M.Sc. Final Year

Physics, MP-06

SOLID STATE PHYSICS AND MATERIAL SCIENCE

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल

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SYLLABI-BOOK MAPPING TABLE

Solid State Physics and Material Science

Syllabi	Mapping in Book
Unit I : Lattice Dynamics and Polarisation Lattice vibration of .monoatomicand diatomic lattice; specific heat of solids, anharmonicity and expansion of solids, Equation of state of solids, phonon mean free path in solids, Elastic waves, Microscopic and macroscopic description of the dielectric behaviour. Polarisation and dielectric constant, Electronic, Ionic, Atomic and orientotional polarisation, Lorentz internal field, static dielectric cqnstant of sol[ds, complex, dielectric constant. Dielectric losses and relaxation time, Debye equations.	**Unit-1:** Lattice Dynamics and Polarisation **(Pages 3-67)**
Unit II : Band Theory of Solids Behaviour of-electron gas in one dimension, density of states, chemical potential, paramagnetism, of free electrons, Hall effect, Fermi energy, Bloch's theorem, Kronig-Penny model, concept of the hole and effective mass, Distinction between conductor, insulator and semiconductor and intrinsic and·extrinsic conductivity.	**Unit-2:** Band Theory of Solids **(Pages 69-102)**
Unit III : Magnetism Element ideas of diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic, ferrimagnetic and fermites, Quantum theory of para and ferromognetism. Origin of magnetic domins. Simple theory and experimental description of Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR), Mossbourer effect and its application in determination of the nature of interatomic forces in crystalline solids with special reference to impure crystal.	**Unit-3:** Magnetism **(Pages 103-132)**
Unit IV : Defects in Crystals Point defects in ionic crystals and metals, Diffusion, ionic conductivity, colour centres (Fand V centres), Excitons. General idea of luminescence, Dislocations and mechanical strength of crystal. Plastic behaviour, Types of dislocations, Stress field of dislocation. Grain boundaries, Ething-types of ething.	**Unit-4:** Defects in Crystals **(Pages 133-180)**
Unit V : Elements of Thin Films Concept of thin films, Electrical conductjon in thin film. Deposition of thin films by thermal evaporations, cathodic sputtering, Evaporation at reduced pressure, Thickness measurement (four probe method, multiple beam interferrometry). Size effect, behavior, Fuchs-Sondheimer model (without derivation).	**Unit-5:** Elements of Thin Film **(Pages 181-196)**

CONTENTS

INTRODUCTION

NOTES

Solid-state physics is the study of rigid matter, or solids, through methods such as quantum mechanics, crystallography, electromagnetism, and metallurgy. It is the largest branch of condensed matter physics. 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. The interdisciplinary field of 'Materials Science', also commonly termed 'Materials Science and Engineering', explains the design and discovery of new materials, particularly solids. The academic origins of materials science branch started when researchers began to use analytical thinking from chemistry, physics, and engineering to understand ancient, phenomenological observations in metallurgy and mineralogy.

The bulk of solid-state physics, as a general theory, is focused on crystals. Primarily, this is because the periodicity of atoms in a crystal (its defining characteristic) facilitates mathematical modelling. Likewise, crystalline materials often have electrical, magnetic, optical, or mechanical properties that can be exploited for engineering purposes. 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 (e.g., 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 (crystalline solids, which include metals and ordinary water ice) or irregularly (an amorphous solid such as common window glass).

This book, *Solid-State Physics And Materials Science* is divided into five units that follow the self-instruction mode with each unit beginning with an Introduction to the unit, followed by an outline of the Objectives. The detailed content is then presented in a simple but structured manner interspersed with Check Your Progress Questions to test the student's understanding of the topic. A Summary along with a list of Key Terms and a set of Self-Assessment Questions and Exercises is also provided at the end of each unit for recapitulation.

UNIT 1 LATTICE DYNAMICS AND POLARISATION

Structure

1.0 INTRODUCTION

Lattice vibration is the fluctuations of atoms in a solid with reference to the equilibrium position. Lattice vibrations can describe elastic properties, thermal properties, optical properties, and sound velocity of materials. In a crystal, the equilibrium positions form a regular lattice. The vibration of these neighbouring atoms is not independent of each other. A regular lattice with harmonic forces between atoms and normal modes of vibrations are called lattice waves. Lattice waves range from low frequencies to high frequencies on the order of 1,013 Hz or even higher. Lattice vibrations can also relate with free electrons in a conducting solid which gives intensification to electrical resistance. Due to the connections between atoms, the displacement of one or more atoms from their equilibrium positions gives rise to a set of vibration waves propagating through the lattice. One such wave is shown in the figure to the right. The amplitude of the wave is given by the displacements of the atoms from their equilibrium positions. The wavelength λ is marked. There is a minimum possible wavelength, given by twice the equilibrium separation a between atoms. Any wavelength shorter than this can be mapped onto a wavelength longer than $2a$, due to the periodicity of the lattice. This can be thought as one consequence of Nyquist–Shannon sampling theorem, the lattice points are viewed as the “Sampling Points” of a continuous wave. Diatomic lattices played an important role in the elucidation of the concepts of element, atom, and molecule in the 19th century, because some of the most common elements, such as hydrogen, oxygen, and nitrogen, occur as diatomic molecules. John Dalton’s original atomic hypothesis assumed that all elements were monatomic and that the atoms in compounds would normally have the simplest atomic ratios with respect to one another. The study of phonons is an important part of condensed matter physics. They play a major role in many of the physical properties of condensed matter systems, such as thermal conductivity and electrical conductivity, as well as play a fundamental role in models of neutron scattering and related effects. Generally, there are two kinds of wave—Mechanical waves and Electromagnetic waves. The waves on strings, sound waves, seismic waves are the examples of mechanical waves; whereas radio waves, light waves, x-rays are the examples of electromagnetic waves. Dielectric constant or relative permittivity, of a material is its (absolute) permittivity expressed as a ratio relative to the vacuum permittivity. Permittivity is a materials property that affects the Coulomb force between two point charges in the material. Relative permittivity is the factor by which the electric field between the charges is decreased relative to vacuum. Similarly, relative permittivity is the ratio of the capacitance of a capacitor using that material as a dielectric, compared with a similar capacitor that has vacuum as its dielectric. Relative permittivity is also commonly known as the dielectric constant, a term still used but deprecated by standards organizations in engineering as well as in chemistry. The historical term for the relative permittivity is dielectric constant. It is still commonly used, but has been deprecated by standards organizations, because of its ambiguity, as some older authors used it for the absolute permittivity $\in$. The permittivity may be quoted either as a static property or as a frequency-dependent variant. It has also been used to refer to only the real component $\in$ of the complex-valued relative permittivity. In this unit, you will study about the lattice vibrations, diatomic lattices, phonons, polarisation, dielectric, Lorentz field, static and complex dielectric constants and Debye equation.

1.1 OBJECTIVES

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

- Describe the lattice vibration of monatomic and diatomic lattice
- Discuss the meaning of anharmonicity and the concept of expansion of solid
- Explain the meaning of elastic wave and phonons
- Discuss the meaning and types of polarisation along with dielectric losses
- Describe the microscopic and macroscopic description of dielectric behaviour
- Analyse the Lorentz field
- Explain static and complex dielectric constants and Debye equation

1.2 LATTICE VIBRATION OF MONATOMIC AND DIATOMIC LATTICE

NOTES

When a lattice is at its equilibrium position then each atom is directed exactly at its lattice site. Now suppose that an atom is displaced from its equilibrium position by an infinitesimal amount. It will tend to regain its equilibrium position, due to the restoring forces acting on it. This causes lattice vibrations. Numerous atoms move simultaneously, therefore, this has to be considered as the motion of the entire lattice.

Lattice vibrations can describe elastic properties, thermal properties, optical properties, and sound velocity of materials. Lattice Vibration is the fluctuations of atoms in a solid with reference to the equilibrium position.

In a crystal, the equilibrium positions form a regular lattice. The vibration of these neighbouring atoms is not independent of each other. A regular lattice with harmonic forces between atoms and normal modes of vibrations are called lattice waves. Lattice waves range from low frequencies to high frequencies on the order of 1,013 Hz or even higher.

Lattice vibrations can also relate with free electrons in a conducting solid which gives intensification to electrical resistance. Due to the connections between atoms, the displacement of one or more atoms from their equilibrium positions gives rise to a set of vibration waves propagating through the lattice. One such wave is shown in the figure to the right. The amplitude of the wave is given by the displacements of the atoms from their equilibrium positions. The wavelength λ is marked.

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There is a minimum possible wavelength, given by twice the equilibrium separation a between atoms. Any wavelength shorter than this can be mapped onto a wavelength longer than 2*a*, due to the periodicity of the lattice. This can be thought as one consequence of Nyquist–Shannon sampling theorem, the lattice points are viewed as the "Sampling Points" of a continuous wave. Not every possible lattice vibration has a well-defined wavelength and frequency. However, the normal modes do possess well-defined wavelengths and frequencies.

Diatomic Lattice

Consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. The diatomic lattice show an important feature which is different from the monoatomic case. Figure 1.1 shows a diatomic lattice with the unit cell composed of two atoms of masses M_1 and M_2 with the distance between two neighbouring atoms *a*.

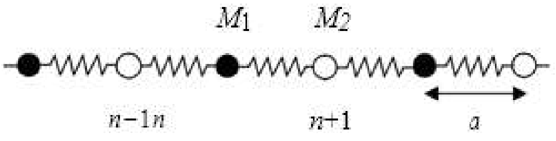


Fig. 1.1 Diatomic Lattice with the Unit Cell

We can evaluate the motion of this lattice in a similar way as for monoatomic lattice. However, in this case because we have two different types of atoms, we should write two equations of motion:

$$M_1 \frac{d^2 u_n}{dt^2} = -C(2u_n - u_{n+1} - u_{n-1}) \qquad ...1.1$$

$$M_2 \frac{d^2 u_{n+1}}{dt^2} = -C(2u_{n+1} - u_{n+2} - u_n) \qquad ... 1.2$$

In analogy with the monoatomic lattice we are looking for the solution in the form of traveling mode for the two atoms:

$$\begin{bmatrix} u_n \\ u_{n+1} \end{bmatrix} = \begin{bmatrix} A_1 e^{iqna} \\ A_2 e^{iq(n+1)a} \end{bmatrix} e^{-i\omega t}, \qquad ..1.3$$

Which is written in the obvious matrix form. Substituting this solution to Equation 1.2, we get

$$\begin{bmatrix} 2C - M_1\omega^2 & -2C\cos qa \\ -2C\cos qa & 2C - M_2\omega^2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = 0. \qquad ...1.4$$

This is a system of linear homogeneous equations for the unknowns A_1 and A_2. A nontrivial solution exists only if the determinant of the matrix is zero. This leads to the secular equation

$$(2C - M_1\omega^2)(2C - M_2\omega^2) - 4C^2\cos^2 qa = 0. \qquad ... 1.5$$

This is a quadratic equation, which can be readily solved:

$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2 qa}{M_1 M_2}}. \qquad ... 1.6$$

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves, as is shown in figure 1.2.

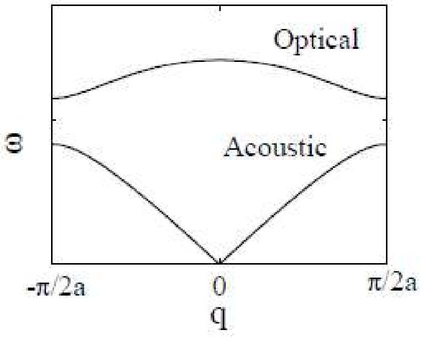


Fig. 1.2 *Dispersion Curves*

The lower curve is called the acoustic branch, while the upper curve is called the optical branch.

1.3 SPECIFIC HEAT OF A SOLID

Failure of classical theory. Blackbody radiation is not the only familiar phenomenon whose explanation requires quantum statistical mechanics. Another is the way in which the internal energy of a solid varies with temperature.

Let us consider the molar specific heat of a solid at constant volume, *Cv*, which is the energy that must be added to one 1 K mol of it, whose volume is held fixed, to raise its temperature by 1 K. The specific heat at constant pressure *Cp* is 3 to 5 per cent higher than *Cv* in solids because it includes the work associated with a volume change as well as the change in internal energy.

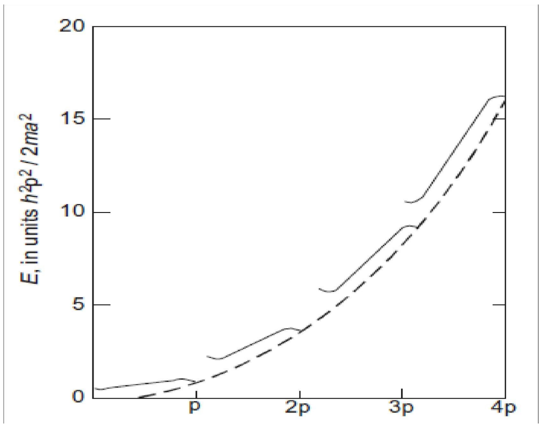


Fig 1.3 *Failure of Classical Theory*

Classical theory of heat

The internal heat energy of a solid resides in the vibrations of its constituent particles which may be atoms, ions or molecules; we shall refer to them as atoms here for convenience. These vibrations may be resolved into components along three perpendicular axes, so that we may represent each atom by three harmonic oscillators. According to classical physics a harmonic oscillator in thermal equilibrium at the temperature *T* has an average energy of *kT*. On this basis each atom in a solid should have 3 *kT* of energy. A kilomole of a solid contains Avogadro's number *N*0 of atoms, and its total internal energy *E* at the temperature *T* accordingly ought to be

$$E = 3N0\ kT = RT$$

where $R = N0\ k = 3.31\times 104$ J/mol.

$$K = 1.99 \text{ Kcal/kmol K}$$

R is the universal gas constant. (We know that in an ideal-gas sample of *n* kilomoles, *PV* = *nRT*.).

Check Your Progress

1. What do you mean by the lattice vibrations?
2. What do you understand by the diatomic lattices?

1.4 ANHARMONICITY AND EXPANSION OF SOLID

It is a tendency of a real crystal to resist compression to a smaller volume than its equilibrium value more strongly than expanding to a larger volume. It occurs due to the shape of the interatomic potential curve. This is a departure from Hooke's Law, as harmonic application does not produce this property. This is termed as anharmonic effect which takes place due to the higher order terms in potential that are generally ignored in harmonic approximation. An example of anharmonic effect is thermal expansion. In case of harmonic approximation, there is no interaction among phonons. When the boundaries are not present, lattice defects and impurities (which also scatter the phonons), the thermal conductivity is infinite. Whereas in anharmonic effect, phonons collide with each other and these collisions limit thermal conductivity which is due to the flow of phonons.

Anharmonicity affects many important phenomena such as thermal expansion and Fourier's law or coherent phonon generation. Heat transport is a prominent pillar of solid state physics and engineering, and it influences many devices and properties. In the past two decades a full chemically specific and atomistic prediction of lattice thermal properties has become possible. The field has benefitted from a positive feedback loop through refined experiments and theories and the same has blossomed at the junction of Physics, Chemistry and Engineering. The anharmonicity of lattice vibration describes various thermal properties of solids including the Lattice Thermal Conductivity (LTC), Coefficient of Thermal Expansion (CTE) and the temperature dependence of phonon frequencies.

1.5 EQUATIONS OF STATE FOR SOLIDS

Every solid (crystalline or amorphous) contains electrons. The important question is that "how the electrons respond when an electric field is applied to it?" That means "how electrical conductivity plays role for different solids?" We already know that the electrons in a crystalline solids are arranged in regular manner. These electrons in crystals are arranged in "Energy Bands" separated by regions in energy for which no wavelike electron orbitals exist. Such forbidden regions are called "*Energy Gaps* (E_g)" or "*Band Gap* (E_g)".

Let us consider two standing waves $\psi_+(x, t)$ and $\psi_-(x, t)$ pile up electrons at different regions, therefore the two standing waves have different potential energy. This is the origin of the "Band Gap" or "Energy Gap". In a constant potential (free electron theory), the energy of the electron as function of the wave vector $\vec{K}$ is given by

$$E = \frac{\hbar^2 K^2}{2m} \qquad ...(1.7)$$

Where $$K = \frac{2\pi}{\lambda} = \frac{P}{\hbar}$$

However, if we consider the motion of an electron in a periodic potential, we can say

(*i*) There exist allowed energy bands separated by forbidden regions; and

(*ii*) The functions $E(K)$ are periodic in $\vec{K}$.

The Figure (1.4) shows the plot of energy E with wave vector K (or wave number) for a free electron.

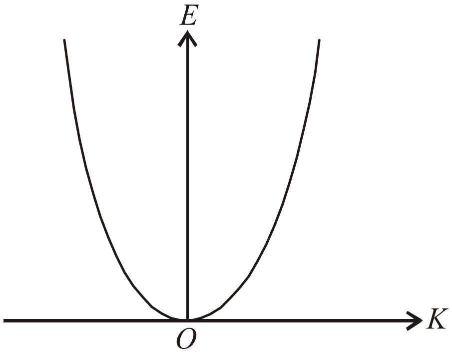


Fig. 1.4 *Energy (E) vs. Wave Vector (K) Graph for a Free Electron*

Figure (1.5) shows the plot of energy E with vector K (or wave number) in a monatomic lattice of lattice constant 'a'. Here, the energy gap (E_g) associated with the first Bragg's reflection at $K = \pm\, \pi/a$. Other forbidden gaps are found at $\pm\, n\pi/a$, where n = 1, 2, 3,.... etc.

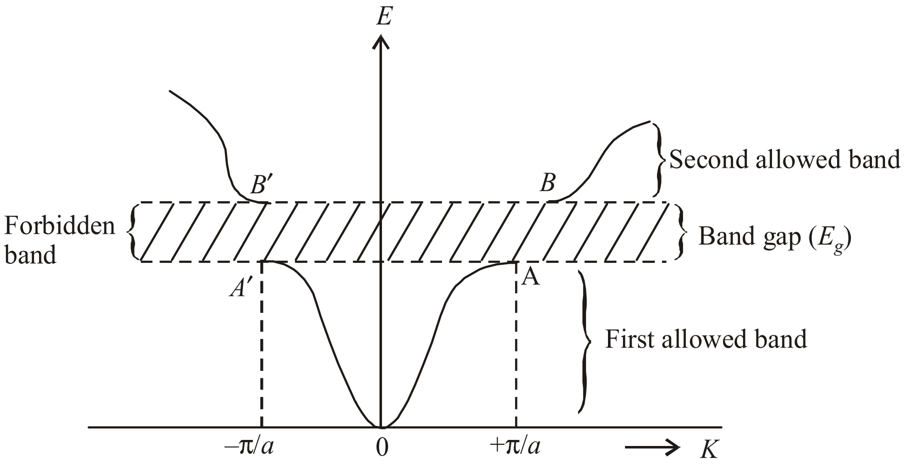


Fig. 1.5 *Energy (E) vs. Wave Vector (K) Graph for a Monatomic Lattice of Lattice Constant 'a'*

1.6 PHONONS

In condensed matter physics, 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 quasi-particle, 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 study of phonons is an important part of condensed matter physics. They play a major role in many of the physical properties of condensed matter systems, such as thermal conductivity and electrical conductivity, as well as play a fundamental role in models of neutron scattering and related effects.

A phonon is the quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency. While normal modes are wave-like phenomena in classical mechanics, phonons have particle-like properties too, in a way related to the wave–particle duality of quantum mechanics.

Three important properties of phonons may be deduced from this technique. First, phonons are bosons, since any number of identical excitations can be created by repeated application of the creation operator $b_k^{\dagger}$. Second, each phonon is a "Collective Mode" caused by the motion of every atom in the lattice. This may be seen from the fact that the creation and annihilation operators, defined here in momentum space, contains sums over the position and momentum operators of every atom when written in position space. Finally, using the position–position correlation function, it can be shown that phonons act as waves of lattice displacement.

Recent research has shown that phonons may have a non-negligible mass and be affected by gravity just as standard particles are. In particular, phonons are predicted to have a kind of negative mass and negative gravity. This can be explained by how phonons are known to travel faster in denser materials. Because the part of a material pointing towards a gravitational source is closer to the object, it becomes denser on that end. From this, it is predicted that phonons would deflect away as it detects the difference in densities, exhibiting the qualities of a negative gravitational field. Although the effect would be too small to measure, it is possible that future equipment could lead to successful results.

Phonons have also been predicted to play a key role in superconductivity in materials and the prediction of superconductive compounds. In 2019, researchers were able to isolate individual phonons without destroying them for the first time.

A lattice vibration carries quantized energy. The quantum of that energy is called a phonon, similar to the photon in electromagnetism. Phonons are specifically relevant for the behaviour of heat and sound transfer in the crystal. The atoms are uniformly arranged in a crystal. The atoms in a crystal can oscillate at particular frequencies when heated. The bonds between the individual atoms can be considered as elastic springs. When one atom of this entangled chain of atoms is pulled or pushed, a wave (or phonon) originates in the crystal as it happens in a rope.

Generally, most of the crystals are filled with a chaotic mixture of phonons comprising different frequencies and propagating in different directions. All waves superimpose each other and form a sea of several phonons.

Phonons are not exactly equivalent to photons, the quantized energy particles of electromagnetic radiation. The photons of different wavelengths majorly don't interact with each other. Whereas, the different phonons can interact and add up when they bump into each other and produce a changed wavelength. Such a property makes them random and hard to control.

The energy of a phonon behaves similar to the photons of a given energy, defined by their frequency, can impart energy into a system only in integer multiples of the basic quanta. Moreover, the heat transfer phenomenon in solids can also be imagined in terms of the propagation of phonons.

In electronic devices, such as computer chips, the process of heat dissipation is quite important to keep components work fine. The ways are designed to control the motion of phonons to get chips cool faster and perform better. On the other hand, some other methods are also designed where the system is allowed to transmit electricity but block heat for thermoelectric devices.

Phonon Momentum

It seems hard to believe that how a wave can carry a momentum but when a phonon interacts with elementary particles such as electron, proton, or neutrons, it seems like it carried a momentum of $hk/2\pi$ (where k is the wave vector). A phonon does not carry any physical momentum. The reason behind this is that a phonon coordinate (except for $k = 0$) includes relative coordinates of the atoms. In a hydrogen molecule (H_2), the internuclear vibrational coordinate $r_1 - r_2$ is a relative coordinate and it does not carry linear momentum. The center of mass coordinate agrees to the uniform mode for $k = 0$ and then it can carry a linear momentum. In crystals, wave vector selection rules guide the allowed transitions between different quantum states. The elastic scattering of an x-ray photon by a crystal is instructed by the wave vector selection rule

$$k' = k + G \tag{1.8}$$

Where G is a vector in the phase space of reciprocal lattice, k is the wave vector of the incident photon, and k' is the wave vector of the scattered photon. In the process of reflection, the crystal as a whole will recoil with the momentum — hG, but this uniform mode of momentum is considered explicitly very rarely.

Equation (1.8) is an example of the rule that the total wave vector of the interacting waves is conserved in a periodic lattice, with the possible addition of a reciprocal lattice vector G. The true momentum of the whole system always is severely conserved. If the scattering of the photon is inelastic, along with the creation of a phonon of wave vector K, then the wave vector selection rule becomes

$$k' + K = k + G\,, \tag{1.9}$$

If a phonon K is absorbed in this process, we have instead of the relation

$$k' = k + K + G\,. \tag{1.10}$$

Relations (1.9) and (1.10) are the natural extensions of (1.8).

1.6.1 Phonon Mean Free Path

For each phonon state (without any interactions between phonons) one may assign some wave vector $\vec{q}$, mode index j and specific energy $\hbar\omega j\,(\vec{q})$. Furthermore, for this wave vector value and mode there exist some displacement pattern of atoms in the lattice determined by the eigenvector $\vec{e}(\vec{q}\,j)$. The group velocities $\vec{v}j(\vec{q})$ of phonons can be obtained from the gradient of $\vec{v}j(\vec{q}) = \Delta\vec{q}\omega j(\vec{q})$ and it is the velocity of this phonon "Wave Packet" (or displacement pattern) in the lattice.

Sometimes one describes the interaction of phonons by using, for example, time-dependent perturbation theory. One assumes that these harmonic phonon states are stationary and interactions occur between these harmonic phonon states.

For instance, in 3-phonon process two phonons may annihilate and third is created or vice versa (energy and crystal-momentum conservation is assumed to be valid). One may thus calculate, for example, the transition rate (one per time unit) due to 3-phonon processes by using Fermi-Golden rule (or some other perturbative technique). The relaxation time $\tau j(\vec{q})$ for each phonon state $\vec{q}j$ is sometimes defined as an inverse of this transition rate.

The mean free path due to 3-phonon processes is defined as $\vec{v}j(\vec{q})\tau j(\vec{q})$, which is the mean distance for phonon to travel until it interacts. Other interactions may also have some effect on mean free path. If the interactions are sufficiently strong this elementary excitation phonon picture starts to become inaccurate and the group velocities etc. are rather ill-defined.

Check Your Progress

3. What are phonons?
4. State the properties of phonons.

1.7 ELASTIC WAVE

In the introduction part, we have discussed the propagation of waves without the transfer of matter through a medium. The propagation of the wave (disturbance) is also accom-panied by the transfer of energy. Therefore, we can say that the propagation of waves means transfer of energy.

For the propagation of any mechanical wave, we require (*a*) a source of disturbance, (*b*) a medium that does carry the wave (*c*) some physical mechanisms through which particles of the said medium can perturbe or influence one another.

Figure 1.6 shows how a mechanical progressive wave has propagated through a string (one end fixed string).

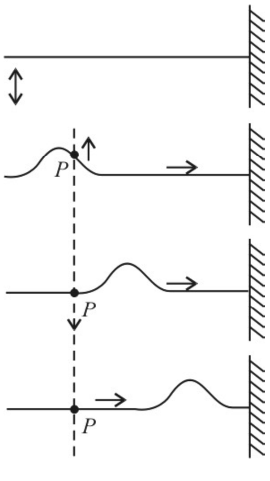


Fig. 1.6 *A travelling wave through a stretched string*

Remember that the pulse travelling through a string is *transverse* in nature; as each point on the pulse moves perpendicular to the direction of wave propagation.

The other class is *longitudinal* waves, where each point of the medium experiences displacement parallel to the direction of the propagation of the wave. For example, the sound waves in air are longitudinal in nature.

A continuous wave pulse may be created by shaking the end of the string, and the result gives us a simple harmonic motion. The nature of the travelling pulse on the said string is *sinusoidal*, as the shape of the pulse is of a sine wave (Fig. 1.7).

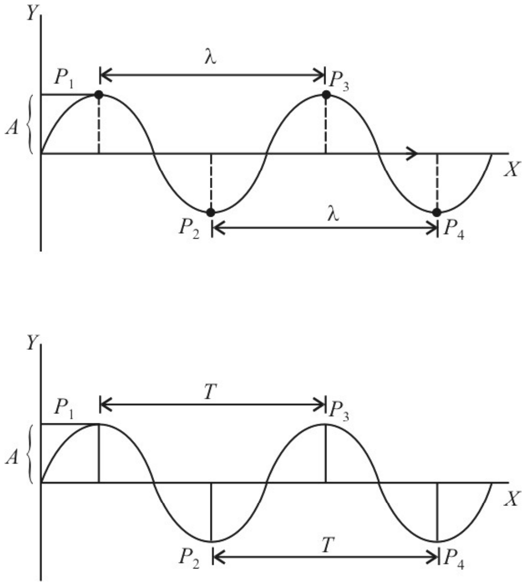


Fig. 1.7 *Wavelength (l) and time-period (T) of a progressive wave (sinusoidal)*

The points (P_1, P_3) with maximum positive displacement of the pulse are called *crests,* while the points (P_2, P_4) with maximum negative displacement of the pulse are called *troughs.*

The length of a wave (wavelength) is defined as “The minimum distance between any two identical points on the wave or the distance between two consecutive crests or troughs’. The wavelength is denoted by λ (lambda, the Greek letter).

The time-period (T) of a sinusoidal wave is defined as “the time taken by a point of the medium to execute one complete oscillation’; is equal to the inverse of the frequency; $T = \frac{1}{\nu}$, where ν is the linear frequency of the sinusoidal wave.

The amplitude (A) of a sinusoidal wave is defined as “The maximum displacement of a point of the medium from its equilibrium position’.

Progressive Wave and Differential Form

Let us visualise a progressive or travelling wave that is propagating along *x*-direction (Fig. 1.8) without interacting with any other waves or particles.

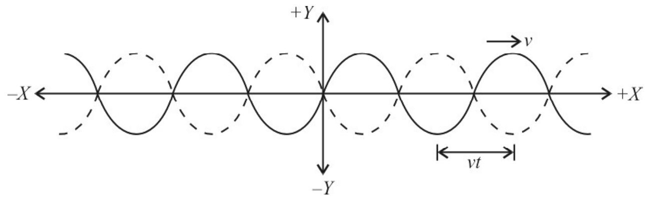


***Fig. 1.8** Propagation of a progressive wave; solid line for* t = *0 and dashed line for* t = t

At $t = 0$, the equation of displacement of such a wave can be described by

$$y(x) = A \sin\left(\frac{2\pi}{\lambda}x\right) \qquad ...(1.11)$$

where A is the amplitude and λ is the wavelength. If the wave moves in the positive x-direction with speed v, the displacement at time t can be described by

$$y(x,\ t) = A \sin\left[\frac{2\pi}{\lambda}(x - vt)\right] \qquad ...(1.12)$$

The speed (v) of the progressive wave is related to the wavelength and time-period or linear frequency by

$$v = \frac{\lambda}{T}\lambda\nu \qquad ...(1.13)$$

If the progressive wave propagates along the negative x-direction, then the displacement equation can be described by

$$y(x,\ t) = A \sin\left[\frac{2\pi}{\lambda}(x + vt)\right] \qquad ...(1.14)$$

Rearranging equation (4.2), we can write

$$y(x,\ t) = A \sin\,(Kx - \omega t) \qquad ...(1.15)$$

where $K = \dfrac{2\pi}{\lambda}$ is called the wave propagation vector, or the wave number and $\omega = \dfrac{2\pi}{T} = 2\pi\nu$; is called the angular frequency of the progressive wave. The above equation is the displacement equation of a progressive or travelling wave.

If the displacement y of a progressive wave is not zero at $x = 0$ and $t = 0$, the general expression for the displacement can be written in the form

$$y\ (x,\ t) = A \sin\,(kx - \omega t + \phi) \qquad ...(1.16)$$

where ϕ is the *phase constant*; it can be obtained from the initial conditions.

To find out the differential form of a progressive wave, we can proceed as follows: Differentiating equation (1.15) with respect to time t, keeping x as constant, we get

$$\left.\frac{dy}{dt}\right|_{x=\text{constant}} = v_l = \frac{\partial y}{\partial t} = -\,\omega\, A \cos\,(kx - \omega t) \qquad ...(1.17)$$

Again by differentiation

$$\left.\frac{dv_y}{dt}\right|_{x=\text{constant}} = a_y = \frac{\partial v_y}{\partial t} = \frac{\partial^2 y}{\partial t^2}$$

$$= -\omega^2 A \sin(Kx - \omega t) = -\omega^2 y \quad ...(1.18)$$

NOTES

From equations (1.17) and (1.18), the maximum values of velocity and acceleration are given by

$$(v_y)_{\max} = \omega A$$

and $$(a_y)_{\max} = \omega^2 A \quad ...(1.19)$$

Differentiating equation 1.15 with respect to position x, keeping t as constant, we get

$$\left.\frac{dy}{dx}\right|_{t=\text{constant}} = \frac{\partial y}{\partial x} = -kA\cos(kx - \omega t) \quad ...(1.20)$$

Again by differentiation

$$\left.\frac{d^2 y}{dx^2}\right|_{t=\text{constant}} = \frac{\partial^2 y}{\partial x^2} = -k^2 A\sin(kx - \omega t) = -k^2 y \quad ...(1.21)$$

Comparing equations 1.18 and 1.21, we get

$$\frac{\partial^2 y}{\partial x^2} = \frac{k^2}{\omega^2}\frac{\partial^2 y}{\partial t^2}$$

or, $$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \quad ...(1.22)$$

where $v = \frac{\omega}{k} = \nu\lambda$ is the velocity of the propagating wave.

Equation 1.22 is the *differential form* of a progressive wave and is often called *linear wave equation.*

Obviously, the solution of the differential equation of progressive wave will be

$$y(x, t) = A\sin\left[\frac{2\pi}{\lambda}(x - vt)\right]$$

or, $$y(x, t) = A\sin(kx - \omega t) \quad ...(1.23)$$

Difference between Elastic (Mechanical) and Electromagnetic Wave

From our previous discussions, we can differentiate the elastic (mechanical) waves and electromagnetic waves by their distinct characteristics.

When an elastic or a mechanical wave propagates, it requires (*a*) a source of disturbance (*b*) a medium that carries the wave and (*c*) some physical mechanism through which the particles of the said medium can perturb or influence other particles. The wave carries energy, and the energy is transmitted through the medium.

When a current flows through a transmission line due to voltage difference, it shows a wave-like behaviour. The existence of voltage across the transmission line produces an electric field in space between the cables. This helps us to understand the propagation of electromagnetic waves in space. Thus, as the current and voltage propagate through a transmission line in the form of waves, the electric and magnetic fields must exhibit the same nature.

Therefore, the electromagnetic waves can propagate through space (vacuum), whereas the mechanical waves can propagate through some medium. Most of the properties and behaviours of mechanical waves and electromagnetic waves are similar to each other.

We can differentiate categorically elastic waves and electromagnetic waves as follows:

Elastic (Mechanical) Waves	*Electromagnetic Waves*
1. A medium is necessary for the propagation of an elastic wave. magnetic wave.	1. Medium is not necessary for the propagation of an electro-
2. An elastic wave is longitudinal in nature.	2. An electromagnetic wave is transverse in nature.
3. As an elastic wave is longitudinal in nature, it cannot be polarised	3. As an electromagnetic wave is transverse in nature, it can be polarised
4. The speed of propagation of an elastic wave is much smaller than an electromagnetic wave. For example, the speed of a sound wave is about 333 m/s.	4. The speed of propagation of an electromagnetic wave is much higher than an elastic wave. For example, the speed of a light wave is about 2.998×10^8 m/s

Fig. 1.9 *Difference between Elastic and Electrogenetic Waves*

[**Note:** The relation between the particle velocity and wave velocity is given by $\frac{dy}{dt} = -v\frac{dy}{dx}$ where $\frac{dy}{dt}$ is the particle velocity and v is the wave velocity.]

1.8 POLARISATION AND DIELECTRIC CONSTANT

Dielectric loss is a major problem involving heat generation and is dominating in high voltage application.

When an ac voltage is applied to a pure dielectric material like vacuum or purified gases, there is no consumption of energy. As a result, the charging current leads the applied voltage by an angle 90° as shown in Figure 1.10(*a*) and the polarisation of the dielectric is in phase with the voltage.

But, when an ac voltage is applied to commercial dielectrics, the charging current does not lead the applied voltage by exactly 90°; but, is always less than 90° as shown in Figure 1.10(*b*).

The complementary angle $\delta = 90 - \theta$ is called the dielectric loss angle. This angle is a measure of the power or heat dissipated in each cycle. In most of the dielectrics this angle δ is negligible.

NOTES

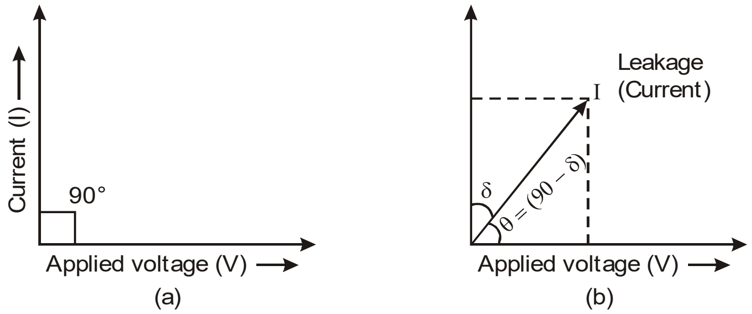


Fig. 1.10 *Dielectric Loss*

The dielectric power loss for a dielectric material used in a capacitor with capacitance C and applied voltage V is given by

$$P = VI\cos\theta$$

where V is the applied voltage in volts

I is the current through the capacitor in amp.

The value of I is given by the relation

$$I = \frac{V}{X_C}, \text{ where, } X_C \text{ is the capacitive reactance}$$

given by $$X_C = \frac{1}{2\pi fC}$$

$$\therefore \quad P = V\frac{V}{X_C}\cos(90^\circ - \delta) \qquad [\because \theta = 90^\circ - \delta]$$

$$= V^2\, 2\pi f C\, \sin\delta \qquad [\because \cos(90^\circ - \delta) = \sin\delta]$$

But, since δ is negligibly small in most of the dielectrics

$$\sin\delta = \tan\delta$$

$$\therefore \quad P = 2\pi V^2 f C\, \tan\delta$$

Here, tanδ is called the power factor. It is also referred to as tangent loss. When the factors like voltage, frequency and capacitance are constant, the dielectric loss is dependent only on δ. The dielectric loss should be low in a dielectric material.

Factors Affecting Dielectric Loss

The dielectric loss increases with:

1. High frequency of the applied voltage.
2. High applied voltage.
3. High temperature and humidity.

Dielectric breakdown

Whenever the voltage applied to a dielectric material exceeds a critical value, a large amount of current flows through it. As a result of this, the dielectric loses its insulating property. This phenomena is known as dielectric breakdown.

Thus, breakdown indicates the failure of the dielectric material.

The electric field at which this breakdown occurs is called the dielectric strength. Also,

$$\text{Dielectric strength} = \frac{\text{Breakdown voltage}}{\text{Thickness of the dielectric}}$$

It is expressed in kV/cm. Dielectric strength decreases with increase of temperature and humidity.

Important types of dielectric breakdown and their mechanism by which, the breakdown takes place are briefly explained below.

Important types of breakdown

1. Intrinsic breakdown.
2. Thermal breakdown.
3. Electrochemical breakdown.
4. Discharge breakdown.
5. Defect breakdown.

1. Intrinsic Breakdown

When the electric field applied to a dielectric material exceeds a critical value, there is an electric breakdown due to physical deterioration of the dielectric material. When the applied field is large, some of the electrons from the valence band cross over the conduction band giving rise to large conduction current. As a result of this, a large current flows through the dielectric and the subsequent breakdown is called as an intrinsic breakdown or zener breakdown.

Note:
- The liberation of electrons from the valence band due to large charge displacement by the higher electric field is called internal field emission of electrons.

The liberated electrons moving under high accelerating electric force collide with atoms or molecules of the dielectric and release more electrons by continuous breaking of covalent bonds. As a result of this, a large current flows through the dielectric and the subsequent breakdown is called as *avalanche breakdown.*

Characteristics or Properties

1. This can occur at any temperature.
2. This requires large electric field to occur.
3. Mostly this kind of breakdown occurs in thin samples only.
4. This does not depend on the electrode configuration and the shape of the material.

2. Thermal Breakdown

When there is excessive increase in the temperature of the dielectric a local melting occurs due to less heat dissipation than heat generated. Hence, mobility of charge carriers is increased, and enormous current flows through the material thus, leading to thermal breakdown.

Characteristics or Properties

1. This can occur only at high temperatures.
2. The breakdown time is of the order of few milli seconds.
3. Mostly this occur in lossy dielectrics.
4. The strength of the electric field to create dielectric breakdown depends upon the material size and shape.
5. Since dielectric loss is directly proportional to frequency, the electric field to create dielectric breakdown will be smaller for alternating fields and higher for (static) dc fields.

3. Electrochemical Breakdown

Dielectric breakdown due to the formation of electro chemical reaction or chemical reaction in a dielectric material is called electrochemical breakdown. This electrochemical breakdown is closely related to the thermal breakdown. An increase of temperature results in an increase of mobility of ions and also an increase in leakage current. Hence, electrochemical reaction takes place and thus, leading to dielectric breakdown.

A chemical reaction within the dielectric material can occur not only by the application of the electric field but also can occur by so many ways.

Characteristics or Properties

1. This type of breakdown is accelerated by atmospheric air. For example, rubber gets converted to rubber oxide in the ozone atmosphere with the formation of cracks on it. Since it is converted into oxide, its dielectric properties get degraded.
2. To avoid this type of breakdown foreign materials should not be mixed with pure insulating materials.
3. This type of breakdown is highly favoured at high temperatures; at which, the stability of chemical properties decreases.
4. This breakdown is very common in dielectric materials with permanent dipoles. The dipoles produce a large leakage current, and subsequently leading to this breakdown.
5. Electrochemical breakdown is accelerated by humidity.

4. Discharge Breakdown

Discharge breakdown occurs due gaseous discharge taking place in occluded gas bubbles. Since, the ionisation potential of gaseous atoms are smaller than the solid atoms of the dielectric material, the gaseous atoms ionise first and bombard the solid atoms of the dielectric causing electrical deterioration resulting in breakdown.

Characteristics or Properties

1. This type of breakdown is highly favoured where there are a large number of occluded gas bubbles.
2. This can occur even at low voltages.

5. Defect Breakdown

The presence of cracks or pores at the surface of the material leads to defect breakdown due to the collection of moisture and other impurities at these defect sites.

Characteristics or Properties

The life of the insulation of the dielectric material depends upon, the number of discharges taking place inside the material.

Properties of a good dielectric material

To avoid breakdown, the dielectric material should possess the following properties.

1. It should have high resistivity to reduce leakage current. (like sulphur).
2. It should have high dielectric strength. (like mica).
3. It should have high mechanical strength. (like steel).
4. It should have high fire resistance. (like silica).
5. It should have high chemical inertness. (like platinum) [i.e., it should be resistant to oils, liquids, gas, acids and alkalies].
6. It should have low thermal expansion. (like invar).
7. It should have high thermal conductivity. (like silver).
8. It should have low dielectric loss. (like vacuum).
9. It should have low water absorption quality. (like paraffin wax).
10. It should have high quality surface finish. (like ebonite).

Types of Dielectric Materials

Dielectric materials can be solids, liquids or gases. A high vacuum can also be used as a dielectric eventhough its relative dielectric constant is only unity.

Solid dielectrics are most commonly used in electrical engineering and are very good insulators.

Examples: Porcelain, glass, plastics, rubber, cotton, wood, mica etc.

