

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – 1 – Crystal Structure – SPH1316

Syllabus

Unit 1. Crystal Structure:

Introduction – Types of solids – amorphous and crystalline solid - space lattice – The basis and the crystal structure unit cell – primitive lattice cell – Lattice parameter - Symmetry considerations – point groups - Bravais lattices in two dimensions–seven crystal systems – co-ordination number for SC, BCC abd FCC - Miller indices–features of miller indices - Bragg's law –- Rotating crystal method–Powder method–Neutron diffraction.

Unit 2. Magnetic and Dielectric materials:

Magnetic materials: Magnetic moment – dia and paramagnetism – Ferromagnetism – Domain theory of ferromagnetism – Antiferromagnetic – Ferrites -; applications – floppy and magnetic disc devices, magnetic bubble memory. **Dielectric materials**: Electronic, ionic, oriental and space charge polarization – Internal field – Determination of Clausius – Mosotti relation – dielectric loss – dielectric breakdown.

Unit 3. Superconductivity:

Introduction – properties of superconductors – High and low temperatures superconductors - BCS theory - Meissner effect – Levitation – Josephson's effect -SQUID - Type I and Type II superconductivity.

Unit 4 -. Semiconducting materials:

Semiconductors - expressions for the carrier concentration in intrinsic and extrinsic semiconductors – calculation of density of holes and electrons – Fermi level and its variation with temperature – Determination of band gap energy – Hall effect – Determination of Hall coefficient.

Unit 5. Optical properties of solids:

Introduction- Ionic conduction – Optical absorption in metals, Insulators and semiconductors – colour Centres – Excitons – Luminescence – Maser and Laser – applications of lasers.

Course Objective

□ To understand the importance of the crystalline order in solids

 \Box To acquire basic concept of crystalline lattices and the techniques.

 \Box To understand the importance of the dynamics of electrons in the conductance properties of materials

□ To understand the importance of the quantum behaviour of electrons in metals

 $\hfill\square$ To understand the origin of the energy bands in solids and basic notions on their calculation

Course Outcomes

Students should gain basic knowledge of solid state physics. This implies that the student will:

CO1:Have a basic knowledge of crystal systems and spatial symmetries

CO2: Be able to account for how crystalline materials are studied using diffraction, including concepts like form factor, structure

factor, and scattering amplitude.

CO3: Know the principles of structure determination by diffraction.

CO4: Understand the concept of reciprocal space and be able to use it as a tool

CO5: Know the significance of Brillouin zones

Crystal Structure

Types of Solids

- Crystals have an orderly arrangement of their constituent particles. In comparison, amorphous solids have no such arrangement. Their particles are randomly organised.
- Crystals have a specific geometric shape with definite edges. Amorphous solids have no geometry in their shapes
- Crystalline solids have a sharp melting point on which they will definitely melt. An amorphous solid will have a range of temperature over which it will melt, but no definite temperature as such
- Crystals have a long order arrangement of their particles. This means the particles will show the same arrangement indefinitely. Amorphous solids have a short order arrangement. Their particles show a lot of variety in their arrangement.
- Crystalline solids cleavage (break) along particular points and directions. Amorphous solids cleavage into uneven parts with ragged edges.
- Crystals are also known as True Solids, whereas another name for Amorphous Solids is Super-Cooled Liquids.





Fig. 1.1 Types of Solids

Space Lattice and Unit Cells



Fig.1.2 Unit cell

In a solid crystalline material, the atoms or molecules are arranged regularly and periodically in three dimensions. ... If each such unit of atoms or atom in a **crystal** is replaced by a point in **space**, then the resultant points in **space** are called **space lattice**.

"The smallest repeat **unit** of a crystal structure, in 3D, which shows the full symmetry of the structure" Repetition of **unit cell** generates entire crystal. "The 3D arrangement of points in **space** is called **space lattice**"

A **lattice** is an ordered array of points describing the arrangement of particles that form a crystal. The **unit cell** of a crystal is defined by the **lattice** points. The **unit cell** is the smallest part of a crystal that repeated regularly through translation in three dimensions creates the whole crystal.

A **unit cell** is the smallest repeating portion of a crystal lattice. **Unit cells** occur in many different varieties. As one example, the **cubic** crystal system is composed of three different **types** of **unit cells**: (1) simple **cubic** (2) face-centered **cubic** and (3)body-centered **cubic**

Crystal structure is described in terms of the geometry of arrangement of particles in the unit cell. The unit cell is defined as the smallest repeating unit having the full symmetry of the crystal structure.

Primitive and Conventional cell

Primitive cells allow lattice points only at the corners of a cell. Unit cell allows lattice points at corners, face centers and body centers. Conventionally a primitive cell is chosen as the cell with smallest primitive vectors.

There are two distinct types of unit cell: primitive and non-primitive. Primitive unit cells contain only one lattice point, which is made up from the lattice points at each of the corners. ... Lattice points on the face of a unit cell are shared between two-unit cells and are worth 1/2 of a lattice point per unit cell.





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The simplest and most primitive of cells are the prokaryotic cells (pro means before and caryon refers to the nucleus). Prokaryotic cells are much smaller than eukaryotic cells.

In physics, the reciprocal lattice represents the Fourier transform of another lattice (usually a Bravais lattice). In normal usage, the initial lattice (whose transform is represented by the reciprocal lattice) is usually a periodic spatial function in real-space and is also known as the direct lattice.

Types of Crystal Structures

There are 7 Crystal Systems. The structures of all crystals can be classified according to the symmetry of the unit cells. There are in total 7 groups, collectively called Crystal Systems: Tricinic, Monoclinic, Orthorhombic, Tetragonal, Trigonal, Hexagonal, and Cubic.

The 14 Bravais lattices are grouped into seven lattice systems: triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, and cubic. In a crystal system, a set of point groups and their corresponding space groups are assigned to a lattice system.



Fig.1.4 Crystal Systems

Table 1.1

The Seven Crystal	Systems divided	into Fourteen	Bravais Lattices	

System	Bravais	Unit Cell	Characteristic	Examples
	Lattice	Characteristics	elements	
Cubic	Simple	a = b = c	Four 3 fold rotation	NaCl, CaF ₂ ,
	Body-Centered	$\alpha = \beta = \gamma = 90^{\circ}$	axes (along	NaCIO ₃
	Face Centered		cube diagonal)	
Tetragonal	Simple	a=b≠c	One 4-fold rotation	NiSO ₄ , SnO ₂ ,
	Body-Centered	$\alpha = \beta = \gamma = 90^{\circ}$	axis	Indium, White,
				Tin
Orthorhombic	Simple	a≠b≠c	Three mutually	KNO ₃ ,
	Base Centered	$\alpha = \beta = \gamma = 90^{\circ}$	orthogonal 2-	BaSO ₄ ,MgSO ₄ ,
	Body-Centered		fold rotation axes.	Sulphur, Topaz
-	Face Centered			
Monoclinic	Simple	a≠b≠c	One 2- fold rotation	Na ₂ SO ₄ , FeSO ₄ ,
	Base Centered	$\alpha = \beta = 90^{\circ} \neq \gamma$	axis	NO ₂ SO ₃
Triclinic	Simple	a≠b≠c	None	CuSO ₄ , K ₂ Cr ₂ O ₇
		$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$		
Trigonal	Simple	a = b = c	One – fold rotation	CaSO ₄ , Bi, Sb,
(Rhombohedral)		$\alpha = \beta = \gamma \neq 90^{\circ}$	axis	Calcite
Hexagonal	Simple	a = b ≠ c	One – fold rotation	Tourmaline,
		$\alpha = \beta = 90^{\circ}$	axis	Quartz.
		$\gamma = 120^{\circ}$		

Miller Indices

- • Miller indices are used to specify directions and planes.
- • These directions and planes could be in lattices or in crystals.
- • The number of indices will match with the dimension of the lattice or the crystal.
- • E.g. in 1D there will be 1 index and 2D there will be two indices etc.

Notation Summary

- • (h,k,l) represents a point note the exclusive use of commas
- • Negative numbers/directions are denoted with a bar on top of the number
- • [hkl] represents a direction represents a family of directions
- • (hkl) represents a plane
- {hkl} represents a family of planes

Miller Indices for Planes

Procedure

- 1. Identify the plane intercepts on the x, y and z-axes.
- 2. Specify intercepts in fractional coordinates.
- 3. Take the reciprocals of the fractional intercepts.





Coordination Number



Fig. 1.6

Neutron Diffraction

- Neutron scattering is routinely used in modern science to understand material properties on the atomic scale. Originally developed as a tool for physics, the method has led to advances in many areas of science, from clean energy and the environment, pharmaceuticals and healthcare, through to nanotechnology, materials engineering, fundamental physics and IT.
- Neutron process a spin and associated magnetic moment, magnetic interaction between neutron and atomic electrons which is responsible for magnetic properties of moments may be expected.
- Thus, a neutron can be scattered by interaction of its magnetic moment with the atomic or ionic magnetic moment of the sample atom.
- This type of scattering is generally referred to as magnetic scattering.

The goal of modern materials science is to understand the factors that determine the properties of matter on the atomic scale, and then to use this knowledge to optimise those properties or to develop new materials and functionality. This process regularly involves the discovery of fascinating new physics, which itself may lead to previously unthought-of capabilities. Almost all of the major changes in our society, from the dramatic growth of computing and the internet to the steady increase in average life span, have their origin in our understanding and exploitation of the physics and chemistry of materials. To investigate atomic-scale structure and dynamics, scientists use a variety of tools and techniques, often based on the scattering of beams of particles. An "ideal" probe might be one that has a wavelength similar to the spacing between atoms, in order to study structure with atomic resolution, and an energy similar to that of atoms in materials in order to study their dynamics. It would have no charge, to avoid strong scattering by charges on the electrons or the nucleus and allow deep penetration into materials. It would be scattered to a similar extent by both light and heavy atoms and have a suitable magnetic moment so that we can also easily study magnetism. The scattering cross-section would be precisely measurable on an absolute scale, to facilitate comparison with theory and computer modelling. This particle exists - it is the neutron. Unfortunately, it is difficult to produce high-intensity beams of neutrons – which are normally only found strongly bound to protons in the nuclei of atoms. This can be done by fission in a nuclear reactor, where the release of neutrons is the fundamental process that produces heat. A research reactor, such as that at the Institut Laue-Langevin (ILL) in Grenoble, France, is optimised to produce bright beams of neutrons. Another way to produce intense neutron beams is using an accelerator-based source, such as the ISIS facility near Oxford in the UK, where a highenergy beam of protons releases neutrons from tungsten nuclei in a process known as spallation. Both research reactors and "spallation sources" are large and expensive facilities, so there are relatively few in the world.

