the rest mass of an electron, m_e (9.11×10^{-31} kg). In these units, it is usually in the range 0.01 to 10, but can also be lower or higher, for example reaching 1,000 in exotic heavy fermion materials, or anywhere from zero to infinity (depending on definition) in graphene. As it simplifies the more general band theory, the electronic effective mass can be seen as an important basic parameter that influences measurable properties of a solid, including everything from the efficiency of a solar cell to the speed of an integrated circuit.

At the highest energies of the valence band in many semiconductors (Ge, Si, GaAs, ...), and the lowest energies of the conduction band in some semiconductors (GaAs, ...), the band structure $E(\mathbf{k})$ can be locally approximated as,

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2\mathbf{k}^2}{2m^*}$$

Where $E(\mathbf{k})$ is the energy of an electron at wavevector **k** in that band, E_0 is a constant giving the edge of energy of that band, and $\boldsymbol{m^*}$ is a constant, the effective mass.

It can be shown that the electrons placed in these bands behave as free electrons except with a different mass, as long as their energy stays within the range of validity of the approximation given above. As a result, the electron mass in models, such as the Drude model must be replaced with the effective mass.

One remarkable property is that the effective mass can become negative, when the band curves downwards away from a maximum. As a result of the negative mass, the electrons respond to electric and magnetic forces by gaining velocity in the opposite direction compared to normal; even though these electrons have negative charge, they move in trajectories as if they had positive charge and positive mass. This explains the existence of valence band holes, the positive charge, positive mass quasiparticles that can be found in semiconductors.

Howerver, if the band structure has the simple parabolic form then the value of effective mass is unambiguous. Unfortunately, the simple parabolic form is not valid for describing most materials. In such complex materials there is no single definition of 'Effective Mass' but instead multiple definitions, each suited to a particular purpose.

In some important semiconductors (notably, silicon) the lowest energies of the conduction band are not symmetrical, as the constant-energy surfaces are now ellipsoids, rather than the spheres in the isotropic case. Each conduction band minimum can be approximated only by,

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2}{2m_x^*}(k_x - k_{0,x})^2 + \frac{\hbar^2}{2m_y^*}(k_y - k_{0,y})^2 + \frac{\hbar^2}{2m_z^*}(k_z - k_{0,z})^2$$

Where x, y, and z axes are aligned to the principal axes of the ellipsoids, and m_x^*, m_y^* and m_z^* are the inertial effective masses along these different axes. The offsets $k_{0,x}$, $k_{0,y}$, and $k_{0,z}$ reflect that the conduction band minimum is no longer cantered or run at zero wavevector.

In this instance, the electron motion is no longer directly comparable to a free electron; instead the speed of an electron will depend on its direction, and it will accelerate to a different degree depending on the direction of the force. Still, in crystals, such as silicon the overall properties, such as conductivity appear to be isotropic. This is because there are multiple valleys, conduction band minima, each with effective masses rearranged along different axes. The valleys collectively act together to give an isotropic conductivity. It is possible to average the different axes' effective masses together in some way, to regain the free electron picture. However, the averaging method turns out to depend on the purpose:

- For calculation of the total density of states and the total carrier density, via the geometric mean combined with a degeneracy factor g which counts the number of valleys, in silicon $g = 6$:

$$m^*_{\text{density}} = \sqrt[3]{g^2 m_x m_y m_z}$$

For the per valley density of states and per valley carrier density, the degeneracy factor is left out.

- For the purposes of calculating conductivity as in the Drude model, via the harmonic mean,

$$m^*_{\text{conductivity}} = 3\left[\frac{1}{m^*_x} + \frac{1}{m^*_y} + \frac{1}{m^*_z}\right]^{-1}$$

Since the Drude law also depends on scattering time, which varies greatly, this effective mass is rarely used; conductivity is instead usually expressed in terms of carrier density and an empirically measured parameter, carrier mobility.

Pseudopotentials

In physics, a **pseudopotential** or effective potential is used as an approximation for the simplified description of complex systems. Applications include atomic physics and neutron scattering. The pseudopotential approximation was first introduced by Hans Hellmann in 1934.

The pseudopotential is an attempt to replace the complicated effects of the motion of the core, i.e., non-valence electrons of an atom and its nucleus with an effective potential, or pseudopotential, so that the Schrödinger equation contains a modified effective potential term instead of the Coulombic potential term for core electrons normally found in the Schrödinger equation.

The pseudopotential is an effective potential constructed to replace the atomic all electron potential or full potential such that core states are eliminated and the valence electrons are described by pseudo-wavefunctions with significantly fewer nodes. This allows the pseudo-wavefunctions to be described with far fewer Fourier modes, thus making plane-wave basis sets practical to use. In this approach usually only the chemically active valence electrons are dealt with explicitly, while the core electrons are 'Frozen', being considered together with the nuclei as rigid non-polarizable ion cores. It is possible to self-consistently update the pseudopotential with the chemical environment that it is embedded in, having the effect of relaxing the frozen core approximation, although this is rarely done. In codes using local basis functions, like Gaussian, often effective core potentials are used that only freeze the core electrons.

Fermi Pseudopotential

Enrico Fermi introduced a pseudopotential, V, to describe the scattering of a free neutron by a nucleus. The scattering is assumed to be s-wave scattering, and therefore spherically symmetric. Therefore, the potential is given as a function of radius, 'r':

$$V(r) = \frac{4\pi\hbar^2}{m} b\,\delta(r)$$

Where $\hbar$ is the Planck constant divided by 2π, m is the mass, $\delta(r)$ is the Dirac delta function, b is the bound coherent neutron scattering length, and $r = 0$, the center of mass of the nucleus. The Fourier transform of this δ-function leads to the constant neutron form factor.

2.2.7 Lattice Effect on Cohesive Energy of Metals

Cohesive energy is the energy gained by arranging the atoms in a crystalline state, as compared with the gas state. Insulators and semiconductors have large cohesive energies; Since these solids are bound together strongly and have good mechanical strength.

Fundamentally, the **cohesive energy** is defined as the energy that must be given to the solid to separate its constituents into neutral free atoms at rest and at infinite separation with the same electronic configuration.

The **lattice energy** of a **solid** is defined as the energy that must be given to an ionic crystal to separate its constituents into free ions at rest and at infinite separation.

The cohesive energy of a solid refers to the energy required to separate constituent atoms apart from each other and to bring them to an assembly of neutral free atoms. Its value for elements in the periodic table is distributed over a few kJ/mol for inert gas elements to 837 kJ/mol for W having the highest melting point (Kittel, 1967).

Types of Bonds

The properties of a solid can usually be predicted from the valence and bonding preferences of its constituent atoms. There are typically four bonding types for a solid, namely ionic bonding, covalent bonding, metallic bonding, and molecular bonding. In an ideally ionic crystal, its cohesive energy can be calculated by summing up the electrostatic energy for an assembly consisting of ions with unlike charges.

Hydrogen-bonded solids, such as ice, make up another category that is important in a few crystals. There are many examples of solids that have a single bonding type, while other solids have a mixture of types, such as covalent bonding and metallic bonding or covalent bonding and ionic bonding.

Ionic Bonding: The ionic bonding can be defined with reference to sodium chloride which exhibits the ionic form of bonding. There is single electron in the sodium atom in its outermost shell, whereas the chlorine atom essentially requires one electron in order to fill its outer shell. Consequently, the sodium atom donates one electron to chlorine atom thereby forming a sodium ion (Na^+) and a chlorine ion (Cl^-). Therefore, each ion precisely attains a closed outer shell of electrons and hence holds on a spherical shape. Additionally, in order to fill the shells and to hold a spherical shape, the ions of an ionic solid exceptionally have the integer valence. An ion having the positive valence is termed as a 'Cation'. Furthermore, in an ionic solid the cations are typically surrounded by ions having the negative valence and are termed as 'Anions'. Similarly, each anion is also surrounded by the cations. Because the opposite charges attract each other, therefore the preferred and essential bonding occurs when each of the ion holds as many neighbours as possible, which are consistent and constant with the ion radii. Approximately, six or eight nearest neighbours are considered as typical, while the numbers of nearest neighbours typically depend on the size of the ions and not on the bond angles.

Covalent Bonding: The covalent bonding can be defined with reference to the silicon, carbon, germanium, and a few other elements which normally form the covalently bonded solids. In all of these elements, in the outer *sp*-shell there are four electrons which are half filled. The *sp*-shell is referred as a hybrid which is specifically formed from one *s* and one *p* subshell. Basically, in the covalent bond an atom characteristically shares one valence (outer shell) electron with each of its four nearest neighbour atoms. The bonds are considered highly or extremely directional and usually prefer or favour a tetrahedral arrangement. Evidently, a covalent bond is formed by means of two electrons, one from each atom which is distinctively located in the orbitals between the ions. Insulators typically have all their electrons within the shells which are inside the atoms.

Metallic Bonding: Metallic bonds generally classified as having two specific categories or groups. The first category or group is defined as the instance in which the valence electrons are typically from the *sp*-shells of the metal ions; this type of metallic bonding is considered as extremely weak bonding. In the second category or group, the valence electrons are uniquely from the partially filled *d*-shells, and therefore this type of metallic bonding is considered as extremely strong. The *d*-bonds dominate when both the types of bonding exist.

Theoretically, the simple metals are referred as bonded with the *sp*-electrons. The electrons of these metal atoms are defined as the filled in atomic shells except for a few electrons which are defined as in unfilled *sp*-shells. Subsequently, the electrons from the unfilled shells get detached from the metal ion and then freely wander all through the crystal. These detached electrons are termed as the conduction electrons because these electrons are responsible for the electrical conductivity of metals.

The phrase or expression ‘Electron Correlation’ describes about the correlated movements of the electrons; in which the motion of each electron precisely depends on the positions of the neighbouring electrons. Additionally, the electrons have or possess the strong and powerful short-range order with one another.

Cohesive energy is referred as the certain specific type of energy exceptionally gained by means of specifically arranging the atoms in a precise crystalline state, as compared with the gas state. Insulators and semiconductors are considered to have substantial and significant cohesive energies therefore these solids are strongly bounded together having excellent mechanical strength. Metals which have electrons in the *sp*-bonds are considered to have extremely small quantity of cohesive energies. This type of metallic bond is considered as weak bond and the crystals are hardly held together. Basically, the single crystals of the simple metals, such as sodium are considered as mechanically weak.

Molecular Binding: The Dutch physicist Johannes D. van der Waals initially proposed about the concept of force that distinctively binds the molecular solids. Characteristically, in between any two atoms or molecules there is a force of attraction (F) that uniquely varies or fluctuates according to the inverse seventh power of the distance R between the centres of the atoms or molecules and is given as:

NOTES

$$F = -C/R^7, \text{ where C is a constant.}$$

This force is termed as the van der Waals force, which rapidly declines or decreases with the distance *R* and is considered as extremely weak. When the atoms or the molecules have a net charge, then there is precisely a strong force whose strength and power uniquely varies or fluctuates according to the Coulomb's law as the inverse second power of the separation distance and is given as:

$$F = -C'/R^2, \text{ where } C' \text{ is a constant.}$$

This force precisely provides the unique molecular binding in the ionic crystals and also some of the molecular binding in the metals. Specifically, the Coulomb's law cannot be applied to the atoms or the molecules without a net charge. Additionally, the molecules having a dipole moment, for example water possess a strong attractive force because of the interactions between the dipoles. For the atoms and the molecules with neither net charges nor dipole moments, the van der Waals force typically provides and supports the crystal binding. Though the force of gravity also acts and exists between the neutral atoms and the molecules, but it is considerably too weak to bind the molecules into the crystals.

Hydrogen Bonding: Hydrogen bonding is considered extremely significant in a few crystals, particularly in ice. In hydrogen bonding, a hydrogen atom with its lone electron usually forms a single covalent bond along with an electronegative atom. In the hydrogen bond, the atom is precisely ionized to a proton. The proton is then positioned between the two anions and joins them. Hydrogen bonding typically occurs precisely with only the most or highly electronegative ions, namely nitrogen, oxygen, and fluorine. In water, evidently the hydrogen links pairs of oxygen ions. In nature, the water is found in several different crystal structures, but all of them have the specific feature or characteristic that the hydrogen atoms uniquely position between the pairs of oxygen. Another hydrogen-bonded solid is referred as the Hydrogen Fluoride (HF), in which the hydrogen atom (proton) uniquely links pairs of fluorines.

Bond Effects of the Crystal Lattice Energy of a Solid

The effects of the crystal lattice potential on bonding can be defined with lattice energy. The lattice energy is the energy change on formation of one mole of an ionic compound from its constituent ions in the gaseous state. It is a measure of the cohesive forces that bind ions. Lattice energy is relevant to many practical properties including solubility, hardness, and volatility. The derivation of lattice energy is usually deduced from the Born–Haber cycle.

The formation of a crystal lattice is exothermic, i.e., the value of $\Delta H_{Lattice}$ is negative because it corresponds to the coalescing of infinitely separated gaseous ions in vacuum to form the ionic lattice.

The concept of lattice energy was originally developed for rock salt structured and sphalerite structured compounds like NaCl and ZnS, where the ions occupy high symmetry crystal lattice sites. In the case of NaCl, lattice energy is the energy released by the reaction.

$$Na^+ (g) + Cl^- (g) \rightarrow NaCl (s)$$

Which would amount to –786 kJ/mol.

2.2.8 Wave Functions for Wave Vector

A **wave function** is a mathematical description of the quantum state of an isolated quantum system. The wave function is a complex-valued probability amplitude, and the probabilities for the possible results of measurements made on the system can be derived from it. The most common symbols for a wave function are the Greek letters ψ and Ψ, for lower case and capital case psi, respectively.

The wave function is a function of the degrees of freedom corresponding to some maximal set of commuting observables. Once such a representation is chosen, the wave function can be derived from the quantum state.

In physics, a **wave vector** or **wavevector** is a vector which helps to describe a wave. Like any vector, it has a magnitude and direction, both of which are equally significant. Its magnitude is either the wavenumber or angular wavenumber of the wave (inversely proportional to the wavelength), and its direction is ordinarily the direction of wave propagation.

Some particles, like electrons and photons, have nonzero spin, and the wave function for such particles include spin as an intrinsic, discrete degree of freedom; other discrete variables can also be included, such as isospin. When a system has internal degrees of freedom, the wave function at each point in the continuous degrees of freedom (for example, a point in space) assigns a complex number for each possible value of the discrete degrees of freedom (for example, Z-component of spin) – these values are often displayed in a column matrix (for example, a 2×1 column vector for a non-relativistic electron with spin 1/2).

According to the superposition principle of quantum mechanics, wave functions can be added together and multiplied by complex numbers to form new wave functions and form a Hilbert space. The inner product between two wave functions is a measure of the overlap between the corresponding physical states and is used in the foundational probabilistic interpretation of quantum mechanics, the Born rule, relating transition probabilities to inner products. The Schrödinger equation determines how wave functions evolve over time, and a wave function behaves qualitatively like other waves, such as water waves or waves on a string, because the Schrödinger equation is mathematically a type of wave equation. This explains the name 'Wave Function' and gives rise to wave–particle duality. However, the wave function in quantum mechanics describes a kind of physical phenomenon, still open to different interpretations, which fundamentally differs from that of classic mechanical waves.

In solid-state physics, the 'Wave Vector' also called **k**-vector of an electron or hole in a crystal is the wavevector of its quantum mechanical wave function. These electron waves are not ordinary sinusoidal waves, but they do have a kind of envelope function which is sinusoidal, and the wave vector is defined via that envelope wave.

2.2.9 Experimental Methods in Fermi Surface Studies

Electronic Fermi surfaces have been measured through observation of the oscillation of transport properties in magnetic fields H, for example the de Haas–van Alphen effect (dHvA) and the Shubnikov–de Haas effect (SdH). The former is an oscillation in magnetic susceptibility and the latter in resistivity. The oscillations are periodic versus $1/H$ and occur because of the quantization of energy levels in the plane perpendicular to a magnetic field, a phenomenon first predicted by Lev Landau. The new states are called Landau levels and are separated by an energy $\hbar\omega_c$ where $\omega_c = eH/m^*c$ is called the cyclotron frequency, '*e*' is the electronic charge, m^* is the electron effective mass and *c* is the speed of light. In a notable result, Lars Onsager proved that the period of oscillation ΔH is related to the cross-section of the Fermi surface (typically given in $Å^{-2}$) perpendicular to the magnetic field direction $A_\perp$ by the equation,

$$A_\perp = \frac{2\pi e \Delta H}{\hbar c}$$

Thus, the determination of the periods of oscillation for various applied field directions allows mapping of the Fermi surface. Observation of the dHvA and SdH oscillations requires magnetic fields large enough that the circumference of the cyclotron orbit is smaller than a mean free path. Therefore, dHvA and SdH experiments are usually performed at high-field facilities like the High Field Magnet Laboratory in Netherlands, Grenoble High Magnetic Field Laboratory in France, the Tsukuba Magnet Laboratory in Japan or the National High Magnetic Field Laboratory in the United States.

The most direct experimental technique to resolve the electronic structure of crystals in the momentum-energy space, and, consequently, the Fermi surface, is the Angle Resolved PhotoEmission Spectroscopy (ARPES). An example of the Fermi surface of superconducting cuprates measured by ARPES.

With positron annihilation it is also possible to determine the Fermi surface as the annihilation process conserves the momentum of the initial particle. Since a positron in a solid will thermalize prior to annihilation, the annihilation radiation carries the information about the electron momentum. The corresponding experimental technique is called Angular Correlation of electron positron Annihilation Radiation (ACAR) as it measures the angular deviation from 180 degree of both annihilation quanta. In this way it is possible to probe the electron momentum density of a solid and determine the Fermi surface. Furthermore, using spin polarized positrons, the momentum distribution for the two spin states in magnetized materials can be obtained. ACAR has many advantages and disadvantages compared to other experimental techniques. It does not rely on UHV conditions (Ultra-High Vacuum Condition), cryogenic temperatures, high magnetic fields or fully ordered alloys. However, ACAR needs samples with a low vacancy concentration as they act as effective traps for positrons. In this way, the first determination of a smeared Fermi surface in a 30% alloy was obtained in 1978.

2.2.10 Cyclotron Resonance in Metals External Orbits

Cyclotron resonance describes the interaction of external forces with charged particles experiencing a magnetic field, thus already moving on a circular path. It is named after the cyclotron, a cyclic particle accelerator that utilizes an oscillating electric field tuned to this resonance to add kinetic energy to charged particles.

The cyclotron frequency or gyrofrequency is the frequency of a charged particle moving perpendicular to the direction of a uniform magnetic field *B*, constant magnitude and direction. Since that motion is always circular, the cyclotron frequency is given by equality of centripetal force and magnetic Lorentz force,

$$\frac{mv^2}{r} = qBv$$

with the particle mass *m*, its charge *q*, velocity *v*, and the circular path radius *r*, also called gyroradius. The gyroradius (also known as radius of gyration, Larmor radius or cyclotron radius) is the radius of the circular motion of a charged particle in the presence of a uniform magnetic field.

The angular speed of the rotation is then,

$$\omega = \frac{v}{r} = \frac{qB}{m}.$$

Giving the rotational frequency (being the cyclotron frequency) as,

$$f = \frac{\omega}{2\pi} = \frac{qB}{2\pi m}$$

It is notable that the cyclotron frequency is independent of the radius and velocity and therefore independent of the particle's kinetic energy; all particles with the same charge-to-mass ratio rotate around magnetic field lines with the same frequency. This is only true in the non-relativistic limit and underpins the principle of operation of the cyclotron.

The cyclotron frequency is also useful in non-uniform magnetic fields, in which (assuming slow variation of magnitude of the magnetic field) the movement is approximately helical - in the direction parallel to the magnetic field, the motion is uniform, whereas in the plane perpendicular to the magnetic field the movement is, as previously circular. The sum of these two motions gives a trajectory in the shape of a helix.

This expression is derived for the SI Units.

Gaussian Units

In some cases, the cyclotron frequency is given in Gaussian units. In Gaussian units, the Lorentz force differs by a factor of 1/*c*, the speed of light, which leads to:

$$\omega = \frac{v}{r} = \frac{qB}{mc}.$$

For materials with little or no magnetism (i.e. $\mu \approx 1$) $H \approx B$, so we can use the easily measured *H* instead of *B*:

$$\omega = \frac{qH}{mc}$$

Note that converting this expression to SI units introduces a factor of the vacuum permeability.

Effective Mass

For some materials, the motion of electrons follows loops that depend on the applied magnetic field, but not exactly the same way. For these materials, we define a cyclotron effective mass, m^* so that:

$$\omega = \frac{qB}{m^*}$$

2.2.11 de Haas–Van Alphen Effect

The de Haas–Van Alphen effect, often abbreviated to DHVA, is a quantum mechanical effect in which the magnetic susceptibility of a pure metal crystal oscillates as the intensity of the magnetic field B is increased. It can be used to determine the Fermi surface of a material. Other quantities also oscillate, such as the electrical resistivity (Shubnikov–de Haas effect), specific heat, and sound attenuation and speed. It is named after Wander Johannes de Haas and his student Pieter M. van Alphen. The DHVA effect comes from the orbital motion of itinerant electrons in the material. An equivalent phenomenon at low magnetic fields is known as Landau diamagnetism.

The differential magnetic susceptibility of a material is defined as,

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

Where H is the applied external magnetic field and M the magnetization of the material, such that $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$, where μ_0 is the vacuum permeability. For practical purposes, the applied and the measured field are approximately the same $\mathbf{B} \approx \mu_0 \mathbf{H}$ (if the material is not ferromagnetic).

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

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

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

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

Theory

Experimentally it was discovered in 1930 by W.J. de Haas and P.M. van Alphen under careful study of the magnetization of a single crystal of bismuth. The magnetization oscillated as a function of the field. The inspiration for the experiment was the recently discovered Shubnikov–de Haas effect by Lev Shubnikov and

De Haas, which showed oscillations of the electrical resistivity as function of a strong magnetic field. Evidently, de Haas thought that the magnetoresistance should behave in an analogous manner.

The theoretical prediction of the phenomenon was formulated before the experiment in the same year, by Lev Landau, but he discarded it as he thought that the magnetic fields necessary for its demonstration could not yet be created in a laboratory. The effect was described mathematically using Landau quantization of the electron energies in an applied magnetic field. A strong homogeneous magnetic field — typically several teslas — and a low temperature are required to cause a material to exhibit the DHVA effect.

After the 1950s, the DHVA effect gained wider relevance after Lars Onsager (1952), and independently, Ilya Lifshitz and Arnold Kosevich (1954), pointed out that the phenomenon could be used to image the Fermi surface of a metal. In 1954, Lifshitz and Aleksei Pogorelov determined the range of applicability of the theory and exceptionally described how to determine the shape of any arbitrary convex Fermi surface by measuring the extremal sections. Lifshitz and Pogorelov also found a relation between the temperature dependence of the oscillations and the cyclotron mass of an electron.

By the 1970s, the Fermi surface of most metallic elements had been reconstructed using de Haas–Van Alphen and Shubnikov–de Haas effects. Other techniques to study the Fermi surface include the Angle Resolved PhotoEmission Spectroscopy (ARPES).

Check Your Progress

1. What is Fermi surface?
2. Define semiconductors on the basis of the Fermi levels.
3. Why in an *n*-type semiconductor the Fermi level is greater than that of the intrinsic semiconductor?
4. Give the equation for Fermi level for *n*-type semiconductor.
5. What is a hole?
6. Define the effective mass of a particle?
7. How the effective mass of electrons or electron holes in a solid is stated?
8. State the terms cohesive energy and lattice energy.
9. How electronic Fermi surfaces are measured?
10. What does cyclotron resonance describe?
11. State about the de Haas–Van Alphen effect.

2.3 TRANSPORT PROPERTIES OF METALS

As per the free electron theory of metals, the free electrons are considered as an ideal gas of free particles which when in thermal equilibrium, obey Maxwell-Boltzmann statistics. When a non-equilibrium state is established by allowing electric or thermal currents to flow, i.e., then the problem is to investigate how the equilibrium distribution would be modified by small electric or thermal current. It is also essential to consider the kinetic behaviour of the electrons as being that of free particles subjected to instantaneous collisions which serve to return the distribution to equilibrium condition, and to express the final result for electrical and thermal conductivity in terms of mean free path between these randomizing collisions. In a state of steady flow of heat or electricity, the distribution function of velocity components and spatial coordinates of the electrons will be different from that in thermal equilibrium in the absence of flow. The theory of transport phenomena is concerned with determining this distribution function for given external fields.

The transport properties of solids are closely related to the energy dispersion relations $E(\vec{k})$ in the solid materials and in particular to the behaviour of $E(\vec{k})$near the Fermi level. Conversely, the analysis of transport measurements provides a great deal of information on $E(\vec{k})$. Although transport measurements do not generally provide the most sensitive tool for studying $E(\vec{k})$, such measurements are fundamental to solid state physics because they can be carried out on nearly all materials and therefore provide a valuable tool for characterizing materials.

2.3.1 The Boltzmann Equation

The Boltzmann Equation or Boltzmann Transport Equation (BTE) describes the statistical behaviour of a thermodynamic system not in a state of equilibrium, devised by Ludwig Boltzmann in 1872. The classic example of such a system is a fluid with temperature gradients in space causing heat to flow from hotter regions to colder ones, by the random but biased transport of the particles making up that fluid. In the modern literature the term Boltzmann equation is often used in a more general sense, referring to any kinetic equation that describes the change of a macroscopic quantity in a thermodynamic system, such as energy, charge or particle number.

The equation arises not by analysing the individual positions and momenta of each particle in the fluid but rather by considering a probability distribution for the position and momentum of a typical particle, i.e., the probability that the particle occupies a given very small region of space, mathematically the volume element $d^3\mathbf{r}$, cantered at the position **r**, and has momentum nearly equal to a given momentum vector **p**, thus occupying a very small region of momentum space $d^3\mathbf{p}$, at an instant of time.

The Boltzmann equation can be used to determine how physical quantities change, such as heat energy and momentum, when a fluid is in transport. One may also derive other properties and characteristics to fluids, such as viscosity, thermal conductivity, and electrical conductivity, by treating the charge carriers in a material as a gas.

The equation is a nonlinear integro-differential equation, and the unknown function in the equation is a probability density function in six-dimensional space of a particle position and momentum.

The Phase Space and Density Function

The set of all possible positions **r** and momenta **p** is called the phase space of the system; in other words, a set of three coordinates for each position coordinate x, y, z, and three more for each momentum component p_x, p_y, p_z. The entire space is

6-dimensional: a point in this space is $(\mathbf{r}, \mathbf{p}) = (x, y, z, p_x, p_y, p_z)$, and each coordinate is parameterized by time t. The small volume 'Differential Volume Element' is written,

$$\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p} = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z$$

Since the probability of N molecules, which all have $\mathbf{r}$ and $\mathbf{p}$ within $\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p}$, is in question, at the heart of the equation is a quantity f which gives this probability per unit phase space volume, or probability per unit length cubed per unit momentum cubed, at an instant of time t. This is a probability density function: $f(\mathbf{r}, \mathbf{p}, t)$, defined so that,

$$\mathrm{d}N = f(\mathbf{r}, \mathbf{p}, t)\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p}$$

This is the number of molecules which all have positions lying within a volume element $\mathrm{d}^3\mathbf{r}$ about $\mathbf{r}$ and momenta lying within a momentum space element $\mathrm{d}^3\mathbf{p}$ about $\mathbf{p}$, at time t. Integrating over a region of position space and momentum space gives the total number of particles which have positions and momenta in that region:

$$\begin{aligned} N &= \int\limits_{\text{momenta}} \mathrm{d}^3\mathbf{p} \int\limits_{\text{positions}} \mathrm{d}^3\mathbf{r}\, f(\mathbf{r}, \mathbf{p}, t) \\ &= \iiint\limits_{\text{momenta}} \quad \iiint\limits_{\text{positions}} f(x, y, z, p_x, p_y, p_z, t)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z \end{aligned}$$

Which is a 6-fold integral. While f is associated with a number of particles, the phase space is for one-particle, not all of them, which is usually the case with deterministic many-body systems, since only one $\mathbf{r}$ and $\mathbf{p}$ is in question. It is not part of the analysis to use $\mathbf{r}_1$, $\mathbf{p}_1$ for particle 1, $\mathbf{r}_2$, $\mathbf{p}_2$ for particle 2, etc., up to $\mathbf{r}_N$, $\mathbf{p}_N$ for particle N.

It is assumed the particles in the system are identical, so each has an identical mass m.

Solving the Equation

Exact solutions to the Boltzmann equations have been proven to exist in some cases; this analytical approach provides insight, but is not generally usable in practical problems.

Instead, numerical methods, including finite elements and lattice Boltzmann methods, are generally used to find approximate solutions to the various forms of the Boltzmann equation. Example applications range from hypersonic aerodynamics in rarefied gas flows to plasma flows. An application of the Boltzmann equation in electrodynamics is the calculation of the electrical conductivity - the result is in leading order identical with the semiclassical result.

Close to local equilibrium, solution of the Boltzmann equation can be represented by an asymptotic expansion in powers of Knudsen number, the Chapman-Enskog expansion. The first two terms of this expansion give the Euler equations and the Navier-Stokes equations. The higher terms have singularities. The problem of developing mathematically the limiting processes, which lead from the atomistic view represented by Boltzmann's equation to the laws of motion of continua, is an important part of Hilbert's sixth problem.

2.3.2 Electrical Conductivity

NOTES

Electrical conductivity or specific conductance is the reciprocal of electrical resistivity. It represents a material's ability to conduct electric current. It is commonly signified by the Greek letter σ (Sigma), but κ (Kappa) (especially in electrical engineering) and γ (Gamma) are sometimes used. The SI unit of electrical conductivity is Siemens per metre (S/m).

In an ideal case, cross-section and physical composition of the examined material are uniform across the sample, and the electric field and current density are both parallel and constant everywhere. Many resistors and conductors do in fact have a uniform cross section with a uniform flow of electric current, and are made of a single material, so that this is a good model, as shown in Figure (2.16).

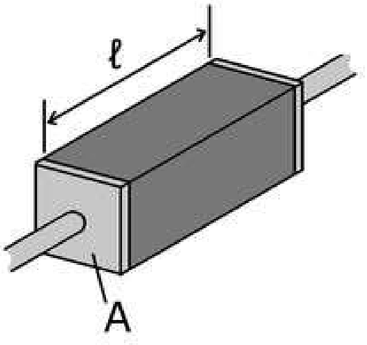


Fig. 2.16 *Resistive Material with Electrical Contacts on Both Ends*

Figure (2.16) shows s piece of resistive material with electrical contacts on both ends.

When this is the case, the electrical resistivity ρ (Greek: rho) can be calculated by:

$$\rho = R\frac{A}{\ell}$$

Where,

R = Electrical Resistance of a Uniform Specimen of the Material

l = Length of the Specimen

A = Cross-Sectional Area of the Specimen

The resistivity can be expressed using the SI unit Ohm metre (ΩÅ.m), i.e., Ohms multiplied by square metres for the cross-sectional area then divided by metres for the length.

Metals possess a high density of conduction electrons. The aluminium atom has three valence electrons in a partially filled outer shell. In metallic aluminium, the three valence electrons per atom are stated asthe conduction electrons. The number of conduction electrons is considered constant, which does not depend on either temperature or impurities. Metals conduct electricity at all temperatures, but for most metals the conductivity is best at low temperatures. Divalent atoms, such as magnesium or calcium, donate both valence electrons to become conduction electrons, while monovalent atoms, such as lithium or gold, donate one. The number of conduction electrons alone does not determine conductivity; it depends on electron mobility as well. Silver, with only one conduction electron per atom, is a better conductor than aluminium with three, for the higher mobility of silver compensates for its fewer electrons.

In metals, such as sodium and aluminium, the atoms donate all their valence electrons to the conduction band. The resulting ions are small, occupying only 10–15 percent of the volume of the crystal. The conduction electrons are free to roam through the remaining space. A simple model, which often describes well the properties of the conduction electrons, treats them as interacting neither with the ions nor with each other. The electrons are approximated as free particles wandering easily through the crystal. This concept was first proposed by the German scientist Arnold Johannes Wilhelm Sommerfeld. It works quite well for those metals, known as simple metals, whose conduction electrons are donated from *sp*-shells—for example, aluminium, magnesium, calcium, zinc, and lead. They are called simple since they are precisely and appropriately explained by the simple theory of Sommerfeld.

2.3.3 Calculation of Relaxation Time

The Boltzmann equation that describes the probability density function for electrons in a solid is,

$$\frac{\partial f}{\partial t} = -\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f - \vec{v} \cdot \nabla_{\vec{r}} f + \left.\frac{\partial f}{\partial t}\right|_{collisions}$$

If an external force is applied, the system will move out of equilibrium. If this external force is removed, the collision term will cause scattering events that return the system to equilibrium. In the relaxation time approximation, the collision term is assumed to have the form,

$$\left.\frac{\partial f(\vec{k})}{\partial t}\right|_{collision} = \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}.$$

Here f_0 is the Fermi function,

$$f_0(\vec{k}) = \frac{1}{1 + \exp\left(\frac{E(\vec{k})-\mu}{k_B T}\right)}$$

This form for the collision term ensures that the probability density function returns to the Fermi function if all forces are removed. If there are no external forces and the electrons are uniformly distributed in space $\nabla_{\vec{r}} f = 0$, then the Boltzmann equation becomes,

$$\frac{\partial f(\vec{k})}{\partial t} = \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}.$$

NOTES

This equation describes a system that starts in some initial non-equilibrium probability density function $f(\vec{k}, t = 0)$ at time $t = 0$ and returns to equilibrium in a relaxation time $\tau(\vec{k})$. Some $\vec{k}$ states decay more quickly than others. Typically, the states far from the Fermi energy decay the fastest. To include the possibility that there is a temperature gradient or a concentration gradient in the problem, the temperature and the chemical potential can depend on $\vec{r}$.

$$\frac{\partial f(\vec{k},\vec{r},t)}{\partial t} = -\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f(\vec{k},\vec{r},t) - \vec{v} \cdot \nabla_{\vec{r}} f(\vec{k},\vec{r},t) + \frac{f_0(\vec{k},\vec{r}) - f(\vec{k},\vec{r},t)}{\tau(\vec{k})}.$$

Often, we consider steady state conditions in which the external fields are considered constant for a much longer time than the relaxation time. Under steady state conditions, $\frac{\partial f}{\partial t} = 0$ and we can solve for $f(\vec{r},\vec{k},t)$,

$$f(\vec{k},\vec{r}) = f_0(\vec{k},\vec{r}) - \tau(\vec{k})\left(\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f(\vec{k},\vec{r}) + \vec{v} \cdot \nabla_{\vec{r}} f(\vec{k},\vec{r})\right)$$

If the system is close to equilibrium, then $f(\vec{k},\vec{r})$ will be almost similar as $f_0(\vec{k},\vec{r})$. We can consider the relaxation time as a small parameter. To first order in τ, $f(\vec{k},\vec{r})$ is,

$$f(\vec{k},\vec{r}) \approx f_0(\vec{k},\vec{r}) - \tau(\vec{k})\left(\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f_0(\vec{k},\vec{r}) + \vec{v} \cdot \nabla_{\vec{r}} f_0(\vec{k},\vec{r})\right)$$

Basically, when the derivatives of Fermi function are taken then, we assume that the $\vec{k}$ dependence arises only through the dispersion relation $E(\vec{k})$ and that the temperature and the chemical potential can depend on the position $\vec{r}$. Here we assume that the dispersion relation does not depend on position so that the material is uniform in space. The derivatives of the Fermi function are,

$$\nabla_{\vec{k}} f_0(\vec{k},\vec{r}) = \frac{\partial f_0}{\partial E}\nabla_{\vec{k}} E(\vec{k}),$$

$$\nabla_{\vec{r}} f_0(\vec{k},\vec{r}) = \frac{\partial f_0}{\partial T}\nabla_{\vec{r}} T + \frac{\partial f_0}{\partial \mu}\nabla_{\vec{r}} \mu.$$

Where,

$$\frac{\partial f_0}{\partial \mu} = -\frac{\partial f_0}{\partial E} = \frac{T}{E(\vec{k}) - \mu}\frac{\partial f_0}{\partial T} = \frac{\exp\left(\frac{E(\vec{k})-\mu}{k_B T}\right)}{k_B T\left(\exp\left(\frac{E(\vec{k})-\mu}{k_B T}\right) + 1\right)^2}.$$

The partial derivatives $\frac{\partial f_0}{\partial \mu}, = \frac{\partial f_0}{\partial E}$ and $\frac{\partial f_0}{\partial T}$ are all functions that are only non-zero for energies $E(\vec{k})$ close to the chemical potential. This means that only the state of matter that is near the Fermi surface will contribute to the transport properties.

2.3.4 Ideal Resistance

The electrical resistance of an object is defined as a measure of its opposition to the flow of electric current. Its reciprocal quantity is termed as the electrical conductance which is typically used to measure the electric current when it passes through the medium. Electrical resistance has some concepts analogous with the mechanical friction. The SI unit of electrical resistance is the Ohm (Ω), while electrical conductance is measured in Siemens (S), formerly called 'Mhos' and was then represented by ℧.

The resistance *R* of an object is defined as the ratio of voltage *V* across it to current *I* through it, while the conductance *G* is the reciprocal. This can be represented as,

$$R = \frac{V}{I}, \qquad G = \frac{I}{V} = \frac{1}{R}$$

For a broad range of materials and their properties, *V* and *I* are directly proportional to each other and therefore *R* and *G* are considered as constants, even though they will depend on the size and shape of the object, the material it is made of and the significant factors, such as temperature or strain. This characteristic proportionality is termed as 'Ohm's Law' and materials that satisfy these conditions are called 'Ohmic Materials'.

Principally, an '**Ideal Resistor**' strictly follow the **Ohm's Law** given by ***V* = *I R*** for any value of ***V*** and ***I***.

An ideal resistor should not possess inductance and/or capacitance, i.e., an ideal resistor should not have any phase difference to the oscillating/alternating voltage applied across it and current flowing through it.

Ideal resistance is therefore considered as the **pure resistance** without any **reactance**.

Ideal value of the resistance is specified as zero which specifies that there is no loss of power, and the zero voltage drops across the resister. Consequently, due to this reason when the ideal resistance is used then the heat is not produced.

2.3.5 Carrier Mobility

In solid state physics, term **carrier mobility** is generally referred to both electron mobility and hole mobility. The electron mobility characterises how fast an electron can move through a metal or semiconductor when pulled by an electric field. There is an analogous quantity for holes, called hole mobility.

Electron mobility and hole mobility are defined as the unique or special cases of **electrical mobility** of **charged particles** in a fluid under an applied electric field.

When an electric field E is applied across a piece of material, then the electrons respond by moving with an average velocity called the drift velocity, ν_d. Then the electron mobility μ is defined as,

$$\nu_d = \mu E$$

Electron mobility is almost always specified in units of cm^2/(V·s). This is different from the SI unit of mobility, m^2/(V·s). They are related by 1 m^2/(V·s) = 104 cm^2/(V·s).

The electron mobility is defined by the equation of the form:

$$\nu_d = \mu_e E$$

Where,

E = Magnitude of the Electric Field Applied to a Material.

ν_d = Magnitude of the Electron Drift Velocity or the Electron Drift Speed caused due to the Electric Field.

μ_e = Electron Mobility.

The hole mobility is defined by the similar form of equation as,

$$\nu_d = \mu_h E$$

Both the electron mobility and hole mobility are stated as positive by the definition.

Charge transport mechanisms are considered as the theoretical models that aim to quantitatively describe the electric current flow through a given medium. Crystalline solids and molecular solids are two opposite extreme cases of materials that exhibit substantially different transport mechanisms. Additionally, in atomic solids transport is intra-molecular, also known as band transport, while in molecular solids the transport is inter-molecular, also known as hopping transport. The two different mechanisms result in different **charge mobilities**.

Considering the Ohm's law and by the definition of conductivity, the following common expression can be possibly derived for current as a function of **carrier mobility** μ and applied electric field $\boldsymbol{E}$:

$$I = GV = \sigma \frac{A}{\ell} V$$

$$= \sigma \boldsymbol{AE} = \boldsymbol{en}\, \mu\, \boldsymbol{AE}$$

The relationship $\sigma = \boldsymbol{en}\,\mu$ holds when the concentration of localized states is significantly higher as compared to the concentration of **charge carriers** and we also assume that the hopping events are independent from each other.

Normally, the **carrier mobility** μ depends on temperature T, on the applied electric field *E*, and the concentration of localized states N. Depending on the model, increased temperature may either increase or decrease carrier mobility, applied electric field can increase mobility by contributing to thermal ionization of trapped charges, and increased concentration of localized states increases the mobility as well. Charge transport in the same material may have to be described by different models, depending on the applied field and temperature.

2.3.6 Impurity Scattering

The ionized impurity scattering is the scattering of charge carriers by ionization in the lattice. The most primitive models can be conceptually understood as a particle responding to unbalanced local charge that arises near a crystal impurity; similar to an electron encountering an electric field. This effect is the mechanism by which doping decreases mobility.

In the current quantum mechanical picture of conductivity the ease with which electrons traverse a crystal lattice is dependent on the near perfectly regular spacing of ions in that lattice. Only when a lattice contains perfectly regular spacing can the ion-lattice interaction (scattering) lead to almost transparent behaviour of the lattice. Impurity atoms in a crystal have an effect similar to thermal vibrations where conductivity has a direct relationship between temperature.

A crystal with impurities is less regular than a pure crystal, and a reduction in electron mean free paths occurs. Impure crystals have lower conductivity than pure crystals with less temperature sensitivity in that lattice.

Lattice scattering is the scattering of ions by interaction with atoms in a lattice. This effect can be qualitatively understood as phonons colliding with charge carriers.

In the current quantum mechanical picture of conductivity, the ease with which electrons traverse a crystal lattice is dependent on the near perfectly regular spacing of ions in that lattice. Only when a lattice contains perfectly regular spacing can the ion-lattice interaction (scattering) lead to almost transparent behaviour of the lattice.

In the quantum understanding, an electron is viewed as a wave traveling through a medium. When the wavelength of the electrons is larger than the crystal spacing, the electrons will propagate freely throughout the metal without collision.

Semiconductors are doped with donors and/or acceptors, which are typically ionized, and are thus charged. The Coulombic forces will deflect an electron or hole approaching the ionized impurity. This is known as ionized impurity scattering. The amount of deflection depends on the speed of the carrier and its proximity to the ion. The more heavily a material is doped, the higher the probability that a carrier will collide with an ion in a given time, and the smaller the mean free time between collisions, and the smaller the mobility. When determining the strength of these interactions due to the long-range nature of the Coulomb potential, other impurities and free carriers cause the range of interaction with the carriers to reduce significantly compared to bare Coulomb interaction.

If these scatterers are near the interface, the complexity of the problem increases due to the existence of crystal defects and disorders. Charge trapping centers that scatter free carriers form in many cases due to defects associated with dangling bonds. Scattering happens because after trapping a charge, the defect becomes charged and therefore starts interacting with free carriers. If scattered carriers are in the inversion layer at the interface, the reduced dimensionality of the carriers makes the case differ from the case of bulk impurity scattering as carriers move only in two dimensions. Interfacial roughness also causes short-range scattering limiting the mobility of quasi-two-dimensional electrons at the interface.

2.3.7 General Transport Coefficients

A transport coefficient γ (Gamma) measures how rapidly a perturbed system returns to equilibrium.

The transport coefficients occur in transport phenomenon with transport laws,

$$\mathbf{J}_k = \gamma_k \mathbf{X}_k$$

Where,

$\mathbf{J}_k$ is a Flux of the Property k

The Transport Coefficient γ_k of this Property k

$\mathbf{X}_k$, the Gradient Force which acts on the Property k.

Transport coefficients can be expressed via a Green–Kubo relation:

$$\gamma = \int_0^\infty \langle \dot{A}(t)\dot{A}(0) \rangle \, dt$$

Where A is an observable occurring in a perturbed Hamiltonian, $\langle \cdot \rangle$ is an ensemble average and the dot above the A denotes the time derivative. For times 't' that are greater than the correlation time of the fluctuations of the observable the transport coefficient obeys a generalized Einstein relation:

$$2t\gamma = \langle |A(t) - A(0)|^2 \rangle$$

In general, a transport coefficient is a tensor.

2.3.8 Thermal Conductivity

The **thermal conductivity** of a material is a measure of its ability to conduct heat. It is commonly denoted by k, λ (Lambda), or κ (Kappa).

Heat transfer occurs at a lower rate in materials of low thermal conductivity than in materials of high thermal conductivity. For instance, metals typically have high thermal conductivity and are very efficient at conducting heat, while the opposite is true for insulating materials like Styrofoam. Correspondingly, materials of high thermal conductivity are widely used in heat sink applications, and materials of low thermal conductivity are used as thermal insulation. The reciprocal of thermal conductivity is called thermal resistivity.

The defining equation for thermal conductivity is $\mathbf{q} = -k\nabla T$, where is the heat flux, k is the thermal conductivity, and ∇T is the temperature gradient. This is known as Fourier's Law for heat conduction. Although commonly expressed as a scalar, the most general form of thermal conductivity is a second-rank tensor.

However, the tensorial description only becomes necessary in materials which are anisotropic.

Consider a solid material placed between two environments of different temperatures. Let T_1 be the temperature at $x = 0$ and T_2 be the temperature at $x = L$, and suppose $T_2 > T_1$. A possible realization of this scenario is a building on a cold winter day: the solid material in this case would be the building wall, separating the cold outdoor environment from the warm indoor environment. Figure (2.17) illustrates that the thermal conductivity can be defined in terms of the heat flow q across a temperature difference.

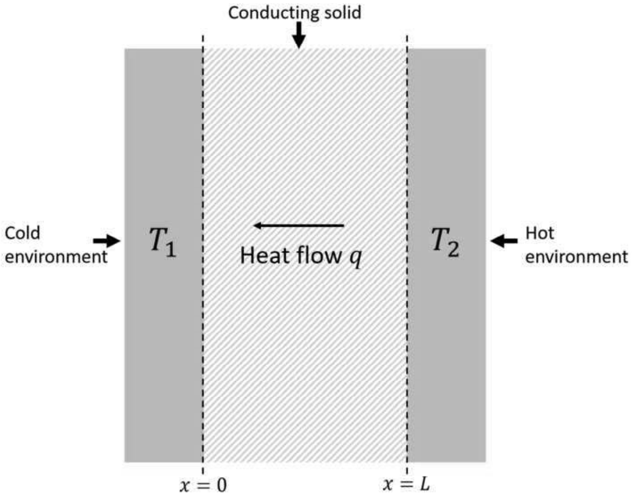


Fig. 2.17 *Thermal Conductivity of the Heat Flow q Across a Temperature Difference*

According to the second law of thermodynamics, heat will flow from the hot environment to the cold one as the temperature difference is equalized by diffusion. This is quantified in terms of a heat flux q, which gives the rate, per unit area, at which heat flows in a given direction (in this case minus x-direction). In many materials, q is observed to be directly proportional to the temperature difference and inversely proportional to the separation distance L:

$$q = -k \cdot \frac{T_2 - T_1}{L}$$

The constant of proportionality k is the thermal conductivity; it is a physical property of the material. In the present scenario, since $T_2 > T_1$ heat flows in the minus x-direction and q is negative, which in turn means that $k > 0$. In general, k is always defined to be positive. The same definition of k can also be extended to gases and liquids, provided other modes of energy transport, such as convection and radiation, are eliminated.

For simplicity, we have assumed here that the k does not vary significantly as temperature is varied from T_2 to T_1.

Other Quantities

In engineering practice, it is common to work in terms of quantities which are derivative to thermal conductivity and implicitly consider design specific features, such as component dimensions.

NOTES

For instance, thermal conductance is defined as the quantity of heat that passes in unit time through a plate of particular area and thickness when its opposite faces differ in temperature by one kelvin. For a plate of thermal conductivity k, area A and thickness L, the conductance is kA / L, measured in W.K^{-1}. The relationship between thermal conductivity and conductance is analogous to the relationship between electrical conductivity and electrical conductance.

Thermal resistance is the inverse of thermal conductance. It is a convenient measure to use in multicomponent design since thermal resistances are additive when occurring in series.

Units

In the International System of Units (SI), thermal conductivity is measured in watts per meter-Kelvin (W/(m.K)), while some standard notations also define the thermal conductivity in watts per centimetre Kelvin (W/(cm.K)).

Measurement

There are several ways to measure thermal conductivity; each is suitable for a limited range of materials. Broadly speaking, there are two categories of measurement techniques: steady state and transient. Steady state techniques infer the thermal conductivity from measurements on the state of a material once a steady state temperature profile has been reached, whereas transient techniques operate on the instantaneous state of a system during the approach to steady state. Lacking an explicit time component, steady state techniques do not require complicated signal analysis (steady state implies constant signals). The disadvantage is that a well-engineered experimental setup is usually needed, and the time required to reach steady state precludes rapid measurement.

In comparison with solid materials, the thermal properties of fluids are more difficult to study experimentally. This is because in addition to thermal conduction, convective and radiative energy transport are usually present unless measures are taken to limit these processes. The formation of an insulating boundary layer can also result in an apparent reduction in the thermal conductivity.

2.3.9 Thermoelectric Effects

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa via a thermocouple. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, heat is transferred from one side to the other, creating a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side.

This effect can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is affected by the applied voltage, thermoelectric devices can be used as temperature controllers.

The term ‘Thermoelectric Effect’ encompasses three separately identified effects: the Seebeck Effect, the Peltier Effect, and the Thomson Effect. The Seebeck and Peltier effects are different manifestations of the same physical process;

textbooks may refer to this process as the Peltier–Seebeck effect, the separation derives from the independent discoveries by French physicist Jean Charles Athanase Peltier and Baltic German physicist Thomas Johann Seebeck. The Thomson effect is an extension of the Peltier–Seebeck model and is credited to Lord Kelvin.

NOTES

Joule heating, the heat that is generated whenever a current is passed through a conductive material, is not generally termed a thermoelectric effect. The Peltier–Seebeck and Thomson effects are thermodynamically reversible, whereas Joule heating is not.

Seebeck Effect

The Seebeck effect is the ElectroMotive Force (EMF) that develops across two points of an electrically conducting material when there is a temperature difference between them. The EMF is called the Seebeck EMF (or Thermo / Thermal / Thermoelectric EMF). The ratio between the EMF and temperature difference is the Seebeck coefficient. A thermocouple measures the difference in potential across a hot and cold end for two dissimilar materials. This potential difference is proportional to the temperature difference between the hot and cold ends. First discovered in 1794 by Italian scientist Alessandro Volta, it is named after the Baltic German physicist Thomas Johann Seebeck, who in 1821 independently rediscovered it. It was observed that a compass needle would be deflected by a closed loop formed by two different metals joined in two places, with an applied temperature difference between the joints. This was because the electron energy levels shifted differently in the different metals, creating a potential difference between the junctions which in turn created an electrical current through the wires, and therefore a magnetic field around the wires. Seebeck did not recognize that an electric current was involved, so he called the phenomenon ‘Thermomagnetic Effect’.

Peltier Effect

When an electric current is passed through a circuit of a thermocouple, heat is evolved at one junction and absorbed at the other junction. This is known as the Peltier Effect. The Peltier effect is the presence of heating or cooling at an electrified junction of two different conductors and is named after French physicist Jean Charles Athanase Peltier, who discovered it in 1834. When a current is made to flow through a junction between two conductors, A and B, heat may be generated or removed at the junction. The total heat generated is not determined by the Peltier effect alone, as it may also be influenced by Joule heating and thermal-gradient effects. The Peltier coefficients represent how much heat is carried per unit charge.

Thomson Effect

In different materials, the Seebeck coefficient is not constant in temperature, and so a spatial gradient in temperature can result in a gradient in the Seebeck coefficient. If a current is driven through this gradient, then a continuous version of the Peltier effect will occur. This Thomson effect was predicted and later observed in 1851 by Lord Kelvin (William Thomson). It describes the heating or cooling of a current-carrying conductor with a temperature gradient.

2.3.10 Phonon Drag

Phonon drag is an increase in the effective mass of conduction electrons or valence holes due to interactions with the crystal lattice in which the electron moves. As an electron moves past atoms in the lattice its charge distorts or polarizes the nearby lattice. This effect leads to a decrease in the electron (or hole, as may be the case) mobility, which results in a decreased conductivity. However, as the magnitude of the Seebeck coefficient increases with phonon drag, it may be beneficial in a thermoelectric material for direct energy conversion applications. The magnitude of this effect is typically appreciable only at low temperatures (<200 K). Phonons are not always in local thermal equilibrium; they move against the thermal gradient. They lose momentum by interacting with electrons (or other carriers) and imperfections in the crystal. If the phonon-electron interaction is predominant, the phonons will tend to push the electrons to one end of the material, losing momentum in the process. This contributes to the already present thermoelectric field. This contribution is most important in the temperature region where phonon-electron scattering is predominant. This happens for,

$$T \approx \frac{1}{5}\theta_{\mathrm{D}}$$

Where θ_D is the Debye temperature. At lower temperatures there are fewer phonons available for drag, and at higher temperatures they tend to lose momentum in phonon-phonon scattering instead of phonon-electron scattering.

This region of the Seebeck coefficient-versus-temperature function is highly variable under a magnetic field.

2.3.11 The Hall Effect

The Hall effect is the production of a voltage difference (the Hall voltage) across an electrical conductor that is transverse to an electric current in the conductor and to an applied magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879.