Liquid dielectric materials are basically of three different types, which include (i) Mineral insulating oils, (ii) Synthetic insulating oils and (iii) Miscellaneous insulating oils.

The function of insulating liquids is to provide electrical insulation and to dissipate heat (cooling agent).

Examples: Transformer oil, cable oil, capacitor oil, vegetable oil, vaseline, silicon liquids. sovol, soutol, etc.

Gaseous dielectric material are used both as an insulator and as a cooling agent.

Examples: Air, hydrogen, nitrogen, helium, sulphurdioxide, propane, methane, sulphur hexafloride, ethane, etc.

Specific Applications of Dielectrics

The dielectric materials based on their nature of state has a variety of applications in electrical engineering field.

The applications of different dielectric materials in capacitors and transformers with their functions are listed below.

Capacitors

The major role of dielectric materials in capacitor is to store electrical energy. Based on the nature of the dielectric material used, the capacitors fall into different groups.

1. Capacitors with vacuum, air or other gases as dielectric are used in radio frequency and low frequency measuring circuits.
2. Capacitors with mineral oil as dielectric are used in high voltage applications, where a large value of capacitance is required.
3. Capacitors with a combination of solid and liquid dielectrics are used in the applications where precision is not so important but a high value capacitance is required.

   In electric power distribution system for power factor correction, these type of capacitors are used. ***Examples:*** Glass, mica, oil impregnated paper dielectric, mineral oil, castor oil etc.
4. Capacitors with only solid dielectrics like sodium, glass, titanium oxide etc, are used in laboratory as standard capacitor.

Transformer

In transformers the dielectrics are used as an insulator as well as a cooling agent.

The applications of different types of solid, liquid and gaseous dielectric material with their function in transformer are listed below.

1. Solid Dielectric Materials

1. Fibrous (class A) materials are used in air cooled and oil cooled transformers.
2. Cotton tape is used for insulating the conductors of oil cooled transformer.
3. High quality synthetic resin bonded paper in the form of cylinders is used as an insulator between core and coils and also between primary and secondary windings.
4. Press board or press paper is used as a filling, and as a packing material between coil.

2. Liquid Dielectric Materials

1. *Transformer oil* - It is a class of mineral insulating oil and is used as a coolant. It also maintains the insulation of the winding.
2. Fluorocarbon liquids are used in large transformers to give high heat transfer rates together with high dielectric strength.

3. Gaseous Dielectric Materials

(*i*) The usage of nitrogen in transformer prevents oxidation and reduces the rate of deterioration.

(*ii*) Sulphur hexafloride dielectric, is an electronegative gas used in transformers. It is non- toxic, non-inflammable and chemically inert.

1.8.1 Polarizability: Electronic, Ionic, Atomic and Orientational

There are four different types of mechanisms through which electrical polarisation can occur in a dielectric material when they are subjected to an external electric field.

They are:

1. Electronic polarisation.
2. Ionic polarisation.
3. Orientation polarisation.
4. Space charge or Interfacial polarisation.
5. Atomic Polarisation

1. Electronic Polarisation

The electronic polarisation occurs, due to the displacement of the positively charged nucleus and the negatively charged electron cloud in opposite directions within a dielectric material upon applying an external electric field E.

Thus, the separation created between the charges induces a dipole. This process occurs throughout the material and the material as a whole will be polarised. Electronic polarisation is more in liquid and solid dielectrics than in gases.

Therefore, the induced dipole moment = $\mu = \alpha_e E$

where α_e is electronic polarisability.

The electronic polarisability for a rare gas atom is given by

$$\alpha_e = \frac{\varepsilon_o(\varepsilon_r - 1)}{N}$$ where N is the number of atoms per unit volume.

Expression for Electronic Polarisability α_e

Let us consider one of the constituent atom of a dielectric material in the absence of an electric field E. Let the radius of the atom be R and its atomic number be Z as shown in Figure 1.11. Here, the nucleus of charge Ze is surrounded by an electronic cloud of charge –Ze. In the atom, the negative charge distribution due to its electron is spherically symmetric.

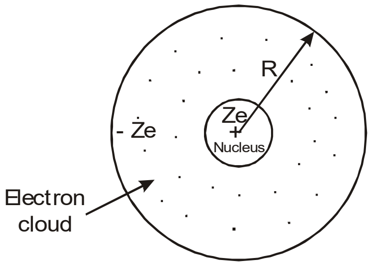


Fig. 1.11 *Atom of a Dielectric Material in the Absence of Electric Field*

Therefore, the charge density for electron cloud is given by

$$\rho = \frac{-Ze}{\frac{4}{3}\pi R^3} = \frac{-3}{4}\left(\frac{Ze}{\pi R^3}\right) \qquad ...(1.24)$$

But, when an electric field is applied, the nucleus and the electron cloud experience a Lorentz force of magnitude ZeE in opposite directions. Hence, the nucleus and the electron cloud are pulled by a distance.

Since, the nucleus is much heavier than the electron cloud it is assumed that only the electron cloud is displaced upon applying an electric field. Let the electron cloud displacement be *x* with respect to the centre of the nucleus.

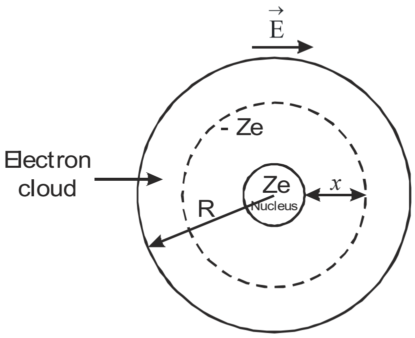


Fig. 1.12 *Atom of a Dielectric Material in the Presence of Electric Field*

Hence, the Lorentz force acting over the electron cloud is – ZeE ...(1.25)

But, according to Gauss theorem a coulomb attractive force is said to act over the nucleus due to the electron cloud in a sphere of radius *x* and this force tends to oppose the displacement.

Thus, the Coulomb force = $\quad Ze \times E$ ...(1.26)

Based on Coulomb's theorem

$$E = \frac{\text{Total charge enclosed in a sphere of radius } x \ (q)}{4\pi\varepsilon_o x^2} \quad ...(1.27)$$

Note: • **Coulomb's Theorem Statement:** The electric field at any point in a charged conductor is $1/\varepsilon_o$ times the surface charge density, i.e., charge per unit area.

But, the total charge enclosed in a sphere of radius *x* is $q = \rho \times \frac{4}{3}\pi x^3$ ...(1.28)

where ρ is negative charge density and $\frac{4}{3}\pi x^3$ is volume of the sphere of radius *x*.

Substituting for ρ from equation (1.24) we get,

$$q = \frac{-3}{4}\left(\frac{Ze}{\pi R^3}\right) \times \frac{4}{3}\pi x^3$$

or $$q = \frac{-Zex^3}{R^3} \quad ...(1.29)$$

Substituting for q in equation (1.29) we get, $E = \frac{-Zex^3}{R^3} \times \frac{1}{4\pi\varepsilon_o x^2}$ ...(1.30)

Hence, equation (1.28) can be given as (substituting for E from equation (1.30))

$$\text{Coulomb force} = Ze \times \frac{-Zex^3}{R^3} \times \frac{1}{4\pi\varepsilon_o x^2} = \frac{-Z^2e^2x}{4\pi\varepsilon_o R^3} \qquad ...(1.31)$$

NOTES

These two forces, i.e., the Lorentz force and the coulomb force are equal in magnitude but opposite in direction. As a result, a equilibrium is reached. Hence, at equilibrium

$$\text{Lorentz force} = \text{Coulomb force}$$

$$-ZeE = \frac{-Z^2e^2x}{4\pi\varepsilon_o R^3} \qquad ...(1.32)$$

or
$$E = \frac{Zex}{4\pi\varepsilon_o R^3} \qquad ...(1.33)$$

Hence,
$$x = \frac{4\pi\varepsilon_o R^3}{Ze} E \qquad ...(1.34)$$

Thus, the displacement of the electron cloud is proportional to the applied field E. Due to this displacement the atom acts as a dipole.

Therefore, the induced dipolement

$$\mu = Ze \times x$$

$$= (Ze)\left(\frac{4\pi\varepsilon_o R^3}{Ze} E\right)$$ (Substituting for x from equation (1.32))

or
$$\mu = 4\pi\varepsilon_o R^3\ E \qquad ...(1.35)$$

But,
$$\mu = \alpha_e E \qquad ...(1.36)$$

Comparing equation (8.12) and (8.13), we have

$$\alpha_e = 4\pi\varepsilon_o R^3 \qquad ...(1.37)$$

Thus, the electronic polarisability is proportional to the volume of the atom and is independent of temperature.

The polarisation vector P = Nμ

$$\therefore \quad P = N\ \alpha_e\ E \qquad ...(1.38)$$

But, we know that
$$P = \varepsilon_o E\ (\varepsilon_r - 1) \qquad ...(1.39)$$

∴ Equating equations (8.15) and (8.16), we get

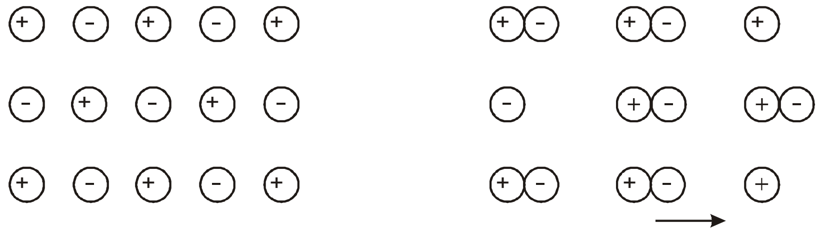
$$N\ \alpha_e\ E = \varepsilon_o E\ (\varepsilon_r - 1)$$

or
$$\alpha_e = \frac{\varepsilon_o(\varepsilon_r - 1)}{N} \qquad ...(1.40)$$

2. Ionic Polarisation

Ionic polarisation occur only in ionic solids such as NaCl which possess ionic bonds. It does not occur in covalent crystals such as diamond, silicon and germanium.

When ionic solids are subjected to an external electric field, the adjacent ions of opposite sign undergo displacement as shown in Figure 1.13. The displacement may cause either an increase or decrease in the distance of separation between the atoms depending upon the location of the ion pair in the lattice.



$E = 0$
Position of ions in the absence of field

$E \neq 0$
Ion displacement due to the applied field

Fig. 1.13 *Ionic Polarisation*

Expression for Ionic Polarisability a_i

Let an electric field E is applied to an ionic solid consisting of one cation and one anion per unit cell. This applied field causes the positive ions and negative ions to get displaced through a distance x_1 and x_2 respectively from their equilibrium position there by inducing a dipolemoment. Thus, the resultant dipolemoment per unit cell is

$$\mu = e\,(x_1 + x_2) \qquad \text{...(1.41)}$$

Due to the application of electric field a restoring force is said to act over the cation and anion.

Thus,

Restoring force $$F = \beta_1 x_1 = \beta_2 x_2 \qquad \text{...(1.42)}$$

Hence, $$x_1 = \frac{F}{\beta_1} \text{ and } x_2 = \frac{F}{\beta_2} \qquad \text{...(1.43)}$$

where β_1 and β_2 are restoring force constants of cation and anion. This restoring force constants depends upon the mass of the ion and angular frequency of the molecule in which the ions are present.

Thus, $$x_1 = \frac{eE}{m\omega_o^2} \quad \text{and} \quad x_2 = \frac{eE}{M\omega_o^2} \qquad \text{...(1.44)}$$

where m is the mass of cation and M the mass of anion.

Substituting equation (1.44) in (1.41), we get

$$\mu = e\left(\frac{eE}{m\omega_o^2} + \frac{eE}{M\omega_o^2}\right)$$

or $$\mu = \frac{e^2E}{\omega_o^2}\left(\frac{1}{m} + \frac{1}{M}\right) \qquad \text{...(1.45)}$$

But, $$\mu = \alpha_i\, E \qquad \text{...(1.46)}$$

$\therefore$ Comparing equations (1.45) and (1.46) we get,

$$\alpha_i\, E = \frac{e^2E}{\omega_o^2}\left(\frac{1}{m} + \frac{1}{M}\right)$$

or $$\alpha_i = \frac{e^2}{\omega_o^{\ 2}}\left(\frac{1}{m}+\frac{1}{M}\right). \qquad ...(1.47)$$

Thus, ionic polarisability is inversely propotional to the square of the natural frequency of the ionic molecule and directly proportional to its reduced mass.

The ionic polarisability is also independent of temperature.

3. Orientation Polarisation (Dipolar Polarisation)

Orientation polarisation occurs in dielectric materials which possess molecules with permanent dipole moment (i.e., in polar molecules).

In the absence of an external electric field, because of random orientation of the dipoles due to thermal agitation the material has net zero dipole moment. But, under the influence of an external applied electric field, each of the dipoles undergo rotation so as to reorient along the direction of the field as shown in figure 1.14. Thus, the material itself develops electrical polarisation.

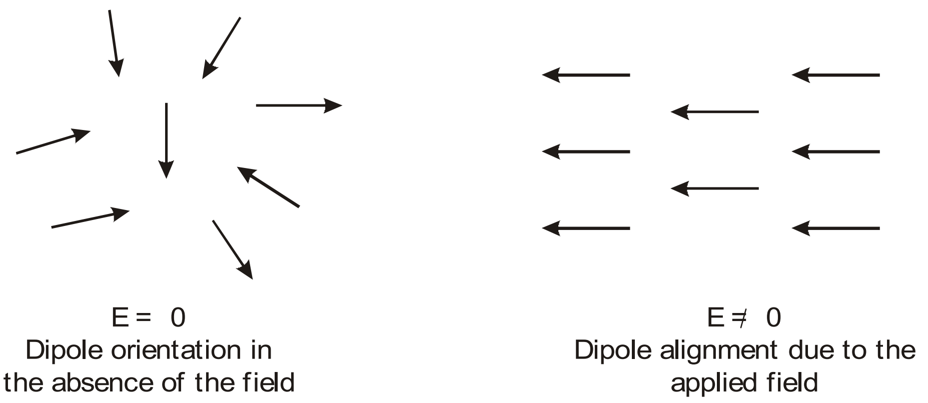


Fig. 1.14 Orientation Polarisation

This polarisation occur in ferroelectric materials such as BaTi O_3 and $PbTiO_3$ and produces a very high dielectric constant in these materials.

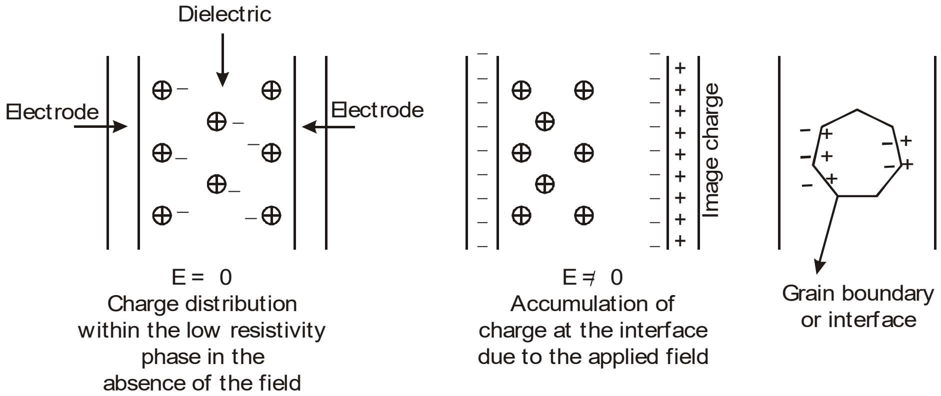
In the case of polar dielectrics, the orientational polarisability α_o is given by

$$\alpha_o = \frac{\mu^2}{3k_BT}$$

where k_B is the Boltzmann constant, T is the temperature and μ is the permanent dipole moment. Thus, the orientational polarisability is inversely proportional to absolute temperature.

4. Space Charge (Interfacial Polarisation)

The space charge polarisation occur in multiphase dielectric materials. When such materials are subjected to an external electric field, especially at high temperature the charges get accumulated at the interface or at the electrodes because of sudden change in conductivity as shown in Figure 1.15.



E = 0
Charge distribution within the low resistivity phase in the absence of the field

E ≠ 0
Accumulation of charge at the interface due to the applied field

Fig. 1.15 Space Charge Polarisation

Since, the accumulation of charges with opposite polarity occurs at opposite parts in the low resistivity phase, it leads to the development of dipole moment within the low resistivity.

Grain boundaries often lead to interfacial polarisation as they can trap charges migrating under the influence of an applied field as shown in figure 1.15. This type of polarisation occur in some materials like $LiTaO_3$, $LiNbO_3$ and in certain glasses containing Li_2O or Na_2O. This polarisation is not an important factor in most common dielectrics used in capacitor and other applications.

Total Polarisability α_T

The total polarisability α_T of a material is thus given by the sum of the electronic, ionic and orientational polarisabilities.

$$\alpha_T = \alpha_e + \alpha_i + \alpha_o$$

Since, the space charge polarisability is very small when compared to other types of polarisabilities it is neglected.

Thus, the total polarisability of a material is given by

$$\alpha_T = 4\pi\varepsilon_o R^3 + \frac{e^2}{\omega_o^2}\left(\frac{1}{m}+\frac{1}{M}\right)+\frac{\mu^2}{3k_B T}$$

[Substituting for α_e, α_i and α_o]

Hence, the total polarisation P is given by

$$P = N\,\alpha_T\,E$$

or

$$P = NE\left[4\pi\varepsilon_o R^3 + \frac{e^2}{\omega_o^2}\left(\frac{1}{m}+\frac{1}{M}\right)+\frac{\mu^2}{3k_B T}\right]$$

The above equation is known as Langevin-Debye equation.

5. Atomic Polarisation

Atomic polarisation arises because there is a relative change in the mean positions of the atomic nuclei within the molecules.

Example 1.1

Copper is a Fcc crystal with a lattice constant 3.6 Å, and atomic number 29. If the average displacement of the electrons relative to the nucleus is 1×10^{-18} m on applying an electric field calculate the electronic polarisation.

Solution:

Given, $x = 1 \times 10^{-18}$ m; $a = 3.61 \times 10^{-10}$ m; Z = 29; P = ?

For Fcc crystal, number of atoms per unit cell is 4.

Number of electrons per m^3 =

$$\frac{(\text{Number of atoms / Unit cell})(\text{Number of electrons / Atom})}{a^3}$$

$$= \frac{4 \times 29}{(3.61 \times 10^{-10})^3} = \mathbf{2.465 \times 10^{30}\ electrons/m^3.}$$

Since, the electron density in copper is equal to the number of atoms per unit volume N = 2.465×10^{30} atoms/m^3.

$$\therefore \quad P = N\mu$$

$$= N \times e \times x \qquad [\because \mu = ex)$$

$$= 2.465 \times 10^{30} \times 1.6 \times 10^{-19} \times 1 \times 10^{-18}$$

$$= 3.944 \times 10^{-7}\ C/m^2$$

$$\therefore \ \mathbf{P = 3.944 \times 10^{-7}\ C/m^2.}$$

Example 1.2

Silicon has a relative permittivity of 11.7 at frequencies high enough to ignore all but its electrical (optical) polarisability. It contains 4.82×10^{28} atoms/m^3. Calculate the dipole moment of each atom in a field of 10^4 Vm^{-1}, and also find the effective distance at this field strength between the center of the electron cloud in each atom and the nucleus.

Solution:

Given, $\varepsilon_r = 11.7$; N = 4.82×10^{28} atoms/m^3; μ = ?; x = ?

Formula $$\alpha_e = \frac{\varepsilon_o(\varepsilon_r - 1)}{N}$$

$$\alpha_e = \frac{8.85 \times 10^{-12}[11.7 - 1]}{4.82 \times 10^{28}} \qquad [\because \varepsilon_o = 8.85 \times 10^{-12} Fm^{-1}]$$

$$\mathbf{\alpha_e = 1.9646 \times 10^{-39}\ Fm^2.}$$

$$\because \quad \mu = \alpha_e E$$

$$= 1.9646 \times 10^{-39} \times 10^4$$

$$= 1.9646 \times 10^{-35}\ Cm^{-3}$$

$$\therefore \quad \mathbf{\mu = 1.9646 \times 10^{-35}\ Cm^{-3}.}$$

Also,

$$\mu = Z\,e\,x$$

$$\therefore \qquad x = \frac{\mu}{Ze} \qquad \text{(For silicon Z = 14)}$$

$$x = \frac{1.9646 \times 10^{-35}}{14 \times 1.6 \times 10^{-19}}$$

$$\therefore \qquad \boldsymbol{x = 8.77 \times 10^{-18}\ \text{m.}}$$

or $$\boldsymbol{x = 8.77 \times 10^{-8}\ \text{Å.}}$$

NOTES

Example 1.3

Calculate the polarisability and relative permittivity in hydrogen gas with a density of 9.8×10^{26} atoms/m^3. Given the radius of the hydrogen atom to be 0.50 Å.

Solution:

Given, $N = 9.8 \times 10^{26}$ atoms/m^3; $R = 0.50 \times 10^{-10}$ m; $\alpha_e = ?$ and $\varepsilon_r = ?$

We know $$\alpha_e = 4\pi\varepsilon_o R^3$$

$$= 4 \times 3.14 \times 8.85 \times 10^{-12} \times (0.50 \times 10^{-10})^3$$

$$\therefore \qquad \boldsymbol{\alpha_e = 1.389 \times 10^{-41}\ \text{Fm}^2.}$$

To find ε_r we know that,

$$\alpha_e = \frac{\varepsilon_o \times (\varepsilon_r - 1)}{N}$$

or $$N\alpha_e = \varepsilon_o \times (\varepsilon_r - 1)$$

$$\frac{N\alpha_e}{\varepsilon_o} = \varepsilon_r - 1$$

$$\therefore \qquad \varepsilon_r = \frac{N\alpha_e}{\varepsilon_o} + 1$$

$$\varepsilon_r = \frac{9.8 \times 10^{26} \times 1.389 \times 10^{-41}}{8.85 \times 10^{-12}} + 1$$

$$\varepsilon_r = 1.5381 \times 10^{-3} + 1$$

$$\therefore \qquad \boldsymbol{\varepsilon_r = 1.0015.}$$

Example 1.4

The electronic polarisability of Argon atom is 1.75×10^{-40} Fm^2. What is the static dielectric constant of solid Argon, if its density is 1.8×10^3 kg/m^3 (given atomic weight of Ar = 39.95 and $N_A = 6.025 \times 10^{26}$/k mole).

Solution:

Given, $\alpha_e = 1.75 \times 10^{-40}$ Fm^2; $\rho = 1.8 \times 10^3$ kgm^{-3}; At. wt = 39.95; $\varepsilon_r = ?$

To find the number of atoms/unit volume

$$N = \frac{N_A\rho}{\text{At.wt}} = \frac{6.025 \times 10^{26} \times 1.8 \times 10^3}{39.95}$$

$$\therefore \qquad \boldsymbol{N = 2.7146 \times 10^{28}\ \text{atoms/m}^3.}$$

NOTES

We know that, $$\varepsilon_r = \frac{N\alpha_e}{\varepsilon_o} + 1$$

$$\varepsilon_r = \frac{2.7146 \times 10^{28} \times 1.75 \times 10^{-40}}{8.85 \times 10^{-12}} + 1$$

$$\varepsilon_r = 0.53679 + 1$$

$$\therefore \quad \boldsymbol{\varepsilon_r = 1.53679.}$$

Piezoelectricity

Piezoelectricity is the electric charge that accumulates in certain solid materials (such as, crystals, certain ceramics, and biological matter, such as bone, DNA and various proteins) in response to applied mechanical stress. The word piezoelectricity means electricity resulting from pressure and latent heat.

The piezoelectric effect results from the linear electromechanical interaction between the mechanical and electrical states in crystalline materials with no inversion symmetry. The piezoelectric effect is a reversible process: materials exhibiting the piezoelectric effect (the internal generation of electrical charge resulting from an applied mechanical force) also exhibit the reverse piezoelectric effect, the internal generation of a mechanical strain resulting from an applied electrical field. For example, lead zirconate titanate crystals will generate measurable piezoelectricity when their static structure is deformed by about 0.1% of the original dimension. Conversely, those same crystals will change about 0.1% of their static dimension when an external electric field is applied to the material. The inverse piezoelectric effect is used in the production of ultrasonic sound waves.

French physicists Jacques and Pierre Curie discovered piezoelectricity in 1880, and it has subsequently been exploited in a number of useful applications, such as the production and detection of sound, piezoelectric inkjet printing, generation of high voltages, clock generator in electronics, microbalances, to drive an ultrasonic nozzle, and ultrafine focusing of optical assemblies.

The nature of the piezoelectric effect is closely related to the occurrence of electric dipole moments in solids. The latter may either be induced for ions on crystal lattice sites with asymmetric charge surroundings (as in $BaTiO_3$ and PZTs) or may directly be carried by molecular groups (as in cane sugar). The dipole density or polarization (dimensionality [$C\bullet m/m^3$]) may easily be calculated for crystals by summing up the dipole moments per volume of the crystallographic unit cell. As every dipole is a vector, the dipole density **P** is a vector field. Dipoles near each other tend to be aligned in regions called Weiss domains. The domains are usually randomly oriented, but can be aligned using the process of poling (not the same as magnetic poling), a process by which a strong electric field is applied across the material, usually at elevated temperatures. Not all piezoelectric materials can be poled.

Of decisive importance for the piezoelectric effect is the change of polarization **P** when applying a mechanical stress. This might either be caused by a reconfiguration of the dipole-inducing surrounding or by re-orientation of molecular dipole moments under the influence of the external stress. Piezoelectricity may then manifest in a variation of the polarization strength, its direction or both, with the details depending on the following:

1. Orientation of **P** within the Crystal
2. Crystal Symmetry
3. Applied Mechanical Stress

The change in **P** appears as a variation of surface charge density upon the crystal faces, i.e., as a variation of the electric field extending between the faces caused by a change in dipole density in the bulk. For example, a 1 cm^3 cube of quartz with 2 kN (500 lbf) of correctly applied force can produce a voltage of 12500 V.

Piezoelectric materials also show the opposite effect, called the converse piezoelectric effect, where the application of an electrical field creates mechanical deformation in the crystal.

Pyro and Ferro Electric Properties of Crystals

Ferroelectricity refers to the creation of large induced dipole moment in a weak electric field as well as the existence of electric polarization even in the absence of an applied electric field.

Crystalline dielectric materials which possess a permanent electric polarization are called ferroelectric materials. Thus it is clear that, ferroelectric materials have electric dipole moment even in the absence of any field.

Examples: Barium Titanate ($BaTiO_3$), Potassium Dihydrogen Phosphate (KDP) (KH_2PO_4), Ammonium Dihydrogen Phosphate (ADP) ($NH_4H_2PO_4$).

Under the action of an external electric field, due to polarization of the material, an internal field gets created. The internal field increases and stabilizes the polarization. As a result, a part of polarization exists even if the field is removed.

Note:

- Ferroelectric, piezoelectric and pyroelectric materials are active dielectrics. i.e., these materials can be adapted to generate, modulate, amplify, convert electric signals and to store electrical energy when subjected to an external electric field. Only non-centrosymmetric crystals exhibit piezoelectic, pyroelectric and ferroelectric behaviour.
- **Piezoelectricity** : This term refers to the creation of electric potential by mechanical stress.
- **Pyroelectricity** : This term refers to the creation of electric potential by thermal stress.

Properties of Ferroelectric Materials

1. The ferroelectric materials exhibit domain structures similar to ferromagnetic materials.
2. These materials possess spontaneous polarization. But, the polarization P is not a linear function of applied field E . Hence these materials are known as non-linear dielectrics.
3 These materials exhibit ferroelectricity only when $T \leq T_C$. T_C is called the ferroelectric Curie temperature or transition temperature.
4. Ferroelecticity usually disappears above the transition temperature and the materials are converted to paraelectric materials. This shows that, above T_C the spontaneous polarization is destroyed by thermal disorder.

5. The condition for spontaneous polarization is given by $\frac{N\alpha_e}{3\varepsilon_0} = 1$.
6. Ferroelectric materials exhibit piezoelectricity and pyroelectricity.

NOTES

Hysteresis

In ferroelectric materials, polarization P is not a linear function of applied electric field E. This is because, the relationship between P and E is complex in nature. In view of this, ferroelectrics are known as non-linear dielectrics. Such materials exhibit hysteresis curve similar to that of ferromagnetic materials. The hysteresis curve exhibited by a ferroelectric material is shown in Figure 1.16.

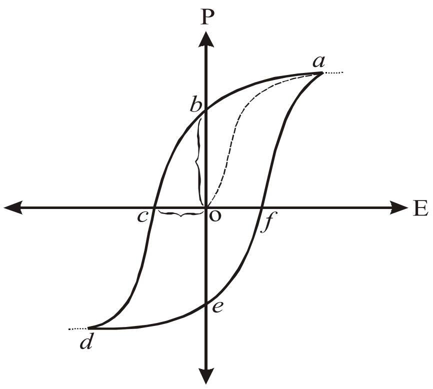


Fig. 1.16 *Ferroelectric hysteresis*

Ferroelectric materials possess spontaneous polarization. Ferroelectricity is a result of dielectric hysteresis. *The lagging of polarization P behind the applied electric field E is called dielectric hysteresis.*

When an increasing electric field is applied to a ferroelectric material the relationship between P and E is shown by the line **oa**. As the value of E is increased continuously, the polarization attains a maximum and saturated value **a** as shown in Figure 1.16.

If now the applied electric field is reduced, the polarization also decreases from the point **a** , but fails to retrace the same path which it had while E was increasing.Thus the new path is **ab**. *But when E becomes zero a small amount of polarization exists in the material. This is known as residual polarization shown by the line* ob. Now the ferroelectric material is said to be spontaneously polarized. *In order to reduce the value of polarisation to zero, a reversing electric field* ***oc*** *should be applied. This field is known as coercive field.*

Further increase in E causes the specimen to get polarised in the opposite direction. This makes P also to increase in the opposite direction and reaches a saturation value again at **d**. Now also, when the field is decreased the curve traces the path **de** instead of **dc**.

Again the specimen gets completely depolarised at **f** when the direction of E is reversed and increased along OE. The curve traces the path up as E is increased further.

Thus, the variation of P *with respect to* E *traced along the closed path* **abcdefa** *in one full cycle of polarization and depolarization is called the hysteresis loop or the hysteresis curve.*

The area enclosed by the curve gives the energy loss per unit volume of the material per cycle.

Note:
- In ordinary dielectrics, the polarization P varies linearly with applied field E ($P = \chi \varepsilon_0 E$). Therefore, the ordinary dielectrics are often known as linear dielectrics.

NOTES

Applications

1. Ferroelectric semiconductors such as $BaTiO_3$ - $SrTiO_3$, $BaTiO_3$ - $PbTiO_3$, $SrTiO_3$ - $PbTiO_3$ are used to make posistors. Posistors are the devices, which are used to measure and control temperature like thermistors.
2. Ferroelectric ceramics are used in the manufacture of capacitors to store electrical energy.
3. Piezoelectric materials are used to make pressure transducers, microphones and ultrasonic transducers.
4. Pyroelectric materials are used to make high sensitive infrared detectors.
5. Electrets (a type of ferroelectric material) are used in capacitors, microphones and gas filters to capture submicron particles by electrostatic attraction.
6. Electrets are also used as bandages over the fractured bones to speed up the healing process.
7. In optical communication, the ferroelectric crystals are used for optical modulation.

1.8.2 Dielectric Loss

Definition - 1 : It is the loss of energy in the form of heat by a dielectric material under the action of an alternating voltage.

Definition - 2 : If a dielectric material is subjected to an alternating voltage, the electrical energy is absorbed by the material and is dissipated in the form of heat. This dissipation of heat energy is called as dielectric loss.

Note: Whenever a dielectric material is subjected to an alternating voltage the molecules will be in a state of electrostatic stress due to polarisation. For each polarity reversal of the applied voltage the stress is also reversed; and this inturn makes the dipoles to switch their orientation. Inorder to do so, the dipoles are required to overcome a sort of internal friction which involves a loss of energy. Thus, the energy loss due to friction is always dissipated as heat by the dielectric material to the surroundings. This is termed as dielectric loss.

Dielectric loss is a major problem involving heat generation and is dominating in high voltage application.

When an ac voltage is applied to a pure dielectric material like vacuum or purified gases, there is no consumption of energy. As a result, the charging current leads the applied voltage by an angle 90° as shown in Figure 1.17(*a*) and the polarisation of the dielectric is in phase with the voltage.

But, when an ac voltage is applied to commercial dielectrics, the charging current does not lead the applied voltage by exactly 90°; but, is always less than 90° as shown in Figure 1.17(*b*).

The complementary angle $\delta = 90 - \theta$ is called the dielectric loss angle. This angle is a measure of the power or heat dissipated in each cycle. In most of the dielectrics this angle δ is negligible.

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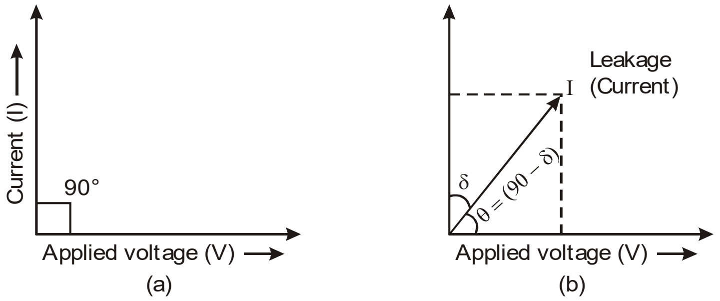

Fig. 1.17 *Dielectric Loss*

The dielectric power loss for a dielectric material used in a capacitor with capacitance C and applied voltage V is given by

$$P = VI \cos\theta$$

where V is the applied voltage in volts

I is the current through the capacitor in amp.

The value of I is given by the relation

$$I = \frac{V}{X_C}, \text{ where, } X_C \text{ is the capacitive reactance}$$

given by $$X_C = \frac{1}{2\pi fC}$$

$$\therefore \quad P = V\frac{V}{X_C}\cos(90^\circ - \delta) \qquad [\because\ \theta = 90^\circ - \delta]$$

$$= V^2\ 2\pi f C\ \ \sin\delta \qquad [\because \cos(90^\circ - \delta) = \sin\ \delta]$$

But, since δ is negligibly small in most of the dielectrics

$$\sin\delta = \tan\delta$$

$$\therefore \quad P = 2\pi V^2 f C\ \ \tan\delta$$

Here, $\tan\delta$ is called the power factor. It is also referred to as tangent loss. When the factors like voltage, frequency and capacitance are constant, the dielectric loss is dependent only on δ. The dielectric loss should be low in a dielectric material.

Factors Affecting Dielectric Loss

The dielectric loss increases with:

1. High frequency of the applied voltage.
2. High applied voltage.
3. High temperature and humidity.

1.8.3 Relaxation Time

Dielectric relaxation is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarisation with respect to a changing electric field in a dielectric medium (e.g., inside capacitors or between two large conducting surfaces). Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (e.g., in inductor or transformer cores). Relaxation in general is a delay or lag in the response of a linear system, and therefore dielectric relaxation is measured relative to the expected linear steady state (equilibrium) dielectric values.

In physics, dielectric relaxation refers to the relaxation response of a dielectric medium to an external, oscillating electric field. This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation.

Debye relaxation

Debye relaxation is the dielectric relaxation response of an ideal, non-interacting population of dipoles to an alternating external electric field. It is usually expressed in the complex permittivity ε of a medium as a function of the field's angular frequency ω:

$$\hat{\varepsilon}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + i\omega\tau}$$

where ε_{∞} is the permittivity at the high frequency limit, $\Delta\varepsilon = \varepsilon_s - \varepsilon_{\infty}$ where ε_s is the static, low frequency permittivity, and τ is the characteristic relaxation time of the medium. Separating into the real part ε' and the imaginary part ε'' of the complex dielectric permittivity yields:

This relaxation model was introduced by and named after the physicist Peter Debye (1913). It is characteristic for dynamic polarisation with only one relaxation time.

1.8.4 Microscopic and Macroscopic Description of Dielectric Behaviour

A dielectric substance is a material which does not conduct electricity i.e., dielectrics are insulators. In such substance the electrons are firmly bound to the atoms of the material. These electrons can, therefore, move through very small distances of the order of atomic dimensions. There are practically no free electrons in dielectrics. Familiar examples are glass, mica, ebonite, paraffine wax and air.

Importance: The importance of dielectric, lies in the fact that dielectric materials are very good insulators. Electric current flows through high tension wires because air (as dielectric) is very good insulator. High voltage transformers are immersed in oil, a high insulator dielectric, to avoid leakage. Porcelain clamps are used at the top of electric poles to insulate the poles from earth. Dielectrics like rubber, plastic etc. are used as cover (sheaths) for underground and overhead cables. Dielectric like mica and paper are used in high quality capacitors employed in radio and television transmission and reception circuits, and other electronic devices.

Non-Polar and Polar Molecules

According to the quantum theory neutral atoms in their ground state consist of a central positively charged nucleus surrounded by a spherically symmetric cloud of equal negative charge of smoothly varying charge density. The radius of this electron cloud constitutes the atomic radius and is of the order of 10^{-10} m. Thus for an atom, in its ground state, the centre of gravity of its negative charge lies exactly at its nucleus which is taken to be a point positive charge. The dipole moment of an atom is, therefore, zero.

For a molecule the positive charge is supposed to be concentrated, at the nuclear points and the negative charge forming a cloud of smoothly varying density around the constituent nuclei. Depending upon the shape of this cloud and variation of charge density inside it, the molecule of dielectric can be classified into two types (i) non-polar molecules and (ii) polar molecules.

(i) **Non-polar molecules:** The molecules in which the centre of gravity of positive charges exactly coincides with that negative charges and the net dipole moment is zero are called non-polar molecules.

(ii) **Polar molecules:** The molecule in which the centre of gravity of positive charges does not coincide with that of the negative charges are known as polar molecules.

Physical Meaning of Polarisation of a Dielectric

As a result of alignment, the dielectric material when placed in an electric field acquires a net dipole moment. This dipole moment being due to the applied electric field is known as induced dipole moment.

When the molecules of a dielectric are aligned completely or partially in the direction of the electric field, the dielectric is said to be polarised. A polarised dielectric is shown in Fig. 1.18.

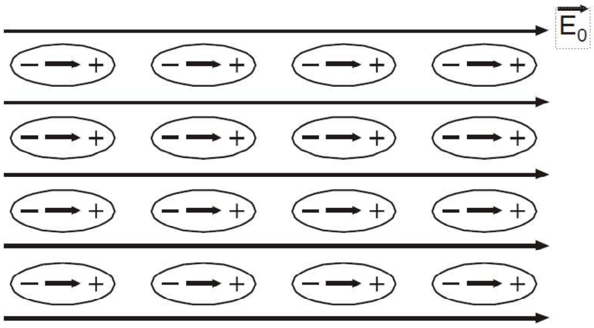

Fig. 1.18

Effect of Electric Field on Non-Polar Dielectric

Fig. 1.19 (a) shows a non-polar molecule. When such a non-polar molecule is placed in an electric field, the centre of the positive charge moves in the direction of the field and the centre of the negative charge in an opposite direction Fig. 1.19 (b). This separation of positive and negative charges continues till the force on either of them due to the external field is completely balanced by the internal force arising due to their relative displacements. The molecule develops a dipole moment known as induced dipole moment. Such a molecule is said to be polarised as shown in Fig. 1.19 (c).

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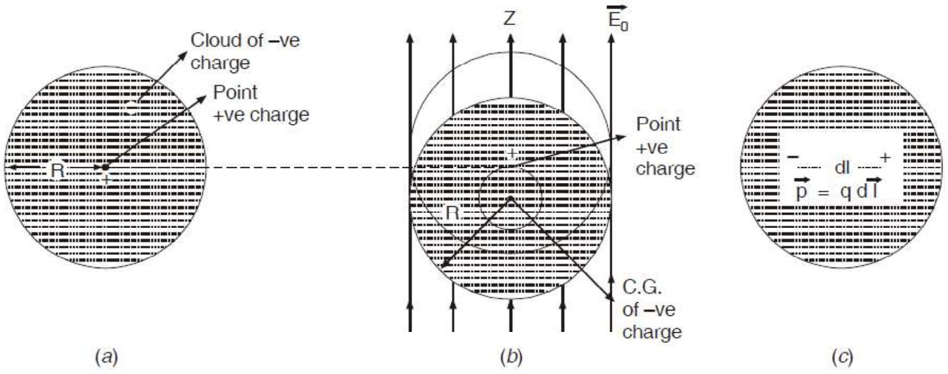


Fig. 1.19 *Induced Dipole Moment*

The induced dipole moment *i.e.* polarisation in non-polar molecules lasts only for the time the electric field is applied. It disappears as soon as the electric field is removed.

Atomic dipole moment

If dl is the separation between the centres of positive and negative charges and q is the positive or negative charge on the atom, then

Atomic dipole moment $\vec{p} = q d\vec{l}$ ...(1.48)

Thus atomic dipole moment is the product of the positive or negative charge on the atom and the distance between the centres of the positive and the negative charges in the direction of the applied electric field.

Atomic polarisability

The net induced electric dipole moment $\vec{p}$ for an atom is proportional to the strength of the applied electric field $\vec{E}_0$ and its direction is also parallel to that of $\vec{E}_0$. Thus, $\vec{p} \propto \vec{E}_0$

$$\therefore \quad \vec{p} = \alpha \vec{E}_0$$

$$\text{or} \quad \alpha = \frac{\vec{p}}{\vec{E}_0} \qquad ...(1.49)$$

α is the constant of proportionality and is known as the atomic polarisability.

Hence atomic polarisability is defined as the electric dipole moment induced in the atom by an electric field of unit strength.

Induced dipole moment ($\vec{p}$):

To calculate the value of induced atomic dipole moment, consider an atom of atomic number Z, then positive charge on the nucleus = + Ze.

As the atom is on whole neutral, the charge carried by all the electrons = –Ze.

It is assumed that the positive charge lies exactly at the centre of sphere of radius R and the negative charge is distributed uniformly in the form of spherical cloud so the centre of gravity of the negative charge also lies exactly at the centre of the sphere and coicides with the centre of gravity of the positive charge as shown in Fig. 1.19 (a). In such a case the atom has zero dipole moment.