IMPORTANT?

Neutrons have No Charge!

- Highly penetrating

Neutrons probe Nuclei!

Light atom sensitive

- Nondestructive
 - Can be used in extremes

Neutrons have a Magnetic Moment!

- Magnetic structure
- Fluctuations
- Magnetic materials

Neutrons have Spin!

- Polarized beams
- Atomic orientation
- Coherent and incoherent scattering

Types of Neutron scattering

Neutron diffraction is the application of neutron scattering to the determination of the atomic /or magnetic structure of a material: A sample to be examined is placed in a beam of thermal, hot or cold neutrons to obtain a diffraction pattern that provides information of the structure.

Elastic neutron scattering

A neutron interaction in which the kinetic energy lost by a neutron in a nuclear collision is transferred to the nucleus. The energy of a **neutron** is reduced more efficiently in collisions with nuclei of similar mass to the neutron, like hydrogen and other elements of low atomic mass.

Inelastic Neutron Scattering

Generally, a **neutron scattering** reaction occurs when a target nucleus emits a single neutron after a neutron-nucleus interaction. In an elastic scattering reaction between a **neutron** and a target nucleus, there is no energy transferred into nuclear excitation.

Advantages

Wavelength comparable with interatomic spacings – Kinetic energy comparable with that of atoms in a solid – Penetrating => bulk properties are measured & sample can be contained – Weak interaction with matter aids interpretation of scattering data - Isotopic sensitivity allows contrast variation – Neutron magnetic moment couples to $B \Rightarrow$ neutron "sees" unpaired electron spins

Disadvantages

Neutron sources are weak \Rightarrow low signals, need for large samples etc – Some elements (e.g. Cd, B, Gd) absorb strongly – Kinematic restrictions (can't access all energy & momentum transfers).

Bragg's Law

An X-ray which reflects from the surface of a substance has travelled less distance than an X-ray which reflects from a plane of atoms inside the crystal. The penetrating

- Sensitive to isotopic substitution

X-ray travels down to the internal layer, reflects, and travels back over the same distance before being back at the surface. The distance travelled depends on the separation of the layers and the angle at which the X-ray entered the material. For this wave to be in phase with the wave which reflected from the surface it needs to have travelled a whole number of wavelengths while inside the material. Bragg expressed this in an equation now known as Bragg's Law:

- $n\lambda = 2d \sin\theta$ (1)
- where n is an integer determined by the order given,
- λ is the wavelength of x-rays, and moving electrons, protons and neutrons,
- d is the spacing between the planes in the atomic lattice, and
- θ is the angle between the incident ray and the scattering planes.
- Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings, are incident upon a crystalline sample, scattered by the atoms in the system and undergo constructive interference in accordance to Bragg's law.









Fig.1.8

Procedure

- The powder diffraction method, by using conventional X-ray sources, was devised independently in 1916 by Debye and Scherrer in Germany and in 1917 by Hull in the United States.
- The technique developed steadily and, half a century later, the 'traditional'applications, such as phase identification, the determination of accurate unit-cell dimensions and the analysis of structural imperfections, were well established.
- There was then a dramatic increase of interest in powder methods during the 1970s, following the introduction by Rietveld in 1967 of his powerful method for refining crystal structures from powder data. This has since been used extensively, initially by using neutron data and later with X-rays, and it was an important step towards extracting 3-dimensional structural information from 1-dimensional powder diffraction patterns, in order to study the structure of crystalline materials. Similarly, techniques which do not involve structural data have been introduced for modelling powder diffraction patterns, to extract various parameters (position, breadth, shape, etc.) which define the individual reflections.
- These are used in most applications of powder diffraction and are the basis of new procedures for characterizing the microstructural properties of materials. Many subsequent advances have been based on this concept and powder diffraction is now one of the most widely used techniques available to materials scientists for studying the structure and microstructure of crystalline solids.



Single crystal Rotating method

4-Circle Gonoimeter (Eulerian or Kappa Geometry)

Fig.1.9

Procedure

Single-crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure. Single crystal X-ray diffractometers consist of three basic elements, an X-ray tube, a sample holder, and an X-ray detector.

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and impact of the electrons with the target material. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K α and K β . K α consists, in part, of K α 1 and K α 2. K α 1 has a slightly shorter wavelength and twice the intensity as K α 2. The specific wavelengths are characteristic of the target material. Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. K α 1 and K α 2 are sufficiently close in wavelength such that a weighted average of the two is used. Molybdenum is the most common target material for single-crystal diffraction, with MoK α radiation = 0.7107Å.

- These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs.
- Single-crystal X-ray diffraction is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice. Bondlengths and angles are directly related to the atomic positions. The crystal structure of a mineral is a characteristic property that is the basis for understanding many of the properties of each mineral.

Applications

- New mineral identification, crystal solution and refinement
- Determination of unit cell, bond-lengths, bond-angles and site-ordering
- Characterization of cation-anion coordination
- With specialized chambers, structures of high pressure and/or temperature phases can be determined
- Determination of crystal-chemical vs. environmental control on mineral chemistry

Limitations

- Must have a single, stable sample, generally between 50-250 microns in size
- Requires optically clear sample
- Data collection generally requires between 24 and 72 hours

Part A

Distinguish Primitive cell and Unit cell Assess the importance of Weigner Seitz cell Interpret the role the Brillouin Zone in Crystal structure Calculate the Coordination number of SC, BCC and FCC Criticize the role of point group in assigning space group Name the basic symmetry operations and mention its role in combinations The intercepts are 3,2,1 and fine (hkl) indices Draw (110) plane in cubic cell Tweet X-rays and differentiate its types Deduce Bragg's law with neat sketch Differentiate the Bravais lattice in 2D and 3D

Part B

Articulate the role of Miller indices in crystal structure How to find Miller Indices and Brief its features Brief the types of symmetry operations and its role in point group and space group Explain Debye Scherrer Camera method with Neat sketch and analyze its applications Enlighten the method of crystal structure determination of single crystal with its advantages and disadvantages

Illuminate the 14 types of Bravais lattice in three dimensional crystal system with neat sketch

References

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- 2. Crystal Structure Determination, Massa, Werner, 2004, Springer
- 3. Crystal Structure, M.Ladd, 1999, Elsevier. ISBN 9781898563631,

UNIT – 2 – Magnetic and Dielectric Materials – SPH1316

Magnetic and Dielectric materials

Magnetic Moment

Origin of Magnetic Moment – Bohr Magneton

- We shall now discuss as to what contribute to the permanent magnetic dipole moment of the atomic constituents of matter. Whenever a charged particle has an angular momentum, it contributes to the permanent dipole moment. In general, these are three contributions to the angular momentum of an atom.
- Orbital angular momentum of the electrons: This corresponds to an permanent orbital angular magnetic dipole moments.
- Electron spin angular momentum. This corresponds to electron spin angular momentum.
- Nuclear spin angular momentum. This corresponds to nuclear magnetic moments.

Orbital angular magnetic dipole moment

• Let us consider an electron describing a circular orbit of radius 'r' with a stationary nuclear at the centre as shown in (fig.2.4) Let the electron rotate with a constant angular velocity of radians per second. Electron revolving in any orbit may be considered as current carrying circular will producing magnetic field perpendicular to its plane. Thus the electronic orbits are associated with a magnetic moment. The orbital magnetic moment of an electron in an atom can be expressed interms of atomic unit of magnetic moment called Bohr magneton, defined as

Electron spin magnetic moment

- The concept of the electron having an angular momentum has been introduced in order to explain the details of atomic spectra. This angular momentum of the electron is referred to as the spin of the electron. Since the electron has a charge, its spin produces a magnetic dipole moment.
- Magnetic lines of force
- These are the liner which are due to the magnetizing field and exist in air even when there is no magnetic substance in the field.



Fig.2.1

Lines of magnetization

If a magnetic substance is kept in a magnetic field, it is magnetised by induction and these lines of force passing within the substance due to magnetisation are known as linear of magnetisation.

Classification of magnetic materials

- Now we are going to study the various types of magnetic materials in terms of the magnetic properties of the atomic dipoles and the interactions between them very first distinction is based on whether the atoms carry permanent magnetic dipoles or not.
- Materials which lack permanent dipoles are called diamagnetic.
- If the atoms of the material carry permanent magnetic dipoles, such a material may be paramagnetic, ferromagnetic, antiferromagnetic or ferrimagnetic, depending on the interaction between the individual dipoles. If the permanent dipoles do not inter act among themselves, the material is paramagnetic.
- If the interaction among permanent dipoles is strong such that all the dipoles line up in parallel, the material is ferromagnetic.
- If the permanent dipoles line up in antiparallel direction, the material is antiferromagnetic or ferrimagnetic. In antiferromagnetic material the magnitudes of permanent dipoles aligned parallel and antiparallel are equal and hence the magnetization vanishes
- In the case of ferrimagnetic materials magnitudes of permanent dipoles aligned antiparallel are not equal thus exhibiting magnetization.
- Before studying the properties of different magnetic materials let us classify them based on their properties.

Properties of diamagnetic materials

- 1. Permanent dipoles are absent.
- 2. Effect is weak and often marked by other kinds of magnetism.
- 3. When placed inside a magnetic field, magnetic lines of forces are repelled.
- 4. Diamagnetic susceptibility is negative

Table 2.1

Magnitude of	Temperature	Examples
susceptibility	dependence	
Small negative	Independent	Organic materials, light elements
Intermediate negative	Below 20k varies with field & temp	Alkali earths, Bismuth
Large negative	Exists only below critical temperatures (Meissner effect)	Superconducting materials

- 5. Magnetic susceptibility is independent of applied magnetic field strength.
- 6. Relative permeability is slightly less than unity.