A Hall effect can also occur across a void or hole in a semiconductor or metal plate, when current is injected via contacts that lie on the boundary or edge of the void or hole, and the charge flows outside the void or hole, in the metal or semiconductor. This Hall effect becomes observable in a perpendicular applied magnetic field across voltage contacts that lie on the boundary of the void on either side of a line connecting the current contacts, it exhibits apparent sign reversal in comparison to the standard ordinary Hall effect in the simply connected specimen, and this Hall effect depends only on the current injected from within the void.

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. It is a characteristic of the material from which the conductor is made, since its value depends on the type, number, and properties of the charge carriers that constitutes the current.

If a specimen (metal or semiconductor) carrying a current I is placed in a transverse magnetic field B, then an electric field E is induced in the direction perpendicular to both I and B. This phenomenon is known as Hall effect and the generated voltage is called the Hall voltage.

Theory

Consider a rectangular slab of a n-type semiconductor material which carries a current *I* along the positive *X*-direction as shown in Figure (2.18). In an *n*-type semiconductor electrons are the majority carries.

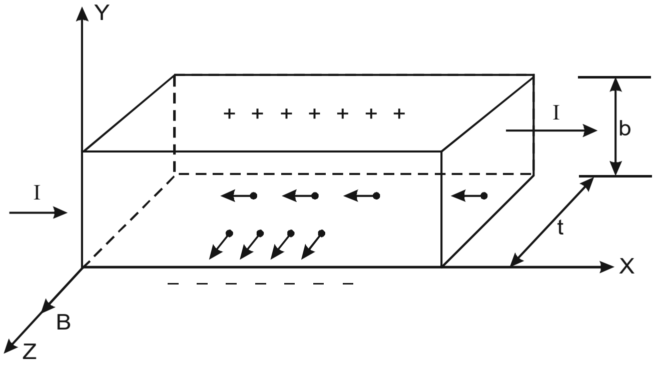


Fig. 2.18 *Hall Effect*

Let a magnetic field B is applied along the positive Z-direction. Under the influence of this magnetic field, the electrons experience a force called Lorentz force given by,

$$F_L = -Bev_d \qquad ...(2.5)$$

Where *e* is the magnitude of charge of the electrons and v_d is the drift velocity.

This Lorentz force is exerted on the electrons in the negative Y-direction. The direction of this force is given by Fleming's left hand rule. Thus, the electrons are therefore deflected downwards and collect at the bottom surface of the specimen.

On the other hand, the top edge of the specimen becomes positively charged due to the loss of electrons. Hence, a potential called the Hall voltage V_H is developed between the upper and lower surfaces of the specimen which establishes an electric field E_H called the Hall field across the specimen in the negative Y-direction.

This electric field excerts an upward force on the electron and is given by,

$$F_E = -eE_H \qquad ...(2.6)$$

At equilibrium, the Lorentz force and the electric force gets balanced. Hence,

$$F_E = F_L$$

Therefore, from Equations (2.6) and (2.7),

$$-eE_H = -Bev_d$$

Or $$E_H = Bv_d \qquad ...(2.7)$$

If b is the width (i.e., the distance between the top and bottom surface) of the specimen, then

$$E_H = \frac{V_H}{b} \qquad ...(2.8)$$

Or $$V_H = E_H\, b \qquad ...(2.9)$$

And $$V_H = Bv_d b \qquad ...(2.10)$$

Let *t* be the thickness of the specimen along the Z-direction. Therefore, its area of cross-section normal to the direction of current is *bt*.

NOTES

If J is the current density, then,

$$J = \frac{I}{bt} \quad ...(2.11)$$

But, J can also be expressed as,

$$J = -n_e ev_d$$ where n_e is the density of electrons. ...(2.12)

$$\therefore \quad v_d = \frac{-J}{n_e e} \quad ...(2.13)$$

Hence, substituting Equation (2.12) in Equation (2.13),

$$V_H = -Bb\frac{J}{n_e e} \quad ...(2.14)$$

But, V_H is also equal to $E_H\,b$

$$\therefore \quad E_H\,b = -Bb\frac{J}{n_e e}$$

Or
$$E_H = \frac{-BJ}{n_e e} \quad ...(2.15)$$

Note: The polarity of Hall voltage for an *n*-type semiconductor is positive at the top surface. For a *p*-type semiconductor the polarity of Hall voltage is positive at the bottom surface. The polarity of the Hall voltage developed at the top and bottom surface of the specimen can be identified by using probes.

Hall Coefficient R_H

The Hall effect is described by means of Hall coefficient R_H. It is given by,

$$R_H = \frac{1}{ne}$$

where n is in general, the carrier concentration.

R_H for n-Type and p-Type Material

A negative sign is used while denoting the Hall coefficient for an *n*-type material i.e.,

It is given by $$R_H = -\frac{1}{n_e e} \quad ...(2.16)$$

where n_e is the density of electrons.

But, for a p-type material a positive sign is used to denote the Hall coefficient. i.e.,

It is given by $$R_H = \frac{1}{n_h e} \quad ...(2.17)$$

where n_h is the density of holes.

Therefore, Equation (2.17) can be written as,

$$E_H = BJ\,R_H$$

i.e.,
$$R_H = \frac{E_H}{JB} \quad ...(2.18)$$

But, we know $E_H = \frac{V_H}{b}$ and $J = \frac{I}{bt}$. Hence Equation (2.18) becomes,

$$R_H = \frac{V_H bt}{IBb}$$

$$\therefore \quad R_H = \frac{V_H t}{IB} \quad ...(2.19)$$

Since, the quantities V_H, *t*, I and B are measurable, the Hall coefficient R_H can be determined.

Experimental Determination of Hall Coefficient

A rectangular slab of thickness *t* and width *b* is placed at right angles to a magnetic field B. A known current I is passed through the material along the X-axis by connecting it to a dc battery, key, a rheostat and a milliammeter as shown in Figure (2.19).

A calibrated voltmeter connected between the opposite ends of the slab measures the Hall voltage V_H. Thus, the Hall field is given by

$$E_H = \frac{V_H}{b}$$

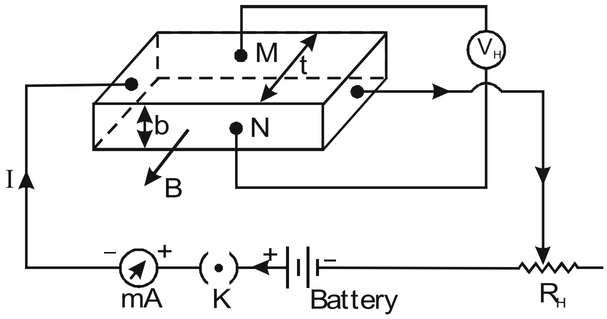


Fig. 2.19 *Experimental Setup to Determine Hall Coefficient*

The current density is given by,

$$J = \frac{I}{bt}$$

Thus, R_H can be calculated using the formula,

$$R_H = \frac{V_H t}{IB}$$

Mobility Determination

For an n-type material the conductivity is given by,

$\sigma_e = n_e e\, \mu_e$ where μ_e is the mobility of electrons.

$$\therefore \quad \mu_e = \frac{\sigma_e}{n_e e} \quad ...(2.20)$$

$$\text{or} \quad \mu_e = -\sigma_e R_H \quad ...(2.21)$$

Similarly, for a p-type material, the conductivity is given by,

$\sigma_h = n_h e\, \mu_h$ where μ_h is the mobility of holes.

$$\therefore \qquad \mu_h = \frac{\sigma_h}{n_h e} \qquad ...(2.22)$$

$$\text{or} \qquad \mu_h = \sigma_h\ R_H \qquad ...(2.23)$$

From the above explanation, it is assumed that all the charge carriers travel with average velocity. But actually, the charge carriers have a random thermal distribution in the velocity.

If this precise distribution is considered, then R_H is defined in general as,

$$R_H = \frac{3\pi}{8ne} = \frac{1.18}{ne} \qquad ...(2.24)$$

Therefore, Equations (2.22) and (2.24) can be written as

$$\mu_e = \frac{-\sigma_e R_H}{1.18} \quad \text{(For } n\text{-type material)} \qquad ...(2.25)$$

$$\text{And} \quad \mu_h = \frac{\sigma_h R_H}{1.18} \quad \text{(For } p\text{-type material)} \qquad ...(2.26)$$

Applications of Hall Effect

The Hall effect can be used for:

1. Determining whether a semiconductor is *n*-type or p-type.
2. Determining the carrier concentration and mobility.
3. Determining the magnetic field B in terms of Hall voltage V_H.
4. Designing the gauss meter and electronic meters based on Hall voltage.

Example 1

The conductivity and the Hall coefficient of a n-type silicon specimen are 112 $\Omega^{-1}m^{-1}$ and 1.25×10^{-13}, m^3C^{-1} respectively. Calculate the charge carrier density and electron mobility.

Solution:

Given, $\sigma_e = 112\ \Omega^{-1}m^{-1}$; $R_H = 1.25 \times 10^{-13}\ m^3C^{-1}$; n_e = ? and μ_e = ?

Formula $\mu_e = \sigma_e\ R_H$

$= 112 \times 1.25 \times 10^{-4}$ **= 0.014 $m^2V^{-1}s^{-1}$.**

We know, $\mu_e = \frac{\sigma_e}{n_e e}$.

$$\therefore \qquad n_e = \frac{\sigma_e}{\mu_e e} = \frac{112}{0.014 \times 1.6 \times 10^{-19}}$$

$$= \frac{112}{2.24 \times 10^{-21}} \ \mathbf{= 5 \times 10^{22}\ electrons/m^3.}$$

Example 2

A semiconducting crystal 12mm long, 1mm wide and 1mm thick has a magnetic flux density of 0.5Wb/m^2 applied from front to back, perpendicular to largest faces. When a current of 20mA flows lengthwise through the specimen, the voltage measured across its width is found to be 37 μv. What is the Hall coefficient of semiconductor and the density of charge carrier.

NOTES

Solution:

Given,

$l = 12\ \text{mm} = 12 \times 10^{-3}\ \text{m}$; $t = 1\ \text{mm} = 1 \times 10^{-3}\ \text{m}$

$b = 1\ \text{mm} = 1 \times 10^{-3}\ \text{m}$, $I = 20\ \text{m A} = 20 \times 10^{-3}\ \text{A}$

$v_H = 37\ \mu\text{V} = 37 \times 10^{-6}\ \text{V}$, $B = 0.5\ \text{Wb/m}^2$.

$R_H = ?$ and $n = ?$

We know

$$R_H = \frac{V_H t}{IB}$$

$$= \frac{37 \times 10^{-6} \times 1 \times 10^{-3}}{20 \times 10^{-3} \times 0.5} = \frac{3.7 \times 10^{-8}}{0.01}$$

$$\mathbf{R_H = 3.7 \times 10^{-6}\ C^{-1}\ m^3.}$$

Example 3

A silicon plate of thickness 1mm, breadth 10mm and length 100mm is placed in a magnetic field of 0.5 Wb/m^2 acting perpendicular to its thickness. If 10^{-2} A current flows along its length, then calculate the Hall coefficient, if Hall voltage developed is 1.83 mV.

Solution:

Given,

$t = 1\ \text{mm} = 1 \times 10^{-3}\ \text{m}$, $b = 10\ \text{mm} = 10 \times 10^{-3}\ \text{m}$

$l = 100\ \text{mm} = 100 \times 10^{-3}\ \text{m}$, $B = 0.5\ \text{Wb/m}^2$

$I = 10^{-2}\ \text{A}$; $V_H = 1.83\ \text{mV} = 1.83 \times 10^{-3}\ \text{V}$.

$R_H = ?$

Formula

$$R_H = \frac{V_H t}{IB} = \frac{1.83 \times 10^{-3} \times 1 \times 10^{-3}}{10^{-2} \times 0.5}$$

$$\therefore \quad \mathbf{R_H = 3.66 \times 10^{-4}\ m^3C^{-1}.}$$

Example 4

The Hall coefficient of certain silicon specimen was found to be -7.35×10^{-5} m^{2}C^{-1} from 100 to 400 K. Determine the nature of the semiconductor if the conductivity was found to be 200 Ω^{-1}m^{-1}. Calculate the density and mobility of the charge carrier.

Solution:

Given, $R_H = -7.35 \times 10^{-5}\text{m}^3\text{C}^{-1}$; $\sigma = 200\ \Omega^{-1}\text{m}^{-1}$; $n_e = ?$ and $\mu_e = ?$

The negative sign of the Hall coefficient indicates that the nature of the semiconductor is *n*-type.

Formula

$$n_e = \frac{1}{R_H e} = \frac{1}{7.35 \times 10^{-5} \times 1.6 \times 10^{-19}}$$

$$\therefore \quad \mathbf{n_e = 8.503 \times 10^{22}\ electrons\ /\ m^3.}$$

Mobility
$$\mu_e = \frac{\sigma}{n_e e} = \frac{200}{8.503 \times 10^{22} \times 1.6 \times 10^{-19}}$$

$\therefore \qquad \boldsymbol{\mu_e = 14.7006 \times 10^{-3} m^2V^{-1}s^{-1}}.$

Or

$$\mu_e = \sigma R_H$$

NOTES

$$= 200 \times 7.35 \times 10^{-5}$$

$\therefore \qquad \boldsymbol{\mu_e = 14.7 \times 10^{-3} m^2V^{-1}s^{-1}}.$

Example 5

A *n*-type semiconductor has Hall coefficient = 4.16 × 10^{-4} m^3C^{-1}. The conductivity is 108 $\Omega^{-1}m^{-1}$. Calculate its charge carrier density n_e and electron mobility at room temperature.

Solution:

Given, $R_H = 4.16 \times 10^{-4}$ m^3C^{-1}; $\sigma = 180\Omega^{-1}m^{-1}$; n_e = ? and μ_ε = ?

$$R_H = \frac{1.18}{n_e e} \qquad \text{(with correction factor for } R_H)$$

$$\therefore \qquad n_e = \frac{1.18}{R_H e} = \frac{1.18}{4.16 \times 10^{-4} \times 1.6 \times 10^{-19}}$$

$\therefore \qquad \boldsymbol{n_e = 1.772 \times 10^{22}/m^3}.$

We know, $\qquad \sigma = n_e e \mu_e$

$$\therefore \qquad \mu_e = \frac{\sigma}{n_e e} = \frac{180}{1.772 \times 10^{22} \times 1.6 \times 10^{-19}}$$

$\therefore \qquad \boldsymbol{M\mu_e = 0.06348\ m^2V^{-1}s^{-1}}.$

Example 6

A rectangular plane sheet of doped silicon has dimensions of 1cm along Y – direction, and 0.5mm along Z – direction. Hall probes are attached on its two surfaces which are parallel to X – Z plane and then a magnetic field of flux density 0.7 Wb/m^2 is applied along Z – direction. A current of 1mA is flowing in it in the X – direction. Calculate the Hall voltage measured by the probes if the Hall coefficient of the material is 1.25 × 10^{-3} m^3 C^{-1}.

Solution:

Given, B = 0.7 Wb/m^2; I = 1 × 10^{-3} A; $R_H = 1.25 \times 10^{-3}$ m^3C^{-1}; b = 1cm = 1 × 10^{-2}m

t = 0.5 mm = 0.5 × 10^{-3} m; V_H = ?

$$V_H = \frac{R_H IB}{t} = \frac{1.25 \times 10^{-3} \times 1 \times 10^{-3} \times 0.7}{0.5 \times 10^{-3}}$$

$$= 1.75 \times 10^{-3} \text{ V}$$

or $\qquad \boldsymbol{V_H = 1.75\ mV}.$

Example 7

The Hall coefficient of a specimen of a doped silicon is found to be 3.66×10^{-4} m^3C^{-1}. The resistivity of the specimen is 8.93 ×10^{-3}Ωm. Find the mobility and density of the charge carrier.

Solution:

Given, $R_H = 3.66 \times 10^{-4}$ m^3C^{-1} ; $\rho = 8.93 \times 10^{-3}\Omega m$; μ = ? and n = ?

Formula

$$R_H = \frac{1}{ne}$$

$$\therefore \quad n = \frac{1}{R_H e} = \frac{1}{3.66 \times 10^{-4} \times 1.6 \times 10^{-19}}$$

$$\mathbf{n = 1.7076 \times 10^{22} / m^3.}$$

Mobility $\mu = \sigma\ R_H$

Or $\mu = \dfrac{R_H}{\rho}$

$$\therefore \quad \mu = \frac{3.66 \times 10^{-4}}{8.93 \times 10^{-3}}$$

Or $\mathbf{\mu = 0.0409\ m^2V^{-1}s^{-1}.}$

NOTES

Example 8

An electric field of 100 V/m is applied to a sample of *n*-type semiconductor whose Hall coefficient is $-0.0125\ m^3C^{-1}$. Determine the current density in the sample, assuming electron mobility to be $0.36\ m^2V^{-1}s^{-1}$.

Solution:

Given, $R_H = -0.0125\ m^3C^{-1}$; $\mu_e = 0.36\ m^2V^{-1}s^{-1}$; $E_H = 100$ V/m; J = ?

We know,

$$R_H = \frac{1}{n_e e}$$

$$\therefore \quad n_e = \frac{1}{R_H e} = \frac{1}{0.0125 \times 1.6 \times 10^{-19}}$$

$$\mathbf{n_e = 5 \times 10^{20} / m^3.}$$

$$\sigma_e = n_e e\ \mu_e = 5 \times 10^{20} \times 1.6 \times 10^{-19} \times 0.36$$

$$\therefore \quad \mathbf{\sigma_e = 28.8\ \Omega^{-1}\ m^{-1}.}$$

We also know $J = \sigma_e E$

$$\therefore \quad J = 28.8 \times 100$$

Or $\mathbf{J = 2880\ A/m^2.}$

2.3.10 Magnetoresistance in the Two Band Model

Typically, there are carriers in two different bands, the applied electric field is the same but their contribution to the current will be different and given by,

$$\mathbf{E} = \frac{1}{\sigma_i}\mathbf{J}_i + \frac{\beta_i}{\sigma_i}\mathbf{H} \times \mathbf{J}_i.$$

Where σ is the conductivity and R = β/σ is the Hall coefficient. It can be inverted by first taking its crossproduct with **H** giving:

$$\mathbf{H} \times \mathbf{E} = \frac{1}{\sigma_i}\mathbf{H} \times \mathbf{J}_i - \frac{\beta_i H^2}{\sigma_i}\mathbf{J}_i$$

Now combining both equations to give:

$$\mathbf{J}_i = \frac{1}{1 + \beta_i^2 H^2}\left(\mathbf{E} - \beta_i \mathbf{H} \times \mathbf{E}\right)$$

Which can also be inverted back to the original form in a similar fashion. We now have an expression for the total current,

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$$

This expression is for a function of applied electric and magnetic field. Consequently, this can again be inverted to give:

$$\mathbf{E} = \frac{1}{\sigma(1+\beta^2 H^2)} (\mathbf{J} + \beta \mathbf{H} \times \mathbf{J})$$

Where,

$$\sigma = \frac{\sigma_1}{1+\beta_1^2 H^2} + \frac{\sigma_2}{1+\beta_2^2 H^2}$$

And,

$$\beta = \frac{1}{\sigma}\left(\frac{\sigma_1\beta_1}{1+\beta_1^2 H^2} + \frac{\sigma_2\beta_2}{1+\beta_2^2 H^2}\right)$$

For low magnetic field we relatively obtain the Hall coefficient denoted as,

$$R = \frac{\sigma_1\beta_1 + \sigma_2\beta_2}{(\sigma_1+\sigma_2)^2} = \frac{\sigma_1^2 R_1 + \sigma_2^2 R_2}{(\sigma_1+\sigma_2)^2}$$

Since it is not easy to find the **magnetoresistance** therefore we consider the equation,

$$\rho = \frac{1}{\sigma(1+\beta^2 H^2)}$$

Which must be in contrast with the **H** = 0 condition, $\rho_0 = \frac{1}{\sigma_1 + \sigma_2}$

After some algebraic manipulations we obtain the following formula by comparing them:

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho - \rho_0}{\rho_0} = \frac{\sigma_1\sigma_2(\beta_1 - \beta_2)^2 H^2}{(\sigma_1+\sigma_2)^2 + H^2(\beta_1\sigma_1 + \beta_2\sigma_2)^2}$$

The magnetoresistance is a positive quantity that vanishes if and only if $\beta_1 = \beta_2$ althrough this must not necessarily specify that the two carriers are the same.

Check Your Progress

12. Define the transport properties of solids.
13. What does the Boltzmann Equation describe?
14. State all the possible positions *r* and momenta *p* for the phase space of the system.
15. What is electrical conductivity or specific conductance?
16. Give the Boltzmann equation that describes the probability density function.
17. What does transport coefficient (Gamma) measures?
18. State about the thermal conductivity giving its defining equation.
19. What is phonon drag?
20. State about Hall effect and Hall coefficient.

2.4 ANSWERS TO ‘CHECK YOUR PROGRESS’

1. The Fermi surface, in condensed matter physics, is abstract interface that defines the allowable energies of electrons in a solid. It was named for Italian physicist Enrico Fermi, who along with English physicist P.A.M. Dirac developed the statistical theory of electrons. Fermi surfaces are important for characterizing and predicting the thermal, electrical, magnetic, and optical properties of crystalline metals and semiconductors. They are closely related to the atomic lattice, which is the underlying feature of all crystalline solids, and to energy band theory, which describes how electrons are distributed in such materials.
2. In semiconductors, the Fermi level is inside a band gap; however, in semiconductors the bands are near enough to the Fermi level to be thermally populated with electrons or holes. In an extrinsic semiconductor, the number of electrons in the conduction and the number of holes in the valence band are not equal. Henceforth, the chances of the occupation of the energy levels in valance and conduction bands are not equal. Therefore, in the case of extrinsic semiconductors, the Fermi level lies close to any of the valance or conduction band.
3. In an *n*-type semiconductor, the Fermi level is greater than that of the intrinsic semiconductor and lies closer to the conduction band than the valence band whereas for *p*-type semiconductors, the Fermi level is below the intrinsic semiconductor and lies closer to the valence band than the conduction band.
4. The Fermi level for *n*-type semiconductor is given as,

   $$E_F = E_C - K_B T \log \frac{N_C}{N_D}$$

   Where,

   E_F = The Fermi Level.
   E_C = The Conduction Band.
   K_B = The Boltzmann Constant.
   T = The Absolute Temperature.
   N_C = The Effective Density of States in the Conduction Band.
   N_D = The Concentration of Donor Atoms.
5. The name hole is given to a missing electron in certain solids, especially semiconductors. Holes affect the electrical, optical, and thermal properties of the solid. Along with electrons, the holes are considered very significant in the field of digital technology because when they are introduced into semiconductors they produce electronic and optical devices.

   Characteristically, an electron hole or a hole is precisiously defined as the lack of an electron at a specified position where one electron could have existed in an atom or atomic lattice. Since in a normal atom or crystal lattice the negative charge of the electrons is balanced by the positive charge of

NOTES

the atomic nuclei, the absence of an electron leaves a net positive charge at the have existed location.

6. A particle's effective mass (often denoted ***m****) is the mass that it seems to have when responding to forces, or the mass that it seems to have when interacting with other identical particles in a thermal distribution. The effective mass is a quantity that is used to simplify band structures by modeling the behaviour of a free particle with that mass. For some materials, the effective mass can be considered to be a simple constant of a material.
7. For electrons or electron holes in a solid, the effective mass is usually stated in units of the rest mass of an electron, m_e (9.11×10^{-31} kg). In these units, it is usually in the range 0.01 to 10, but can also be lower or higher, for example reaching 1,000 in exotic heavy fermion materials, or anywhere from zero to infinity (depending on definition) in graphene.
8. Cohesive energy is the energy gained by arranging the atoms in a crystalline state, as compared with the gas state. Insulators and semiconductors have large cohesive energies; since these solids are bound together strongly and have good mechanical strength. Fundamentally, the cohesive energy is defined as the energy that must be given to the solid to separate its constituents into neutral free atoms at rest and at infinite separation with the same electronic configuration.

   The lattice energy of a solid is defined as the energy that must be given to an ionic crystal to separate its constituents into free ions at rest and at infinite separation.
9. Electronic Fermi surfaces have been measured through observation of the oscillation of transport properties in magnetic fields H, for example the de Haas–van Alphen effect (dHvA) and the Shubnikov–de Haas effect (SdH). The former is an oscillation in magnetic susceptibility and the latter in resistivity.
10. Cyclotron resonance describes the interaction of external forces with charged particles experiencing a magnetic field, thus already moving on a circular path. It is named after the cyclotron, a cyclic particle accelerator that utilizes an oscillating electric field tuned to this resonance to add kinetic energy to charged particles.
11. The de Haas–Van Alphen effect, often abbreviated to DHVA, is a quantum mechanical effect in which the magnetic susceptibility of a pure metal crystal oscillates as the intensity of the magnetic field B is increased. It can be used to determine the Fermi surface of a material. Other quantities also oscillate, such as the electrical resistivity (Shubnikov–de Haas effect), specific heat, and sound attenuation and speed. It is named after Wander Johannes de Haas and his student Pieter M. van Alphen. The DHVA effect comes from the orbital motion of itinerant electrons in the material. An equivalent phenomenon at low magnetic fields is known as Landau diamagnetism.
12. The transport properties of solids are closely related to the energy dispersion relations $E(\vec{k})$ in the solid materials and in particular to the behaviour of $E(\vec{k})$ near the Fermi level. Conversely, the analysis of transport measurements provides a great deal of information on $E(\vec{k})$. Although transport

NOTES

measurements do not generally provide the most sensitive tool for studying $E(\vec{k})$, such measurements are fundamental to solid state physics because they can be carried out on nearly all materials and therefore provide a valuable tool for characterizing materials.

13. The Boltzmann Equation or Boltzmann Transport Equation (BTE) describes the statistical behaviour of a thermodynamic system not in a state of equilibrium, devised by Ludwig Boltzmann in 1872. The equation arises not by analysing the individual positions and momenta of each particle in the fluid but rather by considering a probability distribution for the position and momentum of a typical particle, i.e., the probability that the particle occupies a given very small region of space, mathematically the volume element $d^3\mathbf{r}$, cantered at the position **r**, and has momentum nearly equal to a given momentum vector **p**, thus occupying a very small region of momentum space $d^3\mathbf{p}$, at an instant of time.
14. The set of all possible positions **r** and momenta **p** is called the phase space of the system; in other words, a set of three coordinates for each position coordinate x, y, z, and three more for each momentum component p_x, p_y, p_z. The entire space is 6-dimensional: a point in this space is $(\mathbf{r}, \mathbf{p}) = (x, y, z, p_x, p_y, p_z)$, and each coordinate is parameterized by time t. The small volume 'Differential Volume Element' is written,

$$d^3\mathbf{r}\, d^3\mathbf{p} = dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

15. Electrical conductivity or specific conductance is the reciprocal of electrical resistivity. It represents a material's ability to conduct electric current. It is commonly signified by the Greek letter σ (Sigma), but κ (Kappa) (especially in electrical engineering) and γ (Gamma) are sometimes used. The SI unit of electrical conductivity is Siemens per metre (S/m).
16. The Boltzmann equation that describes the probability density function for electrons in a solid is,

$$\frac{\partial f}{\partial t} = -\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f - \vec{v} \cdot \nabla_{\vec{r}} f + \left.\frac{\partial f}{\partial t}\right|_{collisions}$$

If an external force is applied, the system will move out of equilibrium. If this external force is removed, the collision term will cause scattering events that return the system to equilibrium. In the relaxation time approximation, the collision term is assumed to have the form,

$$\left.\frac{\partial f(\vec{k})}{\partial t}\right|_{collision} = \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}.$$

17. A transport coefficient γ (Gamma) measures how rapidly a perturbed system returns to equilibrium. The transport coefficients occur in transport phenomenon with transport laws,

$$\mathbf{J}_k = \gamma_k \mathbf{X}_k$$

Where, $\mathbf{J}_k$ is a Flux of the Property k, the Transport Coefficient γ_k of this Property k, and $\mathbf{X}_k$, the Gradient Force which acts on the Property k.

18. The thermal conductivity of a material is a measure of its ability to conduct heat. It is commonly denoted by k, λ (Lambda), or κ (Kappa). Heat transfer occurs at a lower rate in materials of low thermal conductivity than in materials of high thermal conductivity. The reciprocal of thermal conductivity is called thermal resistivity. The defining equation for thermal conductivity is $\mathbf{q} = -k\nabla T$, where is the heat flux, k is the thermal conductivity, and ∇T is the temperature gradient. This is known as Fourier's Law for heat conduction. Although commonly expressed as a scalar, the most general form of thermal conductivity is a second-rank tensor. However, the tensorial description only becomes necessary in materials which are anisotropic.
19. Phonon drag is an increase in the effective mass of conduction electrons or valence holes due to interactions with the crystal lattice in which the electron moves. As an electron moves past atoms in the lattice its charge distorts or polarizes the nearby lattice. This effect leads to a decrease in the electron (or hole, as may be the case) mobility, which results in a decreased conductivity.
20. The Hall effect is the production of a voltage difference (the Hall voltage) across an electrical conductor that is transverse to an electric current in the conductor and to an applied magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879. A Hall effect can also occur across a void or hole in a semiconductor or metal plate, when current is injected via contacts that lie on the boundary or edge of the void or hole, and the charge flows outside the void or hole, in the metal or semiconductor.

    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. It is a characteristic of the material from which the conductor is made, since its value depends on the type, number, and properties of the charge carriers that constitutes the current.

2.5 SUMMARY

- In condensed matter physics, the Fermi surface is the surface in reciprocal space which separates occupied from unoccupied electron states at zero temperature.
- The shape of the Fermi surface is derived from the periodicity and symmetry of the crystalline lattice and from the occupation of electronic energy bands.
- The existence of a Fermi surface is a direct consequence of the Pauli exclusion principle, which allows a maximum of one electron per quantum state. The study of the Fermi surfaces of the materials is termed as Fermiology.
- The Fermi surface, in condensed matter physics, is abstract interface that defines the allowable energies of electrons in a solid. It was named for Italian physicist Enrico Fermi, who along with English physicist P.A.M. Dirac developed the statistical theory of electrons.

NOTES

- Fermi surfaces are essential and significant for characterizing and predicting the thermal, electrical, magnetic, and optical properties of crystalline metals and semiconductors. They are closely related to the atomic lattice, which is the underlying feature of all crystalline solids, and to energy band theory, which describes how electrons are distributed in such materials.
- The linear response of a metal to an electric, magnetic or thermal gradient is determined through the shape of the Fermi surface, because currents are due to changes in the occupancy of states near the Fermi energy.
- In reciprocal space, the Fermi surface of an ideal Fermi gas is a sphere of radius,

$$k_F = \frac{p_F}{\hbar} = \frac{\sqrt{2mE_F}}{\hbar}$$

- The state occupancy of fermions like electrons is governed by Fermi–Dirac statistics so at finite temperatures the Fermi surface is accordingly broadened.
- In an extrinsic semiconductor, the number of electrons in the conduction and the number of holes in the valence band are not equal. Henceforth, the chances of the occupation of the energy levels in valance and conduction bands are not equal. Therefore, in the case of extrinsic semiconductors, the Fermi level lies close to any of the valance or conduction band.
- In semiconductors, the Fermi level is inside a band gap; however, in semiconductors the bands are near enough to the Fermi level to be thermally populated with electrons or holes.
- In an *n*-type semiconductor, the Fermi level is greater than that of the intrinsic semiconductor and lies closer to the conduction band than the valence band whereas for *p*-type semiconductors, the Fermi level is below the intrinsic semiconductor and lies closer to the valence band than the conduction band.
- Extrinsic semiconductors are formed by adding suitable impurities to the intrinsic semiconductor. The added impurity is very small of the order of one atom per million atoms of the pure semiconductor. The added impurity may be pentavalent or trivalent.
- Depending on the type of impurity added, the extrinsic semiconductors can be divided into two classes: *n*-type and *p*-type.
- An *n*-type semiconductor is a category of an extrinsic semiconductor. In the case of *n*-type semiconductors, the electron donor atoms play an important role, as these types of semiconductors are doped with the electron donor atoms.
- The donor atoms contribute the free electrons to the semiconductors; therefore, the *n*-type semiconductors have free electrons in plenty when compared to the holes. Basically, the pentavalent atoms are introduced into the semiconductors. Here, the pentavalent atoms refer to the atoms having 5 valence electrons.
- In the case of a *p*-type semiconductor, trivalent impurities are added to the intrinsic semiconductor. Each trivalent impurity generates a hole in the valence band. The hole is receptive towards an electron. In this way, trivalent impurities create a proportional number of holes in the valence band.

NOTES

- The electrons in a static magnetic field move on a curve of constant energy on a plane normal to B. An electron on the Fermi surface will move in a curve on the Fermi surface, because this is a surface of constant energy.
- The orbits that enclose filled states are electron orbits. Orbits that enclose empty states are hole orbits. Orbits that move from zone to zone without closing are open orbits.
- In condensed matter physics, the name **hole** is given to a missing electron in certain solids, especially semiconductors. Holes affect the electrical, optical, and thermal properties of the solid. Along with electrons, the holes are considered very significant in the field of digital technology, because when they are introduced into semiconductors, they produce electronic and optical devices.
- Because a missing electron is considered identical as an added positive electric charge, therefore the holes can characteristically carry a current, similar to that of electrons but in the opposite direction, precisely under an electric field.
- Generally, the 'Holes' moves more slowly as compared to the electrons, even though, since they normally function within the tightly bound valence band instead of the conduction band.
- Characteristically, an electron hole or a hole is precisely defined as the lack of an electron at a specified position where one electron could have existed in an atom or atomic lattice. Because in a normal atom or a crystal lattice the negative charge of the electrons is precisely balanced by means of the positive charge of the atomic nuclei, therefore the absence of an electron leaves a net positive charge at the location of the hole.
- A particle's effective mass (often denoted m^*) is the mass that it seems to have when responding to forces, or the mass that it seems to have when interacting with other identical particles in a thermal distribution.
- The effective mass is a quantity that is used to simplify band structures by modeling the behaviour of a free particle with that mass. For some materials, the effective mass can be considered to be a simple constant of a material.
- For electrons or electron holes in a solid, the effective mass is usually stated in units of the rest mass of an electron, m_e (9.11×10^{-31} kg). In these units, it is usually in the range 0.01 to 10, but can also be lower or higher, for example reaching 1,000 in exotic heavy fermion materials, or anywhere from zero to infinity (depending on definition) in graphene.
- In physics, a pseudopotential or effective potential is used as an approximation for the simplified description of complex systems. Applications include atomic physics and neutron scattering. The pseudopotential approximation was first introduced by Hans Hellmann in 1934.
- The pseudopotential is an attempt to replace the complicated effects of the motion of the core, i.e., non-valence electrons of an atom and its nucleus with an effective potential, or pseudopotential, so that the Schrödinger

equation contains a modified effective potential term instead of the Coulombic potential term for core electrons normally found in the Schrödinger equation.

NOTES

- Cohesive energy is the energy gained by arranging the atoms in a crystalline state, as compared with the gas state. Insulators and semiconductors have large cohesive energies; since these solids are bound together strongly and have good mechanical strength.
- Fundamentally, the cohesive energy is defined as the energy that must be supplied to the solid to separate its constituents into neutral free atoms at rest and at infinite separation with the same electronic configuration.
- The lattice energy of a solid is defined as the energy that must be given to an ionic crystal to separate its constituents into free ions at rest and at infinite separation.
- The wave function is a complex-valued probability amplitude, and the probabilities for the possible results of measurements made on the system can be derived from it.
- The most common symbols for a wave function are the Greek letters ψ and Ψ, for lower case and capital case psi, respectively.
- In physics, a wave vector or wavevector is a vector which helps describe a wave. Like any vector, it has a magnitude and direction, both of which are important. Its magnitude is either the wavenumber or angular wavenumber of the wave (inversely proportional to the wavelength), and its direction is ordinarily the direction of wave propagation.
- Electronic Fermi surfaces have been measured through observation of the oscillation of transport properties in magnetic fields H, for example the de Haas–van Alphen effect (dHvA) and the Shubnikov–de Haas effect (SdH). The former is an oscillation in magnetic susceptibility and the latter in resistivity.
- Cyclotron resonance describes the interaction of external forces with charged particles experiencing a magnetic field, thus already moving on a circular path. It is named after the cyclotron, a cyclic particle accelerator that utilizes an oscillating electric field tuned to this resonance to add kinetic energy to charged particles.
- The de Haas–Van Alphen effect, often abbreviated to DHVA, is a quantum mechanical effect in which the magnetic susceptibility of a pure metal crystal oscillates as the intensity of the magnetic field B is increased.
- The de Haas–Van Alphen effect can be used to determine the Fermi surface of a material. Other quantities also oscillate, such as the electrical resistivity (Shubnikov–de Haas effect), specific heat, and sound attenuation and speed. It is named after Wander Johannes de Haas and his student Pieter M. van Alphen. The DHVA effect comes from the orbital motion of itinerant electrons in the material.
- The transport properties of solids are closely related to the energy dispersion relations $E(\vec{k})$ in the solid materials and in particular to the behaviour of $E(\vec{k})$near the Fermi level. Conversely, the analysis of transport measurements provides a great deal of information on $E(\vec{k})$.

NOTES

- Although transport measurements do not generally provide the most sensitive tool for studying $E(\vec{k})$, such measurements are fundamental to solid state physics because they can be carried out on nearly all materials and therefore provide a valuable tool for characterizing materials.
- The Boltzmann Equation or Boltzmann Transport Equation (BTE) describes the statistical behaviour of a thermodynamic system not in a state of equilibrium, devised by Ludwig Boltzmann in 1872. The classic example of such a system is a fluid with temperature gradients in space causing heat to flow from hotter regions to colder ones, by the random but biased transport of the particles making up that fluid. In the modern literature the term Boltzmann equation is often used in a more general sense, referring to any kinetic equation that describes the change of a macroscopic quantity in a thermodynamic system, such as energy, charge or particle number.
- The equation arises not by analysing the individual positions and momenta of each particle in the fluid but rather by considering a probability distribution for the position and momentum of a typical particle, i.e., the probability that the particle occupies a given very small region of space, mathematically the volume element $d^3\mathbf{r}$, cantered at the position **r**, and has momentum nearly equal to a given momentum vector **p**, thus occupying a very small region of momentum space $d^3\mathbf{p}$, at an instant of time.
- The set of all possible positions **r** and momenta **p** is called the phase space of the system; in other words, a set of three coordinates for each position coordinate x, y, z, and three more for each momentum component p_x, p_y, p_z. The entire space is 6-dimensional: a point in this space is $(\mathbf{r}, \mathbf{p}) = (x, y, z, p_x, p_y, p_z)$, and each coordinate is parameterized by time t. The small volume 'Differential Volume Element' is written,

$$d^3\mathbf{r}\, d^3\mathbf{p} = dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

- Electrical conductivity or specific conductance is the reciprocal of electrical resistivity. It represents a material's ability to conduct electric current. It is commonly signified by the Greek letter σ (Sigma), but κ (Kappa) (especially in electrical engineering) and γ (Gamma) are sometimes used. The SI unit of electrical conductivity is Siemens per metre (S/m).
- The Boltzmann equation that describes the probability density function for electrons in a solid is,

$$\frac{\partial f}{\partial t} = -\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f - \vec{v} \cdot \nabla_{\vec{r}} f + \left.\frac{\partial f}{\partial t}\right|_{collisions}$$

- If an external force is applied, the system will move out of equilibrium. If this external force is removed, the collision term will cause scattering events that return the system to equilibrium. In the relaxation time approximation, the collision term is assumed to have the form,

$$\left.\frac{\partial f(\vec{k})}{\partial t}\right|_{collision} = \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}.$$

- The ionized impurity scattering is the scattering of charge carriers by ionization in the lattice. The most primitive models can be conceptually understood as a particle responding to unbalanced local charge that arises near a crystal impurity; similar to an electron encountering an electric field. This effect is the mechanism by which doping decreases mobility.
- A crystal with impurities is less regular than a pure crystal, and a reduction in electron mean free paths occurs. Impure crystals have lower conductivity than pure crystals with less temperature sensitivity in that lattice.
- Lattice scattering is the scattering of ions by interaction with atoms in a lattice. This effect can be qualitatively understood as phonons colliding with charge carriers.
- A transport coefficient γ (Gamma) measures how rapidly a perturbed system returns to equilibrium.
- The transport coefficients occur in transport phenomenon with transport laws,

  $$\mathbf{J}_k = \gamma_k \mathbf{X}_k$$

  Where, $\mathbf{J}_k$ is a Flux of the Property k, the Transport Coefficient γ_k of this Property k, and $\mathbf{X}_k$, the Gradient Force which acts on the Property k.
- The thermal conductivity of a material is a measure of its ability to conduct heat. It is commonly denoted by k, λ (Lambda), or κ (Kappa).
- Heat transfer occurs at a lower rate in materials of low thermal conductivity than in materials of high thermal conductivity.
- The reciprocal of thermal conductivity is called thermal resistivity.
- The defining equation for thermal conductivity is $\mathbf{q} = -k\nabla T$, where is the heat flux, k is the thermal conductivity, and ∇T is the temperature gradient. This is known as Fourier's Law for heat conduction.
- Although commonly expressed as a scalar, the most general form of thermal conductivity is a second-rank tensor. However, the tensorial description only becomes necessary in materials which are anisotropic.
- In the International System of Units (SI), thermal conductivity is measured in watts per meter-Kelvin (W/(m.K)), while same standard notations also define the thermal conductivity in watts per centimetre kelvin (W/(cm.K)).
- The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa via a thermocouple. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, heat is transferred from one side to the other, creating a temperature difference.
- The term 'Thermoelectric Effect' encompasses three separately identified effects: the Seebeck Effect, the peltier Effect, and the Thomson Effect.
- Joule heating, the heat that is generated whenever a current is passed through a conductive material, is not generally termed a thermoelectric effect. The Peltier–Seebeck and Thomson effects are thermodynamically reversible, whereas Joule heating is not.

- Phonon drag is an increase in the effective mass of conduction electrons or valence holes due to interactions with the crystal lattice in which the electron moves. As an electron moves past atoms in the lattice its charge distorts or polarizes the nearby lattice.
- The phonon drag effect leads to a decrease in the electron (or hole, as may be the case) mobility, which results in a decreased conductivity. However, as the magnitude of the Seebeck coefficient increases with phonon drag, it may be beneficial in a thermoelectric material for direct energy conversion applications.
- The magnitude of this effect is typically appreciable only at low temperatures (<200 K). Phonons are not always in local thermal equilibrium; they move against the thermal gradient.
- The Hall effect is the production of a voltage difference (the Hall voltage) across an electrical conductor that is transverse to an electric current in the conductor and to an applied magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879.
- 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. It is a characteristic of the material from which the conductor is made, since its value depends on the type, number, and properties of the charge carriers that constitutes the current.
- If a specimen (metal or semiconductor) carrying a current I is placed in a transverse magnetic field B, an electric field E is induced in the direction perpendicular to both I and B. This phenomenon is known as Hall effect and the generated voltage is called the Hall voltage.

2.6 KEY TERMS

- **Fermi surface:** The Fermi surface is abstract interface that defines the allowable energies of electrons in a solid. It was named for Italian physicist Enrico Fermi, who along with English physicist P.A.M. Dirac developed the statistical theory of electrons. Fermi surfaces are important for characterizing and predicting the thermal, electrical, magnetic, and optical properties of crystalline metals and semiconductors.
- **Extrinsic semiconductors:** Extrinsic semiconductors are formed by adding appropriate impurities to the intrinsic semiconductor.
- **Conduction band:** The conduction band is an energy band filled with the free electrons.
- **Valence band:** The valence band is an energy band filled with the holes.
- **Forbidden gap:** The forbidden gap is the gap between the conduction band and the valence band.
- **Fermi level:** The Fermi level is the highest energy level that an electron can occupy at absolute 0 (Zero) temperature.
- **Hole:** The name hole is given to a missing electron in certain solids, especially semiconductors. Holes affect the electrical, optical, and thermal properties of the solid.

- **Effective mass:** A particle's effective mass (often denoted ***m****) is the mass that it seems to have when responding to forces, or the mass that it seems to have when interacting with other identical particles in a thermal distribution.
- **Cyclotron resonance:** Cyclotron resonance describes the interaction of external forces with charged particles experiencing a magnetic field, thus already moving on a circular path. It is named after the cyclotron, a cyclic particle accelerator that utilizes an oscillating electric field tuned to this resonance to add kinetic energy to charged particles.
- **Electrical conductivity:** Electrical conductivity or specific conductance is the reciprocal of electrical resistivity and represents a material's ability to conduct electric current. It is commonly signified by the Greek letter σ (Sigma), but κ (Kappa) (especially in electrical engineering) and γ (Gamma) are sometimes used. The SI unit of electrical conductivity is Siemens per metre (S/m).
- **Phonon drag:** Phonon drag is an increase in the effective mass of conduction electrons or valence holes due to interactions with the crystal lattice in which the electron moves. As an electron moves past atoms in the lattice its charge distorts or polarizes the nearby lattice.
- **Hall effect:** The Hall effect is the production of a voltage difference (the Hall voltage) across an electrical conductor that is transverse to an electric current in the conductor and to an applied magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879.

2.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the term Fermi surfaces?
2. What are electrons, holes and open orbits?
3. List some physical properties of holes.
4. State about the effective mass electrons in crystals.
5. Define wave functions for zero wave vector.
6. What is lattice effect and cohesive energy of metals?
7. Why is pseudopotential used?
8. What is the importance of experimental methods in Fermi surface?
9. Define cyclotron resonance in metals.
10. State the de Haas–Van Alphen effect.
11. Why transport properties are significant?
12. State the Boltzmann equation.
13. Brief a note on electrical conductivity, calculation of relaxation time, and impurity scattering.
14. Define general transport coefficients and thermal conductivity.

15. What is thermoelectric effect?
16. State about the phonon drag.
17. How is the Hall voltage calculated?
18. What is magnetoresistance two band model?

Long-Answer Questions

1. Discuss the significance of Fermi surfaces in solid state physics giving appropriate examples.
2. How are the Fermi surfaces constructed? Explain with the help of examples.
3. Discuss the concept of electrons, holes and open orbits giving relevant examples and diagrams.
4. Explain the physical properties of holes.
5. Briefly discuss the effective mass electrons in crystals and the wave functions for zero wave vector.
6. Describe the lattice effect on cohesive energy of metals and pseudopotentials with the help of examples.
7. Elaborate on the experimental methods in Fermi surface studies giving relevant example.
8. Explain in detail about the cyclotron resonance in metals orbits giving relevant example.
9. What is de Haas–Van Alphen effect? Explain giving examples.
10. What is the significance of transport properties of metals? Explain giving examples.
11. Explain and deduce the Boltzmann equation and electrical conductivity with the help of standard equations.
12. Calculate the relaxation time using the Boltzmann equation.
13. Discuss about the impurity scattering and general transport coefficients.
14. Explain the significant features of thermal conductivity, thermoelectric effects, and phonon drag.
15. Discuss in detail about the Hall effect, Hall coefficient and Hall Voltage giving appropriate examples.
16. Elaborate on the magnetoresistances in the two band model.
17. The Hall coefficient of certain silicon specimen was found to be -7.35×10^{-5} m^2C^{-1} from 100 to 400 K. Determine the nature of the semiconductor if the conductivity was found to be 200 $\Omega^{-1}m^{-1}$. Calculate the density and mobility of the charge carrier.

2.8 FURTHER READING

Wahab, M. A. 2005. *Solid State Physics: Structure and Properties of Materials*. New Delhi: Narosa Publishing House.

Kittel, Charles. 1971. *Introduction to Solid State Physics*. New Jersey (US): John Wiley & Sons, Inc.

Pillai, S. O. 2005. *Solid State Physics*. Noida (UP): Wiley India Private Ltd.

Saxena, B. S., P. N. Saxena and R. C. Gupta. 2019. *Fundamentals of Solid State Physics*. Meerut (UP): Pragati Prakashan.

Dekker, A. J. 2008. *Solid State Physics*. Noida (UP): Macmillan Publishers India Pvt. Ltd.

Kakani, S. L. and C. Hemarajani. 2005. *Solid State Physics*. New Delhi: Sultan Chand & Sons Pvt. Ltd.

UNIT 3 SEMICONDUCTORS

NOTES

Structure

3.0 INTRODUCTION

Semiconductors, sometimes referred to as Integrated Circuits (ICs) or microchips, are specifically made from pure elements, typically Silicon or Germanium or compounds, such as Gallium Arsenide. The ICs and electronic discrete components, such as diodes and transistors are also made of semiconductors. Semiconductors are, consequently, termed as the 'Brains of Modern Electronics'.

A semiconductor material holds an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator, such as glass. The resistivity of semiconductor material falls as its temperature rises, subsequently the metals behave in the opposite way. Its conducting properties may be altered and modified in several beneficial methods by introducing the impurities 'Doping' into the crystal structure. When two differently doped regions exist in the same crystal, then uniquely a semiconductor junction is created. Basically, the conductivity of semiconductors may easily be modified or changed by introducing impurities into their crystal lattice. The amount of impurity, or dopant, added to an intrinsic (pure) semiconductor varies its level of conductivity. Doped semiconductors are referred to as extrinsic. By adding impurity to the pure semiconductors, the electrical conductivity may be varied by factors of thousands or millions.

In addition, the semiconductor devices have various useful properties, such as passing current more easily in one direction than the other, showing variable resistance, and having sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by doping and by the application of electrical fields or light, therefore the devices made from semiconductors can be used for amplification, switching, and energy conversion.

Semiconductors in their natural state are referred as the poor conductors because a current requires the flow of electrons, and semiconductors have their valence bands filled, preventing the entire flow of new electrons. Several developed techniques allow semiconducting materials to behave like conducting materials, such as doping or gating. These modifications specifically have two outcomes, namely the *n*-type semiconductors and the *p*-type semiconductors. These refer to the excess or shortage of electrons, respectively. A balanced number of electrons would cause a current to flow throughout the material. The behaviour of charge carriers, which include electrons, ions, and electron holes, at these junctions is the basis of diodes, transistors, and most modern electronics. Some significant examples of semiconductors are Silicon, Germanium, Gallium Arsenide, and elements near the so-called 'Metalloid Staircase' on the periodic table. After Silicon, the Gallium Arsenide is considered as the second most common semiconductor and is used in LASER diodes, solar cells, microwave frequency integrated circuits, and other devices. Silicon is considered as a critical element for fabricating most electronic circuits.

A Schottky defect is defined as an excitation in a crystal lattice leading to point defects named after Walter H. Schottky. In elemental crystals it refers to simple lattice vacancies, also called valency defects. In ionic crystals, this defect forms when oppositely charged ions leave their lattice sites and become incorporated for instance at the surface, creating oppositely charged vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid. Basically, the Schottky defect is formed in ionic crystals when oppositely charged ions leave their lattice sites which leads to the creation of vacancies. These vacancies are further created to maintain a neutral charge in the crystal.

A Frenkel defect is referred as a type of point defect in crystalline solids, named after its discoverer Yakov Frenkel. The defect forms when an atom or smaller ion (usually cation) leaves its place in the lattice, creating a vacancy and becomes an interstitial by lodging in a nearby location.

The Kondo effect describes the scattering of conduction electrons in a metal due to magnetic impurities, resulting in a characteristic change in electrical resistivity with temperature.

In this unit, you will study about the semiconductors, intrinsic conductivity, band gap, law of mass action, intrinsic carrier concentration, semiconductor conductivity, impurity states, thermal ionization of impurities, energy bands in Si and Ge, *n-n* junctions, rectification, polarons, semi-metals mobility of protons, point defects, alloys and dislocations, lattice vacancies, Schottky and Frenkel defects, diffusion, colour centres, magnetic alloys and the Konde effect, order-disorder transformations and crystal growth whiskers.

3.1 OBJECTIVES

After going through his unit, you will be able to:

- Discuss the significance and properties of semiconductors
- Know what intrinsic conductivity is
- Define band gap and law of mass action
- Explain intrinsic carrier concentration
- Understand the semiconductor conductivity and impurity states
- Elaborate on thermal ionization of impurities
- Describe *n-n* junctions and the energy bands in Si and Ge
- State the rectification of half-wave and full wave
- Understand the importance of polarons
- Define the semi-metals mobility of protons and point defects
- State the properties of magnetic alloys, dislocations and lattice vacancies
- Discuss the significant features of Schottky and Frenkel defects
- Explain diffusion phenomena and the Kondo effect
- Define the theoretical characteristics of order-disorder transformations and crystal growth whiskers

3.2 INTRINSIC CONDUCTIVITY

Semiconductors, sometimes referred to as Integrated Circuits (ICs) or microchips, are made from pure elements, typically silicon or germanium, or compounds, such as gallium arsenide. Semiconductors are an essential component of electronic devices, enabling advances in communications, computing, healthcare, military systems, transportation, clean energy, and countless other applications. In a process called doping, small amounts of impurities are added to the pure elements, causing large changes in the conductivity of the material.

Semiconductors are substances with specific properties. The ICs (Integrated Circuits) and electronic discrete components, such as diodes and transistors are made of semiconductors. Common elemental semiconductors are silicon and germanium. Silicon is well-known of these as the silicon forms most of ICs.

Semiconductors are, therefore, termed as the ‘Brains of Modern Electronics’.