An electric field $\vec{E}_0$ is now applied in the Z-direction. The positive charge being firmly fixed in the nucleus is supposed to continue in its original position. On the other hand it is assumed that the negatively charged spherical cloud is not distorted in shape by the external electric field but is only bodily displaced in the negative Z-direction as shown in Fig. 1.19 (b).

In the equilibrium position, let r be the separation between the positively charged nucleus and the centre of negative charge distribution, then

The magnitude of induced dipole moment of the atom $p = Ze\,r$ ...(1.50)

Assuming that the volume charge density ρ in the cloud of negative charge has a uniform value and R is the radius of the atom

$$\rho = \frac{-Ze}{\frac{4}{3}\pi R^3}$$

and charge within a radius of sphere r

$$= \frac{4}{3}\pi r^3 \rho = \frac{-Ze}{\frac{4}{3}\pi R^3}\frac{4}{3}\pi r^3 = -Ze\frac{r^3}{R^3}$$

The field at the nucleus due to negative charge within the sphere of radius r

$$\vec{E} = -Ze\frac{r^3}{R^3}\frac{1}{4\pi\varepsilon_0 r^2}\hat{k} = -\frac{Zer}{4\pi\varepsilon_0 R^3}\hat{k}$$

i.e., the field acts in the negative Z-direction.

The total force on the nucleus due to negatively charged sphere

$$\vec{F} = Ze\vec{E} = -\frac{Zer}{4\pi\varepsilon_0 R^3}(Ze)\hat{k}$$

The charge contained in the sphere of radius r on the boudary of which the positive charge lies is the only charge exerting a net force on the positive charge. The charge contained in the rest of the sphere of the negative charge does not contribute to the force as the positively charged nucleus lies within the negative charge distribution.

The force on the nucleus due to the external electric field $\vec{E}_0$

$$\vec{F}' = ZeE_0\hat{k}$$

along positive Z-axis. As the positive charge is in equilibrium the net force on it is zero.

i.e., $\vec{F} + \vec{F}' = 0$

This is possible when

$$ZeE_0\hat{k} - \frac{Zer(Ze)}{4\pi\varepsilon_0 R^3}\hat{k} = 0.$$

$$Zer = 4\pi\varepsilon_0 R^3 E_0 \qquad ...(1.51)$$

Comparing (1.50) and (1.51), we have

Magnitude of induced atomic dipole moment $p = Zer = 4\pi\varepsilon_0 R^3 E_0$ ...(1.52)

NOTES

Putting $4\pi\varepsilon_0 R^3 = \alpha$, the induced atomic polarisability.

Thus, induced atomic polarisability (α) is defined as atomic dipole moment per unit polarising electric field.

The direction of the dipole moment p is from the negative charge to positive charge i.e., along the direction of the electric field.

Thus, in vector form, Eq. (1.52) is written as

$$\vec{p} = \alpha \vec{E}_0 \qquad ...(1.53)$$

Thus the induced dipole moment is proportional to the external electric field $\vec{E}_0$. As soon $\vec{E}_0$ is removed $\vec{p}$ becomes zero.

Electric Displacement Vector $\vec{D}$ and the Relation

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$

Polarisation density vector $\vec{p}$

The electric field inside a polarised dielectric due to induced polarisation charge is given by

$$\vec{E}_p = -\frac{\vec{p}}{\varepsilon_0} \qquad ...(1.54)$$

Net electric field vector $\vec{E}$

To define and explain the net electric field vector $\vec{E}_0$, we shall calculate the electric field between the plates of a parallel plate capacitor when there is no dielectric between the plates and also when there is a dielectric medium between the plates. When there is no dielectric between the plates the electric field is said to be due to *free charge*.

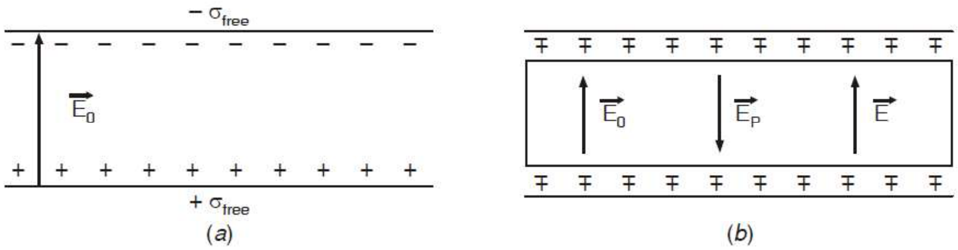


Fig. 1.20

Consider a parallel plate capacitor having a positive charge of surface density $+\sigma_{free}$ at the lower plate and $-\sigma_{free}$ at the upper plate. We denote the charge density due to the external charge supplied to the capacitor as σ_{free} to distinguish it from the induced charge density developed due to polarisation which we call as bound or polarisation charge density and denote it as $+\sigma_{bound}$ or σ_p.

NOTES

When there is no dielectric between the capacitor plates i.e., it is free space or vacuum, electric field between the two plates is given by

$$\vec{E}_0 = -\frac{\sigma_{free}}{\varepsilon_0} \qquad ...(1.55)$$

Electric field between capacitor plates with dielectric

When the space between the capacitor plates is filled with the dielectric, polarisation charge develops, positive on the upper surface and negative on the lower surface. If $\vec{p}$ is the polarisation per unit volume, then for an isotropic dielectric, the polarisation vector $\vec{p}$ is parallel to $\vec{E}_0$ and the average (macroscopic) electric field due to polarisation

$$\vec{E}_p = -\frac{\vec{p}}{\varepsilon_0}$$

i.e., acting opposite to $\vec{E}_0$ within the capacitor and in the dielectric.

The net electric field is given by

$$\vec{E} = \vec{E}_0 + \vec{E}_p = \vec{E}_0 - \frac{\vec{p}}{\varepsilon_0} \qquad ...(1.56)$$

Hence net electric field $\vec{E}$ within the dielectric is defined as the vector sum of the electric field $\vec{E}_0$ due to free charge density σ_{free} and polarisation field $\vec{E}_p$ due to bound charge density σ_p.

Why electric field inside a dielectric decrease?

It is clear from equation (1.56) that the electric field in the dielectric is reduced due to charges induced on its surface by the applied electric field $\vec{E}_0$ as the induced electric field due to dielectric polarisation $\vec{E}_p = -\frac{\vec{p}}{\varepsilon_0}$ acts in a direction opposite to that of $\vec{E}_0$.

Electric Displacement Vector *D*

Relation (1.56) can be put as

$$\vec{E}_0 = \vec{E} + \frac{\vec{p}}{\varepsilon_0}$$

or $$\varepsilon_0 \vec{E}_0 = \varepsilon_0 \vec{E} + \vec{p}$$

The quantity $\varepsilon_0 \vec{E}_0 = \varepsilon_0 \vec{E} + \vec{p}$ within the dielectric is given a special name, the *electric displacement vector* and is denoted by $\vec{D}$

$$\therefore \qquad \vec{D} = \varepsilon_0 \vec{E}_0 = \varepsilon_0 \vec{E} + \vec{p} \qquad ...(1.57)$$

Relation between three electric vector $\vec{E}, \vec{P}$ and $\vec{D}$

Equation (iv) gives the relation between $\vec{E}, \vec{P}$ and $\vec{D}$, the three electric vectors as

NOTES

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$

In free space or vacuum, there is no polarisation ($\vec{p} = 0$)

$$\therefore \qquad \vec{D} = \varepsilon_0 \vec{E}$$

As all the vectors in relation (1.57) act in the same direction we consider their magnitudes and get

$$D = \varepsilon_0 E + P$$

Units: The units of D are the same as those of 9 or $\varepsilon_0 E$ i.e., Cm^{-2}.

Electric Field Between Parallel Plates of Capacitor

Let the electric field between the plates of a parallel plate capacitor without dielectric be $\vec{E}_0$. When a dielectric is introduced between the plates of the parallel plate capacitor polarisation charge develops on the surface of the dielectric. The polarisation charge density is negative near the positive plate of the capacitor and positive near the negative plate of the capacitor. The induced surface charge density due to polarisation $\sigma_p = -P$ where P is the magnitude of the polarisation per unit volume and opposite in sign σ_p. If $\vec{E}$ is the electric field in the dielectric and $\vec{p}$ is the polarisation charge density, then

$$\vec{E}_0 = \vec{E} + \frac{\vec{P}}{\varepsilon_0}$$

or $$\frac{E_0}{E} = 1 + \frac{P}{\varepsilon_0 E} \qquad \text{... (1.58)}$$

or $$\frac{E_0}{E} = 1 + \chi_e \qquad \text{... (1.59)}$$

where $\chi_e = \dfrac{P}{\varepsilon_0 E}$ is known as electric susceptibility (χ_e).

Definition: The ratio of polarisation per unit volume P to the net electric field $\varepsilon_0 E$ as modified by the induced charge on the surface of the dielectric is called electric susceptibility (χ_e).

Moreover, $\dfrac{E_0}{E} = k$, the dielectric constant of the material.

$\therefore$ Eq (1.59) gives,

$$k = 1 + \chi_e \text{ or } \chi_e = (k - 1) \qquad \text{... (1.60)}$$

If ε_r is the relative permittivity of the medium and ε_0 the permittivity of free space (i.e. vacuum), then the absolute permittivity ε is defined as

$$\varepsilon = \varepsilon_r \varepsilon_0 \text{ or } \varepsilon_r = \frac{\varepsilon}{\varepsilon_0}.$$

NOTES

This is nothing but dielectric constant (k) of the medium.

i.e. $\varepsilon_r = k$

$$\therefore \quad E = \frac{E_0}{\varepsilon_r}\left(\text{or } E = \frac{E_0}{k}\right) \quad ...(1.61)$$

Hence, $$1+\frac{P}{\varepsilon_0 E} = \frac{E_0}{E} = \varepsilon_r = k$$

$$\vec{p} = \varepsilon_0(k-1)\ \vec{E} = \varepsilon_0\chi_e\ \vec{E}$$

This equation relates polarisation $\vec{p}$ with dielectric susceptibility χ_e and electric field $\vec{E}$.

Physical Significance of Electric Displacement Vector

The electric field vector $\vec{E}$ depends not only on the magnitude and position of charge but also upon the permittivity of the medium. However electric displacement $\vec{D}$ is an electrical quantity which is independent of the medium. This concept can be understood by considering the Faraday's experiment. A sphere carrying a charge Q was placed inside without touching another hollow sphere. The outer sphere was earthed, for a moment and the inner charged sphere was removed. The charge on outer sphere was found to be equal but opposite to that of the inner sphere. The same result is obtained if spheres of various sizes are chosen or if the space between spheres is filled with different dielectric media. This shows that there was some kind of electric displacement which only depends upon the magnitude of charge Q on inner sphere and is does not depend upon the dielectric media. The S.I. unit of this displacement ψ is equal to the charge. Thus

$$\psi = Q$$

The displacement density D at a point is the displacement per unit area at the point. Thus,

$$D = \frac{\psi}{4\pi r^2}$$

$4\pi r^2$ being the surface area of the sphere of radius r, with the charge at its centre. Now since $\psi = Q$,

$$D = \frac{Q}{4\pi r^2}$$

Multiplying numerator and Denominator by $\in$, we get

$$D = \frac{\in Q}{4\pi r^2} = \in E$$

$$\therefore \quad D = \in E$$

In vector from, $\vec{D} = \in \vec{E}$

Claussius-Mossotti Equation

The electric field inside a dielectric is somewhat less than the externally applied field. It is, therefore necessary to determine the local field or internal field at a point inside the dielectric after it gets polarized. The point where electric field is to be calculated is considered to be enclosed within an imaginary spherical cavity as shown in figure 1.21. The radius of spherical cavity is large as compared to the interatomic spacing.

The net local electric field at the point will be given by

$$E_{\text{loc}} = E_0 = E' + E_1 + E_2... \tag{1.63}$$

where, $E_0 \rightarrow$ The field due to externally applied charges.

$E' \rightarrow$ Field due to the induced charges developed on the faces of dielectric.

$E_1 \rightarrow$ Field due to opposite charges on the inner surface of spherical cavity, and

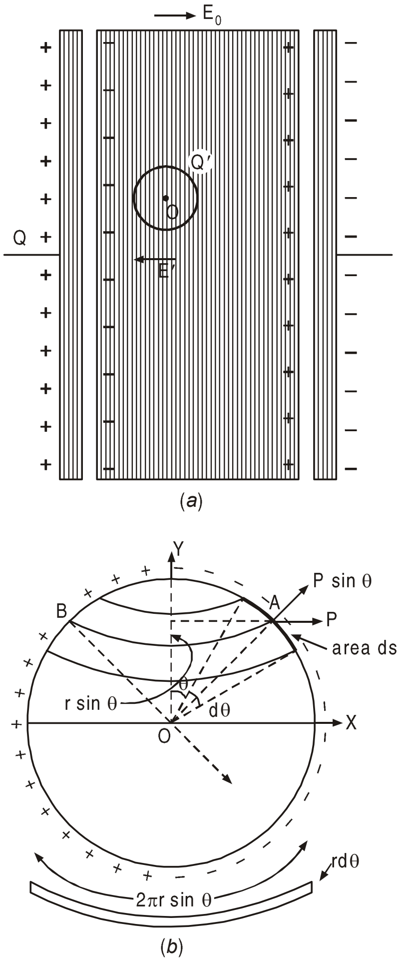
$E_2 \rightarrow$ The field at the centre of cavity due to atomic dipoles inside the cavity.

The effect of E_0 and E' is to produce to net field E, so that

$$E_{\text{loc}} = E + E_1 + E_2$$

The field E_2 at the centre of spherical cavity can be shown to be zero for cubical or spherical symmetry. Hence

$$E_{\text{loc}} = E + E_1$$



(a)

(b)

Fig. 1.21

The contribution E_1 due to charges on inner surface of the spherical cavity can be calculated as under:

Consider an elementary area *ds* at the position *A* on the inner surface of spherical cavity as shown in figure 1.21 (b) Let θ be the angle between *OA* and the *Y*-axis.

The polarization vector $\vec{p}$ has the direction from negative to positive induced charge. The component of *P* normal to the area *ds* is *P* sin θ. By definition, the polarization is the charge per unit area so that *P* sinθ is charge per unit area near *ds*. Thus, the total charge on area *ds* is *P* sinθ *ds*. The force on unit positive charge placed at the centre of cavity due to charge to charge on *ds* is (by Coulomb's law)

$$= \frac{P \sin\theta\, ds}{4\pi \in_0 r^2} \text{ (along } OA)$$

Component of this force along the direction parallel to external field is

$$\frac{P \sin\theta\, ds}{4\pi \in_0 r^2}.\sin\theta$$

For every area *ds* on the right side of the cavity there is another area ds carrying equal positive charge (at *B* is figure) on the left side of the cavity. The vertical components of forces at *O* due to charges on area *ds* at *A* and *B* are equal and opposite and therefore cancel each other. Their horizontal components, however, add together. The net force on unit positive charge at *O* due to the charge on a strip of with *r*dθ and length 2π*r* sinθ (circumference of the strip) is

$$\Delta F = \frac{P \sin\theta}{4\pi \in_0 r^2}.\sin\theta \times (\text{area of the strip})$$

$$= \frac{P \sin^2\theta}{4\pi \in_0 r^2} \times (2\pi r \sin\theta \times r d\theta)$$

$$= \frac{P}{2 \in_0} \sin^3\theta\, d\theta$$

The net force due to the complete spherical cavity is

$$E = \int_0^{\pi} \frac{P}{2 \in_0} - \sin^3\theta\, d\theta$$

Let cosθ = *x*, hence sin θ dθ = – *dx*

when θ = 0, *x* = + 1 and θ = π, *x* = –1

$$\therefore \quad E_1 = -\frac{P}{2 \in_0} \int_{+1}^{-1} x^2 dx = \frac{P}{2 \in_0} \int_{-1}^{+1} x^2 dx = \frac{P}{2 \in_0} \left[\frac{x^3}{3}\right]_{-1}^{+1}$$

$$\therefore \qquad E_1 = \frac{P}{3 \in_0} \qquad \text{... (1.64)}$$

The local field at O is given by

$$E_{\text{loc}} = E + E_1 = E + \frac{P}{3 \in_0} \qquad \text{... (1.65)}$$

NOTES

The field E_{loc} is called **Lorentz field**. Every dipole has a dipole moment $P = \alpha_{\text{e}}\, E_{\text{loc}}$. where α_e is electronic polarizability. If there and n dipoles per unit volume, the dipole moment per unit volume or polarization is

$$\begin{aligned} P &= np \\ &= n\ \alpha_e\ E_{\text{loc}} && \text{... (1.66)} \\ &= n\alpha_e \left[E + \frac{P}{3 \in_0} \right] && \text{... (1.67)} \end{aligned}$$

$$\begin{aligned} \text{But} \qquad D &= \in_0 E + P \\ \in E &= \in_0 E + P \\ \varepsilon_0 \cdot \varepsilon_r E &= \in_0 E + P && (\because\ \text{D} = \in E) \\ \therefore \qquad P &= \in_0 \in_r E - \in_0 E && (\because\ \in\, = \in_0 . \in_r) \\ &= \in_0 [\in_r -1]\, E \end{aligned}$$

$$\therefore \qquad E = \frac{P}{\in_0 (\in_r -1)}$$

Substituting this value of E in equation (1.67), we get,

$$P = n\alpha_e \left[\frac{P}{\in_0\ (\in_r -1)} + \frac{P}{3 \in_0} \right]$$

$$1 = n\alpha_e \left[\frac{1}{\in_0\ (\in_r -1)} + \frac{1}{3 \in_0} \right]$$

$$1 = n\alpha_e \left[\frac{3 \in_0 + \in_0\ (\in_0 -1)}{3 \in^2\ (\in_r -1)} \right]$$

$$1 = \frac{n\alpha_e}{3 \in_0} \left[\frac{\in_r +2}{\in_r -1} \right]$$

which gives

$$\frac{n\alpha_e}{3 \in_0} = \left[\frac{\in_r -1}{\in_r +2} \right] \qquad \text{... (1.68)}$$

This expression is called Claussius–Mossotti relation, and in optics it is the Lorentz equation. The quantity $\left[\dfrac{\in_r - 1}{\in_r + 2} \right]$ is called the volume polarizability.

NOTES

In term of electric susceptibility (χ_e):

Substituting $\varepsilon_r = 1 + \chi_e$ in relation (*vii*), we get

$$\frac{n\alpha_e}{3\in_0} = \frac{(1+\chi_e-1)}{(1+\chi_e+2)} = \frac{\chi_e}{\chi_e+3} \qquad \text{... (1.69)}$$

This relation gives Claussius-Mossotti equation in terms of χ_e, the electric susceptibility of the dielectric.

Molecular Interpretation of Claussius-Mossotti Equation

Claussius–Mossotti's equation is given by

$$\frac{n\alpha_e}{3\in_0} = \frac{\in_r - 1}{\in_r + 2} \qquad \text{... (1.70)}$$

If each dipole is consider to be a sphere of radius *a*, then its dipole moment is given by

$$P = 4\,\pi\in_0 a^3 E_{\text{loc}}$$

But electric dipole moment of a single electric dipole is

$$P = \alpha_e E_{\text{loc}}$$

where, α_e is the electronic polarisability. Equating, we get,

$$\alpha_e = 4\,\pi\in_0 a^3 \qquad \text{...(1.71)}$$

Check Your Progress

5. Define the dielectric loss.
6. What is dielectric breakdown?
7. What do you mean by thermal breakdown?
8. What is electrochemical breakdown?
9. What is ionic polarisation?
10. Define the term ferroelectricity.
11. What do you understand by dielectric hysteresis of ferroelectric materials?
12. State the factors that affect dielectric loss.
13. What is atomic dipole moment?

1.9 LORENTZ INTERNAL FIELD

In this equation, the general form of wave equations despite medium properties will be covered. During the process of deriving we will observe the conditions for relations between the scalar electric potential, *'V'* and vector magnetic potential '$\vec{A}$'. This condition is called Lorentz condition. The procedure to obtain the wave equations include, starting from Maxwell's equation and applying the vector identities and simple manipulations of the obtained equations will result in the wave equations.

NOTES

From Maxwell's second equation,

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{dt}$$

We know that,

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

Therefore,

$$\vec{\nabla} \times \vec{E} = -\frac{\partial}{\partial t}(\vec{\nabla} \times \vec{A})$$

$$\vec{\nabla} \times \vec{E} + \frac{\partial}{\partial t}(\vec{\nabla} \times \vec{A}) = 0$$

$$\vec{\nabla} \times \vec{E} + \vec{\nabla} \times \frac{\partial \vec{A}}{\partial t} = 0$$

$$\vec{\nabla} \times \left[\vec{E} + \frac{\partial \vec{A}}{\partial t}\right] = 0 \qquad (1.72)$$

We know the vector identity that curl of a gradient is zero. Therefore,

$$\vec{\nabla} \times (-\vec{\nabla} V) = 0 \qquad (1.73)$$

Comparing Equations (1.72) and (1.73), we get,

$$\vec{E} + \frac{\partial \vec{A}}{\partial t} = -\vec{\nabla} V$$

$$\vec{E} = -\vec{\nabla} V - \frac{\partial \vec{A}}{\partial t}$$

$$\vec{E} = -\left[\vec{\nabla} V + \frac{\partial \vec{A}}{\partial t}\right] \qquad (1.74)$$

Taking divergence of Equation (1.74), we get,

$$\vec{\nabla}.\vec{E} = \vec{\nabla}.\left[-\left(\vec{\nabla} V + \frac{\partial \vec{A}}{\partial t}\right)\right]$$

$$\vec{\nabla}.\vec{E} = -\left[\nabla^2 V + \frac{\partial}{\partial t}(\vec{\nabla}.\vec{A})\right] \qquad (1.75)$$

But from Maxwell's first equation,

$$\vec{\nabla}.\vec{E} = \frac{\rho_V}{\epsilon}$$

Therefore, equating the above equation with Equation (1.76),

$$\frac{\rho_V}{\epsilon} = -\left[\nabla^2 V + \frac{\partial}{\partial t}(\vec{\nabla}.\vec{A})\right]$$

Or

NOTES

$$\nabla^2 V + \frac{\partial}{\partial t}(\vec{\nabla}.\vec{A}) = -\frac{\rho_V}{\epsilon} \qquad (1.76)$$

So far, we have used Maxwell's equation for electric field and now let us use Maxwell's equation for magnetic field to couple the two fields to arrive at the electromagnetic waves. Considering, Maxwell's fourth equation,

$$\vec{\nabla} \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{dt}$$

But, $\vec{B} = \mu\vec{H}$. Therefore,

$$\vec{\nabla} \times \frac{\vec{B}}{\mu} = \vec{J} + \frac{\partial \vec{D}}{dt}$$

$$\vec{\nabla} \times \vec{B} = \mu\vec{J} + \mu\frac{\partial \vec{D}}{dt}$$

Also, $\vec{D} = \epsilon\vec{E}$

$$\vec{\nabla} \times \vec{B} = \mu\vec{J} + \mu\epsilon\frac{\partial \vec{E}}{dt} \qquad (1.77)$$

Substituting for $\vec{E}$, from Equation (1.77) , we get,

$$\vec{\nabla} \times \vec{B} = \mu\vec{J} + \mu\epsilon\frac{\partial}{dt}\left[-\vec{\nabla}V - \frac{\partial \vec{A}}{\partial t}\right]$$

$$\vec{\nabla} \times \vec{B} = \mu\vec{J} - \mu\epsilon\vec{\nabla}\frac{\partial V}{dt} - \mu\epsilon\frac{\partial^2 \vec{A}}{\partial t^2}$$

But $\vec{B} = \vec{\nabla} \times \vec{A}$, Hence,

$$\vec{\nabla} \times \vec{\nabla} \times \vec{A} = \mu\vec{J} - \mu\epsilon\vec{\nabla}\frac{\partial V}{dt} - \mu\epsilon\frac{\partial^2 \vec{A}}{\partial t^2} \qquad (1.78)$$

Applying vector identity to the LHS of Equation (1.78), we get,

$$\vec{\nabla} \times \vec{\nabla} \times \vec{A} = \vec{\nabla}(\vec{\nabla}.\vec{A}) - \nabla^2\vec{A}$$

$$\vec{\nabla}(\vec{\nabla}.\vec{A}) - \nabla^2\vec{A} = \mu\vec{J} - \mu\epsilon\vec{\nabla}\frac{\partial V}{dt} - \mu\epsilon\frac{\partial^2 \vec{A}}{\partial t^2} \qquad (1.79)$$

Observing Equation (1.79), we find that scalar potential V and vector potential $\vec{A}$ can be separated and decoupled. Therefore for vector potential, $\vec{A}$, Equation (1.78) becomes,

$$-\nabla^2\vec{A} = \mu\vec{J} - \mu\epsilon\frac{\partial^2 \vec{A}}{\partial t^2}$$

Or

$$\nabla^2\vec{A} - \mu\epsilon\frac{\partial^2\vec{A}}{\partial t^2} = \mu\vec{J} \tag{1.80}$$

Similarly, it is good to separate for scalar potential V in terms of $\vec{A}$ because we obtain a relation relating $\vec{A}$ and V known as ***Lorentz condition*** for potentials.

$$\vec{\nabla}(\vec{\nabla}.\vec{A}) = -\mu\epsilon\vec{\nabla}\frac{\partial V}{dt}$$

$$= \vec{\nabla}\left(-\mu\epsilon\frac{\partial V}{dt}\right)$$

$$\vec{\nabla}.\vec{A} = -\mu\epsilon\frac{\partial V}{dt} \tag{1.81}$$

The above relation is known as **Lorentz condition for potentials**.

Recalling Equation (1.81),

$$\nabla^2 V + \frac{\partial}{\partial t}(\vec{\nabla}.\vec{A}) = -\frac{\rho_V}{\epsilon}$$

Substituting for $\vec{\nabla}.\vec{A}$ from Equation (1.80) in Equation (1.81) above,

$$\nabla^2 V + \frac{\partial}{\partial t}\left(-\mu\epsilon\frac{\partial V}{dt}\right) = -\frac{\rho_V}{\epsilon}$$

$$\nabla^2 V - \mu\epsilon\frac{\partial^2 V}{dt^2} = -\frac{\rho_V}{\epsilon} \tag{1.82}$$

Recalling Equation (1.82) as below,

$$\nabla^2\vec{A} - \mu\epsilon\frac{\partial^2\vec{A}}{\partial t^2} = \mu\vec{J}$$

The above two equations are called as ***wave equations***. Equations (1.81) and (1.82) are decoupled equations of $\vec{A}$ and V, whereas Equations (1.82) and (1.81) are coupled equations, in which and are interlinked.

Free Space Wave Equations

In free space, $\rho_V = 0$ and $\vec{J} = 0$ and hence, the wave equations simplify to,

$$\nabla^2 V - \mu\epsilon\frac{\partial^2 V}{dt^2} = -\frac{\rho_V}{\epsilon} \tag{1.83(a)}$$

and

$$\nabla^2\vec{A} - \mu\epsilon\frac{\partial^2\vec{A}}{\partial t^2} = \mu\vec{J} \tag{1.83(b)}$$

NOTES

From electrostatics and magnetostatics,

$$V = -\oint_L \vec{E}.\overrightarrow{dl}$$

and

$$\vec{\nabla} \times \mu\vec{H} = \vec{A}$$

Equation (1.83(a)) can be rewritten as,

$$\nabla^2\vec{E} - \mu\epsilon\frac{\partial^2\vec{E}}{dt^2} = 0 \tag{1.83(c)}$$

And

$$\nabla^2\vec{A} - \mu\epsilon\frac{\partial^2\vec{A}}{\partial t^2} = \mu\vec{J} \tag{1.83(d)}$$

Uniform Plane Waves

Plane waves are waves with same phase at all points of existence. Uniform plane waves are plane waves with constant amplitude.

Consider an electric field wave equation from Equation (1.83(a))

$$\nabla^2\vec{E} - \mu\epsilon\frac{\partial^2\vec{E}}{dt^2} = 0$$

$$\nabla^2\vec{E} = \mu\epsilon\frac{\partial^2\vec{E}}{dt^2}$$

We know that, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and

$\vec{E} = E_x\overrightarrow{a_x} + E_y\overrightarrow{a_y} + E_z\overrightarrow{a_z}$. Therefore,

$$\frac{\partial^2 E_x}{\partial x^2}\overrightarrow{a_x} + \frac{\partial^2 E_y}{\partial y^2}\overrightarrow{a_y} + \frac{\partial^2 E_z}{\partial z^2}\overrightarrow{a_z} = \mu\epsilon\left[\frac{\partial^2 E_x}{\partial t^2}\overrightarrow{a_x} + \frac{\partial^2 E_y}{\partial t^2}\overrightarrow{a_y} + \frac{\partial^2 E_z}{\partial t^2}\overrightarrow{a_z}\right]$$

In the above equation, it should be noted that $\frac{\partial^2 E_y}{\partial y^2} = 0$ and likewise for unequal variables. Splitting the above three dimensional vector equation to a one-dimensional scalar equation,

$$\frac{\partial^2 E_x}{\partial x^2} = \mu\epsilon\frac{\partial^2 E_x}{\partial t^2} \tag{1.84(a)}$$

$$\frac{\partial^2 E_y}{\partial y^2} = \mu\epsilon\frac{\partial^2 E_y}{\partial t^2} \tag{1.84(b)}$$

$$\frac{\partial^2 E_z}{\partial z^2} = \mu\epsilon\frac{\partial^2 E_z}{\partial t^2} \tag{1.84(c)}$$

Also, in free space, where the electromagnetic waves travel, (they can also travel through different medium), $\rho_V = 0$ and $\vec{J} = 0$. Therefore, from Maxwell's first equation,

$$\vec{\nabla}.\vec{D} = 0$$

$$\vec{\nabla}.\epsilon\vec{E} = 0$$

$$\vec{\nabla}.\vec{E} = 0$$

$$\Rightarrow \left(\frac{\partial}{\partial x}\overrightarrow{a_x} + \frac{\partial}{\partial y}\overrightarrow{a_y} + \frac{\partial}{\partial z}\overrightarrow{a_z}\right).\left(E_x\overrightarrow{a_x} + E_y\overrightarrow{a_y} + E_z\overrightarrow{a_z}\right) = 0$$

$$\frac{\partial}{\partial x}E_x + \frac{\partial}{\partial y}E_y + \frac{\partial}{\partial z}E_z = 0$$

Since, E_x is travelling in the x –direction, $\frac{\partial E_y}{\partial y} = \frac{\partial E_z}{\partial z} = 0$. Then, $\frac{\partial E_x}{\partial x}$ represents that no variation of E_x in x-direction and also $\vec{E}$ is independent of y and z. Differentiating with respect to x,

$$\frac{\partial^2 E_x}{\partial x^2} = 0$$

The solution of the above second order differential equation exists only if,

$$E_x = 0 \quad or \quad E_x = K(constant)$$

If $E_x = K$, then E_x is not a wave, but a constant dc line. Hence, a uniform plane wave travelling in x –direction do not have an component of $\vec{E}$. Similarly for the other two directions y and z.

For the magnetic field vector, following the similar approach, from Maxwell's third equation,

$$\vec{\nabla}.\vec{B} = 0$$

$$\vec{\nabla}.\mu\vec{H} = 0$$

$$\vec{\nabla}.\vec{H} = 0$$

$$\Rightarrow \left(\frac{\partial}{\partial x}\overrightarrow{a_x} + \frac{\partial}{\partial y}\overrightarrow{a_y} + \frac{\partial}{\partial z}\overrightarrow{a_z}\right).\left(H_x\overrightarrow{a_x} + H_y\overrightarrow{a_y} + H_z\overrightarrow{a_z}\right) = 0$$

$$\frac{\partial}{\partial x}H_x + \frac{\partial}{\partial y}H_y + \frac{\partial}{\partial z}H_z = 0$$

Since, H_x is travelling in the x –direction, $\frac{\partial H_y}{\partial y} = \frac{\partial H_z}{\partial z} = 0$. $\vec{H}$ is independent of y and z. Therefore,

$$\frac{\partial H_x}{\partial x} = 0 \Rightarrow \frac{\partial^2 H_x}{\partial x^2} = 0$$

Since H_x cannot be constant, to satisfy the above second order differential equation, $H_x = 0$ for uniform plane wave.

Properties of Electromagnetic Waves

Electromagnetic waves transport energy or information from one point to the other. Few examples of electromagnetic waves include the waves in the electromagnetic spectrum as shown in Figure (1.22). Few electromagnetic waves include X-rays, Gamma rays, microwave, TV signals, radar signals, light rays, etc. The electromagnetic waves are also called as Hertzian waves.

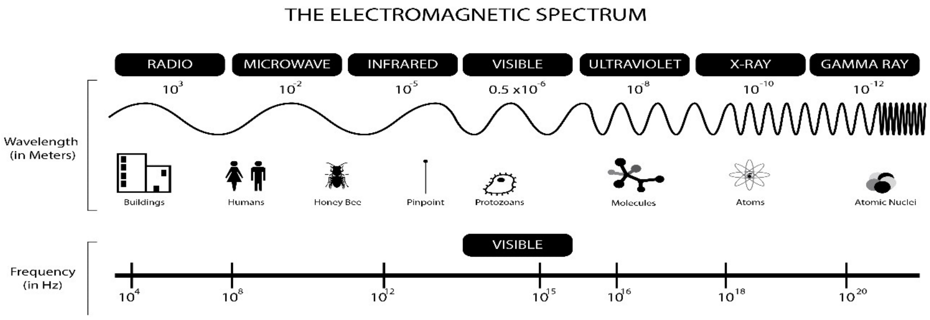


Fig. 1.22 *Electromagnetic Spectrum*

Characteristics of EM Waves

Following are the characteristics of EM waves.

1. They travel at a speed of light in vacuum.
2. They travel similar to the waves with the same their same property.
3. They radiate away from the source
4. They can travel across any medium
5. EM waves are generated by vibration of electrons resulting in energy emission called as electromagnetic radiation.
6. Electromagnetic waves have both electric and magnetic components.
7. Electric and magnetic components are orthogonal (perpendicular) to each other.
8. The direction of wave propagation will be orthogonal to the electric and magnetic waves. Such waves are called Transverse ElectroMagnetic waves (TEM waves).

Parameters of Wave

A simple wave is a sinusoidal signal as represented as in Figure (1.23).

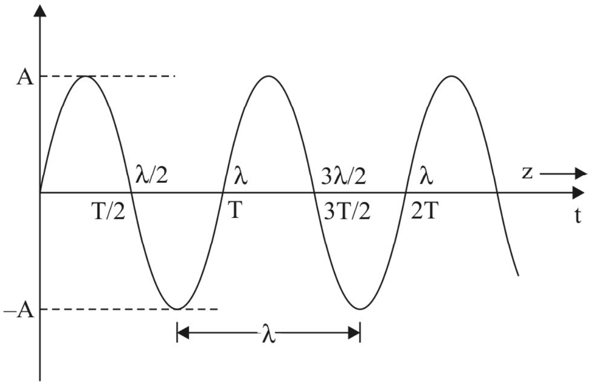


Fig. 1.23 *EM Wave*

Let $\lambda = wavelength\ (m)$

$T = Time\ period\ (S)$

$u = speed\ (m/s)$

$$\therefore \quad u = \frac{\lambda}{T} = f\lambda \qquad [f = 1/T]$$

Let $\omega = angular\ frequency\ (rad/s)$

$\beta = phase\ constant\ or\ wave\ number\ (rad/m)$

$$\omega = 2\pi f\ (rad/s)$$

$$\beta = \frac{\omega}{u} = \frac{2\pi f}{u}$$

$$\beta = \frac{2\pi f}{f\lambda}$$

$$\beta = \frac{2\pi}{\lambda}$$

1.10 STATIC DIELECTRIC CONSTANT

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.

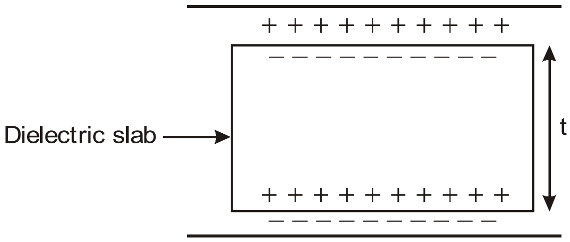


Fig. 1.24 *Dielectric Slab in a Capacitor*

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 7.5. 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

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

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

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

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 1.25 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,

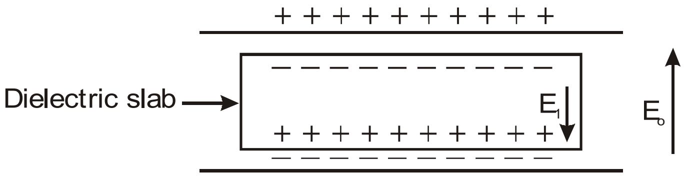


Fig. 1.25 *Fields in a Parallel Plate Capacitor with Dielectric in Between*

$$E_o = \frac{\sigma}{\varepsilon_o} \qquad ...(1.85)$$

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

$$E = E_o - E_1 \qquad ...(1.86)$$

If σ_s is the surface charge density on the slab then, by following equation (1.86), we can write

$$E_1 = \frac{\sigma_s}{\varepsilon_o} \qquad ...(1.87)$$

Therefore, from equations (1.86), (1.87) and (1.88),

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

or
$$\varepsilon_o E = \sigma - \sigma_s \qquad ...(1.88)$$

NOTES

But, $\sigma_s = P$ ($\because$ Polarisation is Charge/Unit Area) ...(1.89)

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

$$D = \sigma \text{ (D is charge/unit area)} \quad ...(1.90)$$

Therefore, Equation (1.89) can be written as

$$\varepsilon_o E = D - P \quad ...(1.91)$$

or

$$D = \varepsilon_o E + P \quad ...(1.92)$$

But, from electrostatics we know

$$D = \varepsilon E = \varepsilon_o \varepsilon_r E \quad ...(1.93)$$

Therefore, Equation (7.19) becomes

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

Rearranging the above equation we can write

$$\varepsilon_o E (\varepsilon_r - 1) = P \quad ...(1.94)$$

or

$$\frac{P}{\varepsilon_o E} = (\varepsilon_r - 1) \quad ...(1.95)$$

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

$$\therefore \quad \chi_e = \varepsilon_r - 1. \quad ...(1.96)$$

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 **Fm^2.**

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

1.10.1 Complex Dielectric Constant

A complex dielectric constant is used to describe the dielectric constant during a periodic variation of the electric field, where the field variation is described by a sine-shaped waveform. It is written in the form

$$\in = \in'' + i.\in''$$

where the real part, $\in'$, is the permittivity component quantifying the stored energy (i.e. the part directly proportional to the field amplitude) and the imaginary part, $\in''$ is the dielectric loss factor, which describes the part of the electric energy that is lost through movement of molecules/ions as a result of the continually changing field (the contribution from this component is proportional to the rate of the electric field change, or the first derivative of the electrical field function). This component also gives rise to a phase difference between the field function and the resulting polarization. Without this component both would be perfectly in phase. Both components depend on the frequency of the field variation.

1.11 DEBYE EQUATION

The Debye-Hückel theory was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes. It was further modified by Lars Onsager in 1927 with the following postulates.

- The solute is completely dissociated, it is a strong electrolyte.
- Ions are spherical and are not polarized by the surrounding electric field.
- The solvent plays no role other than providing a medium of constant relative permittivity (dielectric constant).
- It was assumed that the electric field causes the charge cloud to be distorted away from spherical symmetry.
- There is no electrostriction.
- Individual ions surrounding a 'central' ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach.

The last assumption means that each cation is surrounded by a spherically symmetric cloud of other ions. The cloud has a net negative charge. Similarly each anion is surrounded by a cloud with net positive charge.

Considering the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to derive a theoretical expression to account for the empirical relation known as '**Kohlrausch's Law**', for the molar conductivity, λ_m. The symbol λ (Lambda) is used here.

$$\lambda_m = \lambda_m^0 - K\sqrt{c}$$

Here λ_m^0 is known as the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. Limiting here means 'at the limit of the infinite dilution'. Onsager's expression is,

$$\lambda_m = \lambda_m^0 - (A + B\lambda_m^0)\sqrt{c}$$

Where A and B are constants that depend only on known quantities, such as temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. This is known as the Debye-Hückel-Onsager equation. Figure 1.26 illustrates the graph for strong and weak electrolyte.

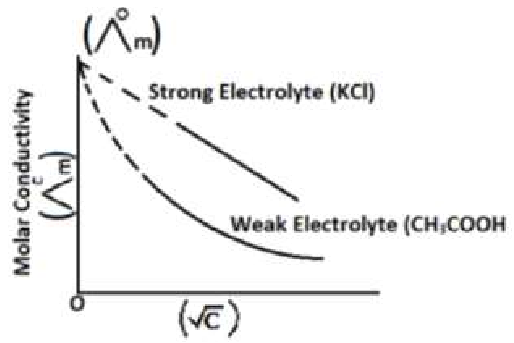


Fig. 1.26 *Graph for Strong and Weak Electrolyte*

Equivalent Conductivity (λ): The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity. It is denoted by λ. (Lambda) symbol.

Strong and Weak Electrolytes

Electrolytes are chemicals that break into ions in water. Aqueous solutions containing electrolytes conduct electricity. Strong electrolytes include the strong acids, strong bases, and salts. These chemicals completely dissociate into ions in aqueous solution.

Weak electrolytes only partially break into ions in water. Weak electrolytes include weak acids, weak bases, and a variety of other compounds. Most compounds that contain nitrogen are weak electrolytes.

Nonelectrolytes do not break into ions in water. Common examples include most carbon compounds, such as sugars, fats, and alcohols.