Paramagnetism

Each electron in an orbit has an orbital magnetic moment and a spin magnetic moment. When shells are unfilled there is not magnetic moment. In the absence of external magnetic field the net moments of the atom are arranged in random directions because of thermal fluctuations. Hence there is no magnetization. When external magnetic field is applied, there is a tendency for the dipoles to align with the field giving rise to an induced positive dipole moment. This induced dipole moment is proportional to the field. The induced magnetism is the source of paramagnetism.

Properties of Paramagnetic materials

- 1. Paramagnetic materials posses permanent magnetic dipoles.
- 2. In the absence of an external applied field, the dipoles are randomly oriented. Hence the not magnetization in any given direction is zero.
- 3. When placed inside be magnetic field, it attracts the magnetic lines of force .
- 4. Paramagnetic susceptibility is positive and depends greatly on temperature as detailed below.

Table 2.2

Magnitude of			Temperature dependence	Examples
Sus	sceptibility			
Small,	positive,	Large	Independent	Alkali metals and
positive			$x = \frac{c}{T}$ curie law	Transition metals Rare earths.
			$or x = \frac{c}{T-Q}$ curie-weiss law	
			where C is curie constant and θ is curie temperature	

5. Spin alignment is random



- 6. Paramagnetic susceptibility is independent of the applied magnetic field strength
- 7. Paramagnetic atoms form a collection of non-interacting magnetic dipoles.

Ferromagnetism

We have known that the permanent magnetic moment is mainly due to the spin magnetic moment. The net spin magnetic moment of ferromagnetic atoms is of the same order as magnetic moment of paramagnetic atoms. However there exists a large magnetization in ferromagnetic substance even in the absence of external applied field. This is due to spontaneous magnetization. There is a special form of interaction called exchange coupling occurring between adjacent atoms.

Properties of ferromagnetic materials

- 1. Due to a special form of interaction called exchange coupling between adjacent atoms, even in the absence of external applied field, exhibits strong magnetization
- 2. When placed inside a magnetic field, it attracts the magnetic lines of forces very strongly.
- 3. Each ferromagnetic material has a characteristic temperature called the ferromagnetic curie temperature θ_f . Ferromagnetic susceptibility depends greatly on temperature above of its properties are quite different as shown below.

Magnitude of susceptibility	Temperature dependence	Examples
Very large positive	$x = \frac{c}{T - Q}$ i) For T > Q _f paramagnetic behavior ii) For T < Q _f ferromagnetic behavior	Iron, cobalt, nickel. gadolinium

1. Spin alignment is parallel in the same direction



- 2. Exhibits hysteresis
- 3. Consists of a number of small regions which are spontaneously magnetized called domains.

DOMAIN Theory of Ferromagnetism: (WEISS Theory)

- Weiss proposed the concept of domains in order to explain the properties of ferromagnetic materials and its Hysteresis Magnetic Domains. The group of atoms organised into tiny bounded regions in the ferromagnetic materials are called magnetic domains. Thus the domain is a region of the ferromagnetic material in which all the magnetic moments are aligned to produce a net magnetic moment in only one direction. Hence behaves likes a magnet with its own magnetic moment and axis. In a demagnetized ferromagnetic material, the domains are randomly oriented and the net magnetisation, in the absence of the field, is zero. These domains are separated from other domains by a wall known as the domain wall or Bloch Wall.
- When a magnetic field is applied to this material, the domains that are parallel to the applied field increase in size at the expand of the other domains in the domain size can also grow due to the movement of domain Walls. Also, all the other domains aline themselves with the field. This results is large net magnetization of the material.

Process of Domain magnetization

- By the motion of domain Walls: The volume of the domains that are favorably oriented with respect to the external field are increased than that are unfavorably oriented as shown in fig 2.13(b). Fig 2.13(a) shows domain arrangement in a virgin specimen when no magnetic field is applied.
- By rotation of domains: As shown in fig 2.13(c), when the applied external magnetic

field is Strong, rotation of the direction of magnetization occurs in the direction of the field.



Fig.2.2. Domain orientation

Types of energy involved in the process of domain growth

Magnetostatic energy

Crystal anisotropy energy

Magnetostrictive energy.

Domain wall energy.

- To study the domain structure clearly, we must know four types of energy involved in the process of domain growth.
- Magnetostatic Energy:
- Magnetostatic energy or magnetic potential energy is the energy present in any ferromaganetic materials when that material produces an external field. This is due to the present of resultant dipole moment in that material even in the absence of external magnetic field.
- The magnetic energy can be reduced by dividing the specimen into two domains as shown in Fig.
- Further subdivisions, as shown in fig 2.16, to N domains, reduces the magnetic energy to 1/N of the magnetic energy of the configuration of fig 2.16 a
- A domain structure shown in fig 2.16 c. has 2000 magnetic energies due to the introduction of triangular domain at the top and bottom of the crystal. These triangular domain are called closure domains.



Fig.2.3

Anisotropy Energy:

- Energy of megnetisation is the function of crystal orientation is crystals have easy and hard direction of magnetisation. For e.g. in Bcc iron, the easy direction is [100], the medium direction is [110], and the hard direction is [111].
- The excess energy required to magnetise a specimen in a particular direction over that it required to magnetise it along the easy direction is called the crystalline anisotropy energy.

Magnetostrictive Energy:

• The change in the dimension of a ferromagnetic material when it is magnetized is known as magnetostriction. This deformation is different along different crystal directions. So if the domains are magnetized in different directions, they will either expand or shrink. This means that work must be done against the elastic restoring force.

Bloch or Domain Wall Energy:

- Consider two domains in magnetic materials. These two domains are separated by Bloch or domain wall. The domains are opposite in direction. The second domain is obtained by rotating the first domain through 180°. The rotation of the domain is carried out gradually due to the existence of exchange force and anisotropy energy.
- The role of exchange force to rotate the dipole which is existing between the adjustment atomic spin is very less.

Magnetic Bubble Memory



- In the magnetic bubble memory, there is on major loop and 157 minor loops as shown in fig . which are arranged from right to left. Each minor loop has 641 bubble sites. Thousands of coded characters may be stored in a single chip.
- Writing Operation
- When a data has to be stored, the bubble from the minor loops are transferred to major loop and if goes to write station. In write station the message is entered and the bubble site again comes to minor loop.
- Reading Operation
- To read the data from the storage, the bubble from minor loops are transferred to major loop and if goes to read station, then it comes to miner loop. The data can be altered by the erase station, if we need to erase it
- Special Features
- It is Non-Volatile
- Bubble sites are moved electronically
- If has high access speed.
- If can store the data even in the absence of electrical power.
- It has high storage capacity than magnetic hard disk.

Floppy Disk (or) Diskette

• Floppy disk are the type of secondary storage devices. It is made up of a Flexible Plastic material and hence called as Floppy Disk. It acts both as an input and output device.

• Structure of Floppy Disk

• A floppy disk is made of flexible plastic which is coated with magnetic oxide. It is provided with a central hole. This hole is used for mounting the disk in the floppy drive unit. It is enclosed in a flexible square envelop (cover). This cover prevents the disk from dust and moisture. There is a small index hole in the cover and there will be a hole in the drive disk. When these two holes matches then only the storage operation starts. There is a opening called Read/Write head aperture slot. The reading and writing operation is done in floppy disk through this opening. The write protect notch is used to prevent writing on the disk by other users, which can be done by covering the notch with a sticker. A 5.25" floppy is as shown in fig. 2.27.



Fig.2.5

Operation

• When the floppy is put into the drive, and when the drive is operated, the disk inside the cover is rotated. There are 200 to 800 tracks on the disk surface, each of which has a designed location number, as shown in fig.2.28. The Read/Write operation is done by the Read/Write head in the drive unit. The head is a small electromagnet with minute gap between the poles.

Writing operation: The floppy disk moves over the gaps as shown in fig.2.29. When it moves, electric pulses from the CPU flow through the write coil of the head and magnetises the iron oxide coating in the disk to the proper pattern.

Reading Operation: When the data are to be read, the magnetised patterns induces pulses of current in the read coil and is amplified then to the CPU. Read/Write of a frequency modulated wave.

Special Advantages:

- Non-volatile storage medium.
- The cost is very low.
- It can be easily handled.

Disadvantages:

- Here the magnetic disk is rotated mechanically.
- It has low storage capacity.
- It has acquired data storage.

Part A

Differentiate Lines of force and lines of induction Differentiate Curie and Neel temperature with X Vs T graph Expound Retentivity, Coercivity and energy product Mention the applications of Hysteresis loop Differentiate Spontaneous and induced magnetization Compare Domain and magnetic bubbles Define dielectric constant and polarization vector Mention the factors can affect Dielectric loss Illuminate dielectric breakdown and its remedies Compare thermal and chemical dielectric breakdown

Criticize about intrinsic breakdown

Part B

Compare Diamagnet, paramagnet and ferromagnet based in its spin behaviour

Illuminate Hysteresis curve (i) Differentiate ferro magnetic materials based on the Hysteresis loop (ii) Brief Domain theory

Describe the energies involved in Weiss/Domain theory

How Bubble memory chip used to store and retrieve information and explain how bubble are propagated in T- bar pattern

Prove that electronic polarization is proportional to the volume of an atom

Examine the types of polarization and deduce the expression

Prove $N\alpha/3\epsilon_0 = \epsilon_r - 1 / \epsilon_r + 2$

References

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UNIT – 3 – Superconductivity – SPH1316

Superconductivity

Properties of Superconducting materials

Zero Electrical Resistance

• The DC electrical resistance of a superconductor at all temperatures below a critical temperature is practically zero. The transition from normal state to superconducting state occurs sharply in pure metals whereas it is not so in impure, HTSC oxides. In HTSC oxides, there exist several superconducting phases.