Semiconductors that exists in pure form without any impurities added are called as intrinsic semiconductors. Consider the semiconductor Silicon, Si with atomic number 14. It has 14 number of protons and 14 number of electrons. The first shell occupies 2 electrons, the second shell occupies 8 electrons and the third shell which could accommodate 18 electrons has only 4 valence electrons. Similarly, germanium with an atomic number of 32 as shown in Figure (3.1(a)) has 4 shells with an outermost shell consisting of 4 valence electrons. These atoms exist in the crystalline structure with bonding as shown in Figure (3.1(b)). One atom of silicon shares the bonding with 4 other atoms thereby filling the 3rd shell of an atom with all 8 electrons creating a stable composition of silicon crystal. This type of bonding is known as covalent bonding.

NOTES

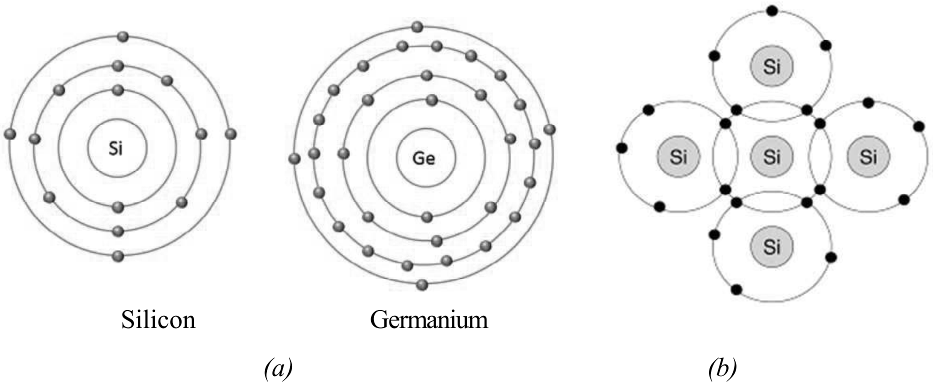


Fig. 3.1 *(a)Atomic Structure of Silicon and Germanium, (b) Crystalline Structure of Silicon*

Intrinsic semiconductors behave as perfect insulators under normal room temperatures. Silicon and germanium that consists of 4 valence electrons in their outermost shells are also known as **tetravalent atoms**. Similarly, atoms with three valence electrons are known as **trivalent atoms** and atoms with five valence electrons are known as **pentavalent atoms**.

Conduction in Intrinsic Semiconductors

When an external energy is supplied to the intrinsic semiconductor crystal, the electrons absorb the energy supplied and gain enough energy to break the covalent bond and are set free to move as free electrons in the crystal. Such free electrons move randomly inside the crystal until they lose their energy and finds a bonding pair of an electron with some other atom. When the electron leaves a covalent bond due to external energy, they leave behind a vacant space known as holes. Electrons are negatively charged and the vacant hole spaces wanting for electrons to occupy the space are considered as positively charged. When the free electrons leave the covalent bonding due to external energy, they form an electron-hole pair.

Figure (3.2) illustrates the conduction in the intrinsic semiconductors.

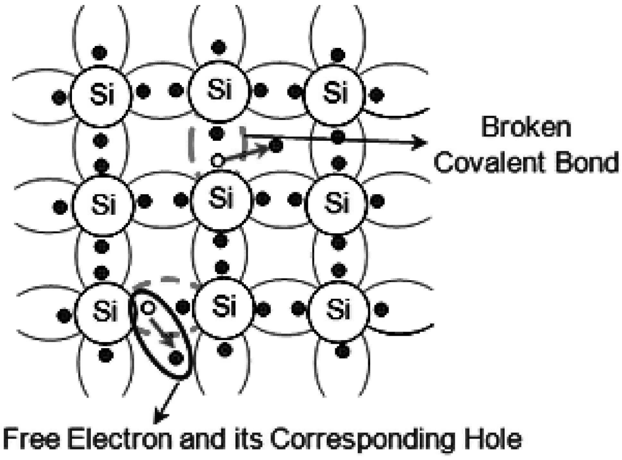


Fig. 3.2 *Conduction Inside Intrinsic Semiconductors*

Electron Current and Hole Current

Current constituted by electrons inside the semiconductor crystal are called an **electron current**. Since electrons are negatively charged, when a potential is applied across the semiconductor crystal, the electrons are attracted towards the positive terminal of the battery.

Current constituted by holes inside a semiconductor crystal are known as **hole current**. Though the holes (vacant spaces) do not move, consequent movement of electrons creates an illusion such that holes move, but in the opposite direction as that of the electron. Electron movement occurs towards the positive polarity of the battery and the hole movement is illusioned to appear as though holes move towards negative terminal of the battery. The movement of holes, i.e., the movement towards a negative terminal (from the positive terminal) is considered as the conventional current movement and hence the hole movement is considered as conventional current flow and the electron movement is considered as the electron flow. The electron and hole current is depicted in Figure (3.3).

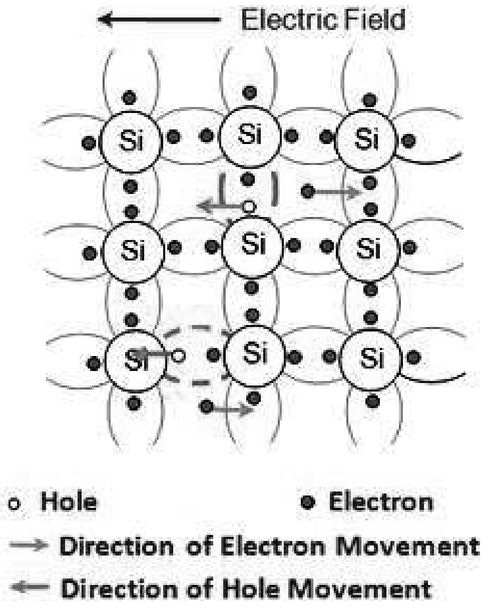


Fig. 3.3 Electron and Hole Current

The hole current is known as the conventional current is opposite to the direction of the electron movement and flows from the positive terminal of the battery to the negative terminal of the battery. The electron current and hole current occur due to two process, they are

- Drift
- Diffusion

Drift Current

The current flow that takes place due to the application of the external potential through a battery results in drifting of the electrons, thereby resulting in drift current. When an external energy is applied to the semiconductor crystal, the electrons gain energy and starts to drift across the crystal and tends move towards the battery terminal (positive terminal). Such currents are said to be drift current caused due to drifting of electrons.

Diffusion Current

NOTES

Diffusion current occurs due to the movement of electrons through diffusion when they move from higher concentration area to a lower concentration area of the semiconductor crystal without applying any external force or energy.

3.2.1 Band Gap

The energy levels of the nucleus and their force of attraction towards the electron shells, can be described using the bands of energy associated with nucleus and electron shells with the help of **energy band diagram.**

Energy band diagram consists of the following three types of the bands:

- Valence Band
- Conduction Band
- Forbidden Band

The diagram shown below in Figure (3.4) shows the energy band diagram associated with an atom.

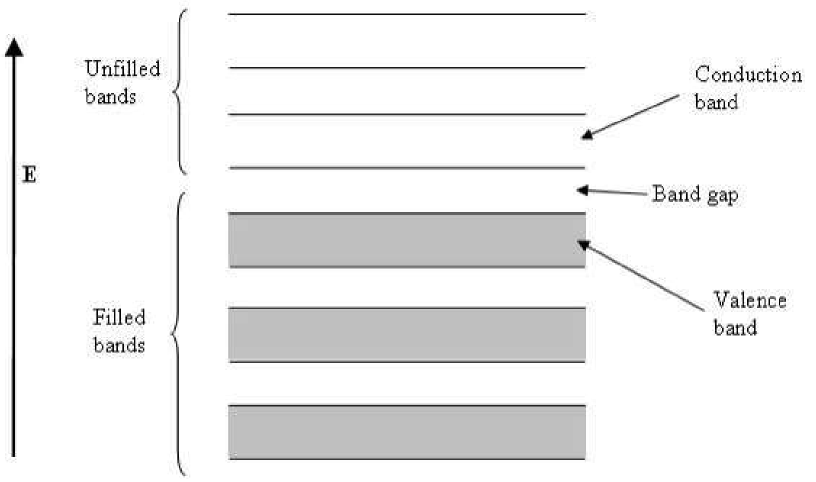


Fig. 3.4 *Energy Band Diagram*

The energy band diagram shown in Figur (3.4) has the nucleus boundary at the bottom of the band diagram. Each shell has a band of energy. The bonding energy between the shells and the nucleus decreases moving farther away from the nucleus energy level. Hence the valence energy band has the least force attraction from the nucleus. The conduction band shown in the Figure (3.4) depicts the energy band in which the electrons are free to move and contribute to the conductivity of the material. The energy gap between the valence band and the conduction band is called as **forbidden energy gap**. Lesser the forbidden energy gap, lesser is the energy required to make the electrons in the valence band to move to the conduction band, i.e., lesser energy is required to dislocate the valence electrons to make it free electrons contributing to the conduction of electricity. The median energy level between the conduction band and the valence band is known as **Fermi level.**

The energy band diagram of the conductor, insulator, and semiconductors are given in Figure (3.5). In conductors, the valence band and conduction band overlap each other. Under normal room temperature, the conductors have free electrons moving between the valence band and conduction band. No external energy is required to dislocate the electrons to make it free and conducting. In semiconductors, there exists a forbidden energy gap. An external energy equivalent to is required to be applied to dislocate electron from valence band to conduction band. In insulators, the forbidden gap between the valence band and the conduction band is larger than the other two materials. The energy required to dislocate the electrons in the valence band to conduction band is sufficient enough to damage the material permanently.

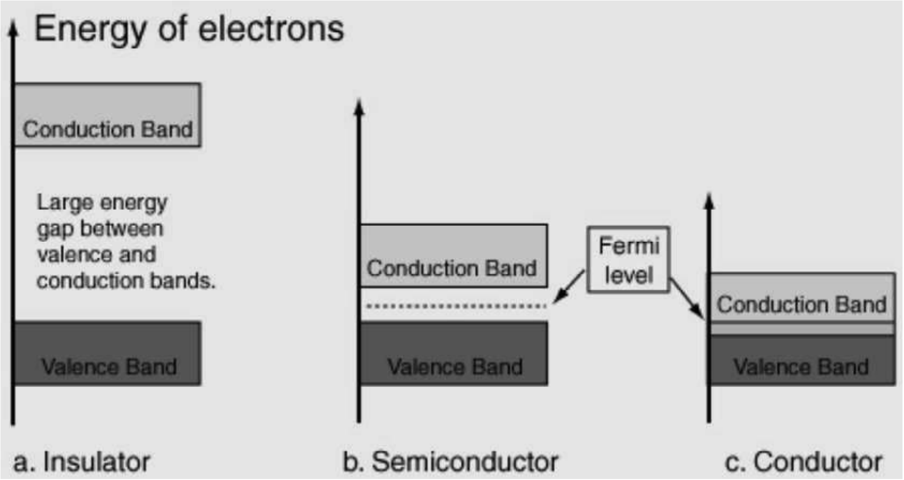


Fig. 3.5 *Energy Band Diagram of Conductor, Semiconductor, and Insulator*

3.2.2 Intrinsic Carrier Concentration and Law of Mass Action

Charge carrier density, also known as **carrier concentration**, denotes the number of charge carriers in per volume. In SI units, it is measured in m^{-3}. As with any density, in principle it can depend on position. However, usually carrier concentration is given as a single number, and represents the average carrier density over the whole or entire material.

Charge carrier densities involve equations concerning the electrical conductivity and related phenomena like the thermal conductivity.

The carrier density is usually obtained theoretically by integrating the density of states over the energy range of charge carriers in the material, for example integrating over the conduction band for electrons, integrating over the valence band for holes.

If the total number of charge carriers is known, the carrier density can be found by simply dividing by the volume. To show this mathematically, charge carrier density is a particle density, so integrating it over a volume V gives the number of charge carriers N in that volume,

$$N = \int_V n(\mathbf{r})\, dV.$$

Where $n(\mathbf{r})$ is the position-dependent charge carrier density.

If the density does not depend on position and is instead equal to a constant n_0, then this equation simplifies to,

$$N = V \cdot n_0.$$

The carrier density is important for semiconductors, where it is an important quantity for the process of chemical doping. Using band theory, the electron density, n_0 is number of electrons per unit volume in the conduction band. For holes, p_0 is the number of holes per unit volume in the valence band. To calculate this number for electrons, we consider that the total density of conduction-band electrons, n_0, is just adding up the conduction electron density across the different energies in the band, from the bottom of the band E_c to the top of the band E_{top}.

$$n_0 = \int_{E_c}^{E_{\text{top}}} N(E)\, dE$$

Because electrons are fermions, the density of conduction electrons at any particular energy, $N(E)$ is the product of the density of states, $g(E)$ or how many conducting states are possible, with the Fermi–Dirac distribution, $f(E)$ which tells us the portion of those states which will actually have electrons in them,

$$N(E) = g(E)\, f(E)$$

In order to simplify the calculation, instead of treating the electrons as fermions, according to the Fermi–Dirac distribution, we rather consider them as a classical non-interacting gas, which is given by the Maxwell–Boltzmann distribution.

A similar expression can be derived for holes. The carrier concentration can be calculated by treating electrons moving back and forth across the bandgap just like the equilibrium of a reversible reaction from chemistry, leading to an electronic **mass action law**. The mass action law defines a quantity $\boldsymbol{n_i}$ called the **intrinsic carrier concentration**, which for undoped materials is given by:

$$\boldsymbol{n_i = n_0 = p_0}$$

The following Table (3.1) lists a few values of the **intrinsic carrier concentration** for intrinsic semiconductors.

Table 3.1 *Some Values the of Intrinsic Carrier Concentration*

Material	**Carrier Density (1/cm^3) at 300K**
Silicon	9.65×10^9
Germanium	2.33×10^{13}
Gallium Arsenide	2.1×10^6

These carrier concentrations will change if these materials are doped. For example, doping pure silicon with a small amount of phosphorus will increase the carrier density of electrons, n. Then, since $n > p$, the doped silicon will be a n-type extrinsic semiconductor. Doping pure silicon with a small amount of boron will increase the carrier density of holes, so then $p > n$, and it will be a p-type extrinsic semiconductor.

3.3 SEMICONDUCTOR CONDUCTIVITY AND IMPURITY STATES

NOTES

A semiconductor material has an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator, such as glass. Its resistivity falls as its temperature rises; metals behave in the opposite way. Its **conducting properties** may be altered in useful ways by introducing **impurities** 'Doping' into the crystal structure. When two differently doped regions exist in the same crystal, a semiconductor junction is created. The behaviour of charge carriers, which include electrons, ions, and electron holes, at these junctions is the basis of diodes, transistors, and most modern electronics. Some examples of semiconductors are silicon, germanium, gallium arsenide, and elements near the so-called 'Metalloid Staircase' on the periodic table. After silicon, gallium arsenide is the second-most common semiconductor and is used in laser diodes, solar cells, microwave-frequency integrated circuits, and others. Silicon is a critical element for fabricating most electronic circuits.

Variable Electrical Conductivity

Semiconductors in their natural state are poor conductors because a current requires the flow of electrons, and semiconductors have their valence bands filled, preventing the entire flow of new electrons. Several developed techniques allow semiconducting materials to behave like conducting materials, such as doping or gating. These modifications have two outcomes: *n*-type and *p*-type. These refer to the excess or shortage of electrons, respectively. A balanced number of electrons would cause a current to flow throughout the material.

High Thermal Conductivity

Semiconductors with high thermal conductivity can be used for heat dissipation and improving thermal management of electronics.

Energy Bands and Electrical Conduction

In insulators and semiconductors, the Fermi level is inside a band gap; however, in semiconductors the bands are near enough to the Fermi level to be thermally populated with electrons or holes.

Semiconductors are defined by their unique electric conductive behaviour, somewhere between that of a conductor and an insulator. The differences between these materials can be understood in terms of the quantum states for electrons, each of which may contain zero or one electron, by the Pauli exclusion principle. These states are associated with the electronic band structure of the material. Electrical conductivity arises due to the presence of electrons in states that are delocalized extending through the material, however in order to transport electrons a state must be partially filled, containing an electron only part of the time. If the state is always occupied with an electron, then it is inert, blocking the passage of other electrons through that state. The energies of these quantum states are critical since a state is partially filled only if its energy is near the Fermi level, as per the Fermi–Dirac statistics.

NOTES

High conductivity in material comes from it having many partially filled states and much state delocalization. Metals are good electrical conductors and have many partially filled states with energies near their Fermi level. On the contrary, the insulators have few partially filled states, hence their Fermi levels sit or position within band gaps with few energy states to occupy. Significantly, an insulator can be made to conduct by increasing its temperature, heating provides energy to promote some electrons across the bandgap, inducing partially filled states in both the band of states beneath the band gap, the valence band, and the band of states above the bandgap, the conduction band. An intrinsic semiconductor has a bandgap that is smaller than that of an insulator and at room temperature, significant numbers of electrons can be excited to cross the band gap.

A pure semiconductor, however, is not very useful, as it is neither a very good insulator nor a very good conductor. However, one important feature of semiconductors and some insulators, known as semi-insulators, is that their conductivity can be increased and controlled by doping with impurities and gating with electric fields. Doping and gating move either the conduction or valence band much closer to the Fermi level and greatly increase the number of partially filled states.

Some wider-bandgap semiconductor materials are sometimes referred to as semi-insulators. When undoped, these have electrical conductivity nearer to that of electrical insulators, however they can be doped making them as useful as semiconductors. Semi-insulators find niche applications in micro-electronics, such as substrates for HEMT (High Electron Mobility Transistor). An example of a common semi-insulator is gallium arsenide. Some materials, such as titanium dioxide, can even be used as insulating materials for some applications, while being treated as wide-gap semiconductors for other applications.

Doping

The conductivity of semiconductors may easily be modified by introducing **impurities** into their **crystal lattice**. The process of adding **controlled impurities** to a semiconductor is known as '**Doping**'. The amount of impurity, or dopant, added to an intrinsic (pure) semiconductor varies its level of conductivity. Doped semiconductors are referred to as extrinsic. By adding impurity to the pure semiconductors, the electrical conductivity may be varied by factors of thousands or millions.

Consider a 1 cm^3 specimen of a metal or semiconductor has the order of 10^{22} atoms. In a metal, every atom donates at least one free electron for conduction, thus 1 cm^3 of metal contains on the order of 10^{22} free electrons, whereas a 1 cm^3 sample of pure germanium at 20 °C contains about 4.2×10^{22} atoms, but only 2.5×10^{13} free electrons and 2.5×10^{13} holes. The addition of 0.001% of arsenic (an impurity) donates an extra 10^{17} free electrons in the same volume and the electrical conductivity is increased by a factor of 10,000.

The materials chosen as suitable dopants depend on the atomic properties of both the dopant and the material to be doped. In general, dopants that produce the desired controlled changes are classified as either electron acceptors or donors.

Semiconductors doped with **donor impurities** are called ***n*-type**, while those doped with **acceptor impurities** are known as ***p*-type**. The *n*-type and *p*-type designations indicate which charge carrier acts as the material's majority carrier. The opposite carrier is called the minority carrier, which exists due to thermal excitation at a much lower concentration compared to the majority carrier.

NOTES

For example, the pure semiconductor silicon has four valence electrons that bond each silicon atom to its neighbours. In silicon, the most common dopants are Group III and Group V elements. Group III elements all contain three valence electrons, causing them to function as acceptors when used to dope silicon. When an acceptor atom replaces a silicon atom in the crystal, a vacant state, an 'Electron Hole' is created, which can move around the lattice and function as a charge carrier. Group V elements have five valence electrons, which allows them to act as a donor; substitution of these atoms for silicon creates an extra free electron. Therefore, a silicon crystal doped with boron creates a *p*-type semiconductor whereas one doped with phosphorus results in an *n*-type material.

During manufacture, dopants can be diffused into the semiconductor body by contact with gaseous compounds of the desired element, or ion implantation can be used to accurately position the doped regions.

3.3.1 Thermal Ionization of Impurities

Thermal ionization, also known as surface ionization or contact ionization, is a physical process whereby the atoms are desorbed from a hot surface, and in the process are ionized.

Thermal ionization is used to make simple ion sources, for mass spectrometry and for generating ion beams. Thermal ionization is extensively used in determining atomic weights, in addition to being used in many geological/nuclear applications.

Electrons are fermions with spin 1/2 → their energy distribution follows Fermi Dirac statistics:

$$f(E) = \frac{1}{\exp\left[\left(E - E_f\right)/k_B T\right] + 1}$$

Distribution function $f(E)$ describes the probability of a state with energy E to be occupied.

Fermi energy E_f is determined by the condition that for the total number of electrons N in the system we have $\int f(E)\, D(E)\, dE = N$ with the density of electronic states $D(E)$.

3.3.2 Extrinsic Semiconductors

An **extrinsic semiconductor** is one that has been doped, i.e., during manufacture of the semiconductor crystal a trace element or chemical called a doping agent has been incorporated chemically into the crystal, for the purpose of giving it different electrical properties than the pure semiconductor crystal, which is called an intrinsic semiconductor. In an extrinsic semiconductor, these foreign dopant atoms in the crystal lattice provide the charge carriers which carry electric current through the crystal. The doping agents used are of two types, resulting in two types of extrinsic semiconductor. An electron donor dopant is an atom which, when incorporated in the crystal, releases a mobile conduction electron into the crystal lattice. An extrinsic semiconductor which has been doped with electron donor atoms is called an *n*-type semiconductor, because the majority of charge carriers in the crystal are negative electrons. An electron acceptor dopant is an atom which accepts an electron from the lattice, creating a vacancy where an electron should be called a hole which can move through the crystal like a positively charged particle. An extrinsic semiconductor which has been doped with electron acceptor atoms is called a *p*-type semiconductor, because the majority of charge carriers in the crystal are positive holes.

Doping is the key to the extraordinarily wide range of electrical behaviour that semiconductors can exhibit, and extrinsic semiconductors are specifically used to make semiconductor electronic devices, such as diodes, transistors, integrated circuits, semiconductor lasers, LEDs (Light Emitting Diodes), and photovoltaic cells. Sophisticated semiconductor fabrication processes like photolithography can implant different dopant elements in different regions of the same semiconductor crystal wafer, creating semiconductor devices on the wafer's surface. For example, a common type of transistor, the *n-p-n* bipolar transistor, consists of an extrinsic semiconductor crystal with two regions of *n*-type semiconductor, separated by a region of *p*-type semiconductor with metal contacts attached to each part.

Intrinsic semiconductors are the purest form of semiconductors. Their conductivity of electricity is limited. They have an equal number of electrons and holes. To make semiconductors practically relevant with better conduction of current, it is important to enhance the conduction capability of semiconductors. One such technique to enhance the conductivity includes the process of **doping**. Doping is a process of adding impurities to the intrinsic semiconductors, such that the conductivity of the semiconductors is improved. The impurity that is added to the semiconductor is called as a dopant. The doped semiconductors are called as extrinsic semiconductors. The type of impurities added may enhance the number of electrons or they may enhance the number of holes. Hence, depending on the type of impurities, the extrinsic semiconductors can be classified as,

- *n*-Type Semiconductors
- *p*-Type Semiconductors.

When an intrinsic semiconductor is added with an impurity with pentavalent atoms, *n*-type semiconductors are formed. When an intrinsic semiconductor is added with a trivalent impurity atom, *p*-type semiconductors are formed. Pentavalent impurity atoms are also known as donor atoms and trivalent atoms are known as acceptor atoms. Atoms that donate atoms to the host atoms are called donor atoms and the atoms that accept an electron from the host atoms are called acceptor atoms.

n-Type Semiconductor

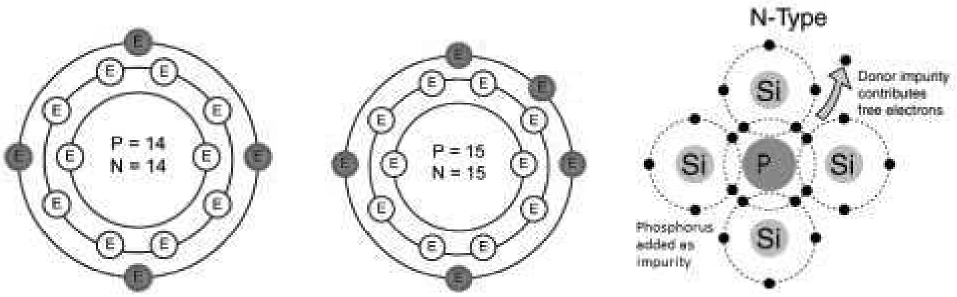


Fig. 3.6 *n-Type Semiconductor*

When a pentavalent impurity atom from Group V of the periodic table, such as Phosphorus (P) or Arsenic (As) is added to the intrinsic silicon atom, *n*-type semiconductors are formed.

When the *n*-type impurity atom (donor atoms) is added with the intrinsic silicon atom, the four valence electrons out of five valence electrons in the impurity atom forms a covalent bond with the four silicon atoms as shown in Figure (3.6). The remaining one valence electrons from the impurity atoms remain as free electron inside the mixture crystal. Similarly, when 1 of phosphorus can generate free electrons of the order of number of free electrons. Number of free electrons required are controlled by the amount of pentavalent impurity added to the intrinsic silicon atom.

The Conductivity of *n*-Type Semiconductors

The mobility of electrons is approximately three times that of the mobility of holes. When more free electrons are added to the intrinsic semiconductor, the average energy level of the semiconductor increases. This makes the electrons move easier from the valence band to the conduction band even with an application of the small amount of an external potential. In addition, the Fermi level, which marks the energy level of electrons is closer to the conduction band as shown in Figure (3.7). In *n*-type semiconductors since the electrons are more than the number of holes, electrons are known as majority carriers and the holes are known as minority carriers. The current constituted by majority carriers (electrons) are predominant and the current constituted by minority carriers (holes) are negligent.

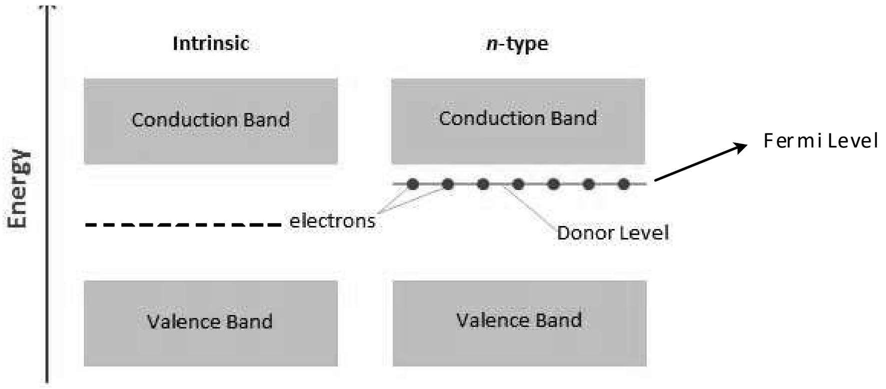


Fig. 3.7 *n-Type Semiconductor Band Diagram*

p-Type Semiconductors

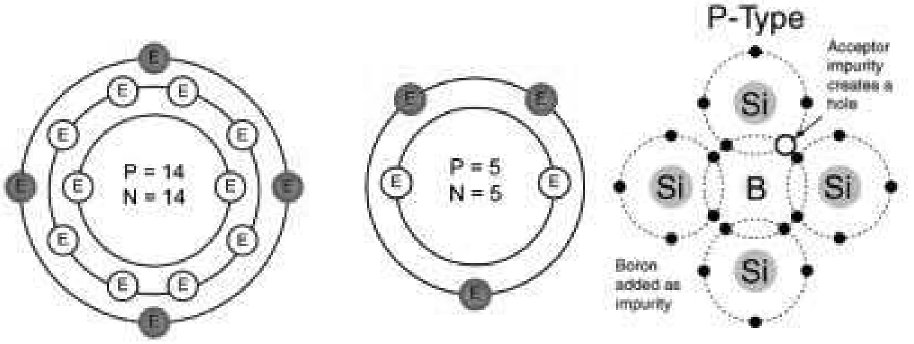


Fig. 3.8 *p-Type Semiconductor*

When a trivalent impurity atom from Group III of the periodic table, such as Boron (B) or Gallium (Ga) is added to the intrinsic silicon atom, then *p*-type semiconductors are formed.

When the p-type impurity atom (acceptor atoms) is added with the intrinsic silicon atom, the three valence electrons of the acceptor atoms form a covalent bond with the three silicon atoms leaving behind one silicon atom form an electro*n*-hole pair as shown in Figure (3.8). The one hole generated due to nonavailability of an electron to fill from the impurity atom forms one electron-hole pair. Similarly, when 1 of Boron can generate electron-hole pairs of the order of number of holes. Number of holes required are controlled by the amount of trivalent impurity added to the intrinsic silicon atom.

The Conductivity of *p*-Type Semiconductors

When more holes are added to the intrinsic semiconductor, the average energy level of the semiconductor decreases. Hence, a larger magnitude of external energy needs to be applied to make the electrons conduct. In other words, to make the electrons move from the valence band to conduction band. However, it is easier to make the electrons conduct in the reverse direction by applying a negative potential. The Fermi level, which marks the energy level of electrons is closer to the valence band as shown in Figure (3.9). In *p*-type semiconductors since the holes are more than the number of electrons, holes are known as majority carriers in *p*-type semiconductors and the electrons are known as minority carriers. The current constituted by majority carriers (holes) are predominant and the current constituted by minority carriers (electrons) are negligent.

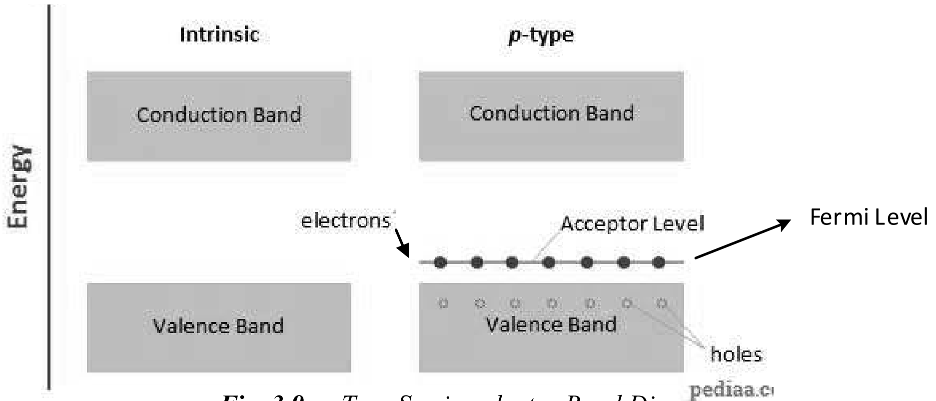


Fig. 3.9 *p-Type Semiconductor Band Diagram*

p-n Junction Diode

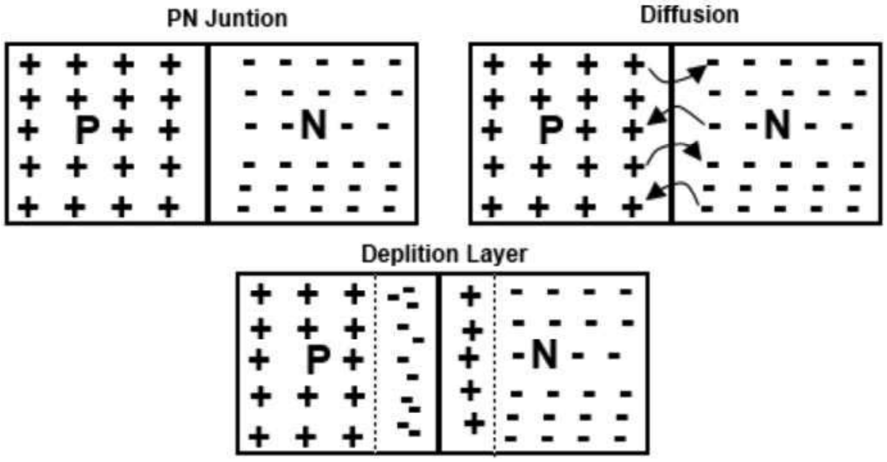


Fig. 3.10 p-n Diffusion

When a *p*-type semiconductor and *n*-type semiconductor are joined together, then diffusion takes place. Since the *p*-type material is highly concentrated with holes leading to an overall high positive charge material and *n*-type a negatively charged material due to the concentration of electrons, when joined together, they together generate a high potential on the *p*-type side and now potential on the *n*-type side. This leads to the process of diffusion making the electrons to move towards the *p*-side. As electrons move towards the *p*-type crossing the junction, they leave behind holes. The electrons spend enough energy to cross over the junction after which they occupy a hole position nearer to the junction. Thus, holes are formed on the *n*-type side of the junction and electrons on the *p*-type junction. Any electron that wants to cross over the junction further must have enough energy to overcome the holes and the junction together. Thus, creates a region of depletion of charges with positive charges on *n*-type and negative charges on *p*-type. The buildup of the depletion region continues until the electrons cannot diffuse further. Once the diffusion stops, the potential difference created by the process of electron diffusion results in approximately 0.7 volts for silicon semiconductors and 0.3 volts for germanium semiconductors. This potential difference created by the process of diffusion is also known as barrier potential. The electrons that require moving to the *p*-type material further must overcome the barrier potential of 0.7V for silicon material. The electrons alone do not possess such amount of energy to cross the barrier potential and hence on the application of an external voltage equal to the barrier potential is required to make the electrons move to the other side of the *p-n* junction.

The barrier potential depends on various factors as follows:

- Type of Semiconductor
- Type of Impurity
- External Atmospheric Temperature
- The Concentration of Intrinsic Semiconductor

3.3.3 Energy Bands in Si (Silicon) and Ge (Germanium)

The band gap or energy band is an energy range in a solid where there is no presence of any electron states. It is the difference in the energy between valence band to the conduction band measured in electron volts in conductors and insulators. According to Bohr's theory, every shell of an atom contains a discrete amount of energy at different levels. Energy band theory explains the interaction of electrons between the outermost shell and the innermost shell. Based on the energy band theory, there are following three different energy bands:

1. Valence Band
2. Forbidden Energy Gap
3. Conduction Band

Germanium and Silicon are the most preferable material whose electrical properties lie in between semiconductors and insulators. The energy band diagram of semiconductor shows that the conduction band is empty and the valence band is completely filled but the forbidden gap between the two bands is very small that is about 1eV. For Germanium, the forbidden gap is 0.72eV and for Silicon, it is 1.1eV. Therefore, the energy band gaps of Silicon and Germanium are 1.1 eV and 0.7 eV. Thus, semiconductor requires small conductivity.

Silicon is a semiconductor material whose number of free electrons is less than conductor but more than that of an insulator. For having this unique characteristic, Silicon has a broad application in the field of electronics. There are two kinds of energy band in Silicon which are conduction band and valence band. A series of energy levels having valence electrons forms the valance band in the solid. At absolute 0^{o}K temperature the energy levels of the valence band are filled with electrons. This band contains maximum amount of energy when the electrons are in valence band, no current flows due to such electrons.

3.3.4 Rectification

A rectifier is an electrical device that converts the Alternating Current (AC), which periodically reverses its direction, to the Direct Current (DC) which flows in only one direction. The reverse operation is performed by means of the inverter. The process of conversion of current is known as '**Rectification**' since it 'Straightens' the direction of current.

Rectification is therefore defined as the process of turning an Alternating Current or AC waveform into a Direct Current or DC waveform, i.e., creating a new signal that has only a single polarity. We know that a DC voltage or current does not have to exhibit a constant value, hence the polarity of the signal never changes.

Half-Wave Rectification

In half-wave rectification of a single-phase supply, either the positive or negative half of the Alternating Current (AC) wave is passed, while the other half is blocked. Because only one half of the input waveform reaches the output, mean voltage is lower. Half-wave rectification requires a single diode in a single-phase supply or three in a three-phase supply. Rectifiers yield a unidirectional but pulsating direct current; half-wave rectifiers produce far more ripple than full-wave rectifiers, and much more filtering is needed to eliminate harmonics of the Alternating Current (AC) frequency from the output. The following Figure (3.11) illustrates the half-wave rectifier.

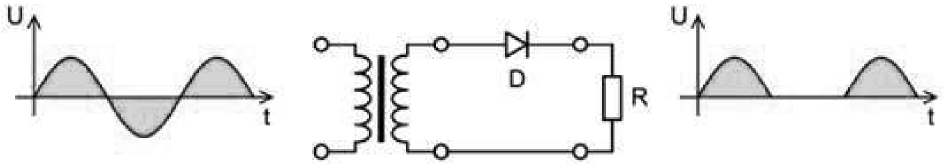


Fig. 3.11 Half-Wave Rectifier

Full Wave Rectification

A full wave rectifier converts the whole of the input waveform to one of constant polarity (positive or negative) at its output. Mathematically, this corresponds to the absolute value function. Full wave rectification converts both polarities of the input waveform to pulsating DC (Direct Current) and yields a higher average output voltage. Two diodes and a center tapped transformer or four diodes in a bridge configuration and any Alternating Current (AC) source (including a transformer without center tap), are needed. Single semiconductor diodes, double diodes with a common cathode or common anode, and four- or six-diode bridges are manufactured as single components. The following Figure (3.12) illustrates the Graetz bridge rectifier, a full-wave rectifier using four diodes.

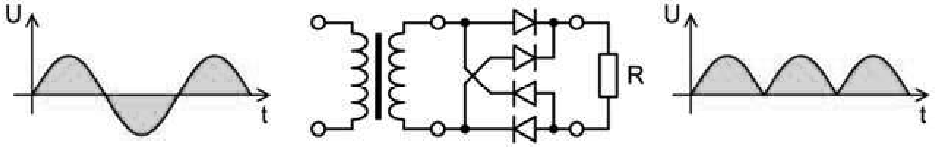


Fig. 3.12 Full Wave Rectification

3.3.5 Polarons

A polaron is a quasiparticle used in condensed matter physics to understand the interactions between electrons and atoms in a solid material. The polaron concept was proposed by Lev Landau in 1933 and Solomon Pekar in 1946 to describe an electron moving in a dielectric crystal where the atoms displace from their equilibrium positions to effectively screen the charge of an electron, known as a phonon cloud. This lowers the electron mobility and increases the electron's effective mass. The general concept of a polaron has been extended to describe other interactions between the electrons and ions in metals that result in a bound state, or a lowering of energy compared to the non-interacting system.

Experimentally, polarons are important to the understanding of a wide variety of materials. The electron mobility in semiconductors can be greatly decreased by the formation of polarons. Organic semiconductors are also sensitive to polaronic effects, which is particularly relevant in the design of organic solar cells that effectively transport charge. Polarons are also important for interpreting the optical conductivity of these types of materials.

The polaron, a fermionic quasiparticle, should not be confused with the polariton, a bosonic quasiparticle analogous to a hybridized state between a photon and an optical phonon.

Polaron Theory

The energy spectrum of an electron moving in a periodical potential of rigid crystal lattice is called the Bloch spectrum, which consists of allowed bands and forbidden bands. An electron with energy inside an allowed band moves as a free electron but has an effective mass that differs from the electron mass in vacuum. However, a crystal lattice is deformable and displacements of atoms (ions) from their equilibrium positions are described in terms of phonons. Electrons interact with these displacements, and this interaction is known as electron-phonon coupling. One of possible scenarios was proposed in the seminal 1933 paper by Lev Landau, which includes the production of a lattice defect, such as an F-center and a trapping of the electron by this defect. A different scenario was proposed by Solomon Pekar that envisions dressing the electron with lattice polarization (a cloud of virtual polar phonons). Such an electron with the accompanying deformation moves freely across the crystal, but with increased effective mass. Pekar coined for this charge carrier the term polaron.

Landau and Pekar formed the basis of polaron theory. A charge placed in a polarizable medium will be screened. Dielectric theory describes the phenomenon by the induction of a polarization around the charge carrier. The induced polarization will follow the charge carrier when it is moving through the medium. The carrier together with the induced polarization is considered as one entity, which is called a polaron.

3.3.6 Semi-Metals Mobility of Protons

A semimetal is a material with a very small overlap between the bottom of the conduction band and the top of the valence band. According to electronic band theory, solids can be classified as insulators, semiconductors, semimetals, or metals. In insulators and semiconductors, the filled valence band is separated from an empty conduction band by a band gap. For insulators, the magnitude of the band gap is larger (for example, > 4 eV) than that of a semiconductor (for example, < 4 eV). Because of the slight overlap between the conduction and valence bands, semimetals have no band gap and a negligible density of states at the Fermi level. A metal, by contrast, has an appreciable density of states at the Fermi level because the conduction band is partially filled.

Temperature Dependency

The insulating/semiconducting states differ from the semimetallic/metallic states in the temperature dependency of their electrical conductivity. With a metal, the conductivity decreases with increases in temperature (due to increasing interaction of electrons with phonons (lattice vibrations)). With an insulator or semiconductor (which have two types of charge carriers – holes and electrons), both the carrier mobilities and carrier concentrations will contribute to the conductivity, and these have different temperature dependencies. Ultimately, it is observed that the conductivity of insulators and semiconductors increase with initial increases in temperature above absolute zero (as more electrons are shifted to the conduction band), before decreasing with intermediate temperatures and then, once again, increasing with still higher temperatures. The semimetallic state is similar to the metallic state but in semimetals both holes and electrons contribute to electrical conduction. With some semimetals, like arsenic and antimony, there is a temperature-independent carrier density below room temperature (as in metals) while, in bismuth, this is true at very low temperatures but at higher temperatures the carrier density increases with temperature giving rise to a semimetal-semiconductor transition. A semimetal also differs from an insulator or semiconductor in that a semimetal's conductivity is always non-zero, whereas a semiconductor has zero conductivity at zero temperature and insulators have zero conductivity even at ambient temperatures (due to a wider band gap).

To classify semiconductors and semimetals, the energies of their filled and empty bands must be plotted against the crystal momentum of conduction electrons. According to the Bloch theorem the conduction of electrons depends on the periodicity of the crystal lattice in different directions.

In a semimetal, the bottom of the conduction band is typically situated in a different part of momentum space (at a different **k**-vector) than the top of the valence band. One could say that a semimetal is a semiconductor with a negative indirect bandgap, although they are seldom described in those terms.

3.3.7 Point Defects

Point defects are defects that occur only at or around a single lattice point. They are not extended in space in any dimension. Strict limits for how small a point defect is, are generally not defined explicitly. However, these defects typically involve at most a few extra or missing atoms. Larger defects in an ordered structure are usually considered dislocation loops. For historical reasons, many point defects, especially in ionic crystals, are called centers, for example a vacancy in many ionic solids is called a luminescence center, a color center, or F-center. These dislocations permit ionic transport through crystals leading to electrochemical reactions. These are frequently specified using Kröger–Vink notation.

Vacancy defects are lattice sites which would be occupied in a perfect crystal but are vacant. If a neighbouring atom moves to occupy the vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. The stability of the surrounding crystal structure guarantees that the neighbouring atoms will not simply collapse around the vacancy. In some materials, neighbouring atoms actually move away from a vacancy, because they experience attraction from atoms in the surroundings. A vacancy (or pair of vacancies in an ionic solid) is sometimes called a Schottky defect.

Interstitial defects are atoms that occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms (mostly impurities) in some crystals can occupy interstices without high energy, such as hydrogen in palladium.

3.3.8 Schottky and Frenkel Defects

A **Schottky defect** is an excitation of the site occupations in a crystal lattice leading to point defects named after Walter H. Schottky. In elemental crystals it refers to simple lattice vacancies, also called valency defects. In ionic crystals, this defect forms when oppositely charged ions leave their lattice sites and become incorporated for instance at the surface, creating oppositely charged vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid.

Schottky defects consist of unoccupied anion and cation sites in a stoichiometric ratio. For a simple ionic crystal of type A^-B^+, a Schottky defect consists of a single anion vacancy (A) and a single cation vacancy (B). For a more general crystal with formula A_xB_y, a Schottky cluster is formed of x vacancies of A and y vacancies of B, thus the overall stoichiometry and charge neutrality are conserved. Conceptually, a Schottky defect is generated if the crystal is expanded by one unit cell, whose a priori empty sites are filled by atoms that diffused out of the interior, thus creating vacancies in the crystal.

Schottky defects are observed most frequently when there is a small difference in size between the cations and anions that make up a material.

A **Frenkel defect** is a type of point defect in crystalline solids, named after its discoverer Yakov Frenkel. The defect forms when an atom or smaller ion (usually cation) leaves its place in the lattice, creating a vacancy and becomes an interstitial by lodging in a nearby location. In elemental systems, they are primarily generated during particle irradiation, as their formation enthalpy is typically much higher than for other point defects, such as vacancies, and thus their equilibrium concentration according to the Boltzmann distribution is below the detection limit. In ionic crystals, which usually possess low coordination number or a considerable disparity in the sizes of the ions, this defect can be generated also spontaneously, where the smaller ion (usually the cation) is dislocated.

Even though Frenkel defects involve only the migration of the ions within the crystal, the total volume and thus the density is not necessarily changed: in particular for close-packed systems, the lattice expansion due to the strains induced by the interstitial atom typically dominates over the lattice contraction due to the vacancy, leading to a decrease of density.

Frenkel defects are exhibited in ionic solids with a large size difference between the anion and cation with the cation usually smaller due to an increased effective nuclear charge.

3.3.9 Crystal Growth Whiskers

A crystal is a solid material whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions. Crystal growth is a major stage of a crystallization process, and consists of the addition of new atoms, ions, or polymer strings into the characteristic arrangement of the crystalline lattice. The growth typically follows an initial stage of either homogeneous or heterogeneous (surface catalyzed) nucleation, unless a ‘Seed’ crystal, purposely added to start the growth, was already present.

The action of crystal growth yields a crystalline solid whose atoms or molecules are close packed, with fixed positions in space relative to each other. The crystalline state of matter is characterized by a distinct structural rigidity and very high resistance to deformation (i.e., changes of shape and/or volume). Most crystalline solids have high values both of Young's modulus and of the shear modulus of elasticity. This contrasts with most liquids or fluids, which have a low shear modulus, and typically exhibit the capacity for macroscopic viscous flow.

There are two stages in the crystallization process, namely nucleation and growth. In the first nucleation stage, a small nucleus containing the newly forming crystal is created. Nucleation occurs relatively slowly as the initial crystal components must impinge on each other in the correct orientation and placement for them to adhere and form the crystal. After successful formation of a stable nucleus, a growth stage ensues in which free particles (atoms or molecules) adsorb onto the nucleus and propagate its crystalline structure outwards from the nucleating site. This process is significantly faster than nucleation. The reason for such rapid growth is that real crystals contain dislocations and other defects, which act as a catalyst for the addition of particles to the existing crystalline structure. By contrast, perfect crystals (lacking defects) would grow exceedingly slowly. On the other hand, impurities can act as crystal growth inhibitors and can also modify crystal habit.

It is generally believed that the mechanical and other properties of the crystal are also pertinent to the subject matter, and that crystal morphology provides the missing link between growth kinetics and physical properties. The necessary thermodynamic apparatus was provided by Josiah Willard Gibbs' study of heterogeneous equilibrium. He provided a clear definition of surface energy, by which the concept of surface tension is made applicable to solids as well as liquids. He also appreciated that an anisotropic surface free energy implied a non-spherical equilibrium shape, which should be thermodynamically defined as the shape which minimizes the total surface free energy.

It may be instructional to note that **whisker growth** provides the link between the mechanical phenomenon of high strength in **whiskers** and the various growth mechanisms which are responsible for their fibrous morphologies. Prior to the discovery of carbon nanotubes, single-crystal whiskers had the highest tensile strength of any materials known. Some mechanisms produce defect-free whiskers, while others may have single screw dislocations along the main axis of growth — producing **high strength whiskers**.

The mechanism behind whisker growth is not well understood but seems to be encouraged by compressive mechanical stresses including mechanically induced stresses, stresses induced by diffusion of different elements, and thermally induced stresses. Metal whiskers differ from metallic dendrites in several respects. Dendrites are fern-shaped like the branches of a tree and grow across the surface of the metal. In contrast, whiskers are fibrous and project at a right angle to the surface of growth, or substrate.

3.3.10 The Kondo Effect

In physics, the Kondo effect describes the scattering of conduction electrons in a metal due to magnetic impurities, resulting in a characteristic change in electrical

NOTES

resistivity with temperature. The effect was first described by Jun Kondo, who applied third-order perturbation theory to the problem to account for ***s-d*** electron scattering. Kondo's model predicted that the scattering rate of conduction electrons off the magnetic impurity should diverge as the temperature approaches 0 K. Experiments in the 1960s by Myriam Sarachik at Bell Laboratories provided the first data that confirmed the Kondo effect. Extended to a lattice of magnetic impurities, the Kondo effect likely explains the formation of heavy fermions and Kondo insulators in intermetallic compounds, especially those involving rare earth elements, such as cerium, praseodymium, and ytterbium, and actinide elements, such as uranium. The Kondo effect has also been observed in quantum dot systems.

Theory

The dependence of the resistivity ρ on temperature T, including the Kondo effect, is written as,

$$\rho(T) = \rho_0 + aT^2 + c_m \ln \frac{\mu}{T} + bT^5$$

Where ρ_0 is the residual resistivity, the term aT^2 shows the contribution from the Fermi liquid properties, and the term bT^5 is from the lattice vibrations: a, b, c_m and μ are constants independent of temperature. Jun Kondo derived the third term with logarithmic dependence on temperature.

Kondo's model was derived using perturbation theory, but later methods used non-perturbative techniques to refine his result. These improvements produced a finite resistivity but retained the feature of a resistance minimum at a non-zero temperature. One defines the Kondo temperature as the energy scale limiting the validity of the Kondo results. The Anderson impurity model and accompanying Wilsonian renormalization theory were an important contribution to understanding the underlying physics of the problem. Based on the Schrieffer-Wolff transformation, it was shown that the Kondo model lies in the strong coupling regime of the Anderson impurity model. The Schrieffer-Wolff transformation projects out the high energy charge excitations in the Anderson impurity model, obtaining the Kondo model as an effective Hamiltonian.

The Kondo effect can be considered as an example of asymptotic freedom, i.e., a situation where the coupling becomes non-perturbatively strong at low temperatures and low energies. In the Kondo problem, the coupling refers to the interaction between the localized magnetic impurities and the itinerant electrons.

3.3.11 Order-Disorder Transformations

In physics, the terms order and disorder designate the presence or absence of some symmetry or correlation in a many particles system. In condensed matter physics, systems typically are ordered at low temperatures; upon heating, they undergo one or several phase transitions into less ordered states. Examples for such an order-disorder transition are:

- Melting of Ice: Solid-Liquid Transition, Loss of Crystalline Order.
- Demagnetization of Iron by Heating Above the Curie Temperature: Ferromagnetic-Paramagnetic Transition, Loss of Magnetic Order.

The degree of freedom that is ordered or disordered can be Translational (Crystalline Ordering), Rotational (Ferroelectric Ordering), or a Spin State (Magnetic Ordering).

The order can consist either in a full crystalline space group symmetry, or in a correlation. Depending on how the correlations decay with distance, long range order or short range order are specified.

If a disordered state is not in thermodynamic equilibrium, the quenched disorder must be specified. For instance, a glass is obtained by quenching (supercooling) a liquid. By extension, other quenched states are called spin glass, orientational glass. In some contexts, the opposite of quenched disorder is annealed disorder.

Check Your Progress

1. What are semiconductors?
2. Define intrinsic semiconductors giving an example.
3. How conduction occurs in intrinsic semiconductors?
4. Define the term band gap.
5. How carrier concentration can be calculated?
6. What is doping?
7. Define the terms polaron and phonon clouds.

3.4 ANSWERS TO ‘CHECK YOUR PROGRESS’

1. Semiconductors, sometimes referred to as Integrated Circuits (ICs) or microchips, are made from pure elements, typically silicon or germanium, or compounds, such as gallium arsenide. In a process called doping, small amounts of impurities are added to these pure elements, causing large changes in the conductivity of the material. Semiconductors are, therefore, termed as the ‘Brains of Modern Electronics’.
2. Semiconductors that exists in pure form without any impurities added are called as intrinsic semiconductors. Consider the semiconductor Silicon, Si with atomic number 14. It has 14 number of protons and 14 number of electrons. The first shell occupies 2 electrons, the second shell occupies 8 electrons and the third shell which could accommodate 18 electrons has only 4 valence electrons. These atoms exist in the crystalline structure with bonding.
3. When an external energy is supplied to the intrinsic semiconductor crystal, the electrons absorb the energy supplied and gain enough energy to break the covalent bond and are set free to move as free electrons in the crystal. Such free electrons move randomly inside the crystal until they lose their energy and finds a bonding pair of an electron with some other atom. When the electron leaves a covalent bond due to external energy, they leave behind a vacant space known as holes. Electrons are negatively charged and the vacant hole spaces wanting for electrons to occupy the space are considered

as positively charged. When the free electrons leave the covalent bonding due to external energy, they form an electron-hole pair.