The equivalent conductivity λ of an electrolyte solution is related to the mobilities of the constituent ions as

$$\lambda = F\,(U_{+} + U_{-}) \qquad \text{...(1.97)}$$

$$U_{+} = \left[U_{+}^{0} - \frac{X}{300}\left(\frac{Z_X e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT}\right)U_{+}^{0}\right]$$

$$U_{-} = \left[U_{-}^{0} - \frac{x}{300}\left(\frac{Z_{-} e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT}\right)U_{-}^{0}\right]$$

Substituting the values of U_{+} and U_{-} in Equation (1.97), we get

$$\lambda = F\left[U_{+}^{0} = \frac{X}{300}\left(\frac{Z_X e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT}U_{+}^{0}\right)\right] + \left[U_{-}^{0} = \frac{X}{300}\left(\frac{Z_{-1} e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT}U_{-}^{0}\right)\right] \text{...(1.98)}$$

Where F - Faraday

X - Distance Traveled by the Ion

e_0 - Charge of the Electric Cloud

η - Viscosity of the Liquid (Here η is for Eta)

Z_0 - Charge of the Ion

∈ - Correction Factor (∈ is for Epsican)

K - Boltzmann Constant

T - Absolute Temperature

λ - Equivalent Conductivity

ω - Dielectric Constant of the Medium (ω is for Omega)

For a Symmetrical Electrolyte, $Z = Z_{+} = Z_{-}$

Therefore, the Equation (1.98) reduces to,

$$\lambda = \left[\left(FU_{+}^{0} - \frac{FXZe_0}{300 \times 6\pi\eta} - \frac{FXZe_0 300 e_0^2 \omega}{300 \times 6 \in KT}\right)\right.$$

$$+FU_{-}^{0}\left(\frac{FXZe_0}{300\times 6\pi\eta}-\frac{FXZe_0 300e_0^2\omega}{300\times 6\in KT}U_{-}^{0}\right)\Bigg]$$

NOTES

$$\lambda = F\left(U_{+}^{0}-U_{-}^{0}\right)-\frac{ZFXZe_0}{300\times 6\pi\eta}-\frac{FXe_0^2\omega}{6\in KT}\left(U_{+}^{0}-U_{-}^{0}\right)$$

$$\lambda = F\left(U_{+}^{0}-U_{-}^{0}\right)-\frac{FXZe_0}{900\pi\eta}-\frac{Xe_0^2\omega}{6\in KT}\left(U_{+}^{0}-U_{-}^{0}\right)$$

But, $\lambda^0 = F\left(U_{+}^{0}+U_{-}^{0}\right)$

$$\lambda = \lambda^0-\left[\frac{FXZe_0}{900\pi\eta}+\frac{xX_0^2\omega}{6\in KT}\lambda^0\right] \quad ...(1.99)$$

Replacing X by the familiar expression,

$$X=\left(\frac{8\pi z^2e_0^2C}{\in KT}\right)^{1/2}\left(\frac{NA}{1000}\right)^{1/2}$$

Then Equation (1.99) becomes,

$$\lambda = \lambda^0-\left[\frac{FZe_0}{900\pi\eta}\left(\frac{8\pi z^2e_0^2C}{\in KT}\right)^{1/2}\left(\frac{NA}{1000}\right)^{1/2}\right.$$

$$\left.+\frac{e_0^2\omega}{6\in KT}\left(\frac{8\pi z^2e_0^2C}{\in KT}\right)^{1/2}\left(\frac{NA}{1000}\right)^{1/2}\lambda^0\right] \quad ...(1.100)$$

Equation (1.100) is the Debye-Hückel-Onsagar equation for a symmetrical electrolyte.

Validity and Extension of the Theory and Activity of Ions in Solution

The verification of the Debye-Hückel-Onsager equation is more difficult for electrolytes of unsymmetrical valence types (different Z^+ and Z^- values) since determination of the value of ω can be done only on knowing the mobility's of the individual ions at infinite dilution and also the transference numbers of the ions. For $CaCl_2$ and $LaCl_3$ dilute solutions, the results are in close agreement with the requirements of the theoretical equation at concentrations λ against square root of the concentration up to 4×10^{-5} equivalents per liter. The higher the valence type of the electrolyte, the lower is the limit of concentration at which the Onsager equation is applicable. It has been observed for aqueous solutions of various electrolytes that there is good agreement between the experimental slopes and theoretically calculated values.

The validity for Onsager theory is also provided by conductance measurements of a number of electrolytes made at 0^0C and 100^0C. At both temperatures, the observed slope of the plot of agrees with the calculated result within the limits of experimental error.

Thus the Onsager equation represents the dependence of the concentration of the equivalent conductance electrolytes. The shapes of the curves indicate that in sufficiently dilute solutions the slopes would be very close to the theoretical Onsager values.

The effect of concentration on equivalent conductance can be studied from the plots of λ^0 values versus square root of the concentration of the electrolyte.

It has been found that different types of plots are obtained depending on the nature of the electrolyte.

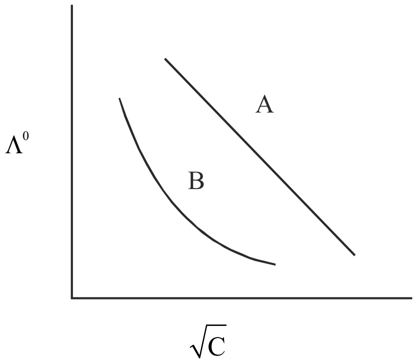


Fig. 1.27 *Concentration of Different Electrolyte*

Validity for Non-Aqueous Solvents

For methyl alcohol solutions, chlorides and thiocyanates of the alkali metals, the experimental values closely agree with the theoretical values. But nitrate solutions, tetra alkyl ammonium salts and salts of higher valence types show appreciable deviations. The discrepancies are more prominent when the dielectric constant of the medium is low. The conductance of KI in a number of solvents was determined and the slopes of the plots of λ against square root of C was found out. At higher dielectric constants, there is close agreement between the experimental and calculated slopes. But at lower dielectric constants, greater discrepancies are observed. The deviation from theoretical Onsager behaviour for non-aqueous solutions occurs because many strong electrolytes which are completely dissociated in water behave as weak, incompletely dissociated electrolytes in solvents of low dielectric constant.

Activity Coefficients of Different Electrolytes

The activity coefficients of different electrolytes can be determined based on measurements of vapor pressure, freezing point, solubility or electromotive force. The results obtained by the various methods are in good agreement with each other and hence they may be regarded as reliable.

The activity coefficients deviate appreciably from unity. The values always decrease at first as the concentration is increased, but they generally pass through a minimum and then increase again. The activity coefficients often exceed unity at high concentrations so that the mean activity of the electrolyte is actually greater than the concentration. The deviations from ideal behaviour at high concentrations are in the opposite direction to those which occur at low concentrations.

(a) The electrolytes of the same valence type have almost identical activity coefficients in dilute solutions.

(b) The deviation from ideal behaviour at a given concentration is greater if the product of the valences of the ions constituting the electrolyte is higher.

NOTES

Check Your Progress

14. What is electric susceptibility?
15. Define the uniform plane waves.
16. What is complex dielectric constant?

1.12 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Lattice vibrations can describe elastic properties, thermal properties, optical properties, and sound velocity of materials. Lattice Vibration is the fluctuations of atoms in a solid with reference to the equilibrium position.
2. Consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. The diatomic lattice show an important feature which is different from the monoatomic case.
3. In condensed matter physics, a phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, specifically in solids and some liquids.
4. Important properties of phonons are as follows:
    (i) Phonons are bosons.
    (ii) Each phonon is a "Collective Mode" caused by the motion of every atom in the lattice.
    (iii) Phonons act as waves of lattice displacement.
5. Dielectric loss is a major problem involving heat generation and is dominating in high voltage application.
6. Whenever the voltage applied to a dielectric material exceeds a critical value a large amount of current flows through it. As a result of this, the dielectric loses its insulating property. This phenomena is known as dielectric breakdown.
7. When there is excessive increase in the temperature of the dielectric a local melting occurs due to less heat dissipation than heat generated. Hence, mobility of charge carriers is increased, and enormous current flows through the material thus, leading to thermal breakdown.
8. Dielectric breakdown due to the formation of electro chemical reaction or chemical reaction in a dielectric material is called electrochemical breakdown.
9. Ionic polarisation occur only in ionic solids, such as NaCl which possess ionic bonds. It does not occur in covalent crystals such as diamond, silicon and germanium.
10. Ferroelectricity refers to the creation of large induced dipole moment in a weak electric field as well as the existence of electric polarization even in the absence of an applied electric field.

11. Ferroelectric materials possess spontaneous polarization. Ferroelectricity is a result of dielectric hysteresis. The lagging of polarization P behind the applied electric field E is called dielectric hysteresis.
12. The dielectric loss increases with high frequency of the applied voltage, high applied voltage, high temperature and humidity.
13. Atomic dipole moment is the product of the positive or negative charge on the atom and the distance between the centres of the positive and the negative charges in the direction of the applied electric field.
14. The ratio of polarisation to the net electric field $\varepsilon_0 E$ as modified by the induced charges on the surface of the dielectric is called susceptibility.
15. Plane waves are waves with same phase at all points of existence. Uniform plane waves are plane waves with constant amplitude.
16. A complex dielectric constant is used to describe the dielectric constant during a periodic variation of the electric field, where the field variation is described by a sine-shaped waveform.

1.13 SUMMARY

- Lattice vibrations can describe elastic properties, thermal properties, optical properties, and sound velocity of materials. Lattice Vibration is the fluctuations of atoms in a solid with reference to the equilibrium position.
- Lattice vibrations can also relate with free electrons in a conducting solid which gives intensification to electrical resistance. Due to the connections between atoms, the displacement of one or more atoms from their equilibrium positions gives rise to a set of vibration waves propagating through the lattice.
- Consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. The diatomic lattice show an important feature which is different from the monoatomic case.
- In condensed matter physics, a phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, specifically in solids and some liquids.
- The internal heat energy of a solid resides in the vibrations of its constituent particles which may be atoms, ions or molecules; we shall refer to them as atoms here for convenience. These vibrations may be resolved into components along three perpendicular axes, so that we may represent each atom by three harmonic oscillators.
- It is a tendency of a real crystal to resist compression to a smaller volume than its equilibrium value more strongly than expanding to a larger volume. It occurs due to the shape of the interatomic potential curve. This is a departure from Hooke's Law, as harmonic application does not produce this property. This is termed as anharmonic effect which takes place due to the higher order terms in potential that are generally ignored in harmonic approximation.

NOTES

- The anharmonicity of lattice vibration describes various thermal properties of solids including the Lattice Thermal Conductivity (LTC), Coefficient of Thermal Expansion (CTE) and the temperature dependence of phonon frequencies.
- The electrons in a crystalline solids are arranged in regular manner. These electrons in crystals are arranged in "Energy Bands" separated by regions in energy for which no wavelike electron orbitals exist. Such forbidden regions are called "*Energy Gaps* (*Eg*)*"* or "*Band Gap* (*Eg*)".
- 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.
- A phonon is the quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency.
- Phonons have also been predicted to play a key role in superconductivity in materials and the prediction of superconductive compounds. In 2019, researchers were able to isolate individual phonons without destroying them for the first time.
- For each phonon state (without any interactions between phonons) one may assign some wave vector $\vec{q}$, mode index j and specific energy $\hbar\omega j(\vec{q})$. Furthermore, for this wave vector value and mode there exist some displacement pattern of atoms in the lattice determined by the eigenvector $e \times \ \vec{e}(\vec{q}j)$.
- The propagation of the wave (disturbance) is accompanied by the transfer of energy. Therefore, we can say that the propagation of waves means transfer of energy.
- When an elastic or a mechanical wave propagates, it requires (*a*) a source of disturbance (*b*) a medium that carries the wave and (*c*) some physical mechanism through which the particles of the said medium can perturb or influence other particles.
- Dielectric loss is a major problem involving heat generation and is dominating in high voltage application.
- The complementary angle $\delta = 90 - \theta$ is called the dielectric loss angle. This angle is a measure of the power or heat dissipated in each cycle. In most of the dielectrics this angle d is negligible.
- Whenever the voltage applied to a dielectric material exceeds a critical value a large amount of current flows through it. As a result of this, the dielectric loses its insulating property. This phenomena is known as dielectric breakdown.
- When there is excessive increase in the temperature of the dielectric a local melting occurs due to less heat dissipation than heat generated. Hence, mobility of charge carriers is increased, and enormous current flows through the material thus, leading to thermal breakdown

NOTES

- Dielectric breakdown due to the formation of electro chemical reaction or chemical reaction in a dielectric material is called electrochemical breakdown.
- Discharge breakdown occurs due gaseous discharge taking place in occluded gas bubbles.
- The presence of cracks or pores at the surface of the material leads to defect breakdown due to the collection of moisture and other impurities at these defect sites.
- The electronic polarisation occurs, due to the displacement of the positively charged nucleus and the negatively charged electron cloud in opposite directions within a dielectric material upon applying an external electric field E.
- Ionic polarisation occur only in ionic solids, such as NaCl which possess ionic bonds. It does not occur in covalent crystals such as diamond, silicon and germanium.
- Orientation polarisation occurs in dielectric materials which possess molecules with permanent dipole moment (i.e., in polar molecules).
- The space charge polarisation occur in multiphase dielectric materials. When such materials are subjected to an external electric field, especially at high temperature the charges get accumulated at the interface or at the electrodes because of sudden change in conductivity.
- The piezoelectric effect results from the linear electromechanical interaction between the mechanical and electrical states in crystalline materials with no inversion symmetry.
- The piezoelectric effect is a reversible process: materials exhibiting the piezoelectric effect (the internal generation of electrical charge resulting from an applied mechanical force) also exhibit the reverse piezoelectric effect, the internal generation of a mechanical strain resulting from an applied electrical field.
- Ferroelectric materials possess spontaneous polarization. Ferroelectricity is a result of dielectric hysteresis. The lagging of polarization P behind the applied electric field E is called dielectric hysteresis.
- Dielectric loss is a major problem involving heat generation and is dominating in high voltage application. When an AC voltage is applied to a pure dielectric material like vacuum or purified gases, there is no consumption of energy. As a result, the charging current leads the applied voltage by an angle 90° and the polarization of the dielectric is in phase with the voltage.
- Dielectric relaxation is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarisation with respect to a changing electric field in a dielectric medium (e.g., inside capacitors or between two large conducting surfaces).
- Dielectric substance is a material which does not conduct electricity i.e., dielectrics are insulators. In such substance the electrons are firmly bound to the atoms of the material. These electrons can, therefore, move through very small distances of the order of atomic dimensions.

- When the molecules of a dielectric are aligned completely or partially in the direction of the electric field, the dielectric is said to be polarised.
- The ratio of polarisation per unit volume P to the net electric field $\varepsilon_0 E$ as modified by the induced charge on the surface of the dielectric is called electric susceptibility (χ_e).
- Plane waves are waves with same phase at all points of existence. Uniform plane waves are plane waves with constant amplitude.
- Electromagnetic waves transport energy or information from one point to the other. Few examples of electromagnetic waves include the waves in the electromagnetic spectrum. Few electromagnetic waves include X-rays, Gamma rays, microwave, TV signals, radar signals, light rays, etc. The electromagnetic waves are also called as Hertzian waves.
- The dielectric constant or relative permittivity ε_r is defined as, the ratio between the permittivity of the medium **e** and the permittivity of free space $\boldsymbol{\varepsilon_0}$.
- A complex dielectric constant is used to describe the dielectric constant during a periodic variation of the electric field, where the field variation is described by a sine-shaped waveform.
- The verification of the Debye-Hückel-Onsager equation is more difficult for electrolytes of unsymmetrical valence types (different Z^+ and Z^- values) since determination of the value of w can be done only on knowing the mobility's of the individual ions at infinite dilution and also the transference numbers of the ions.
- The activity coefficients of different electrolytes can be determined based on measurements of vapour pressure, freezing point, solubility or electromotive force.

1.14 KEY TERMS

- **Lattice vibrations:** Lattice Vibration is the fluctuations of atoms in a solid with reference to the equilibrium position.
- **Phonons:** A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, specifically in solids and some liquids.
- **Dielectric loss:** Dielectric loss is a major problem involving heat generation and is dominating in high voltage application.
- **Dielectric breakdown:** Whenever the voltage applied to a dielectric material exceeds a critical value a large amount of current flows through it. As a result of this, the dielectric loses its insulating property. This phenomena is known as dielectric breakdown.
- **Discharge breakdown:** Discharge breakdown occurs due gaseous discharge taking place in occluded gas bubbles.

- **Ionic polarization:** Ionic polarisation occurs only in ionic solids, such as NaCl which possess ionic bonds. It does not occur in covalent crystals, such as diamond, silicon and germanium.
- **Orientation polarization:** Orientation polarisation occurs in dielectric materials which possess molecules with permanent dipole moment (i.e., in polar molecules).
- **Space charge polarization:** The space charge polarisation occur in multiphase dielectric materials.
- **Polarisation:** 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 up to the critical value.
- **Clausius–Mossotti's relation:** The Clausius–Mossotti's relation connects the relative permittivity of a dielectric to the polarizability 'a' of the atoms or molecules constituting the dielectric.
- **Dielectric constant:** The dielectric constant or relative permittivity is defined as, the ratio between the permittivity of the medium and the permittivity of free space.
- **Polarisation vector:** It is defined as the induced dipole moment per unit volume of the dielectric. The polarisation P is also defined as the induced surface charge per unit area.
- **Susceptibility:** It is the ratio of polarisation to the net electric field as modified by the induced charges on the surface of the dielectric is called susceptibility.
- **Uniform plane waves:** Uniform plane waves are plane waves with constant amplitude.

1.15 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What do you mean by anharmonicity?
2. What do you mean by phonon mean free path?
3. What does an elastic or a mechanical wave require while propagating?
4. What do you understand by the polarizability?
5. Define dielectric loss angle.
6. Mention the effect of electric field on non-polar dielectric.
7. Why does the electric field inside a dielectric decrease?
8. State the Claussius-Mossotti equation.
9. What are weak and strong electrolytes?

Long-Answer Questions

1. Describe the meaning of phonons and phonon momentum.
2. Differentiate between elastic (mechanical) and electromagnetic waves.
3. Discuss the dielectric constant with the help of appropriate examples.
4. Differentiate between the dielectric breakdown and intrinsic breakdown.
5. Explain the polarizability on the basis of electronic, ionic and piezo.
6. Analyse the pyro and ferro electric properties of crystals. Give appropriate examples.
7. Describe the Lorentz field.

1.16 FURTHER READING

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UNIT 2 BAND THEORY OF SOLIDS

NOTES

Structure

2.0 INTRODUCTION

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. 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. In condensed matter physics, the electronic 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 (transistors, solar cells, etc.). 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. The 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. Although, electronic band structures are usually associated with crystalline materials, quasi-crystalline and amorphous solids may also exhibit band gaps. These are somewhat more difficult to study theoretically since they lack the simple symmetry of a crystal, and it is not usually possible to determine a precise dispersion relation. As a result, virtually all of the existing theoretical work on the electronic band structure of solids has focused on crystalline materials.

The main assumption of the free electron model to describe the delocalized electrons in a metal can be derived from the Fermi gas. Since interactions are neglected due to screening effect, the problem of treating the equilibrium properties and dynamics of an ideal Fermi gas reduces to the study of the behaviour of single independent particles. In these systems the Fermi temperature is generally many thousands of kelvins, so in human applications the electron gas can be considered degenerate. The maximum energy of the fermions at zero temperature is called the Fermi energy. The Fermi energy surface in reciprocal space is known as the Fermi surface.

A free Fermi gas is a physical model assuming a collection of non-interacting fermions in a constant potential well. Fermions are elementary or composite particles with half-integer spin, thus follow Fermi-Dirac statistics. The equivalent model for integer spin particles is called the Bose gas (an ensemble of non-interacting bosons). At low enough particle number density and high temperature, both the Fermi gas and the Bose gas behave like a classical ideal gas. The total energy of the Fermi gas at absolute zero is larger than the sum of the single-particle ground states because the Pauli principle implies a sort of interaction or pressure that keeps fermions separated and moving. For this reason, the pressure of a Fermi gas is non-zero even at zero temperature, in contrast to that of a classical ideal gas. In this unit, you will study about the band theory of solids, Kronig–Penney model, semiconductors, Fermi energy, Hall effect and intrinsic and extrinsic conductivity.

2.1 OBJECTIVES

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

- Describe the band theory of solids
- Explain the behaviour of one dimensional electron gas
- Discuss the density of states and chemical potential
- State the concept of Fermi energy
- Explain the Hall effect and Kronig-Penney model
- Differentiate between conductors, semiconductors and insulators
- Describe intrinsic and extrinsic conductivity

2.2 BAND THEORY

In the case of a single isolated atom, the electron in any orbit as shown in Figure 2.1 have a definite energy. As a result, they occupy discrete energy levels, as shown in Figure 2.2(a).

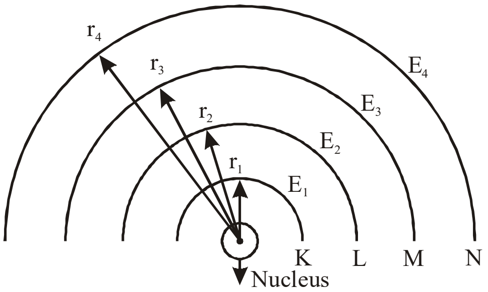

Fig. 2.1 *The energy Levels of a Single Isolated Atom*

The pauli exclusion principle allows each energy level to contain only two electrons. For example, the 2s level of a single atom contains one energy level with two electrons and 2p level contains 3 energy levels with two electrons in each level thus, with a total of six electrons as shown in Figure 2.2(a).

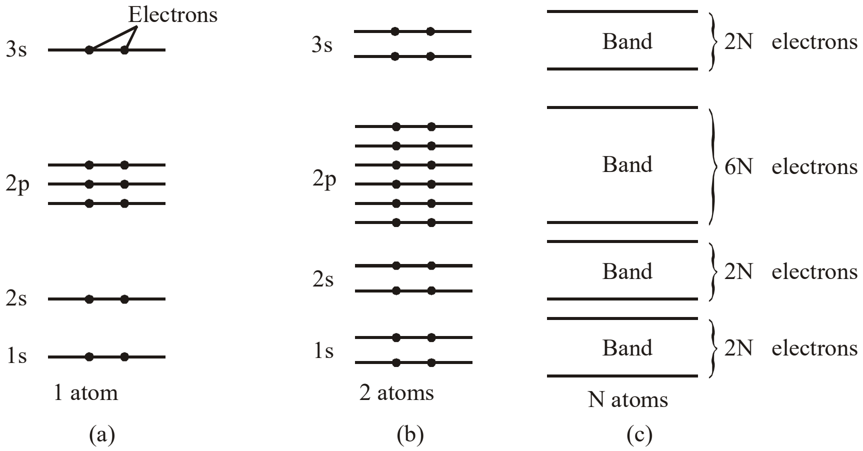

Fig. 2.2 *The Energy Levels Broaden Into Energy Bands*

Band Structure in Solid

Let us consider the formation of bands in a solid sodium.

The single energy level of an isolated sodium (Z = 11) based on the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$ is shown in Figure 2.2(a).

When an another sodium is brought close to it, the electrons will be subjected to the effect of an additional field. As a result, each energy level is split in to two as shown in Figure 2.2(b). Similarly, when three atoms come close together, the original level splits into three levels and so on.

More generally, when a solid is formed by bringing N atoms together, the Pauli principle still demands that only two electrons in the entire solid should have the same energy. Hence, in a solid the different split energy levels of electrons come together to form continuous bands of energies as shown in Figure 2.2(c).

Consequently, the 2s band in a solid sodium contain N discrete energy levels and 2N electrons, two in each energy level. Similarly, each of the 2p level contain N energy levels and 2N electrons. Hence, a broad 2p band will contain 3N energy levels and 6N electrons since the three 2p bands overlap.

Hence in general, each energy band has a total of N individual levels and each energy band can hold a maximum of $2(2l + 1)$ N electrons.

[Each energy level can hold $2\ (2l + 1)$ electrons. 2 corresponds to the electrospin and $(2l + 1)$ corresponds to the orientation of the electron orbital angular momentum].

The result is that, electrons in any orbit of atom within a solid can have a range of energies rather than a single value. *Thus, the range of energies possessed by an electron in a solid is known as energy band.* i.e., Each energy level of an isolated atom becomes a band in a solid as shown in Figure 2.2(c).

Check Your Progress

1. What is the band theory of solids?
2. Define the band structure in solids.

2.3 BEHAVIOUR OF ELECTRON GAS: ONE-DIMENSIONAL

The free electron models of metals give us a good deal of insight into several properties of metals. Yet there are many other important properties that these models do not explain. In particular, they do not tell us why, when chemical elements crystallize to become solids, some are good *conductors*, some are *insulators,* and yet others are *semiconductors* with electrical properties that vary greatly with temperature. These differences are not minor, but rather remarkable. The resistivity may vary from 10^{-8} ohm-m for a good conductor to 10^{-22} ohm-m for a good insulator.

We can understand the differences between insulators and conductors by extending the free electron model to take into account the interaction of the electrons with the positive ion lattice. In the quantum mechanical free electron (QMFE) model, we assumed that the potential energy inside the solid was uniform. It would be more realistic to assume it is a periodic (alternating uniformly) function of x, y and z. This is reasonable because of the periodic distribution of the lattice ions in crystalline solid.

When the interaction between the electrons and the lattice ions is considered, we will find some unusual properties possessed by the electrons in the crystal.

1. QMFE model gave rise to a series of discrete energy states about 10^{-15} eV apart, which ranged from $E \approx O$ to $E = E_F$, the Fermi level. This range of energy levels can be called a *band* of energies, and the energy levels are so close together that they are referred to as quasi continuous. In the band of the QMFE model there were an infinite number of unoccupied energy states above the Fermi level that could be occupied by excited electrons. When we introduce the potential of the lattice ions, we will see that bands of this type have upper and lower limits of allowable energies. If a band is not

filled with electrons, then the electrons may be excited into the empty states and contribute to electrical or thermal conduction. If, however, a band is filled, then there are no states to be occupied and the electrons cannot be excited. For conductors, we will see that the behavior of the electrons in the occupied band of highest energy is almost identical to that predicted by the QMFE model, but not so for insulators and semiconductors. The band theory model will solve the questions concerning the differences between conductors and insulators.

2. The electrons respond to an externally applied electric or magnetic field as if they were endowed with an effective mass m^*, which may be greater or smaller than that of the free electron, or even be negative. By this we mean that the electrons can be treated as free in responding to an external electric and magnetic field provided that we assign to them a mass different from the true mass.
3. There are situations in which instead of conduction by electrons it is convenient to attribute the conduction to charge carriers with a positive charge +, called *hole.*

   There are several methods (or models) to show the existence of bands and to find the shape of the band. Some work well for certain materials, some with others, Quantitative band calculations must take into account the particular crystal structure, atomic configuration, and type of bonding. These details belong to the realm of solid-state physics research. Our purpose there is simply to show the existence of bands and the general characteristics. This can be achieved with idealized models and by using qualitative arguments.

2.4 DENSITY OF STATES

Electron Density of States

On combining the *Bohr mo*del and the *de Broglie wave*, we have

$$\lambda = \frac{h}{p} \qquad \text{...(2.1)}$$

This is known as the *de Broglie wavelength.* Using the definition of wavevector $k = 2\pi/\lambda$, we have

$$k = \frac{p}{\eta} \qquad \text{...(2.2)}$$

Knowing the momentum $p = mv$, the possible energy states of a free electron is obtained

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\eta^2 k^2}{2m} \qquad \text{...(2.3)}$$

which is called the *dispersion relation* (energy or frequency-wavevector relation).

Effective Mass

In reality, an electron in a crystal experiences complex forces from the ionized atoms. We imagine that the atoms in the linear chain form the electrical periodic potential. If the free electron mass m is replaced by the effective mass m^*, we can treat the motion of electrons in the conduction band as free electrons. An exact defined value of the wavevector k, however, implies complete uncertainty about the electron's position in real space. Mathematically, localization can be described by expressing the state of the electron as a wave packet, in other words, a *group velocity*. The group velocity of electrons in Figure 2.3 is the slope of the dispersion relation.

$$v_g = \frac{\partial \omega}{\partial k} \qquad \text{... (2.4)}$$

Since the wavelength is twice the lattice constant a, the boundaries at the zone in k-space is $k = \pm \pi/a$. The frequency ω associated with a wavevector of energy E is

$$E = \omega\eta \text{ and } k = \frac{p}{\eta} \qquad \text{...(2.5)}$$

where the two equations are known as the *Planck-Einstein relations.*

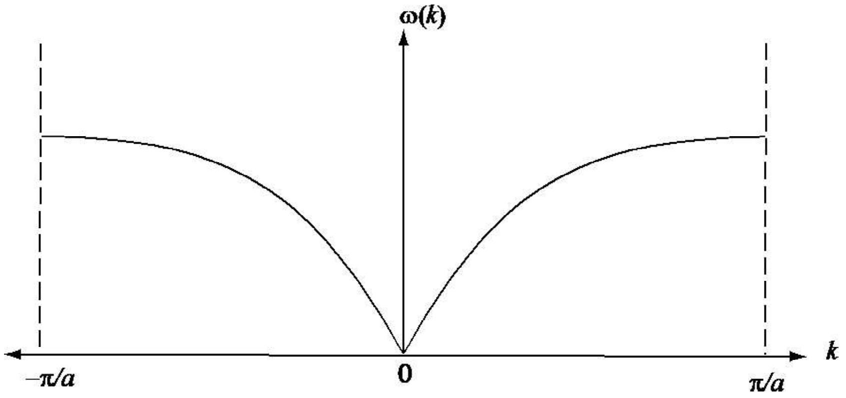

Fig. 2.3 *Dispersion relation of a group of electrons with a nearest neighbor interaction. Note that ω is linear for small k, and that ∂ω/∂k vanishes at the boundaries of the Brillouin zone (k = ± π/a)*

$$v_g = \frac{1}{\eta}\frac{\partial E}{\partial k} \qquad \text{...(2.6)}$$

The derivative of Equation 2.6 with respect to time is

$$\frac{\partial v_g}{\partial t} = \frac{1}{\eta}\frac{\partial^2 E}{\partial k \partial t} = \frac{1}{\eta}\frac{\partial^2 E}{\partial k^2}\frac{\partial k}{\partial t} \qquad \text{...(2.7)}$$

From Equation 2.5 we have $mv_g = \eta k$ and $m\partial v_g |\partial t = \eta \partial k| \partial t$. The force acting on the group of electrons is then

$$F = m\frac{\partial v_g}{\partial t} = \eta\frac{\partial k}{\partial t} \qquad \text{...(2.8)}$$

Combining Equations 2.7 and 2.8 yields

$$F = \frac{\eta^2}{\partial^2 E \partial k^2}\frac{\partial v_g}{\partial t} \qquad ...(2.9)$$

NOTES

This indicates that there is an effective mass m^*, which will replace the electron mass m.

$$\frac{1}{m^*} = \frac{1}{\eta^2}\frac{\partial^2 E}{\partial k^2} \qquad ...(2.10)$$

The effective mass m^* is the second order of derivative of energy with respect to wavevector, which is representative of the local curvature of the *dispersion relation* in three dimensional space. The effective mass is a tensor and may be obtained experimentally or numerically.

Density of States

Thermoelectric materials typically exhibit the directional behavior. Therefore, in general we have

$$E = \frac{\eta^2}{2}\left(\frac{k_x^2}{m_x} + \frac{k_y^2}{m_y}\frac{k_z^2}{m_z}\right) \qquad ...(2.11)$$

where m_x, m_y, and m_z are the principal effective masses in the x-, y-, z-directions and here k is the magnitude of the wavevector.

$$k^2 = k_x^2 + k_y^2 + k_z^2 \qquad ...(2.12)$$

This represents the surface of a sphere with radius k in k-space. We introduce a new wavevectors

k' and an effective mass m' as

$$E = \frac{\eta^2 k'^2}{2m'} = \frac{\eta^2}{2m'}(k_x'^2 + k_y'^2 + k_z'^2) \qquad ...(2.13)$$

Equating Equations 2.11 and 2.13, we have a relationship between the original wavevector and the new wavevector as

$$k_x = \sqrt{\frac{m_x}{m'}}\,k_x', k_y = \sqrt{\frac{m_y}{m'}}k_y', k_z = \sqrt{\frac{m_z}{m'}}k_z' \qquad ...(2.14)$$

In Fig 2.4, we have the volume of a thin shell of radius k and thickness dk.

$$dk = dk_x\, dk_y\, dk_z = \sqrt{\frac{m_x m_y m_z}{m'^3}}\, dk_x' dk_y' dk_z' = \sqrt{\frac{m_x m_y m_z}{m'^3}}\, 4\pi k'^2 dk' \quad ...(2.15)$$

The volume of the smallest wavevector in a crystal of volume L^3 is $(2p/L)^3$ since L is the largest wavelength. The *number of states* between k and $k + dk$ in three-dimensional space is then obtained (see Fig 2.4)

$$N(k)dk \frac{-2.4\pi k'^2}{\left(\frac{2\pi}{r}\right)^3}\sqrt{\frac{m_x m_y m_z}{m'^3}}dk' \qquad ...(2.16)$$

where the factor of 2 accounts for the electron spin (Pauli Exclusion Principle). Now the density of states $g(k)$ is obtained by dividing the number of states N by the volume of the crystal L^3.

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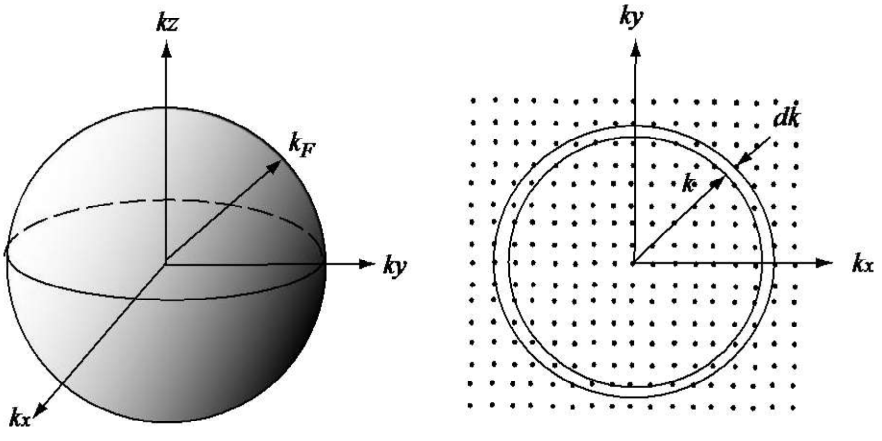
$$g(k)dk\frac{k}{2}\sqrt{\frac{m_x m_y m_z}{m'^3}}dk' \quad ...(2.17)$$



(a) (b)

Fig 2.4 *A constant energy surface in* k*-space: (a) three-dimensional view, (b) lattice points for a spherical band in two-dimensional view.*

From Equation 2.13 we have

$$k' = \frac{\sqrt{2m'}}{\eta}E^{\frac{1}{2}} \quad ...(2.18)$$

Differentiating this gives

$$\frac{dk'}{dE} = \frac{\sqrt{2m'}}{2\eta}E^{-\frac{1}{2}} \quad ...(2.19)$$

Replacing this into Equation 2.17, m' is eliminated. The *density of states per valley* is finally obtained as

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m_d^*}{\eta^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}} \quad ...(2.20)$$

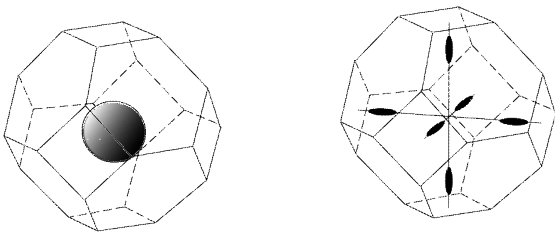
where

$$m_d^* = (m_x m_y m_z)^{\frac{1}{3}} \quad ...(2.21)$$

which is called the *density-of-states effective mass*, and *mx*, *my*, and *mz* are the *principal effective masses* in the x-, y-, z-directions. Most actual band structures for semiconductors have ellipsoidal energy surfaces which require longitudinal and transverse effective masses in place of the three principal effective masses (Fig 2.5). Therefore, the density-of-states effective mass is expressed as

$$m_d^* = (m_l m_t^2)^{\frac{1}{3}} \quad ...(2.22)$$

where m_l is the *longitudinal effective mass* and m_t is the *transverse effective mass*.



(a) (b)

***Fig 2.5** Constant electron energy surfaces in the* Brillouin zones *(space or* k-*space): (a) a* spherical band *such as GaAs; (b) an* ellipsoidal band *such as Si. Si has six identical conduction bands.*

2.5 CHEMICAL POTENTIAL

So far our discussions were mainly confined to closed systems. Now our attention will be on open systems. An open system as defined is one where both exchange of energy and matter takes place. Gibbs free energy is a function of pressure, temperature and volume. Again these parameters are interrelated for a system of fixed composition and we can write $G = f(P, T)$; $G = f(V, T)$; $G = f(P, V)$ and $G = f(P, T)$ is more convenient. But for an open system quantities of components may also vary, so as free energy which is an extensive property will also be dependent on the amount of components. Let a system contain n_1 moles of A, n_2 moles of B, n_3 moles of C etc., then its free energy

$$G = f(P, T, n_1, n_2, n_3, ...)$$

If all the variables undergo change, the total differential will be given by,

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, n_3, ...} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, n_3, ...} dT + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, ...} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, n_3, ...} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{P, T, n_1, n_2, ...} dn_3 + ...$$

It is already known that

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, n_3 ...} = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, n_3 ...} = -S$$

Hence, the equation becomes

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, ...} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, n_3, ...} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{P, T, n_1, n_2, ...} dn_3 + ... \quad ...(2.23)$$

[$\left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, ...}$ means except n_1 all other parameters, i.e., P, T, n_2, n_3 ··· have been kept constant during differentiation.]

The change in free energy per mole addition of a component keeping other components fixed at a fixed temperature is called the partial molar free energy. Hence, $\left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_J}$ for the *i*th component is the partial molar free energy of the *i*th component and also called its chemical potential and is denoted by the symbol m_i.

The chemical potential (m_i) is thus the rate of increase in Gibbs free energy per mole of the component added. But while measuring chemical potential one must take care of two things

(1) Suppose to a given solution containing several components we add very small amount of component *i* and measure its chemical potential. Again chemical potential can also be measured by adding large amount of component *i*. What makes the difference then? In the first case the composition is unaltered (i.e., concentration of components does not vary or if varies that too a negligible amount) but in the second case the composition is altered (i.e., large variations in concentrations of components due to increment in volume). Thus, chemical potential of the same component having same kind of other components vary. Thus, small amount of component should be added to a large amount of system so that the composition remains practically unaltered.

(2) Suppose we want to measure chemical potential of water. This can be done by adding 1 mole water to 1 kg of pure water, 1 kg of sugar solution or 1 kg of salt solution and so on. In these cases the chemical potential of water will not however be the same because in all the three cases the composition is different. Although chemical potential is independent of masses but it is dependent on the composition of a system.

Now at constant temperature and pressure, the equation (2.23) can be rewritten as

$$dG_{P,\ T} = m_1 dn_1 + m_2 dn_2 + m_3 dn_3 + ... = \sum_{i=1}^{N} \mu_i dn_i \qquad ...(2.24)$$

Now suppose at constant P and T we have increased the constituents in the same proportion Dx. That is, component A is increased by an amount $n_1\Delta x$ moles, B by n_2Dx moles, C by $n_3\Delta x$ moles. Hence, $dn_1 = n_1$Dx, $dn_2 = n_2$Dx, $dn_3 = n_3$Dx or in general $dn_i = n_i$Dx.

Now as G is an extensive property, it will also increase by an amount GDx, i.e.

$$dG = G\text{D}x$$

Hence, equation (2.24) under this condition

$$dG = \mu_1 n_1 \text{D}x + \mu_2 n_2 \text{D}x + \mu_3 n_3 \text{D}x + ... + \mu_i n_i \text{D}x$$

or $$G\mathrm{D}x = \mu_1 n_1 \mathrm{D}x + \mu_2 n_2 \mathrm{D}x + \mu_3 n_3 \mathrm{D}x + \ldots + \mu_i n_i \mathrm{D}x$$

Hence, $$G = \mathrm{m}_1 n_1 + \mathrm{m}_2 n_2 + \mathrm{m}_3 n_3 + \ldots + \mathrm{m}_i n_i = \sum_{i=1}^{N} \mu_i n_i \qquad ..(2.25)$$

The complete differentiation of (2.25) will give,

$$dG = \mathrm{m}_1 dn_1 + n_1 d\mathrm{m}_1 + \mathrm{m}_2 dn_2 + n_2 d\mathrm{m}_2 + \mathrm{m}_3 dn_3 + n_3 d\mathrm{m}_3 + \ldots + \mathrm{m}_i dn_i + n_i d\mathrm{m}_i +$$

$$= (\mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \ldots\ \mu_i\, .\, dn_i) + (n_1\, d\mu_1 + n_2\, d\mu_2 + n_3\, d\mu_3 + \ldots\ n_i\, d\mu_i) \qquad ...(2.26)$$

Now subtracting (2.25) from (2.26) we get,

$$n_1\, d\mu_1 + n_2\, \mathrm{d}\mu_2 + n_3\, d\mu_3 + \ldots\ n_i\, d\mu_i = 0$$

or, $$\sum_{i=1}^{N} n_i\, d\mu_i = 0 \qquad ..(2.27)$$

Thus, we have got three very useful relations for chemical potentials with the composition of the system.

(*i*) $G = \mu_1\, n_1 + \mu_2\, n_2 + \mu_3\, n_3 + \ldots = \sum_{i=1}^{N} \mu_i\, n_i$

(*ii*) $dG = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \ldots = \sum_{i=1}^{N} \mu_i\, dn_i$

(*iii*) $0 = n_1\, d\mu_1 + n_2\, d\mu_2 + n_3\, d\mu_3 + \ldots = \sum_{i=1}^{N} n_i\, d\mu_i$

These three equations are commonly known as *Gibbs–Duhem relations*.

For a pure substance obviously chemical potential $\mu = \frac{G}{n}$, i.e., free energy per mole.

One of the important application of Gibbs-Duhem equation is prediction of condition of equilibrium. For simplicity we consider the phase of a component in equilibrium having free energies $\bar{G}_1$ and $\bar{G}_2$. Now at equilibrium, if an intinitenimal amount (*dn*) gm-moles of a component passes from phase 1 to phase 2. Then from Gibbs-Duhem relationship

$$\mu_1\, dn_1 + \mu_2\, dn_2 = dG = 0 \quad \text{or} \quad \mu_1(-\,dn) + \mu_2(dn) = 0$$

$$\text{or} \quad \mu_1 = \mu_2 \quad \text{or} \quad \bar{G}_1 = \bar{G}_2$$

The chemical potential or partial molal free energy of a component in every phase must be the same under conditions of equilibrium.