Fig.3.1

- Diamagnetic Property (Meissner Effect): When a weak magnetic field is applied to a superconducting material at a temperature below transition temperature ($T < T_c$), the magnetic flux lines are excluded from the material ($\mathbf{B} = 0$). So the superconductor acts as an ideal diamagnet. The ejection of magnetic lines of force, when the superconducting material is cooled below its T_c in a weak magnetic field is called Meissner effect.
- Effect of Heavy Magnetic Field: Below T_c , superconductivity can be destroyed by the application of strong magnetic field. At any temperature, the minimum magnetic field required to destroy superconductivity is called critical field (H_c) of the material. Thus the value of H_c depends upon the temperature of the superconducting material and is given by $H_c = H_0 [1 - (T^2 / Tc^2)]$ where, H_0 is the critical field at 0 K, T is the temperature of the material and T_c is the transition temperature. From the graph, we know that, when the temperature of the material increases from 0 K, the value of Hc decreases and at $T = T_c$, $H_c = 0$. Also the value of H_c is different for different materials.



Fig.3.2

- Effect of Heavy Current (Silsbee's rule): We know that a current carrying conductor has a magnetic field around it. When heavy current flows through a superconductor it will set up the magnetic field which destroys the superconducting property of the superconductor. According to Silsbee's rule, the critical current (I_c) flowing through a superconducting wire of radius r is $I_c = 2\pi r H_c$ where, H_c is the critical field at T K.
- Effect of Pressure: Some materials which behave as normal conductors at normal pressure can undergo phase transition and behave as superconductors under the application of external pressure. *e.g.*
- Cesium becomes a superconductor at 110 kilo bar pressure and its $T_c = 1.5 \text{ K}$
- Silicon becomes a superconductor at 165 kilo bar pressure and its $T_c = 8.3$ K
- Effect of Isotope: The transition temperature of the given superconducting material varies with its mass number or isotopic mass and this effect is known as Isotope effect. Maxwell found that, T_c is inversely proportional to the square root of the atomic mass (M) of the isotope of the single superconductor.
- Entropy: Entropy is a measure of degree of disorderness of the given system. The entropy of a superconducting material is found to be lower than that of the normal conducting material which indicates that in the superconducting state the electrons are in the more ordered state than they are in the normal conducting state.
- Specific heat capacity: The specific heat capacity of a normal conductor (C_n) consists of two contributions, one from the conduction band electrons and the other from the lattice.
- Energy gap: Specific heat capacity measurements provided the first indication of an energy gap (Δ) in superconductors. The energy gap of a superconductor is of different nature than that of a semiconductor or a conductor. In case of semiconductors, the energy gap is tied to the lattice and it corresponds to the energy difference between the valence band and the conduction band (~1eV); whereas in superconductors, the energy gap (Δ) is tied to the Fermi energy and this gap in the spectrum of allowed energy states separates the excited states from the ground states. In conventional superconductors, Δ~1meV while in HTSC, Δ~1to 10 meV.

London Penetration Depth (λ): When a superconducting material is placed in a magnetic field, a current is set up on the surface of the material and a magnetic field is produced everywhere within the material. This magnetic field opposes the applied external magnetic field. So the applied magnetic field penetrates some distance into the superconductor. This distance is called London Penetration depth (λ). It is also defined as the effective depth to which a magnetic field penetrates a superconductor.

Coherence Length (ξ):

The paired electrons (Cooper pairs) are not scattered because of their peculiar properties of smoothly riding imperfection. Also there is no exchange of energy

between them. Mean time, they can maintain their coupled motion up to certain distance (about 10^{-6} m). This distance is called Coherence Length. It is also refereed as the distance between two electrons of the Cooper pair within the highly coherent superconducting state.

Ginzburg Landau Parameter (k): It is the ratio of London penetration depth (λ) to coherence length (ξ).

Flux Quantization: The magnetic flux ϕ through a superconducting ring is quantized in terms of h/2e. This phenomenon is said to be flux quantization. A closed superconducting ring (loop) can enclose magnetic flux only in integral multiples of a fundamental quantum of flux. This fundamental quantum of flux is called Fluxon (ϕ_0).

Theory of Superconductivity

- A number of theories have been put forward to describe the phenomenon of superconductivity viz. London theory, Ginzburg and Landau theory and BCS theory. BCS theory explains most of the phenomena associated with superconductivity in natural manner but alone could not explain the anomalous behavior of HTSC. To explain the HTSC, several theories have been proposed like Resonance Valence Bond (RVB) theory, Interlayer tunneling model, Boson Fermion model *etc*. None of these models provide satisfactory explanation of the anomalous features of HTSC oxides. However, the efforts to understand the HTSC oxides pairing mechanism with enhancing future prospects for new HTSC materials and their novel applications are still under research and are in progress.
- The theory of super conductivity can be considered in two stages like macroscopic and microscopic. The first stage is to accept the macroscopic description of a superconductor as a body which has no magnetic and electric fields ($\mathbf{B} = 0 = \mathbf{E}$) and to develop the thermodynamic consequences without making any assumptions. The second stage is the microscopic description of a superconductor formulated by Bardeen, Cooper and Schrieffer (BCS) on the basis of advanced quantum theory.

London's Theory (Macroscopic)

• London formulated a more general description of electro-dynamic behavior of superconductor. At an extremely low temperature, vibrations of the nucleus and free electrons of certain atoms slow down so much and they synchronize with the passing waves of electrons in the flow of electric current. When this happens resistance to electric current disappears.

BCS Theory (Microscopic)

Electron-Lattice- Electron (Electron-Phonon- Electron) Interaction:

Bardeen found that, an electron moving through a crystal lattice has a self energy accompanied with "Virtual Phonon" of energy hu. Let us consider an electron of wave vector \mathbf{K}_1 moving through a crystal lattice. This electron can distort the lattice and a virtual phonon of wave vector \mathbf{q} is emitted. Thus \mathbf{K}_1 is scattered as $(\mathbf{K}_1 - \mathbf{q})$. Consider a second electron of wave vector \mathbf{K}_2 is moving through a crystal lattice and close to the previous electron wave vector \mathbf{K}_1 . Now the virtual phonon \mathbf{q} is absorbed by this second electron and \mathbf{K}_2 is scattered as $(\mathbf{K}_2 + \mathbf{q})$. Thus the second electron interacts with the first electron *via* lattice deformation and the exchange of virtual phonon between the two electrons. This type of interaction is called **Electron-Lattice-Electron (Electron-Phonon-Electron) Interaction.**



Fig.3.3

Total wave vector before interaction = Total wave vector after interaction

 $K_1 + K_2 = (K_1 - q) + (K_2 + q) = K_1 + K_2$

- Thus net wave vector of the two electrons (pair of electrons) is conserved and the momentum is transferred between these two electrons. So these two electrons together form a pair called Cooper pair.
- The energy of the Cooper pair (E_{cp}) is less than the total energy of separated electrons (E_{sep}) in the normal state. $(E_{cp} < E_{sep})$. So the binding energy of the Cooper pair (E) is the energy difference between the normal state and paired state $(E=E_{sep} E_{cp})$. Also this energy is required to break the Cooper pair. At $T > T_c$, all the free electrons are in the separated position. At $T < T_c$, electron-lattice-electron interaction is stronger than electron-electron repulsive coulomb interaction. So the free electrons tend to pair up (formation of Cooper pair). Then the pairing is complete at T = 0 K.

Existence of Energy Gap:

• Fermi Energy (E_F) is the highest energy to which the electrons are filled in a metal. The corresponding energy level is called Fermi Energy level. The loci of the end points of the wave vectors corresponding to the Fermi level trace out a surface called **Fermi Surface**. The binding energy of the Cooper pair ($E = E_{sep} - E_{cp}$) appears as the superconducting energy gap at the Fermi surface. At the Fermi surface, the normal electron states are above the energy gap while superconducting states are below the energy gap. According to BCS theory, this energy gap at absolute zero is predicted to be $D = 3.5 \text{ K}_{B} \text{ T}_{c}$ where K_{B} is the Boltzmann constant.

- The width of the energy gap (D) is a function of temperature. At $T > T_c$, Cooper pairing is dissolved and hence the energy gap reduces to zero (D = 0). At T = 0 K, all the free electrons are formed in a Cooper pair and hence the energy gap reaches the maximum (D = maximum)s. The energy gaps for typical superconductors (~10⁻⁴eV) are much smaller than the energy gaps for typical semiconductors (~1eV). This prediction of the superconducting energy gap was verified experimentally by studying absorption of electromagnetic radiation by superconductors.
- Major accomplishments of BCS theory
- BCS theory explained Meissner effect, coherence length, penetration depth, flux quantization and energy gap parameter.
- It has solved the problem of electron energy where there is attractive interaction.
- It gives the expression for the transition temperature (McMillan's formula),
- $T_c = 1.14 \ \theta_D \ exp \ [-1/V.N(E_F)]$ where θ_D Debye temperature, V- net attractive potential of the electron, $N(E_F)$ density of states at the Fermi level.

MAGLEV

The most important application of superconductors is maglev or Magnetic Levitation Train. Maglev coaches do not slide over steel rails but float on a 4 inch air cushion over a strongly magnetized track. The principle behind this is electromagnetic forces between the superconducting magnets. This train consists of superconducting magnets placed on each side of the train. It can run in a guide way (rail) which consists of series of "8" shaped coil. Initially the train slide on the rails. When the train moves, the superconducting magnets on each side of the train will induce a current in the "8" shaped coils kept in the guide way. This induced current generates a magnetic force in the coils in such a way that, the lower half of the "8" shaped coil has the same magnetic pole as that of the superconducting magnet in the train, while the upper half has the opposite magnetic pole. Hence, the total upward magnetic force acts on the train and the train is levitated or raised above the wheels. Now the train floats in the air. By an alternatively changing the poles of the superconducting magnets in the train, alternating currents can be induced in the "8" shaped coils. Thus alternating series of north and south magnetic poles are produced in the coils, which pulls and pushes the superconducting magnets in the train and hence the train is further moved. Because of no mechanical friction, speeds up to 500 Km/hr can be easily achieved.



Fig.3.4 MagLev

Josephson Effect

Josephson junction is the sophisticated sandwich structures of superconducting films usually of Niobium, separated by extremely thin insulating oxide layer of thickness approximately equal to 10 Å. In 1962, B.D.Josephson predicted theoretically that Cooper pair tunneling is possible through a very thin insulating layer that is sandwiched between two superconducting films. The tunneling may be made to result either a dc voltage (D.C Josephson effect) or with an ac voltage (A.C Josephson effect) across the tunnel barrier. This phenomenon is known as Josephson Effect. When a constant nonzero dc potential is maintained across the barrier, ac component exists along the dc component, whereas the dc component persists even after the removal of applied dc potential.