4. Each shell has a band of energy. The bonding energy between the shells and the nucleus decreases moving farther away from the nucleus energy level. Hence the valence energy band has the least force attraction from the nucleus. The energy gap between the valence band and the conduction band is called as forbidden energy gap. Lesser the forbidden energy gap, lesser is the energy required to make the electrons in the valence band to move to the conduction band, i.e., lesser energy is required to dislocate the valence electrons to make it free electrons contributing to the conduction of electricity.
5. The carrier concentration can be calculated by treating electrons moving back and forth across the bandgap just like the equilibrium of a reversible reaction from chemistry, leading to an electronic mass action law. The mass action law defines a quantity n_i called the intrinsic carrier concentration, which for undoped materials is given by:

   $$n_i = n_0 = p_0$$
6. The conductivity of semiconductors may easily be modified by introducing impurities into their crystal lattice. The process of adding controlled impurities to a semiconductor is known as 'Doping'. The amount of impurity, or dopant, added to an intrinsic (pure) semiconductor varies its level of conductivity. Doped semiconductors are referred to as extrinsic.
7. A polaron is a quasiparticle used in condensed matter physics to understand the interactions between electrons and atoms in a solid material. The polaron concept was proposed by Lev Landau in 1933 and Solomon Pekar in 1946 to describe an electron moving in a dielectric crystal where the atoms displace from their equilibrium positions to effectively screen the charge of an electron, known as a phonon cloud. This lowers the electron mobility and increases the electron's effective mass.

3.5 SUMMARY

- Semiconductors, sometimes referred to as Integrated Circuits (ICs) or microchips, are made from pure elements, typically silicon or germanium, or compounds, such as gallium arsenide. In a process called doping, small amounts of impurities are added to these pure elements, causing large changes in the conductivity of the material.
- Semiconductors are an essential component of electronic devices, enabling advances in communications, computing, healthcare, military systems, transportation, clean energy, and countless other applications.
- Semiconductors are substances with specific properties. The ICs (Integrated Circuits) and electronic discrete components, such as diodes and transistors are made of semiconductors. Common elemental semiconductors are silicon and germanium. Silicon is well-known of these as the silicon forms most of ICs.

- Semiconductors are, therefore, termed as the ‘Brains of Modern Electronics’.
- Semiconductors that exists in pure form without any impurities added are called as intrinsic semiconductors.
- Consider the semiconductor Silicon, Si with atomic number 14. It has 14 number of protons and 14 number of electrons. The first shell occupies 2 electrons, the second shell occupies 8 electrons and the third shell which could accommodate 18 electrons has only 4 valence electrons.
- Similarly, germanium with an atomic number of 32 has 4 shells with an outermost shell consisting of 4 valence electrons. These atoms exist in the crystalline structure with bonding.
- Intrinsic semiconductors behave as perfect insulators under normal room temperatures.
- Silicon and germanium that consists of 4 valence electrons in their outermost shells are also known as tetravalent atoms. Similarly, atoms with three valence electrons are known as trivalent atoms and atoms with five valence electrons are known as pentavalent atoms.
- When an external energy is supplied to the intrinsic semiconductor crystal, the electrons absorb the energy supplied and gain enough energy to break the covalent bond and are set free to move as free electrons in the crystal. Such free electrons move randomly inside the crystal until they lose their energy and finds a bonding pair of an electron with some other atom. When the electron leaves a covalent bond due to external energy, they leave behind a vacant space known as holes.
- Electrons are negatively charged and the vacant hole spaces wanting for electrons to occupy the space are considered as positively charged. When the free electrons leave the covalent bonding due to external energy, they form an electron-hole pair.
- Current constituted by electrons inside the semiconductor crystal are called an electron current.
- Since electrons are negatively charged, when a potential is applied across the semiconductor crystal, the electrons are attracted towards the positive terminal of the battery.
- Current constituted by holes inside a semiconductor crystal are known as hole current. Though the holes (vacant spaces) do not move, consequent movement of electrons creates an illusion such that holes move, but in the opposite direction as that of the electron.
- The current flow that takes place due to the application of the external potential through a battery, results in drifting of the electrons, thereby resulting in drift current.
- When an external energy is applied to the semiconductor crystal, the electrons gain energy and starts to drift across the crystal and tends move towards the battery terminal (positive terminal). Such currents are said to be drift current caused due to drifting of electrons.

NOTES

- Diffusion current occurs due to the movement of electrons through diffusion when they move from higher concentration area to a lower concentration area of the semiconductor crystal without applying any external force or energy.
- Each shell has a band of energy. The bonding energy between the shells and the nucleus decreases moving farther away from the nucleus energy level. Hence the valence energy band has the least force attraction from the nucleus.
- The energy gap between the valence band and the conduction band is called as forbidden energy gap. Lesser the forbidden energy gap, lesser is the energy required to make the electrons in the valence band to move to the conduction band, i.e., lesser energy is required to dislocate the valence electrons to make it free electrons contributing to the conduction of electricity.
- The median energy level between the conduction band and the valence band is known as Fermi level.
- Charge carrier density, also known as carrier concentration, denotes the number of charge carriers in per volume. In SI units, it is measured in m^{-3}.
- Charge carrier densities involve equations concerning the electrical conductivity and related phenomena like the thermal conductivity.
- The carrier concentration can be calculated by treating electrons moving back and forth across the bandgap just like the equilibrium of a reversible reaction from chemistry, leading to an electronic mass action law. The mass action law defines a quantity n_i called the intrinsic carrier concentration, which for undoped materials is given by:

  $$n_i = n_0 = p_0$$
- A semiconductor material has an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator, such as glass. Its resistivity falls as its temperature rises; metals behave in the opposite way. Its conducting properties may be altered in useful ways by introducing impurities 'Doping' into the crystal structure.
- When two differently doped regions exist in the same crystal, a semiconductor junction is created. The behaviour of charge carriers, which include electrons, ions, and electron holes, at these junctions is the basis of diodes, transistors, and most modern electronics.
- Semiconductors in their natural state are poor conductors because a current requires the flow of electrons, and semiconductors have their valence bands filled, preventing the entire flow of new electrons.
- Several developed techniques allow semiconducting materials to behave like conducting materials, such as doping or gating. These modifications have two outcomes: *n*-type and *p*-type. These refer to the excess or shortage of electrons, respectively.
- Semiconductors with high thermal conductivity can be used for heat dissipation and improving thermal management of electronics.

- In insulators and semiconductors, the Fermi level is inside a band gap; however, in semiconductors the bands are near enough to the Fermi level to be thermally populated with electrons or holes.
- Semiconductors are defined by their unique electric conductive behaviour, somewhere between that of a conductor and an insulator.
- The conductivity of semiconductors may easily be modified by introducing impurities into their crystal lattice. The process of adding controlled impurities to a semiconductor is known as 'Doping'.
- The amount of impurity, or dopant, added to an intrinsic (pure) semiconductor varies its level of conductivity. Doped semiconductors are referred to as extrinsic.
- Thermal ionization, also known as surface ionization or contact ionization, is a physical process whereby the atoms are desorbed from a hot surface, and in the process are ionized.
- The band gap or energy band is an energy range in a solid where there is no presence of any electron states. It is the difference in the energy between valence band to the conduction band measured in electron volts in conductors and insulators.
- According to Bohr's theory, every shell of an atom contains a discrete amount of energy at different levels. Energy band theory explains the interaction of electrons between the outermost shell and the innermost shell.
- A polaron is a quasiparticle used in condensed matter physics to understand the interactions between electrons and atoms in a solid material.
- The polaron concept was proposed by Lev Landau in 1933 and Solomon Pekar in 1946 to describe an electron moving in a dielectric crystal where the atoms displace from their equilibrium positions to effectively screen the charge of an electron, known as a phonon cloud. This lowers the electron mobility and increases the electron's effective mass.
- A semimetal is a material with a very small overlap between the bottom of the conduction band and the top of the valence band. According to electronic band theory, solids can be classified as insulators, semiconductors, semimetals, or metals.
- In insulators and semiconductors, the filled valence band is separated from an empty conduction band by a band gap.
- Point defects are defects that occur only at or around a single lattice point. They are not extended in space in any dimension.
- Interstitial defects are atoms that occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms (mostly impurities) in some crystals can occupy interstices without high energy, such as hydrogen in palladium.
- A Schottky defect is an excitation of the site occupations in a crystal lattice leading to point defects named after Walter H. Schottky. In elemental crystals it refers to simple lattice vacancies, also called valency defects.

- In ionic crystals, this defect forms when oppositely charged ions leave their lattice sites and become incorporated for instance at the surface, creating oppositely charged vacancies. These vacancies are formed in stoichiometric units basically to maintain an overall neutral charge in the ionic solid.
- A Frenkel defect is a type of point defect in crystalline solids, named after its discoverer Yakov Frenkel. The defect forms when an atom or smaller ion (usually cation) leaves its place in the lattice, creating a vacancy and becomes an interstitial by lodging in a nearby location.
- The crystal whisker growth provides the link between the mechanical phenomenon of high strength in whiskers and the various growth mechanisms which are responsible for their fibrous morphologies.
- In physics, the Kondo effect describes the scattering of conduction electrons in a metal due to magnetic impurities, resulting in a characteristic change in electrical resistivity with temperature. The effect was first described by Jun Kondo, who applied third-order perturbation theory to the problem to account for ***s-d*** electron scattering.

3.6 KEY TERMS

- **Semiconductors:** Semiconductors, sometimes referred to as Integrated Circuits (ICs) or microchips, are made from pure elements, typically silicon or germanium, or compounds, such as gallium arsenide. In a process called doping, small amounts of impurities are added to these pure elements, causing large changes in the conductivity of the material. Semiconductors are, therefore, termed as the 'Brains of Modern Electronics'.
- **Intrinsic semiconductors:** Semiconductors that exists in pure form without any impurities added are called as intrinsic semiconductors.
- **Electron current:** Current constituted by electrons inside the semiconductor crystal are called an electron current.
- **Hole current:** Current constituted by holes inside a semiconductor crystal are known as hole current.
- **Drift current:** The current flow that takes place due to the application of the external potential through a battery, results in drifting of the electrons, thereby resulting in drift current.
- **Diffusion current:** Diffusion current occurs due to the movement of electrons through diffusion when they move from higher concentration area to a lower concentration area of the semiconductor crystal without applying any external force or energy.
- **Charge carrier density:** Charge carrier density, also known as carrier concentration, denotes the number of charge carriers in per volume. In SI units, it is measured in m^{-3}. Charge carrier densities involve equations concerning the electrical conductivity and related phenomena like the thermal conductivity.

- **Doping:** The conductivity of semiconductors may easily be modified by introducing impurities into their crystal lattice. The process of adding controlled impurities to a semiconductor is known as 'Doping'. The amount of impurity, or dopant, added to an intrinsic (pure) semiconductor varies its level of conductivity. Doped semiconductors are referred to as extrinsic.
- **Schottky defect:** A Schottky defect is an excitation of the site occupations in a crystal lattice leading to point defects named after Walter H. Schottky. In elemental crystals it refers to simple lattice vacancies, also called valency defects.
- **Frenkel defect:** A Frenkel defect is a type of point defect in crystalline solids, named after its discoverer Yakov Frenkel. The defect forms when an atom or smaller ion (usually cation) leaves its place in the lattice, creating a vacancy and becomes an interstitial by lodging in a nearby location.

3.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the term semiconductors.
2. What is intrinsic conductivity?
3. State the concept of band gap.
4. Define the law of mass action.
5. What is the importance of intrinsic carrier concentration?
6. Why is semiconductor conductivity used?
7. Define impurity states for semiconductors.
8. State about the thermal ionization of impurities.
9. Specify the energy bands for Si and Ge.
10. Define the term rectification.
11. What are polarons?
12. Define the semi-metals mobility of protons.
13. What does point defects specify?
14. State the Schottky and Frenkel defects for solids.
15. What is Konde effect?
16. Define the term crystal growth whiskers.
17. How order-disorder transformations happen?

Long-Answer Questions

1. Discuss briefly about the characteristic features of semiconductors giving appropriate examples.
2. Explain intrinsic conductivity giving appropriate examples.
3. Describe band gap with the help of energy band concept.

4. Briefly explain intrinsic carrier concentration and law of mass action with the help of examples.
5. Explain in detail the semiconductor conductivity and impurity states for *n*-type and *p*-type semiconductors.
6. Briefly explain doping with reference to semiconductor impurities.
7. What does thermal ionization of impurities state? Explain giving examples.
8. Explain in detail the extrinsic semiconductors with reference to *n*-type and *p*-type semiconductors conductivity.
9. What are energy bands? Explain the energy bands on the basis of Si and Ge properties.
10. Differentiate between half-wave rectification and full wave rectification giving examples.
11. Discuss the significance of polarons with reference to electron mobility in semiconductors.
12. Explain the semi-metals mobility of protons giving examples.
13. Why are vacancy and interstitial point defects used? Explain with the help of crystal structure.
14. Explain the Schottky defect and Frenkel defect giving appropriate examples.
15. Discuss the significant properties of crystal growth whiskers.
16. Explain the implications of Kondo effect in physics.
17. How the order-disorder transformations designate the symmetry or correlation in the particles system? Explain giving examples.

3.8 FURTHER READING

Wahab, M. A. 2005. *Solid State Physics: Structure and Properties of Materials*. New Delhi: Narosa Publishing House.

Kittel, Charles. 1971. *Introduction to Solid State Physics*. New Jersey (US): John Wiley & Sons, Inc.

Pillai, S. O. 2005. *Solid State Physics*. Noida (UP): Wiley India Private Ltd.

Saxena, B. S., P. N. Saxena and R. C. Gupta. 2019. *Fundamentals of Solid State Physics*. Meerut (UP): Pragati Prakashan.

Dekker, A. J. 2008. *Solid State Physics*. Noida (UP): Macmillan Publishers India Pvt. Ltd.

Kakani, S. L. and C. Hemarajani. 2005. *Solid State Physics*. New Delhi: Sultan Chand & Sons Pvt. Ltd.

UNIT 4 SUPERCONDUCTIVITY: OPTICAL PHENOMENON, EXPERIMENTAL AND THEORETICAL SURVEYS

Structure

4.0 INTRODUCTION

Superconductivity is defined as a set of established physical properties observed in certain materials specifically at the state when the electrical resistance vanishes, and the magnetic flux fields are expelled from the material. Any material exhibiting these properties is termed as a superconductor. Fundamentally, a superconductor has a characteristic critical temperature below which the resistance drops abruptly or suddenly to zero. An electric current through a loop of superconducting wire can persist indefinitely with no power source.

The superconductivity phenomenon was discovered by Dutch physicist Heike Kamerlingh Onnes in the year 1911. Similar to ferromagnetism and atomic spectral lines, the superconductivity is referred as a phenomenon which can only be explained by quantum mechanics. Superconductivity is typically characterized by the Meissner effect, which explains the complete ejection of magnetic field lines from the interior of the superconductor during its transitions into the superconducting state. A superconductor is of two types, namely Type-I superconductors, and Type-II superconductors. In the Type-I superconductors, the specifications include that it has a single critical field above which all superconductivity is lost and below which the magnetic field is completely expelled from the superconductor. In the Type-II superconductors, the specifications include that it has two critical fields between which it allows partial penetration of the magnetic field through the isolated points, termed as the vortices.

In superconducting materials, the characteristics of superconductivity occur when the temperature 'T' is lowered below a critical temperature 'T_C'. The value of this critical temperature varies from material to material.

The Meissner effect or Meissner–Ochsenfeld effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state when it is cooled below the critical temperature. This expulsion will repel a nearby magnet. The German physicists Walther Meissner and Robert Ochsenfeld discovered this phenomenon in 1933 by measuring the magnetic field distribution outside superconducting tin and lead samples.

As per the thermodynamics of the superconducting transition, the transition between the normal and superconducting state is thermodynamically reversible. BCS theory or Bardeen–Cooper–Schrieffer theory, named after John Bardeen, Leon Cooper, and John Robert Schrieffer, is the first microscopic theory of superconductivity since Heike Kamerlingh Onnes's 1911 discovery. The theory describes superconductivity as a microscopic effect caused due to the condensation of Cooper pairs. The theory is also used in nuclear physics to describe the pairing interaction between nucleons in an atomic nucleus.

The optical phenomena states that an F-center or Farbe center or color center is a type of crystallographic defect in which an anionic vacancy in a crystal lattice is occupied by one or more unpaired electrons. The term F-center or Farbe center is derived from the original German 'Farbzentrum', where 'Farbe' means 'Color' and 'Zentrum' means 'Center'. Electrons in such a vacancy in a crystal lattice tend to absorb light in the visible spectrum such that a material that is usually transparent becomes coloured.

An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge. An exciton can form when a material absorbs a photon of higher energy than its bandgap.

In this unit, you will study about the superconductivity, experimental survey, occurrence of superconductivity, destruction of superconductivity by magnetic fields, Meissner effect, heat capacity, energy gap, microwave gap, microwave and infrared properties, isotope effect, theoretical survey, thermodynamics of superconducting transition, London equation, coherence length, BSC theory of superconductivity, BCS ground state, persistent current, single particle tunnelling, Josephson effect and flux quantization, type H superconductors vertex state, optical phenomena in insulators, colour centres, excitons, weakly and tightly bound excitons, exciton waves, excitons in molecular crystals, solid state quantum electronics, principles of MASER action, three level Maser, Ruby Laser, semiconductor junction Laser, photoconductivity traps, space charge effect, crystal counters, luminescence, study of breakdown in solid dielectrics at low, high and intermediate temperatures, influence of annealing, temperature, effect of thickness of electrode edge effects and time log.

4.1 OBJECTIVES

After Going through this unit, you will be able to:

- Understand the concept of superconductivity
- Explain the occurrence and destruction of superconductivity by magnetic fields
- State the Meissner effect, heat capacity and energy gap
- Describe the microwave and infrared properties and isotope effect
- Discuss the thermodynamics of superconducting transition
- State the London equation and coherence length
- Know the BSC theory of superconductivity and BCS ground state
- Explain the Josephson effect and flux quantization
- Define the optical phenomena in insulators, colour centres and excitons
- Discuss the principles of MASER, three level Maser, Ruby Laser and semiconductor junction Laser
- Elaborate on the photoconductivity traps, space charge effect and crystal counters
- Understand the principle of luminescence
- Describe about the breakdown in solid dielectrics at low, high and intermediate temperatures
- Know the influence of annealing and effect of temperature

4.2 OCCURRENCE OF SUPERCONDUCTIVITY

***Superconductivity** is a phenomenon in which certain metals, alloys and ceramics conduct electricity without resistance when, it is cooled below a certain temperature called the critical temperature.*

Superconductivity is a set of physical properties observed in certain materials where electrical resistance vanishes and magnetic flux fields are expelled from the material. Any material exhibiting these properties is a superconductor. Unlike an ordinary metallic conductor, whose resistance decreases gradually as its temperature is lowered even down to near absolute zero, a superconductor has a characteristic critical temperature below which the resistance drops abruptly to zero. An electric current through a loop of superconducting wire can persist indefinitely with no power source.

The superconductivity phenomenon was discovered in 1911 by Dutch physicist Heike Kamerlingh Onnes and it is still an exciting field of discovery and technological applications. This new state was first discovered in mercury when cooled below 4.2 K. Since then, a large number and wide variety of metals, alloys, binary and ternary chemical compounds have been found to show superconductivity at various temperatures.

Like ferromagnetism and atomic spectral lines, superconductivity is a phenomenon which can only be explained by quantum mechanics. It is characterized by the Meissner effect, the complete ejection of magnetic field lines from the interior of the superconductor during its transitions into the superconducting state. The occurrence of the Meissner effect indicates that superconductivity cannot be understood simply as the idealization of perfect conductivity in classical physics.

A superconductor is of two types, namely Type-I superconductors, and Type-II superconductors. In the Type-I superconductors, the specifications include that it has a single critical field above which all superconductivity is lost and below which the magnetic field is completely expelled from the superconductor. In the Type-II superconductors, the specifications include that it has two critical fields between which it allows partial penetration of the magnetic field through the isolated points, termed as the vortices.

In 1986, it was discovered that some Cuprate-Perovskite Ceramic materials have a critical temperature above 90 K (–183 °C). Such a high transition temperature is theoretically impossible for a conventional superconductor, leading the materials to be termed high-temperature superconductors. The economically available coolant liquid nitrogen boils at 77 K, and thus the existence of superconductivity at higher temperatures than this facilitates many experiments and applications that are less practical at lower temperatures.

In the following sections fundamental terms and phenomena of superconductors, its properties, types and its applications are discussed in brief.

4.2.1 Properties of Superconductors

Few significant properties of superconductors are explained in brief in this section.

1. Electrical Resistance

The electrical resistance of a superconducting material is very low and is of the order of 10^{-7} Ωm.

2. Effect of Impurities

When impurities are added to superconducting elements, the superconducting property is not lost, but the T_c value is lowered.

3. Effect of Pressure and Stress

Certain materials are found to exhibit the superconductivity phenomena on increasing the pressure over them. For example, Cesium is found to exhibit superconductivity phenomena at $T_c = 1.5$ K on applying a pressure of 110 Kbar.

In superconductors, the increase in stress results in increase of the T_c value.

4. Isotope Effects

The critical or transition temperature T_c value of a superconductor is found to vary with its isotopic mass. This variation in T_c with its isotopic mass is called the isotopic effect.

The relation between T_c and the isotopic mass is given by,

$$T_c \propto^{al} \frac{1}{\sqrt{M}} \text{ where M is the isotopic mass.}$$

Which states that the transition temperature is inversely proportional to the square root of the isotopic mass of a single superconductor.

5. Magnetic Field Effect

If a sufficiently strong magnetic field is applied to a superconductor at any temperature below its critical temperature T_c, the superconductor is found to undergo a transition from the superconducting state to the normal state.

*This minimum magnetic field required to destroy the superconducting state is called the **critical magnetic field H_c**.*

The critical magnetic field of a superconductor is a function of temperature. The variation of H_c with temperature is given by,

$$H_c = H_o\left[1-\left(\frac{T}{T_c}\right)^2\right] \qquad ...(4.1)$$

Where H_o is the critical field at T = 0 K. The critical field decreases with increasing temperature and, becoming zero at $T = T_c$.

Figure (4.1) shows the variation of critical field H_c as a function of temperature. The material is said to be in the superconducting state within the curve and is non superconducting (i.e., normal state) in the region outside the curve.

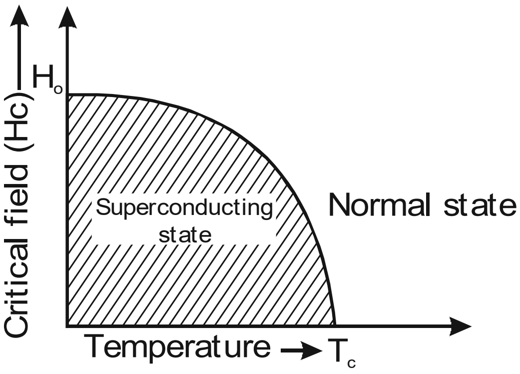


Fig. 4.1 Dependence of H_c on T

6. Critical Current Density J_c and Critical Current I_c

The critical current density is an another important characteristic feature of the superconducting state.

When the current density through a superconducting sample exceeds a critical value J_c, the superconducting state is found to disappear in the sample. This happens because, the current through the superconductor itself generates a magnetic field, and at a sufficiently high current density the magnetic field will start exceeding the critical magnetic field H_c thereby making the superconducting state to disappear in the material.

Hence, the critical current density can be defined as the maximum current that can be permitted in a superconducting material without destroying its superconductivity state. The critical current density is a function of temperature, i.e., colder the temperature for a superconductor the more is the current it can carry.

For a thin long cylindrical superconducting wire of radius *r* the relation between critical current I_c and critical magnetic field H_c is given by,

$$I_c = 2\ \pi r\ H_c$$

Similarly, the relation between critical current density J_c and critical current I_c is given by,

$$J_c = \frac{I_c}{A}$$

Where A is the superconducting specimen's cross-sectional area.

7. Persistent Current

When current is made to flow through a superconducting ring (say a loop of lead wire) which is at a temperature either equal to its T_c value or less than its T_c value, it was observed that the current was flowing through the material without any significant loss in its value.

This steady flow of current in a superconducting ring without any potential deriving it, is called the persistent current.

8. Meissner Effect (Diamagnetic Property)

*The complete expulsion of all the magnetic field by a superconducting material is called the **"Meissner Effect".***

When a superconducting material is placed in a magnetic field ($H > H_c$) at room temperature, the magnetic field is found to penetrate normally throughout the material, Figure (4.2(*a*)).

However, if the temperature is lowered below T_c and with $H < H_c$ the material is found to reject all the magnetic field penetrating through it as shown in Figure (4.2(*b*)).

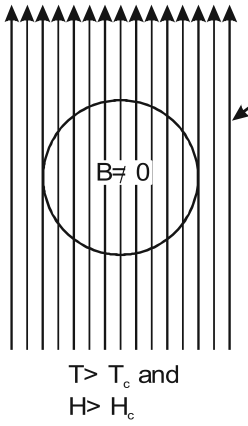


Fig. 4.2(a) *Normal State*

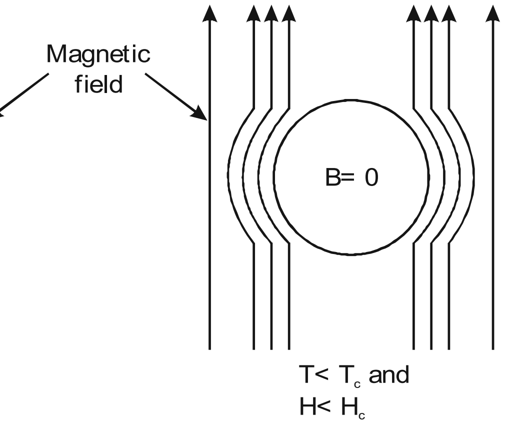


Fig. 4.2(b) *Superconducting State*

The above process occurs due to the development of surface current which inturn results in the development of magnetization M within the superconducting material. Hence, as the developed magnitation and the applied field are equal in magnitude but opposite in direction they cancel each other everywhere inside the material. Thus, below T_c a superconductor is a perfectly diamagnetic substance ($\chi_m = -1$).

The Meissner effect is a distinct characteristic of a superconductor from a normal perfect conductor. In addition, this effect is exhibited by the superconducting materials only when the applied field is less than the critical field H_c.

To Prove $\chi_m = -1$ for Superconductors

We know that, for a magnetic material the magnetic induction or magnetic flux density B is given by,

$$B = \mu_o (M + H) \qquad ...(4.2)$$

Where μ_o is the Permeability of Free Space.

M is the Intensity of Magnetisation.

And, H is the Applied Magnetic Field.

But, we know that for a superconductor B = 0

Therefore, Equation (4.2) can be written as,

$$0 = \mu_o (M + H)$$

$$\because \quad \mu_o \neq 0$$

$$M + H = 0$$

$$\text{or} \quad M = -H$$

$$\textbf{or} \quad \frac{\mathbf{M}}{\mathbf{H}} = \mathbf{-1}$$

Hence, $\chi_m = -1$ where $\chi_m = \frac{M}{H}$ is called the '**Magnetic Susceptibility**'.

Thus this means that, for a superconductor the susceptibility is negative and maximum, i.e., a superconductor exhibits perfect diamagnetism.

Three Important Factors to Define a Superconducting State

In general, the superconducting state is defined by three important factors:

1. Critical Temperature T_c.
2. Critical Current Density J_c.
3. Critical Magnetic Field H_c.

Each of the above three parameters is very dependent on the other two properties. To sustain superconducting state in a material it is required to have both the current density and magnetic field, as well as the temperature, to remain below their critical values; and all of which depend on the material.

The relationship between T_c, J_c and H_c is shown in the phase diagram given in the Figure (4.3).

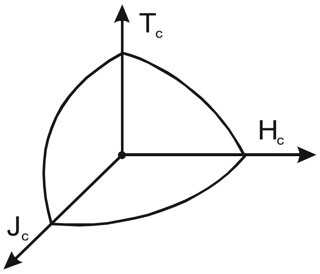


Fig. 4.3 *Critical Surface Phase Diagram*

The highest values for H_c and J_c occur at 0 K, while the highest value for T_c occurs when H and J are zero. Thus, the plot of all these three parameters represents a critical surface.

Within the surface the material is superconducting and outside the surface the material is said to be in the normal state.

Example 1

For mercury of mass number 202, the α value is 0.50 and T_c is 4.2 K. Find the transition temperature for the isotope of mercury of mass number 200.

Solution:

Given

Mass Number $M_1 = 202$

$\alpha = 0.5$

$T_{c1} = 4.2$ K

Mass Number $M_2 = 200$

$T_{c2} = ?$

We know, $M^\alpha T_{c1} = \text{Constant}$

Using this,

$$M_1^\alpha T_{c1} = M_2^\alpha T_{c2}$$

or

$$T_{c2} = \left(\frac{M_1}{M_2}\right)^\alpha T_{c1} = \left(\frac{202}{200}\right)^{0.5} \times 4.2 \qquad \left[\because \alpha = \frac{1}{2}\right]$$

$$= 1.004987 \times 4.2$$

$$\mathbf{T_{c2} = 4.2209\ K.}$$

Example 2

The critical temperature of Nb is 9.15 K. At zero Kelvin the critical field is 0.196 T. Calculate the critical field at 6 K.

Solution:

Given, $T_c = 9.15$ K; $T = 6$ K; $H_o = 0.196$ T; $H_c = ?$

$$H_c = H_o\left(1-\left(\frac{T}{T_c}\right)^2\right) = 0.196\left[\left[\left(1-\left(\frac{6}{9.15}\right)^2\right)\right]\right]$$

$$= 0.196\ [1 - 0.4299]$$

$$= 0.196\ [0.5701]$$

$$\therefore \qquad \mathbf{H_c = 0.1117\ T.}$$

Example 3

The critical temperature for a metal with isotopic mass 199.5 is 4.185 K. Calculate the isotopic mass if the critical temperature falls to 4.133 K.

Solution:

Given, $M_1 = 199.5$; $T_{c1} = 4.185$ K; $T_{c2} = 4.133$ K; $M_2 = ?$

Formula

$$M_1^{\alpha}\ T_{c1} = M_2^{\alpha}\ T_{c2}$$

$$\therefore \qquad M_2^{\alpha} = (199.5)^{\alpha}\ \frac{4.185}{4.133}$$

$$M_2^{0.5} = (199.5)^{0.5} \times 1.01258$$

$$\left[\because \alpha = \frac{1}{2}\right]$$

$$\sqrt{M_2} = \sqrt{199.5} \times 1.01258 = 14.124 \times 1.01258$$

$$M_2 = (14.301)^2$$

$$\therefore \qquad \mathbf{M_2 = 204.55.}$$

Example 4

Calculate the critical current through a long thin superconducting wire of radius 0.5 mm. The critical magnetic field is 13.2 kA/m.

Solution:

Given, $H_c = 7.2 \times 10^3$ A/m; $r = 0.5 \times 10^{-3}$m; $I_c = ?$

Formula

$$I_c = 2\pi r\ H_c$$

$$= 2 \times 3.14 \times 0.5 \times 10^{-3} \times 7.2 \times 10^3$$

$$\therefore \qquad \mathbf{I_c = 22.608\ A.}$$

Example 5

Superconducting Sn has a critical temperature of 3.7 K at zero magnetic field and a critical field of 0.0306 T at 0 K. Find the critical field at 2 K.

Solution:

Given, $T_c = 3.7$ K; $H_o = 0.0306$ T; $H_c = ?$; $T = 2$ K

Formula

$$H_c = H_o\left[1-\left(\frac{T}{T_c}\right)^2\right] = 0.0306\left[1-\left(\frac{2.0}{3.7}\right)^2\right]$$

$$= 0.0306\ (1 - 0.29218) = 0.0306 \times 0.70782$$

$$\therefore \quad \mathbf{H_c = 0.021659\ Tesla.}$$

Example 6

Calculate the critical current for a superconducting wire of lead having a diameter of 1 mm at 4.2 K. Critical temperature for lead is 7.18 K and $H_c\ (0) = 6.5 \times 10^4$ A/m.

Solution:

Given, $H_o = 6.5 \times 10^4$ A/m; $T_c = 7.18$ K; $r = 0.5 \times 10^{-3}$ m; T = 4.2 K; $I_c = ?$; $H_c = ?$

Formula

$$H_c = H_o\left[1-\left(\frac{T}{T_c}\right)^2\right] = 6.5 \times 10^4\left[1-\left(\frac{4.2}{7.18}\right)^2\right]$$

$$= 6.5 \times 10^4\ (1 - 0.34217) = 6.5 \times 10^4 \times 0.65783$$

$$\therefore \quad \mathbf{H_c = 42.758\ kA/m.}$$

$$I_c = 2\pi r\ H_c = 2 \times 3.14 \times 0.5 \times 10^{-3} \times 42.758 \times 10^3$$

$$\therefore \quad \mathbf{I_c = 134.26\ A.}$$

Example 7

The critical field for vanadium is 10^5 Am^{-1} at 8.58 K and 2×10^5 Am^{-1} at 0 K. Determine the T_c value.

Solution:

Given, $H_c = 10^5$ Am^{-1}; $H_o = 2 \times 10^5$ Am^{-1}; T = 8.58 K; $T_c = ?$

Formula

$$H_c = H_o\left[1-\left(\frac{T}{T_c}\right)^2\right]$$

$$\therefore \quad \left(\frac{H_c}{H_o}\right) = 1-\left(\frac{T}{T_c}\right)^2$$

$$\left(\frac{T}{T_c}\right)^2 = 1-\left(\frac{H_c}{H_o}\right)$$

$$\therefore \quad T_c = \frac{T}{\sqrt{1-\left(\frac{H_c}{H_o}\right)}} = \frac{8.58}{\sqrt{1-\frac{10^5}{2\times 10^5}}} = \frac{8.58}{\sqrt{1-0.5}} = \frac{8.58}{\sqrt{0.5}} = \frac{8.58}{0.7071}$$

$$\therefore \quad \mathbf{T_c = 12.133\ K.}$$

4.2.2 Thermodynamics of Superconducting Transition

The term 'Superconductivity' is specifically defined as a set of established physical properties specifically studied in specific materials where the electrical resistance disappears, and from the material the fields of magnetic flux are expelled. The theoretical model that was first conceived for superconductivity was completely classical, and it is principally summarized using the London constitutive equations. It was put forward by the brothers Fritz Wolfgang London and Heinz London in the year 1935, shortly after the discovery that magnetic fields are expelled from superconductors. A key triumph or victory of the equations of this theory is their capability to explain the Meissner effect, wherein a material exponentially expels all internal magnetic fields as it crosses the superconducting threshold. By using the London equation, one can obtain the dependence of the magnetic field inside the superconductor on the distance to the surface.

In thermodynamics, the term phase transitions or phase changes are defined as the physical processes of transition between a state of a medium, uniquely identified and characterised by means of some specific parameters, and another one, with different values of the parameters. Commonly the term is used to refer to changes among the basic common states of matter, namely the solid, the liquid, and the gas, as well as plasma in rare cases.

Characteristically, the phase of a thermodynamic system and the states of matter have uniform physical properties. During a phase transition of a given medium, certain properties of the medium change, often discontinuously, as a result of the change of external conditions, such as temperature, pressure, or others. For example, a liquid may become gas upon heating to the specified boiling point, resulting in an abrupt change in volume. The measurement of the external conditions at which the transformation occurs is termed as the phase transition. Phase transitions commonly occur in nature and are used today in many technologies. Phase transitions usually occur when the thermodynamic free energy of a system is non-analytic for certain range of thermodynamic variables. Characteristically, the phase transitions can occur and are specifically defined for the non-thermodynamic systems, where temperature is not a parameter.

Ehrenfest Classification

Paul Ehrenfest classified phase transitions based on the behaviour of the thermodynamic free energy as a function of other thermodynamic variables. Under this notion the phase transitions were labelled by the lowest derivative of the free energy that is discontinuous at the transition. First-order phase transitions exhibit a discontinuity in the first derivative of the free energy with respect to some thermodynamic variable. The various solid/liquid/gas transitions are classified as first-order transitions because they involve a discontinuous change in density, which is the (inverse of the) first derivative of the free energy with respect to pressure. Second-order phase transitions are continuous in the first derivative, the order parameter which is the first derivative of the free energy with respect to the external field, is continuous across the transition, but exhibit discontinuity in a second derivative of the free energy. These include the ferromagnetic phase transition in materials, such as iron, where the magnetization, which is the first derivative of the free energy with respect to the applied magnetic field strength, increases continuously from zero as the temperature is lowered below the Curie temperature. The magnetic susceptibility, the second derivative of the free energy with the field, changes discontinuously. Under the Ehrenfest classification the phase transition can be specifically defined as a form where in principle there are precisely third, fourth, and higher-order phase transitions.

The Ehrenfest classification implicitly allows for continuous phase transformations, where the bonding character of a material changes, but there is no discontinuity in any free energy derivative. An example of this can be observed at the supercritical liquid-gas boundaries.

Modern Classifications

In the modern classification scheme, phase transitions are divided into following two broad categories, named similarly to the Ehrenfest classes:

1. **First-Order Phase Transitions:** First-order phase transitions are those that involve a latent heat. During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy per volume. During this process, the temperature of the system will stay constant as heat is added, the system is in a 'Mixed-Phase Regime' in which some parts of the system have completed the transition and others have not. Familiar examples are the melting of ice or the boiling of water, the water does not instantly turn into vapour, but forms a turbulent mixture of liquid water and vapour bubbles. Yoseph Imry and Michael Wortis showed that quenched disorder can broaden a first-order transition, i.e., the transformation is completed over a finite range of temperatures, but phenomena like supercooling and superheating exists and hysteresis is observed on thermal cycling.
2. **Second-Order Phase Transitions:** Second-order phase transitions are also called 'Continuous Phase Transitions'. They are characterized by a divergent susceptibility, an infinite correlation length, and a power law decay of correlations near criticality. Examples of second-order phase transitions are the ferromagnetic transition, superconducting transition, for a Type-I superconductor the phase transition is second-order at zero external field and for a Type-II superconductor the phase transition is second-order for both normal-state-mixed-state and mixed-state-superconducting-state transitions, and the superfluid transition. In contrast to viscosity, thermal expansion and heat capacity of amorphous materials show a relatively sudden change at the glass transition temperature which enables accurate detection using differential scanning calorimetry measurements. Lev Landau gave a phenomenological theory of second-order phase transitions.

   The variation of specific heat with temperature is often a good analysis of phase transitions in matter. Historically, it is Ehrenfest who first classified phase transitions based on the variation of the thermodynamic free energy with some state variable, such as temperature. The order of a transition was defined as the lowest derivative of free energy (with respect to some variable) that was discontinuous at the transition. If the first derivative of free energy were discontinuous, such as the case of a solid-liquid transition where the density is discontinuous, then the transition is called first order. In the case of ferromagnetic transition of Fe for example, the susceptibility, i.e., the second derivative of free energy with field, is discontinuous and one would classify this as a second order phase transition. However, there are many cases in nature where rather than discontinuous jumps in thermodynamic variables, there is a divergence, such as in the heat capacity of a superconductor. The modern classification of phase transitions is based on the existence or lack thereof of a latent heat. If a phase transition involves a Latent Heat 'L', i.e., the substance absorbs or releases heat without a change in temperature, then it is called a 'First-Order Phase Transition'. In the absence of a latent heat, the phase transition is a 'Second-Order Phase Transition'. The variation of the enthalpy in the vicinity of a first order phase transition is shown below in Figure (4.4).

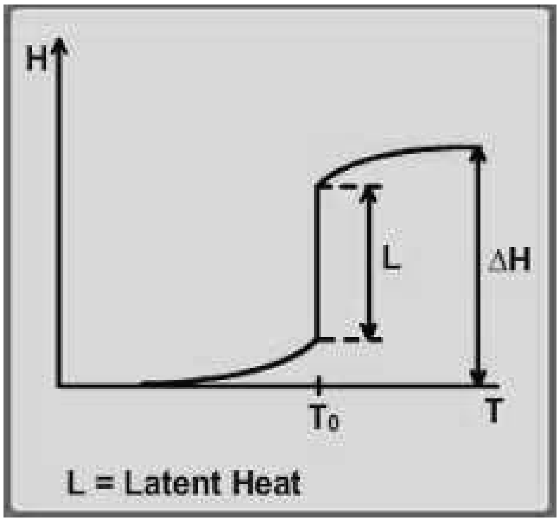


Fig. 4.4 *Variation of the Enthalpy of a First-Order Phase Transition*

The Figure (4.4) illustrates the schematic variation of enthalpy in the case of a transition involving a Latent Heat 'L'. For a Type-I superconductor, in general, there is an entropy change at the transition temperature 'T' and therefore a latent heat, making the Transition First-Order. However, in zero magnetic field, the entropy change is zero and hence the Transition is Second-Order.

4.3 DESTRUCTION OF SUPERCONDUCTIVITY BY MAGNETIC FIELDS MEISSNER EFFECT

The Dutch physicist Heike Kamerlingh Onnes discovered the unique phenomenon of superconductivity in the year 1911. Kamerlingh Onnes also stated that the electrical resistivity of a mercury wire can suddenly disappear when it is typically cooled below a temperature of around 4 K (–269 °C); absolute zero is 0 K, this is the temperature at which all matter loses its disorder. Subsequently, he also discovered that it is possible for a superconducting material to return back to the normal state, i.e., non-superconducting state either by applying or passing an appropriately larger current through it or by passing or applying an appropriately stronger magnetic field to it.

As per the Encyclopaedia Britannica, "The term superconductivity refers to the complete disappearance of electrical resistance in various solids when they are cooled below a characteristic temperature. This temperature, called the transition temperature, varies for different materials but generally is below 20 K (–253 °C)".

Superconductivity is essentially a specific phenomenon which can be studied or described by means of quantum mechanics, similar to ferromagnetism and atomic spectral lines. Consequently, the characteristic properties of the superconductivity state are described/characterised through the **Meissner effect**, when there is entire/complete ejection of the magnetic field lines from the interior of the superconductor during the period of its transitions into the superconducting state. In the classical physics, the existence of the Meissner effect specifies that the term superconductivity is not simply the idealization of perfect conductivity.

Response to a Magnetic Field

A **superconductor** can be **Type-I superconductor**, meaning it has a single critical field, above which all superconductivity is lost and below which the magnetic field is completely expelled from the superconductor; or **Type-II superconductor**, meaning it has two critical fields, between which it allows partial penetration of the magnetic field through isolated points. These points are called **vortices**. Furthermore, in multicomponent superconductors it is possible to have a combination of the two behaviours.

By Theory of Operation

It is conventional if it can be explained by the BCS theory or its derivatives, or unconventional, otherwise. Alternatively, a superconductor is termed as unconventional if the superconducting order parameter transforms according to a non-trivial irreducible representation of the point group or space group of the system.

BCS theory or Bardeen–Cooper–Schrieffer theory is named after John Bardeen, Leon Cooper, and John Robert Schrieffer and is referred as the first microscopic theory of superconductivity since Heike Kamerlingh Onnes's 1911 discovery. The theory describes superconductivity as a microscopic effect caused by a condensation of Cooper pairs. The theory is also used in nuclear physics to describe the pairing interaction between nucleons in an atomic nucleus.

By Critical Temperature

A superconductor is generally considered high-temperature if it reaches a superconducting state above a temperature of 30 K (–243.15 °C); as in the initial discovery by Georg Bednorz and K. Alex Müller. It may also reference materials that transition to superconductivity when cooled using liquid nitrogen, i.e., at only $T_c > 77$ K, although this is generally used only to emphasize that liquid nitrogen coolant is sufficient. Low temperature superconductors refer to materials with a critical temperature below 30 K. One exception to this rule is the iron pnictide group of superconductors which display behaviour and properties typical of high-temperature superconductors, yet some of the group have critical temperatures below 30 K.

By Material

Superconductor material classes include chemical elements, for example Mercury or Lead, Alloys, such as Niobium–Titanium, Germanium–Niobium, and Niobium Nitride, Ceramics, such as YBCO and Magnesium Diboride, Superconducting Pnictides, such as Fluorine-Doped LaOFeAs or Organic Superconductors Fullerenes and Carbon Nanotubes.

Yttrium Barium Copper Oxide (YBCO) is a family of crystalline chemical compounds, famous for displaying high-temperature superconductivity. It includes the first material ever discovered to become superconducting above the boiling point of liquid nitrogen (77 K) at about 92 K.

Physical Properties of Superconductors

Several physical properties of superconductors vary from material to material, such as the critical temperature, the value of the superconducting gap, the critical magnetic field, and the critical current density at which superconductivity is destroyed. On the other hand, there is a class of properties that are independent of the underlying material. The **Meissner effect**, the **quantization** of the **magnetic flux** or permanent currents, i.e., the **state of zero resistance** are the most important examples. The existence of these 'Universal' properties is rooted in the nature of the broken symmetry of the superconductor and the emergence of off-diagonal long range order. Superconductivity is a thermodynamic phase, and thus possesses certain distinguishing properties.

Meissner Effect

The **Meissner effect** or **Meissner–Ochsenfeld effect** is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state when it is cooled below the critical temperature. This expulsion will repel a nearby magnet.

The German physicists Walther Meissner and Robert Ochsenfeld discovered this phenomenon in 1933 by measuring the magnetic field distribution outside superconducting tin and lead samples. The samples, in the presence of an applied magnetic field, were cooled below their superconducting transition temperature, whereupon the samples cancelled nearly all interior magnetic fields. They detected this effect only indirectly because the magnetic flux is conserved by a superconductor, when the interior field decreases, the exterior field increases. The experiment demonstrated for the first time that superconductors were more than just perfect conductors and provided a uniquely defining property of the superconductor state. The ability for the expulsion effect is determined by the nature of equilibrium formed by the neutralization within the unit cell of a superconductor.

A superconductor with little or no magnetic field within it is said to be in the **Meissner state**. The Meissner state breaks down when the applied magnetic field is too strong. Superconductors can be divided into two classes according to how this breakdown occurs.

Following Figure (4.5) illustrates the diagram of the Meissner effect, the magnetic field lines are represented as arrows, and are excluded from a superconductor when it is below its Critical Temperature T_C, i.e., $T < T_C$.

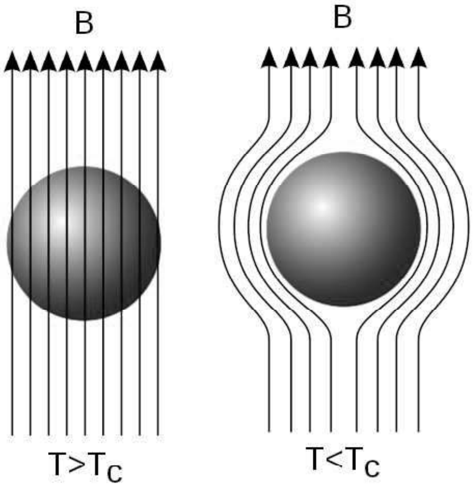


Fig. 4.5 *Diagram of the Meissner Effect*

In Type-I superconductors, superconductivity is abruptly destroyed when the strength of the applied field rises above a critical value H_c. Depending on the geometry of the sample, one may obtain an intermediate state consisting of a baroque pattern of regions of normal material carrying a magnetic field mixed with regions of superconducting material containing no field.

In Type-II superconductors, raising the applied field past a critical value H_{c1} leads to a mixed state, also known as the vortex state, in which an increasing amount of magnetic flux penetrates the material, but there remains no resistance to the electric current as long as the current is not too large. At a second critical field strength H_{c2}, superconductivity is destroyed. The mixed state is caused by vortices in the electronic superfluid, sometimes called fluxons because the flux carried by these vortices is quantized. Most pure elemental superconductors, except niobium and carbon nanotubes, are Type-I Super Conductors, while almost all impure and compound superconductors are Type-II Super Conductors.

Explanation of Meissner Effect

The Meissner effect was given a phenomenological explanation by the brothers Fritz and Heinz London, who showed that the electromagnetic free energy in a superconductor is minimized provided,

$$\nabla^2 \mathbf{H} = \lambda^{-2} \mathbf{H}$$

Where H is the magnetic field and λ is the London penetration depth.

This equation, known as the **'London Equation'**, predicts that the magnetic field in a superconductor decay exponentially from whatever value it possesses at the surface. This exclusion of magnetic field is a manifestation of the superdiamagnetism emerged during the phase transition from conductor to superconductor, for example by reducing the temperature below critical temperature.

In a weak applied field, i.e., less than the critical field that breaks down the superconducting phase, a superconductor expels nearly all magnetic flux by setting up electric currents near its surface, as the magnetic field H induces magnetization M within the London penetration depth from the surface. These surface currents shield the internal bulk of the superconductor from the external applied field. As the field expulsion, or cancellation, does not change with time, the currents producing this effect termed as persistent currents or screening currents do not decay with time.

Near the surface, within the London penetration depth, the magnetic field is not completely cancelled. Each superconducting material has its own characteristic penetration depth.

Any perfect conductor will prevent any change to magnetic flux passing through its surface due to ordinary electromagnetic induction at zero resistance. However, the Meissner effect is distinct from this, when an ordinary conductor is cooled so that it makes the transition to a superconducting state in the presence of a constant applied magnetic field, the magnetic flux is expelled during the transition. This effect cannot be explained by infinite conductivity, but only by the London equation. The placement and subsequent levitation of a magnet above an already superconducting material do not demonstrate the Meissner effect, while an initially stationary magnet later being repelled by a superconductor as it is cooled below its critical temperature does.

The persisting currents that exist in the superconductor to expel the magnetic field is commonly misconceived as a result of Lenz's Law or Faraday's Law. A reason this is not the case is that no change in flux was made to induce the current. Another explanation is that since the superconductor experiences zero resistance, there cannot be an induced EMF in the superconductor. The persisting current therefore is not a result of Faraday's Law.

When a superconductor is placed in a weak external magnetic field H, and cooled below its transition temperature, the magnetic field is ejected. The Meissner effect does not cause the field to be completely ejected but instead, the field penetrates the superconductor but only to a very small distance, characterized by a parameter λ, called the London penetration depth, decaying exponentially to zero within the bulk of the material. The Meissner effect is a defining characteristic of superconductivity. For most superconductors, the London penetration depth is on the order of 100 nm.

Perfect Diamagnetism

Superconductors in the Meissner state exhibit perfect diamagnetism or superdiamagnetism meaning that the total magnetic field is very close to zero deep inside them, many penetration depths from the surface. This means that their volume magnetic susceptibility is $\chi_v = -1$. Diamagnetics are defined by the generation of a spontaneous magnetization of a material which directly opposes the direction of an applied field. However, the fundamental origins of diamagnetism in superconductors and normal materials are very different. In normal materials diamagnetism arises as a direct result of the orbital spin of electrons about the nuclei of an atom induced electromagnetically by the application of an applied field. In superconductors the illusion of perfect diamagnetism arises from persistent screening currents which flow to oppose the applied field, the Meissner effect, not solely the orbital spin.

4.3.1 Heat Capacity, Energy Gap and Microwave Gap

Heat capacity or thermal capacity is a physical property of matter, defined as the amount of heat to be supplied to an object to produce a unit change in its temperature. The SI unit of heat capacity is Joule per Kelvin (J/K).

Heat capacity is an extensive property. The corresponding intensive property is the specific heat capacity, found by dividing the heat capacity of an object by its mass. Dividing the heat capacity by the amount of substance in moles yields its molar heat capacity. The volumetric heat capacity measures the heat capacity per volume. In architecture and civil engineering, the heat capacity of a building is often referred to as its thermal mass.

The heat capacity of an object, denoted by C, is the limit,

$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$$

Where ΔQ is the amount of heat that must be added to the object of mass *M* in order to raise its temperature by ΔT.

The value of this parameter usually varies considerably depending on the starting Temperature 'T' of the object and the Pressure 'P' applied to it. In particular, it typically varies dramatically with phase transitions, such as melting or vaporization. Therefore, it should be considered a function C (P, T) of those two variables.

Exponential Heat Capacity

The exponential heat capacity can be explained with the help of vanadium. As the vanadium is warmed toward its critical temperature, the heat capacity of vanadium increases 100-fold in just 4 K, as shown below in Figure (4.6). This exponential increase suggests an **energy gap** which must be bridged by thermal energy. This energy gap evidence was part of the experimental motivation for the BCS (Bardeen–Cooper–Schrieffer) theory of superconductivity.

From comparisons with other methods of determining the band gap, it is found that the constant '*b*' in the exponential heat capacity expression is one-half the band gap energy. If the slope of the line in the illustration is determined by scaling, it is about *b* = 7.4k, corresponding to an energy gap of about 1.3 meV. This is slightly lower than the value obtained by other methods. The value predicted for vanadium from its critical temperature of 5.38 K by the BCS theory is 1.6 meV, and the measured value is close to that.

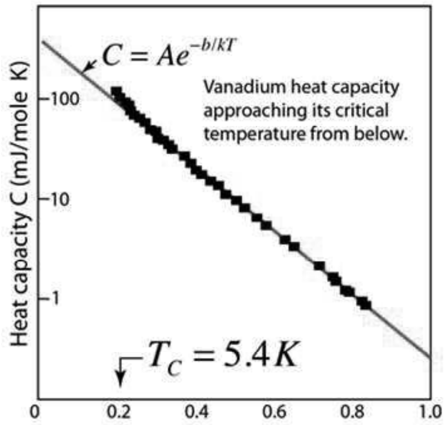


***Fig. 4.6** Heat Capacity of Vanadium approaching its Critical Temperature*

Energy Gap

In solid state physics, an **energy gap** is an energy range in a solid where no electron states exist, i.e., an energy range where the density of states vanishes.

If an energy gap exists in the band structure of a material, then it is termed as the **band gap**. The physical properties of semiconductors are to a large extent determined by their band gaps, but also for insulators and metals the band structure, and thus any possible band gaps govern their electronic properties.