Check Your Progress

3. What is effective mass?
4. What is partial molar free energy?

2.6 PARAMAGNETISM OF A FREE ELECTRON

Paramagnetism is due to the presence of unpaired electrons in the material, so 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.

The discussion above makes no assumptions about the detail of the *density of states* within the conduction band. Despite this simplification, it predicts the magnetisation reasonably accurately and demonstrates the fact that the magnetisation of a metal is independent of temperature. We can derive a more accurate formula if we use the density of states according to the *free electron gas* model of a metal, *i.e.* treat the delocalised electrons of the atom as independent from the atom cores (nuclei and localised inner-shell electrons) and allow them to move freely like a gas. This model predicts the number N of states per volume element at a particular energy E as

$$N(E)=1/3\pi^2(2meE/\hbar^2)^{3/2} \qquad \text{... (2.28)}$$

and thus the density of states D(E) (density here refers to how densely packed the states are on an energy scale) as

$$D(E)=dN/dE=1/2p^2(2me/\hbar^2)^{3/2}\sqrt{E} \qquad \text{...(2.29)}$$

When placed in a magnetic field, the potential energy of the parallel and anti-parallel aligned moments is shifted down and up, respectively, by the magnetic interaction p_mB, resulting in a relative shift of $2p_mB$ between the parabola segments for the two different orientations. The Fermi energy still applies across the whole electron gas, resulting in a larger population of electrons with parallel aligned moments than anti-parallel ones. The (anti-)parallel population is

$$N_{\uparrow\uparrow,\uparrow\downarrow}=1/2\int_{-pmB}^{Ef} f(E)D(E^{-+}p_mB)dE \qquad \text{...(2.30)}$$

where the density of states D has been shifted according to the strength of the magnetic interaction, but the Fermi distribution remains unchanged since it applies to the electron gas as a whole. The integral consists of a part corresponding to the number of states in the absence of an external field and an almost trapezoidal area near the Fermi energy which is affected by the shift:

$$N_{\uparrow\uparrow,\uparrow\downarrow}\approx 1/2\int_{-pmB}^{Ef} f(E)D(E^{-+}p_mB)dE - 1/2p_mBD(E_F) \qquad \text{...(2.31)}$$

The magnetisation arises from the population difference:

$$M=p_m(N_{\uparrow\uparrow}-N_{\uparrow\downarrow})=p^2{}_mD(E_F)B \qquad \text{...(2.32)}$$

The density of states at the Fermi energy $D(E_F)$ in the free electron gas model is $D(E_F)=3N/2E_F$, so the magnetisation becomes

$$M_{metal}=3Np^2{}_mB/2E_F \qquad \text{...(2.33)}$$

It confirms the result from the less sophisticated model apart from a factor 3/2.

2.7 HALL EFFECT

NOTES

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.

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 2.6. In an n-type semiconductor electrons are the majority carries.

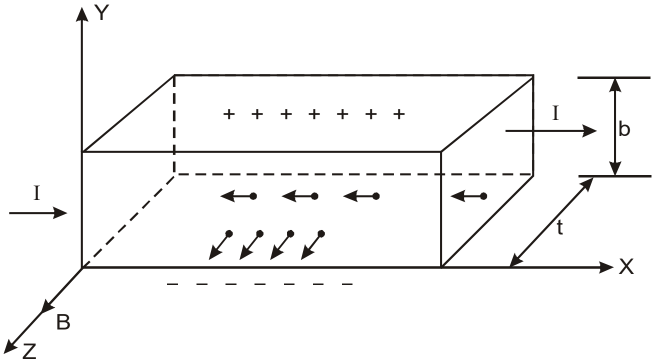


Fig. 2.6 *Hall Effect*

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

$$F_L = -Bev_d \quad ...(2.34)$$

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

$$F_E = -eE_H \quad ...(2.35)$$

At equilibrium, the Lorentz force and the electric force gets balanced. Hence,

$$F_E = F_L$$

Therefore, from Equations (2.35) and (2.36)

$$-eE_H = -Bev_d$$

or

$$E_H = Bv_d \quad ...(2.36)$$

If b is the width (i.e., the distance between the top and bottom surface) of the specimen, then

$$E_H = \frac{V_H}{b} \qquad ...(2.37)$$

or $$V_H = E_H\, b \qquad ...(2.38)$$

and $$V_H = Bv_d b \qquad ...(2.39)$$

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.

If J is the current density, then,

$$J = \frac{I}{bt} \qquad ...(2.40)$$

But, J can also be expressed as

$$J = -n_e e v_d$$ where n_e is the density of electrons. ...(2.41)

$$\therefore \quad v_d = \frac{-J}{n_e e} \qquad ...(2.42)$$

Hence, substituting Equation (2.41) in Equation (2.42)

$$V_H = -Bb\,\frac{J}{n_e e} \qquad ...(2.43)$$

But, V_H is also equal to E_H b

$$\therefore \quad E_H\, b = -Bb\frac{J}{n_e e}$$

or $$E_H = \frac{-BJ}{n_e e} \qquad ...(2.44)$$

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 $$R_H = -\frac{1}{n_e e} \qquad ...(2.45)$$

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 $$R_H = \frac{1}{n_h e} \qquad \text{...(2.46)}$$

NOTES

where n_h is the density of holes.

Therefore, Equation (2.46) can be written as

$$E_H = BJ\,R_H$$

i.e., $$R_H = \frac{E_H}{JB} \qquad \text{...(2.47)}$$

But, we know $E_H = \frac{V_H}{b}$ and $J = \frac{I}{bt}$. Hence Equation (2.47) becomes,

$$R_H = \frac{V_H bt}{IBb}$$

$$\therefore \quad R_H = \frac{V_H t}{IB} \qquad \text{...(2.48)}$$

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 2.7.

A calibrated voltmeter connected between the opposite ends of the slab measures the Hall voltage V_H. Thus, the Hall field is given by

$$E_H = \frac{V_H}{b}$$

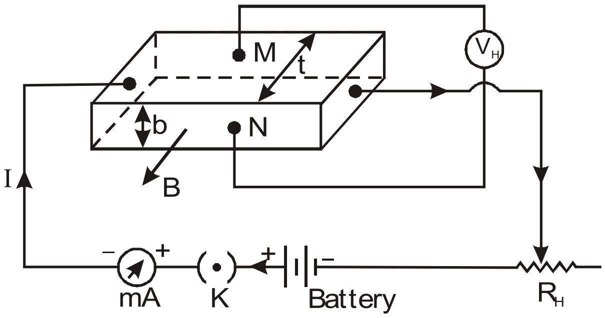


Fig. 2.7 Experimental Setup to Determine Hall Coefficient

The current density is given by

$$J = \frac{I}{bt}$$

Thus, R_H can be calculated using the formula

$$R_H = \frac{V_H t}{IB}$$

NOTES

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.

$$\therefore \quad \mu_e = \frac{\sigma_e}{n_e e} \qquad ...(2.49)$$

$$\text{or} \quad \mu_e = -\sigma_e R_H \qquad ...(2.50)$$

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.

$$\therefore \quad \mu_h = \frac{\sigma_h}{n_h e} \qquad ...(2.51)$$

$$\text{or} \quad \mu_h = \sigma_h R_H \qquad ...(2.52)$$

In the above discussion, it is assumed that all the charge carriers travel with average velocity. But actually, the charge carriers have a random thermal distribution in velocity.

With this distribution taken into consideration, R_H is defined in general as

$$R_H = \frac{3\pi}{8ne} = \frac{1.18}{ne} \qquad ...(2.53)$$

Therefore, Equations (2.51) and (2.53) can be written as

$$\mu_e = \frac{-\sigma_e R_H}{1.18} \quad \text{(For n-type material)} \qquad ...(2.54)$$

$$\text{And} \quad \mu_h = \frac{\sigma_h R_H}{1.18} \quad \text{(For p-type material)} \qquad ...(2.55)$$

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 2.1

The conductivity and the Hall coefficient of a n-type silicon specimen are 112 $\Omega^{-1}m^{-1}$ and $1.25 \times 10^{-13}\ m^3C^{-1}$ 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 $\mu_e = ?$

Formula $\mu_e = \sigma_e\ R_H$

$= 112 \times 1.25 \times 10^{-4}$ **$= 0.014\ m^2V^{-1}s^{-1}$.**

We know $\mu_e = \dfrac{\sigma_e}{n_e e}$.

$$\therefore \quad n_e = \frac{\sigma_e}{\mu_e e} = \frac{112}{0.014 \times 1.6 \times 10^{-19}}$$

$$= \frac{112}{2.24 \times 10^{-21}} = \mathbf{5 \times 10^{22}\ electrons/m^3.}$$

Example 2.2

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.

Solution:

Given,

$l = 12 \text{ mm} = 12 \times 10^{-3}$ m; $t = 1 \text{ mm} = 1 \times 10^{-3}$ m

$b = 1 \text{ mm} = 1 \times 10^{-3}$ m, $I = 20 \text{ m A} = 20 \times 10^{-3}$ A

$v_H = 37\ \mu V = 37 \times 10^{-6}$ V, $B = 0.5$ Wb/m^2.

$R_H = ?$ and $n = ?$

We know

$$R_H = \frac{V_H t}{IB}$$

$$= \frac{37\times10^{-6}\times1\times10^{-3}}{20\times10^{-3}\times0.5} = \frac{3.7\times10^{-8}}{0.01}$$

$$\mathbf{R_H = 3.7 \times 10^{-6}\ C^{-1}\ m^3.}$$

Example 2.3

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, calculate the Hall coefficient, if Hall voltage developed is 1.83 mV.

Solution:

Given,

$t = 1 \text{ mm} = 1 \times 10^{-3}$ m, $b = 10 \text{ mm} = 10 \times 10^{-3}$ m

$l = 100 \text{ mm} = 100 \times 10^{-3}$ m, $B = 0.5$ Wb/m^2

$I = 10^{-2}$ A; $V_H = 1.83 \text{ mV} = 1.83 \times 10^{-3}$ V.

$R_H = ?$

Formula

$$R_H = \frac{V_H t}{IB} = \frac{1.83\times10^{-3}\times1\times10^{-3}}{10^{-2}\times0.5}$$

$$\therefore \quad \mathbf{R_H = 3.66 \times 10^{-4}\ m^3C^{-1}.}$$

Example 2.4

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, $R_H = -7.35 \times 10^{-5}$m^{3}C^{-1}; $\sigma = 200\ \Omega^{-1}m^{-1}$; $n_e = ?$ and $\mu_e = ?$

The negative sign of the Hall coefficient indicates that the nature of the semiconductor is n-type.

NOTES

Formula $n_e = \frac{1}{R_H e} = \frac{1}{7.35\times10^{-5}\times1.6\times10^{-19}}$

$\therefore$ $\mathbf{n_e = 8.503\times10^{22}}$ **electrons / m^3.**

Mobility $\mu_e = \frac{\sigma}{n_e e} = \frac{200}{8.503\times10^{22}\times1.6\times10^{-19}}$

$\therefore$ $\mathbf{\mu_e = 14.7006\times10^{-3} m^2V^{-1}s^{-1}.}$

or

$\mu_e = \sigma\, R_H$

$= 200\times7.35\times10^{-5}$

$\therefore$ $\mathbf{\mu_e = 14.7\times10^{-3} m^2V^{-1}s^{-1}.}$

Example 2.5

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, $R_H = 4.16\times10^{-4}\ m^3C^{-1}$; $\sigma = 180\Omega^{-1}m^{-1}$; n_e = ? and μ_ε = ?

$R_H = \frac{1.18}{n_e e}$ (with correction factor for R_H)

$\therefore$ $n_e = \frac{1.18}{R_H e} = \frac{1.18}{4.16\times10^{-4}\times1.6\times10^{-19}}$

$\therefore$ $\mathbf{n_e = 1.772\times10^{22}/m^3.}$

We know $\sigma = n_e e \mu_e$

$\therefore$ $\mu_e = \frac{\sigma}{n_e e} = \frac{180}{1.772\times10^{22}\times1.6\times10^{-19}}$

$\therefore$ $\mathbf{M\mu_e = 0.06348\ m^2V^{-1}s^{-1}.}$

Example 2.6

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 parallel to X – Z Plane and 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 × 10^{-3} m^3C^{-1}; b = 1cm = 1 × 10^{-2}m

t = 0.5 mm = 0.5 × 10^{-3} m; V_H = ?

$$V_H = \frac{R_H IB}{t} = \frac{1.25\times10^{-3}\times1\times10^{-3}\times0.7}{0.5\times10^{-3}}$$

$= 1.75\times10^{-3}$ V

or $\mathbf{V_H = 1.75\ mV.}$

Example 2.7

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 $8.93\times10^{-3}\Omega m$. 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

$$R_H = \frac{1}{ne}$$

$$\therefore \quad n = \frac{1}{R_H e} = \frac{1}{3.66\times10^{-4}\times1.6\times10^{-19}}$$

$$\mathbf{n = 1.7076 \times 10^{22} / m^3.}$$

Mobility $\mu = \sigma R_H$

or $\mu = \dfrac{R_H}{\rho}$

$$\therefore \quad \mu = \frac{3.66\times10^{-4}}{8.93\times10^{-3}}$$

or $\mathbf{\mu = 0.0409\ m^2V^{-1}s^{-1}.}$

Example 2.8

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

$$R_H = \frac{1}{n_e e}$$

$$\therefore \quad n_e = \frac{1}{R_H e} = \frac{1}{0.0125\times1.6\times10^{-19}}$$

$$\mathbf{n_e = 5 \times 10^{20} / m^3.}$$

$$\sigma_e = n_e e\, \mu_e = 5 \times 10^{20} \times 1.6 \times 10^{-19} \times 0.36$$

$$\therefore \quad \mathbf{\sigma_e = 28.8\ \Omega^{-1}\ m^{-1}.}$$

We also know $J = \sigma_e E$

$\therefore$ $J = 28.8 \times 100$

or $\mathbf{J = 2880\ A/m^2.}$

2.8 FERMI ENERGY

We know 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,

$$e^{\left(\frac{2E_F}{k_B T}\right)} = \left(\frac{m_h^*}{m_e^*}\right)^{3/2} e^{\left(\frac{E_v + E_c}{k_B T}\right)} \qquad ...(2.56)$$

Taking logarithm on both sides,

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

[The RHS of Equation (2.56) has been written using the formula ln (*a*b) = ln*a* + lnb].

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

$$\therefore \quad ME_F = \frac{3k_B T}{4}\ln\left(\frac{m_h^*}{m_e^*}\right) + \frac{E_v + E_c}{2} \qquad ...(2.57)$$

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

$$E_F = \frac{E_v + E_c}{2}\text{, Since} \quad \ln(1) = 0 \qquad ...(2.58)$$

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

...(2.59)

As shown in Figure 2.8(*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 2.8. At T = 0 K, the Fermi level lies exactly in the middle of forbidden gap as shown in Figure 2.8(*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, in actual case $m_e^* > m_h^*$. 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. Thus the Fermi level gets raised slightly as shown in Figure 2.8(*b*) as T increases.

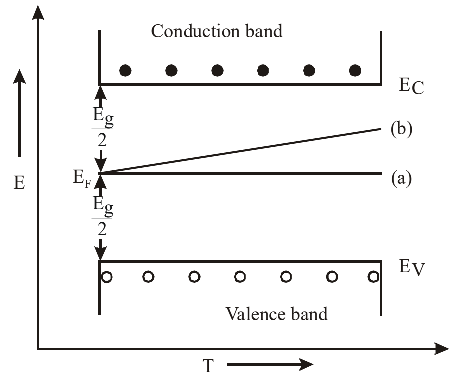


Fig. 2.8 *Position of Fermi Level in an Intrinsic Semiconductor at Various Temperatures*

Check Your Progress

5. What is the cause of paramagnetism?
6. What is Hall effect?

2.9 BLOCH'S THEOREM

For a free electron with $E_{p\,=}$ constant, the space part of the wave function $\psi(x,t)$, *called the eigenfunction* $X(x)$, *is written as*

$$X(x) = e^{\pm ibx} \qquad ...(2.60)$$

If the spacing of the ions in the *x* direction in a solid is *d*, then the potential energy of an electron at a point X distance from the origin is equal to the potential energy at a point *x+d* from the origin. This potential energy is equal in turn to that it point *x+2d* from the origin, and so on. Therefore, we can generalize and take any point x in the lattice and state that the potential energy at that point is equal to the potential energy at point *x+d* or, state mathematically, $E_P(x) = E_P(x+d)$. This is known as periodic potential. There is a theorem by Bloch which state that for a particle moving in a periodic potential, the eigen functions *X(x)* are of the form

$$X(x) = 14_k(x)e^{ibx} \qquad ...(2.61)$$

where

$$14k(x)=14_k(x+ d)$$

These eigen functions are plane waves modulated by a function $14_k(x)$, *where* $14_k(x)$ has the same periodicity as the potential energy. Because the potential energy $E_P(x) = E_P(x+d)$, one expects that the probability of finding a particle at a given *x* is the same.

In quantum mechanics the potential energy is often called the potential.

As that of finding it at *x+d.* This is guaranteed by the periodicity of 14_k and can be seen in the following expression for the probability density.

$$X^*(x)X(x) = 14^*_k(x)e^{-ikx}\ 14_k(x)e^{ikx} \qquad ...(2.62)$$

$$14^*_k(x)\ 14_k(x)$$

Therefore, when

$$14_k(x) = 14_k(x+d)$$

then

$$X^*(x)X(x) = X^*(x+d)X(x+d) \qquad \ldots(2.63)$$

The specific from of the function $14_k(x)$ will depend on the form of the function $E_p(x)$. We will now consider an idealized, one-dimensional periodic potential.

2.10 KRONIG-PENNEY MODEL

The Kronig–Penney model (named after Ralph Kronig and William Penney) is a simple, idealized quantum-mechanical system that consists of an infinite periodic array of rectangular potential barriers.

Consider a particle of mass m having a total energy E moving in a one-dimensional potential $V(x)$. The state of the particle described by the wavefunction $\psi(x)$ satisfies the time-independent Schrödinger equation,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x) = 0 \qquad \ldots(2.64)$$

The solutions of the above equation give the energy eigenfunctions $\psi_n(x)$ belonging to different energy eigenvalues E_n for the particle.

Equation (2.64) can be solved exactly only when (i) the potential function $V(x)$ is stated explicitly and (ii) the boundary conditions imposed on the system, i.e., on the wavefunction $\psi(x)$ are known exactly.

The nature of the states of the particle is determined completely by the energy of the particle and the nature of the potential function $V(x)$. We encounter the following results with respect to the energy eigenvalues and states:

(i) The eigenvalues form a *discrete-spectrum* corresponding to *bound* states.

(ii) The eigenvalues form a *continuous spectrum* corresponding to unbound states.

(iii) The eigenvalues form a mixed spectrum consisting of a discrete spectrum for some range of energy E and a continuous spectrum outside that range.

In the sections to follow we shall illustrate the above results by considering some important problems of one-dimensional motion.

The important properties of one-dimensional motion that we find are:

(i) In case of bound states, the energy spectrum is not only discrete but is non-degenerate also.

(ii) The eignfunction $\psi_n(x)$ for a bound state has 'n' number of nodes if the ground state corresponds to $n = 0$ and $(n - 1)$ number of nodes if the ground state corresponds to $n = 1$.

2.11 CONCEPTS OF HOLE AND EFFECTIVE MASS

NOTES

In this section, we will discuss the concept of hole and effective mass.

Hole

The concept that electrons near the top of the band have negative effective mass leads to a very interesting feature that has a tremendous importance in the operation of all semiconductor devices.

At T = 0 K, the band structure of a semiconductor is characterized by a fully occupied valence band and a completely empty conduction band. The semiconductor ideally is an insulator with zero conductivity at T = 0 K. As the temperature is raised, some electrons in the valence band can receive enough thermal energy and be excited into the conduction band because the energy gap between the two bands is rather narrow.

The result is that there are some electrons in an otherwise empty conduction band and some unoccupied states in an otherwise filled valence band. An empty state in the valence band is called a *hole*.

The electrons in the conduction band can move under the influence of an external electric field because they have available to them many empty higher energy states, and they can contribute to the current density *J*. Similarly, the electrons in the valence band can move into the empty states (holes) left by the electrons that were excited into the conduction band. We will assume, based on our previous discussion, that the empty states at the top of the valence band are *negative effective mass states*.

The interesting and important feature that we mentioned before is that *the conduction by the electrons in the valence band as they move into the empty negative mass states is completely equivalent to the conduction by particles of positive charge and positive mass. The number of such +q, +m particles is equal to the number of available empty states, that is, the number of "holes"*. Basically, what we are saying is that when considering the contribution to the electric current from the valence band, we ignore the electrons, and instead we treat it as if conduction took place via positively charged holes.

Convention is that it is negative if the predominant type of carrier is the electron, and positive if it is the hole. Regardless of the complexities involved in the calculation of R_H when both types of carriers are present, it should be clear that R_H could never be positive if holes were not a reality. Some examples of the value of the Hall coefficient are listed in Table 2.1.

Table 2.1 *Value of Hall Coefficients*

	R_H
Solid	(m^3/C)
Lithium	-17×10^{-11}
Sodium	-25×10^{-11}
Beryllium	$+24 \times 10^{-11}$
Zinc	$+3 \times 10^{-11}$
Cadmium	$+6 \times 10^{-11}$

It can be seen in this table that some well-known metal conduct electricity with holes as the predominant charge carrier.

We conclude this with a comment about the behaviour of holes. Consider the situation, where a few electrons have been excited into the conduction band of the semiconductor leaving behind an equal number of holes at the top of the valence band. As we indicated earlier in this section, if additional energy is provided to the charge carriers of the semiconductor, such as by the application of an external electric field, the electrons in the valence band will move up into the empty states (the holes). When this happens, the holes move down from their initial position in the valence band. Because we have decided to ignore the electrons in the valence band and instead consider only the holes, we conclude that when energy is provided to the carriers in the valence band, the holes move down, or putting if differently, the energy of the holes *increases downward* from the top of the valence band. This fact will be used to calculate the hole concentration in the valence band of a semiconductor.

Effective Mass

When an electric field $\mathcal{E}$ acts on a free electron, it exerts a force $e\mathcal{E}$, that, from Newton's law, will produce acceleration inversely proportional to its mass, $a = e\varepsilon/m$. What happens when the electron to be accelerated is not free but happens to be in a crystal under the influence of the potential of the lattice ions? The answer is that it will still accelerate according to Newton's law; however, the electron responds as if it had some *effective mass*, which is different from its true mass. As we will show, this is because is not the only electric field acting on the electron inside the crystal.

We will introduce this concept by using a semi-classical picture: an argument that is half classical and half quantum mechanical. The quantum mechanical part lies in the fact that the motion of an electron is governed by a wave, and that the velocity of the electron is equal to the group velocity v_{group} of the wave, that is, the velocity of the envelope, of the wave packet. In our treatment of matter waves and wave packets , we saw that the group velocity is given by;

$$v_{group} = \frac{dE}{dp} \qquad ...(2.65)$$

where E is the energy of the particle and p is its momentum.

NOTES

In the case of a free particle, we can readily show that the group velocity is equal to the particle velocity. For a free particle, the energy

$$E + \frac{1}{2}m\upsilon_{particle} = \frac{p^2}{2m} \qquad ...(2.66)$$

Therefore

$$\upsilon_{\text{group}} = \frac{\text{dE}}{\text{dp}} = \frac{\text{d}}{\text{dp}}\left(\frac{\text{p}^2}{2\text{m}}\right) = \frac{\text{p}}{\text{m}} = \frac{\text{M}\upsilon_{\text{particle}}}{\text{m}} = \upsilon_{\text{particle}} \qquad ...(2.67)$$

Although we have shown that group $\upsilon_{\text{group}} = \text{M}\upsilon_{\text{particle}}$ for the free particle case only, it can be shown that the relation holds even when the particle is not free, such as the case of an electron in a lattice.

Equation 2.67 defines the group velocity in terms of the energy *E* and the momentum *p* of the particle. As we have seen in the Kronig-Penney model, the energy is often expressed in terms of the wave vector *k*. It is convenient, therefore, to define the group of velocity in terms of *E* and *k*. This can be done by using de Broglie's relation $p = h/\lambda$ and the fact that $\lambda = 2\pi/k$. Combining equations we have $p = hk$ and hence $dp = hdk$. Substituting this result for *dp* in Equation 2.67, we obtain

$$\upsilon_{\text{group}} = \frac{1}{h}\frac{dE}{dk} \qquad ...(2.68)$$

The classical part of the argument uses the definition from mechanics that if a force does not work *dW* on a particle, the energy of that particle increases by the same amount *dE=dW*. Applying this to the present case, we have

$$dE = dW = e\mathcal{E}\,dx = e\mathcal{E}\frac{dx}{dt}\,dt = e\mathcal{E}\,v_{\text{g}}\,dt \qquad ...(2.69)$$

The rate at which the energy of the particle is changing is therefore

$$\frac{dE}{dt} = e\mathcal{E}\,v_{\text{g}} \qquad ...(2.70)$$

We also know from Newton's law that when a force acts on a particle, it will be accelerated. By definition, the acceleration *a* is

$$a = \frac{\text{d}\upsilon_{\text{particle}}}{dt} = \frac{dv_{\text{g}}}{\text{dt}}$$

Substituting for υ_{g} we

$$a = \frac{1}{h}\frac{d}{dt}\frac{dE}{dk}$$

Interchanging the order of the differentiation of *E*, we may write

$$a = \frac{1}{h}\frac{d}{dk}\frac{dE}{dt} \qquad ...(2.71)$$

Substituting Eq. 2.70 for *dE/dt* in Eq. 2.71 yields

$$a = \frac{e\mathcal{E}}{h}\,\frac{dv_{\text{g}}}{\text{dt}}$$

From Eq. 2.69, it follows that

$$a = \frac{1}{h^2}\frac{d^2E}{dk^2}\, e\mathcal{E}$$

Rearranging terms, we get

$$e\mathcal{E} = \frac{h^2}{\frac{d^2E}{dk^2}}\, a \qquad \text{...(2.72)}$$

Noting that is the force of the externally applied electric field, we conclude that Eq. 2.72 has the form $F = m^*a$, where

$$m^* = \frac{h^2}{\frac{d^2E}{dk^2}} \qquad \text{...(2.73)}$$

The response of the electron in the solid to an externally applied electric field is as if it had an effective mass m^* given by the expression in Eq. 2.73. Let us see if Eq. 2.73 gives the correct result for the free electron case. For the free electron we have

$$\mathrm{E} = \frac{h^2k^2}{2m} \qquad \text{...(2.74)}$$

and

$$\frac{dE}{dk} = \frac{h^2k}{m}\,; \quad \frac{h^2E}{dk^2} = \frac{h^2}{m}$$

Substitute this result into Eq. 2.73 and we obtain

$$m^* = \frac{h^2}{\frac{d^2}{m}} = m \qquad \text{...(2.75)}$$

When the electron is free, the effective mass is the true mass, as it should be. However, when the electron is in a crystal, m^* is different from m because the energy is not proportional to k^2, as we saw in the Kronig-Penney model.

Check Your Progress

7. What is the Kronig-Penney model?
8. How is the band structure of a semiconductor characterized at T = 0 K?

2.12 DISTINCTION BETWEEN CONDUCTORS, SEMICONDUCTORS AND INSULATORS

The effective number of free electrons in a solid in the energy bands is given by

$$n_{eff} = \Sigma f_K = \left(\frac{a}{\pi}\right)\int_{-K'}^{+K'} f_K\, dK$$

$$= \left(\frac{2am}{\pi\hbar^2}\right)\int_0^{K'}\left(\frac{d^2E}{dK^2}\right)dK$$

$$= \left(\frac{2am}{\pi\hbar^2}\right)\left(\frac{dE}{dK}\right)_{K=K'}$$

where, '*a*' is the lattice constant and $E = \frac{\hbar^2K^2}{2m}$. From the above equation, we can say

(*i*) The effective numbers of electrons holds maximum value for a band filled to the inflection point of the $E - K$ curve, because at the point of inflection, $\frac{dE}{dK}$ is maximum, and

(*ii*) The effective number of electrons in a fully filled band vanishes, as $\frac{dE}{dK} = 0$ the top of the band.

Figure (2.9) shows energy (*K*) vs. wave vector (*K*) diagram for the energy band filled up to K' states at $T = 0$K.

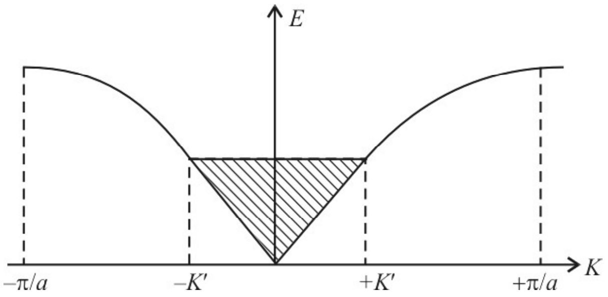


Fig. 2.9 *Energy (*E*) vs. wave vector (*K*) graph for energy band filled up to* K′ *states at* T = *0K*

Metal

A solid is said to be a '*metal*', if the energy band is incompletely filled or partly filled. When an external electric field is applied, the electrons within the metal acquire additional energy from the external applied field and goes to the higher energy states (which is empty) lying close to the filled levels in the incompletely (partly) filled band. This incompletely (partly) filled band which is responsible for the conduction of electrons are termed as '*conduction band*', and the electrons are called 'free electrons'. It is obvious that the electrons in the energy band in a metal are odd in number.

Semiconductor

A substance of which the width of the forbidden energy gap between the valance band and conduction band is proportionally higher than that of a metal is called a '*semiconductor'*. The semiconductor shows an electrical conductivity larger than that of an insulator but less than that of a metal. It is obvious that the electrons in the energy band in a semiconductor are even in number. An intrinsic (pure) semiconductor becomes an insulator at $T = 0$K.

NOTES

Insulator

A substance of which a certain number of energy bands are completely filled, and the other energy bands are completely empty, is called an '*insulator*'. The number of electrons in the outer most shell are even for an insulator. The forbidden energy gap between the valance band (topmost filled band) and conduction band (lowermost empty band) is so wide that a negligible number of thermally excited electrons can jump from valance band to conduction band at room temperature in an insulator. As only a negligible number of electrons are available in the conduction band, the substance is a bad conductor of electricity.

2.12.1 Intrinsic and Extrinsic Conductivity

In this section, we will study about the conductivity of intrinsic and extrinsic semiconductors.

Intrinsic Conductivity

In an intrinsic semiconductor, since the electrons move in nearly empty conduction band while holes move in nearly full valence band, the properties such as mobility, conductivity, etc. of electrons are, in general, different from those of holes. Let *vdn,* pn and *n* denote the drift velocity, mobility and concentration of electrons respectively in the conduction band. Then current density due to electrons is given by

$$J_n = nev_{dn} \qquad \ldots(2.76)$$

where *e* is the electronic charge. We can write drift velocity for the electrons as

$$v_{dn} = \mu_n \mathcal{E}$$

Therefore, from Eq. (2.76), we obtain

$$J_n = ne\mu_n \mathcal{E} \qquad \ldots(2.77)$$

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

$$J_n = \sigma_n \mathcal{E},$$

where an represents the electronic conductivity of the material, we get

$$\sigma_n = ne\mu_n \qquad \ldots(2.78)$$

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

$$\sigma_p = pe\mu_p \qquad \ldots(2.79)$$

where p and μ_p represent the concentration and mobility of holes respectively. Thus the total conductivity of the material is

$$\begin{aligned} \sigma &= \sigma_n + \sigma_p \\ &= e\,(n\mu_n + p\mu_p) \end{aligned} \qquad \ldots(2.80)$$

For an intrinsic semiconductor,

$n = p = n_i$

Therefore, Eq. (2.80) becomes

$$\sigma = en_i\ (\mu_n + \mu_p) \qquad \text{...(2.81)}$$

It is important to note that, in semiconductors, the movement of carriers or the flow of current is, in fact, the consequence of the following two processes:

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

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

In the above treatment, we have considered only the drift current contribution. The diffusion current contribution is absent in semiconductors having a uniform distribution of impurities.

Variation of Conductivity with Temperature

Assuming mobilities to be independent of temperature, the temperature dependence of conductivity arises because of the variation of intrinsic carrier concentration, *n*^ with temperature. It will be proved that *ni* is given by

$$n_i = \frac{2(2\pi kT)^{3/2}}{h^3} \left(m_n^* m_p^*\right)^{3/4} \exp\left(-\frac{E_g}{2kT}\right) \qquad \text{...(2.82)}$$

where m_n* and m * represent the effective masses of an electron and a hole respectively, *E* is the band gap, *k* is the Boltzmann's constant and *T* is the absolute temperature. Substituting *ni* from Eq. (2.82) into (2.81), we get

$$\sigma = e(\mu_n + \mu_p)\ \frac{2(2\pi kT)^{3/2}}{h^3} \left(m_n^* m_p^*\right)^{3/4} \exp\left(-\frac{E_g}{2kT}\right) \qquad \text{...(2.83)}$$

which gives

$$\ln \sigma = -\left(\frac{E_g}{2k}\right)\frac{1}{T} + \frac{3}{2}\ln T + \text{constant} \qquad \text{...(2.84)}$$

The first term on the right hand side is the dominant term. The plot of Ina versus 1/7 is a straight line as shown in Fig. 2.10. The slope of the line gives an estimate of the band gap of the semiconductor.

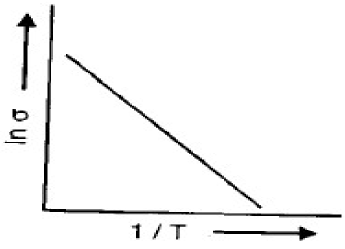


Fig 2.10 *Plot of lns versus 1/T*

Extrinsic Conductivity

The electrical conductivity of an n-type semiconductor can be calculated from

$$\sigma = en\mu_n \cong e\, N_d^{+}\, \mu_n \qquad ...(2.85)$$

where it has been assumed that the conduction is mainly due to electrons. Knowing the electron concentration, n, and the electron mobility μ_n, at any given temperature, the electrical conductivity can be calculated by using the above equation. The temperature dependence of electrical conductivity for an n-type germanium is shown in Fig. 2.11.

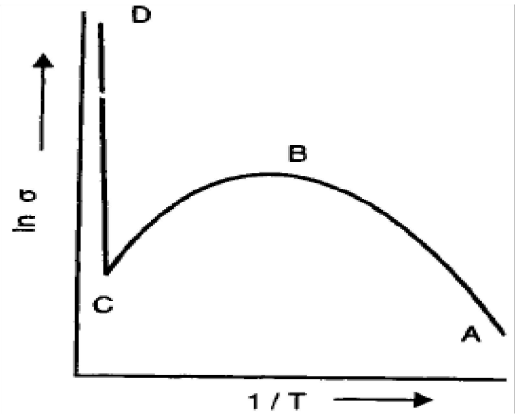


Fig 2.11 *Conductivity versus temperature for a typical n-type germanium sample*

The following conclusions can be drawn from this curve:

(i) Starting from the very low temperature (about 10 K) corresponding to the point A, the conductivity increases with rise in temperature. This is due to the increase in the number of conduction electrons as a result of ionization of the donors. The conductivity attains a maximum value (point B) when all the donors are ionized. The temperature corresponding to this is about 50 K for a moderately doped n-type germanium.

(ii) The conductivity decreases with further increase in temperature up to about room temperature (point C) and is attributed to the decrease in the value of mobility with rise in temperature. There is also an increase in the intrinsic conductivity but to a lesser extent.

(iii) The sharp rise in conductivity from C to D is due to the large increase in intrinsic conductivity which offsets the decrease in mobility.

The electrical conductivity of a p-type semiconductor is given by

$$\sigma_p = ep\mu_p \cong eN_a^{-}\, \mu_p \qquad ...(2.86)$$

where the conduction due to minority carriers has been ignored. The variation of conductivity with temperature is similar to that for the n-type semiconductor.

It also follows from Eqs. (2.80) and (2.86) that the increase in concentration of either type of impurity atoms increases the conductivity of a semiconductor. For impurity concentration ranging from 10^{20} to 10^{22} m^{-3}, the resistivity of Si and Ge varies from 10^{-3} to 10^{-1} ohm-m. If doping is heavy (10^{23} to 10^{24} atoms/m3), the conductivity of semiconductors becomes comparable to metals. Such semiconductors are called *degenerate semiconductors* and find applications in high power and high frequency devices.

Check Your Progress

9. Define conduction band and free electrons.
10. When does an intrinsic (pure) semiconductor become an insulator?

NOTES

2.13 ANSWERS TO 'CHECK YOUR PROGRESS'

1. In the case of a single isolated atom, the electrons in any orbit have a definite energy. As a result, they occupy discrete energy levels. The Pauli exclusion principle allows each energy level to contain only two electrons.
2. The electrons in any orbit of atom within a solid can have a range of energies rather than a single value. Thus, the range of energies possessed by an electron in a solid is known as energy band. i.e., each energy level of an isolated atom becomes a band in a solid.
3. The effective mass m^* is the second order of derivative of energy with respect to wavevector, which is representative of the local curvature of the *dispersion relation* in three dimensional space. The effective mass is a tensor and may be obtained experimentally or numerically.
4. The change in free energy per mole addition of a component keeping other components fixed at a fixed temperature is called the partial molar free energy.
5. Paramagnetism is due to the presence of unpaired electrons in the material, so most atoms with incompletely filled atomic orbitals are paramagnetic, although exceptions such as copper exist.
6. 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.
7. The Kronig–Penney model (named after Ralph Kronig and William Penney) is a simple, idealized quantum-mechanical system that consists of an infinite periodic array of rectangular potential barriers.
8. At T = 0 K, the band structure of a semiconductor is characterized by a fully occupied valence band and a completely empty conduction band.
9. When an external electric field is applied, the electrons within the metal acquire additional energy from the external applied field and goes to the higher energy states (which is empty) lying close to the filled levels in the incompletely (partly) filled band. This incompletely (partly) filled band which is responsible for the conduction of electrons are termed as '*conduction band*', and the electrons are called 'free electrons'.
10. An intrinsic (pure) semiconductor becomes an insulator at $T = 0$K.

2.14 SUMMARY

NOTES

- In the case of a single isolated atom, the electrons in any orbit have a definite energy. As a result, they occupy discrete energy levels. The Pauli exclusion principle allows each energy level to contain only two electrons.
- The electrons in any orbit of atom within a solid can have a range of energies rather than a single value. Thus, the range of energies possessed by an electron in a solid is known as energy band. i.e., each energy level of an isolated atom becomes a band in a solid.
- The free electron models of metals give us a good deal of insight into several properties of metals. Yet there are many other important properties that these models do not explain. In particular, they do not tell us why, when chemical elements crystallize to become solids, some are good *conductors*, some are *insulators,* and yet others are *semiconductors* with electrical properties that vary greatly with temperature.
- QMFE model gave rise to a series of discrete energy states about 10^{-15} eV apart, which ranged from $E \approx O$ to $E = E_{F,}$ the Fermi level. This range of energy levels can be called a *band* of energies, and the energy levels are so close together that they are referred to as quasicontinuous.
- The effective mass m^* is the second order of derivative of energy with respect to wavevector, which is representative of the local curvature of the *dispersion relation* in three dimensional space. The effective mass is a tensor and may be obtained experimentally or numerically.
- An open system as defined is one where both exchange of energy and matter takes place. Gibbs free energy is a function of pressure, temperature and volume. Again these parameters are interrelated for a system of fixed composition and we can write $G = f(P, T)$; $G = f(V, T)$; $G = f(P, V)$ and $G = f(P, T)$ is more convenient. But for an open system quantities of components may also vary, so as free energy which is an extensive property will also be dependent on the amount of components.
- One of the important application of Gibbs-Duhem equation is prediction of condition of equilibrium.
- Paramagnetism is due to the presence of unpaired electrons in the material, so 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.
- 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.
- If the spacing of the ions in the x direction in a solid is d, then the potential energy of an electron at a point X distance from the origin is equal to the potential energy at a point $x+d$ from the origin. This potential energy is equal in turn to that it point $x+2d$ from the origin, and so on.

- The Kronig–Penney model (named after Ralph Kronig and William Penney) is a simple, idealized quantum-mechanical system that consists of an infinite periodic array of rectangular potential barriers.
- At T = 0 K, the band structure of a semiconductor is characterized by a fully occupied valence band and a completely empty conduction band. The semiconductor ideally is an insulator with zero conductivity at T = 0 K. As the temperature is raised, some electrons in the valence band can receive enough thermal energy and be excited into the conduction band because the energy gap between the two bands is rather narrow.
- The electrons in the conduction band can move under the influence of an external electric field because they have available to them many empty higher energy states, and they can contribute to the current density J. Similarly, the electrons in the valence band can move into the empty states (holes) left by the electrons that were excited into the conduction band.
- When the electron is free, the effective mass is the true mass.
- A solid is said to be a '*metal*', if the energy band is incompletely filled or partly filled. When an external electric field is applied, the electrons within the metal acquire additional energy from the external applied field and goes to the higher energy states (which is empty) lying close to the filled levels in the incompletely (partly) filled band. This incompletely (partly) filled band which is responsible for the conduction of electrons are termed as '*conduction band*', and the electrons are called 'free electrons'.
- A substance of which the width of the forbidden energy gap between the valance band and conduction band is proportionally higher than that of a metal is called a '*semiconductor'.*
- A substance of which a certain number of energy bands are completely filled, and the other energy bands are completely empty, is called an '*insulator*'.
- In an intrinsic semiconductor, since the electrons move in nearly empty conduction band while holes move in nearly full valence band, the properties such as mobility, conductivity, etc. of electrons are, in general, different from those of holes.

2.15 KEY TERMS

- **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.
- **Hall effect:** 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.
- **Fermi Energy:** The Fermi energy is a concept in quantum mechanics usually referring to the energy difference between the highest and lowest occupied single-particle states in a quantum system of non-interacting fermions at absolute zero temperature.

- **Effective Mass:** In solid state physics, a particle's effective mass 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.

NOTES

2.16 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the band theory of solids.
2. What do you mean by the band structure in solids?
3. State the Kronig-Penney model.
4. State the concept of Fermi energy.
5. What are the applications of Hall Effect?
6. State Bloch's theorem.
7. Mention the electric conductivity of n-type and p-type semiconductors.