Fig. 3.4 Josephson Junction



Fig.3.5 I-V graph

Applications of Josephson junction:

- Josephson junction is capable of switching signals from one circuit to another with a switching time of I picoseconds (10^{-12}sec) . (ie) it acts as a fastest switching element.
- Moreover, it is cable of storing information, smaller in size, lighter in weight; hence they may provide the basis for the architecture of the fastest computers in future. Josephson junction computer has been fabricated with a volume of $1.25 \times 10^{-4} \text{m}^3$ and a cycle time of 2 nano sec; which is 10 times faster than the high speed semiconductor based computer.
- It is used to produce microwave with a frequency 10¹² Hz, when the applied potential is 1 mill Volt.
- It is used in the precision determination of (\hbar/e) .
- The A.C Josephson effect is used to measure very low temperature based on the variation of frequency of the emitted radiation with temperature.
- Josephson junction is used in the construction of SQUIDs. SQUIDs are used in Magnetocardiography (MCG), Magneto encephalography (MEG) and in MRI.

SQUIDS

SQUIDS means Superconducting Quantum Interference Device and also called Double Junction Quantum Interferometer. It can measure the feeble fields (weak magnetic fields) corresponding to extremely small electric currents generated by heart and brain. The principle behind this is small change in magnetic field produces variation in the flux quantum.

It consists of superconducting ring or loop with "weak link or junction".

Weak link is a thin region which has very low critical current I_c . Weak link acts as a gate, since it allows super current at $I < I_c$ and it blocks super current at $I > I_c$. Weak link is prepared such that it allows only a single fluxon



Fig.3.6

Applications of SQUID:

- By measuring the current through the SQUID, one can measure the value of e/h accurately.
- SQUID is used to detect very tiny magnetic field and hence it is used as a magnetometer.
- MRI (Magnetic Resonance Imaging) scanning, employing SQUID, is used to measure the field in the micro Tesla region, where as the ordinary MRI is used to measure the field from one to several Tesla.
- Based on these sensors we have, magnetocardiography (MCA), Magneto encephalography (MEG), etc.
- They can be used in the finest precision instruments at the forefront of meteorology.
- A novel application of SQUID is the magnetic marker monitoring method, which is used to trace the path of orally applied drugs.

Cryotron

- It is a magnetically operated current switch where the current through one superconducting element can be altered by the magnetic field produced by another superconducting element. Consider a superconducting material (Tantalum-Ta) is surrounded by another superconducting material (Niobium-Nb) and the whole arrangement is placed in a low temperature bath (T < Tc). The critical field of Tantalum–Ta is less than the critical field of Niobium-Nb.
- At an operating temperature, the magnetic field produced by the superconducting material Niobium-Nb may exceed the critical field of Tantalum–Ta. Hence, the superconducting material Tantalum–Ta becomes normal conductor since the critical field of Tantalum–Ta is less than the critical field of Niobium-Nb. But Niobium-Nb will not become normal conductor. Hence, the current in material Ta can be controlled by the current in Niobium-Nb and the system can acts as a relay or switching element.



Fig.3.7 Cryotron

Part A

Substantiate Meissner effect with neat sketch Prove superconductor are perfect diamagnet Show fluxon in diagrammatically Compare Ac and DC Josephson effect Differentiate Hard and soft superconductor Analyze the application of SQUID Evaluate the principle held behind magnetically levitated train Examine the drawback of London theory How superconductor are classified based on Landau theory If Mass number of Silicon is 199.5 with Tc 4.185 K calculate it Tc when the mass number changed to 203.4 and comment your result The critical magnetic field of 0.5 diameter of superconducting wire is 4000 Tesla. Calculate its critical current

Part B

Explain the following properties of superconductors (i) Critical temperature (ii) Critical magnetic field

(iii) London Penetration depth (iv) Skin effect (v) Ginzburg Landau parameter (vi) Effect of pressure

and impurities

Demonstrate BSC theory and its major accomplishments

Assess Josephson junction and Josephson effect and its types

Brief applications of superconductors (i) MAGLEV (ii) SQUID (iii) Cryotron

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UNIT – 4 – Semiconducting Materials – SPH1316

Semiconducting materials

Types of Semiconductor

Semiconductors are classified into two types. Intrinsic semiconductors and Extrinsic semiconductors.

a) Intrinsic Semiconductors: A semiconductor in an extremely pure form is known as Intrinsic semiconductor. The vacant conduction band is separated by a forbidden energy gap E_g from the filled valence band. So at absolute zero (0⁰k), there is no electric conduction. Fermi level is at the middle of valance band and conduction band.





Extrinsic Semiconductors: When an impurity is added to an intrinsic semiconductor its conductivity changes. This process of adding impurity to a semiconductor is called Doping and the impure semiconductor is called extrinsic semiconductor. Depending on the type of impurity added, extrinsic semiconductors are further classified as n-type and p-type semiconductor.

n-type semiconductor

When an impurity (electron) is added to an intrinsic semiconductor its conductivity changes and is called n-type semiconductor. This extra electron is forming a new energy level called **donor energy level** and is situated just below the conduction band. Fermi level is at the middle of donor energy level and conduction band.

p-type semiconductor

When an impurity (hole) is added to an intrinsic semiconductor its conductivity changes and is called p-type semiconductor. This extra hole is forming a new energy level called **acceptor energy level** and is situated just above the valance band. Fermi level is at the middle of acceptor energy level and conduction band.



Fig.4.2 n type and p type semiconductor

CARRIER (ELECTRON AND HOLE) CONCENTRATION OF INTRINSIC SEMICONDUCTOR

- At absolute zero temperature, the valence band is completely occupies by electrons but the conduction band is completely empty. The completely filled band does not conduct current. Thus, at low temperatures, the pure (intrinsic) semiconductor gives an extremely high resistance to electric conduction.
- At finite temperature, the electrons in the valence band get excited and they will move to the conduction band. So holes are produced in the valence band. The probability of occupation of electrons in the conduction band and holes in the valence band are described by the Fermi distribution function .i.e..,

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

- where, E_F is the Fermi Energy
 - K_B is the Boltzman's constant
- T is the temperature of the intrinsic semiconductor
- The density of states of conduction and valence bands.

• Electron Concentration of Intrinsic Semiconductor

Generally, the band gap (E-E_F) is of the order of 1 eV. For electrons at the bottom of the conduction band, exp (E-E_F)/(K_{R-T}=e²⁰ ≫ 1. For other electrons in the conductions band, this factor will be still higher. Thus, the value +1 in the denominator is negligible. This approximation is called Boltzman approximation.

$$f(E) \sim \frac{1}{\exp\left(\frac{E-E_F}{K_BT}\right)} = \exp\left(\frac{E_F - E}{K_BT}\right)$$
(2)

The concentration of electron in the conduction band is

$$n_e = n = \int_{E_c}^{\infty} f(E) N_e(E) dE$$

The concentration of holes in the valence band is,

$$n_n = p = \int_{-\infty}^{E_v} \left(1 - f(E)\right) N_h(E) dE \qquad (4)$$

Where, $N_e(E)$ is the electron density (number of electrons per unit volume) of states near the conduction band and

 N_h (E) is the hole density of states near the valence band.

For an intrinsic semiconductor, n = p.

The electron density of states in the conduction band is

$$N_{e}(E) = \frac{4\pi}{h^{3}} \left(2m_{e}^{*} \right)^{3/2} (E - E_{c})^{1/2} \quad (5)$$

Where m_e^* is the effective mass of electron in conduction band.

Substituting equations (2) and (5) in equation (3), we get,

$$n_{e} = \frac{4\pi}{h^{3}} \left(2m_{e}^{*}\right)^{\frac{3}{2}} \int_{E_{c}}^{\infty} \left(E - E_{c}\right)^{\frac{1}{2}} \cdot \exp\left(\frac{E_{c} - E}{K_{R}T}\right) \cdot dE$$
(6)
Let $\exp\left(\frac{E_{F} - E}{K_{R}T}\right) = \exp\left(\frac{E_{F} - E_{c} + E_{c} - E}{K_{R}T}\right)$
$$= \exp\left(\frac{E_{F} - E_{c}}{K_{R}T}\right) \cdot \exp\left(\frac{E_{c} - E}{K_{R}T}\right)$$

Substituting this in equation (6), we get,

$$n_{e} = \frac{4\pi}{h^{5}} (2m_{e}^{*})^{\frac{5}{2}} \int_{E_{c}}^{\infty} (E - E_{c})^{\frac{1}{2}} . exp\left(\frac{E_{F-E_{c}}}{K_{B}T}\right) . exp\left(\frac{E_{c}-E}{K_{B}T}\right) . dE$$
(7)
$$Let\left(\frac{E-E_{c}}{K_{B}T}\right) = x \qquad \text{Therefore } E - E_{c} = x.K_{B}T$$

Differentiating the above equation, we get, $dE = K_B T.dx$

Also
$$(E - E_c)^{\frac{1}{2}} = x^{1/2} \cdot K_B^{1/2} T^{1/2}$$

When $E = E_{c}x = 0$ and when $E = \infty$, $x = \infty$

Substituting the above values in equation (7), we get,



Fig. 4.3 Density of states of conduction and valence bands of Intrinsic Semiconductor

$$n_{e} = \frac{4\pi}{h^{3}} (2m_{e}^{*})^{3/2} \int_{0}^{\infty} x^{\frac{1}{2}} K_{B}^{1/2} T^{1/2} .\exp\left(\frac{E_{F} - E_{c}}{K_{R}T}\right) e^{-x} .K_{B}T .dx$$

$$= \frac{4\pi}{h^{5}} (2m_{h}^{*} K_{B}T)^{3/2} .exp\left(\frac{E_{F} - E_{c}}{K_{R}T}\right) \int_{0}^{\infty} x^{1/2} e^{-x} .dx$$

$$Now \int_{0}^{\infty} x^{1/2} e^{-x} dx = \frac{\pi}{2}^{1/2}$$

$$n_{e} = \frac{4\pi}{h^{3}} (2m_{e}^{*} K_{B}T)^{3/2} .exp\left(\frac{E_{F} - E_{c}}{K_{R}T}\right) .(\frac{\pi}{2}^{1/2})$$

$$n_{e} = 2\left(\frac{2\pi m_{e}^{*} K_{B}T}{h^{2}}\right) \exp\left(\frac{E_{F} - E_{c}}{K_{B}T}\right)$$
(8)

This is the concentration of electron in the conduction band of intrinsic semiconductor.