For **superconductors** the **energy gap** is a region of suppressed density of states around the Fermi energy, with the size of the energy gap much smaller than the energy scale of the band structure. The superconducting energy gap is a key aspect in the theoretical description of superconductivity and thus features prominently in BCS theory. Here, the size of the energy gap indicates the energy gain for two electrons upon formation of a Cooper pair. If a conventional superconducting material is cooled from its metallic state, at higher temperatures, into the superconducting state, then the superconducting energy gap is absent above the critical temperature T_C, it starts to open upon entering the superconducting state at T_C, and it grows upon further cooling. BCS theory predicts that the size Δ of the superconducting energy gap for conventional superconductors at zero temperature scales with their critical temperature,

T_C: $\Delta (T = 0) = 1.764\, k_B T_C$ (with Boltzmann Constant k_B).

Microwave Gap

Solid state technology has produced several devices capable of producing, amplifying, detecting, and controlling microwaves. Significant among these are the Gunn diode and the tunnel or Esaki diode. Another type of device, the MASER, acronym for 'Microwave Amplification by Stimulated Emission of Radiation' has proved useful in such areas as radio astronomy, microwave radiometry, and long-distance communications.

Microwave frequencies range between 10^9 Hz (1 GHz) to 1000 GHz with respective wavelengths of 30 to 0.03 cm.

Many **semiconductor** processing techniques use **microwaves** to generate plasma for such purposes as reactive ion etching and Plasma-Enhanced Chemical Vapour Deposition (PECVD).

Microwave radiation is used in Electron Paramagnetic Resonance (EPR or ESR) spectroscopy, typically in the X-band region (~9 GHz) in conjunction typically with magnetic fields of 0.3 T. This technique provides information on unpaired electrons in chemical systems, such as free radicals or transition metal ions, such as Cu(II).

In the **microwave Photonic Band Gap (PBG) materials**, the magnetic permeability μ varies periodically within the material. This material is fabricated using a periodic arrangement of arrays of magnetic nanowires. As for dielectric or metallic PBG, the band gap behaviour varies with the geometrical parameters fixing the spatial periodicity of the magnetic structure. The magnetic photonic band gap is induced by the presence of a ferromagnetic resonance effect in the vicinity of the band gap.

4.3.2 Microwave and InfraRed (IR) Properties

Microwave is a form of ElectroMagnetic (EM) radiation with wavelengths ranging from about one meter to one millimeter corresponding to frequencies between 300 MHz and 300 GHz respectively. Different sources define different frequency ranges as microwaves; the above broad definition includes both UHF (Ultra High Frequency) and EHF (Extremely High Frequency), the millimeter wave bands. A more common definition in Radio Frequency (RF) engineering is the range between 1 and 100 GHz, wavelengths between 0.3 m and 3 mm. In all the conditions, the microwaves include the entire SHF (Super High Frequency) band, 3 to 30 GHz, or 10 to 1 cm, at minimum. Frequencies in the microwave range are often referred to by their IEEE (Institute of Electrical and Electronics Engineers) radar band designations: S, C, X, Ku, K, or Ka band, or by similar NATO or EU designations.

The prefix **micro-** in microwave does not mean that it is a wavelength in the micrometer range, instead it indicates that microwaves are 'Small', i.e., having shorter wavelengths, compared to the radio waves used prior to microwave technology. Microwaves travel by line-of-sight and follow the earth's surface as ground waves or reflect from the ionosphere, consequently the terrestrial microwave communication links are limited by the visual horizon to about 40 miles (64 km). Microwaves are widely used in modern technology, for example in point-to-point communication links, wireless networks, microwave radio relay networks, radar, satellite and spacecraft communication, medical diathermy and cancer treatment, remote sensing, radio astronomy, particle accelerators, spectroscopy, industrial heating, collision avoidance systems, garage door openers and keyless entry systems, and for cooking food in microwave ovens.

Microwaves occupy a place in the electromagnetic spectrum with frequency above ordinary radio waves and below infrared light. The Microwaves have the Wavelength of 1 mm – 1 m, Frequency (Hz) as 300 GHz – 300 MHz, and the Photon Energy (eV) as 1.24 meV – 1.24 μeV.

At the high end of the band, the microwaves are absorbed by gases in the atmosphere. Although at the low end of the band the microwaves can pass through building walls. Therefore, on the surface of the Earth, microwave communication links are limited by the visual horizon to about 30–40 miles (48–64 km). Microwaves are absorbed by moisture in the atmosphere, and the attenuation increases with frequency, becoming a significant factor (rain fade) at the high end of the band.

Beginning at about 40 GHz, atmospheric gases also begin to absorb microwaves, consequently above this frequency microwave transmission is limited to a few kilometers. A spectral band structure causes absorption peaks at specific frequencies. Above 100 GHz, the absorption of electromagnetic radiation by Earth's atmosphere is extremely significant and consequently it is in effect opaque, until the atmosphere becomes transparent again in the so-called infrared and optical window frequency ranges. A microwave oven passes microwave radiation at a frequency near 2.45 GHz (12 cm) through food, causing dielectric heating primarily by absorption of the energy in water. Water in the liquid state possesses many molecular interactions that broaden the absorption peak. In the vapour phase, isolated water molecules absorb at around 22 GHz, almost ten times the frequency of the microwave oven.

High-power microwave sources use specialized vacuum tubes to generate microwaves. These devices operate on different principles from low-frequency vacuum tubes, using the ballistic motion of electrons in a vacuum under the influence of controlling electric or magnetic fields, and include the Magnetron used in Microwave Ovens, Klystron, Traveling Wave Tube (TWT), and Gyrotron. These devices work in the Density Modulated Mode (DMM), rather than the Current Modulated Mode (CMM). This means that they work on the basis of clumps of electrons flying ballistically through them, rather than using a continuous stream of electrons.

Low-power microwave sources use solid state devices, such as the field effect transistor at least at lower frequencies, tunnel diodes, Gunn diodes, and IMPATT diodes (IMPact ionization Avalanche Transit Time diode). A MASER (Microwave Amplification by Stimulated Emission of Radiation) is a solid state device which amplifies microwaves using similar principles to the Laser, which amplifies higher frequency light waves, i.e., the MASER produces coherent electromagnetic waves through amplification by stimulated emission.

All warm objects emit low level microwave black-body radiation, depending on their temperature, so in meteorology and remote sensing, microwave radiometers are used to measure the temperature of objects or terrain. The sun and other astronomical radio sources, such as 'Cassiopeia A' emit low level microwave radiation which carries information about their makeup, which is studied by radio astronomers using receivers called radio telescopes. Cassiopeia A (Cas A) is a SuperNova Remnant (SNR) in the constellation Cassiopeia and the brightest extrasolar radio source in the sky at frequencies above 1 GHz. The Cosmic Microwave Background Radiation (CMBR) is considered as a weak microwave noise filling empty space which is a major source of information on cosmology's Big Bang theory of the origin of the Universe.

Microwave Frequency Measurement: Microwave frequency can be measured by either electronic or mechanical techniques. Frequency counters or high frequency heterodyne systems can be used. Here the unknown frequency is compared with harmonics of a known lower frequency by use of a low-frequency generator, a harmonic generator and a mixer. The accuracy of the measurement is limited by the accuracy and stability of the reference source. Mechanical methods require a tunable resonator, such as an absorption wavemeter, which has a known relation between a physical dimension and frequency.

Solid State Microwave Devices

The development of semiconductor electronics in the 1950s led to the first solid state microwave devices which worked by a new principle; negative resistance. The feedback oscillator and two-port amplifiers which were used at lower frequencies became unstable at microwave frequencies, and negative resistance oscillators and amplifiers based on one-port devices, such as diodes were more significant.

The tunnel diode invented in 1957 by Japanese physicist Leo Esaki could produce a few milliwatts of microwave power. Its invention set off a search for better negative resistance semiconductor devices for use as microwave oscillators, resulting in the invention of the IMPATT diode in 1956 by W.T. Read and Ralph L. Johnston and the Gunn diode in 1962 by J. B. Gunn. Diodes are the most widely used microwave sources today.

Two low-noise solid state negative resistance microwave amplifiers were developed; the Ruby MASER invented in 1953 by Charles H. Townes, James P. Gordon, and H. J. Zeiger, and the Varactor Parametric Amplifier developed in 1956 by Marion Hines. These were used for low noise microwave receivers in radio telescopes and satellite ground stations. The MASER led to the development of atomic clocks, which keep time using a precise microwave frequency emitted by atoms undergoing an electron transition between two energy levels.

Microwave Integrated Circuits

The period from the 1970s to the present has been considered as the development of tiny inexpensive active **solid state microwave components** which can be mounted on **circuit boards**, allowing circuits to perform significant **signal processing** at **microwave frequencies**. This has made possible satellite television, cable television, GPS (Global Positioning System) devices, and modern wireless devices, such as smartphones, Wi-Fi, and Bluetooth which connect to networks using microwaves.

Microstrip, a type of transmission line usable at microwave frequencies, was invented with printed circuits in the 1950s. The low-cost circuits were fabricated on Printed Circuit Boards PCBs) that allowed microstrip versions of capacitors, inductors, resonant stubs, splitters, directional couplers, diplexers, filters and antennas to be made, thus allowing compact microwave circuits to be constructed.

Transistors that operated at microwave frequencies were developed in the 1970s. The semiconductor Gallium Arsenide (GaAs) has a much higher electron mobility than silicon, so devices fabricated with this material can operate at 4 times the frequency of similar devices of silicon. The GaAs was used to make the first microwave transistors, and it has dominated microwave semiconductors ever since. MESFETs (MEtal-Semiconductor Field-Effect Transistors), fast GaAs field effect transistors using Schottky junctions for the gate were developed with cut-off frequencies of 100 GHz and are now the most widely used active microwave devices.

GaAs can be made semi-insulating, allowing it to be used as a substrate on which circuits containing passive components, as well as transistors, can be fabricated by lithography. By 1976 this led to the first Integrated Circuits (ICs) which functioned at microwave frequencies, called Monolithic Microwave Integrated Circuits (MMIC). The word ‘Monolithic’ was added to distinguish these from microstrip PCB circuits, which were termed as ‘Microwave Integrated Circuits (MIC)’. Since then, the silicon MMICs have also been developed, and nowadays the MMICs are considered very significant for both analog and digital high-frequency electronics, enabling the production of single-chip microwave receivers, broadband amplifiers, modems, and microprocessors.

InfraRed (IR) Properties

InfraRed (IR), sometimes also termed as infrared light, is an ElectroMagnetic Radiation (EMR) with wavelengths longer than those of visible light. It is therefore invisible to the human eye. IR is generally understood to encompass wavelengths from around 1 millimeter (300 GHz) to the nominal red edge of the visible spectrum, around 700 nanometers (frequency 430 THz), although the longer IR wavelengths are often designated rather as terahertz radiation. Black-body radiation from objects near room temperature is almost all at infrared wavelengths. As a form of electromagnetic radiation, IR propagates energy and momentum, with properties corresponding to both those of a wave and of a particle, the photon.

Infrared radiation was discovered in 1800 by astronomer Sir William Herschel, who discovered a type of invisible radiation in the spectrum lower in energy than red light, by means of its effect on a thermometer. Slightly more than half of the energy from the Sun was eventually found, through Herschel’s studies, to arrive on Earth in the form of infrared. The balance between absorbed and emitted infrared radiation has an important effect on Earth’s climate.

Infrared radiation is emitted or absorbed by molecules when changing rotational-vibrational movements. It excites vibrational modes in a molecule through a change in the dipole moment, making it a useful frequency range for study of these energy states for molecules of the proper symmetry. Infrared spectroscopy examines absorption and transmission of photons in the infrared range.

Infrared Radiation and the Electromagnetic Spectrum

Infrared radiation extends from the nominal red edge of the visible spectrum at 700 nanometers (nm) to 1 millimeter (mm). This range of wavelengths corresponds to a frequency range of approximately 430 THz down to 300 GHz. Beyond infrared is the microwave portion of the electromagnetic spectrum.

Infrared has the Wavelength of about 700 nm – 1 mm, the Frequency (Hz) as 300 GHz – 430 THz, and the Photon Energy (eV) as 1.7 eV – 1.24 meV.

Generally, the objects emit infrared radiation across a spectrum of wavelengths, but sometimes only a limited region of the spectrum is of significance because sensors usually collect radiation only within a specific bandwidth. Thermal infrared radiation also has a maximum emission wavelength, which is inversely proportional to the absolute temperature of object, in accordance with Wien's displacement law.

Characteristically, the infrared part of the electromagnetic spectrum covers the range from roughly 300 GHz to 400 THz (1 mm – 750 nm) and it can be divided into three parts, namely Far InfraRed (FIR), Mid InfraRed (MIR) and Near InfraRed (NIR).

Far InfraRed (FIR): The Far InfraRed (FIR) ranges from 300 GHz to 30 THz (1 mm – 10 μm). The lower part of this range may also be called microwaves or terahertz waves. This radiation is typically absorbed by the rotational modes in gas phase molecules, by molecular motions in liquids, and by phonons in solids. The water in Earth's atmosphere absorbs so strongly in this range that it renders the atmosphere in effect opaque. However, there are certain wavelength ranges within the opaque range that allow partial transmission and can be used for astronomy. The wavelength ranges from approximately 200 μm up to a few mm is often referred to as Submillimetre Astronomy, reserving Far InfraRed (FIR) for wavelengths below 200 μm.

Mid InfraRed (MIR): The Mid InfraRed (MIR) specifically ranges from 30 to 120 THz (10–2.5 μm). Hot objects, such as the black-body radiators, can radiate strongly in this range, and human skin at normal body temperature radiates strongly at the lower end of this region. This radiation is absorbed by molecular vibrations, where the different atoms in a molecule vibrate around their equilibrium positions. This range is sometimes called the fingerprint region, since the Mid InfraRed (MIR) absorption spectrum of a compound is very specific for that compound.

Near InfraRed (NIR): The Near InfraRed (NIR) ranges from 120 to 400 THz (2,500–750 nm). Physical processes that are relevant for this range are similar to those for visible light. The highest frequencies in this region can be detected directly by some types of photographic film and by many types of solid state image sensors for infrared photography and videography.

4.3.3 Isotope Effect

Isotopes are two or more types of atoms that have the same atomic number, the number of protons in their nuclei, and position in the periodic table and hence belong to the same chemical element, and that differ in nucleon numbers or mass numbers due to different numbers of neutrons in their nuclei. While all isotopes of a given element have almost the same chemical properties, they have different atomic masses and physical properties.

The number of protons within the atom's nucleus is called atomic number and is equal to the number of electrons in the neutral (non-ionized) atom. Each atomic number identifies a specific element, but not the isotope; an atom of a given element may have a wide range in its number of neutrons. The number of nucleons (both protons and neutrons) in the nucleus is the atom's mass number, and each isotope of a given element has a different mass number. For example, Carbon-12, Carbon-13, and Carbon-14 are three isotopes of the element Carbon with mass numbers 12, 13, and 14, respectively. The atomic number of Carbon is 6, which means that every carbon atom has 6 protons so that the neutron numbers of these isotopes are 6, 7 and 8, respectively.

Some isotopes/nuclides are radioactive, and are therefore referred to as radioisotopes or radionuclides, whereas others have never been observed to decay radioactively and are referred to as stable isotopes or stable nuclides. For example, ^{14}C is a radioactive form of carbon, whereas ^{12}C and ^{13}C are stable isotopes. There are about 339 naturally occurring nuclides on Earth, of which 286 are primordial nuclides, meaning that they have existed since the Solar System's formation.

Primordial nuclides include 34 nuclides with very long half-lives, over 100 million years, and 252 that are formally considered as 'Stable Nuclides', because they have not been observed to decay. In most of the situations, if an element has stable isotopes, then those isotopes predominate in the elemental abundance found on Earth and in the Solar System. However, in the cases of three elements (Tellurium, Indium, and Rhenium) the most abundant isotope found in nature is actually one (or two) extremely long-lived radioisotope(s) of the element, despite these elements having one or more stable isotopes.

Theory predicts that many apparently 'Stable' isotopes/nuclides are radioactive, with extremely long half-lives. Some stable nuclides are in theory energetically susceptible to other known forms of decay, such as alpha decay or double beta decay, but no decay products have yet been observed, and so these isotopes are said to be 'Observationally Stable'. The predicted half-lives for these nuclides often greatly exceed the estimated age of the universe, and in fact, there are also 31 known radionuclides with half-lives longer than the age of the universe. Adding in the radioactive nuclides that have been created artificially, there are 3,339 currently known nuclides. These include 905 nuclides that are either stable or have half-lives longer than 60 minutes.

The first evidence for multiple isotopes of a stable (non-radioactive) element was found by J. J. Thomson in 1912 as part of his exploration into the composition of canal rays, the positive ions. Thomson channelled streams of neon ions through parallel magnetic and electric fields, measured their deflection by placing a photographic plate in their path, and computed their mass to charge ratio using a method that became known as the Thomson's parabola method. Each stream created a glowing patch on the plate at the point it struck. Thomson observed two separate parabolic patches of light on the photographic plate which suggested two species of nuclei with different mass to charge ratios.

F. W. Aston subsequently discovered multiple stable isotopes for numerous elements using a mass spectrograph. In 1919, Aston studied neon with sufficient resolution to show that the two isotopic masses are very close to the integers 20 and 22 and that neither is equal to the known molar mass (20.2) of Neon Gas. This is an example of Aston's whole number rule for isotopic masses, which states that large deviations of elemental molar masses from integers are primarily due to the fact that the element is a mixture of isotopes. Aston showed that the molar mass of chlorine (35.45) is a weighted average of the almost integral masses for the two isotopes ^{35}Cl and ^{37}Cl.

The theoretical analysis of isotope effects strongly depends on transition state theory, which assumes a single potential energy surface for the reaction, and a barrier between the reactants and the products on this surface, on top of which resides the transition state.

Isotope Effect and Superconductivity

Isotope effect studies have been vital to the development of the microscopic theory of superconductivity. The first piece of evidence about the existence of isotope effect in mercury was reported in 1950 by Maxwell and independently by Reynold *et al*. They found that the critical temperature T_C of mercury varies as an inverse function of isotopic mass. The argument that isotope mass enters into the formation of the superconducting phase implies that superconductivity is not purely electronic in origin. In the same year, Frohlich proposed that same electron lattice interaction responsible for the scattering of conduction electrons by lattice vibrations provides a necessary glue between electrons. Frohlich's theory got a strong base from the experimental observation of isotope effect and played a key role in understanding microscopic mechanism of superconductivity. In 1956, Cooper demonstrated that a pair of electrons can interact above a Fermi surface with an interaction of a kind that might be expected due to phonon and screened coulomb fields. If there is a net attraction between the electrons, it turns out that they can form bound states, though their energy is larger than zero. The properties of non-interacting system of bound pairs are very suggestive of those which could produce superconducting state. However, the existence of electron pairs does not necessarily imply a phonon mediated pairing. Certainly, Bose condensation, as considered by Schafroth is also a possible mechanism for superconductivity, but unfortunately the model was not able to explain one of the important experimentally observed property of isotope effect discovered earlier by Maxwell and Reynold. Finally in 1957 Bardeen, Cooper and Schrieffer, in view of experimental observation of isotope effect in mercury discovered by Maxwell and Reynold followed by theoretical consideration of Frolich and inadequacy of Schafroths condensation, put forward first successful microscopic theory, which explains most of the physical properties observed in conventional superconductors.

Magnetic Isotope Effects

Magnetic isotope effects arise when a chemical reaction involves spin-selective processes, such as the radical pair mechanism. The result is that some isotopes react preferentially, depending on their nuclear spin quantum number 'I'.

4.4 LONDON EQUATION

In the Meissner effect, it is already discussed that one of the conditions of the superconducting state is that Magnetic Flux Density (B) = 0 inside the superconductors. This means that the magnetic flux cannot penetrate inside the superconductor. But experimentally it is not true. The magnetic flux does not suddenly goes to zero inside the surface. H. London and F. London has explained the phenomenon of flux penetration inside the superconductors.

This is already shown that the Meissner effect implies that the value of magnetic susceptibility $\chi = —1/4\Pi$ in CGS unit system in the superconducting state or, in SI, $\chi = -1$. Is it possible to modify a constitutive equation of electrodynamics (such as Ohm's law) by some method to get the Meissner effect? The modification in the Maxwell equations in not required. In the normal state of a metal electrical conduction is described by Ohm's law which is given by, $J = \sigma E$. Here J is the Current Density in a Resistive Material, E is the Electric Field and σ (Sigma) is the conductivity. This formula of Ohm's law is due to Gustav Kirchhoff. Now, we need to do the modification in this to describe conduction and the Meissner effect in the superconducting state. Let us first make a postulate and then see what happens next.

We put a postulate that when the current density is superconducting it is directly proportional to the vector potential A of the local magnetic field, where B = curl A. The gauge of A will be identified. In CGS units the constant of proportionality can be written as $—c/4\Pi\lambda_L^2$.

Here *c* is the speed of light and λ_L is a constant with the dimensions of length.

The theoretical model that was first conceived for superconductivity was completely classical: it is summarized by London equations. It was put forward by the brothers Fritz and Heinz London in 1935, shortly after the discovery that magnetic fields are expelled from superconductors. A major triumph of the equations of this theory is their ability to explain the Meissner effect, wherein a material exponentially expels all internal magnetic fields as it crosses the superconducting threshold. By using the London equation, one can obtain the dependence of the magnetic field inside the superconductor on the distance to the surface.

The two constitutive equations for a superconductor by London are:

$$\frac{\partial \mathbf{j}}{\partial t} = \frac{ne^2}{m}\mathbf{E}, \qquad \nabla \times \mathbf{j} = -\frac{ne^2}{m}\mathbf{B}.$$

The first equation follows from Newton's second law for superconducting electrons.

Magnetic Levitation (Maglev)

Magnetic levitation or maglev is the process by which an object is suspended above another object with no other support but magnetic fields.

We know that, a diamagnetic substance repels a magnetic field. Thus, the perfect diamagnetic property of superconductors make them suitable for achieving friction less motion in motors and bearing.

The phenomena of magnetic levitation is based on Meissner effect.

How to Achieve Magnetic Levitation?

The magnetic levitation is brought about by enormous repulsion between two highly powerful magnetic fields.

If a small magnet is brought near a superconductor it will be repelled. This repulsion takes place due to the induced currents in the superconductor which is being generated by the magnetic field of the magnet. Because of zero resistance property of the superconductor this current persists and thus, the field due to this induced current repels the field due to the magnet. As a result, the magnet floats freely (i.e., levitated) above the superconductor.

Thus, the levitation of the magnet or maglev demonstrates two critical properties of superconductors: (i) Zero Resistance and (ii) Meissner Effect.

Applications

Magnetically levitated vechiles are called maglev vehicles. The utility of such levitation in vechiles is that, in the absence of contact between the moving and stationary systems, the friction is eliminated. With such an arrangement great speeds could be achieved with very low energy consumption.

1. Maglev Train

The levitation is based on two techniques: (i) ElectroMagnetic Suspension (EMS) and (ii) ElectroDynamic Suspension (EDS).

In attractive EMS the electromagnets installed on the train bogies attract the iron rails (guideways). The vechile magnets wrap around the iron guideways and the attractive upward force lifts the train.

In EDS levitation is achived by creating a repulsive force between the train and guideways.

The basic idea of maglev train is to levitate it with magnetic fields so that there is no physical contact between the train and the rails (guideways). Consequently the maglev train can travel at very high speed. These trains travel at a speed of about 500 km/h.

2. A similar magnetic propulsion system is being used to launch the satellite into orbits directly from earth without the use of rockets.

4.4.1 Josephson Effect and its Application

Josephson Junction: *Two superconductors separated by a very thin strip of an insulator Figure (4.7) forms a Josephson junction.*

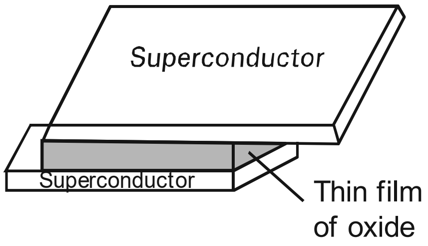


Fig. 4.7 *Josephson Junction*

Josephson Effect

The wave nature of moving particles makes the electrons to tunnel through the barrier (insulator), i.e., the electrons can tunnel from one superconductor to the other. As a consequence of the tunneling of electrons (Cooper pairs) across the insulator, there is a net current across the junction. This is called as ***D.C. Josephson effect.*** The current flows even in the absence of a potential difference.

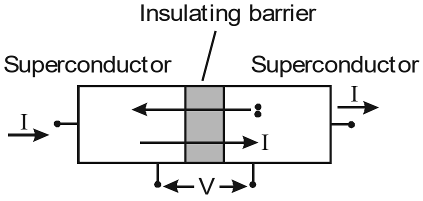


Fig. 4.8 *Josephson Junction with an Applied External Voltage (V)*

The magnitude of the current depends on, the thickness of the insulator, the material nature and on the temperature.

On the other hand, when a potential difference V is applied between the two sides of the junction Figure (4.8), there will be an oscillation of the tunneling current with angular frequency $\nu = \frac{2eV}{h}$. This is called the ***A.C. Josephson effect.*** Thus, according to A.C. Josephson effect, the junction generates an A.C. current at a frequency of $\frac{2eV}{h}$ Hz per volt.

Note: Cooper pair is a bound pair of electrons formed by the interaction between the electrons with opposite momenta and spin in a phonon field.

Application of Josephson Junction

Josephson junctions are used in sensitive magnetometers called SQUID-Superconducting QUantum Interference Device.

A SQUID is formed by connecting two Josephson junctions in parallel, Figure (4.9).

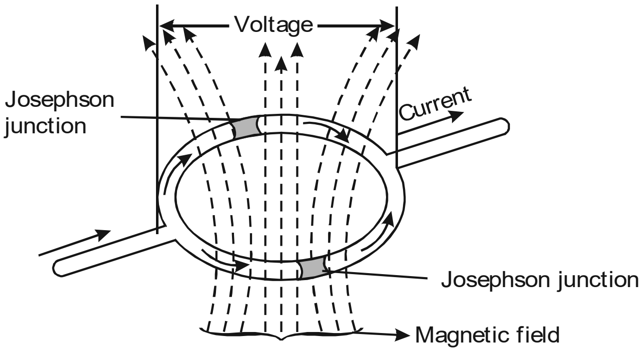


Fig. 4.9 *SQUID*

When current is passed into this arrangement, the current splits flowing across the two opposite arc. The current through the circuit will have a periodicity which is very sensitive to the magnetic flux passing normally through the closed circuit. As a result, extremely small magnetic flux can be detected with this device.

This device can also be used to detect voltages as small as 10^{-15} V.

Magnetic field changes as small as 10^{-21}T can be detected.

Weak magnetic fields produced by biological currents such as those in the brain can also be detected using SQUID's.

SQUID detectors are used to measure the levels of iron in liver, so that iron built up can be treated before much harm is done to the body.

Other Applications of Superconductors

1. Superconductors can be used to transmit electrical power over very long distances, without any power loss or any voltage drop.
2. Superconducting generators has the benefit of small size and low energy consumption than the conventional generators.
3. Superconducting coils are used in NMR (Nuclear Magnetic Resonance) imaging equipments which are used in hospitals, for scanning the whole body to diagnose medical problems.
4. Very strong magnetic fields can be generated with coils made of high – T_c superconducting materials.
5. Superconductors can act as relay or switching system in a computer. They can also be used as a memory or storage element in computers.

   Cryotron : It is a relay or switch made of superconductors whose size can be made very small. In addition, these switches consume a very little current.

   The cryotron consists of two superconducting materials A and B. Let the material A be inside the coil of wire B as shown in Figure (4.10).

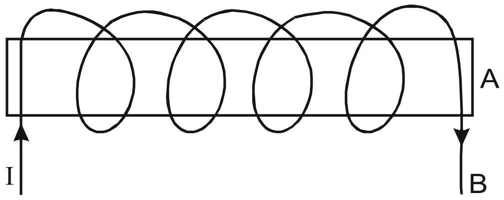
   

   Fig. 4.10 *Cryotron*

   Let the critical field of the material A be H_{cA} and that of B be H_{cB} respectively and also, let $H_{cA} < H_{cB}$. If a current I is passed through the material B, the current induces a magnetic field H. If this induced field H happens to be greater than H_{cA} then the superconducting property of the material A gets destroyed.

   Hence, the resistivity increases and the contact is broken. Thus, the current in A can be controlled by the current in B and hence, this system can act as a relay or switch element.
6. Very fast and accurate computers can be constructed using superconductors and the power consumption is also very low.
7. Ore separation can be done efficiently using superconducting magnets.

Example 8

A voltage of 5.9 μV is applied across a Josephson junction. What is the frequency of the radiation emitted by the junction?

Solution:

Given, V = 5.9 × 10^{-6} V; ν = ?

Formula $$\nu = \frac{2eV}{h} = \frac{2\times 1.6\times 10^{-19}\times 5.9\times 10^{-6}}{6.62\times 10^{-34}}$$

$$\boldsymbol{\nu = 2.851 \times 10^{9}\ \text{Hz.}}$$

4.4.2 Coherence Length

In condensed matter physics coherence length is the propagation distance over which a coherent wave (e.g., an electromagnetic wave) maintains a specified degree of coherence. Wave interference is strong when the paths taken by all of the interfering waves differ by less than the coherence length. A wave with a longer coherence length is closer to a perfect sinusoidal wave. Coherence length is important in holography and telecommunications engineering. Coherence length is usually applied to the optical regime.

In radio-band systems, the coherence length is approximated by,

$$L = \frac{c}{n\,\Delta f} = \frac{\lambda^2}{n\Delta\lambda},$$

Where c is the speed of light in vacuum, n is the refractive index of the medium, and Δf is the bandwidth of the source or λ is the signal wavelength and $\Delta\lambda$ is the width of the range of wavelengths in the signal.

The coherence length can be measured using a Michelson interferometer and is the optical path length difference of a self-interfering Laser beam which corresponds to a $1/e = 37\%$ fringe visibility, where the fringe visibility is defined as,

$$V = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}},$$

Where I is the fringe intensity.

Multimode Helium–Neon Lasers have a typical coherence length of 20 cm, while the coherence length of single-mode lasers can exceed 100 m. Semiconductor Lasers reach some 100 m, but small, inexpensive semiconductor Lasers have shorter lengths, with one source claiming 20 cm. Single mode fibre Lasers with line widths of a few kHz can have coherence lengths exceeding 100 km. Similar coherence lengths can be reached with optical frequency combs due to the narrow line width of each tooth. Non-zero visibility is present only for short intervals of pulses repeated after cavity length distances up to this long coherence length.

4.4.3 BSC Theory of Superconductivity

In 1957, the American physicists, John Bardeen, Leon N Cooper and John Robert Schrieffer proposed a microscopic theory (i.e., a quantum theory) to account for the observed properties of superconductors, which is known as BCS theory.

This theory involves the electron interactions through phonon as mediators (Refer Figure 4.11). This theory is based on the formation of Cooper pairs which is purely a quantum mechanical concept.

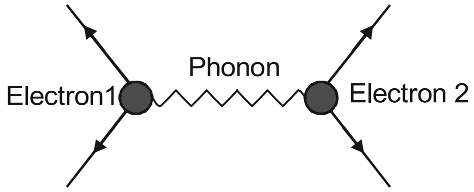


Fig. 4.11 *Electron-Lattice-Electron Interaction*

When an electron comes near a positive ion core of the lattice, it experiences an attractive force because of the opposite charge polarity between the electron and the ion core. Due to this interaction (Electron-Lattice Interaction) the ion core will be displaced from its position which is called 'Lattice Distortion'. The distortion causes an increase in the density of ions in the distorted region. The higher density of ions in the distorted region may attract an another electron. Thus, the second electron does not see the bare electron (i.e., the first electron) since it is screened by positive ions. Hence, the second electron will be attracted towards the first electron through the distorted lattice (Lattice-Electron Interaction) which tends to reduce the energy of the first electron. Thus, this process is looked upon as an equivalent to the interaction between two electrons via the lattice. *Since the lattice vibrations are quantized in terms of phonons, the process is called electron-lattice-electron interaction via the phonon field. A pair of electrons thus coupled through a phonon is called a Cooper pair.*

Since there is a reduction of energy during the interaction, it is treated as equivalent to estabilishing an attractive force between the two electrons. This attractive force is maximum if the two electrons have equal and opposite spins and momentum.

At temperatures below the critical temperature ($T < T_c$) the attractive force dominates the usual coulombic repulsive force between the two electrons thus leading to the formation of Cooper pairs. At this stage, the Cooper pairs of electrons in materials do not encounter any scattering by the lattice points. As a result, the resistivity vanishes and the conductivity becomes very high (almost infinity) leading to superconducting state of the material.

The BCS theory is supported by the fact that, the good conductors such as Au, Ag and Cu do not exhibit superconductivity. The reason given is that, the electrons in these metals move so freely in the lattice that the electron lattice interaction is virtually absent. Thus, the possibility of formation of Cooper pairs is negligible and, hence, the occurrence of superconductivity.

The distance among the lattice points in a superconductor upto which the Cooper pair of electrons can maintain the coupled motion is called the coherent length. This is found to be of the order of 10^{-6}m.

The base of a quantum theory of superconductivity was put by the classic papers of Bardeen, Cooper, and Schrieffer in 1957. The "BCS Theory of Superconductivity" is applicable with a very wide range, from He atoms in their condensed phase, to Type-I and Type-II metallic superconductors. It is also applicable to superconductors based on planes of cuprite ions with high-temperature. After that, there is a "BCS Wavefunction" which is composed of the particles in pairs k↓ and -k↓. If these are treated by the BCS theory then it gives the well-known electronic superconductivity which is observed in metals and exhibits the energy gaps. This pairing is called as an s-wave pairing. There are certainly other forms of particle pairing which are possible with the BCS theory, but we do not need to consider here any forms other than the BCS wave-function. In this chapter, we are discussing the specific achievements of BCS theory with a BCS wavefunction, some of which are given below:

1. If there is an attractive interaction between electrons then it can separate ground state from excited states by an energy gap. The critical magnetic field, the thermal properties, and most of the electromagnetic properties are due to the energy gap.
2. The interaction of electron-lattice-electron can lead to an energy gap of a certain magnitude which can be observed. The indirect interaction takes place when one electron interacts with the lattice and deforms it. Then a second electron sees the deformed lattice and adapts itself to take advantage of the deformation to lower its energy. Hence, the second electron interacts with the first electron through the lattice deformation.
3. The penetration depth and the coherence length came out as natural consequences of the BCS theory. For magnetic fields that vary slowly in space, the London equation is obtained. So, the most important phenomenon in superconductivity called the Meissner effect is obtained naturally.
4. The transition temperature criteria of an element or alloy involves the electron density of orbitals $D(E_F)$ of one spin at the Fermi level and the electron-lattice interaction U. This can be estimated from the electrical resistivity as the resistivity at room temperature is an estimate of the electron-phonon interaction. For $UD(\varepsilon_F) << 1$ the BCS theory predicts that

   $$T_c = 1.14\theta \exp[-1/UD(\varepsilon_F)]$$

   Where T_c, is the Debye temperature and U is an attractive interaction. The result for T_c is satisfied by the experimental data qualitatively. There is an interesting apparent anomaly that the higher the resistivity at room temperature the higher is U, and so, it is more likely that the metal will be a superconductor when cooled.
5. Magnetic flux obtained from a superconducting ring is quantized and the effective unit of charge is $2e$ instead of e. The ground state of BCS involves the pairs of electrons. Hence, the flux quantization in terms of the pair charge $2e$ is an outcome of the theory.

4.4.4 BCS Ground State

The ground state of a Fermi gas of non-interacting electrons is the filled Fermi Sea. This state allows very small excitation. We can create an excited state by just taking an electron from the Fermi surface and putting it just above the Fermi surface. The BCS theory shows that if there is an appropriate attractive interaction between electrons then the new ground state is superconducting and it is separated by a finite energy gap E_g from its lowest excited state.

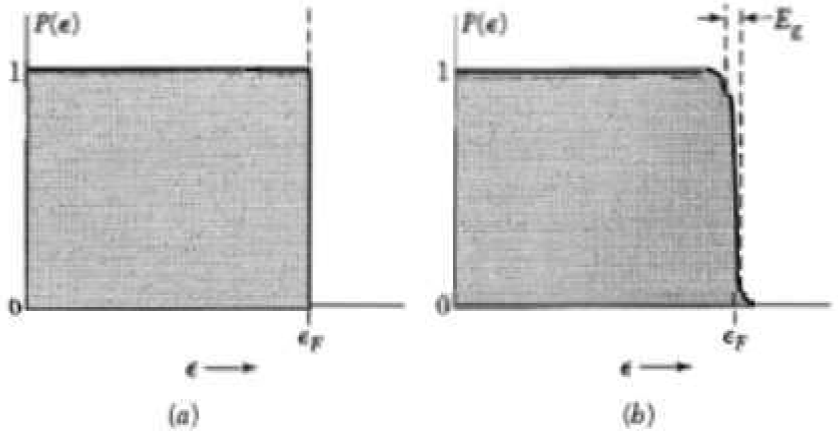


Fig. 4.12 *(a) Probability P that an Orbital of Kinetic Energy E is Occupied in the Ground State of the Noninteracting Fermi Gas; (b) the BCS Ground State Differs from the Fermi State in a Region of the Width of the Order of the Energy Gap Ep. Both Curves are for Absolute Zero.*

The formation of the BCS ground state is shown in Figure (4.12). The BCS state in (b) contains the mixtures of one-electron orbitals from above the Fermi energy T_F. At first look, the BCS state appears to have higher energy than the Fermi state. The comparison of Figure (4.12) (b) with (a) clearly shows that the kinetic energy of the BCS state is higher than that of the Fermi state. But the attractive potential energy of the BCS state, which is not represented in the figure reacts to lower the total energy of the BCS state in comparison to the Fermi state.

When the ground state of BCS of a many-electron system is defined in terms of the occupancy of one-particle orbitals. The orbitals which are near T_F are filled somewhat like a Fermi-Dirac distribution for some finite temperature.

The main feature of the BCS state is that the one-particle orbitals are occupied in the pairs that are if an orbital with wavevector k and spin up is occupied, then the orbital with wavevector -k and spin down is also occupied. 1f k$\downarrow$ is vacant, then -k$\downarrow$ is also vacant. These pairs are called Cooper pairs. They have zero spin and have many attributes of Bosons.

4.5 SINGLE PARTICLE TUNNELLING

Quantum tunnelling is the quantum mechanical phenomenon where a wavefunction can propagate through a potential barrier. The transmission through the barrier can be finite and depends exponentially on the barrier height and barrier width.

The wavefunction may disappear on one side and reappear on the other side. The wavefunction and its first derivative are continuous. In steady-state, the probability flux in the forward direction is spatially uniform. No particle or wave is lost. Tunnelling occurs with barriers of thickness around 1–3 nm and smaller.

Tunnel Junction: A simple barrier can be created by separating two conductors with a very thin insulator. These are tunnel junctions, the study of which requires understanding quantum tunnelling. Josephson junctions take advantage of quantum tunnelling and the superconductivity of some semiconductors to create the Josephson effect. This has applications in precision measurements of voltages and magnetic fields, as well as the multijunction solar cell.

The Superconducting Tunnel Junction (STJ) — also known as a Superconductor–Insulator–Superconductor (SIS) tunnel junction— is an electronic device consisting of two superconductors separated by a very thin layer of insulating material. Current passes through the junction via the process of quantum tunnelling. The STJ is a type of Josephson junction, though not all the properties of the STJ are described by the Josephson effect.

These devices have a wide range of applications, including high-sensitivity detectors of electromagnetic radiation, magnetometers, high speed digital circuit elements, and quantum computing circuits.

All currents flowing through the STJ pass through the insulating layer via the process of quantum tunnelling. There are two components to the tunnelling current. The first is from the tunnelling of Cooper pairs. This supercurrent is described by the ac and dc Josephson relations, first predicted by Brian David Josephson in 1962.

The second is the quasiparticle current, which, in the limit of zero temperature, arises when the energy from the bias voltage eV exceeds twice the value of superconducting energy gap Ä. At finite temperature, a small quasiparticle tunnelling current — called the subgap current — is present even for voltages less than twice the energy gap due to the thermal promotion of quasiparticles above the gap.

If the STJ is irradiated with photons of frequency f the dc current-voltage curve will exhibit both Shapiro steps and steps due to photon-assisted tunnelling. Shapiro steps arise from the response of the supercurrent and occur at voltages equal to $nhf/(2e)$ where h is Planck's constant, e is the electron charge, and n is an integer. Photon-assisted tunnelling arises from the response of the quasiparticles and gives rise to steps displaced in voltage by nhf/e relative to the gap voltage.

4.5.1 Type II Superconductors Vertex State

Based on the coolants to achieve superconductivity phenomena in materials, the superconductors fall in to two categories.

1. Low Temperature Superconductors.
2. High Temperature Superconductors.

Low Temperature Superconductors

Superconductors that require liquid helium as coolant are called as Low Temperature Superconductors (LTS or Low – T_c*). Liquid helium temperature is 4.2 K above absolute zero.*

High Temperature Superconductors

Superconductors having their T_c *values above the temperature of liquid nitrogen (77 K or –196°C) are called the High Temperature Superconductors (HTS or High-*T_c*).*

After the discovery of superconducting in mercury (4K) by Heike Kammerling onnes, the critical temperature had been gradually increased from 4K of Hg to 23 K in the compound Nb_3Ge first discovered in 1973. This remained a record until 1986.

On January 27, 1986, a new era of superconductivity science and technology begin. J. George Bednorz and K.A. Muller using a variant of the materials synthesized by Michel, smashed the long-stand 23K temperature record with a compound of barium, lanthanum, copper and oxygen that at 30 K is a very indicator of superconductivity.

Similar materials with higher transition temperature (High-T_c) soon followed in the history of superconductors when $Y_1Ba_2\,Cu_3\,O_{7-\delta}$ (Y BCO) or the so called 1-2-3 compound was discovered in 1987. The 1-2-3 compound was the first oxide superconductor to have transition temperature above liquid nitrogen temperature.

Soon after the discovery of superconductivity in YBCO material, more than 50 superconducting cuprates are now known. Extensive research to find high-T_c superconductivity in other families of materials has been unsuccessful. The highest transition temperature currently known is 138 K in a thallium doped mercuric cuprate comprised of the elements Hg, Tl, Ba, Ca, Cu and oxygen.

Examples for high temperature superconductors are listed in Table 4.1.

Table 4.1 *Examplefor High* T_c *Superconductors*

Material	T_c's in K
1. $Pb_2YSr_2\,Cu_3\,O_8$	77
2. Y – Ba – Cu – O ($Y_1Ba_2\,Cu_3\,O_7$)	93 – 95
3. Tl (Bi) – Ba(Sr) – Ca – Cu – O	122 – 125
4. Hg – Ba – Ca – Cu – O	130 – 135

High T_c Superconducting Oxide

The structure of the most intensily studied high T_c material (1-2-3) is explained in brief in this section.

It is found that, the superconductivity in $Y_1\,Ba_2\,Cu_3\,O_{7-x}$ system is due to $Y_1\,Ba_2\,Cu_3\,O_7$ and its T_c is $\simeq$ 90 K. The detailed structural investigations by single crystal X-ray and neutron powder diffraction techniques have shown that

$Y\,Ba_2\,Cu_3\,O_7$ is an orthorhombically distorted perovskite with a tripled cell along the c-axis as shown in Figure (4.13(a)). The lattice parameters are a = 3.823 Å, b = 3.86 Å and c = 11.681 Å.

Substitutional studies on $Y_1\,Ba_2\,Cu_3\,O_7$ have indicated that Y can be replaced by other magnetic rare earth, retaining the superconducting characteristics.

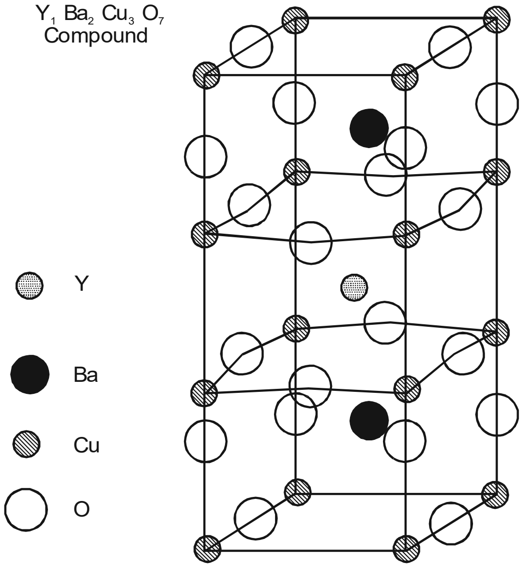


Fig. 4.13(a) *Structure of $Y_1\,Ba_2\,Cu_3\,O_7$ Compound–Orthorhombic*

Two more superconducting phases have been identified in the Y-Ba-Cu-O system having compositions $Y\,Ba_2\,Cu_3\,O_8$ and $Y_2\,Ba_4\,Cu_7\,O_{14}$ with $T_c \sim 80$ K and 40K, respectively.

Neutron and X-ray diffraction measurements showed that, the orthorhombic to tetragonal phase transition in $Y\,Ba_2\,Cu_3\,O_{7-x}$ occurs above 700°C. T_c also drops down drastically in the range $x = 0.5 - 0.6$ and becomes zero at $x = 0.65$ and the structure changes to tetragonal symmetry whereby the superconductivity also disappears in the compound.

It was observed that, the decrease in the superconducting transition temperature is due to a disordering of the oxygen chains, which implies that the Cu-O chains play a major role in the mechanism for high temperature superconductivity.

The structure difference between the orthorhombic and tetragonal Figure (4.13(*b*)) arises from the distribution of oxygen vacancies in the Cu(1) plane, i.e., in the tetragonal phase O_1 will be absent. One major advantage of high T_c superconductors is that, the liquid nitrogen can be used as a coolant to replace the more expensive liquid helium coolant.

The high temperature superconductors currently have only limited practical applications. The reason is, most of the high-T_c superconductors are ceramics which are brittle. But, in thin film technology these materials can find their applications in the electronic field such as high speed computers.

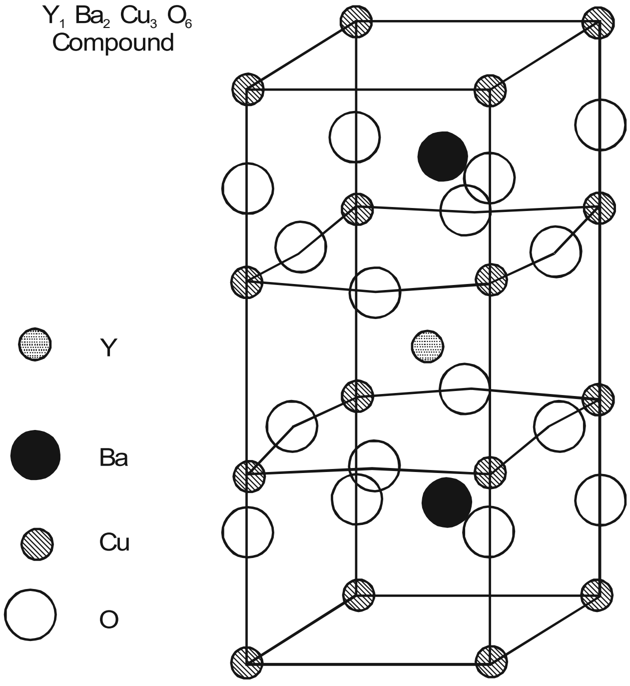


Fig. 4.13(b) *Structure of $Y_1 Ba_2 Cu_3 O_6$ Compound–Tetragonal*

Check Your Progress

1. What is superconductivity?
2. Define persistent current.
3. Which three important factors define a superconducting state?
4. How Paul Ehrenfest classified phase transitions?
5. Define the basic concept of Meissner effect and Meissner state.
6. In solid state physics, what is an energy gap and a band gap?
7. State about the microwave and infrared radiations.
8. What is magnetic levitation or maglev?
9. Define the term coherence length.
10. What is BCS theory and lattice distortion?
11. State about the quantum tunnelling, tunnel junctions and Superconducting Tunnel Junction (STJ).

4.6 OPTICAL PHENOMENA IN INSULATORS: COLOUR CENTRES AND EXCITONS

Optical property of a material is defined as its interaction with electromagnetic radiation in the visible. Visible light is one form of electromagnetic radiation with wavelengths ranging from 0.39 to 0.77 μm. Light can be considered as having waves and consisting of particles called photons. Basically, the optical properties provide an important tool for studying energy band structure, impurity levels, excitons, localized defects, lattice vibrations, and certain magnetic excitations in insulators.

1. Excitons

An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

An exciton can form when a material absorbs a photon of higher energy than its bandgap. This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively charged electron hole, an abstraction for the location from which an electron was moved. The electron in the conduction band is then less attracted to this localized hole due to the repulsive Coulomb forces from large numbers of electrons surrounding the hole and excited electron. These repulsive forces provide a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound electron and hole. The wavefunction of the bound state is said to be hydrogenic, an exotic atom state akin to that of a hydrogen atom. However, the binding energy is much smaller and the particle's size much larger than a hydrogen atom. This is because of both the screening of the Coulomb force by other electrons in the semiconductor, i.e., its relative permittivity, and the small effective masses of the excited electron and hole. The recombination of the electron and hole, i.e., the decay of the exciton, is limited by resonance stabilization due to the overlap of the electron and hole wave functions, resulting in an extended lifetime for the exciton.

The electron and hole may have either parallel or antiparallel spins. The spins are coupled by the exchange interaction, giving rise to exciton fine structure. In periodic lattices, the properties of an exciton show momentum (**k**-vector) dependence.

The concept of '**Excitons**' was first proposed by Yakov Frenkel in 1931, when he described the excitation of atoms in a '**Lattice of Insulators**'. He proposed that this excited state would be able to travel in a particle-like fashion through the lattice without the net transfer of charge.

Excitons are often treated in the two limiting cases of small dielectric constant versus large dielectric constant corresponding to Frenkel exciton and Wannier–Mott exciton, respectively.

Frenkel Exciton

In materials with a relatively small dielectric constant, the Coulomb interaction between an electron and a hole may be strong and the excitons thus tend to be small of the same order as the size of the unit cell. Molecular excitons may even be entirely located on the same molecule, as in fullerenes.

The Frenkel exciton, named after Yakov Frenkel, has a typical binding energy on the order of 0.1 to 1 eV. Frenkel excitons are typically found in alkali halide crystals and in organic molecular crystals composed of aromatic molecules, such as Anthracene and Tetracene. Another example of Frenkel exciton includes on-site ***d-d*** excitations in transition metal compounds with partially filled ***d***-shells. While ***d-d*** transitions are in principle forbidden by symmetry, they become weakly allowed in a crystal when the symmetry is broken by structural relaxations or other effects. Absorption of a photon resonant with a ***d-d*** transition leads to the creation of an electron-hole pair on a single atomic site, which can be treated as a Frenkel exciton.

Wannier–Mott Exciton

In semiconductors, the dielectric constant is generally large. Consequently, electric field screening tends to reduce the Coulomb interaction between electrons and holes. The result is a Wannier–Mott exciton, which has a radius larger than the lattice spacing. Small effective mass of electrons that is typical of semiconductors also favours large exciton radii. As a result, the effect of the lattice potential can be incorporated into the effective masses of the electron and hole. Likewise, because of the lower masses and the screened Coulomb interaction, the binding energy is usually much less than that of a hydrogen atom, typically on the order of 0.01eV. This type of exciton was named for Gregory Wannier and Nevill Francis Mott. Wannier–Mott excitons are typically found in semiconductor crystals with small energy gaps and high dielectric constants, but have also been identified in liquids, such as Liquid Xenon. They are also known as Large Excitons.

In single wall carbon nanotubes, excitons have both Wannier–Mott and Frenkel character. This is due to the nature of the Coulomb interaction between electrons and holes in one dimension. The dielectric function of the nanotube itself is large enough to allow for the spatial extent of the wave function to extend over a few to several nanometers along the tube axis, while poor screening in the vacuum or dielectric environment outside of the nanotube allows for large (0.4 to 1.0eV) binding energies.

Often more than one band can be chosen as source for the electron and the hole, leading to different types of excitons in the same material. Even high-lying bands can be effective as femtosecond two-photon experiments have shown. At cryogenic temperatures, many higher excitonic levels can be observed approaching the edge of the band, forming a series of spectral absorption lines that are in principle similar to hydrogen spectral series.

Equations for 3D Semiconductors

In a bulk semiconductor, the Wannier exciton has an energy and a radius associated with it, specifically termed as **Exciton Rydberg Energy** and **Exciton Bohr Radius**, respectively. For the energy, we have,

$$E(n) = -\frac{\left(\frac{\mu}{m_0 \varepsilon_r^2}\mathrm{Ry}\right)}{n^2} \equiv -\frac{R_{\mathrm{X}}}{n^2}$$

where Ry is the **Rydberg** unit of **energy**, the Rydberg constant, ε_r is the static relative permittivity, $\mu = (m_e^* m_h^*)/(m_e^* + m_h^*)$ is the reduced mass of the electron and hole, and m_0 is the electron mass. Concerning the radius, we have,

$$r_n = \left(\frac{m_0 \varepsilon_r a_{\mathrm{H}}}{\mu}\right) n^2 \equiv a_{\mathrm{X}} n^2$$

where a_{H} is the **Bohr radius**.