Long-Answer Questions

1. Discuss briefly the band theory of solids with the help of examples.
2. Analyse the Kronig-Penney model giving examples.
3. Explain the properties of electrons when the interaction between them and the lattice ions is considered.
4. Explain paramagnetism of a free electron.
5. Describe the Hall Effect.

2.17 FURTHER READING

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UNIT 3 MAGNETISM

NOTES

Structure

3.0 INTRODUCTION

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 include most chemical elements and some compounds; they 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, so 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. Materials that are called "Paramagnets" are most often those that exhibit, at least over an appreciable temperature range, magnetic susceptibilities that adhere to the Curie or Curie–Weiss laws. In principle any system that contains atoms, ions, or molecules with unpaired spins can be called a paramagnet, but the interactions between them need to be carefully considered. Paramagnets do not retain any magnetization in the absence of an externally applied magnetic field because thermal motion randomizes the spin orientations. Some paramagnetic materials retain spin disorder even at absolute zero, meaning they are paramagnetic in the ground state, i.e. in the absence of thermal motion.

Ferromagnetism is the strongest type and is responsible for the common phenomenon of magnetism in magnets encountered in everyday life. Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets, or are attracted to magnets. In physics, several different types of magnetism are distinguished.

Ferromagnetism is very important in industry and modern technology, and is the basis for many electrical and electromechanical devices such as electromagnets, electric motors, generators, transformers, and magnetic storage such as tape recorders, and hard disks, and non-destructive testing of ferrous materials. Permanent magnets (materials that can be magnetized by an external magnetic field and remain magnetized after the external field is removed) are either ferromagnetic or ferromagnetic, as are the materials that are noticeably attracted to them. Only a few substances are ferromagnetic. The common ones are iron, cobalt, nickel and most of their alloys, and some compounds of rare earth metals.

Ferromagnetic materials can be divided into magnetically "Soft" materials like annealed iron, which can be magnetized but do not tend to stay magnetized, and magnetically "Hard" materials, which do. Permanent magnets are made from "Hard" ferromagnetic materials such as alnico, and ferromagnetic materials such as ferrite that are subjected to special processing in a strong magnetic field during manufacture to align their internal microcrystalline structure, making them very hard to demagnetize. Ferromagnetism is an unusual property that occurs in only a few substances. The common ones are the transition metals iron, nickel, cobalt and their alloys, and alloys of rare earth metals. It is a property not just of the chemical make-up of a material, but of its crystalline structure and microstructure. There are ferromagnetic metal alloys whose constituents are not themselves ferromagnetic, called Heusler alloys, named after Fritz Heusler. In this unit, you will study about the classification of magnetic materials, quantum theory of paramagnetism, origin of magnetic domain, Nuclear Magnetic Resonance, Electron Paramagnetic Resonance and Mossbauer Effect.

3.1 OBJECTIVES

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

- State the classification of magnetic materials
- Discuss the quantum theory of paramagnetism
- Explain the Weiss molecular field theory
- Interpret the ferromagnetic domains
- Describe the Nuclear Magnetic Resonance and Electron Paramagnetic Resonance
- Discuss the Mossbauer effect and the applications of Mossbauer spectroscopy

3.2 ELEMENT IDEAS OF MAGNETISM

Magnetic materials are classified into different categories based on their magnetic parameters (like 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 classified broadly into the following three categories.

1. Diamagnetic materials,
2. Paramagnetic materials, and
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, and
5. Ferrimagnetic materials.

Materials which lack permanent dipoles are called diamagnetic.

If the atoms or molecules of a material have permanent dipoles, such a material may be paramagnetic,ferromagnetic,antiferromagnetic or ferrimagnetic, depending on the interaction between the individual dipoles.

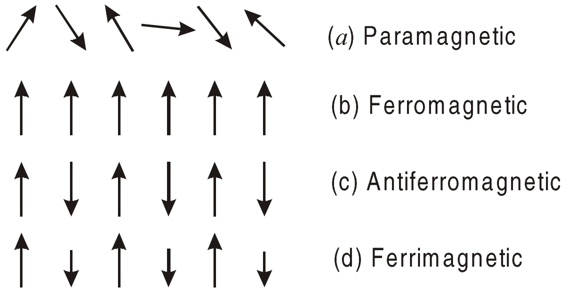


Fig. 3.1 *Illustration of Arrangement of Permanent Magnetic Dipoles in a Paramagnetic, Ferromagnetic, Antiferromagnetic and Ferrimagnetic Material*

If the interaction between the permanent dipoles is either negligible or if they do not interact among themselves as shown in Figure 3.1(*a*), the materials is paramagnetic.

If the magnetic dipoles interact in such a way they tend to orient in the same direction as shown in Figure 3.1(*b*), the material is ferromagnetic.

If the neighbouring dipoles orient in opposite directions and if the dipoles are of equal magnitude as shown in Figure 3.1(*c*), the materials is antiferromagnetic.

On the otherhand, if the neighbouring dipoles are of different magnitude and orient themselves in anti-parallel direction as shown in Figure 3.1(*d*), then the material is ferrimagnetic.

Table 3.1 Summary of Classification of Magnetic Materials on the Basis of Orientation of Dipoles

NOTES

Classification	Permanent dioples	Interaction between neighbouring dipoles
Diamagnetic	Absent	—
Paramagnetic	Present	Negligible.
Ferromagnetic	Present	Parallel orientation.
Antiferromagnetic	Present	Anti-parallel orientation of equal magnitude.
Ferrimagnetic	Present	Anti-parallel orientation of unequal magnitude.

It has been observed through many studies in the past that electrons revolve around the nucleus in circular orbits. A moving electron can be considered as an electric current whereas it also demonstrates a magnetic dipole moment normal to the plane in which the electron is orbiting. As the direction of the revolution of an electron flips the direction of the magnetic moment also turns in the opposite direction. Now, according to Langevin's theory, the paired electrons in the atoms of a diamagnetic substance revolve in such a way that the magnetic moments caused by them cancel out each other. As a result, no net magnetic moment is obtained by the orbital motion of the electrons. Therefore, it can be stated that all electrons are paired in an atom of a diamagnetic material. When a magnetic field is applied perpendicular to the plane of the orbiting electron, the angular velocity of the revolving electron would change without any change in the radius. The change in the angular velocity will depend upon the direction of the magnetic field. The variation in the angular velocity causes a variation in the magnetic moment of the atom.

3.3 QUANTUM THEORY OF PARAMAGNETISM

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.

General Properties of Paramagnetic Materials

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.
10. **Examples**: Platinum, aluminium, copper sulphate, magenese sulphate and the salts of iron and nickel.

Check Your Progress

1. How are the magnetic materials classified?
2. State the quantum theory of paramagnetism.
3. Mention the general properties of paramagnetic materials.

3.4 ORIGIN OF MAGNETIC DOMAIN

Pierre-Ernest Weiss (25 March 1865, Mulhouse – 24 October 1940, Lyon) was a French physicist specialized in magnetism. He developed the domain theory of ferromagnetism in 1907. Weiss also developed the molecular or mean field theory, which is often called Weiss-mean-field theory, which lead to the discovery of the Curie-Weiss law.

According to Weiss, in a real gas, the molecules are mutually influenced by their magnetic moments and consequently, there should exist a molecular field, within the gas. This field, produced at any point by all the neighbouring molecules, is proportional to the same logic as the intensity of magnetization. Let this internal molecular field be represented by H_i. Then,

$$H_i = \lambda M$$

Here, λ is molecular field coefficient. M is the magnetization.

Then, the effecting field is,

$$H_e = H + H_i = H + \lambda M$$

According to Langevin's theory of paramagnetism,

$$M = nm^2 \mu_0 H / 3KT = \mu_0 M^2_s H/3nkT$$

m = Magnetic moment of each atoms.

n = Number of atoms per unit volume.

H = Magnetic field intensity.

K = Boltzmann's constant.

T = Absolute temperature.

$M_s = nm$ = Saturation value of magnetization.

Weiss replaced H by H_e. Therefore,

$$M = \mu_0 M^2_s (H + \lambda M) / 3nkT \qquad ...3.1$$

Now,

Volume susceptibility $\chi_m = M/H = \mu_0\, nm^2 (H + \lambda M)/3kTH$

i.e., $\chi_m = \mu_0 nm^2 /3kT = + \lambda\mu_0 nm^2 /2kT\, \chi_m$

Or $\chi_m = (1 - \lambda\, \mu_0 nm^2 /2kT) = \mu_0 nm^2 /3kT$

$$\chi_m = (\mu_0 nm^2 /3kT) = (\mu_0 nm^2 /3k) / \mathrm{T} - \lambda\, \mu_0 nm^2 /(T - \lambda\, \mu_0 nm^2 /3k) = C/T - \theta \qquad ...3.2$$

Equation 3.2 is known as Curie-Weiss law. The constant θ is known as Curie temperature. Curie-Weiss law shows that below Curie temperature ($T < \theta$), susceptibility becomes negative. However, it should be noted that for most of the paramagnetic substances, Curie temperature is quite low so that a situation for which $T < \theta$ is rare.

Langevin's theory of paramagnetism was modified by Weiss through introducing the concept of internal fields. Weiss supposed that in a real gas, the molecules influence each other via their magnetic moments. A molecular field should exist within the gas. This field at any point, contributed by all the coordinating molecules, is directly proportional to the intensity of magnetization.

At that time, Weiss also introduced a theoretical concept of ferromagnetic domains. The atoms of the ferromagnetic material align in the same direction in a small region due to certain mutual exchange interaction. It was named as a domain. Therefore, Weiss's theory of ferromagnetism is also known as domain theory of ferromagnetism. Some main points of this theory are the following:

(1) The size of the domains aligned fairly along the direction of the applied magnetic field at the cost of the domains oriented in another direction. The domains aligned opposite to the applied field get reduced. Overall, the domain boundaries (also known as domain walls) move to expand the domain in a favorable orientation.

(2) Likewise, domains rotate and orient themselves along the external magnetic field. When a weak external field is applied, the process of magnetization in the material happens mostly because of the growing domain, however, in the case of a strong magnetic field, the material is mostly magnetized through domain alignment. After that when the field is removed, the domain walls do not get back their original positions, therefore, the material is not demagnetized completely. Some residual magnetism remains in this. Thereafter, in 1907, Weiss postulated molecular field theory to deduce the prominent features of ferromagnetism.

3.4.1 Ferromagnetism 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 3.2.

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.

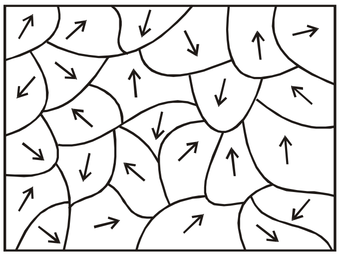
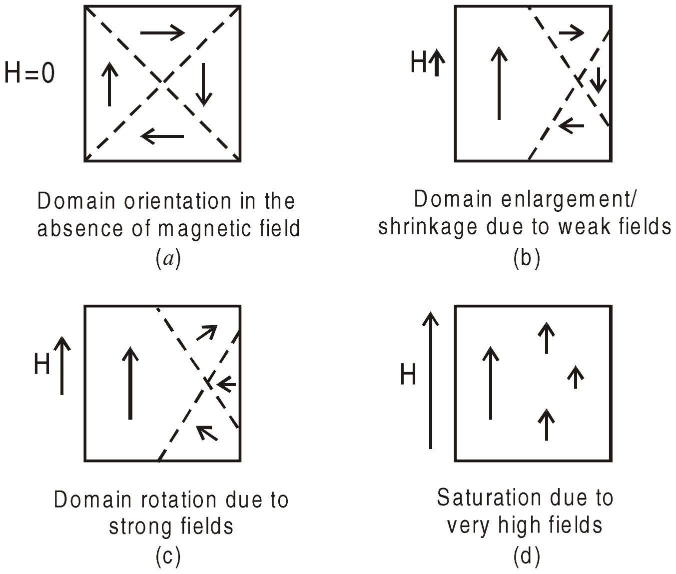


Fig. 3.2 *Random Orientation of Magnetic Moments of the Domains*

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 3.3. 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 3.3(*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. 3.3 *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 or
2. Due to the rotation of domains magnetic moments and
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 (Figure 3.3(*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 (Figure 3.3(*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 (Figure 3.3(*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.

Check Your Progress

4. Define the Weiss molecular field theory.
5. What do you mean by the ferromagnetism domains?
6. State the effect of external magnetic field on the domains.

3.5 NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.

The energy of radio frequency wave having frequency of 10^7 to 10^8 cycle per second is about 6.6×10^{-20} to 6.6×10^{-19} ergs. The energy is too small to rotate, vibrate or excite an atom or molecule but sufficient to affect the nuclear spin of atoms in a molecule. Thus, by absorption of radio frequency radiation direction of spin of nuclei of atoms in a molecule may change.

Without a magnetic field, the spin state of nuclei is degenerate, i.e. of same energy, and energy level transition is not possible. But when an external magnetic field is applied, the degeneracy is broken and the radio frequency radiation can cause transition between the energy levels.

The nuclear spin, is the resultant of angular momenta of all the nuclear particles, the protons and neutrons. The protons and neutrons by virtue of their spin on their own axis posses the angular momentum $\frac{1}{2}\left(\frac{h}{2\pi}\right)$. The nuclear spin is given by $\sqrt{I(I+1)}\frac{h}{2\pi}$ where I is the spin quantum number. The net spin of a nucleus depends on the number of particles. The rules of determining net spin of a nucleus are as follows:

NOTES

1. A nucleus with odd mass number has a half integral spin $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \text{ etc.}\right)$.
2. A nucleus with odd number of protons and odd number of neutrons has an integral spin. (1, 2, 3, etc.)
3. A nucleus with even number of protons and even number of neutrons has zero spin.

Thus ^{12}C, ^{16}O which have net spin zero will not respond to NMR. On the other hand, for ^{13}C which has odd mass number ($N = 7$ and $P = 6$) the spin is $\frac{1}{2}$ and respond to NMR and so is the case with ^{1}H and ^{11}B.

NMR techniques helps us to study the shape and structure of molecules. The most important application of NMR is in the study of hydrogen atoms in organic molecules.

Radio Frequency Absorption: The Cause and Effect

A nucleus is positively charged. Any electrical charge in motion sets up a magnetic field and hence a nucleus due to its motion (spinning) also generates a magnetic field and possesses magnetic moment. The magnetic moment, μ, is proportional to its spin angular momentum,

$$\mu = \gamma \times \text{spin angular momentum}$$

$$= \gamma \times \sqrt{I(I+1)}\frac{h}{2\pi}$$

where h is Planck's constant and ν is called the gyromagnetic ratio, a fundamental nuclear constant.

Now, when a nucleus is placed in a homogeneous external field of strength say H_O, it will behave as a magnet and tend to orient itself in relation to the field. For a nucleus with spin quantum number I, the number of possible orientations is given by $(2I + 1)$.

Thus, a proton with spin quantum number 1/2 there is a possibility $\left(2 \times \frac{1}{2} + 1 = 2\right)$ of two orientations with respect to the axis of the external field.

The two orientations will be

(*i*) Alignment with the field, and

(*ii*) Alignment against the field.

In the absence of an external magnetic field, these orientation are of equal energy. When external magnetic field is applied, energy levels split corresponding to $m_I = -\frac{1}{2}$ (antiparallel to the direction of magnetic field) and to $m_I = +\frac{1}{2}$ (parallel to the direction of magnetic field). The energy for a particular level is given by

NOTES

$$E = \pm \frac{\gamma h}{2\pi}\ \mathrm{mH_0}\ (\text{‘}m\text{’ is the magnetic quantum number})$$

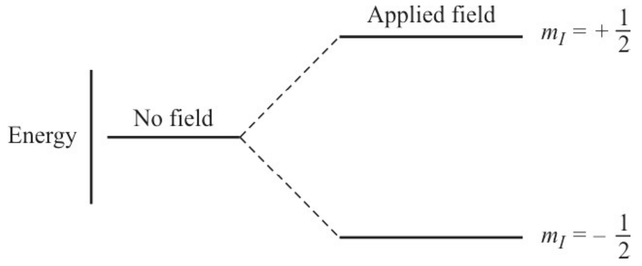


Fig. 3.4 *Energy level splitting of spin $\frac{1}{2}$ nucleus in an applied magnetic field*

Thus, energy with $m_I = -\frac{1}{2}$ and $+\frac{1}{2}$ respectively, is

$$E_1 = -\frac{1}{2}\left(\frac{\gamma h}{2\pi}\right)\mathrm{H_0}$$

and $$E_2 = +\frac{1}{2}\left(\frac{\gamma h}{2\pi}\right)\mathrm{H_0}$$

When the nucleus absorbs energy it is promoted from a lower energy state E_1 to higher energy state E_2, i.e., the nucleus precessing in the aligned orientation, passes into opposed orientation. From higher energy opposed orientation it can come back to the lower energy aligned orientation by losing energy. The transition from one energy state to the other is called flipping. The difference in energy $\Delta E(E_2 - E_1)$ changes the magnetic moment from parallel state $m_I = +\frac{1}{2}$ to antiparallel state $m_I = -\frac{1}{2}$.

$$\Delta E = E_2 - E_1 = h\nu$$

or $$\nu = \frac{E_2 - E_1}{h} = \frac{\frac{1}{2}(\gamma H/2\pi)H_0 + \frac{1}{2}(\gamma h/2\pi)H_0}{h}$$

or $$\nu = \frac{\gamma}{2\pi}H_0$$

where ν = Frequency in cycle per sec. or Hz,

H_0 = Strength of applied magnetic field in gauss,

γ = Nuclear constant or gyromagnetic ratio and is equal to 26750 for the proton.

It is therefore seen that the frequency absorbed or emitted by a nucleus in its transition from one energy level to the other is directly proportional to the applied magnetic field (H_0).

The stronger the applied field, greater will be the tendency of the nuclear magnet to remain lined up with it and higher will be the frequency needed to flip the proton to the higher energy state.

Now when the nuclei is irradiated with a beam of electromagnetic radiation of desired frequency, the lower energy nuclei will absorb it and move to higher energy state. The precessing proton will absorb energy from the radio-frequency region only if the precessing frequency is exactly equal to the frequency of radio frequency region, i.e., when the quantum energy ($h\nu$) of the radiation matches up the energy difference between the two energy states at the applied field strength H_0. When this occurs, the nucleus and the radio frequency beam are said to be in resonance. Hence, the term nuclear magnetic resonance (NMR).

In NMR techniques, mainly organic compounds are exposed to a powerful magnetic field. The different sets of protons will precess at different frequencies (protons might have different environment around it) and now if these precessing protons are irradiated with steadily changing frequencies at some frequency/frequencies resonance condition will be established leading to absorption. In NMR it is the absorption of energy which is detected. It is, however, more convenient to keep the radio frequency constant and change the magnetic field strength constantly. At some value of the field strength resonance condition will occur and energy of the radiation will be absorbed. The absorption will produce a signal. The signal at the detector is amplified and recorded as a band in the spectrum. Such a spectrum is called Nuclear Magnetic Resonance Spectrum.

All protons of a compound however, do not absorb at the same applied field. The absorption depends on the magnetic field a proton feels. One set of protons might have different environment to other protons. Thus, at a given radio frequency, different protons (different sets of equivalent protons) will require slightly different applied magnetic field strength to have some effective field strength which causes absorption. Therefore, in the NMR spectra the number of signals at different applied field strengths is equal to the number of different sets of equivalent protons.

Absorption Line Width in NMR

The width of absorption line is affected by a number of factors such as:

1. **The Homogeneous field:** The absorption line width is mainly controlled by applied magnetic field H_0. If the applied field H_0 (which may be 1 - 2 inch long) is not constant throughout the sample medium, the frequency of absorption for different part of the sample will be different resulting in wide absorption line. This ultimately may lead to an overlap with neighbouring peaks causing wrong interpretation.
2. **Relaxation:** Relaxation process involves some non-radiative transitions through which nucleus returns from upper state to lower energy state or lower spin state. The relaxation may be due to (*i*) spin-spin interaction (*ii*) spin-lattice interaction.
    (*i*) **Spin-spin relaxation:** For two nuclei in close proximity if the magnetic field strength of one nuclei is the same as that required to induce transition in other nuclei, energy may be transferred from one nuclei to

the other. The total energy however, is always conserved but the energy is spread from one nuclei to the other causing line broadening in NMR spectra. Such phenomena is more prominent in solids.

(*ii*) **Spin-lattice relaxation (Longitudinal relaxation):** In this case, the energy of a nucleus in its higher energy state is transferred to crystal lattice as translational, rotational or vibrational energy. The total energy of the system is, however, always conserved. Such a spread of energy also causes line broadening. Smaller the time the nuclei is in the excited state, greater is the line width.

Number of Signals

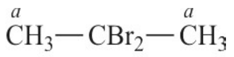
Equivalent and Non-Equivalent Protons

A set of protons having identical environments are called equivalent protons while the protons with different environments are known as non-equivalent protons. Protons with different environment absorb at different applied field strength, whereas protons with identical environment absorb at the same field strength.

It should be remembered that, magnetically equivalent protons are also chemically equivalent. Therefore, equivalent protons simply mean chemically equivalent protons.

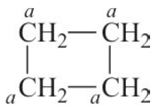
The number of signals in a PMR as we deal with mainly proton, NMR is replaced by PMR (Proton Magnetic Resonance). Spectrum tells us how may kinds of protons are present in a given molecule.

For example



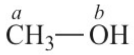
$\overset{a}{CH_3}-CBr_2-\overset{a}{CH_3}$ All protons equivalent, only 1 PMR signal

2, 2-Dibromopropane



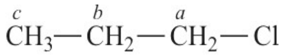
All protons equivalent, only 1 PMR signal

Cyclobutane



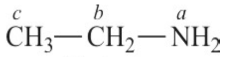
$\overset{a}{CH_3}-\overset{b}{OH}$ Two kinds of protons, two PMR signals

Methyl alcohol



$\overset{c}{CH_3}-\overset{b}{CH_2}-\overset{a}{CH_2}-Cl$ Three kinds of protons, three PMR signals

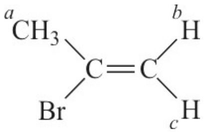
n-Propyl chloride



$\overset{c}{CH_3}-\overset{b}{CH_2}-\overset{a}{NH_2}$ Three kinds of protons, three PMR signals

Ethylamine

Again, chemically equivalent protons must also be stereo-chemically equivalent. For example in case of 2-bromopropene, $CH_3-C(Br)=CH_2$



From the structure, it is expected that there will be two sets of equivalent protons and hence two PMR signals. But the stereochemical formula reveals three sets of protons as H^b and H^C are not in exactly similar environments and three PMR signals are obtained.

Chemical Shift

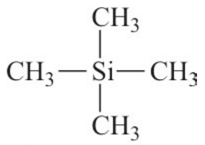
The number of signals in a PMR spectrum tell us how many kinds of protons are present in a given molecule.

The positions of the signals indicate the nature of protons, viz., aliphatic, vinylic, aromatic adjacent to some electron attracting or electron releasing group etc. The protons absorb at different applied field strengths due to different electronic environments around it. It is really the electronic environment which dictates the position of absorption by protons.

Rotation of electrons, especially the π-electrons, around a nuclei generates magnetic field. Again when a molecule is placed in a magnetic field the electrons around the nuclei are perturbed, their rotations are influenced and secondary magnetic fields or induced magnetic field are generated. The induced magnetic field of electrons in turn can either oppose or reinforce the applied field at the proton. If the induced field opposes the applied field, then the proton is said to be **shielded**. If on the other hand the induced field reinforces the applied field, the proton will feel a much higher field strength and proton is said to be **deshielded**. Shielding shifts the absorption upfield and deshielding shifts the absorption downfield to have an effective field strength for absorption.

The shifts in the position of NMR or PMR signals (compared with a standard reference) resulting from the shielding and deshielding by electrons are called chemical shifts.

For measurement of chemical shifts there must be some standard signal with respect to which the measurement should be made. For this purpose, tetramethyl silane (TMS), $(CH_3)_4$ Si, is used as the reference or standard compound.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3$$

Tetramethyl silane

TMS is used as reference compound because:

1. TMS has 12 equivalent protons and hence gives only one very intense signal.
2. The electronegativity of silicon is very low (1.8 compared to 2.5 for carbon), therefore shielding of equivalent electrons in TMS is more compared to almost all other organic compounds. Consequently, with reference to TMS signal, almost all other signals appear in the downfield direction.
3. TMS is chemically inert and has a low boiling point (27 ºC or 300 K) and thus can easily be removed after measuring a spectrum.
4. It is miscible with almost all organic substances.

The NMR signal of a particular proton in a molecule appears at different field strengths compared to TMS signal. This difference in the absorption position of the proton with reference to the TMS signal is called the chemical shift (δ-value). Equivalent protons give same chemical shift, conversely, protons with same chemical shifts are called equivalent protons. Non-equivalent protons have different chemical shifts. The magnitude of δ is given by

NOTES

$$\delta = \frac{H_0(\text{reference}) - H_0(\text{sample})}{H_0(\text{reference})}$$

Now, $$\nu = \frac{\gamma}{2\pi}H_0$$

Hence, in terms of frequency unit

$$\delta = \frac{\nu\,(\text{sample}) - \nu\,(\text{reference})}{\nu\,(\text{reference})} = \frac{\Delta\nu}{\nu\,(\text{reference})}$$

where Δν is the frequency shift.

The value of H_0 for reference is usually greater than H_0 for the sample, hence, δ will be positive. The chemical shift, δ is dimensionless and is expressed in parts per million (ppm).

An alternative system which is generally used for defining the position of the resonance relative to the reference is assigned Tau (τ) scale. On this scale, the reference is assigned an arbitrary position of 10 and the value of other resonances is given by

$$\tau = 10 - \delta$$

and 'δ' has the same significance as defined. In the δ scale, position of the TMS signal is taken as 0.00 ppm and most chemical shifts have values between 0 and 10. A small magnitude of δ means a small downfield shift and vice versa.

On the τ scale, the signal for the standard reference TMS is taken as 10 ppm and in most chemical shifts it is taken as 10 ppm and most chemical shifts have values between 0 and 10. A small magnitude of τ represents a low-field absorption and vice versa.

NMR signal is usually plotted with magnetic field strength increasing to the right. Hence, signal for highly shielded TMS appears at the extreme right of the spectrum with δ = 0.00 ppm. Greater the deshielding of protons, larger will be the value of δ (or smaller value of τ). For most of the organic compounds, signal appears downfield to the left of TMS signal. The relationship between TMS signal, δ and τ values and the effect of shielding and deshielding on chemical shifts has been depicted (Fig. 3.5).

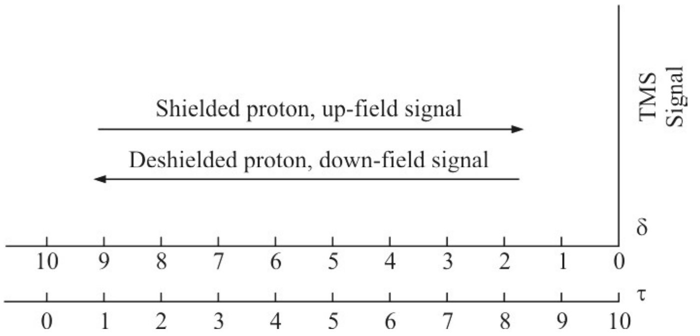
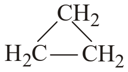


Fig. 3.5 *The relationship between TMS signal, d and t values and their effect on shielding and deshielding on chemical shifts*

Table 3.2 *Typical Proton Chemical Shifts*

NOTES

Types of protons		*Chemical shift,* δ	*ppm* τ
Cyclo-propane		0.2	9.8
Primary	$R—CH_3$	0.9	9.1
Secondary	R_2CH_2	1.3	8.7
Tertiary	R_3CH	1.5	8.5
Vinylic	$—\overset{\vert}{C}{=}CH$	4.6–5.8	5.4–4.2
Acetylenic	$—C{\equiv}CH$	2–3.5	8–6.5
Aromatic	Ar—H	6–8.5	4–1.5
Alkyl Fluoride	$—\underset{\vert}{\overset{\vert}{CH}}—F$	4–4.5	6–5.5
Alkyl Chloride	— CH— Cl	3–4	7–6
Alkyl Bromide	$—\underset{\vert}{\overset{\vert}{CH}}—Br$	2.5–4	7.5–6
Alkyl Iodide	— CH — I	2–4	8–6
Alcohols	$—\overset{\vert}{CH}—OH$	3.4–4	6.6–6
Ethers	$—\overset{\vert}{CH}—O—R$	3.3–4	6.7–6
Esters	$—\underset{\vert}{\overset{\vert}{CH}}—COOR$	2–2.2	8–7.8
Acids	—CH—COOH	2–2.5	8–7.5
Hydroxy	R — OH	1–5.5	9–4.5
Phenolic	Ar — OH	4–12	6 to –12
Aldehydic	RCHO	9–10	1–0
Carbonylic	RCOOH	10.5–12	– 0.5 to – 2
Amine	$R — NH_2$	1–5	9–5

Factors Influencing Chemical Shift

There are mainly three factors influencing chemical shifts:

1. Inductive effect,
2. Anisotropic effect,
3. Hydrogen bonding.

1. **Inductive Effect:** The protons in a molecule are surrounded by moving electrons which shield these protons from the applied magnetic field. But if the electron density around the proton is reduced, the shielding effect is also reduced, conversely if the electron density around the proton is increased there will be greater deshielding. An electronegative atom attached to a molecule will withdraw an electron, thus reducing the electron

density around the proton and deshielding it. Greater the electronegativity of the atom, greater is the deshielding caused to the proton.

For example

$$\overset{b}{CH_3} \rightarrow\!\!- \overset{a}{CH_2} \rightarrow\!\!- Cl \qquad\qquad \overset{b}{CH_3} \rightarrow\!\!- \overset{a}{CH_2} \rightarrow\!\!- F$$

Ethyl chloride Ethyl fluoride

For two of the above compounds two signals are expected. However, deshielding for proton '*a*' in ethyl chloride is less than that of proton '*a*' of ethyl fluoride as '*F*' is more electronegative than 'Cl'.

Again as the distance of electronegative element increases, the deshielding effects also reduce. Thus, for proton '*b*' there will be less deshielding compared to proton '*a*'.

On the other hand, an electron releasing group (such as alkyl) increases the electron density around the proton and gives rise to its shielding.

2. **Anisotropic Effects (Space Effect):** The shielding and deshielding effects on a proton due to induced magnetic field in other parts of a molecule operating through space are known as anisotropic effects. Such effects are observed in compounds having π bonds. For example, alkynes, benzene, annulene, aldehydes, etc.

   When a magnetic field is applied to a molecule having π-electrons, these electrons begin to circulate at right angles to the direction of the applied field thereby producing induced magnetic field which influences the nearby proton causing shielding or deshielding. The shielding or deshielding which takes place will depends upon the orientation of the proton with respect to the π-bond producing the induced field.

3. **Hydrogen Bonding:** In case of hydrogen bonding, the hydrogen bonded proton is attached to a highly electronegative element. For example, in case of phenol $C_6H_5—\ddot{\underset{\cdot\cdot}{O}}—H$, the hydrogen is bonded to the more electronegative 'O' atom and hence the electron is pulled by 'O' and consequently there is small electron density around hydrogen bonded proton. Being less shielded, the field felt by the proton is more and resonance will occur down field. In case of intermolecular hydrogen bonding the effect is not pronounced.

Solvents used in NMR

The solvent used in NMR should be (1) chemically inert toward the sample, (2) it should be free from proton, and (3) it must be capable of dissolving at least 10% of the substance under investigation. The common solvents used in NMR spectroscopic study are carbon tetrachloride (CCl_4), carbon disulfide (CS_2), deuterated chloroform ($CDCl_3$), deuterated water (D_2O), trifluoroacetic acid (CF_3COOH), dimethyl sulfoxide (DMSO) etc.

However, it is still observed that NMR spectrum of even a completely deuterated solvent shows one or more peaks. It is due to the presence of minor impurities in the solvent.

Interpretation of NMR Spectra

NMR spectrum gives very valuable information about the structure of the molecule. The total information gathered can be summarised as follows:

1. The number of signals in the PMR spectrum tells us how many kinds of protons in different chemical environments are present.
2. The positions of signals tell us the electronic environments of each kind of atom.
3. The intensities of different signals tell us about the relative number of protons of different kinds.
4. The splitting of signals tells us about the environment of the absorbing proton with respect to the environments of the neighbouring protons.

Peak Area and Proton Counting

In a NMR spectrum the number of signals or peaks represents the different kinds of protons. The area of each peak tells the number of protons in each set. Squares under each peak are counted from the spectra and the ratio between various kinds of protons is found out. These ratios are then converted to whole numbers. These whole numbers or some multiplies of it tell the number of protons in various NMR signals.

For example, in the NMR spectra of acetaldehyde. Two signals are obtained, showing two different types of protons in the compound. The areas under the two peaks are found to be in the ratio of 3 : 1. Hence, in acetaldehyde, 3 protons are of one kind and 1 proton is of another kind.

Splitting of Signals

In the NMR spectra when the resolution is very high, instead of single peak, the peaks are found to consist of fine structures. For example, the NMR spectra of ethanol $CH_3—CH_2—OH$.

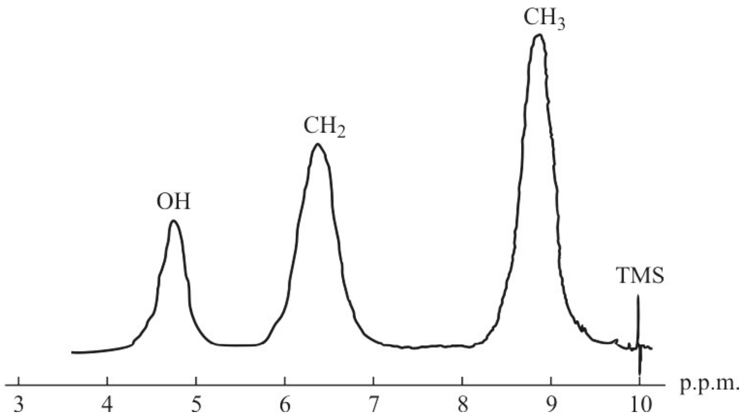


***Fig. 3.6* (a)** *1 HNMR spectrum of ethanol*

NOTES

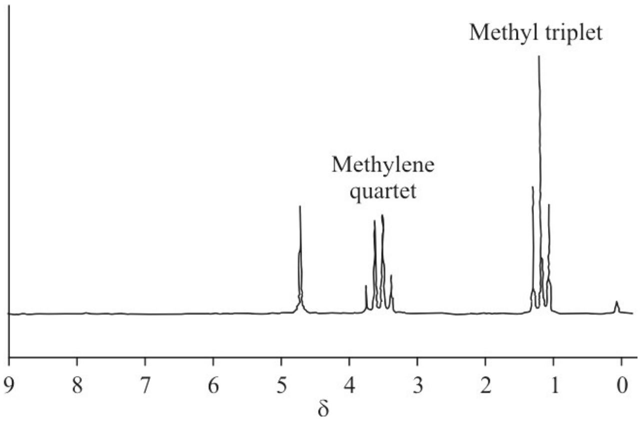


***Fig. 3.6 (b)** 1 HNMR spectrum of ethanol at high resolution instruments*

In this case, the peak for CH_2 produces four closely packed absorption lines and CH_3 group three. This is due to interaction between the neighbouring nuclei, i.e., spin-spin coupling.

The spins of two protons (— CH_2—) can couple with the adjacent methyl group (— CH_3) in three different ways relative to the external field. The three different ways of alignments are

(*i*) ↑ ↑ (Reinforcing)
(*ii*) ↓ ↑ ↑ ↓ (Not effecting)
(*iii*) ↓ ↓ (Opposing)

↑ External Field

Thus, a triplet of peaks results in the intensity ratio of 1 : 2 : 1 which corresponds to distribution ratio of alignment.

Similarly, the spin of three protons (CH_3—) can couple with the adjacent methylene group (—CH_2—) in four different ways relative to the external field.

(*i*) ↑ ↑ ↑ (Strongly reinforcing)
(*ii*) ↑ ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↑ (Weakly reinforcing)
(*iii*) ↓ ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↓ (Weakly opposing)
(*iv*) ↓ ↓ ↓ (Strongly opposing)

↑ External Field

The quartet of peaks results with an intensity ratio of 1 : 3 : 3 : 1 which corresponds to the distribution ratio of all the alignments.

Mathematically, it can be shown that, the relative intensities of the individual lines of a multiplet correspond to the numerical coefficient of the lines in the binomial expression.

$$(1+x)^n = 1 + x \text{ if } n = 1$$

when $n = 2$

$$(1+x)^2 = 1 + 2x + x^2.$$

Thus, the lines of the triplet have relative intensities 1 : 2 : 1

for $n = 3$

$$(1 + x)^3 = 1 + 3x^2 + 3x + x^3$$

Thus, the lines of the quartet formed due to the influence of three equivalent protons will have relative intensities 1 : 3 : 3 : 1.

The splitting of a signal is due to the different environment of the absorbing proton with respect to nearby protons and not with respect to electrons.

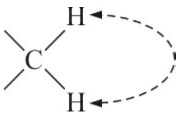
The mutual coupling between — OH and — CH_2 — does not take place. It is because the — OH proton is rapidly exchanging, i.e., does not stay in the same environment long enough for its coupling with — CH_2 — protons and hence — OH proton is seen as a singlet.

Coupling Constant (J)

The distance between the peaks in a given multiplet (fine structures) is a measure of magnitude of splitting effect. This is known as coupling constant and is designated by the symbol J, which is expressed in cycle per second or Hertz (Hz). Whereas chemical shift is dependent on applied field, the coupling constant is independent of the applied field but depends on the structure of a molecule.

In case of mutually coupled protons the magnitude of splitting of signal of one proton by the other is the same. The coupling constant is determined by the nature of the bond and the spatial relations between the protons.

1. For protons attached to the same carbon atom (i.e., geminal protons), the value of J varies from 0–20 Hz depending on bond angle and overall structure of the molecule.



$J = 0 – 20$ Hz

2. For protons attached to adjacent carbon atoms (i.e., vicinal protons), the value of J depends on the dihedral angle.

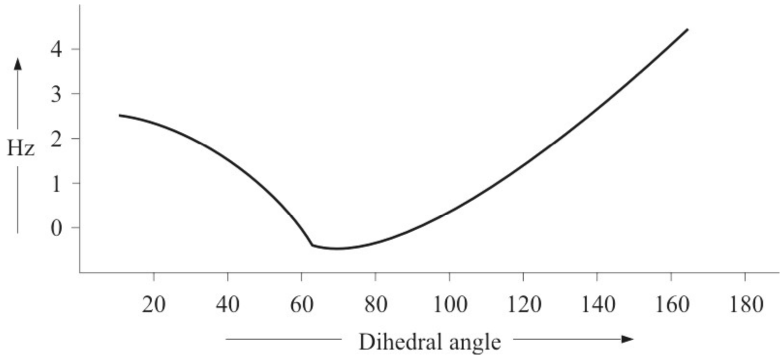
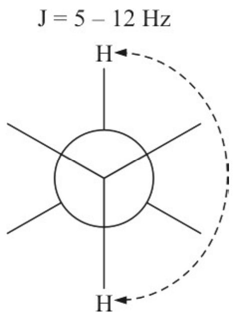


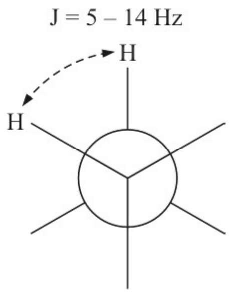
Fig. 3.7 *Variation of J with dihedral angle*

For 0º and 180º, coupling constants is higher. At 90º 'J' is slightly negative.

In case of ethane (C_2H_6), which has freely rotating groups, protons with anti conformation have 'J' value 5–12 Hz while protons with gauche conformation have $J = 2 – 4$ Hz.



Anti



Gauche

Coupling constants are a measure of the effectiveness of spin-spin coupling and are helpful in determining complex molecular structures.

Applications of NMR Spectroscopy

NMR spectroscopy is used for detailed investigations of an unknown compound.

1. Identification of isomers and conformers
2. Identification of double bond character
3. Detection of aromaticity
4. Detection of hydrogen bonding
5. Detection of electronegative atom or group
6. Quantitative analysis

3.5.1 Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) is similar to the nuclear magnetic resonance (NMR) as they both illustrate the case of resonance of an atomic particle as a result of high-frequency electromagnetic radiation absorption when an external magnetic field is present. NMR is related to nucleus, whereas EPR is related to the unpaired electron.

After applying an external magnetic field, spin energy levels split, and electrons spin either aligned to or opposite to the direction of the magnetic field. An energy difference (ÄE) takes place due to the splitting of the spin energy levels. Consequently, the number of electrons aligned parallel to the external magnetic field and occupying the lower energy level becomes more than those aligned antiparallel to the external magnetic field and occupying the upper energy level.

Spectrometer Structure

A conventional continuous wave (cw) spectrometer is represented in Figure 3.7. The figure is composed of four groups:

1. Source components
2. Magnet system
3. Detection system
4. Modulation system

The first group, source components, produces the electromagnetic radiation and holds the sample to be subjected to the incident waves. It also controls and guides the incident microwaves. The function of magnet system is to help in providing the required magnetic field which is necessary for splitting the energy level. The modulation system and the detection system amplify and record the received signal.