Hole Concentration of Intrinsic Semiconductor

For holes at the top of the valence band, $\exp\left(\frac{E_{-E_F}}{K_RT}\right) \ll 1$. For other holes in the valence band this factor will be still lower. Now,

$$\begin{split} \left[1-f(E)\right] &= 1 - \frac{1}{1 + exp\left(\frac{E-E_F}{K_BT}\right)} \\ &= \frac{1 + exp\left(\frac{E-E_F}{K_BT}\right) - 1}{1 + exp\left(\frac{E-E_F}{K_BT}\right)} \quad = \frac{exp\left(\frac{E-E_F}{K_BT}\right)}{1 + exp\left(\frac{E-E_F}{K_BT}\right)} \end{split}$$

The exponential factor in the denominator is negligible, since $exp\left(\frac{E_{-E_F}}{K_RT}\right) \ll 1$.

$$[1 - f(E)] \cong exp\left(\frac{E_{-EF}}{K_{R}T}\right)$$
(9)

The hole density of states in the valence band is,

$$N_h(E) = \frac{4\pi}{h^3} (2m_h^*)^{3/2} (E_v - E)^{1/2}$$
(10)

Where m_h^* is the effective mass of hole in the valence band.

Substituting equation (9) and (10) in equation (4), we get,

$$n_{h} = \frac{4\pi}{h^{3}} (2m_{h}^{*})^{\frac{3}{2}} \int_{-\infty}^{E_{v}} (E_{v} - E)^{\frac{1}{2}} exp\left(\frac{E_{-EF}}{K_{R}T}\right) . dE$$
(11)

Let
$$exp\left(\frac{E_{-EF}}{K_{R}T}\right) = exp\left(\frac{E_{-E_{V}}+E_{V}-E_{F}}{K_{R}T}\right)$$
$$= exp\left(\frac{E_{-E_{V}}}{K_{R}T}\right) \cdot exp\left(\frac{E_{V}-E_{F}}{K_{R}T}\right)$$

Substituting this in equation (11), we get,

$$n_{h=P} = \frac{4\pi}{h^{8}} (2m_{h}^{*})^{\frac{8}{2}} \int_{-\infty}^{E_{v}} (E_{v} - E)^{\frac{1}{2}} exp\left(\frac{E_{-E_{v}}}{K_{R}T}\right) \cdot exp\left(\frac{E_{v-E_{F}}}{K_{R}T}\right) \cdot dE$$
(12)
Let $\frac{E_{v} - E}{K_{R}T} = x$ $E_{v} - E = x \cdot K_{B}T$

Differentiating the above equation, we get, $-dE = K_B T \cdot dx$

$$d\mathbf{E} = -K_B T.\,dx$$

(13)

$$(E_v - E)^{1/2} = x^{1/2} K_B^{1/2} T^{1/2}$$

When $E = -\infty$, $x = \infty$ and when $E = E_v$, x = 0

Substituting the above values in equation (12), we get

$$n_{h=P} = \frac{4\pi}{h^{3}} (2m_{h}^{*})^{\frac{5}{2}} \int_{\infty}^{0} x^{\frac{1}{2}} K_{B}^{\frac{1}{2}} T^{\frac{1}{2}} e^{-x} exp\left(\frac{E_{v-EF}}{K_{R}T}\right) \cdot (-K_{B}T) dx$$

$$= \frac{-4\pi}{h^{5}} (2m_{e}^{*}K_{B}T)^{\frac{5}{2}} exp\left(\frac{E_{v-EF}}{K_{R}T}\right) \int_{\infty}^{0} x^{\frac{1}{2}} e^{-x} dx$$
Now
$$\int_{\infty}^{0} x^{\frac{1}{2}} e^{-x} dx = -\int_{0}^{\infty} x^{\frac{1}{2}} e^{-x} dx = -\frac{\pi^{\frac{1}{2}}}{2}$$

$$n_{h} = \frac{-4\pi}{h^{5}} (2m_{h}^{*}K_{B}T)^{3/2} \cdot exp\left(\frac{E_{v-EF}}{K_{R}T}\right) \cdot \left(-\frac{\pi}{2}^{1/2}\right)$$

$$n_{h} = 2\left(\frac{2\pi m_{h}^{*}K_{B}T}{h^{2}}\right)^{3/2} \cdot exp\left(\frac{E_{v-EF}}{K_{R}T}\right)$$
(13)

This is the concentration of hole in the valence band of intrinsic semiconductor.

Fermi Energy of Intrinsic Semiconductor

 $n_e = n_h(i.e, n = p)$ For an intrinsic semiconductor,

$$2\left(\frac{2\pi m_{e}^{*}K_{B}T}{h^{2}}\right)^{3/2} \cdot \exp\left(\frac{E_{F-EC}}{K_{R}T}\right) = 2\left(\frac{2\pi m_{h}^{*}K_{B}T}{h^{2}}\right)^{3/2} \cdot \exp\left(\frac{E_{v-EF}}{K_{R}T}\right)$$
$$(m_{e}^{*})^{3/2} \exp\left(\frac{E_{F-EC}}{K_{R}T}\right) = (m_{h}^{*})^{3/2} \exp\left(\frac{E_{v-EF}}{K_{R}T}\right)$$

Taking logarithm on both sides, we get,

$$\begin{split} \log(m_{e}^{*})^{3/2} + \left(\frac{E_{F-E_{C}}}{K_{R}T}\right) &= \log(m_{h}^{*})^{\frac{3}{2}} + \left(\frac{E_{v-E_{F}}}{K_{R}T}\right) \\ \left(\frac{E_{F-E_{C}}}{K_{R}T}\right) - \left(\frac{E_{v-E_{F}}}{K_{R}T}\right) &= \frac{3}{2}\log(m_{h}^{*}) - \frac{3}{2}\log(m_{e}^{*}) \\ &\frac{2E_{F} - (E_{c} + E_{v})}{K_{R}T} &= \frac{3}{2}\log\left(\frac{m_{h}^{*}}{m_{e}^{*}}\right) \\ 2E_{F} - (E_{c} + E_{v}) &= \frac{3}{2}K_{B}T\log\left(\frac{m_{h}^{*}}{m_{e}^{*}}\right) \\ 2E_{F} &= (E_{c} + E_{v}) + \frac{3}{2}K_{B}T\log\left(\frac{m_{h}^{*}}{m_{e}^{*}}\right) \end{split}$$

$$E_F = \left(\frac{E_c + E_v}{2}\right) + \frac{3}{4} K_B T \log\left(\frac{m_h^*}{m_g^*}\right) \tag{14}$$

CARRIER (ELECTRON AND HOLE) CONCENTRATION OF INTRINSIC SEMICONDUCTOR IN TERMS OF BAND GAP ENERGY

Then from equation (14),

$$E_F - E_c = \left(\frac{E_c + E_v}{2}\right) + \frac{3}{4}K_B T \log\left(\frac{m_h^*}{m_s^*}\right) - E_c = \left(\frac{E_v - E_c}{2}\right) + \frac{3}{4}K_B T \log\left(\frac{m_h^*}{m_s^*}\right)$$

The above equation is divided by $K_B T.we$ get,

$$\left(\frac{E_F - E_C}{K_R T}\right) = \frac{-E_g}{2K_R T} + \frac{3}{4} \log\left(\frac{m_h^*}{m_s^*}\right) \tag{15}$$

Where $E_g = E_c - E_v$ is the energy of the forbidden gap.

Substituting equation (15) in equation (8), we get,

$$n_{e} = n = 2 \left(\frac{2\pi m_{e} {}^{*} K_{B} T}{h^{2}}\right)^{3/2} \exp\left[\frac{-E_{g}}{2K_{R} T} + \frac{3}{4} \log\left(\frac{m_{h} {}^{*}}{m_{s} {}^{*}}\right)\right]$$

$$n_{e} = n = 2 \left(\frac{2\pi m_{e} {}^{*} K_{B} T}{h^{2}}\right)^{3/2} \exp\left[\frac{-E_{g}}{2K_{R} T}\right] \exp\left[\log\left(\frac{m_{h} {}^{*}}{m_{e} {}^{*}}\right)^{3/4}\right]$$

$$n_{e} = n = 2 \left(\frac{2\pi m_{e} {}^{*} K_{B} T}{h^{2}}\right)^{3/2} \left(\frac{m_{h} {}^{*}}{m_{s} {}^{*}}\right)^{3/4} \cdot \exp\left(\frac{-E_{g}}{2K_{R} T}\right)$$

$$n_{e} = n = 2 \left(\frac{2\pi K_{B} T}{h^{2}}\right)^{3/2} \left(m_{e} {}^{*} m_{h} {}^{*}\right)^{3/4} \exp\left(\frac{-E_{g}}{2K_{R} T}\right)$$
(16)

Also from equation (14),

$$\begin{split} E_v - E_F &= E_v - \left[\frac{E_c + E_v}{2} + \frac{3}{4}K_BT\log\left(\frac{m_h^*}{m_s^*}\right)\right] \\ &= \left(\frac{E_v - E_c}{2}\right) - \frac{3}{4}K_BT\log\left(\frac{m_h^*}{m_s^*}\right) \end{split}$$

The above equation is divided by $K_B T$, we get,

$$\frac{E_{v-E_F}}{K_BT} = \frac{-E_g}{2K_BT} - \frac{3}{4}\log\left(\frac{m_h^*}{m_s^*}\right) \tag{17}$$

Substituting equation (17) in equation (13), we get,

$$n_{h} = p = 2 \left(\frac{2\pi m_{h}^{*} K_{B} T}{h^{2}} \right)^{3/2} \cdot exp \left[\frac{-E_{g}}{2K_{B} T} - \frac{3}{4} \log \left(\frac{m_{h}^{*}}{m_{s}^{*}} \right) \right]$$

$$n_h = p = 2 \left(\frac{2\pi m_h^* K_B T}{h^2}\right)^{3/2} \cdot exp\left[\frac{-E_g}{2K_B T}\right] \exp\left[\log\left(\frac{m_h^*}{m_g^*}\right)^{3/4}\right]$$

$$n_{h} = p = 2\left(\frac{2\pi m_{h}^{*}K_{B}T}{h^{2}}\right)^{\frac{5}{2}} \left(\frac{m_{h}^{*}}{m_{s}^{*}}\right)^{\frac{5}{4}} \exp\left(\frac{-E_{g}}{2K_{B}T}\right)$$
$$n_{h} = p = 2\left(\frac{2\pi K_{B}T}{h^{2}}\right)^{3/2} \left(m_{s}^{*}m_{h}^{*}\right)^{3/4} \exp\left(\frac{-E_{g}}{2K_{B}T}\right)$$
(18)

From equation (16) and (18), we get,

$$n = p = 2 \left(\frac{2\pi K_B T}{h^2}\right)^{3/2} \left(m_g^* m_h^*\right)^{3/4} exp\left(\frac{-E_g}{2K_B T}\right)$$
(19)

Therefore, the concentration of electron in the conduction band and hole in the valence band depend upon the temperature of the intrinsic semiconductor.