Consequently, for example in GaAs, we have relative permittivity of 12.8 and effective electron and hole masses as $0.067m_0$ and $0.2m_0$, respectively, and that gives us $R_{\mathrm{X}} = 4.2$ meV and $a_{\mathrm{X}} = 13$ nm.

Equations for 2D Semiconductors

In two dimensional (2D) materials, the system is quantum confined in the direction perpendicular to the plane of the material. The reduced dimensionality of the system has an effect on the binding energies and radii of Wannier excitons. In fact, excitonic effects are enhanced in such systems.

For a simple screened Coulomb potential, the binding energies take the form of the 2D hydrogen atom,

$$E(n) = -\frac{R_{\mathrm{X}}}{\left(n - \frac{1}{2}\right)^2}.$$

In most of the 2D semiconductors, the Rytova–Keldysh form is a more accurate approximation to the exciton interaction given by the form,

$$V(r) = -\frac{\pi}{2r_0}\left[\mathrm{H}_0\left(\frac{\kappa r}{r_0}\right) - \mathrm{Y}_0\left(\frac{\kappa r}{r_0}\right)\right]$$

Where r_0 is the screening length, κ the average dielectric constant of the surrounding media, and r the exciton radius. For this potential, no general expression for the exciton energies may be found. One must instead turn to numerical procedures, and it is precisely this potential that gives rise to the non-hydrogenic Rydberg series of the energies in 2D semiconductors

2. Colour Centres

The term 'Colour Centre' refers to the defect in the regular spacing of atoms within a solid that absorbs visible light of a particular colour or InfraRed (IR) or UltraViolet (UV) radiation, thus providing a **characteristic colour** to the solid. Each colour centre involves the absence of an atom from the place it would normally occupy in the solid and the relation of an electron with such an empty place or vacancy. Solids without colour centres may still have colour if impurity atoms or other structures that absorb light are present.

There are many types of colour centres. The best understood one, called an F-Centre or Farbe Centre or Color Center is a type of crystallographic defect in which an anionic vacancy in a crystal lattice is occupied by one or more unpaired electrons. Electrons in such a vacancy in a crystal lattice tend to absorb light in the visible spectrum such that a material that is usually transparent becomes coloured.

The term F-Centre or Farbe Centre is adopted from the original German word 'Farbzentrum', where 'Farbe' means 'Color' and 'Zentrum' means 'Center'. An F-center, Farbe center is used to identify many compounds, especially Zinc Oxide (Yellow).

Typically, the F-Centre or Farbe Centre results from the absence of a negatively charged ion from a particular point in an ionic solid. This vacancy, which acts like a positively charged particle, attracts and traps an electron, and their combination constitutes an F-Centre. The electron so trapped can absorb only certain colours of light. F-Centres in sodium chloride absorb only Blue Light, giving the solid a Yellow-Orange Tinge. Sodium chloride is usually colourless, however, because its electrons are not free to move to vacancies formed by removal of negative chloride ions from the solid. X-rays striking the solid, for example, may produce colour centres by freeing electrons. Following Figure (4.14) illustrates the F-center in a Sodium Chloride or NaCl crystal.

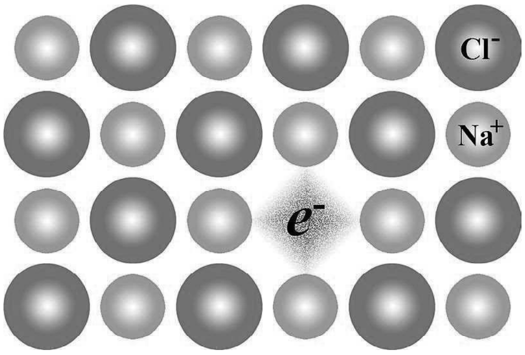


Fig. 4.14 *F-Center in a Sodium Chloride (NaCl) Crystal*

Color centers can occur naturally in compounds (particularly metallic oxides) because when heated to high temperature the ions become excited and are displaced from their normal crystallographic positions, leaving behind some electrons in the vacated spaces. This effect is also exhibited by ionic compounds containing metal-excess defects. The formation of F-centers is the reason that some crystals, such as lithium chloride, potassium chloride, and zinc oxide become pink, lilac and yellow, respectively, when heated.

Exciton Waves

Exciton can be defined as the combination of an electron and a positive hole, an empty electron state in a valence band, which is free to move through a nonmetallic crystal as a unit. An exciton is, therefore, a two-body composite quasiparticle formed of an electron and hole, is a fundamental optical excitation in condensed matter systems. Since its discovery nearly a century ago, a measurement of the **excitonic wave function** is stated. Excitons are typically the electrically neutral energetic pairs of electrons and holes, created by the absorption of **photons** in a solid, the specific **exciton wave** type.

4.6.1 Weakly and Tightly Bound Excitons

Excitons are lowest excited states of the electronic subsystem of pure crystals. Impurities can bind excitons, and when the bound state is shallow, the oscillator strength for producing bound excitons is so high that impurity absorption can compete with intrinsic exciton absorption even at rather low impurity concentrations. This phenomenon is generic and applicable both to the large radius, the Wannier–Mott excitons, and molecular, the Frenkel excitons.

Normally, excitons in a semiconductor have a very short lifetime due to the close proximity of the electron and hole. However, by placing the electron and hole in spatially separated quantum wells with an insulating barrier layer in between so called 'Spatially Indirect' excitons can be created. In contrast to ordinary or spatially direct, these spatially indirect excitons can have large spatial separation between the electron and hole, and thus possess a much longer lifetime. This is often used to cool excitons to very low temperatures in order to study Bose–Einstein condensation or rather its two-dimensional analog.

4.7 SOLID STATE QUANTUM ELECTRONICS: PRINCIPLES OF MASER ACTION

Solid state physics is the study of rigid matter or solids, through methods, such as quantum mechanics, crystallography, electromagnetism and metallurgy, and is considered as the largest branch of condensed matter physics. Fundamentally, the solid state physics studies how the large scale properties of solid materials result from their atomic scale properties. Thus, solid state physics forms a theoretical basis of materials science. It also has direct applications, for example in the technology of transistors and semiconductors.

Quantum electronics a branch of physics that deals with the interaction of radiation with discrete energy levels in substances, as in a MASER or Laser. A quantum particle like an electron can be described by a wave function, which associates to each point in space a probability amplitude. Applying the Born rule to these amplitudes gives a probability density function for the position that the electron will be found to have when an experiment is performed to measure it. The Schrödinger equation relates the collection of probability amplitudes that pertain to one moment of time to the collection of probability amplitudes that pertain to another. Analytic solutions of the Schrödinger equation are known for very few relatively simple model Hamiltonians including the quantum harmonic oscillator, the particle in a box, the dihydrogen cation, and the hydrogen atom.

The significant consequence of the mathematical rules of quantum is the phenomenon of quantum interference, for example a coherent light source, such as a Laser beam, illuminates a plate pierced by two parallel slits, and the light passing through the slits is observed on a screen behind the plate. The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles. However, the light is always found to be absorbed at the screen at discrete points, as individual particles rather than waves; the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit and not through both slits.

Quantum method is often the only theory that can reveal the individual behaviors of the subatomic particles that make up all forms of matter, i.e., electrons, protons, neutrons, photons, and others. Solid state physics and materials science are dependent upon quantum theory.

Uncertainty Principle

One consequence of the basic quantum formalism is the uncertainty principle. In its most familiar form, this states that no preparation of a quantum particle can imply simultaneously precise predictions both for a measurement of its position and for a measurement of its momentum. Both position and momentum are observables, meaning that they are represented by Hermitian operators.

Principles of MASER Action

The term MASER, an acronym for ‘Microwave Amplification by Stimulated Emission of Radiation’, is a device that produces coherent electromagnetic waves through amplification by stimulated emission. The first MASER was built by Charles H. Townes, James P. Gordon, and Herbert J. Zeiger at Columbia University in 1953. MASERs are used as the timekeeping device in atomic clocks, and as extremely low-noise microwave amplifiers in radio telescopes and deep space spacecraft communication ground stations.

Modern MASERs can be designed to generate electromagnetic waves at not only microwave frequencies but also radio and infrared frequencies. For this reason Charles Townes suggested replacing ‘Microwave’ with the word ‘Molecular’ as the first word in the acronym MASER.

As per the Encyclopedia Britannica, “The MASER, an acronym derived from ‘Microwave (or Molecular) Amplification by Stimulated Emission of Radiation’, is a device that produces and amplifies electromagnetic radiation mainly in the microwave region of the spectrum. The MASER operates according to the same basic principle as the LASER, the name of which is formed from the acronym for ‘Light Amplification by Stimulated Emission of Radiation’ and shares many of its characteristics”.

The LASER works by the same principle as the MASER but produces higher frequency coherent radiation at visible wavelengths. The MASER was the forerunner of the Laser, inspiring theoretical work by Townes and Arthur Leonard Schawlow that led to the invention of the LASER in 1960 by Theodore Maiman. When the coherent optical oscillator was first imagined in 1957, it was originally called the ‘Optical MASER’. This was ultimately changed to LASER.

Theoretical Principles of a MASER

The theoretical principles governing the operation of a MASER were first described by Joseph Weber of the University of Maryland, College Park at the Electron Tube Research Conference in June 1952 in Ottawa, with a summary published in the June 1953 Transactions of the Institute of Radio Engineers Professional Group on Electron Devices, and simultaneously by Nikolay Basov and Alexander Prokhorov from Lebedev Institute of Physics at an All-Union Conference on Radio-Spectroscopy held by the USSR Academy of Sciences in May 1952, subsequently published in October 1954.

Independently, Charles Hard Townes, James P. Gordon, and H. J. Zeiger built the first Ammonia MASER at Columbia University in 1953. This device used stimulated emission in a stream of energized ammonia molecules to produce amplification of microwaves at a frequency of about 24.0 gigahertz. Townes later worked with Arthur L. Schawlow to describe the principle of the Optical MASER or LASER of which Theodore H. Maiman created the first working model in 1960.

Technology

The MASER is based on the principle of stimulated emission proposed by Albert Einstein in 1917. When atoms have been induced into an excited energy state, they can amplify radiation at a frequency particular to the element or molecule used as the masing medium, similar to what occurs in the lasing medium in a Laser. By putting such an amplifying medium in a resonant cavity, feedback is created that can produce coherent radiation.

Following are some common types of MASERs.

- Atomic Beam MASERs
- Ammonia MASER
  - o Free Electron MASER
  - o Hydrogen MASER
- Gas MASERs
- Rubidium MASER
  - o Liquid-Dye and Chemical Laser
- Solid State MASERs
- Ruby MASER
  - o Whispering-Gallery Modes Iron-Sapphire MASER
- Dual Noble Gas MASER - The dual noble gas of a masing medium which is nonpolar.

MASERs serve as high precision frequency references. These ‘Atomic Frequency Standards’ are one of the many forms of atomic clocks. Masers were also used as low-noise microwave amplifiers in radio telescopes, though these have largely been replaced by amplifiers based on FETs (Field Effect Transistors).

4.7.1 Three Level MASER

A solid state MASER in which three energy levels are used is specifically defined as the ‘Three Level MASER’. The effective operation has been obtained with crystals of Gadolinium Ethyl Sulfate and crystals of Potassium Chromecyanide at the temperature of Liquid Helium.

Bloembergen's Three Level MASER: The three level method of population inversion was initially proposed by Basov and Prokhorov who suggested it for application in a molecular beam apparatus. Bloembergen subsequently suggested that the method could be readily applicable to diamagnetic solids containing weak concentration of paramagnetic ions presented the theoretical treatment of the Three Level MASER.

In a three level MASER, a transition between two energy levels is saturated in order to produce an induced emission of power at a lower frequency corresponding to a transition between an intermediate energy level and one or the other of the two saturated levels. In some situations, it is possible to obtain for the same system an induced emission of power at two frequencies given by the resonances between the intermediate energy level and both of the saturated levels. Additionally, in the absence of inhomogeneous broadening of the spectral line, a net induced emission can be obtained at certain portions of a resonant line and a net absorption at other frequencies within the line widths. Such effects become significant where $T_1 = T_2$ which is true for ordinary gaseous systems and individual spin systems in a majority of very dilute paramagnetic solids.

4.7.2 Ruby Laser

A Ruby Laser is a solid state Laser that uses a synthetic ruby crystal as its gain medium. The first working Laser was a 'Ruby Laser' made by Theodore H. 'Ted' Maiman at Hughes Research Laboratories on May 16, 1960.

Ruby Lasers produce pulses of coherent visible light at a wavelength of 694.3 nm, which is a deep red color. Typical Ruby Laser pulse lengths are on the order of a millisecond.

A Ruby Laser most often consists of a ruby rod that must be pumped with very high energy, usually from a flashtube, to achieve a population inversion. The rod is often placed between two mirrors, forming an optical cavity, which oscillate the light produced by the ruby's fluorescence, causing stimulated emission. Ruby is one of the few solid state Lasers that produce light in the visible range of the spectrum, lasing at 694.3 nanometers, in a deep red color, with a very narrow linewidth of 0.53 nm.

The Ruby Laser is referred as a 'Three Level Solid State Laser'. The active Laser medium (Laser Gain/Amplification Medium) is a synthetic ruby rod that is energized through optical pumping, typically by a xenon flashtube. Ruby has very broad and powerful absorption bands in the visual spectrum, at 400 and 550 nm, and a very long fluorescence lifetime of 3 milliseconds. This allows for very high energy pumping, since the pulse duration can be much longer than with other materials. While ruby has a very wide absorption profile, its conversion efficiency is much lower than other mediums.

Ruby also absorbs some of the light at its lasing wavelength. To overcome this absorption, the entire length of the rod needs to be pumped, leaving no shaded areas near the mountings. The active part of the ruby is the dopant, which consists of chromium ions suspended in a synthetic sapphire crystal. The dopant often comprises around 0.05% of the crystal and is responsible for all the absorption and emission of radiation. Depending on the concentration of the dopant, synthetic ruby usually comes in either pink or red.

4.7.3 Semiconductor Junction Laser

A Laser Diode (LD), also termed as Injection Laser Diode or ILD, or Diode Laser, is a **semiconductor** device similar to a light-emitting diode in which a diode pumped directly with electrical current can create lasing conditions at the **diode's junction**.

Driven by voltage, the doped p–n transition allows for recombination of an electron with a hole. Due to the drop of the electron from a higher energy level to a lower one, radiation, in the form of an emitted photon is generated. This is spontaneous emission. Stimulated emission can be produced when the process is continued and further generates light with the same phase, coherence and wavelength.

The choice of the semiconductor material determines the wavelength of the emitted beam, which in today's Laser Diodes range from InfraRed (IR) to the UltraViolet (UV) spectrum. Laser diodes are the most common type of Lasers produced, with a wide range of uses that include fiber optic communications, barcode readers, Laser pointers, CD/DVD/Blu-ray disc reading/recording, Laser printing, Laser scanning and light beam illumination.

Laser diodes form a subset of the larger classification of semiconductor p–n junction diodes. Forward electrical bias across the Laser diode causes the two species of charge carrier, holes and electrons, to be 'Injected' from opposite sides of the p–n junction into the depletion region. Holes are injected from the p-doped, and electrons from the n-doped, semiconductor. A depletion region, devoid of any charge carriers, forms as a result of the difference in electrical potential between n-type and p-type semiconductors wherever they are in physical contact. Due to the use of charge injection in powering most diode Lasers, this class of Lasers is sometimes termed 'Injection Lasers', or 'Injection Laser Diode (ILD)'. As diode Lasers are semiconductor devices, they may also be classified as Semiconductor Lasers.

4.8 PHOTOCONDUCTIVITY TRAPS

Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation, such as visible light, UltraViolet (UV) light, InfraRed (IR) light, or Gamma radiation.

When light is absorbed by a material, such as a semiconductor, the number of free electrons and holes increases, resulting in increased electrical conductivity. To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap, or to excite the impurities within the band gap. When a bias voltage and a load resistor are used in series with the semiconductor, a voltage drop across the load resistors can be measured when the change in electrical conductivity of the material varies the current through the circuit.

Classic examples of photoconductive materials include the following:

Photographic Film: Kodachrome, Fujifilm, Agfachrome, Ilford, etc., based on Silver Sulfide and Silver Bromide.

Conductive Polymer Polyvinylcarbazole: The Conductive Polymer Polyvinylcarbazole is used extensively in Photocopying (Xerography).

Lead Sulfide: Lead Sulfide is used in Infrared Detection applications, such as the U.S. Sidewinder and Soviet (now Russian) Atoll Heat-Seeking Missiles.

Selenium: Selenium is used in early Television and Xerography.

When a photoconductive material is connected as part of a circuit, it functions as a resistor whose resistance depends on the light intensity. In this context, the material is called a photoresistor, also called light-dependent resistor or photoconductor. The most common application of photoresistors is as photodetectors, i.e., devices that measure light intensity. Photoresistors are not the only type of photodetector, other types include Charge Coupled Devices (CCDs), photodiodes and phototransistors, but they are among the most common. Some photodetector applications in which photoresistors are often used include camera light meters, streetlights, clock radios, infrared detectors, nanophotonic systems and low-dimensional photo-sensors devices.

Trap in Photoconductivity

In physics, **trap** is any location within a solid, generally a semiconductor or an insulator, that restricts the movement of electrons and holes, i.e., equivalent positive electrical charges that result from the absence of an electron within a crystal structure. A trap consists of either a chemical impurity or an imperfection in the regular spacing of the atoms that make up the solid. Traps play a significant role in photoconduction, luminescence, and the operation of various electronic devices because the ability of a solid to carry an electrical current depends on the flow of electrons and holes through the solid.

A trap can capture and immobilize an electron or hole and prevent its recombination with the carrier of opposite charge as an electron hole pair. Electrons and holes may break free from traps quickly, or they may remain there for an extended period of time, for example several months or longer. Charge carriers can be released from traps by the addition of energy, such as irradiating the solid with light or by heating it.

Negative Photoconductivity

Some materials exhibit deterioration in photoconductivity upon exposure to illumination. One important example is Hydrogenated Amorphous Silicon (a-Si:H) in which a metastable reduction in photoconductivity is observable. Other materials that were reported to exhibit negative photoconductivity include Molybdenum Disulfide, Graphene, Indium Arsenide Nanowires, Decorated Carbon Nanotubes, and Metal Nanoparticles.

4.8.1 Space Charge Effect

Space charge is a concept in which excess electric charge is treated as a continuum of charge distributed over a region of space, either a volume or an area, rather than distinct point like charges. This model typically applies when charge carriers have been emitted from some region of a solid, the cloud of emitted carriers can form a space charge region if they are sufficiently spread out, or the charged atoms or molecules left behind in the solid can form a space charge region.

Space charge only occurs in dielectric media (including vacuum) because in a conductive medium the charge tends to be rapidly neutralized or screened. The sign of the space charge can be either negative or positive. This situation is perhaps most familiar in the area near a metal object when it is heated to incandescence in a vacuum. This effect was first observed by Thomas Edison in light bulb filaments, where it is sometimes called the Edison effect. Space charge is a significant phenomenon in many vacuum and solid state electronic devices.

When a metal object is placed in a vacuum and is heated to fluorescence or glow, then the energy is sufficient to cause electrons to 'Boil' away from the surface atoms and surround the metal object in a cloud of free electrons. This is called thermionic emission. The resulting cloud is negatively charged and can be attracted to any nearby positively charged object, thus producing an electric current which passes through the vacuum.

Space charge can result from a range of phenomena, but following are the most important:

1. Combination of the current density and spatially inhomogeneous resistance.
2. Ionization of species within the dielectric to form hetero charge.
3. Charge injection from electrodes and from a stress enhancement.
4. Polarization in structures, such as water trees. 'Water Tree' is a name given to a tree-like figure appearing in a water-impregnated polymer insulating cable.

In the Alternating Current (AC) most carriers injected at electrodes during a half of cycle are ejected during the next half cycle, so the net balance of charge on a cycle is practically zero. However, a small fraction of the carriers can be trapped at levels deep enough to retain them when the field is inverted. The amount of charge in AC should increase slower than in Direct Current (DC) and become observable after longer periods of time.

Hetero Charge and Homo Charge

Hetero charge means that the polarity of the space charge is opposite to that of neighbouring electrode, and homo charge is the reverse situation. Under high voltage application, a hetero charge near the electrode is expected to reduce the breakdown voltage, whereas a homo charge will increase it. After polarity reversal under AC conditions, the homo charge is converted to hetero space charge.

Mathematical Explanation

If the 'Vacuum' has a pressure of 10^{-6} mmHg or less, then the main vehicle of conduction is electrons. The emission current density (*J*) from the cathode, as a function of its thermodynamic temperature *T*, in the absence of space charge, is given by Richardson's law:

$$J = (1 - \tilde{r})A_0T^2 \exp\left(\frac{-\phi}{kT}\right)$$

Where,

- $A_0 = \frac{4\pi e m_\mathrm{e} k^2}{h^3} \approx 1.2 \times 10^6 \,\mathrm{A\,m^{-2}K^{-2}}$
- e = Elementary Positive Charge (i.e., Magnitude of Electron Charge)
- m_e = Electron Mass
- k = Boltzmann's Constant = $1.38 \times 10^{"23}$J/K
- h = Planck's Constant = $6.62 \times 10^{"34}$ J s
- ϕ = Work Function of the Cathode
- ø = Mean Electron Reflection Coefficient

The reflection coefficient can be as low as 0.105 but is usually near 0.5. For tungsten, $(1 - \breve{r})\, A_0 = 0.6$ to 1.0×10^6 A $\mathrm{m^{-2}\,K^{-2}}$, and $\phi = 4.52$ eV. At 2500 °C, the emission is 28207 A/m^2.

The emission current is many times greater than that normally collected by the electrodes, except in some pulsed valves, such as the cavity magnetron. Most of the electrons emitted by the cathode are driven back to it by the repulsion of the cloud of electrons in its neighbourhood. This is called the **space charge effect**. In the limit of large current densities, *J* is given by the Child–Langmuir equation.

4.8.2 Crystal Counters

Crystal counters are defined as an instrument used for detecting and measuring the intensity of high-energy radiation, in which particles collide with a crystal and momentarily increase its conductivity. Basically, a crystal counter is a particle detector in which the sensitive material is a dielectric or non-conducting crystal mounted between two metallic electrodes. It is defined as a solid state ionization chamber where the ionization is released by the particle which is a measure of its energy.

The first implementation of a crystal counter is attributed to van Heerden, who demonstrated that Silver Chloride crystals when cooled to low temperatures were capable of detecting Gamma (γ) Rays, Alpha (α) particles and Beta (β) particles. This is fully spectroscopic device and not the integrated device.

4.8.3 Luminescence

Luminescence is spontaneous emission of light by a substance not resulting from heat or 'Cold Light'. It is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions or stress on a crystal.

This distinguishes luminescence from incandescence, which is light emitted by a substance as a result of heating. Historically, radioactivity was thought of as a form of 'Radio Luminescence', although it is today considered to be separate since it involves more than electromagnetic radiation.

The following are types of luminescence:

- **Chemiluminescence:** The emission of light as a result of a chemical reaction.
  - o Bioluminescence, a result of biochemical reactions in a living organism.
  - o Electrochemiluminescence, a result of an electrochemical reaction.
  - o Lyoluminescence, a result of dissolving a solid (usually heavily irradiated) in a liquid solvent.
  - o Candoluminescence, is light emitted by certain materials at elevated temperatures, which differs from the black body emission expected at the temperature in question.
- **Crystalloluminescence:** Produced during crystallization.
- **Electroluminescence:** A result of an electric current passed through a substance.
  - o Cathodoluminescence, a result of a luminescent material being struck by electrons.
- **Mechanoluminescence:** A result of a mechanical action on a solid.
  - o Triboluminescence, generated when bonds in a material are broken when that material is scratched, crushed, or rubbed.
  - o Fractoluminescence, generated when bonds in certain crystals are broken by fractures.
  - o Piezoluminescence, produced by the action of pressure on certain solids.
  - o Sonoluminescence, a result of imploding bubbles in a liquid when excited by sound.
- **Photoluminescence:** A result of absorption of photons.
  - o Fluorescence, photoluminescence as a result of singlet–singlet electronic relaxation (typical lifetime: nanoseconds).
  - o Phosphorescence, photoluminescence as a result of triplet–triplet electronic relaxation (typical lifetime: microseconds to hours).
- **Radioluminescence:** A result of bombardment by ionizing radiation.
- **Thermoluminescence:** The re-emission of absorbed energy when a substance is heated.
  - o Cryoluminescence, the emission of light when an object is cooled, an example of this is wulfenite.

Luminescence occurs in some minerals when they are exposed to low powered sources of UltraViolet (UV) or InfraRed (IR) electromagnetic radiation, for example, portable UV lamps, at atmospheric pressure and atmospheric temperatures. This property of these minerals can be used during the process of mineral identification at rock outcrops in the field or in the laboratory.

4.9 STUDY OF BREAKDOWN IN SOLID DIELECTRICS AT LOW, HIGH AND INTERMEDIATE TEMPERATURES

Solid dielectric materials are used in all kinds of electrical circuits and devices to insulate one current carrying part from another when they operate at different voltages. A good dielectric should have low dielectric loss, high mechanical strength, should be free from gaseous inclusion, and moisture, and be resistant to thermal and chemical deterioration. Solid dielectrics have higher breakdown strength compared to liquids and gases.

Analysis of the breakdown of solid dielectrics are of extreme importance in insulation studies. When breakdown occurs, solids get permanently damaged while gases fully and liquids partly recover their dielectric strength after the applied electric field removed. The mechanism of breakdown is a complex phenomenon in the case of solids and varies depending on the time of application of voltage as shown in Figure (4.15).

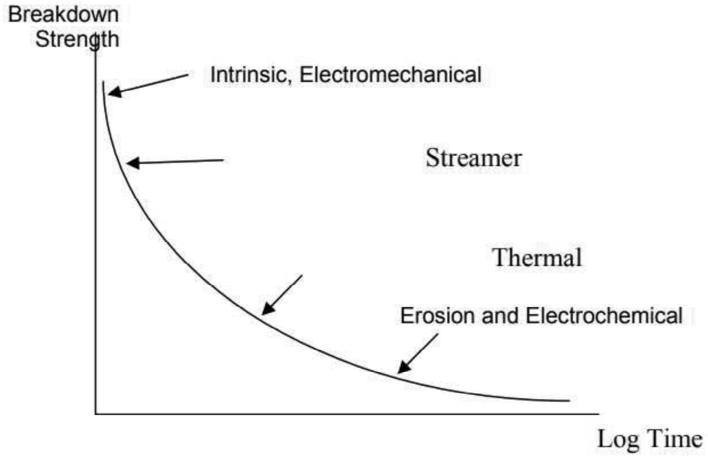


***Fig. 4.15** Variation of Breakdown Strength with Time after Application of Voltage*

The various breakdown mechanisms can be classified as follows:

1. Intrinsic or Ionic Breakdown
2. Electromechanical Breakdown
3. Failure due to Treeing and Tracking
4. Thermal Breakdown
5. Electrochemical Breakdown
6. Breakdown due to Internal Discharges

Electrical breakdown or dielectric breakdown is a process that occurs when an electrical insulating material, subjected to a high enough voltage, suddenly becomes an electrical conductor and electric current flows through it. All insulating materials undergo breakdown when the electric field caused by an applied voltage exceeds the material's dielectric strength. The voltage at which a given insulating object becomes conductive is called its breakdown voltage and depends on its size and shape. Under sufficient electrical potential, electrical breakdown can occur within solids, liquids, gases or vacuum. However, the specific breakdown mechanisms are different for each kind of dielectric medium.

Electrical breakdown may be a momentary event, as in an electrostatic discharge, or may lead to a continuous electric arc if protective devices fail to interrupt the current in a power circuit. In this case electrical breakdown can cause catastrophic failure of electrical equipment, and fire hazards.

Dielectric Strength and Breakdown Voltage

The electric field strength, in volts per meter, at which breakdown occurs is an intrinsic property of the insulating material called its dielectric strength. The electric field is usually caused by a voltage difference applied across the material. The applied voltage required to cause breakdown in a given insulating object is called the object's breakdown voltage. The electric field created in a given insulating object by an applied voltage varies depending on the size and shape of the object and the location on the object where the voltage is applied, so in addition to the material's dielectric strength, the breakdown voltage depends on these factors.

In a flat sheet of insulator between two flat metal electrodes, the electric field E is proportional to the voltage difference V divided by the thickness D of the insulator, so in general the breakdown voltage V_b is proportional to the dielectric strength E_{ds} and the length of insulation between two conductors,

$$V_b = DE_{ds}$$

However, the shape of the conductors can influence the breakdown voltage.

Breakdown Process

Breakdown is a local process, and in an insulating medium subjected to a high voltage difference begins at whatever point in the insulator the electric field first exceeds the local dielectric strength of the material. Since the electric field at the surface of a conductor is highest at protruding parts, sharp points and edges, in a homogeneous insulator like air or oil adjacent to a conductor breakdown usually starts at these points. If the breakdown is caused by a local defect in a solid insulator, such as a crack or bubble in a ceramic insulator, it may remain limited to a small region; this is called partial discharge. In a gas adjacent to a sharp pointed conductor, local breakdown processes, corona discharge or brush discharge, can allow current to leak off the conductor into the gas as ions. However, usually in a homogeneous solid insulator after one region has broken down and become conductive there is no voltage drop across it, and the full voltage difference is applied to the remaining length of the insulator. Since the voltage drop is now across a shorter length, this creates a higher electric field in the remaining material, which causes more material to break down. So, the breakdown region rapidly, within microseconds, spreads in the direction of the voltage gradient from one end of the insulator to the other, until a continuous conductive path is created through the material between the two contacts applying the voltage difference, allowing a current to flow between them.

Electrical breakdown can also occur without an applied voltage, due to an electromagnetic wave. When a sufficiently intense electromagnetic wave passes through a material medium, the electric field of the wave can be strong enough to cause temporary electrical breakdown. For example, a laser beam focused to a small spot in air can cause electrical breakdown and ionization of the air at the focal point.

Breakdown Mechanism

Breakdown mechanisms differ in solids, liquids, and gasses. Breakdown is influenced by electrode material, sharp curvature of conductor material, resulting in locally intensified electric fields, the size of the gap between the electrodes, and the density of the material in the gap.

Solids: In solid materials, such as in power cables a long-time partial discharge typically precedes breakdown, degrading the insulators and metals nearest to the voltage gap. Ultimately the partial discharge chars through a channel of carbonized material that conducts current across the gap.

Liquids: Possible mechanisms for breakdown in liquids include bubbles, small impurities, and electrical superheating. The process of breakdown in liquids is complicated by hydrodynamic effects, since additional pressure is exerted on the fluid by the non-linear electrical field strength in the gap between the electrodes.

In liquefied gases used as coolants for superconductivity, such as Helium at 4.2 K or Nitrogen at 77 K, bubbles can induce breakdown.

In oil-cooled and oil-insulated transformers the field strength for breakdown is about 20 kV/mm, as compared to 3 kV/mm for dry air. Despite the purified oils used, small particle contaminants are blamed.

Gases: Electrical breakdown occurs within a gas when the dielectric strength of the gas is exceeded. Regions of intense voltage gradients can cause nearby gas to partially ionize and begin conducting. This is done deliberately in low pressure discharges, such as in fluorescent lights. The voltage that leads to electrical breakdown of a gas is approximated by Paschen's Law.

Partial discharge in air causes the 'Fresh Air' smell of ozone during thunderstorms or around high voltage equipment. Although air is normally an excellent insulator, when stressed by a sufficiently high voltage, an electric field of about 3×10^6 V/m or 3 kV/mm, air can begin to break down, becoming partially conductive. Across relatively small gaps, breakdown voltage in air is a function of gap length times pressure. If the voltage is sufficiently high, complete electrical breakdown of the air will culminate in an electrical spark or an electric arc that bridges the entire gap.

4.9.1 Influence of Annealing and Temperature

Annealing is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable. It involves heating a material above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time and then cooling.

In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to a change in ductility and hardness. As the material cools it recrystallizes. For many alloys, including carbon steel, the crystal grain size and phase composition, which ultimately determine the material properties, are dependent on the heating rate and cooling rate. Hot working or cold working after the annealing process alters the metal structure, so further heat treatments may be used to achieve the properties required. With knowledge of the composition and phase diagram, heat treatment can be used to adjust from harder and more brittle to softer and more ductile.

In the case of ferrous metals, such as steel, annealing is performed by heating the material, generally until glowing, for a while and then slowly letting it cool to room temperature in still air. Copper, Silver and Brass can be either cooled slowly in air, or quickly by quenching in water.

Thermodynamics

Annealing occurs by the diffusion of atoms within a solid material, so that the material progresses towards its equilibrium state. Heat increases the rate of diffusion by providing the energy needed to break bonds. The movement of atoms has the effect of redistributing and eradicating the dislocations in metals and to a lesser extent in ceramics. This alteration to existing dislocations allows a metal object to deform more easily, increasing its ductility.

The amount of process initiating Gibbs free energy in a deformed metal is also reduced by the annealing process, this reduction of Gibbs free energy is termed stress relief.

The relief of internal stresses is a thermodynamically spontaneous process, however, at room temperatures, it is a very slow process. The high temperatures at which annealing occurs serve to accelerate this process.

The reaction that facilitates returning the cold-worked metal to its stress-free state has many reaction pathways, mostly involving the elimination of lattice vacancy gradients within the body of the metal. The creation of lattice vacancies is governed by the Arrhenius equation, and the migration/diffusion of lattice vacancies are governed by Fick's laws of diffusion.

In steel, there is a decarburation mechanism that can be described as three distinct events, namely the reaction at the steel surface, the interstitial diffusion of carbon atoms and the dissolution of carbides within the steel.

Stages

The three stages of the annealing process that proceed as the temperature of the material is increased are recovery, recrystallization, and grain growth. The first stage is recovery, and it results in softening of the metal through removal of primarily linear defects called dislocations and the internal stresses they cause. Recovery occurs at the lower temperature stage of all annealing processes and before the appearance of new strain free grains. The grain size and shape do not change. The second stage is recrystallization, where new strain free grains nucleate and grow to replace those deformed by internal stresses. If annealing is allowed to continue once recrystallization has completed, then grain growth, the third stage occurs. In grain growth, the microstructure starts to coarsen and may cause the metal to lose a substantial part of its original strength. This can however be regained with hardening.

The high temperature of annealing may result in oxidation of the metal's surface, resulting in scale. If scale must be avoided, annealing is carried out in a special atmosphere, such as with endothermic gas, a mixture of carbon monoxide, hydrogen gas, and nitrogen gas. Annealing is also done in forming gas, a mixture of hydrogen and nitrogen. The magnetic properties of Mu-Metal Espey Cores are introduced by annealing the alloy in a hydrogen atmosphere.

In the semiconductor industry, silicon wafers are annealed to repair atomic level disorder from steps like ion implantation. In the process step, dopant atoms, usually boron, phosphorus or arsenic, move into substitutional positions in the crystal lattice, which allows these dopant atoms to function properly as dopants in the semiconducting material.

4.9.2 Effect of Thickness of Electrode Edge Effects and Time Lag

An electrode is an electrical conductor used to make contact with a nonmetallic part of a circuit, for example a semiconductor, an electrolyte, a vacuum or air. Fundamentally, an electrode in an electrochemical cell and is referred to as either an anode or a cathode, words that were coined by William Whewell at Faraday's request. The anode is now defined as the electrode at which electrons leave the cell and oxidation occurs indicated by a minus symbol, "", and the cathode as the electrode at which electrons enter the cell and reduction occurs indicated by a plus symbol, '+'. Each electrode may become either the anode or the cathode depending on the direction of current through the cell. A bipolar electrode is an electrode that functions as the anode of one cell and the cathode of another cell.

Using electrodes that are porous increases the reactive surface area but also the distance that ions and electrons have to travel. Thicker electrodes, through their larger surface area, reduce the activation overpotential but increase the ohmic losses. There will therefore be an electrode thickness for which the voltage losses are minimal, corresponding to a maximum energy efficiency.

Theoretically the mechanism of spark breakdown is considered as a function of ionization processes under uniform field conditions. In practical engineering designs, the breakdown due to rapidly changing voltages or impulse voltages is of great importance. Actually, there is a time difference between the application of a voltage sufficient to cause breakdown and the occurrence of breakdown itself. This time difference is called as the **time lag**. In considering the time lag observed between the application of a voltage sufficient to cause breakdown and the actual breakdown the two basic processes of concern are the appearance of avalanche initiating electrons and the temporal growth of current after the criterion for static breakdown is satisfied.

In the case of slowly varying fields, there is usually no difficulty in finding an initiatory electron from natural sources, for example cosmic rays, detachment of gaseous ions, etc. However, for impulses of short duration (around 1 microsecond), depending on the gap volume, natural sources may not be sufficient to provide an initiating electron while the voltage is applied, and in the absence of any other source, breakdown will not occur.

The time t_s which elapses between the application of a voltage greater than or equal to the static breakdown voltage (V_s) to the spark gap and the appearance of a suitably placed initiatory electron is called the statistical time lag of the gap, the appearance being usually statistically distributed. After such an electron appears, the time t_f required by the ionisation processes to generate a current of a magnitude which may be used to specify breakdown of the gap is known as the formative time lag. The sum $t_f + t_s = t$ is the total time lag.

The ratio V/Vs, which is greater than unity, is called the impulse ratio, and clearly depends on $t_s + t_f$ and the rate of growth of the applied voltage.

Check Your Progress

12. What is exciton?
13. Define the term colour centres.
14. What is F-centre or Farbe centre?
15. State about MASER.
16. What is Ruby Laser?
17. Define the term Laser Diode (LD).
18. State bout the photoconductivity.
19. Define photoconductivity trap.
20. What are crystal counters?
21. State about the breakdown of solid dielectrics.
22. What is annealing?

4.10 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Superconductivity is a phenomenon in which certain metals, alloys and ceramics conduct electricity without resistance when, it is cooled below a certain temperature called the critical temperature. Basically, superconductivity is a set of physical properties observed in certain materials where electrical resistance vanishes and magnetic flux fields are expelled from the material. Any material exhibiting these properties is a superconductor. The superconductivity phenomenon was discovered in 1911 by Dutch physicist Heike Kamerlingh Onnes and it is still an exciting field of discovery and technological applications.
2. When current is made to flow through a superconducting ring (say a loop of lead wire) which is at a temperature either equal to its T_c value or less than its T_c value, it was observed that the current was flowing through the material

without any significant loss in its value. This steady flow of current in a superconducting ring without any potential deriving it, is called the persistent current.

3. Following three important factors define a superconducting state:
    - Critical Temperature T_c.
    - Critical Current Density J_c.
    - Critical Magnetic Field H_c.

    Each of the above three parameters are very dependent on the other two properties. To sustain superconducting state in a material it is required to have both the current density and magnetic field, as well as the temperature, to remain below their critical values; and all of which depend on the material.
4. Paul Ehrenfest classified phase transitions based on the behaviour of the thermodynamic free energy as a function of other thermodynamic variables. Under this scheme, phase transitions were labelled by the lowest derivative of the free energy that is discontinuous at the transition. First-order phase transitions exhibit a discontinuity in the first derivative of the free energy with respect to some thermodynamic variable. The various solid/liquid/gas transitions are classified as first-order transitions because they involve a discontinuous change in density, which is the (inverse of the) first derivative of the free energy with respect to pressure. Second-order phase transitions are continuous in the first derivative, the order parameter which is the first derivative of the free energy with respect to the external field, is continuous across the transition, but exhibit discontinuity in a second derivative of the free energy.
5. The Meissner effect or Meissner–Ochsenfeld effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state when it is cooled below the critical temperature. This expulsion will repel a nearby magnet. The German physicists Walther Meissner and Robert Ochsenfeld discovered this phenomenon in 1933 by measuring the magnetic field distribution outside superconducting tin and lead samples.

    A superconductor with little or no magnetic field within it is said to be in the Meissner state. The Meissner state breaks down when the applied magnetic field is too strong. Superconductors can be divided into two classes according to how this breakdown occurs.

    The Meissner effect was given a phenomenological explanation by the brothers Fritz and Heinz London, who showed that the electromagnetic free energy in a superconductor is minimized provided,

    $$\nabla^2 \mathbf{H} = \lambda^{-2} \mathbf{H}$$

    Where H is the magnetic field and λ is the London penetration depth.
6. In solid state physics, an energy gap is an energy range in a solid where no electron states exist, i.e., an energy range where the density of states vanishes. If an energy gap exists in the band structure of a material, then it is termed as

the band gap. The physical properties of semiconductors are to a large extent determined by their band gaps, but also for insulators and metals the band structure, and thus any possible band gaps govern their electronic properties.

7. Microwave is a form of ElectroMagnetic (EM) radiation with wavelengths ranging from about one meter to one millimeter corresponding to frequencies between 300 MHz and 300 GHz, respectively. Microwaves occupy a place in the electromagnetic spectrum with frequency above ordinary radio waves and below infrared light. The Microwaves have the Wavelength of 1 mm – 1 m, Frequency (Hz) as 300 GHz – 300 MHz, and the Photon Energy (eV) as 1.24 meV – 1.24 μeV.

   InfraRed (IR), sometimes also termed as infrared light, is an ElectroMagnetic Radiation (EMR) with wavelengths longer than those of visible light. It is therefore invisible to the human eye. IR is generally understood to encompass wavelengths from around 1 millimeter (300 GHz) to the nominal red edge of the visible spectrum, around 700 nanometers (frequency 430 THz), although the longer IR wavelengths are often designated rather as terahertz radiation. Infrared radiation was discovered in 1800 by astronomer Sir William Herschel, who discovered a type of invisible radiation in the spectrum lower in energy than red light, by means of its effect on a thermometer. Infrared radiation extends from the nominal red edge of the visible spectrum at 700 nanometers (nm) to 1 millimeter (mm). This range of wavelengths corresponds to a frequency range of approximately 430 THz down to 300 GHz. Beyond infrared is the microwave portion of the electromagnetic spectrum. Infrared has the Wavelength of about 700 nm – 1 mm, the Frequency (Hz) as 300 GHz – 430 THz, and the Photon Energy (eV) as 1.7 eV – 1.24 meV. Characteristically, the infrared part of the electromagnetic spectrum covers the range from roughly 300 GHz to 400 THz (1 mm – 750 nm) and it can be divided into three parts, namely Far InfraRed (FIR), Mid InfraRed (MIR) and Near InfraRed (NIR).

8. Magnetic levitation or maglev is the process by which an object is suspended above another object with no other support but magnetic fields. We know that a diamagnetic substance repels a magnetic field. Thus, the perfect diamagnetic property of superconductors makes them suitable for achieving friction less motion in motors and bearing. The phenomenon of magnetic levitation is based on Meissner effect.

9. Coherence length is the propagation distance over which a coherent wave (e.g., an electromagnetic wave) maintains a specified degree of coherence. Wave interference is strong when the paths taken by all of the interfering waves differ by less than the coherence length. A wave with a longer coherence length is closer to a perfect sinusoidal wave.

10. In 1957, the American physicists, John Bardeen, Leon N Cooper and John Robert Schrieffer proposed a microscopic theory (i.e., a quantum theory) to account for the observed properties of superconductors, which is known as BCS theory. This theory involves the electron interactions through phonon as mediators. This theory is based on the formation of Cooper pairs which is purely a quantum mechanical concept.

When an electron comes near a positive ion core of the lattice, it experiences an attractive force because of the opposite charge polarity between the electron and the ion core. Due to this interaction (electron-lattice interaction) the ion core will be displaced from its position which is called lattice distortion. The distortion causes an increase in the density of ions in the distorted region. The higher density of ions in the distorted region may attract an another electron.

11. Quantum tunnelling is the quantum mechanical phenomenon where a wavefunction can propagate through a potential barrier. The transmission through the barrier can be finite and depends exponentially on the barrier height and barrier width. The wavefunction may disappear on one side and reappear on the other side. The wavefunction and its first derivative are continuous.

    Tunnel junctions are described on the basis of quantum tunnelling, where a simple barrier can be created by separating two conductors with a very thin insulator. The Superconducting Tunnel Junction (STJ) — also known as a Superconductor–Insulator–Superconductor (SIS) tunnel junction— is an electronic device consisting of two superconductors separated by a very thin layer of insulating material. Current passes through the junction via the process of quantum tunnelling. The STJ is a type of Josephson junction, though not all the properties of the STJ are described by the Josephson effect.

12. An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

    An exciton can form when a material absorbs a photon of higher energy than its bandgap. This excites an electron from the valence band into the conduction band. The concept of 'Excitons' was first proposed by Yakov Frenkel in 1931, when he described the excitation of atoms in a 'Lattice of Insulators'. He proposed that this excited state would be able to travel in a particle-like fashion through the lattice without the net transfer of charge.

13. The term 'Colour Centre' refers to the defect in the regular spacing of atoms within a solid that absorbs visible light of a particular colour or InfraRed (IR) or UltraViolet (UV) radiation, thus providing a characteristic colour to the solid. Each colour centre involves the absence of an atom from the place it would normally occupy in the solid and the relation of an electron with such an empty place or vacancy. Solids without colour centres may still have colour if impurity atoms or other structures that absorb light are present.

14. There are many types of colour centres. The best understood one, called an F-Centre or Farbe Centre or Color Center is a type of crystallographic defect in which an anionic vacancy in a crystal lattice is occupied by one or more unpaired electrons. Electrons in such a vacancy in a crystal lattice tend to absorb light in the visible spectrum such that a material that is usually transparent becomes coloured. Typically, the F-Centre or Farbe Centre

results from the absence of a negatively charged ion from a particular point in an ionic solid.

The term F-Centre or Farbe Centre is adopted from the original German word 'Farbzentrum', where 'Farbe' means 'Color' and 'Zentrum' means 'Center'. An F-center, Farbe center is used to identify many compounds, especially Zinc Oxide (Yellow).

15. The term MASER, an acronym for 'Microwave Amplification by Stimulated Emission of Radiation', is a device that produces coherent electromagnetic waves through amplification by stimulated emission. The first MASER was built by Charles H. Townes, James P. Gordon, and Herbert J. Zeiger at Columbia University in 1953. Modern MASERs can be designed to generate electromagnetic waves at not only microwave frequencies but also radio and infrared frequencies.

    As per the Encyclopedia Britannica, "The MASER, an acronym derived from 'Microwave (or Molecular) Amplification by Stimulated Emission of Radiation', is a device that produces and amplifies electromagnetic radiation mainly in the microwave region of the spectrum. The MASER operates according to the same basic principle as the LASER, the name of which is formed from the acronym for 'Light Amplification by Stimulated Emission of Radiation' and shares many of its characteristics".

16. A Ruby Laser is a solid state Laser that uses a synthetic ruby crystal as its gain medium. The first working Laser was a 'Ruby Laser' made by Theodore H. 'Ted' Maiman at Hughes Research Laboratories on May 16, 1960. Ruby Lasers produce pulses of coherent visible light at a wavelength of 694.3 nm, which is a deep red color. Typical Ruby Laser pulse lengths are on the order of a millisecond. The Ruby Laser is a Three Level Solid State Laser. The active Laser medium (Laser Gain/Amplification Medium) is a synthetic ruby rod that is energized through optical pumping, typically by a xenon flashtube. Ruby has very broad and powerful absorption bands in the visual spectrum, at 400 and 550 nm, and a very long fluorescence lifetime of 3 milliseconds.

17. A Laser Diode (LD), also termed as Injection Laser Diode or ILD, or Diode Laser, is a semiconductor device similar to a light-emitting diode in which a diode pumped directly with electrical current can create lasing conditions at the diode's junction. Driven by voltage, the doped p–n transition allows for recombination of an electron with a hole. Due to the drop of the electron from a higher energy level to a lower one, radiation, in the form of an emitted photon is generated. This is spontaneous emission. Stimulated emission can be produced when the process is continued and further generates light with the same phase, coherence and wavelength.

18. Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation, such as visible light, UltraViolet (UV) light, InfraRed (IR) light, or Gamma radiation. When light is absorbed by a material, such as a semiconductor, the number of free electrons and holes increases, resulting in increased electrical conductivity.

19. In physics, trap is any location within a solid, generally a semiconductor or an insulator, that restricts the movement of electrons and holes, i.e., equivalent positive electrical charges that result from the absence of an electron within a crystal structure. A trap consists of either a chemical impurity or an imperfection in the regular spacing of the atoms that make up the solid. A trap can capture and immobilize an electron or hole and prevent its recombination with the carrier of opposite charge as an electron hole pair.
20. Crystal counters are defined as an instrument used for detecting and measuring the intensity of high-energy radiation, in which particles collide with a crystal and momentarily increase its conductivity. Basically, a crystal counter is a particle detector in which the sensitive material is a dielectric or non-conducting crystal mounted between two metallic electrodes. It is defined as a solid state ionization chamber where the ionization is released by the particle which is a measure of its energy.
21. The breakdown of solid dielectrics are of extreme importance in insulation studies. When breakdown occurs, solids get permanently damaged while gases fully and liquids partly recover their dielectric strength after the applied electric field removed. The mechanism of breakdown is a complex phenomenon in the case of solids and varies depending on the time of application of voltage. Electrical breakdown or dielectric breakdown is a process that occurs when an electrical insulating material, subjected to a high enough voltage, suddenly becomes an electrical conductor and electric current flows through it. The voltage at which a given insulating object becomes conductive is called its breakdown voltage and depends on its size and shape. Breakdown mechanisms differ in solids, liquids, and gasses. Breakdown is influenced by electrode material, sharp curvature of conductor material, resulting in locally intensified electric fields, the size of the gap between the electrodes, and the density of the material in the gap.
22. Annealing is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable. It involves heating a material above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time and then cooling. In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to a change in ductility and hardness. As the material cools it recrystallizes.

4.11 SUMMARY

- Superconductivity is a phenomenon in which certain metals, alloys and ceramics conduct electricity without resistance when, it is cooled below a certain temperature called the critical temperature.
- Superconductivity is a set of physical properties observed in certain materials where electrical resistance vanishes, and magnetic flux fields are expelled from the material. Any material exhibiting these properties is a superconductor.

- Unlike an ordinary metallic conductor, whose resistance decreases gradually as its temperature is lowered even down to near absolute zero, a superconductor has a characteristic critical temperature below which the resistance drops abruptly to zero.
- The superconductivity phenomenon was discovered in 1911 by Dutch physicist Heike Kamerlingh Onnes and it is still an exciting field of discovery and technological applications.
- The electrical resistance of a superconducting material is very low and is of the order of 10^{-7} Ωm.
- The critical or transition temperature T_c value of a superconductor is found to vary with its isotopic mass. This variation in T_c with its isotopic mass is called the isotopic effect.
- When current is made to flow through a superconducting ring (say a loop of lead wire) which is at a temperature either equal to its T_c value or less than its T_c value, it was observed that the current was flowing through the material without any significant loss in its value. This steady flow of current in a superconducting ring without any potential deriving it, is called the persistent current.
- The complete expulsion of all the magnetic field by a superconducting material is called the "Meissner Effect".
- In general, the superconducting state is defined by the following three important factors:

  1. Critical Temperature T_c.
  2. Critical Current Density J_c.
  3. Critical Magnetic Field H_c.

  Each of the above three parameters is very dependent on the other two properties. To sustain superconducting state in a material it is required to have both the current density and magnetic field, as well as the temperature, to remain below their critical values; and all of which depend on the material.
- The theoretical model that was first conceived for superconductivity was completely classical, it is summarized by London constitutive equations. It was put forward by the brothers Fritz and Heinz London in 1935, shortly after the discovery that magnetic fields are expelled from superconductors.
- By using the London equation, one can obtain the dependence of the magnetic field inside the superconductor on the distance to the surface.
- In thermodynamics, phase transitions or phase changes are the physical processes of transition between a state of a medium, identified by some parameters, and another one, with different values of the parameters.
- Paul Ehrenfest classified phase transitions based on the behaviour of the thermodynamic free energy as a function of other thermodynamic variables. Under this scheme, phase transitions were labelled by the lowest derivative of the free energy that is discontinuous at the transition.
- First-order phase transitions exhibit a discontinuity in the first derivative of the free energy with respect to some thermodynamic variable. The various

solid/liquid/gas transitions are classified as first-order transitions because they involve a discontinuous change in density, which is the (inverse of the) first derivative of the free energy with respect to pressure.

- Second-order phase transitions are continuous in the first derivative, the order parameter which is the first derivative of the free energy with respect to the external field, is continuous across the transition, but exhibit discontinuity in a second derivative of the free energy.
- First-order phase transitions are those that involve a latent heat. During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy per volume.
- Second-order phase transitions are also called 'Continuous Phase Transitions'. They are characterized by a divergent susceptibility, an infinite correlation length, and a power law decay of correlations near criticality.
- A superconductor can be Type-I superconductor, meaning it has a single critical field, above which all superconductivity is lost and below which the magnetic field is completely expelled from the superconductor; or Type-II superconductor, meaning it has two critical fields, between which it allows partial penetration of the magnetic field through isolated points. These points are called vortices.
- Superconductor material classes include chemical elements, for example Mercury or Lead, Alloys, such as Niobium–Titanium, Germanium–Niobium, and Niobium Nitride, Ceramics, such as YBCO and Magnesium Diboride, Superconducting Pnictides, such as Fluorine-Doped LaOFeAs or Organic Superconductors Fullerenes and Carbon Nanotubes.
- Yttrium Barium Copper Oxide (YBCO) is a family of crystalline chemical compounds, famous for displaying high-temperature superconductivity. It includes the first material ever discovered to become superconducting above the boiling point of liquid nitrogen (77 K) at about 92 K.
- The Meissner effect or Meissner–Ochsenfeld effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state when it is cooled below the critical temperature. This expulsion will repel a nearby magnet.
- A superconductor with little or no magnetic field within it is said to be in the Meissner state. The Meissner state breaks down when the applied magnetic field is too strong. Superconductors can be divided into two classes according to how this breakdown occurs.
- The Meissner effect was given a phenomenological explanation by the brothers Fritz and Heinz London, who showed that the electromagnetic free energy in a superconductor is minimized provided,

$$\nabla^2 \mathbf{H} = \lambda^{-2} \mathbf{H}$$

Where H is the magnetic field and λ is the London penetration depth.