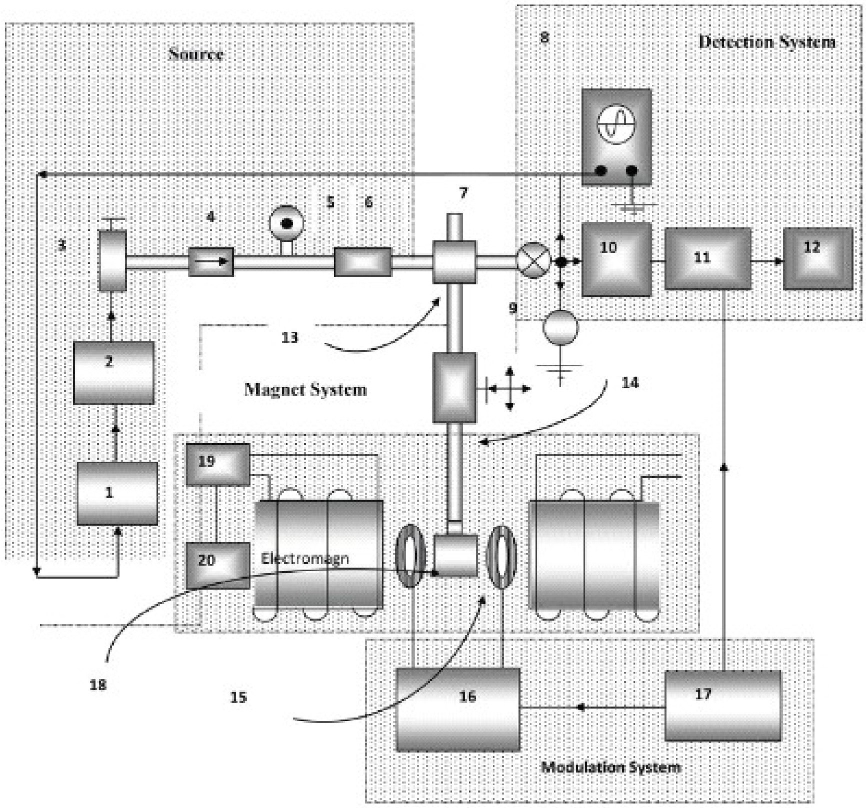


Fig 3.8 *Block diagram of a typical X-band EPR spectrometer employing 100 kHz phase-sensitive detection. (1) Automatic frequency control. (2) Microwave source power supply. (3) Microwave source (klystron or Gunn diode). (4) Isolator. (5) Frequency counter. (6) Attenuator. (7) Terminating load. (8) Oscilloscope. (9) Detector crystal. (10) 100 kHz signal amplifier. (11) 100 kHz signal detector. (12) Pen recorder and data bank (or computer). (13) Circular or hybrid tee. (14) Cavity system. (15) 100 kHz modulation coils. (16) 100 kHz power amplifier. (17) 100 kHz oscillator. (18) Resonant cavity. (19) Magnet power supply. (20) Field scan drive [3].*

The higher the frequency is used, the more intensive magnetic field is needed to reach the resonance.

3.6 MÖSSBAUER EFFECT

Mossbauer Effect is concerned with the phenomenon of resonance fluorescence of gamma rays. It is comparable to resonance fluorescence in optical regions, but involves intra nuclear rather than electronic energy levels. An important characteristic of this radiation, under optimum conditions of measurement, is the extreme sharpness of the lines.

The resonance gamma ray of ^{67}Zn, e.g. has a width at half height of only 4.8 × 10^{-11} eV, but with a photon energy of approximately 93 keV, less than 1 part in 10^{15}. This may be compared with the Zn K_α X-ray which has a half height width of 4.7 × 10^{-8} eV for a photon of 8.6 keV, or about 1 part in 10^{11}.

The recoil energy of nucleus emitting γ-rays destroys the exact conditions for observing resonant absorption and scattering by the same type of nucleus. Assuming free recoil of the radiating nucleus, the nuclear recoil energy is $E^2/M.c^2$, where E is the energy of the -rays.

R.L. Mossbauer (1958) demonstrated resonance absorption in ^{191}Ir by a different system. He used source and ^{191}Ir as the absorber, both cooled at low temperature. The source decays by β emission to an excited state at 129 KeV of the stable . The half life of this state is 1.3 x sec and its natural width = 3 x The recoil energy of the free nucleus would be 0.047 eV corresponding to a Doppler shift = 3.6 x . Mossbauer therefore made an important discovery that emission of 129 KeV y-radiation of ^{191}Ir is sometimes not accompanied by the recoil of the nucleus. The recoil momentum and energy are transferred to the crystal as a whole, and even for a tiny crystalline source the effect of this recoil energy is negligible.

By far the greatest amount of work has been done on ^{57}Fe, with ^{61}Ni and ^{119}Sn following. There are about 32 elements in which the effect has been observed, and 17 more in which it is to be expected. *The importance of chemistries is enough to ensure this technique a place among instrumental methods. The theory of recoilless emission shows that Mossbauer Effect is most likely to occur it.*

The energy E is small: The best example is the 14.4 KeV transition of ^{57}Fe. The latter is therefore most extensively studied element. This is because the nuclear energy levels of ^{57}Fe are most easily accessible. This nuclide has a metastable energy level 14.4 KeV above the stable ground state, and it is the -rays emitted in the transition between these levels that are readily absorbed by normal ^{57}Fe nuclei. The excited nuclei are obtained by spontaneous decay of ^{57}Co (half life – 267 days). So the source material in the Mossbauer experiment with Fe is made of ^{57}Co plated on a suitable support. The absorber can be ordinary Fe in any chemical form.

The decay scheme of ^{191}Ir and ^{57}Fe are given in Fig. 3.9.

For Fe, the characteristic temperature is ~ 420 K. About 1 percent of the ^{191}Ir transitions at 80K are recoilless, in contrast to ~ 70 percent for the 14.4 keV ^{57}Fe transitions at room temperature. The natural widths and life times of excited states are 5 x eV and 1.3 x sec for the 129 keV level of ^{191}Ir, and 4.6 x sec for the 14.4 129 keV level of ^{57}Fe.

The sources are ^{191}Os and ^{57}Fe. The energies, spins, and parities of various states are given.

(1) The temperature of the crystal source is small.

(2) The Debye temperature QD of the crystal lattice is high.

Since the frequency bands are so narrow, extremely slight changes in the energy states of the absorbing nuclei can shift the frequency at which absorption can occur by more than the width of the line of the primary radiation, so that no absorption is expected to take place. The effect of the state of chemical combination on the nuclear levels can be just this order of magnitude.

Such a chemical shift can be observed and measured by imposing a transitional motion on either the emitter or the absorber in such a manner that the resulting Doppler effect just compensates for the chemical shift.

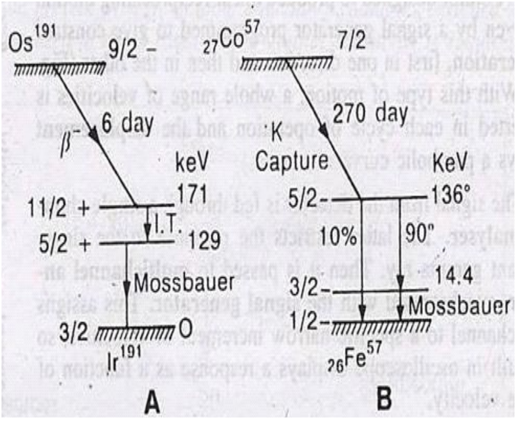


***Fig 3.9** the Mossbauer Transitions of 129 keV (^{191}Ir) and 14.4 keV (^{57}Fe)*

Mossbauer Spectroscopy

Atomic resonance fluorescence and absorption phenomena are well known. The resonance scattering of the 3527 Å ultraviolet line of the mercury spectrum by mercury vapour is a striking example of resonance fluorescence. The resonant absorption of the mercury radiation by mercury vapour occurs, because of the fact that the energy *hv* of the incident photon coincides with the difference in energy of the two states of the mercury atom. The excited atoms of the absorber re-radiate the mercury line, but there is no correlation between the direction of emission of the light and the direction of the incident radiation. The effect is equivalent to resonant scattering. Occurrence of quantized levels in the case of nuclei, gives the possibility of observing resonance fluorescence and absorption in them as well.

Kuhn (1929) suggested that such type of scattering experiments may also be conducted with -rays. A number of attempts to observe resonance scattering with -radiations were made, but all without success. The resonance fluorescence is observed very easily with visible light, but not with -radiation. This is due to the fact that when an atom or nucleus radiates a photon, the atom or nucleus must recoil to conserve momentum. The recoiling atom or nucleus takes some of the available energy , which is equal to the difference in energy of the two states of the radiating atom or nucleus. The problems of nuclear resonance, fluorescence and absorption were, therefore, complicated due to the large amount of recoil energies given to the nucleus by the emitted radiations (-ray).

If E is the energy of emitted photon (E < , its momentum is E/c. The atom or nucleus recoils with a momentum (E/c) in the opposite direction because the conservation of linear momentum demands that the -ray photon momentum and the nuclear recoil momentum should be equal and opposite. The kinetic energy of the recoil particle is given by , when M is the mass of the atom or nucleus. The energy of the photon is given by,

$$\mathrm{E} = \mathrm{hv} = E_0 - \frac{E^2}{2Mc^2} \qquad \text{...(3.3)}$$

$$\mathrm{E} = E_0 - \mathrm{E} = \frac{E^2}{2Mc^2} \qquad \text{...(3.4)}$$

This shows that during the emission, the -ray energy is reduced in its value due to recoil. Equation (3.4) also indicates that energy shift $E_0 - E$ increases as E^2 and it is much more pronounced for high energy photons. For mercury line of 2537 Å, E ~ 5McV, M ~ 180 a.m.u. and $E_0 - E < 10^{-10}$ corresponding to $E/E_0 \sim 10^{-11}$. For a y-ray of energy ~ 0.5 MeV emitted by nucleus of mass number A ~ 100, $E/E_0 \sim 2 \times 10^{-6}$ which is much greater than the value of mercury ultraviolet line of 2537 Å.

When a gamma ray photon strikes a nucleus of mass M in the process of absorption from ground state A to first excited state B, it again transfers a recoil energy of $E^2/M.c^2$. In this process the width of energy levels A and B are also involved. In other words, the degree of resonance scattering depends on the value of E/E_0 in comparison with the natural width Γ of the excited state radiating the line. If we take transitions between ground state and the first excited level B, the problem becomes much simplified as only B levels will have a width and A will be sharp. The line width is related to its life time as

$$\Gamma.\ \Gamma_B = \mathrm{h}. \qquad \text{...(3.5)}$$

The resonance fluorescence in a particular nucleus can be observed only when some of the protons excite the nucleus from its state A to B and provide a recoil energy as well to the nucleus. The condition for the overlap of energy of photons (-rays) and energy of state B of width Γ_B for fluorescence emission will be given by,

$$2\mathrm{E} \leq \Gamma_P \qquad \text{...(3.6)}$$

Applications of Mossbauer Spectroscopy

(1) Isomer shift or chemical shift: Isomer shift (IS) in the Mossbauer spectra reflects differences in the s-electron density around the emitter and absorber nuclei. Since the hyperfine splitting of line width are of the same order (~ 10^{-9} eV) as those which changes in chemical environment, the technique is of great importance in the investigation of molecular structure. Generally, the IS decreases as the s-electron density and hence the oxidation state increases. For example, isomer shift for iron and tin compounds in their different states of oxidation are given below:

(a) Iron, $_{26}Fe^0$: (Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$).

State of oxidation	2	3	4	6
		$Fe^2(3d^6 4s^0)$	$Fe^3(3d^5 4s^0)$	
Isomer shift (IS) (mms^{-1})	1.5	0.7	0.2	-0.6

(b) Tin, $_{50}Sn^0$: (Electronic configuration Kr $4d^{10}$ $5s^2$ $5p^2$

State of oxidation	2	3	4	6
		$Sn^{2+}(5s^2 5p^0)$	$Sn^{IV}(5sp^3)$	$Sn^{4+}(5s^0 4p^0)$
Isomer shift (IS) (mms^{-1})		3.7	2.1	0

The velocity results can be qualitatively explained by assuming that s-electron shielding is governed by the formal d-electron charge state. For a more precise correlation, actual or effective charge state of the ion in the crystal is to be known. *However, it is difficult to know, because it depends upon several factors such as nature and number of ligands, the co-ordination number, the molecular structure, difference in electronegativities, degree of ionicity etc.*

The main factor responsible for affecting the magnitude of chemical shift or isomer shift is the electron density at the nucleus. In case of p and d-orbitals, the electron density at their nuclei is zero and so s-orbital density is only important. The observation of chemical shift permits measurement of relative s-electron density and this gives an idea about the bond character of atoms or ions chemically attached to the Mossbauer nucleus. For example, outermost electronic configuration of ^{119}Sn is $5s^2$ $5p^2$. It indicates that 4+ state of tin has no outer s-electrons, while in 2+ state it is known that higher $5p^2$ electrons are removed leaving two s-electrons. In its 4-covalent state, where the compound obtained have **tetrahedral structure (sp^3 hybridisation)** there is only one s-electron. The isomer shift or chemical shift reflects these structures almost linearly. Thus we can easily ascertain the **valence state** of an unknown tin compound from the Mossbauer spectrum.

(2) **Co-ordination chemistry of iron cyanides** : **Prussian blue** obtained by adding potassium ferrocyanide to a ferric salt solution was supposed to be ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ and **Turnbull's blue**, formed by the addition of potassium ferricyanide to a ferrous salt solution, was supposed to be ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$. Mossbauer spectra, using $^{57}Fe^*$ have shown in that both the compounds has high spin Fe^{3+} and low spin Fe^{11} corresponding to one and the same substance, viz ferric ferrocyanide, $Fe_4(III)[Fe(II)(CN)_6]_3$.

Similarly, in the case of complex, $Na_4[Fe(CN)_6]$ the iron atom has been found to have octahedral symmetry and a single line spectrum is obtained. In the complex, $Na_2\{Fe(CN)_5NO].2H_2O$, the distorted configuration causes the line to split into a doublet, which is probably due to an extensive bonding in Fe-N-O linkage. The bonding abilities of some ligands have been found to decrease in the order $NO^+ > CO > CN^- > SO_4^{2-} > P(C_6H_5)_2 > NO_2^- > NH_3$, as obtained by the Mossbauer spectra.

Check Your Progress

7. What do you mean by Nuclear Magnetic Resonance Spectroscopy?
8. Name the factors influencing chemical shifts.
9. How should be the solvents used in NMR?
10. Name the applications of NMR spectroscopy.

3.7 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Magnetic materials are classified into different categories based on their magnetic parameters (like χ and μ_r) and their microscopic magnetic structure under different and their microscopic magnetic structure under different environmental conditions (i.e., under the influence of magnetic field, temperature, etc.).
2. 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.
3. Paramagnetic materials experience a feeble attractive force when brought near the pole of a magnet. They are attracted towards the stronger parts of an inhomogeneous magnetic field.
4. According to Weiss, in a real gas, the molecules are mutually influenced by their magnetic moments and consequently, there should exist a molecular field, within the gas. This field, produced at any point by all the neighbouring molecules, is proportional to the same logic as the intensity of magnetization.
5. According to 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.
6. In the absence of an external magnetic field the relative orientation of the magnetic moments of various domains will be completely random. When an external magnetic field is applied, depending on the strength of the applied magnetic field, the magnetization effect may take place in different kind of stages.
7. Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.
8. There are mainly three factors influencing chemical shifts:
   (i) Inductive effect
   (ii) Anisotropic effect
   (ii) Hydrogen bonding

9. The solvent used in NMR should be (1) chemically inert toward the sample, (2) it should be free from proton, and (3) it must be capable of dissolving at least 10% of the substance under investigation.
10. NMR spectroscopy is used for detailed investigations of an unknown compound.
    (i) Identification of isomers and conformers
    (ii) Identification of double bond character
    (iii) Detection of aromaticity
    (iv) Detection of hydrogen bonding
    (v) Detection of electronegative atom or group
    (vi) Quantitative analysis

3.8 SUMMARY

- Magnetic materials are classified into different categories based on their magnetic parameters (like χ and μ_r) and their microscopic magnetic structure under different and their microscopic magnetic structure under different environmental conditions (i.e., under the influence of magnetic field, temperature, etc.).
- 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.
- Paramagnetic materials experience a feeble attractive force when brought near the pole of a magnet. They are attracted towards the stronger parts of an inhomogeneous magnetic field.
- Pierre-Ernest Weiss (25 March 1865, Mulhouse – 24 October 1940, Lyon) was a French physicist specialized in magnetism. He developed the domain theory of ferromagnetism in 1907. Weiss also developed the molecular or mean field theory, which is often called Weiss-mean-field theory.
- According to Weiss, in a real gas, the molecules are mutually influenced by their magnetic moments and consequently, there should exist a molecular field, within the gas. This field, produced at any point by all the neighbouring molecules, is proportional to the same logic as the intensity of magnetization.
- According to 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.
- In the absence of an external magnetic field the relative orientation of the magnetic moments of various domains will be completely random. When an external magnetic field is applied, depending on the strength of the applied

magnetic field, the magnetization effect may take place in different kind of stages.

- Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.
- A nucleus is positively charged. Any electrical charge in motion sets up a magnetic field and hence a nucleus due to its motion (spinning) also generates a magnetic field and possesses magnetic moment. The magnetic moment, μ, is proportional to its spin angular momentum.
- The stronger the applied field, greater will be the tendency of the nuclear magnet to remain lined up with it and higher will be the frequency needed to flip the proton to the higher energy state.
- All protons of a compound however, do not absorb at the same applied field. The absorption depends on the magnetic field a proton feels.
- A set of protons having identical environments are called equivalent protons while the protons with different environments are known as non-equivalent protons. Protons with different environment absorb at different applied field strength, whereas protons with identical environment absorb at the same field strength.
- The shielding and deshielding effects on a proton due to induced magnetic field in other parts of a molecule operating through space are known as anisotropic effects.
- In case of hydrogen bonding, the hydrogen bonded proton is attached to a highly electronegative element.
- The solvent used in NMR should be (1) chemically inert toward the sample, (2) it should be free from proton, and (3) it must be capable of dissolving at least 10% of the substance under investigation.
- The distance between the peaks in a given multiplet (fine structures) is a measure of magnitude of splitting effect. This is known as coupling constant and is designated by the symbol J, which is expressed in cycle per second or Hertz (Hz).
- NMR is related to nucleus, whereas EPR is related to the unpaired electron.
- Mossbauer Effect is concerned with the phenomenon of resonance fluorescence of gamma rays. It is comparable to resonance fluorescence in optical regions, but involves intra nuclear rather than electronic energy levels. An important characteristic of this radiation, under optimum conditions of measurement, is the extreme sharpness of the lines.

3.9 KEY TERMS

- **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.

- **Ferromagnetism:** Ferromagnetism is a phenomenon in which a material gets magnetized to a very large extent in the presence of an external field.
- **Weiss molecular field theory:** According to Weiss, in a real gas, the molecules are mutually influenced by their magnetic moments and consequently, there should exist a molecular field, within the gas.
- **Ferromagnetism domains:** According to domain concept, a specimen of ferromagnetic material consists of different region which are spontaneously magnetised below the Curie temperature.

3.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. State the classification of magnetic materials.
2. Mention the general properties of paramagnetic materials.
3. What is the Weiss molecular field theory?
4. Mention the ferromagnetism domains.
5. What is the effect of external magnetic field on the domains?
6. State the factors which affect the width of absorption line in NMR.
7. What is Mossbauer Effect?

Long-Answer Questions

1. Discuss the classification of magnetic materials. Give appropriate examples.
2. Analyse the Langevin's theory of paramagnetism.
3. Explain the quantum theory of paramagnetism.
4. Describe the ferromagnetism with the help of examples.
5. Analyse the Weiss molecular field theory.
6. Discuss the ferromagnetism domains.
7. Describe the cause and effect of radio frequency absorption.
8. Illustrate the spectrometer structure.
9. Explain the applications of Mossbauer spectroscopy.

3.11 FURTHER READING

NOTES

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UNIT 4 DEFECTS IN CRYSTALS

NOTES

Structure

4.0 INTRODUCTION

Metals can have various types of defects. A point defect is any defect that involves only a single particle (a lattice point) or sometimes a very small set of points. A line defect is restricted to a row of lattice points, and a plane defect involves an entire plane of lattice points in a crystal. A vacancy occurs where an atom is missing from the normal crystalline array; it constitutes a tiny void in the middle of a solid. In this unit, we will study in detail about the point and line defects, types of colour centres in crystals, general idea of luminescence, mechanical strength of crystal, plastic behaviour of solids, grain boundary and etching.

4.1 OBJECTIVES

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

- Discuss the point defects in a crystal along with their types
- Explain different types of colour centres in crystals
- Discuss the general idea of luminescence
- Describe the mechanical strength of crystal
- Analyse the plastic behaviour of solids
- Describe the types of dislocation and stress field of dislocation
- Explain the terms grain boundary and etching

4.2 POINT DEFECT IN IONIC CRYSTAL AND METAL

The defects which take place due to imperfect packing of atoms during crystallisation are known as point defects.

As the name implies, they are imperfect point like regions in the crystal. Thus they are also referred as zero dimensional imperfections.

The most common point defects in a crystal are discussed in brief in this section.

Vacancies

A vacancy is the simplest point defect in a crystal. This refers to a missing atom or a vacant atomic site as shown in Figure 4.1 . *Such defects may arise either from imperfect packing density crystallisation process or from thermal vibration of atoms at high temperature.*

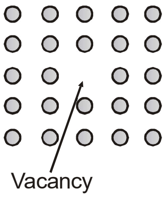

Fig. 4.1

When the thermal energy due to the vibration gets increased among atoms, it can result in a particular atom acquiring sufficient energy to escape, thereby creating a vacancy.

The vacancies may be single or divacancies (two atoms missing) or trivacancies (three atoms missing) and so on.

The number of vacancies n_v per cubic meter is given by

$$n_v = ne^{\frac{-E_a}{k_B T}}$$

where n is the number of lattice points per cubic meter, E_a is the energy needed to produce a vacancy, T is the temperature in kelvin and k_B is the Boltzmann constant.

Interstitial Defects

This type of defect is formed when an extra atom occupies the normally unoccupied site or voids (*i.e., interstitial position*). This is shown in Figure 4.2. S*uch atoms may be impurities or deliberately addded alloying elements.*

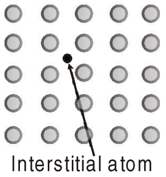

Fig. 4.2

Self Interstitial Defects

This defect occurs when an atom is displaced from its normal position within the crystal to an interstital position. This defect is shown in Figure 4.3.

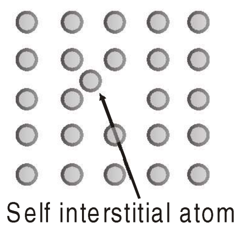

Fig. 4.3

Substitutional Defects

This defect occurs whenever a foreign atom substitutes or replaces the position of a parent (matrix) atom in the crystal lattice.

Such substitutional atoms may be smaller or larger than the atom being replaced. It may be an imputrity or deliberately added alloying element. This type of defect is shown in Figure 4.4.

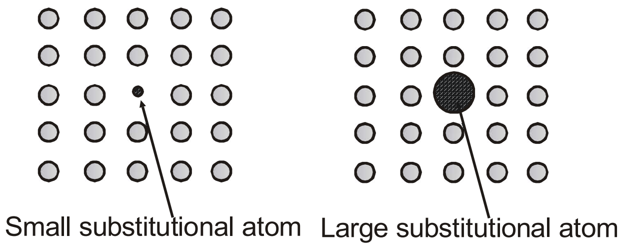

Fig. 4.4 *Substitutional defects*

Schottky Defect

Whenever a pair of positive and negative ions are missing from a crystal the defect is known as schottky defect.That is a pair of missing ion (one cation and one anion) vacancies is termed as schottky defect as shown in Figure 4.5(a). In this type of defect, the crystal is electrically neutral.

Frenkel Defect

Frenkel defect occurs whenever a cation (positive ion) moves from a normal lattice point to an interstitial site. This is shown in Figure 4.5(b).

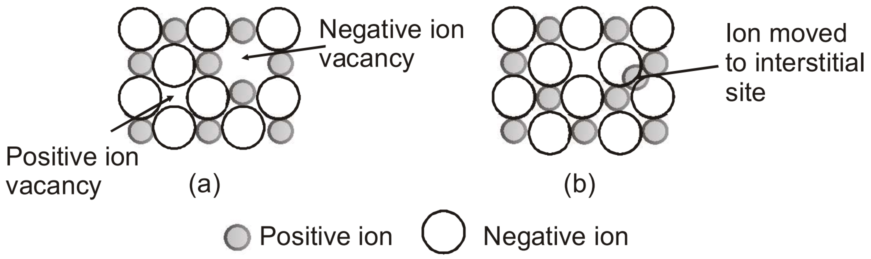

Fig. 4.5 *Schottky and Frenkel defect*

This type of defect is more common in ionic crystals and can occur only for cation (positive ion), because of their smaller size as compared to the size of anion. Frenkel defect is a combination of vacancy and interstitial defect. A Frenkel imperfection does not change the overall electrical neutrality of the crystal.

Equilibrium Concentration of Point Defects

The equilibrium concentration for vacancies of point imperfections in one mole of a crystal is given by

$$\frac{n}{N} = e^{\left(\frac{-\Delta H_f}{RT}\right)}$$

and $\frac{n}{N} = e^{\left(\frac{-\Delta H_f}{2RT}\right)}$ for schottky defects.

n – Number of point imperfections in one mole.

N – Avagadro number (6.023×10^{23} gm/mole).

ΔH_f – Enthalpy of formation of the point imperfection. This is equal to the work done to create a point imperfection in the crystal. It is expressed in kJ/mol or eV/point imperfection.

R – Gas constant.

T – Absolute temperature of the crystal.

Check Your Progress

1. What do you mean by point defects?
2. How is a vacancy created?

4.3 DIFFUSION IN THE CRYSTAL

It is assumed that any given atom moves about its mean position in the crystal lattice due to thermal vibration. This vibration causes vacancy motion and contributes to dislocation motion. Atomic vibrations and vacancies allow atoms to move through a sold. This motion of matter through other matter is called diffusion. In other words diffusion is the shifting of atoms and molecules to new sites within a material resulting in the uniformity of composition as a result of thermal agitation.

Applications of Diffusion

Given below are the applications of diffusion:

1. Diffusion is fundamental to phase changes, e.g., γ to α iron
2. Joining of materials by diffusion bonding, e.g., welding, brazing, soldering, galvanizing and metal cladding.
3. Important in heat treatment like homogenizing treatment of castings, recovery, recrystallization and precipitation of phases
4. Production of strong bodies by powder metallurgy (sintering)

5. Surface treatment of steels, e.g., case hardening
6. Oxidation of metals
7. Doping of semiconductors

Classification of Diffusion

1. Self diffusion : Atoms jumping in pure metals,
2. Inter-diffusion : Observed in binary metal alloys such as the Cu-Ni system.
3. Volume diffusion : Atomic movement in bulk in materials.
4. Grain-boundary diffusion : Atomic movement along the grain boundaries alone.
5. Surface diffusion : Atomic movement along the surface of a phase.

Diffusion Mechanisms

Several atomic mechanisms have been proposed to explain diffusion. All of them are based on the vibrational energy of atoms in a solid. Vacancy mechanism, interstitial mechanism and direct-interchange mechanism are the common diffusion mechanisms.

1. Vacancy Mechanism

This is very important mechanism for diffusion in (FCC, BCC, HCP) metals. Diffusion can occur by atoms moving into adjacent sites that are vacant. Diffusion by the vacancy mechanism in a pure solid is illustrated in Fig. 4.6 (a). The atoms surrounding the vacant site shift their equilibrium positions to adjust for the change in binding that accompanies the removal of a metal ion and its valency election. Assuming that the vacancies move through the lattice and produce random shifts of atoms from one lattice position to another as a result of atom jumping. Over a period of time such diffusion produces concentration changes. Vacancies are continually being created and destroyed at the surface, grain boundaries and suitable interior positions such as dislocations. The rate of diffusion, therefore, increases rapidly with increasing temperature.

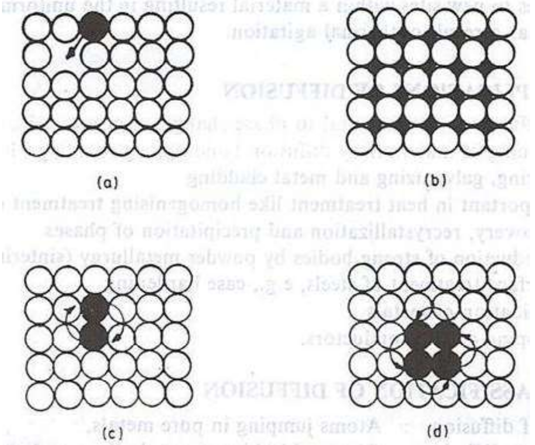

Fig. 4.6 *Diffusion mechanisms (a) Vacancy mechanism (b)Interstitial mechanism (c) Two atoms interchange (d) Four atoms interchange*

NOTES

atoms is called self diffusion because the moving atom and the solid are the same chemical-element. Copper and nickel are mutually soluble in all proportions in the solid state and form substitutional solid solutions e.g., plating of nickel on copper. Figure 4.7 also shows the vacancy mechanism for atomic diffusion.

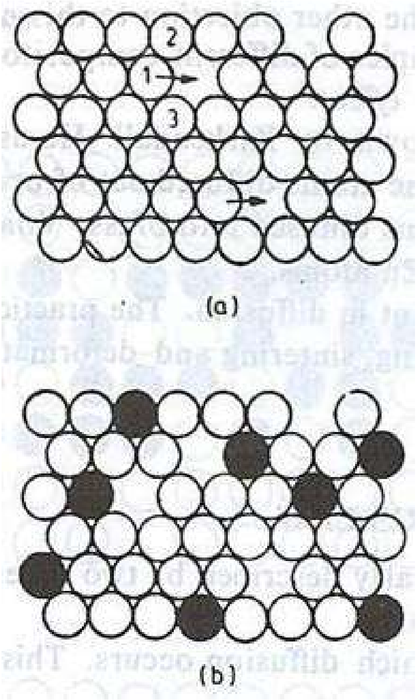

Fig. 4.7 *The Vacancy Mechanism for Atomic Diffusion (a) Pure Solid Solution (b) Substitutional Solid Solution*

o A Atoms

● B Atoms

2. Interstitial Mechanism

Interstitial may occur when a solid is composed of two or more elements whose atomic radii differ significantly. The large atoms occupy lattice sites while the smaller ones fit into the voids created by the large atoms. These voids are called interstices. The diffusion mechanism in this case is similar to vacancy diffusion except that the interstitial atoms stay on interstitial sites. This is shown in Fig. 4.6 (b). An activation energy is associated with interstitial diffusion because, to arrive at the vacant site, it must squeeze past neighbouring atoms with energy supplied by the vibrational energy of the moving atoms. Consequently, interstitial diffusion is a thermally activated process. This process is simpler since the presence of vacancies is not required for the solute atom to move.

This mechanism is important in two cases:

(a) The presence of very small atoms in the interstices of the lattice greatly affect the mechanical properties of metals.

(b) Oxygen, nitrogen and hydrogen can be diffused in metals easily at low temperatures.

3. Direct Interchange Mechanism

As illustrated in Fig. 4.6 (c) and (d), two or more adjacent atoms jump past each other and exchange positions, but the number of sites remains constant. This may be two-atom or four-atom (Zenner-ring) interchange (for BCC). This mechanism results is severe local distortion due to the displacement of the atoms surrounding the jumping pairs. Much more energy is required in this case for atom jumping. The other objection to this mechanism is that a number of diffusion couples of different compositions are produced. This is also called Kirkendall's effect.

NOTES

The inequality of diffusion was first shown by Kirkendall. He used an -brass/copper couple and showed that zinc atoms diffused out of brass into copper more rapidly than copper atoms diffused into brass. Voids can be observed in brass due to a net loss of Zn atoms.

Theoretically, this effect is very important in diffusion. The practical importance of this effect is in metal cladding, sintering and deformation of metals (creep).

Diffusion Coefficient: Fick's Law

Solid state diffusion can be mathematically described by two differential equations called Fick's first and second laws.

Ficks first aw describes the rate at which diffusion occurs. This states that

$$dn = -D \frac{dc}{dx} a \, dt$$

wheredn =Amount of metal in kg that crosses a plane normal to the direction of diffusion.

de/dx = Slope of concentration gradient.

D = Diffusion co-efficient

a = Area of plane across which diffusion takes place.

dt = Duration of diffusion

J = The flux or the number of atoms moving from unit area of one plane to unit area ofaAnother per unit time. It is proportional to the concentration gradient.

The equation becomes

$$\frac{dn}{dt} = D \frac{de}{dx} a$$

$$\therefore \qquad J = -\frac{1}{a}\frac{dn}{dt} = -D\frac{dc}{dx}$$

The negative sign indicates that flow occurs down the concentration gradient. A large negative slope corresponds to a high diffusion rate. The B atoms will diffuse from the left side in accordance with Fick's first law. The net migration of B atoms to the right side means that the concentration will decrease on the left side of the solid and increase on the right side as diffusion progresses.

Fick's Second Law – Time Dependence

Fick's first law allows the calculation of the instantaneous mass flow rate (flux) past any plane in a solid but gives no information about the time dependence of the concentration. The time dependence is contained in Fick's second law, which can be derived using Fick's first law and the law of conservation of mass. The derivation is beyond the scope of this book.

Fick's second law is given by the following equation:

$$\frac{de}{dt} = \frac{d}{dx}\left[D\left(\frac{de}{dx}\right)\right] = D\left(\frac{d^2e}{dx^2}\right)$$

Figure 4.8 is a schematic illustration of the time dependence of diffusion. The curve labeled corresponds to the concentration profile at a given instant of time. At a later time , the concentration profile has changed. This change is due to the diffusion of *B* atoms that has occurred in the time interval . The curve represents the concentration profile at a still later time. The diffusion process is trying to distribute B atoms uniformly throughout the solid solution. Figure 4.8 also shows the concentration gradient becoming less negative as time increases. This means that the diffusion rate becomes slower as the diffusion process progresses.

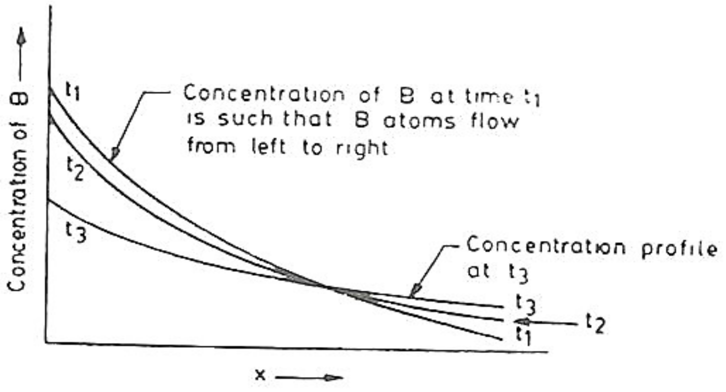

Fig 4.8 *Schematic Illustration of the Time Dependence of Diffusion*

Factors Affecting the Diffusion Coefficient

The diffusion coefficient is affected by concentration, but this effect is generally small when compared to the effect of temperature. The diffusion mechanisms, as discussed earlier, assumed that atoms jumped from one lattice position to another. The rate at which atoms jumped depended on their vibrational frequency, the crystal structure, activation energy and temperature. The activation energy depends on the energies of the bonds which are formed between the jumping atoms and their neighbours. The bond energies depend on the concentration.

Self-Diffusion

We know that diffusion can occur by atoms moving into adjacent sites that are vacant. For an atom to move past other atoms, energy is required. This is the activation energy for vacancy motion.

If the solid is composed of a single element (pure copper for example), the movement of the atoms is called self-diffusion because the moving atom and the solid are the same chemical element.

Self-diffusion is very important for annealing and creep. Radioactive tracers have proved to be very useful in determining self-diffusion coefficients.

Inter-Diffusion

This takes place in binary metallic alloys, e.g. the copper-nickel system. It is contrary to self-diffusion. If nickel had been plated onto the surface of copper, atomic diffusion would bring about nickel homogenization within the copper, after a sufficient time, at elevated temperatures.

Diffusion Couple

A diffusion couple consists of two solids of different compositions in contact with one another, so that each tries to diffuse into the other. This is called inter-diffusion and is responsible for diffusion welding.

A diffusion couple (Fig. 4.9) consists of two solids (metal *A* and metal *B*) in contact with one another. The rate of diffusion of *A* into *B* and *B* into *A* for any given value of x can be determined by Fick's first law.

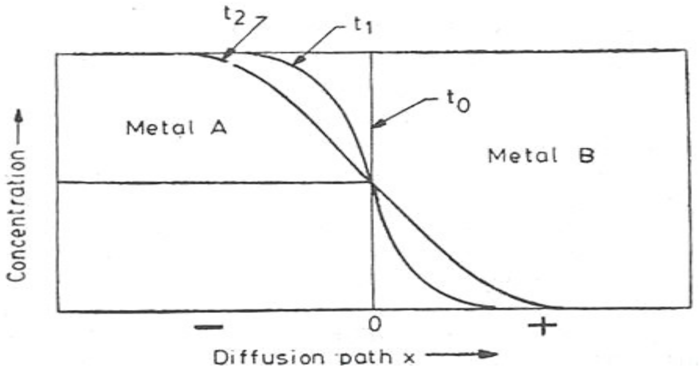

Fig. 4.9 *Diffusion Couple*

The concentration-distance profiles at different lengths of diffusion time are shown in Fig. 4.9. Time is the instant at which diffusion begins and concentration profiles show a step change at the contact surface. *A* and *B* diffuse diffuse into each other and the concentration profiles change with time as shown by curves and . The concentration of either *A* or *B*, as a function of *x* and *t*, can be found from the solution of Fick's second law as applied to the diffusion couple.

The diffusion couple provides one method of experimentally determining the coefficient of diffusion *D*.

Diffusion with Constant Concentration (Case-Hardening)

Case-hardening is a process in which one element (usually in gaseous form) is diffused into another (a solid), the diffusion being limited to a small region near the surface. The properties of this region are changed as a result. Generally, surface regions become harder and brittle whereas the core remains ductile.

This process is governed by Fick's second law. Diffusion of gas atoms into the solid takes place by one of the diffusion mechanisms (usually the interstitial mechanism). The depth to which the atoms of gas penetrate increases with time. Thus, the depth of interstitial alloy increases as diffusion progresses.

For example, nitrogen can be dissolved in the interstitial sites of an iron crystal and the resulting Fe-N alloy is stonger, harder and more brittle than the original iron. The interstitial atoms inhibit dislocation motion and the nitrogen concentration would be highest near the surface in accordance with concentration profiles. This diffusion of nitrogen into iron is called nitriding. Iron and steel can also be case-hardened by carbon, in which case the process is called carburizing.

Check Your Progress

3. What is diffusion?
4. What affects the diffusion coefficient?
5. What is self-diffusion?

4.4 IONIC CONDUCTIVITY

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.,
$$\sigma = \frac{J}{E} \qquad ...(4.1)$$

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
$$a = \frac{eE}{m} \qquad ...(4.2)$$

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

$$v_d = a\tau \qquad ...(4.3)$$

where τ is called the mean free time.

Substituting equation (4.2) in (4.3), we get

NOTES

$$v_d = \frac{eE\tau}{m} \qquad ...(4.4)$$

The current density is given by

$$J = nev_d \qquad ...(4.5)$$

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

Hence, substituting equation (4.4) in (4.5), we get

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

$$\therefore \qquad J = \frac{ne^2\tau}{m}.E \qquad ...(4.6)$$

But, J is also expressed as

$$J = \sigma E \qquad ...(4.7)$$

Therefore, substituting for J in equation (4.6) from equation (4.7)

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

$$\text{or} \qquad \sigma = \frac{ne^2\tau}{m} \qquad ...(4.8)$$

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

Expression for σ in Terms of k_BT

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

$$\tau = \frac{\lambda}{v} \qquad ...(4.9)$$

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

$$\frac{1}{2}mv^2 = \frac{3}{2}k_BT$$

(where k_B is the Boltzmann constant)

$$\text{or} \qquad m = \frac{3k_BT}{v^2} \qquad ...(4.10)$$

Substituting equation (4.10) for m and equation (4.9) for τ in equation (4.8)

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

$$\therefore \qquad \sigma = \frac{ne^2\lambda v}{3k_BT} \qquad ...(4.11)$$

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 ...(1)

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

$$= \frac{\text{Atomic weight}}{D}\ \mathbf{m^3} \qquad ...(2)$$

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). ...(3)

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 = $\frac{N_A \times D}{\text{Atomic weight}}$ ...(4)

Hence, substituting equation (4) in (1) we get,

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

Number of free electrons / Atom × $\mathbf{\frac{N_A \times D}{\text{Atomic weight}}}$ **m^{-3}.**

Example 4.1

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}; $\sigma = 6.22 \times 10^7\ \Omega^{-1}$ m^{-1}; J = ?; μ = ?

Formula

$$J = nev_d$$
$$= 5.9 \times 10^{28} \times 1.6 \times 10^{-19} \times 0.625$$
$$\therefore \quad \mathbf{J = 5.9 \times 10^{9}\ Am^{-2}}$$

NOTES

We know

$$\sigma = ne\mu$$
$$\therefore \quad \mu = \frac{\sigma}{ne} = \frac{6.22\times10^{7}}{5.9\times10^{28}\times1.6\times10^{-19}}$$
$$\boldsymbol{\mu = 6.588 \times 10^{-3}\ m^{2}\ V^{-1}s^{-1}.}$$

Example 4.2

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 × 10^{28} m^{-3}; A = 1.05 mm^2 = 1.05 × 10^{-6} m^2; I = 1A.

Formula

$$J = nev_d$$
$$\therefore \quad v_d = \frac{J}{ne} = \frac{I}{Ane} \qquad \left[\because J = \frac{I}{A}\right]$$
$$v_d = \frac{1}{1.05\times10^{-6}\times8.5\times10^{28}\times1.6\times10^{-19}}$$
$$\mathbf{v_d = 7.002 \times 10^{-5}\ ms^{-1}.}$$

Example 4.3

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, μ = 3.5 × 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 4.4

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 × 10^{28} m^{-3}; ρ = 1.435 × 10^{-8} Ω − m; τ = ?

Formula

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

NOTES

$$\therefore \quad \tau = \frac{m\sigma}{ne^2} = \frac{m}{\rho ne^2} \qquad \left[\because \sigma = \frac{1}{\rho}\right]$$

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

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

Example 4.5

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

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

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

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

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

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

To calculate v (thermal velocity)

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

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

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

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

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

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

Example 4.6

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 mm = 1× 10^{-3} m ; V = 1 V ; T = 300 K ; μ = 0.04 $m^2 V^{-1}s^{-1}$;

v = ? ; v_d = ?

NOTES

Formula

Thermal velocity

$$v = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\times1.38\times10^{-23}\times300}{9.11\times10^{-31}}} = \sqrt{1.36333\times10^{10}}$$

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

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

Drift velocity v_d

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

or $$v_d = E\mu$$

But, $$E = \frac{V}{t} = \frac{1}{1\times10^{-3}} = \mathbf{1000 \text{ Vm}^{-1}.}$$

∴ $$v_d = 1000 \times 0.04$$

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

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

Example 4.7

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

Solution:

Given,Atomic weight = 63.5; density D = 8.93 × 10^3 kgm^{-3}; τ = 2.48 × 10^{-14} s;

σ = ?