EXPERIMENTAL DETERMINATION OF BAND GAP OF A

SEMICONDUCTOR

The diode is immersed in an oil bath that in turn is kept in a heating mantle. A thermometer is also kept in the oil path such that its measure bulb is just at the height of diode. The diode is reversed biased with the help of DC voltage obtained from a DC power supply and the current that flows through the reverse diode is measured with a milliammeter. The Circuit diagram of this experiment is shown in the Fig.2.18(a).

The power supply is switched on and the voltage is adjusting say five volts. The current through the diode and the room temperature are noted. The power supply in switched off and the heating mantle is switched on. The oil bath is heated up to 65° C. The oil is stirred well. The temperature of oil bath stabilized say at 75° C.

The power supply is again switched on and the voltage is kept at 5V. The temperature (say 75^{0} C) and the corresponding current through the diode are noted.

Now the oil bath is allowed to cool slowly. As the temperature falls, the current through the diode decreases. The current falls for various temperatures (any convenient interval) are noted down.

The calculations are completed and a graph is plotted taking 1000/T on X-axis and log I_0 on Y-axis. A straight line is obtained as shown in the Fig.2.18 (b). The slow of the straight line is determined and using it the band gap is calculated using the following equation.

Care should be taken while performing the experiment the diode and the thermometer are placed at the same level in the oil bath. The maximum temperature of the diode should not be beyond 80° C. Reading of the current and temperature to be taken simultaneously.



Fig. 4.4 (a) Circuit diagram

(b) Expermental graph

Hall Effect





- The standard geometry for doing an experiment in its most simple form is as follows:
- A magnetic field <u>**B**</u> is employed perpendicular to the current direction <u>*i*</u>, as a consequence a *potential difference* (i.e. a *voltage*) develops at right angles to both vectors.
- In other words: A **Hall voltage** U_{Hall} will be measured perpendicular to <u>B</u> and <u>j</u>.In yet other words: An electrical field <u>E_{Hall}</u> develops in y-direction That is already the essence of the Hall effect.

Hall effect is a very useful phenomenon and helps to

- Determine the Type of Semiconductor
- Calculate the Carrier Concentration
- Determine the Mobility (Hall Mobility)
- Measure Magnetic Flux Density

Part A

Explain the properties of semiconductors Analyze the role of Fermi level in semiconductors Classify the types of semiconductors Compare p and n type semiconductors Evaluate the role of temperature in Fermi level Elucidate Band gap and its dependent factors Illuminate Hall effect and mention its applications Write the expression of electron and hole concentration in pure semiconductor and mention its major changes Draw energy band profile of intrinsic and extrinsic semiconductors Draw and explain band profile of p and n type semiconductors Mention the role of acceptor and donor energy levels Analyze the applications of semiconductor based on their properties

Part B

Deduce the expression of electron density in Intrinsic semiconductors

Deduce the expression of electron and hole density in Intrinsic semiconductors and comment your

results

Defend the role of temperature in Fermi level assignment in intrinsic semiconductor

Deduce the carrier concentration of n-type semiconductor

Deduce the carrier concentration of p-type semiconductor

Analyze the methodology to find energy gap

Derive Hall coefficient in term of Hall voltage

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UNIT – 5 – Optical Properties of Solids – SPH1316

Optical properties of Solids

Optical Absorption

- OPTICAL ABSORPTION IN METALS
- We know that, when a metal is exposed to light then the metal gets heated after some time. Why?

Reason

- Conduction band electrons in metals are able to interact with an optical electric field. Their motion is damped by collisions with the vibrating lattice and so some of the light energy is transferred to the lattice. In this manner, the material is heated.
- Skin depth and skin layer
- A perfect metal is a material having an infinite conductivity. It can be shown that electromagnetic wave propagating in a metal gets attenuated by a factor of 1/e when it has travelled a distance.

$$\boldsymbol{\delta} = \frac{2}{(\omega \chi \sigma)^{1/2}}$$

Where χ - is the magnetic susceptability



Fig.5.1

- Optical absorption in dielectrics (Insulators)
- In dielectric, the electrons are effectively bound to the atoms (or) molecules that compose the material. (The availability of free electrons is very less). The applied field induces a polarisation in the material. Upon relaxation some of the energy in the polarisation is coupled to the lattice and the material in heated.
- When light is allowed to fall on a dielectric, the covalent bonds are broken and the electrons in the valance band absorbs the light energy and moves to conduction band thereby creating a hole in valence band. While it returns from conduction band to valance band it may radiate the energy in two processes.
- Radiative transition
- It is the process in which the electrons in conduction band recombines with the holes in valance band and reradiate the energy in the form of light.

• Non-radiate transition

- In this process, the electrons in conduction band will have collision with the lattice points in the dielectric material and thereby radiate the energy in the form of heat.
- In either case phonons are generated and the material is heated.

OPTICAL ABSORPTION IN SEMI-CONDUCTORS

- Semiconductors possess charges of all kinds, bound and free and so exhibit some of the optical properties characteristic of each. The most important transition for the semiconductor materials are those between the valence band and the conduction band. The energy transition depends on the energy band gap (Eg) between the valence band and conduction band.
- The energy band gap of a semiconductor is given by

$$\underline{E}_{g} = \underline{h}\underline{U} = \underbrace{hc}{\underline{h}}\underline{L}$$

Absorption edge $(\lambda) = \frac{hc}{E_{a}}$ and at this wavelength there exists a sharp edge in

the absorption spectrum.

Absorption edge (λ) is inversely proportional to the energy band gap (ie) the materials having small energy band gap (Eg) will absorb, the lower wavelength and allow the higher wavelength of light.

Traps

- In an intrinsic semiconductor electron-hole pairs are generated due to breaking of covalent bands. The concentration of electrons 'n' in the conduction band is equal to the concentration of holes 'p' in the valence band.
- $n = p = n_i$
- where $n_i \rightarrow$ is the intrinsic carrier concentration. The value of n_i varies exponentially with temperature.
- The recombination of electron-hole pair occurs at the same rate at which the thermal generation occurs. when an electron in the conduction band makes a transition into a vacant state in the valence band recombination takes place.
- The energy released in the recombination which is about E_g, may be emitted as a photon. When a photon is released, the process is called rediative recombination. Instead energy may be released as heat at the crystal lattice in the form of quantized lattice vibrations which are called Phonons. The absence of photon emission indicates a non-radiative process. There are two types of recombination processes
- Trapping center
- Recombination center

Colour centres

• Insulators that are transparent because of the large band gap appear coloured some times. This colour results from selective absorption of some portion of the visible spectrum by

imperfections in the crystal. Such imperfections in a crystal which selectively absorb certain colours in the visible, spectrum are called colour centres. These colour centres gives rise to energy states in the forbidden gap. Colour centres are the lattice defects (or) crystal imperfections which absorb the visible light, so that the crystal is coloured.

- Pure ionic crystals like NaCl, KCl etc., are transparent when visible light is passed through them. These crystals may be made to appear coloured by any of the following ways.
- Adding impurities
- Adding metal ions
- By bombarding the crystals with x-ray, γ -ray, neutron (or) electron
- Electrolysis

Types of Colour Centres are

- There are various types of colour centres and they are listed as below:
- F-centre
- *F*[']-centre
- R₁-centre
- R₂-centre
- M-centre
- V-centre etc.

F Centre:

- The colour centre in which an electron as trapped at a negative at a vacancy is called F-Centre.
- The simplest colour centre is the F- centre in an alkali halide and consist of an electron trapped at a negative halogen ion vacancy.
- If a colourless NaCl crystal is heated, in the presence of sodium Vapour, then the NaCl crystal will absorb the sodium atoms from the sodium vapour. Each of the excess sodium atom absorbed from the sodium vapour may then ionize into positive sodium ion and an electron
- $Na \rightarrow Na^+ + e^-$
- Thus a number of Na⁺ ions, and an equal number of negative ion vacancies will be created to keep the crystal as a whole. Since, the negative ion vacancies represent a net positive
- charge within the crystal, they attract the electrons and captures it. This trapped electron will be shared by all the positive (Na⁺) ions nearby the vacant site as shown in Fig 4:8.



Fig.5.2

Properties of F-Centre

- Coloured crystals are less dense than uncoloured crystals which indicates
- that the introduction of vacancies leaser the density.
- The width of the F-band increases with temperature.
- F-absorption band is independent of the metal ions added to it.
- In stoichimetric crystals. The hands are formed due to irradiation of ultraviolet radiations.
- x-rays etc. ٠

F' Centre

An electron with two electrons trapped in it is called F'-Centre.

When the temperature of the F-Centre is decreased, than the F-Centre will be destroyed and the electron from one F-Centre will be captured by another F-Centre to form a new colour centre called F'-Centre, Fig (4.9)



Figure 4.9 F¹-Centre



R1, R2 and M-Centres:

When the crystals containing F-Centres, are irradiated with light, under a suitable temperature range, coagulation will occur. Due to coagulation, various colour centres viz., R1, R2 and M-centers are produced as shown in fig 4.10.