- Superconductors in the Meissner state exhibit perfect diamagnetism or superdiamagnetism meaning that the total magnetic field is very close to zero deep inside them, many penetration depths from the surface. This means that their volume magnetic susceptibility is $\chi_v = -1$. Diamagnetics are defined by the generation of a spontaneous magnetization of a material which directly opposes the direction of an applied field.

- Heat capacity or thermal capacity is a physical property of matter, defined as the amount of heat to be supplied to an object to produce a unit change in its temperature. The SI unit of heat capacity is Joule per Kelvin (J/K).
- Heat capacity is an extensive property. The corresponding intensive property is the specific heat capacity, found by dividing the heat capacity of an object by its mass.
- Dividing the heat capacity by the amount of substance in moles yields its molar heat capacity. The volumetric heat capacity measures the heat capacity per volume. The heat capacity of an object, denoted by C, is the limit,

  $$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$$

  Where ΔQ is the amount of heat that must be added to the object of mass *M* in order to raise its temperature by ΔT.
- In solid state physics, an energy gap is an energy range in a solid where no electron states exist, i.e., an energy range where the density of states vanishes.
- If an energy gap exists in the band structure of a material, then it is termed as the band gap. The physical properties of semiconductors are to a large extent determined by their band gaps, but also for insulators and metals the band structure, and thus any possible band gaps govern their electronic properties.
- For superconductors the energy gap is a region of suppressed density of states around the Fermi energy, with the size of the energy gap much smaller than the energy scale of the band structure.
- The superconducting energy gap is a key aspect in the theoretical description of superconductivity and thus features prominently in BCS theory. Here, the size of the energy gap indicates the energy gain for two electrons upon formation of a Cooper pair.
- In the microwave Photonic Band Gap (PBG) materials, the magnetic permeability μ varies periodically within the material. This material is fabricated using a periodic arrangement of arrays of magnetic nanowires. As for dielectric or metallic PBG, the band gap behaviour varies with the geometrical parameters fixing the spatial periodicity of the magnetic structure. The magnetic photonic band gap is induced by the presence of a ferromagnetic resonance effect in the vicinity of the band gap.
- Microwave is a form of ElectroMagnetic (EM) radiation with wavelengths ranging from about one meter to one millimeter corresponding to frequencies between 300 MHz and 300 GHz, respectively.
- Microwaves occupy a place in the electromagnetic spectrum with frequency above ordinary radio waves and below infrared light. The Microwaves have the Wavelength of 1 mm – 1 m, Frequency (Hz) as 300 GHz – 300 MHz, and the Photon Energy (eV) as 1.24 meV – 1.24 μeV.

- InfraRed (IR), sometimes also termed as infrared light, is an ElectroMagnetic Radiation (EMR) with wavelengths longer than those of visible light. It is therefore invisible to the human eye.
- IR is generally understood to encompass wavelengths from around 1 millimeter (300 GHz) to the nominal red edge of the visible spectrum, around 700 nanometers (frequency 430 THz), although the longer IR wavelengths are often designated rather as terahertz radiation.
- Infrared radiation was discovered in 1800 by astronomer Sir William Herschel, who discovered a type of invisible radiation in the spectrum lower in energy than red light, by means of its effect on a thermometer.
- Infrared radiation extends from the nominal red edge of the visible spectrum at 700 nanometers (nm) to 1 millimeter (mm). This range of wavelengths corresponds to a frequency range of approximately 430 THz down to 300 GHz. Beyond infrared is the microwave portion of the electromagnetic spectrum.
- Infrared has the Wavelength of about 700 nm – 1 mm, the Frequency (Hz) as 300 GHz – 430 THz, and the Photon Energy (eV) as 1.7 eV – 1.24 meV.
- Characteristically, the infrared part of the electromagnetic spectrum covers the range from roughly 300 GHz to 400 THz (1 mm – 750 nm) and it can be divided into three parts, namely Far InfraRed (FIR), Mid InfraRed (MIR) and Near InfraRed (NIR).
- Magnetic levitation or maglev is the process by which an object is suspended above another object with no other support but magnetic fields. We know that a diamagnetic substance repels a magnetic field. Thus, the perfect diamagnetic property of superconductors makes them suitable for achieving friction less motion in motors and bearing. The phenomenon of magnetic levitation is based on Meissner effect.
- Two superconductors separated by a very thin strip of an insulator forms a Josephson junction.
- Coherence length is the propagation distance over which a coherent wave (e.g., an electromagnetic wave) maintains a specified degree of coherence. Wave interference is strong when the paths taken by all of the interfering waves differ by less than the coherence length. A wave with a longer coherence length is closer to a perfect sinusoidal wave.
- Coherence length is important in holography and telecommunications engineering. Coherence length is usually applied to the optical regime.
- In 1957, the American physicists, John Bardeen, Leon N Cooper and John Robert Schrieffer proposed a microscopic theory (i.e., a quantum theory) to account for the observed properties of superconductors, which is known as BCS theory.
- This theory involves the electron interactions through phonon as mediators. This theory is based on the formation of Cooper pairs which is purely a quantum mechanical concept.

- When an electron comes near a positive ion core of the lattice, it experiences an attractive force because of the opposite charge polarity between the electron and the ion core. Due to this interaction (electron-lattice interaction) the ion core will be displaced from its position which is called lattice distortion. The distortion causes an increase in the density of ions in the distorted region. The higher density of ions in the distorted region may attract an another electron.
- Quantum tunnelling is the quantum mechanical phenomenon where a wavefunction can propagate through a potential barrier. The transmission through the barrier can be finite and depends exponentially on the barrier height and barrier width. The wavefunction may disappear on one side and reappear on the other side. The wavefunction and its first derivative are continuous.
- In steady-state, the probability flux in the forward direction is spatially uniform. No particle or wave is lost. Tunnelling occurs with barriers of thickness around 1–3 nm and smaller.
- A simple barrier can be created by separating two conductors with a very thin insulator. These are tunnel junctions, the study of which requires understanding quantum tunnelling.
- Josephson junctions take advantage of quantum tunnelling and the superconductivity of some semiconductors to create the Josephson effect.
- The Superconducting Tunnel Junction (STJ) — also known as a Superconductor–Insulator–Superconductor (SIS) tunnel junction— is an electronic device consisting of two superconductors separated by a very thin layer of insulating material. Current passes through the junction via the process of quantum tunnelling. The STJ is a type of Josephson junction, though not all the properties of the STJ are described by the Josephson effect.
- Optical property of a material is defined as its interaction with electromagnetic radiation in the visible. Visible light is one form of electromagnetic radiation with wavelengths ranging from 0.39 to 0.77 μm. Light can be considered as having waves and consisting of particles called photons. Basically, the optical properties provide an important tool for studying energy band structure, impurity levels, excitons, localized defects, lattice vibrations, and certain magnetic excitations in insulators.
- An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.
- An exciton can form when a material absorbs a photon of higher energy than its bandgap. This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively charged electron hole, an abstraction for the location from which an electron was moved.
- The electron in the conduction band is then less attracted to this localized hole due to the repulsive Coulomb forces from large numbers of electrons

surrounding the hole and excited electron. These repulsive forces provide a stabilizing energy balance.

- The electron and hole may have either parallel or antiparallel spins. The spins are coupled by the exchange interaction, giving rise to exciton fine structure. In periodic lattices, the properties of an exciton show momentum (k-vector) dependence.
- The concept of 'Excitons' was first proposed by Yakov Frenkel in 1931, when he described the excitation of atoms in a 'Lattice of Insulators'. He proposed that this excited state would be able to travel in a particle-like fashion through the lattice without the net transfer of charge.
- Excitons are often treated in the two limiting cases of small dielectric constant versus large dielectric constant corresponding to Frenkel exciton and Wannier–Mott exciton, respectively.
- The term 'Colour Centre' refers to the defect in the regular spacing of atoms within a solid that absorbs visible light of a particular colour or InfraRed (IR) or UltraViolet (UV) radiation, thus providing a characteristic colour to the solid.
- Each colour centre involves the absence of an atom from the place it would normally occupy in the solid and the relation of an electron with such an empty place or vacancy. Solids without colour centres may still have colour if impurity atoms or other structures that absorb light are present.
- There are many types of colour centres. The best understood one, called an F-Centre or Farbe Centre or Color Center is a type of crystallographic defect in which an anionic vacancy in a crystal lattice is occupied by one or more unpaired electrons. Electrons in such a vacancy in a crystal lattice tend to absorb light in the visible spectrum such that a material that is usually transparent becomes coloured.
- The term F-Centre or Farbe Centre is adopted from the original German word 'Farbzentrum', where 'Farbe' means 'Color' and 'Zentrum' means 'Center'. An F-center, Farbe center is used to identify many compounds, especially Zinc Oxide (Yellow).
- Typically, the F-Centre or Farbe Centre results from the absence of a negatively charged ion from a particular point in an ionic solid. This vacancy, which acts like a positively charged particle, attracts and traps an electron, and their combination constitutes an F-Centre. The electron so trapped can absorb only certain colours of light.
- F-Centres in sodium chloride absorb only Blue Light, giving the solid a Yellow-Orange Tinge. Sodium chloride is usually colourless, however, because its electrons are not free to move to vacancies formed by removal of negative chloride ions from the solid.
- The term MASER, an acronym for 'Microwave Amplification by Stimulated Emission of Radiation', is a device that produces coherent electromagnetic waves through amplification by stimulated emission. The first MASER was built by Charles H. Townes, James P. Gordon, and Herbert J. Zeiger at Columbia University in 1953.

- MASERs are used as the timekeeping device in atomic clocks, and as extremely low-noise microwave amplifiers in radio telescopes and deep space spacecraft communication ground stations.
- Modern MASERs can be designed to generate electromagnetic waves at not only microwave frequencies but also radio and infrared frequencies. For this reason, Charles Townes suggested replacing 'Microwave' with the word 'Molecular' as the first word in the acronym MASER.
- As per the Encyclopedia Britannica, "The MASER, an acronym derived from 'Microwave (or Molecular) Amplification by Stimulated Emission of Radiation', is a device that produces and amplifies electromagnetic radiation mainly in the microwave region of the spectrum. The MASER operates according to the same basic principle as the LASER, the name of which is formed from the acronym for 'Light Amplification by Stimulated Emission of Radiation' and shares many of its characteristics".
- The MASER is based on the principle of stimulated emission proposed by Albert Einstein in 1917. When atoms have been induced into an excited energy state, they can amplify radiation at a frequency particular to the element or molecule used as the masing medium, similar to what occurs in the lasing medium in a Laser. By putting such an amplifying medium in a resonant cavity, feedback is created that can produce coherent radiation.
- MASERs serve as high precision frequency references. These 'Atomic Frequency Standards' are one of the many forms of atomic clocks. Masers were also used as low-noise microwave amplifiers in radio telescopes, though these have largely been replaced by amplifiers based on FETs (Field Effect Transistors).
- In a three level MASER, a transition between two energy levels is saturated in order to produce an induced emission of power at a lower frequency corresponding to a transition between an intermediate energy level and one or the other of the two saturated levels.
- A Ruby Laser is a solid state Laser that uses a synthetic ruby crystal as its gain medium. The first working Laser was a 'Ruby Laser' made by Theodore H. 'Ted' Maiman at Hughes Research Laboratories on May 16, 1960.
- Ruby Lasers produce pulses of coherent visible light at a wavelength of 694.3 nm, which is a deep red color. Typical Ruby Laser pulse lengths are on the order of a millisecond.
- The Ruby Laser is a Three Level Solid State Laser. The active Laser medium (Laser Gain/Amplification Medium) is a synthetic ruby rod that is energized through optical pumping, typically by a xenon flashtube. Ruby has very broad and powerful absorption bands in the visual spectrum, at 400 and 550 nm, and a very long fluorescence lifetime of 3 milliseconds.
- A Laser Diode (LD), also termed as Injection Laser Diode or ILD, or Diode Laser, is a semiconductor device similar to a light-emitting diode in which a diode pumped directly with electrical current can create lasing conditions at the diode's junction.

- Driven by voltage, the doped p–n transition allows for recombination of an electron with a hole. Due to the drop of the electron from a higher energy level to a lower one, radiation, in the form of an emitted photon is generated. This is spontaneous emission. Stimulated emission can be produced when the process is continued and further generates light with the same phase, coherence and wavelength.
- Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation, such as visible light, UltraViolet (UV) light, InfraRed (IR) light, or Gamma radiation.
- When light is absorbed by a material, such as a semiconductor, the number of free electrons and holes increases, resulting in increased electrical conductivity. To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap, or to excite the impurities within the band gap.
- When a bias voltage and a load resistor are used in series with the semiconductor, a voltage drop across the load resistors can be measured when the change in electrical conductivity of the material varies the current through the circuit.
- In physics, trap is any location within a solid, generally a semiconductor or an insulator, that restricts the movement of electrons and holes, i.e., equivalent positive electrical charges that result from the absence of an electron within a crystal structure.
- A trap consists of either a chemical impurity or an imperfection in the regular spacing of the atoms that make up the solid. Traps play a significant role in photoconduction, luminescence, and the operation of various electronic devices because the ability of a solid to carry an electrical current depends on the flow of electrons and holes through the solid.
- A trap can capture and immobilize an electron or hole and prevent its recombination with the carrier of opposite charge as an electron hole pair. Electrons and holes may break free from traps quickly, or they may remain there for an extended period of time, for example several months or longer. Charge carriers can be released from traps by the addition of energy, such as irradiating the solid with light or by heating it.
- Space charge is a concept in which excess electric charge is treated as a continuum of charge distributed over a region of space, either a volume or an area, rather than distinct point like charges. This model typically applies when charge carriers have been emitted from some region of a solid, the cloud of emitted carriers can form a space charge region if they are sufficiently spread out, or the charged atoms or molecules left behind in the solid can form a space charge region.
- Space charge only occurs in dielectric media (including vacuum) because in a conductive medium the charge tends to be rapidly neutralized or screened.
- The sign of the space charge can be either negative or positive. This situation is perhaps most familiar in the area near a metal object when it is heated to

incandescence in a vacuum. This effect was first observed by Thomas Edison in light bulb filaments, where it is sometimes called the Edison effect.

- Crystal counters are defined as an instrument used for detecting and measuring the intensity of high-energy radiation, in which particles collide with a crystal and momentarily increase its conductivity.
- Basically, a crystal counter is a particle detector in which the sensitive material is a dielectric or non-conducting crystal mounted between two metallic electrodes. It is defined as a solid state ionization chamber where the ionization is released by the particle which is a measure of its energy.
- The first implementation of a crystal counter is attributed to van Heerden, who demonstrated that Silver Chloride crystals when cooled to low temperatures were capable of detecting Gamma (γ) Rays, Alpha (α) particles and Beta (β) particles. This is fully spectroscopic device and not the integrated device.
- Luminescence is spontaneous emission of light by a substance not resulting from heat or 'Cold Light'. It is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions or stress on a crystal. This distinguishes luminescence from incandescence, which is light emitted by a substance as a result of heating.
- Historically, radioactivity was thought of as a form of 'Radio Luminescence', although it is today considered to be separate since it involves more than electromagnetic radiation.
- Analysis of the breakdown of solid dielectrics are of extreme importance in insulation studies. When breakdown occurs, solids get permanently damaged while gases fully and liquids partly recover their dielectric strength after the applied electric field removed.
- The mechanism of breakdown is a complex phenomenon in the case of solids and varies depending on the time of application of voltage.
- Electrical breakdown or dielectric breakdown is a process that occurs when an electrical insulating material, subjected to a high enough voltage, suddenly becomes an electrical conductor and electric current flows through it.
- All insulating materials undergo breakdown when the electric field caused by an applied voltage exceeds the material's dielectric strength.
- The voltage at which a given insulating object becomes conductive is called its breakdown voltage and depends on its size and shape.
- Under sufficient electrical potential, electrical breakdown can occur within solids, liquids, gases or vacuum. However, the specific breakdown mechanisms are different for each kind of dielectric medium.
- Breakdown mechanisms differ in solids, liquids, and gasses. Breakdown is influenced by electrode material, sharp curvature of conductor material, resulting in locally intensified electric fields, the size of the gap between the electrodes, and the density of the material in the gap.
- Annealing is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness,

making it more workable. It involves heating a material above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time and then cooling.

- In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to a change in ductility and hardness. As the material cools it recrystallizes.

4.12 KEY TERMS

- **Superconductivity:** Superconductivity is a phenomenon in which certain metals, alloys and ceramics conduct electricity without resistance when, it is cooled below a certain temperature called the critical temperature.
- **Isotopic effect:** The critical or transition temperature T_c value of a superconductor is found to vary with its isotopic mass. This variation in T_c with its isotopic mass is called the isotopic effect.
- **Persistent current:** When current is made to flow through a superconducting ring (say a loop of lead wire) which is at a temperature either equal to its T_c value or less than its T_c value, it was observed that the current was flowing through the material without any significant loss in its value. This steady flow of current in a superconducting ring without any potential deriving it, is called the persistent current.
- **Meissner effect:** The complete expulsion of all the magnetic field by a superconducting material is called the "Meissner Effect".
- **Meissner state**: A superconductor with little or no magnetic field within it is said to be in the Meissner state. The Meissner state breaks down when the applied magnetic field is too strong. Superconductors can be divided into two classes according to how this breakdown occurs.
- **Microwave:** Microwave is a form of ElectroMagnetic (EM) radiation with wavelengths ranging from about one meter to one millimeter corresponding to frequencies between 300 MHz and 300 GHz, respectively. The Microwaves have the Wavelength of 1 mm – 1 m, Frequency (Hz) as 300 GHz – 300 MHz, and the Photon Energy (eV) as 1.24 meV – 1.24 μeV.
- **InfraRed (IR):** InfraRed (IR), sometimes also termed as infrared light, is an ElectroMagnetic Radiation (EMR) with wavelengths longer than those of visible light. Infrared has the Wavelength of about 700 nm – 1 mm, the Frequency (Hz) as 300 GHz – 430 THz, and the Photon Energy (eV) as 1.7 eV – 1.24 meV.
- **Magnetic levitation or maglev:** Magnetic levitation or maglev is the process by which an object is suspended above another object with no other support but magnetic fields. The phenomenon of magnetic levitation is based on Meissner effect.
- **Josephson junction:** Two superconductors separated by a very thin strip of an insulator forms a Josephson junction.
- **Quantum tunnelling:** Quantum tunnelling is the quantum mechanical phenomenon where a wavefunction can propagate through a potential barrier.

The transmission through the barrier can be finite and depends exponentially on the barrier height and barrier width.

- **Tunnel junction:** A simple barrier can be created by separating two conductors with a very thin insulator, these are tunnel junctions.
- **Exciton:** An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids.
- **MASER:** The term MASER, an acronym for 'Microwave Amplification by Stimulated Emission of Radiation', is a device that produces coherent electromagnetic waves through amplification by stimulated emission. The first MASER was built by Charles H. Townes, James P. Gordon, and Herbert J. Zeiger at Columbia University in 1953.

4.13 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What is superconductivity?
2. Where does superconductivity occur?
3. State about Meissner effect.
4. Define the concept of heat capacity, energy gap and microwave gap.
5. What is the importance of microwave and infrared radiations?
6. State the isotope effect
7. Derive the London equation.
8. Define the importance of coherence length.
9. Who stated the BSC theory of superconductivity?
10. What is BCS ground state?
11. Define the terms persistent current, single particle tunnelling and Josephson effect.
12. What do you mean by optical phenomena in insulators?
13. State about colour centres and excitons.
14. What is MASER?
15. Give the significance of Ruby Laser and semiconductor junction Laser.
16. What are photoconductivity traps?
17. Define space charge effect, crystal counters and luminescence.
18. How the breakdown in solid dielectrics occurs?
19. What is annealing?
20. How the temperature effects electrode?

Long-Answer Questions

1. Briefly discuss the theory and significance of superconductivity giving appropriate examples.
2. Specify about the occurrence and destruction of superconductivity by magnetic fields with the help of examples.
3. Discuss the importance of Meissner effect.
4. Explain the significant properties of heat capacity, energy gap and microwave gap.
5. Briefly explain the microwave and infrared properties and their specific wavelengths.
6. Explain the terms isotope effect and thermodynamics of superconducting transition giving appropriate examples.
7. Discuss the concept of London equation and coherence length with the help of relevant examples.
8. Briefly explain the BSC theory of superconductivity and BCS ground state giving appropriate examples.
9. Brief a note on persistent current, single particle tunnelling, Josephson effect and flux quantization.
10. Discuss the optical phenomena in insulators with the help of examples.
11. Explain the concept of colour centres, excitons and exciton waves with the help of relevant examples.
12. Briefly explain the principles of MASER, three level Maser, Ruby Laser, and semiconductor junction Laser giving appropriate examples.
13. Discuss briefly about the photoconductivity traps and space charge effect.
14. Explain briefly about the crystal counters and luminescence giving relevant examples.
15. How can the breakdown in solid dielectrics at different temperatures be studied? Explain giving specific examples.
16. Discuss the influence of annealing and effect of temperature with the help of examples.

4.14 FURTHER READING

Wahab, M. A. 2005. *Solid State Physics: Structure and Properties of Materials*. New Delhi: Narosa Publishing House.

Kittel, Charles. 1971. *Introduction to Solid State Physics*. New Jersey (US): John Wiley & Sons, Inc.

Pillai, S. O. 2005. *Solid State Physics*. Noida (UP): Wiley India Private Ltd.

Saxena, B. S., P. N. Saxena and R. C. Gupta. 2019. *Fundamentals of Solid State Physics*. Meerut (UP): Pragati Prakashan.

Dekker, A. J. 2008. *Solid State Physics*. Noida (UP): Macmillan Publishers India Pvt. Ltd.

Kakani, S. L. and C. Hemarajani. 2005. *Solid State Physics*. New Delhi: Sultan Chand & Sons Pvt. Ltd.

UNIT 5 MAGNETISM AND MAGNETIC RESONANCE

NOTES

Structure

5.0 INTRODUCTION

Magnetism is a specific group of physical attributes that are typically mediated by magnetic fields. Electric currents and the magnetic moments of elementary particles give rise to a magnetic field, which acts on other currents and magnetic moments. Magnetism is one aspect of the combined phenomenon of electromagnetism. The most familiar effects occur in ferromagnetic materials, which are strongly attracted by magnetic fields and can be magnetized to become permanent magnets, which precisely produces magnetic fields. Demagnetizing a magnet is also possible. Only a few substances are ferromagnetic of which the most common ones are Iron, Cobalt and Nickel and their Alloys. The prefix 'Ferro-' refers to Iron, because permanent magnetism was first observed in Lodestone, a form of natural Iron ore called Magnetite, Fe_3O_4.

All substances exhibit some type of magnetism. Magnetic materials are classified according to their bulk susceptibility. Ferromagnetism is responsible for most of the effects of magnetism that we observe in our everyday life. Paramagnetic substances, such as Aluminium and Oxygen, are weakly attracted to an applied magnetic field; diamagnetic substances, such as Copper and Carbon, are weakly repelled; while antiferromagnetic materials, such as Chromium and Spin Glasses, have a more complex relationship with a magnetic field. The force of a magnet on paramagnetic, diamagnetic, and antiferromagnetic materials is usually too weak to be felt and can be detected only by laboratory instruments, therefore, these substances are often described as non-magnetic.

The magnetic state or the magnetic phase of a material typically depends on temperature, pressure, and the applied magnetic field. A material may exhibit more than one form of magnetism as these variables change. The strength of a magnetic field practically and continually decreases with distance, though the exact mathematical relationship between strength and distance varies. Different configurations of magnetic moments and electric currents can result in complicated magnetic fields.

Diamagnetism can be observed in all materials and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. However, in a material with paramagnetic properties, i.e., with a tendency to enhance an external magnetic field, the paramagnetic behaviour dominates. In a diamagnetic material, there are no unpaired electrons, hence the intrinsic electron magnetic moments cannot produce any bulk effect. In a paramagnetic material there are unpaired electrons, i.e., atomic or molecular orbitals with exactly one electron in them. A ferromagnet, like a paramagnetic substance, has unpaired electrons. However, in addition to the electrons' intrinsic magnetic moment's tendency to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered-energy state. Thus, even in the absence of an applied field, the magnetic moments of the electrons in the material spontaneously line up parallel to one another. Every ferromagnetic substance has its own individual temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties.

Because of the magnetic moments of atoms in a ferromagnetic material the ferromagnetic materials behave like tiny permanent magnets. They stick together and align themselves into small regions of more or less uniform alignment termed as magnetic domains or Weiss domains.

Magnetic resonance is a process by which a physical excitation or resonance is set up by means of magnetism. This process was used to develop Magnetic Resonance Imaging (MRI) and Nuclear Magnetic Resonance (NMR) spectroscopy technology.

Nuclear Magnetic Resonance (NMR) is a physical phenomenon in which nuclei in a strong constant magnetic field are perturbed by a weak oscillating magnetic field and respond by producing an electromagnetic signal with a characteristic frequency of the magnetic field at the nucleus. This process occurs near resonance, when the oscillation frequency matches the intrinsic frequency of the nuclei, which depends on the strength of the static magnetic field, the chemical environment, and the magnetic properties of the isotope involved. NMR is also routinely used in advanced medical imaging techniques, such as in Magnetic Resonance Imaging (MRI). The Nuclear Magnetic Resonance (NMR) spectroscopy or the Magnetic Resonance Spectroscopy (MRS) is a spectroscopic technique specifically used for analysing the local magnetic fields around atomic nuclei.

In this unit, you will study about the magnetism, diamagnetism and paramagnetism, quantum theory of paramagnetism, spin waves and magnons, ferromagnetic order, antiferromagnetic order, ferromagnetic domains, magnetic resonance, Nuclear Magnetic Resonance (NMR), line width hyperfine splitting, nuclear quadrupole resonance, ferromagnetic resonance and antiferromagnetic resonance.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the basic concept of magnetism
- Differentiate between diamagnetism and paramagnetism
- Elaborate on the quantum theory of paramagnetism
- Describe the spin waves and magnons
- Explain the ferromagnetic order and the antiferromagnetic order
- Know what ferromagnetic domains are
- Discuss the basic principles of magnetic resonance
- Explain the significant properties of Nuclear Magnetic Resonance (NMR)
- Understand the line width hyperfine splitting
- Elaborate on nuclear quadrupole resonance
- Differentiate between the ferromagnetic resonance and antiferromagnetic resonance

5.2 MAGNETISM

Magnetism is referred as a specific class having physical characteristics that are intermediated by means of magnetic fields. Electric currents and the magnetic moments of elementary particles generate a magnetic field, which acts on other currents and magnetic moments. Magnetism is one aspect of the combined phenomenon of electromagnetism. The most familiar effects occur in ferromagnetic materials, which are strongly attracted by magnetic fields and can be magnetized to become permanent magnets, producing magnetic fields themselves. Demagnetizing a magnet is also possible. Only a few substances are ferromagnetic; the most common ones are iron, cobalt and nickel and their alloys. The rare earth metals, such as neodymium and samarium are less common examples. The prefix ‘Ferro’ refers to Iron, because permanent magnetism was first observed in lodestone, a form of natural Iron ore called Magnetite, Fe_3O_4.

Fundamentally, the magnetism is the force exerted by magnets when they attract or repel each other. All magnets have north and south poles. Opposite poles are attracted to each other, while the similar poles repel each other.

All substances exhibit some type of magnetism; hence the magnetic materials are classified according to their bulk susceptibility. Ferromagnetism is responsible for most of the effects of magnetism encountered in everyday life, but there are actually several types of magnetism. Paramagnetic substances, such as Aluminium and Oxygen, are weakly attracted to an applied magnetic field; diamagnetic substances, such as Copper and Carbon, are weakly repelled; while antiferromagnetic materials, such as Chromium and Spin Glasses, have a more complex relationship with a magnetic field. The force of a magnet on paramagnetic, diamagnetic, and antiferromagnetic materials is usually too weak to be felt and can be detected only by laboratory instruments, therefore in everyday life, these substances are often described as non-magnetic.

The magnetic state or magnetic phase of a material depends on temperature, pressure, and the applied magnetic field. A material may exhibit more than one form of magnetism as these variables change.

The strength of a magnetic field almost always decreases with distance, though the exact mathematical relationship between strength and distance varies. Different configurations of magnetic moments and electric currents can result in complicated magnetic fields.

Magnetism, at its origin, evolves from following two sources:

1. Electric Current.
2. Spin Magnetic Moments of Elementary Particles.

The magnetic properties of materials are primarily due to the magnetic moments of their atoms' orbiting electrons. The magnetic moments of the nuclei of atoms are typically thousands of times smaller than the electrons' magnetic moments, therefore they are negligible in the context of the magnetization of materials. Nuclear magnetic moments are however very significant in other contexts, especially in Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI).

Ordinarily, the enormous number of electrons in a material are arranged such that their magnetic moments, both orbital and intrinsic cancel out. This is due to some extent to electrons combining into pairs with opposite intrinsic magnetic moments as a result of the Pauli exclusion principle and combining into filled subshells with zero net orbital motion. In both cases, the electrons preferentially adopt arrangements in which the magnetic moment of each electron is cancelled by the opposite moment of another electron. Moreover, even when the electron configuration is such that there are unpaired electrons and/or non-filled subshells, it is often the case that the various electrons in the solid will contribute magnetic moments that point in different, random directions so that the material will not be magnetic.

Sometimes, either spontaneously or owing to an applied external magnetic field, each of the electron magnetic moments will be on average lined up. A suitable material can then produce a strong net magnetic field.

The magnetic behaviour of a material depends on its structure, particularly its electron configuration, for the reasons stated above, and also on the temperature. At high temperatures, random thermal motion makes it more difficult for the electrons to maintain alignment.

Classification of Magnetic Materials

Magnetic materials are classified into different categories based on their magnetic parameters, such as c and m_r, and their microscopic magnetic structure under different environmental conditions, i.e., under the influence of magnetic field, temperature, etc.

Based on whether the atoms carry permanent magnetic dipoles or not, and also on the basis of effect of temperature and magnetic field on the magnetic properties; all materials are broadly classified into the following three categories.

1. Diamagnetic Materials
2. Paramagnetic Materials
3. Ferromagnetic Materials

Two more classes of materials have structure very close to ferromagnetic materials but possess quite different magnetic effects. They are:

4. Antiferromagnetic Materials
5. Ferrimagnetic Materials

Following are the three broad categories of magnetism.

Diamagnetism: Diamagnetism appears in all materials and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. However, in a material with paramagnetic properties, i.e., with a tendency to enhance an external magnetic field the paramagnetic behaviour dominates. Thus, despite its universal occurrence, diamagnetic behaviour is observed only in a purely diamagnetic material.

Paramagnetism: In a paramagnetic material there are unpaired electrons, i.e., atomic or molecular orbitals with exactly one electron in them. While paired electrons are required by the Pauli exclusion principle to have their intrinsic 'Spin' magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an unpaired electron is free to align its magnetic moment in any direction. When an external magnetic field is applied, these magnetic moments will tend to align themselves in the same direction as the applied field, thus reinforcing it.

Ferromagnetism: A ferromagnet, like a paramagnetic substance, has unpaired electrons. However, in addition to the electrons' intrinsic magnetic moment's tendency to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered-energy state. Thus, even in the absence of an applied field, the magnetic moments of the electrons in the material spontaneously line up parallel to one another. Every ferromagnetic substance has its own individual temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order. Ferromagnetism only occurs in a few substances; common ones are Iron, Nickel, Cobalt, their Alloys, and some alloys of rare earth metals.

Following are the two more classes of magnetic materials.

Antiferromagnetism: The antiferromagnetism type of magnetism can be explained with reference to solids, such as Manganese Oxide (MnO) in which the adjacent ions, the Manganese ions Mn^{2+}, typically act as tiny magnets and get spontaneously aligned at relatively or comparatively low temperatures either into opposite or into antiparallel arrangements throughout the material with the purpose to exhibit approximately no external magnetism.

Depending upon the temperature, the antiferromagnetic solid materials show unique behaviour in an applied magnetic field. Consequently. the solids show no response to the external field at exceptionally low temperature because the atomic magnet's antiparallel ordering is firmly maintained. Subsequently, at the higher temperatures some of the atoms of the solids break down and are free of the orderly or systematic arrangement for aligning with the external field. This type of alignment produces the weak magnetism characteristics in the solids when achieve their peak at the Néel temperature. Above the Néel temperature, the thermal tension gradually prevents the alignment or orientation of the atoms of the solid materials with the magnetic field, therefore, the weak magnetism that is produced in the solids through the alignment of the atoms decreases continuously as temperature increases.

Ferrimagnetism: Ferrimagnetism can be defined as typical behaviour of solid materials termed as 'Ferrites'. The occurrence of ferrimagnetism can be characteristically observed when the two different types of magnetic ions are present. A ferrimagnetic material is a specific material that has number of atoms with opposing magnetic moments, as in antiferromagnetism. For ferrimagnetic materials, these moments are unequal in magnitude so a spontaneous magnetization remains, for example this can occur when the number of atoms consist of different atoms or ions, such as Fe^{2+} and Fe^{3+}.

Ferrimagnetism has often been confused with ferromagnetism. The oldest known magnetic substance, Magnetite (Fe_3O_4), was typically classified as a ferromagnet before Louis Néel discovered ferrimagnetism in the year 1948. Since the discovery, numerous uses have been found for ferrimagnetic materials, such as hard drive platters and biomedical applications.

Ferrimagnetism has the same physical origins as ferromagnetism and antiferromagnetism. In ferrimagnetic materials, the magnetization is also caused by a combination of dipole-dipole interactions and exchange interactions resulting from the Pauli exclusion principle. The main difference is that in ferrimagnetic materials there are different types of atoms in the material's unit cell. Ferrimagnets have a critical temperature above which they become paramagnetic just as ferromagnets do. At this temperature, specifically termed as the 'Curie Temperature' there is a second order phase transition, and the system can no longer maintain a spontaneous magnetization. This is because at higher temperatures the thermal motion is strong enough and consequently it exceeds the tendency of the dipoles to align.

5.2.1 Diamagnetism

A diamagnetic material is the solid material whose atoms do not have or exhibit permanent magnetic dipole moment. When an external magnetic field is applied to a diamagnetic material, such as Bismuth or Silver then a weak magnetic dipole moment is induced or generated in the direction that is opposite to the applied field. Fundamentally, since all the materials are essentially considered as diamagnetic in nature, hence a weak repulsive force is generated in the magnetic field through the current of the orbiting electron. However, some of the materials possess stronger paramagnetic properties hence they are capable to overcome of their natural diamagnetic qualities. These paramagnetic materials have unpaired electrons, such as Iron and Nickel.

Basically, a diamagnetic material has extremely low or minimal magnetic effect because of the absence of any unpaired electrons in them. Alternatively, the diamagnetic materials can be explained through the Lenz's law, which states that diamagnetic materials get induced dipoles in the presence of an external magnetic field, and this happens in such an order that the magnetic field and the induced dipoles repel each other.

Diamagnetism was first discovered when Anton Brugmans observed in 1778 that 'Bismuth' was repelled by magnetic fields. In 1845, Michael Faraday demonstrated that it was a property of matter and concluded that every material responded, in either a diamagnetic or paramagnetic way, to an applied magnetic field. Therefore, the characteristic features of diamagnetic material or diamagnets was uniquely defined by Michael Faraday. Additionally, with the introduction and establishment of the modern-day periodic table which explained the specific properties of elements of each group of the periodic table, it was proved by the scientists that most of the elements are 'Diamagnetic', like Gold, Silver, Copper, etc. Furthermore, the semiconductors are considered as the best diamagnetic materials. The semiconductors also exhibit the diamagnetic field and therefore this ideal diamagnetism in the superconductor is termed as the 'Meissner Effect'.

A simple rule of thumb is used for determining whether a particle (atom, ion, or molecule) is paramagnetic or diamagnetic. If all electrons in the particle are paired, then the substance made of this particle is termed as diamagnetic else if it has unpaired electrons, then the substance is termed as paramagnetic.

All materials are inherently diamagnetic. The orbital motion of electrons create tiny atomic current loops, which produce magnetic field. Under such a condition, when an external magnetic field is applied to a material, these current loops will tend to align in such a way as to oppose the applied field.

Thus diamagnetism can be viewed as, the result of Lenz`s law, i.e., an induced magnetic field tend to oppose the change which created it.

Diamagnetism occurs in substances whose atom consists of an even number of electrons. The electrons of such atoms are paired. The electrons in each pair have orbital motion as well as spin motions in opposite sense. Thus, the resultant magnetic dipole moment is zero.

General Properties of Diamagnetic Materials

1. Diamagnetic materials experience a repelling force when brought near the pole of a strong magnet.
2. In a non-uniform magnetic field, they are repelled away from stronger parts of the field.
3. These materials do not retain the magnetic properties when the external field is removed.
4. The magnetic susceptibility χ of these materials is always negative.
5. The relative permeability μ_r is always less than one (i.e., $\mu_r < 1$).
6. In the absence of an external magnetic field, the net magnetic dipole moment over each atom or molecule of a diamagnetic material is zero. This is due to the pairing of electrons.
7. Both susceptibility and relative permeability are independent of applied magnetic field and temperature.
8. **Examples**: Bismuth, Copper, Lead, Zinc and Rare Gases.

NOTES

5.2.2 Paramagnetism

Paramagnetism is a form of magnetism whereby some materials are weakly attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field. Paramagnetic materials typically include most chemical elements and some compounds. Additionally, the paramagnetic materials have a relative magnetic permeability slightly greater than 1, i.e., a small positive magnetic susceptibility and hence are attracted to magnetic fields. The magnetic moment induced by the applied field is linear in the field strength and rather weak. It typically requires a sensitive analytical balance to detect the effect and modern measurements on paramagnetic materials are often conducted with a SQUID magnetometer.

Paramagnetism is due to the presence of unpaired electrons in the material, consequently most atoms with incompletely filled atomic orbitals are paramagnetic, although exceptions, such as Copper exist. Due to their spin, unpaired electrons have a magnetic dipole moment and act like tiny magnets. An external magnetic field causes the electrons' spins to align parallel to the field, causing a net attraction. Paramagnetic materials include Aluminium, Oxygen, Titanium, and Iron Oxide (FeO).

In contrast to ferromagnets, paramagnets do not retain any magnetization in the absence of an externally applied magnetic field because thermal motion randomizes the orientations of spin. Certain paramagnetic materials retain spin disorder even at absolute zero signifying that they are paramagnetic in the ground state, i.e., in the absence of thermal motion. Consequently, the total magnetization drops to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetization because only a small fraction of the spins will be oriented by the field. This fraction is proportional to the field strength, and this explains the linear dependency. The attraction experienced by ferromagnetic materials is non-linear and much stronger, as a result it is easily observed, for instance the attraction between a refrigerator magnet and the iron of the refrigerator itself.

The Bohr–Van Leeuwen theorem proves that there cannot be any diamagnetism or paramagnetism in a purely classical system. The paramagnetic response has then two possible quantum origins, either coming from permanent magnetic moments of the ions or from the spatial motion of the conduction electrons inside the material.

Curie's Law

For low levels of magnetization, the magnetization of paramagnets approximately follows the Curie's law. This law implies that the susceptibility 'χ' of paramagnetic materials is inversely proportional to their temperature, i.e., that materials become more magnetic at lower temperatures. The mathematical expression is given by:

$$\mathbf{M} = \chi\mathbf{H} = \frac{C}{T}\mathbf{H}$$

Where,

M = The Resulting Magnetization, measured in Amperes/meter (A/m)

χ = The Volume Magnetic Susceptibility (Dimensionless)

$\mathbf{H}$ = The Auxiliary Magnetic Field (A/m)

$\boldsymbol{C}$ = The Absolute Temperature, measured in Kelvins (K)

$\boldsymbol{T}$ = The Material-Specific Curie Constant (K).

Curie's law is valid under the commonly encountered conditions of low magnetization ($\mu_B H \leq k_B T$) but does not apply in the high-field/low-temperature regime where saturation of magnetization occurs ($\mu_B H \geq k_B T$) and magnetic dipoles are all aligned with the applied field. When the dipoles are aligned, increase in the external field will not increase the total magnetization since there can be no further alignment.

Pauli Paramagnetism

For some alkali metals and noble metals, conduction electrons are weakly interacting and delocalized in space forming a 'Fermi Gas'. For these materials, one contribution to the magnetic response comes from the interaction between the electron spins and the magnetic field known as 'Pauli Paramagnetism'. For a small magnetic field **H**, the additional energy per electron from the interaction between an electron spin and the magnetic field is given by,

$$\Delta E = -\mu_0 \mathbf{H} \cdot \boldsymbol{\mu}_e = -\mu_0 \mathbf{H} \cdot \left(-g_e \frac{\mu_{\mathrm{B}}}{\hbar} \mathbf{S}\right) = \pm \mu_0 \mu_{\mathrm{B}} H.$$

Where m_0 is the vacuum permeability, m_e is the electron magnetic moment, m_B is the Bohr magneton, $\hbar$ is the reduced Planck constant, and the g-factor cancels with the spin $\mathbf{S} = \pm\hbar/2$. The ± indicates that the sign is positive (negative) when the electron spin component in the direction of **H** is parallel (antiparallel) to the magnetic field.

General Properties of Paramagnetic Materials

1. The paramagnetic materials are weakly attracted by the magnetic field.
2. In the non-uniform external magnetic field, paramagnetic materials shift from week field region to a strong field region.
3. When the net atomic dipole moment of an atom is not zero, then the atoms of paramagnetic substances exhibit permanent dipole moment due to unpaired spin.
4. The intensity of magnetization is exceptionally small, positive and directly proportional to the magnetizing field.
5. Magnetic susceptibility χ is small and positive.
6. The relative permeability is slightly greater than 1, the field inside the material is greater than the magnetizing field.
7. Magnetic field lines become denser inside the paramagnetic materials.
8. Magnetization of paramagnetic materials is inversely proportional to absolute temperature (T).
9. Paramagnetic materials observe Curie's law, according to which magnetic susceptibility is inversely proportional to its absolute temperature.

10. Magnetic dipole moment of paramagnetic substances is small and parallel to the magnetizing field.
11. **Examples:** Platinum, Aluminium, Copper Sulphate, Manganese Sulphate and the Salts of Iron and Nickel.

5.3 QUANTUM THEORY OF PARAMAGNETISM

According to classical theory the atoms of the paramagnetic gas are assumed to be small permanent magnets due to circulating electrons. In the absence of the external magnetic field, the magnetic axes of the atoms are uniformly distributed in all directions. When the magnetic field is applied then the atoms will tend to orient themselves with their magnetic axes in the direction of the field.

In **quantum theory**, the permanent magnetic moment of an atom or ion is not freely rotating but with respect to applied field it is restricted to a finite set of orientations. If 'N' be the number of atoms per unit volume of the medium and 'J' be the total angular momentum quantum number of each atom, then the possible component of the magnetic moment is given as follows.

The magnetic moment is given by,

$$M_J \, g \, \mu_B$$

Where $M_J = J, (J-1), \ldots -(J-1), -J$

$=$ Magnetic Quantum Number associated with J.

$\therefore$ Potential Energy of a Magnetic Dipole having Component $M_J \, g \, \mu_B$ along H,

$$= -M_J \, g \, \mu_B \, H$$

Therefore, from statistical mechanics the total magnetic moment per unit volume or the magnetisation along the field direction can be written as,

$$M = N \sum_{-J}^{+J} M_J \, g \, \mu_B \; e^{M_J g \mu_B}/KT \; / \; \sum_{-J}^{+J} \; e^{M_J g \mu_B}/KT$$

Where,

g = Lande's Splitting Factor

$= 1 + J(J+1) + S(S+1) - L(L+1) / 2(J(J+1)$

μ_B = Bohr Magneton

L = Total Orbital Angular Momentum of Each Atom

S = Total Spin Angular Momentum of Each Atom

Paramagnetism is a result of the presence of some unpaired electrons and from the realignment of the electron orbits caused by the external magnetic field. In paramagnetic materials, the magnetic fields due to the orbiting and spinning electrons do not cancel out. Thus there will be a net intrinsic moment.

Properties of Paramagnetism

1. Paramagnetic materials experience a feeble attractive force when brought near the pole of a magnet.
2. They are attracted towards the stronger parts of an inhomogeneous magnetic field.
3. These materials possess some permanent dipole moment which arise due to some unpaired electrons.
4. In the absence of an external magnetic field, the dipoles are randomly oriented. Thus the net magnetization is zero.
5. When these materials are placed in an external magnetic field, realignment of the electron orbits and magnetic dipoles take place resulting in a small magnetization.
6. These materials do not retain the magnetic properties when the external field is removed.
7. The magnetic susceptibility χ is small and positive.
8. The permeability is slightly greater than one (i.e., $\mu_r > 1$).

   It is given by, $\chi = \frac{C}{T-\theta}$ where C is the Curie`s Constant, T is the Absolute Temperature and θ is Curie Temperature.
9. When the temperature is less than Curie Temperature, Paramagnetic materials become Diamagnetic material.

Check Your Progress

1. What is magnetism?
2. Define the terms magnetic state and strength of a magnetic field.
3. How magnetic materials are classified into different categories?
4. Give the specific features of diamagnetism, paramagnetism and ferromagnetism.
5. State the properties of antiferromagnetism and ferrimagnetism.
6. Define Curie's law and its mathematical expression.

5.4 SPIN WAVES AND MAGNONS

A spin wave is a propagating disruption in the reference of a magnetic material. These low-lying collective excitations occur in magnetic lattices with continuous symmetry. From the equivalent quasi-particle point of view, spin waves are known as magnons, which are bosonic modes of the spin lattice that correspond roughly to the phonon excitations of the nuclear lattice. As temperature is increased, the thermal excitation of spin waves reduces a ferromagnet’s spontaneous magnetization. The energies of spin waves are typically only μ_e V in keeping with typical Curie points at room temperature and below.

Spin waves are observed through four experimental methods: inelastic neutron scattering, inelastic light scattering (Brillouin scattering, Raman scattering and inelastic *X*-ray scattering), inelastic electron scattering (spin-resolved electron energy loss spectroscopy), and spin-wave resonance (ferromagnetic resonance).

The simplest way of understanding spin waves is to consider the Hamiltonian $\mathcal{H}$ for the Heisenberg ferromagnet:

$$\mathcal{H} = -\frac{1}{2}J\sum_{i,j}\mathbf{S}_i \cdot \mathbf{S}_j - g\mu_{\mathrm{B}}\sum_i \mathbf{H} \cdot \mathbf{S}_i$$

Where *J* is the exchange energy, the operators *S* represent the spins at Bravais lattice points, *g* is the Landé *g*-factor, μ_B is the Bohr magneton and **H** is the internal field which includes the external field plus any "Molecular" field. Note that in the classical continuum case and in 1 + 1 dimensions Heisenberg ferromagnet equation has the form,

$$\mathbf{S}_t = \mathbf{S} \times \mathbf{S}_{xx}.$$

In 1 + 1, 2 + 1 and 3 + 1 dimensions this equation admits several integrable and non-integrable extensions like the Landau-Lifshitz equation, the Ishimori equation, and so on. For a ferromagnet $J > 0$ and the ground state of the Hamiltonian $|0\rangle$ is that in which all spins are aligned parallel with the field **H**. That $|0\rangle$ is an Eigen state of $\mathcal{H}$ can be verified by rewriting it in terms of the spin-raising and spin-lowering operators given by:

$$S^{\pm} = S^x \pm iS^y$$

Resulting in,

$$\mathcal{H} = -\frac{1}{2}J\sum_{i,j} S_i^z S_j^z - g\mu_{\mathrm{B}} H \sum_i S_i^z - \frac{1}{4}J\sum_{i,j}(S_i^+ S_j^- + S_i^- S_j^+)$$

Where *z* has been taken as the direction of the magnetic field. The spin-lowering operator S^- annihilates the state with minimum projection of spin along the *Z*-axis, while the spin-raising operator S^+ annihilates the ground state with maximum spin projection along the *Z*-axis.

5.5 FERROMAGNETIC ORDER AND ANTIFERROMAGNETIC ORDER

The magnetism of metals and other materials are determined by the orbital and spin motions of the unpaired electrons and the way in which unpaired electrons align with each other. All magnetic substances are paramagnetic at sufficiently high temperature, where the thermal energy exceeds the interaction energy between spins on neighbouring atoms. Below a certain critical temperature, spins can adopt different kinds of ordered arrangements.

In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighbouring spins (on different sublattices) pointing in opposite directions.

This is, like ferromagnetism and ferrimagnetism, a manifestation of ordered magnetism.

Generally, **antiferromagnetic order** may exist at sufficiently low temperatures, but vanishes at and above the Néel temperature – named after Louis Néel, who had first identified this type of magnetic ordering. Above the Néel temperature, the material is typically paramagnetic. Following Figure (5.1) illustrates the antiferromagnetic order.

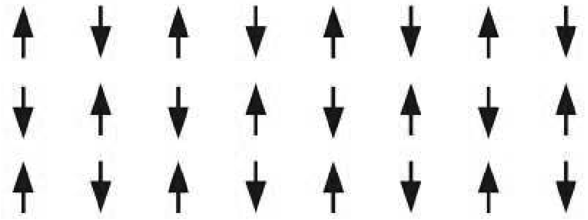


Fig. 5.1 *Antiferromagnetic Order*

Ferromagnetism is the basic mechanism by which certain materials, such as iron form permanent magnets or are attracted to magnets. Historically, the term ferromagnetism was used for any material that could exhibit spontaneous magnetization, a net magnetic moment in the absence of an external magnetic field, i.e., any material that could become a magnet. However, in a landmark paper in 1948, Louis Néel showed there are two levels of **magnetic alignment** or **ordering** that result in this behaviour. One is **ferromagnetism ordering** in the strict sense, where all the magnetic moments are aligned. The other is **ferrimagnetism**, where some magnetic moments point in the opposite direction but have a smaller contribution, so there is still a spontaneous magnetization.

In **ferromagnetic ordering**, all the spins within a magnetic domain, typically hundreds of unit cells in width, have the same orientation. Following Figure (5.2) illustrates the ferromagnetic order in which all the molecular magnetic dipoles are pointed in the same direction.

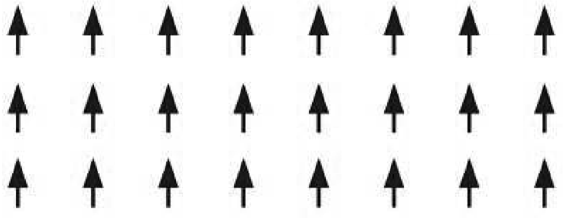


Fig. 5.2 *Ferromagnetic Order*

5.5.1 Ferromagnetic Domains

The magnetization and hysteresis observed in a ferromagnetic material is explained using the concept of domain proposed by Weiss in 1907.

According to this domain concept, a specimen of ferromagnetic material consists of different region which are spontaneously magnetised below the Curie temperature. *These spontaneously magnetised or self magnetised regions in a ferromagnetic material is called domains*. Each domain is separated by the other domain by domain walls which has finite dimension.

At finite temperature ($T < T_c$), and in the absence of an external magnetic field, the direction of magnetization of each domain have random orientation in space as shown in Figure (5.3).

Because of this randomness, the resultant magnetic moment of the material as a whole (which is the vectorial sum of the magnetic moment of the constituent domains) turn out to be zero. Figure (5.3) illustrates the random orientation of the magnetic moments of the domains.

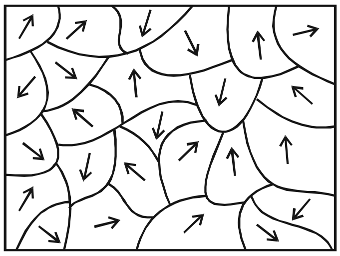
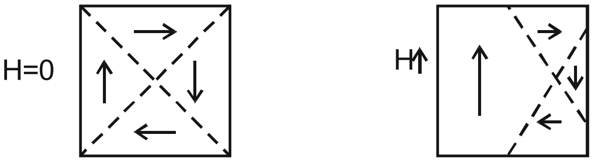


Fig. 5.3 *Random Orientation of Magnetic Moments of the Domains*

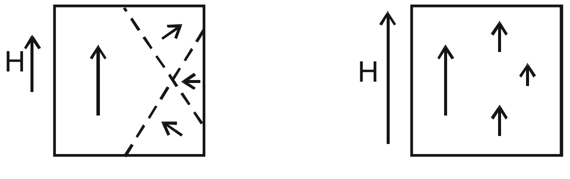
Effect of External Magnetic Field on The Domains

A symbolic representation of the response of the domains to the magnetic field is shown in Figure (5.4). In the absence of an external magnetic field the relative orientation of the magnetic moments of various domains will be completely random as shown in Figure (5.4(*a*)).