R1-Centre:

It is the colour centre formed due to the combinations of an F –centre and vacant site



R2-Centre:

It is the colour centre formed due to the combination is the centre as shown in fig.

M-Centre:

It is the colour centre formed due to the combination of an F-Centre with positive and negative vacant sites as shown in fig.

V-Centres:

V-Centre: Trapping of a hole at a positive ion vacancy is called V-Centres.

EXCITONS

- An electron-hole bound state formed by the electro static attraction that exists between an electron and a hole is called as exciton.
- When photons of long wavelength region is absorbed by a crystal, there will not be photoconductivity. Since the crystals does not show extra electrical conductivity due to absorption of photons. That the absorption does not give rise to an electronic transition from the filled valence band into the empty conduction band, but instead gives rise to an excited state (or) level below the conduction band level called exciton bands.



The combination of an electron in an excited state (black dot) and the hole left behind in the filled valance band (open circle) is called an excition.

•
$$+ O \rightarrow Exciton$$

The electron in the excited state does not become free even after leaving the filled valence band but it still bound to some extent by the coulomb field produced by the hole it left behind. Thus the combination of an electron in an excited state just below the conduction band and the associated hole forming the band state level is called an exciton.

This bound electron hole pair as a whole is neutral and will not contribute to any electrical conduction to the crystal, but will transfer its energy from one ion to the next ion.

$+ O \rightarrow Exciton$

[Bound electron – hole pair] \rightarrow Exciton

Types of Excitons

There are classified into two types as

- (i) Strongly bound excitons
- (ii) Weakly bound excitons

Strongly bound excitons:

This type of excitons are called as frenkel excitons.

This electron-hole interparticle distance is small in comparision with atomic radius (a > r) as shown in fig. 4.6. This implies that the electron and hole are found on or near the same atom. Coupling between the neighbouring sites permits hopping of the exciton from one atom to another.

Example: NaCl, KBr etc. has strongly bound excitons.



Weakly bound excitons:

This model of excitons is due to Mott and Wannier. The excitons which its electron-hole interparticle distance is large compared to lattice constant (r > a).

Example: Cu₂O.



Fig.5.7

Luminescence

- A Material which absorbs energy and then spontaneously emits visible (or) near-visible radiation is known as luminescence.
- When a material absorbs energy in some form (like excitation by light, particle bombardment, chemical reaction, heat, high energy electrons, high alternating electric field etc.,) a fraction of absorbed energy may re-emitted in me form of electromagnetic radiation.
- Mechanism
- In luminescence, the input energy excites electrons of a luminescent material from the valance band into the conduction band. When an excited electron in the conduction band (higher energy state) drops to the valence band (lower energy state), it recombines with a hole in the valence band. The recombination process may lead to the emission of a photon.
- Thus, in general, the emission of light by an electron-hole recombination process is called

luminescence.

- Depending on the method of excitation we may distinguish between the various types of luminescence.
- **Photo luminescence** Excitation of electrons by the absorption of photons
- **Cathode luminescence** Excitation of electrons by high-energy electron bombardment of the material.
- Electroluminescence Excitation of electrons by the application electric field.
- Thermoluminescence Excitation of electrons by the application of High temperature.
- Chemiluminescence Excitation of electron due to chemical reaction.
- Photoluminescence

In photoluminescence, energy is transformed to the crystal by the absorption of a photon. In luminescent materials, the activator ion* itself absorbs the photon directly. The same energy levels are involved in both absorption and emission. Hence the absorption and emission wavelengths are expected to be identical. But the emission peak is red shifted compared to the absorption peak. This phenomenon is known as stokes shift







Fig.5.9

Application

• The stokes shit, find commercial application in fluorescent lamps. In these lamps an electric discharge is passed through a mixture of argon and mercury vapour. An appreciable amount of radiant energy emitted is in the ultraviolet. Since the walls of the discharge tube are coated with a suitable luminescing material), the ultraviolet radiation is converted into useful visible radiation, thereby increasing the luminous efficiency of the lamp.

Types

Based on time delay between excitation (generation of an electron-hole pair) and de excitation (recombination of an electron-hole pair) the photoluminescence process can be classified as

- Fluorescence Fast photoluminescence
- Phosphorescence -Slow Photoluminescence.

Fluorescence

- If the emission of radiation due to recombination is instantaneous (i.e) if the omission occurs during excitation or within 10^{-8} sec of excitation then the process is called fluorescence. Thus is fluorescence, the emission of light stops with 10^{-8} sec after the excitation is turned off.
- The life time of an election in an excited state is 10^{-8} sec for which the return to the ground state is

accompanied by the emission of radiation.

• In fluorescence, the electron-hole recombination taxes place directly and the emission of light radiation occurs very quickly and hence this process can be termed as fast photoluminescence.

Applications

- The emission of light from a fluorescent tube is based on fluorescence process. This tube contain a gas mixture of argon and mercury. This argon and mercury gas become excited by the electrical discharge process and emit light mainly in the ultraviolet region, which is absorbed by the fluorescent coating on the tube. The excited electrons in the florescent coating material then recombine, resulting in the emission at light in the visible Spectrum.
 - Fluorescence excited by ultraviolet light is used to identify minerals and biochemical compounds.

Phosphorescence

- In some materials emission of light radiation continues for periods upto seconds (or) minutes after the excitation is turned off.
- This type of light emission for which there is a delay between excitation and de-excitation (emission), which provides on after glow is called phosphorescence and the materials are called phosphors. Here the emission taxes longer than 10^{-8} sec.
- The delay in emission is due to the fact that the excited electrons are trapped in various ways at discrete energy levels which are introduced by added impurities called activators. These discrete impurity levels are in the energy gap between the conduction band and valence band of the host material.

• Thus, in phosphorescence, the electron hole recombination takes place indirectly via impurity levels in me bandgap and the emission of light radiation occurs rather slowly. Hence this process can be termed as slow photoluminescence.



Fig.5.10

- The phosphorescence consist of the following events. They are,
- A electron-hole pair (EHP) is formed due to absorption of incoming photon of energy $hv_1 > E_g$. This process is called "Photogeneration".
- The excited electron in the conduction band gives some of its energy to the lattice by scattering until it comes to the bottom edge of conduction band.
- The electron is then trapped by the impuring level E_t and remains trapped until it can be thermally re-excited to the conduction band.
- The electron wanders in the bottom edge of the conduction band for a very small function of time.
- Finally, recombination occurs as the electron falls to an empty state in the valence band, releasing a light photon of energy hv_2 which is approximately the bandgap energy.

Phosphors

- Materials which can produce luminescence are called Phosphors. Phosphors have the capability of absorbing high energy (short wavelength) radiation and spontaneously emitting low energy (longer wavelength) light radiation. The emission spectra of phosphors are controlled industrially by certain added impurities called "activators" Eg: ZnS (Zinc Sulfide)
- – Small amounts of Cu in the ZnS phosphor act as activator with luminescence occurring in the green region.
- – Mn that gives luminescence in the red region.
- – When ZnS is activated with Silver, it will emit blue light

Cathodoluminescence

- When high energetic electron beam hits the solid, the electron-hole pair is created in the solid. During the recombination of electron-hole pairs, the light is emitted. This process of emission of light is called photoluminescence.
- Explanation
- When high energetic electron beam form a hot cathode hits the solid, some electrons are scattered back and some of them will penetrate into the solid. During penetration, the incident electrons so called primary electrons will remove the electrons from the covalent bonds and are called secondary electrons inside the solid and thus create electron-hole pairs.
- The secondary electrons created will go to the energy level (E_c) below the conduction band energy level and the holes created will be in the energy level (E_v) above the valence band energy level. Now, during recombination of electron and hole pairs, the energy is emitted in the form of light and the phenomenon is called cathode-luminescence.

Electroluminescence

When the electrons are excited from valence band to conduction band by applying d.c (or) a.c field and if they emit light during de excitation then it is called Electro-luminescence.

- Mechanism:
- The Phosphor particles namely ZnS: Cu are suspended in a non-conducting transparent insulating binding medium of high dielectric constant. This medium is sandwiched in between two electrodes, namely, highly transparent (SnO₂) and a metal electrode. As a result, there is no complete conduction path between the two electrodes and hence, the de-

excitation could not take place. When an ac voltage is applied between the two electrodes, a short burst of light is emitted for every half cycle for a period of 10^{-3} S.



Fig.5.11

Applications

- The fluorescent materials are used in display devices such as CRT, LED, LCD, etc.
- A fluorescent lamp consists of a thin coating of a fluorescent material like magnesium tungstate, Zinc Silicate, Cadmium borate or Zinc beryllium Silicate. When ultraviolet radiations are made to fall on such type of materials, they absorb the incident radiation and reemit the light having the wavelength in the visible region, and hence increases the luminous flux.
- When x-rays are made to fall on a glass coated with barium platinocynaide, it produces a fluorescent light. Therefore, it is used as detector for x-rays.
- The yellow-brown tint of a washed fabric is removed by adding certain fluorescent chemicals with washing power. These fluorescent chemicals are used to increase the whiteness of the fabric.
- Fluorescent Paints are prepared by adding some fluorescent chemicals to the paints. When they are illuminated by light during the night time, they become visible.
- Watch dials and clocks are coated with certain fluorescent chemicals like radium compounds.

Part A

Analyze the optical absorption in insulator Explain skin depth and in which material it is applicable Examine the reason behind electron trapping Elucidate the formation of excitons Explain the nature of light propagation in semiconductors Compare Frenkel and Mott Wannier excitons Illuminate the principle behind colour centers Differentiate F and V colour centers Irradiate the types of Luminescence with its principle Differentiate Phosphorescence and Fluorescence

Part B

What is meant by absorption? Explain the phenomena of absorption of light in metals, insulators and semiconductors

(i)Write a note on Colour centers with neat sketch

(ii)Compare Traps and excitons

Explain about luminescence? Explain how photoluminescence takes place in characteristic luminescent materials?

Compare Injection, Photo and cathode luminescence

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