Domain orientation in the absence of magnetic field
(*a*)

Domain enlargement/ shrinkage due to weak fields
(b)



Domain rotation due to strong fields
(c)

Saturation due to very high fields
(d)

Fig. 5.4 *Domain Response to the Field*

When an external magnetic field is applied, depending on the strength of the applied magnetic field, the magnetization effect may take place in any one of the following three stages.

1. Due to domain wall movement.
2. Due to the rotation of domains magnetic moments.
3. Due to both of the above two process.

NOTES

1. When the applied field is weak, the domains which have their resultant magnetic moments in a direction parallel to (atleast favourably oriented to) the direction of the applied field expand their size at the cost of other domains with unfavourably oriented magnetic moments. Thus the domain areas of unfavourably oriented magnetic moments diminish (Refer Figure 5.4(*b*)) thereby providing a large net magnetization.
2. When the field becomes strong, the domain's magnetic moments rotate partially and tend to align in the direction of the magnetic field (Refer Figure 5.4(*c*)). This results in further increase in the magnetization of the material.
3. When the field become very strong, the magnetic moments of each and every domain undergo required amount of rotation so as to align perfectly along the direction of the field (Refer Figure 5.4(*d*)). *This indicates the ultimate stage of magnetization. This state of magnetization is called saturation.* Beyond this saturation stage, further increase in magnetization is impossible, no matter how strong the field is.

5.6 NUCLEAR MAGNETIC RESONANCE

Nuclear Magnetic Resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like IR (InfraRed) and UV (UltraVoilet) spectroscopy this method is non-destructible one and permits the recovery of the sample for further evaluation.

As implied in the name, nuclear magnetic resonance is concerned with the magnetic properties of certain nuclei, notably the nucleus of the hydrogen atom– the proton. Studying an organic molecule by NMR spectroscopy enables us to record difference in the magnetic properties of the various nuclei present, and to deduce in large measure what are the positions of these nuclei with in the molecule. We can for proton NMR deduce how many different kinds of hydrogen environments there are in the molecule, and also which hydrogen atoms are present an neighbouring carbon atoms. We can also measure how many hydrogen atoms are present in each of these environments.

Nuclei are characterized by nuclear spin quantum, *I*, which have the values 1/2, 1, 3/ 2... expressed in units of $\frac{h}{2\pi}$. For a given nucleus with spin number *I*, there are 2/+ 1 orientations possible in a magnetic field. It has been found that the nuclei with even atomic numbers and even mass numbers, i.e., both *p* and *n* even have zero nuclear spins. Such nuclei do not exhibit nuclear magnetic resonance. The nuclei with zero spin are ^{4}He, ^{12}C and ^{16}O. Nuclei with both *p* and *n* odd, i.e., with charge odd and mass even, have integral spins. The examples are ^{2}H, ^{14}N (Spin 1) and ^{10}B (Spin 3). The nuclei with odd mass have half integral spin. The examples are ^{1}H, ^{15}N, ^{13}C and ^{17}O. However, very commonly one consider the hydrogen nuclei (^{1}H).

NOTES

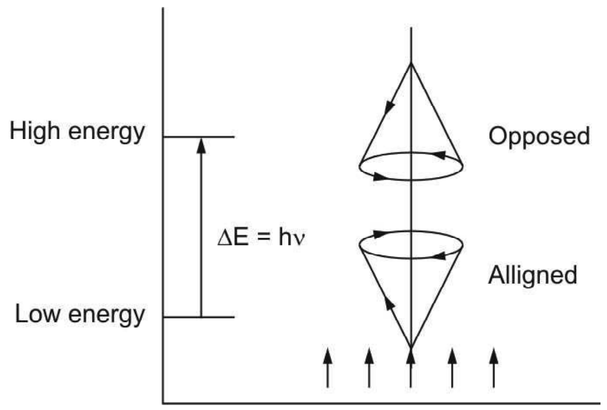


Fig. 5.5 *NMR Study of Hydrogen Nuclei*

The proton behaves like a spinning magnet and it precesses like a top around the axis of an applied magnetic field and can do so in two principal orientations, either aligned with the field (low energy) or opposed to the field (high energy) as shown in Figure. (5.5), where, B_0 is the external magnetic field. The spinning frequency of the nucleus does not change, but the speed of precession does. The precessional frequency, v, is directly proportional to the strength of the external field B_0; that is

$$v \propto B_0'$$

For example, a proton when exposed to an external magnetic field of 1.4 T (≡ 14.000 gauss) will precess ~60 million times per second, so that $v = 60$ MHz: in doing so it will take up one of the two orientations with respect to the axis of the external field–aligned or opposed. If a proton is precessing in the aligned orientation, it can absorb energy and pass to the opposed orientation; subsequently it can lose this extra energy and relax back into the aligned position. If we irradiate the precessing nuclei with a beam of radio-frequency energy of the correct frequency, the low-energy nuclei may absorb this energy and move to a higher energy state. The precessing proton will only absorb energy from the radio-frequency source if the precessing frequency is the same as the frequency of the radio-frequency beam; when this occurs, the nucleus and the radio-frequency beam are said to be in resonance; hence the term Nuclear Magnetic Resonance (NMR). In an applied magnetic nuclei like the proton precess at a frequency v, which is proportional to the strength of the applied field. The exact frequency is given by,

$$v = \mu\beta_N B_0/ht$$

Where B_0 = Strength of the Applied External Field

h = Planck's Constant

μ = Magnetic Moment of the Particular Nucleus

I = Spin Quantum Number

β_N = Nuclear Magneton Constant.

Chemical Shift

The field at a nucleus due to the field of the magnet is modified by the induced diamagnetic electronic currents. These set up a secondary magnetic field. Let B_0

be the magnetic field in the bulk of the specimen and B be the field actually experienced by the nuclei. The B is related to B_0 by the relation,

$$B = B_0 (1 - \sigma')$$

Where σ' is the screening constant which depends on the environment of the nuclei. The displacement of resonance caused by the additional field at the nucleus is proportional to the strength of the applied field and is called the chemical shift. In fact, chemical shift is a measure of the difference between the σ' values for different chemical positions. The shielding constant σ may be defined as,

$$\sigma = \sigma' \times 10^6 = \frac{B - B_{ref}}{B_{ref}} \times 10^6$$

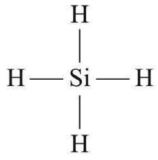
Where B is strength of the magnetic field at which resonance occurs and B_{ref} is the field at which the nucleus in reference surroundings gives resonance at the same frequency. Chemical shifts δ are given as,

$$\delta = \sigma - \sigma_{ref} = \frac{B - B_{ref}}{B_{ref}} \times 10^6$$

With protons a very convenient reference compound is, TetraMethyl Silane (TMS) and the quantity $\pi = 10 - \delta$ has been introduced so that

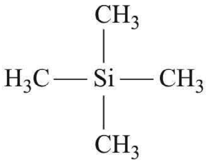
$$\tau(\text{ppm}) = 10 - \frac{\Delta(\text{Me}_4\text{Si}) \times 10^6}{\text{Oscillator Frequency}}$$

Where Δ is the displacement in frequency between the sample resonance and the Me_4Si resonance. On this scale, τ is positive for all but very acidic protons. This scale is most widely used for work with protons and is measured in parts per million (ppm). To measure pressional frequency of a group of nuclei in absolute units is extremely difficult and rarely required. Most commonly the differences in frequency are measured with respect to some reference group of nuclei. For protons the universally accepted reference is tetra methylsilane, TMS (TetraMethyl Silane) is chosen because it contains 12 protons in magnetically equivalent positions and thus gives an intense sharp signal. TMS is chemically inert and has a low boiling point so that it can easily be removed from a recoverable sample of valuable organic compound. TMS is soluble in most organic solvents and is added as an internal standard (≈ percent).



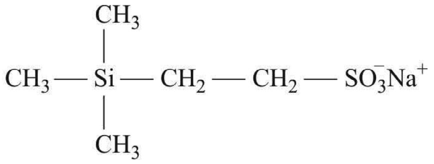
SiH_4

I
Silane



$Si(CH_3)_4$

II
Tetramethyl Silane
(TMS)



$(CH_3)_3Si{-}CH_2{-}CH_2{-}SO_3^-Na^+$

III
Sodium salt of
3-(Trimethyl silyl)-
Propanesulphonic acid

TMS is not soluble in water or in D_2O, therefore, for polar substances sodium salt of propane sulphonic acid is used as reference. Chemical shift is important because it enable us to ascertain what types of hydrogens are present in a molecule by measuring the shift involved and comparing it with known standards run under the same conditions.

Experimental Arrangement

The experimental method for the determination of nuclear magnetic resonance was developed independently by F M Purcell and Bloch in 1946. A simplified diagram of a nuclear magnetic resonance spectrometer is shown in Figure (5.6). A magnetic field B varying from 0 to 10.000 gauss is applied and this field produces an equidistant splitting of the nuclear energy levels. Transitions between the energy levels are stimulated by radiation from the radio frequency transmitter which sends out electromagnetic radiation from the transmitter coil. The sample will absorb the radiation if the frequency of the oscillating field. The transitions are detected in the indicator. Usually, a cathode ray oscillograph is used as indicator.

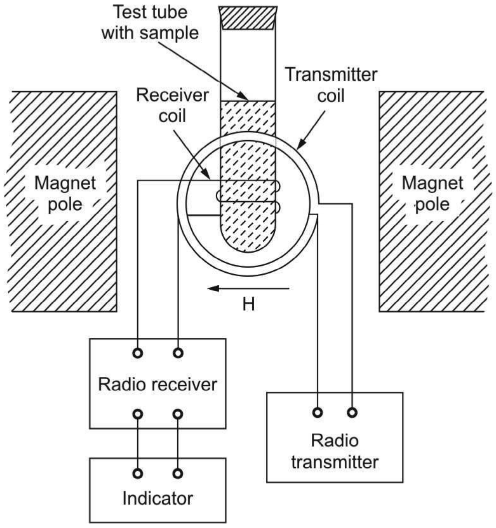


Fig. 5.6 *Schematic Representation of an NMR Spectrometer*

The resonance condition is achieved by superimposing a small variable magnetic field. The low resolution NMR spectrum of ethyl alcohol or ethanol is shown in Figure (5.7). This absorption spectrum is historically significant because it was the first compound which was studied by Packard in 1951. He was able to detect three different values for the precessional frequencies of the protons. He thus, demonstrated that these corresponded to three different chemical environments for the protons an ethanol (CH_3, CH_2 and OH).

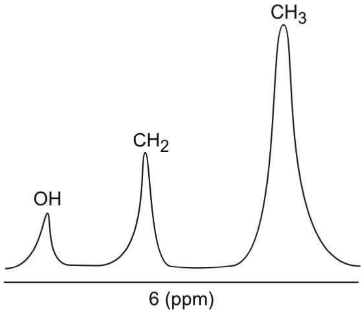


Fig. 5.7 *NMR Spectrum of Ethanol*

The NMR spectra helps us to know the types of hydrogen atoms in the molecule, which is given by the number of peaks in the NMR spectra. Secondly the number of hydrogen atoms of each type can be determined by finding the ratio of the relative area under each peak. The area under the peaks in ethanol molecule is in the ratio of 1: 2: 3.

Spin-Spin Splitting: When the NMR spectrum of ethanol is recorded at high resolution, the CH_2 peak is split into four lines and that for CH_3 into three lines. This splitting is not a chemical shift is proved by the fact the observed splitting does not depend on the strength of the applied field. The effect is caused by the interaction of the nuclear spins of one set of equivalent protons with those of another set. This is called spin-spin coupling. Further the splitting of an NMR line due to interaction of the spins is measured by the spin-spin coupling constant *J*.

Let us consider a proton A which has another Proton *X* in its neighbourhood. Now the proton *X* can have either its nuclear magnet aligned with proton A or opposed to it. Thus, the proton *X* can either increase the net magnetic field experienced by A (*X* aligned) or decrease it (*X* opposed). The two spin orientations of *X* create two different magnetic fields around proton A. Therefore, the proton A comes to resonance not once but twice thus producing doublet as shown in Figure (5.8).

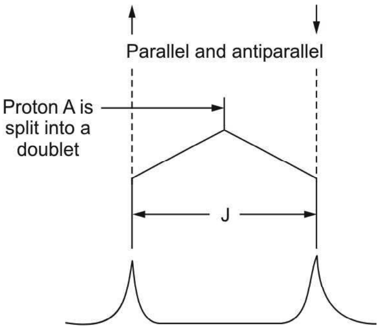


Fig. 5.8 *Spin Compling be Hower Neighbour Proton x*

Similarly a proton A sees two neighbouring protons *X* and *X*′ the A can see three different possible combinations of spins (*i*) The nuclear spins *X* and *X*′ both be parallel to A (↑↑); (*ii*) Both can be anti-parallel to A (↓↓) (*iii*) One can be parallel and another anti-parallel and this can arise in two ways–*X* parallel with *X*′ anti-parallel (↑↓) or *X* antiparallel and *X*′ parallel (↓↑). Three distinct situations are thus created. The probability of the first two states arising is equal while the third state since it can occur in two ways has twice the probability to occur than the first two. This is shown in Figure (5.9).

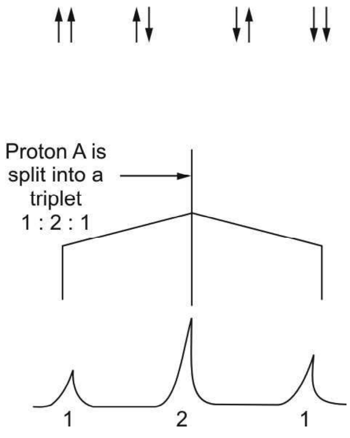


Fig. 5.9 *Spin Coupling between Proton and Two Neighbour Protons X and X*′

In general if there are n number of equivalent protons interacting with the neighbouring proton the absorption will be split into $n + 1$ lines and their relative intensities will be proportional to the coefficients of the binomial expansion of $(1 + x)^m$ where $m = n - 1$. Alternatively these coefficients can also be calculated using Pascal's triangle.

$$\begin{array}{ccccccccccccc}
 & & & & & & 1 & & & & & & \\
 & & & & & 1 & & 1 & & & & & \\
 & & & & 1 & & 2 & & 1 & & & & \\
 & & & 1 & & 3 & & 3 & & 1 & & & \\
 & & 1 & & 4 & & 6 & & 4 & & 1 & & \\
 & 1 & & 5 & & 10 & & 10 & & 5 & & 1 & \\
1 & & 6 & & 15 & & 20 & & 15 & & 6 & & 1
\end{array}$$

Pascal's Triangle

A high resolution NMR spectrum of ethanol is more complicated than the ordinary low resolution spectrum. With higher resolution the lines in the spectrum are split into multiplets. The absorption line due to methyl (CH_3) protons is split into three components (1 : 2 : 1) because the neighbouring methylene group (CH_2) contains two protons each with spin $\frac{1}{2}$. We can think of the first methylene proton splitting the methyl proton resonance into a doublet as shown in Figure (5.10).

Then the second methylene proton splits the doublet into a triplet with the center line twice as intense as the other two. The two methylene protons produce the same spin-spin splitting because there is rapid rotation of around the C–C bond.

The absorption line due to methylene protons is split into four components by three protons of the neighbouring CH_3 group.

The relative intensities will be 1 : 3 : 3 : 1.

In the high resolution spectrum recorded in presence of trace amounts of acid the proton in the hydroxyl group does not cause splitting because it undergoes chemical change so rapidly with protons in other molecules that it does not produce splitting effect.

Fig. 5.10 *High Resolution NMR Spectra Ethanol*

5.6.1 Line Width Hyperfine Splitting

The 'Hyperfine Splitting' occurs due to hyperfine coupling, the EPR (Electron Paramagnetic Resonance) analogy to NMR's J coupling, and further splits the fine structure occurring from spin-orbit interaction and relativistic effects of the spectra of atoms with unpaired electrons. Although hyperfine splitting applies to multiple spectroscopy techniques, such as Nuclear Magnetic Resonance (NMR), this splitting is essential and most relevant in the utilization of Electron Paramagnetic Resonance (EPR) spectroscopy.

Hyperfine splitting is typically utilized in EPR spectroscopy to provide information about a molecule, most often radicals. The number and identity of nuclei can be determined, as well as the distance of a nucleus from the unpaired electron in the molecule. Hyperfine coupling is caused by the interaction between the magnetic moments arising from the spins of both the nucleus and electrons in atoms. As shown in Figure (5.11), in a single electron system the electron with its own magnetic moment moves within the magnetic dipole field of the nucleus. In the Figure (5.11), B refers to the magnetic field, μ refers to the dipole moment, 'N' refers to the nucleus, and 'e' refers to the electron.

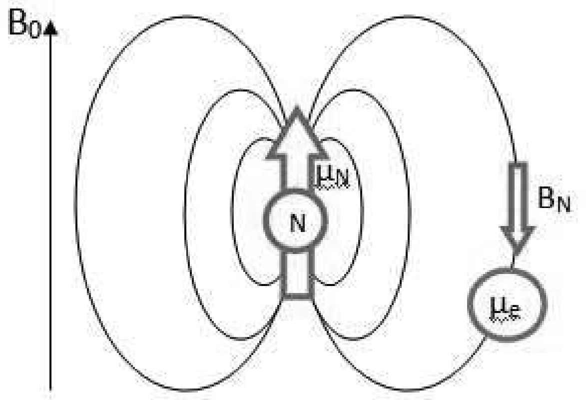


Fig. 5.11 *B is Magnetic Field, μ is Dipole Moment, 'N' refers to the Nucleus, 'e' refers to the Electron*

This spin interaction in turn causes splitting of the fine structure of spectral lines into smaller components termed as hyperfine structure. Hyperfine structure is approximately 1000 times smaller than fine structure. Figure (5.12) shows a comparison of fine structure with hyperfine structure splitting for hydrogen, though this is not to scale.

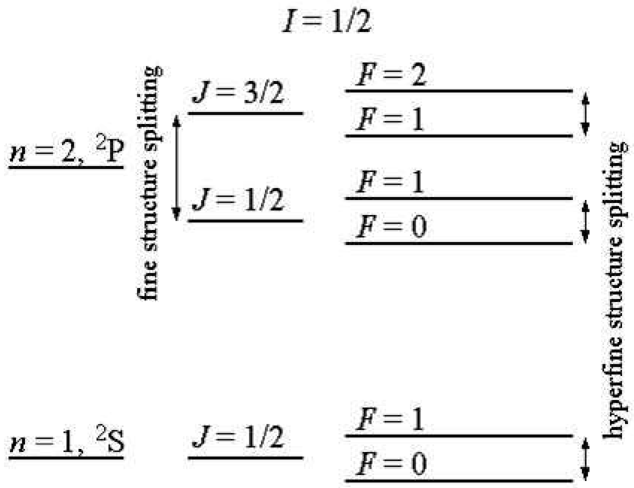


Fig. 5.12 *Splitting Diagram of Hydrogen*

The total angular momentum of the atom is represented by F with regards to hyperfine structure. This is given by the relation,

$$\boldsymbol{F = J + I}$$

Where I is the ground state quantum number and J refers to the energy levels of the system.

These hyperfine interactions between dipoles are especially relevant in EPR. The spectra of EPR are derived from a change in the spin state of an electron. Without the additional energy levels arising from the interaction of the nuclear and electron magnetic moments, only one line would be observed for single electron spin systems. This process is known as hyperfine splitting (hyperfine coupling) and may be thought of as a Zeeman effect occurring due to the magnetic dipole moment of the nucleus inducing a magnetic field. The line width of ESR resonance depends on the relaxation time of the spin state under study.

The coupling patterns due to hyperfine splitting are identical to that of NMR. The number of peaks resulting from hyperfine splitting of radicals may be predicted by the following equations where M_i is the number of equivalent nuclei:

# of Peaks = $M_i I + 1$ for Atoms having One Equivalent Nuclei

# of Peaks = $(2M_1I_1 + 1)\,(2M_2I_2 + 1)$ for Atoms with Multiple Equivalent Nuclei

5.6.2 Nuclear Quadrupole Resonance

Nuclear Quadrupole Resonance or NQR spectroscopy is a chemical analysis technique related to Nuclear Magnetic Resonance (NMR). Unlike NMR, NQR transitions of nuclei can be detected in the absence of a magnetic field, and for this reason NQR spectroscopy is referred to as 'Zero Field NMR'. The NQR resonance is mediated by the interaction of the Electric Field Gradient (EFG) with the quadrupole moment of the nuclear charge distribution. Unlike NMR, NQR is applicable only to solids and not liquids, because in liquids the quadrupole moment averages out. Because the EFG at the location of a nucleus in a given substance is determined primarily by the valence electrons involved in the particular bond with other nearby nuclei, the NQR frequency at which transitions occur is unique for a given substance. A particular NQR frequency in a compound or crystal is proportional to the product of the nuclear quadrupole moment, a property of the nucleus, and the EFG in the neighbourhood of the nucleus. It is this product which is termed the nuclear quadrupole coupling constant for a given isotope in a material and can be found in tables of known NQR transitions. In NMR, an analogous but not identical phenomenon is the coupling constant, which is also the result of an internuclear interaction between nuclei in the analyte.

Definition: Nuclear Quadrupole Resonance (NQR) spectroscopy is a unique method to describe chemical compounds containing Quadrupolar Nuclei (QN). Similar as in Nuclear Magnetic Resonance (NMR) the sample under investigation is irradiated with strong Radio Frequency (RF) pulses to induce and detect transitions between sublevels of nuclear ground states.

NMR refers to the situation where the sublevel energy splitting is predominantly due to nuclear interaction with an applied static magnetic field, while

NOTES

NQR refers to the instance where the predominant splitting is due to an interaction with Electric Field Gradients (EFG) within the material. Quadrupole splitting is possible if the charge distribution of the nucleus has an electric quadrupole moment. This is possible if the spin quantum number I is greater than 1/2. The electric quadrupole moment of the nucleus interacts with the EFG which is caused by a non-spherical charge distribution of the environment of the nucleus.

Principle

Any nucleus with more than one unpaired nuclear particle, protons or neutrons, will have a charge distribution which results in an electric quadrupole moment. Allowed nuclear energy levels are shifted unequally due to the interaction of the nuclear charge with an electric field gradient supplied by the non-uniform distribution of electron density, for example from bonding electrons and/or surrounding ions. As in the case of NMR, irradiation of the nucleus with a burst of RF (Radio Frequency) electromagnetic radiation may result in absorption of some energy by the nucleus which can be viewed as a perturbation of the quadrupole energy level. Unlike the NMR case, NQR absorption takes place in the absence of an external magnetic field. Application of an external static field to a quadrupolar nucleus splits the quadrupole levels by the energy predicted from the Zeeman interaction. The technique is very sensitive to the nature and symmetry of the bonding around the nucleus. It can characterize phase transitions in solids when performed at varying temperature. Due to symmetry, the shifts become averaged to zero in the liquid phase, therefore NQR spectra can only be measured for solids.

Derivation of Resonance Frequency

To derive the resonance frequency, consider a nucleus with a non-zero quadrupole moment **Q** and charge density ρ(**r**), which is surrounded by a potential **V**(**r**). This potential may be produced by the electrons whose probability distribution might be non-isotropic in general. The potential energy in this system equals to the integral over the charge distribution ρ(**r**) and the potential **V**(**r**) within a domain ***D***, and the equation is given by:

$$U = -\int_{\mathcal{D}} d^3 r \rho(\mathbf{r}) V(\mathbf{r})$$

One can write the potential as a Taylor-expansion at the center of the considered nucleus. This method corresponds to the multipole expansion in Cartesian coordinates.

Applications of Nuclear Quadrupole Resonance Spectroscopy

Several research have been conducted to define the techniques for using NQR to detect explosives. Units have been successfully designed to detect landmines and explosives concealed in luggage. A detection system consists of a Radio Frequency (RF) power source, a coil to produce the magnetic excitation field and a detector circuit which monitors for a RF NQR response coming from the explosive component of the object.

Another practical use for NQR is measuring the Water/Gas/Oil coming out of an Oil Well in real time. This particular technique allows local or remote monitoring of the extraction process, calculation of the well's remaining capacity and the water/detergents ratio the input pump must send to efficiently extract oil.

Due to the strong temperature dependence of the NQR frequency, it can be used as a precise temperature sensor with resolution on the order of 10^{-4} °C.

5.6.3 Ferromagnetic Resonance and Antiferromagnetic Resonance

FerroMagnetic Resonance or **FMR** is defined as coupling between an electromagnetic wave and the magnetization of a medium through which it passes. This coupling induces a significant loss of power of the wave. The power is absorbed by the precession magnetization, the Larmor precession, of the material and lost as heat. For this coupling to occur, the frequency of the incident wave must be equal to the precession frequency of the magnetization, the Larmor frequency, and the polarization of the wave must match the orientation of the magnetization.

This effect can be used for various applications, such as spectroscopic techniques or conception of microwave devices.

The FMR spectroscopic technique is used to probe the magnetization of ferromagnetic materials. It is a standard tool for probing spin waves and spin dynamics. FMR is very broadly similar to Electron Paramagnetic Resonance (EPR), and also somewhat similar to Nuclear Magnetic Resonance (NMR), except that FMR probes the sample magnetization resulting from the magnetic moments of dipolar coupled but unpaired electrons, while NMR probes the magnetic moment of atomic nuclei that are screened by the atomic or molecular orbitals surrounding such nuclei of non-zero nuclear spin.

The FMR resonance is also the basis of various high-frequency electronic devices, such as resonance isolators or circulators.

Ferromagnetic resonance was experimentally discovered by V. K. Arkad'yev when he observed the absorption of UHF (Ultra High Frequency)radiation by ferromagnetic materials in 1911. A qualitative explanation of FMR along with an explanation of the results from Arkad'yev was offered up by Ya. G. Dorfman in 1923 when he suggested that the optical transitions due to Zeeman splitting could provide a way to study ferromagnetic structure.

A 1935 paper published by Lev Landau and Evgeny Lifshitz predicted the existence of ferromagnetic resonance of the Larmor precession, which was independently verified in experiments by J. H. E. Griffiths (UK) and E. K. Zavoiskij (USSR) in the year1946.

Explanation

FerroMagnetic Resonance or FMR occurs from the precessional motion of the magnetization **M**, usually quite large, of a ferromagnetic material in an external magnetic field **H**. The magnetic field exerts a torque on the sample magnetization which causes the magnetic moments in the sample to precess. The precession frequency of the magnetization depends on the orientation of the material, the strength of the magnetic field, as well as the macroscopic magnetization of the sample; the effective precession frequency of the ferromagnet is much lower in value from the precession frequency observed for free electrons in EPR. Moreover, linewidths of absorption peaks can be greatly affected both by dipolar-narrowing and exchange-broadening (quantum) effects. Furthermore, not all absorption peaks observed in FMR are caused by the precession of the magnetic moments of electrons in the ferromagnet. Thus, the theoretical analysis of FMR spectra is far more complex than that of EPR or NMR spectra.

NOTES

The basic setup for an FMR experiment is a microwave resonant cavity with an electromagnet. The resonant cavity is fixed at a frequency in the super high frequency band. A detector is placed at the end of the cavity to detect the microwaves. The magnetic sample is placed between the poles of the electromagnet and the magnetic field is swept while the resonant absorption intensity of the microwaves is detected. When the magnetization precession frequency and the resonant cavity frequency are the same, absorption increases sharply which is indicated by a decrease in the intensity at the detector.

Furthermore, the resonant absorption of microwave energy causes local heating of the ferromagnet. In samples with local magnetic parameters varying on the nanometre scale this effect is used for spatial dependent spectroscopy investigations.

The resonant frequency of a film with parallel applied external field B is given by the Kittel formula:

$$f = \frac{\gamma}{2\pi}\sqrt{B(B + \mu_0 M)}$$

Where M is the magnetization of the ferromagnet and γ is the gyromagnetic ratio.

Antiferromagnetic Resonance

Antiferromagnetic resonance is a specific type of electron magnetic resonance. The ‘Antiferromagnetic Resonance’ is proved and established as a sharp rise in the absorption of electromagnetic energy passing through antiferromagnetic material for certain resonant values of the frequency ***v*** and of the intensity of the applied magnetic field **H**. Antiferromagnetic materials typically have an ordered arrangement of magnetic moments for the atoms (ions). Elementary magnetic moments having the same orientation in antiferromagnetic materials form the so called sublattices, in the simplest case two lattices. In antiferromagnetic resonance, the resonant vibrations are excited in the magnetization vectors of the sublattices with respect both to one another and to the direction of the applied field H. The form of the dependence of *v* on the effective magnetic fields in antiferromagnetic materials is very complicated and varies for different crystal structures. As a rule, a single value of an applied field corresponds to two antiferromagnetic resonance frequencies. Antiferromagnetic resonance frequencies lie in the range of 10 to 1000 gigahertz. The antiferromagnetic resonance facilitates to establish or calculate the values of the effective magnetic fields to be determined in an antiferromagnetic material.

Check Your Progress

7. What is spin wave?
8. Define Nuclear Magnetic Resonance (NMR) technique.
9. What is hyperfine splitting?
10. State about the Nuclear Quadrupole Resonance or NQR spectroscopy.
11. Define the terms ferromagnetic resonance and antiferromagnetic resonance.

5.7 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Magnetism is referred as a specific class having physical characteristics that are intermediated by means of magnetic fields. Electric currents and the magnetic moments of elementary particles generate a magnetic field, which acts on other currents and magnetic moments. Magnetism is, therefore, one aspect of the combined phenomenon of electromagnetism. Fundamentally, the magnetism is the force exerted by magnets when they attract or repel each other. All magnets have north and south poles. Opposite poles are attracted to each other, while the similar poles repel each other.
2. The magnetic state or magnetic phase of a material depends on temperature, pressure, and the applied magnetic field. A material may exhibit more than one form of magnetism as these variables change.

   The strength of a magnetic field almost always decreases with distance, though the exact mathematical relationship between strength and distance varies. Different configurations of magnetic moments and electric currents can result in complicated magnetic fields.
3. Magnetic materials are classified into different categories based on their magnetic parameters, such as χ and μ_r, and their microscopic magnetic structure under different environmental conditions, i.e., under the influence of magnetic field, temperature, etc.
4. Following are the specific features of diamagnetism, paramagnetism and ferromagnetism:

   Diamagnetism: Diamagnetism appears in all materials and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. Despite its universal occurrence, diamagnetic behaviour is observed only in a purely diamagnetic material.

   Paramagnetism: In a paramagnetic material there are unpaired electrons, i.e., atomic or molecular orbitals with exactly one electron in them. While paired electrons are required by the Pauli exclusion principle to have their intrinsic 'Spin' magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an unpaired electron is free to align its magnetic moment in any direction.

   Ferromagnetism: A ferromagnet, like a paramagnetic substance, has unpaired electrons. Every ferromagnetic substance has its own individual temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order.

5. Following are the significant properties of antiferromagnetism and ferrimagnetism:

   Antiferromagnetism: The antiferromagnetism type of magnetism can be explained with reference to solids, such as Manganese Oxide (MnO) in which the adjacent ions, the Manganese ions Mn^{2+}, typically act as tiny magnets and get spontaneously aligned at relatively or comparatively low temperatures either into opposite or into antiparallel arrangements throughout the material with the purpose to exhibit approximately no external magnetism. Depending upon the temperature, the antiferromagnetic solid materials show unique behaviour in an applied magnetic field.

   Ferrimagnetism**:** Ferrimagnetism can be defined as typical behaviour of solid materials termed as 'Ferrites'. The occurrence of ferrimagnetism can be characteristically observed when the two different types of magnetic ions are present. A ferrimagnetic material is a specific material that has number of atoms with opposing magnetic moments. For ferrimagnetic materials, these moments are unequal in magnitude so a spontaneous magnetization remains, for example this can occur when the number of atoms consist of different atoms or ions, such as Fe^{2+} and Fe^{3+}. Ferrimagnets have a critical temperature above which they become paramagnetic. At this temperature, specifically termed as the 'Curie Temperature' there is a second order phase transition, and the system can no longer maintain a spontaneous magnetization.

6. For low levels of magnetization, the magnetization of paramagnets approximately follows the Curie's law. This law implies that the susceptibility 'χ' of paramagnetic materials is inversely proportional to their temperature, i.e., that materials become more magnetic at lower temperatures. The mathematical expression is given by:

   $$\mathbf{M} = \chi\mathbf{H} = \frac{C}{T}\mathbf{H}$$

   Where,

   M = The Resulting Magnetization, measured in Amperes/meter (A/m)

   χ = The Volume Magnetic Susceptibility (Dimensionless)

   H = The Auxiliary Magnetic Field (A/m)

   C = The Absolute Temperature, measured in Kelvins (K)

   T = The Material-Specific Curie Constant (K).

   Curie's law is valid under the commonly encountered conditions of low magnetization ($\mu_B H \leq k_B T$) but does not apply in the high-field/low-temperature regime where saturation of magnetization occurs ($\mu_B H \geq k_B T$) and magnetic dipoles are all aligned with the applied field. When the dipoles are aligned, increasing the external field will not increase the total magnetization since there can be no further alignment.

7. A spin wave is a propagating disruption in the reference of a magnetic material. These low-lying collective excitations occur in magnetic lattices with continuous symmetry. From the equivalent quasi-particle point of view, spin waves are known as magnons, which are bosonic modes of the spin lattice that correspond roughly to the phonon excitations of the nuclear lattice. As temperature is increased, the thermal excitation of spin waves reduces a ferromagnet's spontaneous magnetization.
8. Nuclear Magnetic Resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like IR (InfraRed) and UV (UltraVoilet) spectroscopy this method is non-destructible one and permits the recovery of the sample for further evaluation.

   Nuclear Magnetic Resonance (NMR) is concerned with the magnetic properties of certain nuclei, notably the nucleus of the hydrogen atom–the proton. Studying an organic molecule by NMR spectroscopy enables us to record difference in the magnetic properties of the various nuclei present, and to deduce in large measure what are the positions of these nuclei within the molecule.
9. The 'Hyperfine Splitting' occurs due to hyperfine coupling, the EPR analogy to NMR's J coupling, and further splits the fine structure occurring from spin-orbit interaction and relativistic effects of the spectra of atoms with unpaired electrons. Hyperfine splitting is typically utilized in EPR spectroscopy to provide information about a molecule, most often radicals. The number and identity of nuclei can be determined, as well as the distance of a nucleus from the unpaired electron in the molecule. Hyperfine coupling is caused by the interaction between the magnetic moments arising from the spins of both the nucleus and electrons in atoms.
10. Nuclear Quadrupole Resonance or NQR spectroscopy is a chemical analysis technique related to Nuclear Magnetic Resonance (NMR). Unlike NMR, NQR transitions of nuclei can be detected in the absence of a magnetic field, and for this reason NQR spectroscopy is referred to as 'Zero Field NMR'. The NQR resonance is mediated by the interaction of the Electric Field Gradient (EFG) with the quadrupole moment of the nuclear charge distribution. Unlike NMR, NQR is applicable only to solids and not liquids, because in liquids the quadrupole moment averages out.
11. FerroMagnetic Resonance or FMR is defined as coupling between an electromagnetic wave and the magnetization of a medium through which it passes. This coupling induces a significant loss of power of the wave. The power is absorbed by the precession magnetization, the Larmor precession, of the material and lost as heat. For this coupling to occur, the frequency of the incident wave must be equal to the precession frequency of the magnetization, the Larmor frequency, and the polarization of the wave must match the orientation of the magnetization.

    Antiferromagnetic resonance is a specific type of electron magnetic resonance. The 'Antiferromagnetic Resonance' is proved and established as a sharp rise in the absorption of electromagnetic energy passing through antiferromagnetic material for certain resonant values of the frequency ***v*** and of the intensity of the applied magnetic field **H**. Antiferromagnetic materials typically have an ordered arrangement of magnetic moments for the atoms (ions). In antiferromagnetic resonance, the resonant vibrations are excited in the magnetization vectors of the sublattices with respect both to one another and to the direction of the applied field H. Antiferromagnetic resonance frequencies lie in the range of 10 to 1000 gigahertz.

5.8 SUMMARY

- Magnetism is referred as a specific class having physical characteristics that are intermediated by means of magnetic fields. Electric currents and the magnetic moments of elementary particles generate a magnetic field, which acts on other currents and magnetic moments. Magnetism is one aspect of the combined phenomenon of electromagnetism.
- The most familiar effects occur in ferromagnetic materials, which are strongly attracted by magnetic fields and can be magnetized to become permanent magnets, producing magnetic fields themselves. Demagnetizing a magnet is also possible.
- The prefix ferro- refers to Iron, because permanent magnetism was first observed in Lodestone, a form of natural iron ore called Magnetite, Fe_3O_4.
- Fundamentally, the magnetism is the force exerted by magnets when they attract or repel each other. All magnets have north and south poles. Opposite poles are attracted to each other, while the similar poles repel each other.
- The magnetic state or magnetic phase of a material depends on temperature, pressure, and the applied magnetic field. A material may exhibit more than one form of magnetism as these variables change.
- The strength of a magnetic field almost always decreases with distance, though the exact mathematical relationship between strength and distance varies. Different configurations of magnetic moments and electric currents can result in complicated magnetic fields.
- Magnetism, at its origin, evolves from following two sources:
  1. Electric Current.
  2. Spin Magnetic Moments of Elementary Particles.
- The magnetic properties of materials are primarily due to the magnetic moments of their atoms' orbiting electrons. The magnetic moments of the nuclei of atoms are typically thousands of times smaller than the electrons' magnetic moments, therefore they are negligible in the context of the magnetization of materials.
- Nuclear magnetic moments are very significant especially in Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI).
- The magnetic behaviour of a material depends on its structure, particularly its electron configuration, for the reasons stated above, and also on the

temperature. At high temperatures, random thermal motion makes it more difficult for the electrons to maintain alignment.

- Magnetic materials are classified into different categories based on their magnetic parameters, such as χ and μ_r, and their microscopic magnetic structure under different environmental conditions, i.e., under the influence of magnetic field, temperature, etc.
- Based on whether the atoms carry permanent magnetic dipoles or not, and also on the basis of effect of temperature and magnetic field on the magnetic properties; all materials are broadly classified into the following three categories.
  1. Diamagnetic Materials
  2. Paramagnetic Materials
  3. Ferromagnetic Materials
- Two more classes of materials have structure very close to ferromagnetic materials but possess quite different magnetic effects. They are:
  1. Antiferromagnetic Materials
  2. Ferrimagnetic Materials
- Diamagnetism appears in all materials and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field.
- In a material with paramagnetic properties, i.e., with a tendency to enhance an external magnetic field the paramagnetic behaviour dominates.
- Despite its universal occurrence, diamagnetic behaviour is observed only in a purely diamagnetic material.
- In a paramagnetic material there are unpaired electrons, i.e., atomic or molecular orbitals with exactly one electron in them.
- The paired electrons are required by the Pauli exclusion principle to have their intrinsic 'Spin' magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an unpaired electron is free to align its magnetic moment in any direction.
- A ferromagnet, like a paramagnetic substance, has unpaired electrons. However, in addition to the electrons' intrinsic magnetic moment's tendency to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered-energy state. Thus, even in the absence of an applied field, the magnetic moments of the electrons in the material spontaneously line up parallel to one another.
- Every ferromagnetic substance has its own individual temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order.
- Ferromagnetism only occurs in a few substances; common ones are Iron, Nickel, Cobalt, their Alloys, and some alloys of rare earth metals.

- The antiferromagnetism type of magnetism can be explained with reference to solids, such as Manganese Oxide (MnO) in which the adjacent ions, the Manganese ions Mn^{2+}, typically act as tiny magnets and get spontaneously aligned at relatively or comparatively low temperatures either into opposite or into antiparallel arrangements throughout the material with the purpose to exhibit approximately no external magnetism.
- Depending upon the temperature, the antiferromagnetic solid materials show unique behaviour in an applied magnetic field. Consequently. the solids show no response to the external field at exceptionally low temperature because the atomic magnet's antiparallel ordering is firmly maintained.
- At the higher temperatures some of the atoms of the solids break down and are free of the orderly or systematic arrangement for aligning with the external field. This type of alignment produces the weak magnetism characteristics in the solids when achieve their peak at the Néel temperature.
- Above the Néel temperature, the thermal tension gradually prevents the alignment or orientation of the atoms of the solid materials with the magnetic field, therefore, the weak magnetism that is produced in the solids through the alignment of the atoms decreases continuously as temperature increases.
- Ferrimagnetism can be defined as typical behaviour of solid materials termed as 'Ferrites'. The occurrence of ferrimagnetism can be characteristically observed when the two different types of magnetic ions are present.
- A ferrimagnetic material is a specific material that has number of atoms with opposing magnetic moments, as in antiferromagnetism. For ferrimagnetic materials, these moments are unequal in magnitude so a spontaneous magnetization remains, for example this can occur when the number of atoms consist of different atoms or ions, such as Fe^{2+} and Fe^{3+}.
- Ferrimagnetism has often been confused with ferromagnetism. The oldest known magnetic substance, Magnetite (Fe_3O_4), was typically classified as a ferromagnet before Louis Néel discovered ferrimagnetism in 1948.
- Ferrimagnetism has the same physical origins as ferromagnetism and antiferromagnetism. In ferrimagnetic materials, the magnetization is also caused by a combination of dipole-dipole interactions and exchange interactions resulting from the Pauli exclusion principle.
- Ferrimagnets have a critical temperature above which they become paramagnetic just as ferromagnets do. At this temperature, specifically termed as the 'Curie Temperature' there is a second order phase transition, and the system can no longer maintain a spontaneous magnetization. This is because at higher temperatures the thermal motion is strong enough that it exceeds the tendency of the dipoles to align.
- A diamagnetic material is the solid material whose atoms do not have or exhibit permanent magnetic dipole moment.
- Basically, a diamagnetic material has extremely low or minimal magnetic effect because of the absence of any unpaired electrons in them. Alternatively, the diamagnetic materials can be explained through the Lenz's law, which states that diamagnetic materials get induced dipoles in the presence of an

external magnetic field, and this happens in such an order that the magnetic field and the induced dipoles repel each other.

- Diamagnetism was first discovered when Anton Brugmans observed in 1778 that 'Bismuth' was repelled by magnetic fields.
- In 1845, Michael Faraday demonstrated that it was a property of matter and concluded that every material responded, in either a diamagnetic or paramagnetic way, to an applied magnetic field. Therefore, the characteristic features of diamagnetic material or diamagnets was uniquely defined by Michael Faraday.
- The semiconductors are considered as the best diamagnetic materials. The semiconductors also exhibit the diamagnetic field and therefore this ideal diamagnetism in the superconductor is termed as the 'Meissner Effect'.
- A simple rule of thumb is used for determining whether a particle (atom, ion, or molecule) is paramagnetic or diamagnetic. If all electrons in the particle are paired, then the substance made of this particle is termed as diamagnetic else if it has unpaired electrons, then the substance is termed as paramagnetic.
- Paramagnetism is a form of magnetism whereby some materials are weakly attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field.
- The paramagnetic materials have a relative magnetic permeability slightly greater than 1, i.e., a small positive magnetic susceptibility and hence are attracted to magnetic fields.
- Paramagnetism is due to the presence of unpaired electrons in the material, consequently most atoms with incompletely filled atomic orbitals are paramagnetic, although exceptions, such as Copper exist. Due to their spin, unpaired electrons have a magnetic dipole moment and act like tiny magnets.
- An external magnetic field causes the electrons' spins to align parallel to the field, causing a net attraction. Paramagnetic materials include Aluminium, Oxygen, Titanium, and Iron Oxide (FeO).
- For some alkali metals and noble metals, conduction electrons are weakly interacting and delocalized in space forming a 'Fermi Gas'. For these materials, one contribution to the magnetic response comes from the interaction between the electron spins and the magnetic field known as 'Pauli Paramagnetism'.
- In quantum theory, the permanent magnetic moment of an atom or ion is not freely rotating but with respect to applied field it is restricted to a finite set of orientations.
- A spin wave is a propagating disruption in the reference of a magnetic material. These low-lying collective excitations occur in magnetic lattices with continuous symmetry.
- From the equivalent quasi-particle point of view, spin waves are known as magnons, which are bosonic modes of the spin lattice that correspond roughly to the phonon excitations of the nuclear lattice. As temperature is increased,

the thermal excitation of spin waves reduces a ferromagnet's spontaneous magnetization.

- Spin waves are observed through four experimental methods: inelastic neutron scattering, inelastic light scattering (Brillouin scattering, Raman scattering and inelastic X-ray scattering), inelastic electron scattering (spin-resolved electron energy loss spectroscopy), and spin-wave resonance (ferromagnetic resonance).
- Antiferromagnetic order may exist at sufficiently low temperatures but vanishes at and above the Néel temperature – named after Louis Néel, who had first identified this type of magnetic ordering. Above the Néel temperature, the material is typically paramagnetic.
- In ferromagnetic ordering, all the spins within a magnetic domain, typically hundreds of unit cells in width, have the same orientation.
- The magnetization and hysteresis observed in a ferromagnetic material is explained using the concept of domain proposed by Weiss in 1907. According to this domain concept, a specimen of ferromagnetic material consists of different region which are spontaneously magnetised below the Curie temperature.
- These spontaneously magnetised or self magnetised regions in a ferromagnetic material is called domains. Each domain is separated by the other domain by domain walls which has finite dimension.
- Nuclear Magnetic Resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like IR (InfraRed) and UV (UltraVoilet) spectroscopy this method is non-destructible one and permits the recovery of the sample for further evaluation.
- Nuclear Magnetic Resonance (NMR) is concerned with the magnetic properties of certain nuclei, notably the nucleus of the hydrogen atom–the proton. Studying an organic molecule by NMR spectroscopy enables us to record difference in the magnetic properties of the various nuclei present, and to deduce in large measure what are the positions of these nuclei within the molecule.
- The 'Hyperfine Splitting' occurs due to hyperfine coupling, the EPR (Electron Paramagnetic Resonance) analogy to NMR's J coupling, and further splits the fine structure occurring from spin-orbit interaction and relativistic effects of the spectra of atoms with unpaired electrons.
- Although hyperfine splitting applies to multiple spectroscopy techniques, such as Nuclear Magnetic Resonance (NMR), this splitting is essential and most relevant in the utilization of Electron Paramagnetic Resonance (EPR) spectroscopy.
- Hyperfine splitting is typically utilized in EPR spectroscopy to provide information about a molecule, most often radicals. The number and identity of nuclei can be determined, as well as the distance of a nucleus from the unpaired electron in the molecule.

- Hyperfine coupling is caused by the interaction between the magnetic moments arising from the spins of both the nucleus and electrons in atoms.
- Nuclear Quadrupole Resonance or NQR spectroscopy is a chemical analysis technique related to Nuclear Magnetic Resonance (NMR). Unlike NMR, NQR transitions of nuclei can be detected in the absence of a magnetic field, and for this reason NQR spectroscopy is referred to as 'Zero Field NMR'.
- The NQR resonance is mediated by the interaction of the Electric Field Gradient (EFG) with the quadrupole moment of the nuclear charge distribution.
- A particular NQR frequency in a compound or crystal is proportional to the product of the nuclear quadrupole moment, a property of the nucleus, and the EFG in the neighbourhood of the nucleus. It is this product which is termed the nuclear quadrupole coupling constant for a given isotope in a material and can be found in tables of known NQR transitions.
- In NMR, an analogous but not identical phenomenon is the coupling constant, which is also the result of an internuclear interaction between nuclei in the analyte.
- Nuclear Quadrupole Resonance (NQR) spectroscopy is a unique method to describe chemical compounds containing Quadrupolar Nuclei (QN). Similar as in Nuclear Magnetic Resonance (NMR) the sample under investigation is irradiated with strong Radio Frequency (RF) pulses to induce and detect transitions between sublevels of nuclear ground states.
- FerroMagnetic Resonance or FMR is defined as coupling between an electromagnetic wave and the magnetization of a medium through which it passes. This coupling induces a significant loss of power of the wave. The power is absorbed by the precession magnetization, the Larmor precession, of the material and lost as heat.
- Antiferromagnetic resonance is a specific type of electron magnetic resonance.
- The 'Antiferromagnetic Resonance' is proved and established as a sharp rise in the absorption of electromagnetic energy passing through antiferromagnetic material for certain resonant values of the frequency ***v*** and of the intensity of the applied magnetic field **H**.
- Antiferromagnetic materials typically have an ordered arrangement of magnetic moments for the atoms (ions).
- In antiferromagnetic resonance, the resonant vibrations are excited in the magnetization vectors of the sublattices with r1espect both to one another and to the direction of the applied field **H**.
- Antiferromagnetic resonance frequencies lie in the range of 10 to 1000 gigahertz. The antiferromagnetic resonance facilitates to establish or calculate the values of the effective magnetic fields to be determined in an antiferromagnetic material.

5.9 KEY TERMS

- **Magnetism:** Magnetism is referred as a specific class having physical characteristics that are intermediated by means of magnetic fields. Fundamentally, the magnetism is the force exerted by magnets when they attract or repel each other. All magnets have north and south poles. Opposite poles are attracted to each other, while the similar poles repel each other.
- **Diamagnetism:** Diamagnetism appears in all materials and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. Despite its universal occurrence, diamagnetic behaviour is observed only in a purely diamagnetic material.
- **Paramagnetism:** In a paramagnetic material there are unpaired electrons, i.e., atomic or molecular orbitals with exactly one electron in them. While paired electrons are required by the Pauli exclusion principle to have their intrinsic 'Spin' magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an unpaired electron is free to align its magnetic moment in any direction.
- **Ferromagnetism:** A ferromagnet, like a paramagnetic substance, has unpaired electrons. Every ferromagnetic substance has its own individual temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order.
- **Antiferromagnetism:** The antiferromagnetism type of magnetism can be explained with reference to solids, such as Manganese Oxide (MnO) in which the adjacent ions, the Manganese ions Mn^{2+}, typically act as tiny magnets and get spontaneously aligned at relatively or comparatively low temperatures either into opposite or into antiparallel arrangements throughout the material with the purpose to exhibit approximately no external magnetism.
- **Ferrimagnetism:** Ferrimagnetism can be defined as typical behaviour of solid materials termed as 'Ferrites'. The occurrence of ferrimagnetism can be characteristically observed when the two different types of magnetic ions are present. For ferrimagnetic materials, these moments are unequal in magnitude so a spontaneous magnetization remains, for example this can occur when the number of atoms consist of different atoms or ions, such as Fe^{2+} and Fe^{3+}.
- **Pauli paramagnetism:** For some alkali metals and noble metals, conduction electrons are weakly interacting and delocalized in space forming a 'Fermi Gas'. For these materials, one contribution to the magnetic response comes from the interaction between the electron spins and the magnetic field known as 'Pauli Paramagnetism'.
- **Antiferromagnetic order:** Antiferromagnetic order may exist at sufficiently low temperatures but vanishes at and above the Néel temperature – named after Louis Néel, who had first identified this type of magnetic ordering. Above the Néel temperature, the material is typically paramagnetic.

- **Ferromagnetic ordering:** In ferromagnetic ordering, all the spins within a magnetic domain, typically hundreds of unit cells in width, have the same orientation.

5.10 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What is magnetism?
2. Differentiate between diamagnetism and paramagnetism.
3. State the quantum theory of paramagnetism.
4. Why the spin waves and magnons are studied?
5. Define the terms ferromagnetic order and antiferromagnetic order.
6. What are the ferromagnetic domains?
7. State about the magnetic resonance property.
8. What is the importance of Nuclear Magnetic Resonance (NMR)?
9. Why is line width hyperfine splitting used?
10. Define nuclear quadrupole resonance.
11. Differentiate between ferromagnetic resonance and antiferromagnetic resonance.

Long-Answer Questions

1. Briefly discuss the concept and significant properties of magnetism with the help of appropriate examples.
2. How magnetic materials are classified? Explain giving relevant examples.
3. Discuss the properties and important characteristics of diamagnetism and paramagnetism giving significant notations and relevant examples.
4. Explain the quantum theory of paramagnetism.
5. Briefly explain the characteristic features of spin waves and magnons giving appropriate examples.
6. Discuss and differentiate between the ferromagnetic order and the antiferromagnetic order with the help of examples.
7. Explain the basic characteristics of ferromagnetic domains.
8. Briefly explain the significance of magnetic resonance with reference to Nuclear Magnetic Resonance (NMR). Also discuss the significant properties and applications of NMR.
9. Analyse the significance of line width hyperfine splitting.
10. Discuss the concept of Nuclear Quadrupole Resonance (NQR) giving relevant examples.
11. Briefly discuss ferromagnetic resonance and antiferromagnetic resonance giving their characteristic features.

5.11 FURTHER READING

Wahab, M. A. 2005. *Solid State Physics: Structure and Properties of Materials*. New Delhi: Narosa Publishing House.

Kittel, Charles. 1971. *Introduction to Solid State Physics*. New Jersey (US): John Wiley & Sons, Inc.

Pillai, S. O. 2005. *Solid State Physics*. Noida (UP): Wiley India Private Ltd.

Saxena, B. S., P. N. Saxena and R. C. Gupta. 2019. *Fundamentals of Solid State Physics*. Meerut (UP): Pragati Prakashan.

Dekker, A. J. 2008. *Solid State Physics*. Noida (UP): Macmillan Publishers India Pvt. Ltd.

Kakani, S. L. and C. Hemarajani. 2005. *Solid State Physics*. New Delhi: Sultan Chand & Sons Pvt. Ltd.