Formula

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

To find n

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

$$= \frac{1\times6.023\times10^{26}\times8.93\times10^3}{63.5}$$

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

NOTES

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

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

or $\boldsymbol{\sigma = 5.87 \times 10^7\ \text{Sm}^{-1}}$. $[\Omega^{-1} = \text{siemens}]$

Example 4.8

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 = $8.48 \times 10^{28}\ \text{m}^{-3}$]

Solution:

Given, $I = 10$ A; diameter of wire = 0.16×10^{-2} m

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

Formula

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

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

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

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 4.9

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 = 100V/m; $n = 5.8 \times 10^{28}\ \text{m}^{-3}$; $v_d = ?$

Formula

$$v_d = \mu E$$

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

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

$$\therefore \qquad v_d = \mu E$$

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

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

Example 4.10

NOTES

The following datas are given for copper:

(*i*) Density = 8.92×10^3 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 = 8.92×10^3 kg / m^3; Atomic weight = 63.5; $\rho = 1.73 \times 10^{-8}\ \Omega$m;

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

Formula

$$n = \frac{D \times \text{Avagadro number}}{\text{Atomic weight}} = \frac{8.92\times10^3\times6.02\times10^{26}}{63.5}$$

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

$$\tau = \frac{m}{ne^2\rho} = \frac{9.1\times10^{-31}}{8.456\times10^{28}\times\left(1.6\times10^{-19}\right)^2\times1.73\times10^{-8}}$$

$$\therefore \qquad \boldsymbol{\tau} \mathbf{= 2.43 \times 10^{-14}\ s.}$$

$$\mu = \frac{1}{\rho ne} = \frac{1}{1.73\times10^{-8}\times8.456\times10^{28}\times1.6\times10^{-19}}$$

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

Example 4.11

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

$$\rho = \frac{m}{ne^2\tau} \quad n = \frac{\text{Number of atoms per unit cell} \times \text{Number of electrons per unit cell}}{\text{Volume}}$$

$$= \frac{2\times1}{a^3} \qquad (\because \text{volume} = a^3)$$

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

$$\therefore \quad a = \frac{4\times1.85\times10^{-10}}{\sqrt{3}}$$

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

NOTES

$$\therefore \quad n = \frac{2}{\left(4.27\times10^{-10}\right)^3}$$

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

$$\text{Electrical resistivity } \rho = \frac{m}{ne^2\tau} = \frac{9.11\times10^{-31}}{2.57\times10^{28}\times\left(1.6\times10^{-19}\right)^2\times3\times10^{-14}}$$

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

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 4.12

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

$l = 5$ m, I = 15 A

Number of free electron = 3

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

Formula

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

$$= \frac{6.023\times10^{26}\times3\times2.7\times10^3}{26.98}$$

$$\therefore \quad \mathbf{n = 1.81 \times 10^{29}\ electrons/m^3.}$$

$$\mu = \frac{1}{ne\rho} = \frac{1}{1.81\times10^{29}\times1.6\times10^{-19}\times2.7\times10^{-8}}$$

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

$$E = \frac{V}{l} = \frac{IR}{l} = \frac{15\times60\times10^{-3}}{5}$$

$$\mathbf{E = 0.18\ V/m.}$$

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

$$\therefore \quad \mathbf{v_d = 2.302 \times 10^{-4}\ m/sec.}$$

NOTES

Example 4.13

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

Solution:

Given, $l = 1$ cm; $b = 1$ mm; $t = 1$ mm; $T = 300$ K; $\rho = ?$; $R = ?$

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

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

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

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

$$\mathbf{\rho = 0.431\ \Omega m.}$$

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

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

4.5 COLOUR CENTRES IN CRYSTALS

Ionic crystals such as NaCl, KCl etc. in the pure state without imperfections, are transparent throughout the visible region of spectrum. However, the impure salts are often coloured because energy is absorbed in certain regions (called absorption bands) of the visible spectrum owing to the presence of various impurities and point defects.

As mentioned above, presence of vacancies in the crystal causes the absorption band to appear in the range of visible spectrum. When the vacancies capture electrons or holes, they are capable of absorbing light and since the crystal appears coloured because of absorption of light, these are called coloured centres. A colour centre is therefore a lattice defect, which absorbs visible light.

The colour centres can be produced in a number of ways:

- By introduction of chemical impurities;
- By introduction of an excess of the metal ion(we may heat the crystal in the vapour of the alkali metal and then cool it quickly for example; an NaCl crystal heated in the presence of sodium vapour becomes yellow; a KCl crystal heated in potassium vapour becomes magenta);
- By x-ray, γ-rays, neutron and electron bombardment; and
- By electrolysis

- By any above methods energy is given (UV or X-rays or gamma rays, Vapour heating) are used to promote an electron from the valence band to the trap.

Example of Self-Darkening Sunglasses

Colour change can occur merely while the glasses are illuminated, leading to optical bleaching. Glasses may fade in the dark at room temperature when the ultraviolet energy present in sunlight produces darkening, and room temperature leads to fading as soon as ultraviolet light is no longer present.

Let us discuss some types of colour centres.

1. F Centre

The F centre comes from German word Farbe which means colour. We usually produce F centres by heating the crystal in excess alkali vapour or by x- irradiation. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse from the crystal to its surface and combine with Na atoms, forming NaCl. During this process, the Na atom on the surface of the crystal lose electrons. These released electrons diffuse into the crystal and occupy the vacant anionic site and creates F–Centre.

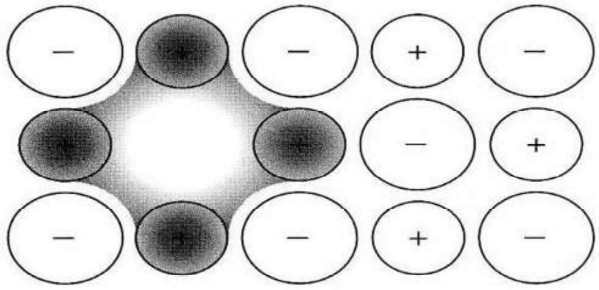

Fig 4.10 *F Centre*

Coagulation of F Centres

If crystals containing F centres are irradiated with light in F band, there is a suitable temperature range(for NaCl and KCl room tempr) in which number of bands appear on the long wave length side of F band. This is because of (-) ion vacancy introduced during creation of F centre, combine with existing (+) ion vacancies forming pairs and therefore combination of F centres occurs.

R1 Centre: F centre combined with a vacant anion site is called R1 Centre. R2 Centre: When two F centres combine it is R2 centre.

2. M Centre

Two Adjacent F centres (with pair of vacancies of opposite spin) form M centre.

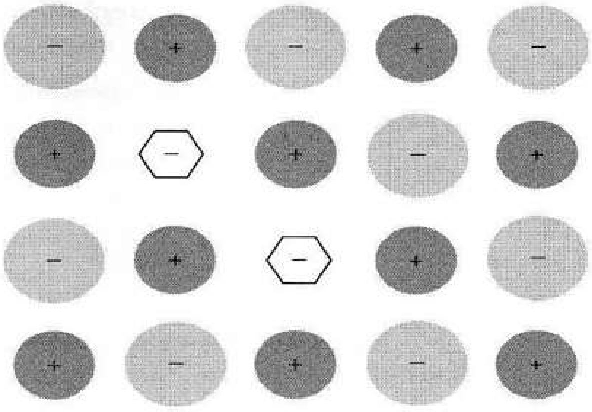

Fig 4.11 M Centre

3. R Centre

Three adjacent F centres form R centres (a group of three negative Ion vacancies in a plane).

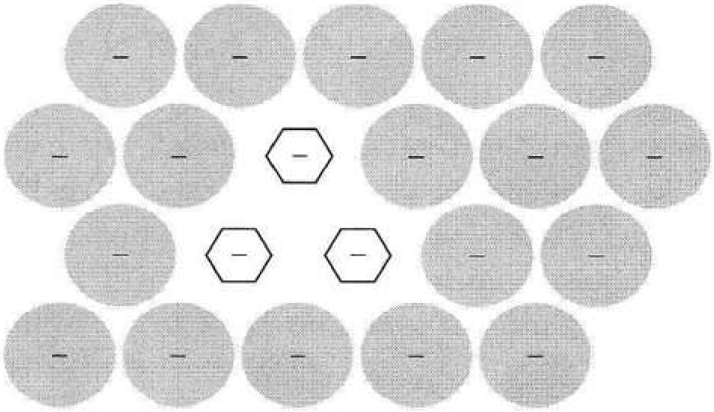

Fig 4.12 R Centre

4. V Centre

This type of colour centres result from an excess of halogen in alkali halides. Mollwo observed new absorption band for KBr when heated in Br^2 vapour. The excess bromine is incorporated in the lattice in the form of negative ions, occupying normal lattice sites. As result of the introduction of extra bromine atoms, positive holes are formed. These holes are most likely to be situated near a positive ion vacancy where they can be trapped. A hole trapped at a positive ion vacancy is called V centre.

4.6 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.

Attraction between the electron and the hole causes their motion to be correlated and the resultant electron-hole pair is known as an exciton. 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.

As in any two particle systems, the exciton motion can be decomposed into two parts: a Center-of-Mass (CM) motion and a relative motion of the two particles about the CM.

With this decomposition, the potential acting on the exciton CM still has translational invariance since the Coulomb interaction depends only on the relative coordinate of the electron and hole.

Within the effective mass approximation, the exciton CM behaves like a free particle with mass

$$M = m_e + m_h$$

The relative motion of the electron and the hole in the exciton is similar to that of the electron and the proton inside the H atom.

Formation of Exciton

An exciton in semiconducting materials can form when a material absorbs a photon of higher energy than its bandgap (hv is greater than Eg).

The photon, excites an electron from the valence band into the conduction band consecutively, this leaves behind a positively charged hole.

The electron in the CB is then effectively attracted to this localized hole by the repulsive Coulomb forces from large numbers of electrons surrounding the hole and excited electron.

This attraction provides a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound electron and hole.

Classification of Excitons

Typically excitons have been studied in the two limiting cases:

(1) **Frenkel excitons:** For strong electron-hole attraction, as in ionic crystals, the electron and the hole are tightly bound to each other within the same or nearest-neighbor unit cells.

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.

This *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.

(2) **Wannier-Mott excitons:** In most semiconductors, the Coulomb interaction is strongly screened by the valence electrons via the large dielectric constant, i.e. electrons and holes are only weakly bound.

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 semiconductors, the dielectric constant is generally large. Consequently this tends to reduce the Coulomb interaction between electrons and holes, which has a radius larger than the lattice spacing

Small effective mass of electrons that is typical of semiconductors also favors large exciton radii

The Wannier-Mott excitons and their properties can be calculated with the effective mass approximation.

Within this approximation, the electron and the hole are consider two particles moving with the effective masses of the conduction and the valence bands, respectively.

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.

Check Your Progress

6. Define electrical conductivity.
7. What do you mean by coloured centres?
8. What is exciton?

4.7 GENERAL IDEAS OF LUMINESCENCE

There are a lot of light-emitting processes occurring in nature. Luminescence is an umbrella term for those kinds of events where light emission is not the result of high temperatures. In this section, we will discuss different forms of luminescence and go into detail in the case of fluorescence.

Light-emitting Processes

Some very common biological or biochemical lab methods are based on the existence of several "…escences" such as phosphorescence, chemiluminescence, bioluminescence and finally fluorescence. The origin of these phenomena lies in the Latin word for see: *-escentia*, which already implies the connection to our visual system. All the "…escences" describe physical, chemical or biological processes that we can perceive with our eyes. We add the suffix "…escence" to words denoting change, action or process like the word convalescence.

So obviously, fluorescence is something we can see and something that concerns a change or a process. We will learn how fluorescence fulfils these conditions later on. First we will take a short look at the other "…escences" which are all luminescence themselves. Luminescence is the generic term for the emission of light which is not an effect of high temperature. So luminescence can be determined as an appearance of cold body radiation. This radiation can either be part of a chemical reaction or a cause of subatomic motions or stress on a crystal. Another way to generate emission is incandescence where light is emitted by a substance as the result of heat (e.g., hot metal).

Chemiluminescence is a light-emitting process based on a chemical reaction where the product has an excited intermediate. This intermediate emits light when falling into the ground state. Unlike fluorescence, electrons in chemiluminescent materials are excited by a chemical reaction and not by the absorption of photons. Chemiluminescence finds its technical application in light sticks for example. A well-known chemiluminescent substance is luminol, which is used in criminalistics to find blood traces. Here Fe^{2+} ions which are present in hemoglobin function as a catalyzer to bring Luminol to its light emitting configuration.

If a living organism emits light we speak of bioluminescence, no matter how this light is produced. There are a lot of organisms that produce light, like glowworms (*Lampyris noctiluca*) or fireflies (*Photinus pyralis*). A very extraordinary organism in a row of several other fungi is the Jack O'Lantern mushroom (*Omphalotus nidiformis*), which glows in the dark. Numerous marine organisms like some corals, algae, crustacaea or even squids emit light, mostly in the blue or green spectrum. Another sea inhabitant is the bioluminating jellyfish *Aequorea victoria*, the source of the Green Fluorescent Protein (GFP). Whereas the firefly, for example uses only a chemiluminescent process to produce light, *A. victoria* uses both a chemiluminescent and a fluorescent process. As scientists found out, the jellyfish generates blue light by a chemical reaction with the help of the protein Aequorin. This blue light is then used to excite the already mentioned GFP in a fluorescence reaction resulting in a green glow.

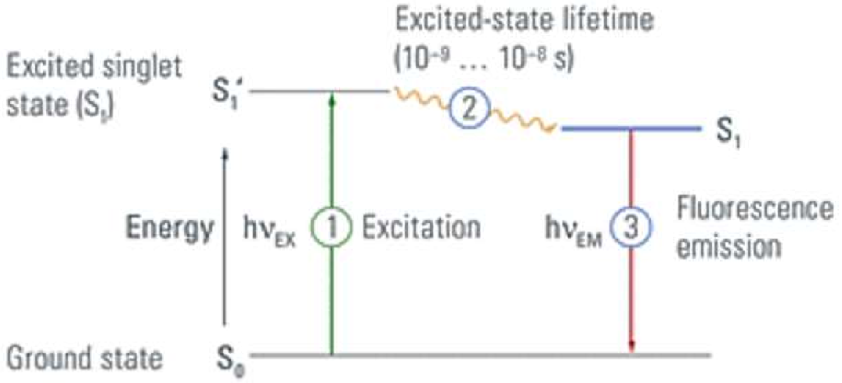

Fig. 4.13 *Fluorescence Jablonski Diagram*

This leads us to the question: "What is fluorescence?" Fluorescence is a process where a substance emits light as an effect of the absorption of light of a shorter wavelength. The difference in wavelengths is called **Stoke's Shift**. In detail, fluorescence occurs if a substance absorbs light in the form of photons. This leads to a shift of electrons to a higher energy level. But this high energy situation is very unstable, which is why electrons tend to return to their ground state. During this procedure energy is released again in the form of photons that can be seen as a glow. In contrast to phosphorescence, electron energy shift is very fast, in fact in the range of nano seconds (Figure 4.13). Any substance which is able to emit light of a distinct wavelength after excitation with another distinct wavelength is called a fluorochrome. These are discussed in the next section. Most fluorescing substances occurring in nature have a broad excitation and emission spectrum, but substances with clearly defined excitation and emission maxima are more useful for fluorescence microscopy.

NOTES

Similar to fluorescence, **phosphorescence** is a light-emitting phenomenon where the phosphorescent material is excited with light. Even though it is closely related to fluorescence, it is much slower. In contrast to fluorescence the re-emission of photons is decelerated by the association of excited electrons energy with a "forbidden" state. Their return to the ground state does not occur as fast as in the case of fluorescence because energy is "trapped". Typical examples of phosphorescent materials are "glow-in-the-dark" toys which can be "charged" with an ordinary light bulb or daylight and then emit light for several minutes or even hours.

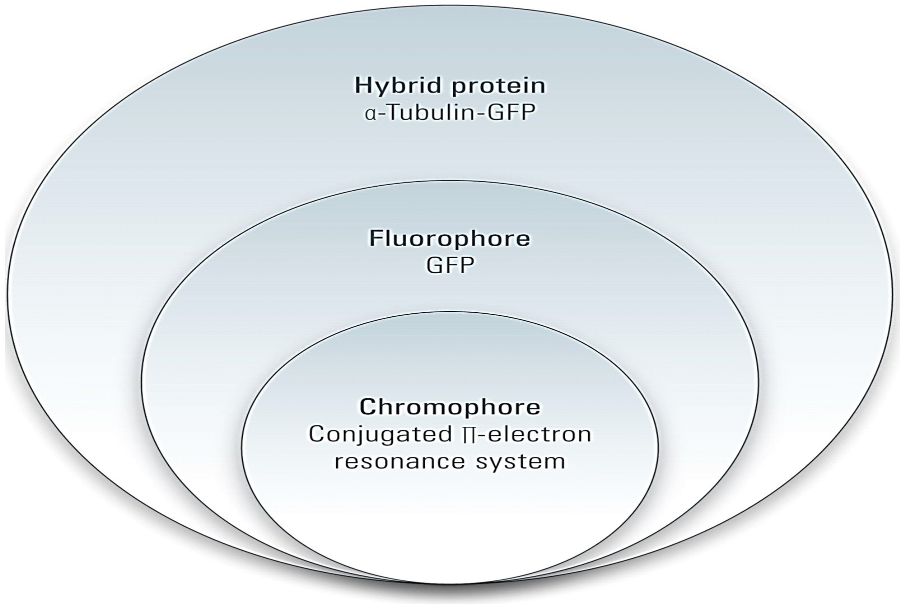

Fig. 4.14 *Hierarchy in Fluorescent Proteins*

Looking a little bit deeper into a fluorophore we reach the chromophore, which is the part of a molecule that defines its color (Figure 4.14). Inside the chromophore, energy level transformation of electrons and the interconnected emission of light (see above) take place. There are at least two forms of chromophore. Either they are built of a conjugated π-electron resonance system (GFP) or of metal complexes (chlorophyll, heme).

Because of its relevance for microscopy, we will take a closer look at the chromophore of GFP. It turns out that for the formation of the GFP chromophore no other cofactors or enzyme components are necessary than molecular oxygen.

NOTES

Defined by the primary structure of the GFP amino acid backbone, it forms spontaneously in a self-catalyzed folding mechanism and is completed by intramolecular rearrangements. Going into detail, the chromophore is made of three relevant amino acids. Ser65, Tyr66 and Gly67 undergo a cyclization, a dehydration and an oxidation successively. The result of these reactions is a conjugated π-electron resonance system, the mature GFP chromophore.

Looking at the entire GFP structure, the cyclic tripeptide sits in the middle of a cylinder. This cylinder is made of 11 strands forming a β-barrel structure, which gives the protein a high stability. The β-barrel structure has a diameter of about 3 nm and a height of about 4 nm (Figure 4.15). All of the FPs known so far have this protecting cylinder which has a great influence on their photophysical properties. In the case of GFP, quantum yield and photostability are relatively high. Furthermore the very compact protein structure leads to a high pH resistance. Specimens with a GFP-tag are comparatively robust concerning temperature and show high tolerance to denaturating substances like paraformaldehyde, urea or guanidinium hydrochloride.

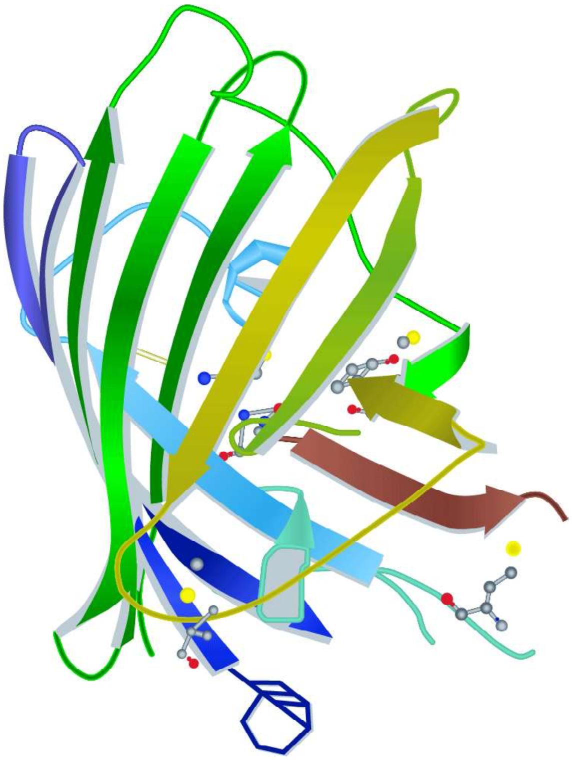

Fig 4.15 *Molecular structure of Green Fluorescent Protein (GFP)*

Check Your Progress

9. What is luminescence?
10. Define fluorescence.
11. What is fluorochrome?

4.8 MECHANICAL STRENGTH OF CRYSTAL

Mechanical strength is determined by the nature of the following points:

- Inter-atomic forces
- Temperature (causes atoms to vibrate)
- Stress state of the material. We shall make calculations of two states of stresses: uniaxial normal stress and shear stress. The stresses required for failure under the two situations will be calculated, and the mechanical strength should be the lower of the two values.

Mechanical Cleavage Stress

Cleavage involves the separation of atomic bonds perpendicular to an applied load/stress. Materials, when exposed to external forces, will deform or fail. This may occur when a material,

- breaks under perpendicular (i.e., normal) stress and the fracture is perpendicular to the applied stress
- consumes little energy and produces a brittle fracture

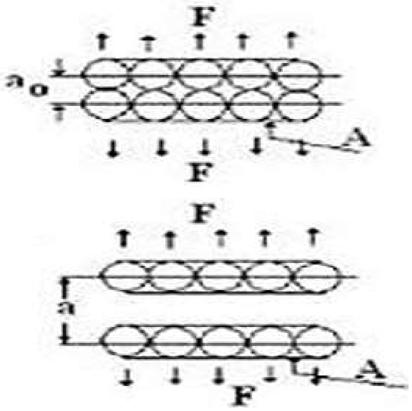

Fig 4.16 *Mechanical Cleavage Stress*

Orowan developed a simple method for obtaining the theoretical tensile strength of a crystal. It is assumed that all atoms separate simultaneously once their separation reaches a critical value.

Mechanical Shear Stress

Another kind of failure can be seen in crystals under application of external forces which is shear.

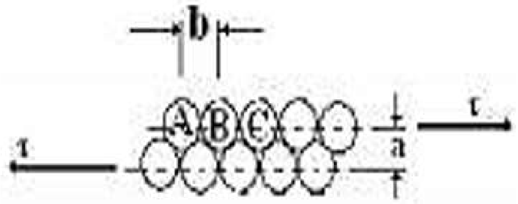

Fig 4.17 *Mechanical Shear Stress*

Shear occurs when a material breaks under "parallel" stress and the fracture path is parallel to the applied stress. It consumes more energy as shear distorts specimen. The bond breakage is sequential. Frenkel performed a simple calculation of the theoretical shear strength of crystals by considering two adjacent and parallel lines of atoms subjected to a shear stress.

4.9 PLASTIC BEHAVIOUR

In this section, we will study the plastic behaviour of solids.

Tensile Strength

Tensile strength is a measurement of the force required to pull something such as rope, wire, or a structural beam to the point where it breaks.

The tensile strength of a material is the maximum amount of tensile stress that it can take before failure, for example breaking.

There are three typical definitions of tensile strength:

- **Yield strength** - The stress a material can withstand without permanent deformation. This is not a sharply defined point. Yield strength is the stress which will cause a permanent deformation of 0.2% of the original dimension.
- **Ultimate strength** - The maximum stress a material can withstand.
- **Breaking strength** - The stress coordinate on the stress-strain curve at the point of rupture.

Typical Tensile Strengths

Table 4.1 *Typical Tensile Strength of some Materials*

Material	Yield strength (MPa)	Ultimate strength (MPa)	Density (g/cm^3)
Structural steel ASTM A36 steel	250	400	7.8
Steel, API 5L X65 (Fikret Mert Veral)	448	531	7.8
Steel, high strength alloy ASTM A514	690	760	7.8
Maraging_Steel, Grade 350	2400	2500	8.1
Steel Wire			7.8
Steel, Piano wire	c. 2000		7.8
High density polyethylene (HDPE)	26-33	37	0.95
Polypropylene	12-43	19.7-80	0.91
Stainless steel AISI 302 - Cold-rolled	520	860	8.03;
Cast iron 4.5% C, ASTM A-48	130 (??)	200	7.3;
Titanium Alloy (6% Al, 4% V)	830	900	4.51
Aluminium Alloy 2014-T6	400	455	2.7

Note: Multiwall carbon nanotubes have the highest tensile strength of any material yet measured, with labs producing them at a tensile strength of 63 GPa, still well below their theoretical limit of 300 GPa. However, as of 2004, no macroscopic object constructed of carbon nanotubes has had a tensile strength remotely approaching this figure, or substantially exceeding that of high-strength materials like Kevlar.

NOTES

Toughness

In materials science and metallurgy, toughness is the ability of a material to absorb energy and plastically deform without fracturing. One definition of material toughness is the amount of energy per unit volume that a material can absorb before rupturing. This measure of toughness is different from that used for fracture toughness, which describes load bearing capabilities of materials with flaws. It is also defined as a material's resistance to fracture when stressed.

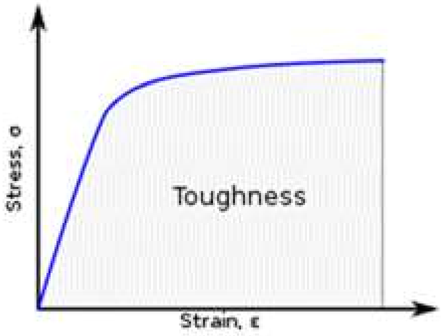

Fig. 4.18 *Toughness as defined by the Area under the Stress-Strain Curve*

In materials science and metallurgy, toughness is the ability of a material to absorb energy and plastically deform without fracturing. One definition of material toughness is the amount of energy per unit volume that a material can absorb before rupturing. This measure of toughness is different from that used for fracture toughness, which describes load bearing capabilities of materials with flaws. It is also defined as a material's resistance to fracture when stressed.

Toughness requires a balance of strength and ductility.

Toughness and Strength

Toughness is related to the area under the stress–strain curve. In order to be tough, a material must be both strong and ductile. For example, brittle materials (like ceramics) that are strong but with limited ductility are not tough, conversely, very ductile materials with low strengths are also not tough. To be tough, a material should withstand both high stresses and high strains. Generally speaking, strength indicates how much force the material can support, while toughness indicates how much energy a material can absorb before rupturing.

Toughness Tests

The toughness of a material can be measured using a small specimen of that material. A typical testing machine uses a pendulum to deform a notched specimen of defined cross-section. The height from which the pendulum fell, minus the height to which it rose after deforming the specimen, multiplied by the weight of the pendulum is a measure of the energy absorbed by the specimen as it was deformed during the impact with the pendulum. The Charpy and Izod notched impact strength tests are typical ASTM tests used to determine toughness.

Unit of Toughness

Tensile toughness or *deformation energy* (U_T) is measured in units of Joule per cubic metre ($J\cdot m^{-3}$) in the SI system and inch-pound-force per cubic inch ($in\cdot lbf\cdot in^{-3}$) in US customary units.

$1.00\ N\cdot m.m^{-3} \simeq 0.000145\ in\cdot lbf\cdot in^{-3}$ and $1.00\ in\cdot lbf\cdot in^{-3} \simeq 6.89\ kN\cdot m.m^{-3}$.

In the SI system, the unit of tensile toughness can be easily calculated by using area underneath the stress–strain ($\sigma - \varepsilon$) curve, which gives tensile toughness value, as given below:

U_T = Area Underneath the Stress–Strain ($\sigma - \varepsilon$) Curve = $\sigma \times \varepsilon$

U_T [=] $P/A \times \Delta L/L = (N\cdot m^{-2})\cdot$(Unit Less)

U_T [=] $N\cdot m\cdot m^{-3}$

U_T [=] $J\cdot m^{-3}$

Elongation

Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.

Plastic Deformation

Fig. 4.19 *Plastic Deformation*

Swebor-brand high-strength low alloy steel plate, showing both sides, after plastic deformation from defeating projectiles in ballistics testing. Note: When exposed to fire, steel first expands and then loses its strength, exceeding critical temperature at 538°C or 1000°F per ASTM E119 unless treated with fireproofing.

This type of deformation is not undone simply by removing the applied force. An object in the plastic deformation range, however, will first have undergone elastic deformation, which is undone simply be removing the applied force, so the object will return part way to its original shape. Soft thermoplastics have a rather large plastic deformation range as do ductile metals such as copper, silver, and gold. Steel does, too, but not cast iron. Hard thermosetting plastics, rubber, crystals, and ceramics have minimal plastic deformation ranges. An example of a material with a large plastic deformation range is wet chewing gum, which can be stretched to dozens of times its original length.

Under tensile stress, plastic deformation is characterized by a strain hardening region and a necking region and finally, fracture (also called rupture). During strain hardening the material becomes stronger through the movement of atomic dislocations. The necking phase is indicated by a reduction in cross-sectional area of the specimen. Necking begins after the ultimate strength is reached. During necking, the material can no longer withstand the maximum stress and the strain in the specimen rapidly increases. Plastic deformation ends with the fracture of the material.

NOTES

Hardness

Hardness is a measure of the resistance to localized plastic deformation induced by either mechanical indentation or abrasion. In general, different materials differ in their hardness; for example hard metals such as titanium and beryllium are harder than soft metals such as sodium and metallic tin, or wood and common plastics. Macroscopic hardness is generally characterized by strong intermolecular bonds, but the behaviour of solid materials under force is complex; therefore, there are different measurements of hardness: scratch hardness, indentation hardness, and rebound hardness.

Hardness is dependent on ductility, elastic stiffness, plasticity, strain, strength, toughness, viscoelasticity, and viscosity.

Common examples of hard matter are ceramics, concrete, certain metals, and super hard materials, which can be contrasted with soft matter.

Scratch Hardness

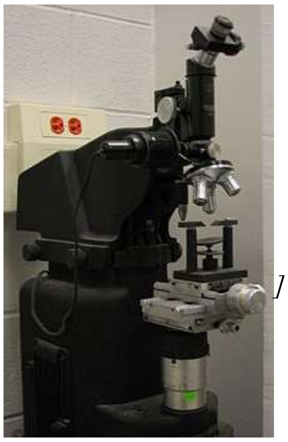

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Fig. 4.20

Hardness Tester

There are three main types of hardness measurements: scratch, indentation, and rebound. Within each of these classes of measurement there are individual measurement scales. For practical reasons conversion tables are used to convert between one scale and another.

Scratch Hardness

Scratch hardness is the measure of how resistant a sample is to fracture or permanent plastic deformation due to friction from a sharp object. The principle is that an object made of a harder material will scratch an object made of a softer material. When testing coatings, scratch hardness refers to the force necessary to cut through the film to the substrate. The most common test is Mohs scale, which is used in mineralogy. One tool to make this measurement is the sclerometer.

Another tool used to make these tests is the pocket hardness tester. This tool consists of a scale arm with graduated markings attached to a four-wheeled carriage. A scratch tool with a sharp rim is mounted at a predetermined angle to the testing surface. In order to use it a weight of known mass is added to the scale arm at one of the graduated markings, the tool is then drawn across the test surface. The use of the weight and markings allows a known pressure to be applied without the need for complicated machinery.

Indentation Hardness

Indentation hardness measures the resistance of a sample to material deformation due to a constant compression load from a sharp object. Tests for indentation hardness are primarily used in engineering and metallurgy fields. The tests work on the basic premise of measuring the critical dimensions of an indentation left by a specifically dimensioned and loaded indenter.

Common indentation hardness scales are Rockwell, Vickers, Shore, and Brinell, amongst others.

Rebound Hardness

Rebound hardness, also known as dynamic hardness, measures the height of the ‘Bounce’ of a diamond-tipped hammer dropped from a fixed height onto a material. This type of hardness is related to elasticity. The device used to take this measurement is known as a scleroscope.

Two scales that measures rebound hardness are the Leeb rebound hardness test and Bennett hardness scale.

Ultrasonic Contact Impedance (UCI) method determines hardness by measuring the frequency of an oscillating rod. The rod consists of a metal shaft with vibrating element and a pyramid-shaped diamond mounted on one end.

Creep

In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods and generally increases as they near their melting point.

The rate of deformation is a function of the material’s properties, exposure time, exposure temperature and the applied structural load. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function — for example creep of a turbine blade could cause the blade to contact the casing, resulting in the failure of the blade. Creep is usually of concern to engineers and metallurgists when evaluating components that operate under high stresses or high temperatures. Creep is a deformation mechanism that may or may not constitute a failure mode. For example, moderate creep in concrete is sometimes welcomed because it relieves tensile stresses that might otherwise lead to cracking.

Unlike brittle fracture, creep deformation does not occur suddenly upon the application of stress. Instead, strain accumulates as a result of long-term stress. Therefore, creep is a "time-dependent" deformation. It works on the principle of Hooke's law (stress is directly proportional to strain).

Fatigue (material)

Fig. 4.21 *Plastic Deformation*

Fracture of an aluminium crank arm. Dark area of striations: slow crack growth. Bright granular area: sudden fracture.

In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface. The crack will continue to grow until it reaches a critical size, which occurs when the stress intensity factor of the crack exceeds the fracture toughness of the material, producing rapid propagation and typically complete fracture of the structure.

Fatigue has traditionally been associated with the failure of metal components which led to the term metal fatigue. In the nineteenth century, the sudden failing of metal railway axles was thought to be caused by the metal crystallising because of the brittle appearance of the fracture surface, but this has since been disproved. Most materials seem to experience some sort of fatigue-related failure such as composites, plastics and ceramics.

To aid in predicting the fatigue life of a component, fatigue tests are carried out using coupons to measure the rate of crack growth by applying constant amplitude cyclic loading and averaging the measured growth of a crack over thousands of cycles. However, there are also a number of special cases that need to be considered where the rate of crack growth is significantly different compared to that obtained from constant amplitude testing. Such as: the reduced rate of growth that occurs for small loads near the threshold or after the application of an overload; and the increased rate of crack growth associated with short cracks or after the application of an underload.

NOTES

If the loads are above a certain threshold, microscopic cracks will begin to initiate at stress concentrations such as holes, Persistent Slip Bands (PSBs), composite interfaces or grain boundaries in metals. The stress values that cause fatigue damage are typically much less than the yield strength strength of the material.

Check Your Progress

12. Define the tensile strength.
13. What do you mean by elongation?
14. What do you understand by plastic deformation of the materials?
15. What is the scratch hardness?

4.10 TYPES OF DISLOCATION

The defects which take place due to dislocation or distortion of atoms along a line in some direction is called as line defect. Movement of dislocation is necessary for plastic deformation.

The dislocation is a boundary between the slipped region and the unslipped region and lies in the slip plane. The structure and behaviour of dislocations affect many of the properties of engineering materials.

Dislocations arise in a crystal as a result of

(a) Growth accidents, (b) Phase transformations, (c) Thermal stresses, (d) External stresses causing plastic flow, and (e) Segregation of solute atoms causing mismatches etc.

Note: **Slip** - The shear displacement of two adjacent planes of atom.

Slip plane - This is the plane between the planes of atoms on which slip occurs.

Slip direction - This is the direction in which slip occurs.

There are two basic types of dislocations. They are: (a) Edge dislocation and (b) Screw dislocation.

Edge Dislocation

Edge dislocation is shown in Figure 4.22. *Edge dislocation is the defect which arise due to the insertion of an extra half plane of atoms.*

If this extra plane of inserted atoms is above the slip plane, the line defect is called positive dislocation and is denoted by the symbol $\perp$. *Instead, if this extra plane is below, the defect is called negative dislocation and is denoted by the symbol* $\top$.

The horizontal line in the symbol represents the slip plane or line of dislocation and the vertical line the incomplete atomic plane.

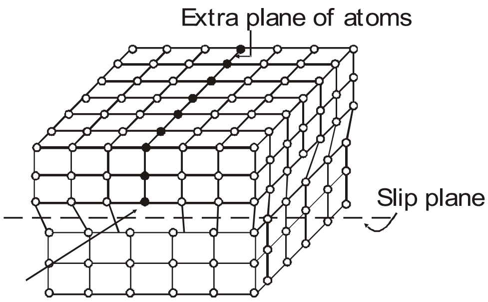


Fig. 4.22: *Positive Edge Dislocations*

The lattice above and below the dislocation line is in the distorted state. For positive dislocation, the lattice above the line is in compression state, whereas below the line it is in tension state,and reverse is the case for negative dislocation.

Burger's Vector

The dislocation lines can also be described by Burger's vector $\vec{b}$. *The vector which indicates the direction and magnitude of the shift of the lattice on the slip plane is called Burger vector.*

Burger vector of a dislocation line can be found by using Burger's loop or circuit method.

Burger's circuit or loop is formed by taking integral lattice translations in each pair of parallel sides in the region of interest. Such a circuit would close itself in a perfect region of the crystal as shown in Figure 4.23. That is a region with no dislocation will form a closed circuit.

In Figure 4.23, consider a point S as the starting point. If we move by atom to atom, 3 steps to the right and 3 steps down and by 3 steps to the left and again 3 steps up, we reach the starting point S. Thus, the circuit gets closed F. That is the start S and finish F of the circuit meet at the same atom.

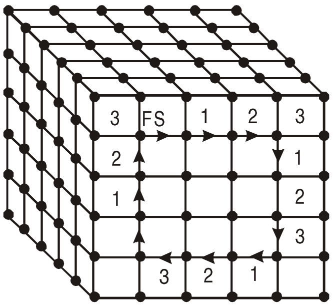


Fig. 4.23 *Burger vector and circuit for a perfect crystal*

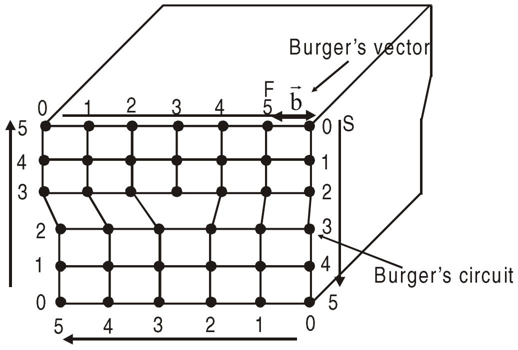


Fig. 4.24 *Burger vector and Burger's circuit for an edge dislocation*

On the other hand, if a Burger circuit is described around the dislocation position of the lattice, the start and finish point will not be coincident as shown in Figure 4.24.

If the circuit fails to close itself in the region containing a dislocation, the closer failure distance i.e., the vector necessary to close the circuit is called Burger's vector $\vec{b}$ of dislocation line.

Let us consider a point S as shown in Figure 4.24, and move down by 5 steps and to the left by 5 steps and move up by 5 steps and again 5 steps to the right. It can be seen that, it ends up at the point F instead of ending at S. Now, we have to move an extra step $\overrightarrow{FS}$ to return to the starting point S inorder to close the circuit. The magnitude and direction of the extra step defines the Burger's vector $\vec{b}$.

Screw Dislocation

Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of crystal forming a spiral ramp around the dislocation line.

If a cylinder as shown Figure 4.25(a) is cut along the plane PQRS and displaced parallel to cut direction as shown in Figure 4.25(b) a screw dislocation results. The axis of the cylinder is the dislocation line. By means of a Burger circuit as shown in Figure 4.26 for a screw dislocation, one can determine the magnitude and direction of the screw dislocation. The Burger vector is parallel to the dislocation line.

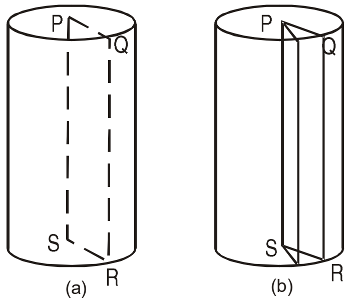


Fig. 4.25 *Screw dislocation*

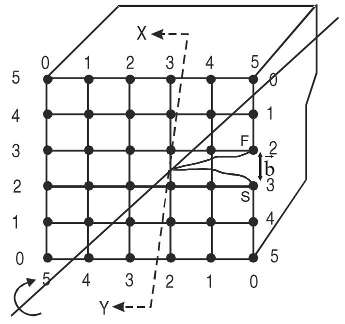


Fig. 4.26 *Burger's vector and circuit for a screw dislocation*

A screw dislocation is continuous helical plane of atoms rather than a series of parallel plane.

The following effects of a screw dislocation are of great importance.

1. The force required to form and move a screw dislocation is probably somewhat greater than that required to initiate an edge dislocation.
2. Plastic deformation is possible under low stress without breaking the continuity of the lattice.
3. Screw dislocation causes distortion of the lattice for a considerable distance from the center of the line and takes the form of spiral distribution of the planes.

Note: In practice, dislocations are oftern considered to be a combination of edge and screw dislocations and are termed as mixed dislocations. For the curved dislocation line as shown Figure 4.27, the dislocation is of the purely screw type at the left where it enters the crystal and of the edge type where it leaves crystal on the right. Within the crystal, the dislocation is a mixture of edge and screw components.

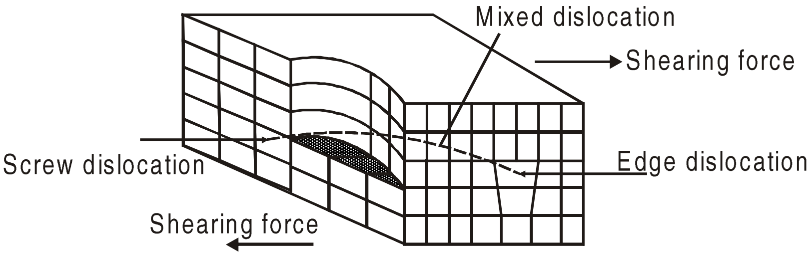


Fig. 4.27 *Mixed dislocation*

4.10.1 Stress Field of Dislocation

The elastic distortion around a straight screw dislocation of infinite length can be represented in terms of a cylinder of elastic material deformed as defined by Volterra. The following illustration shows the basic geometry.

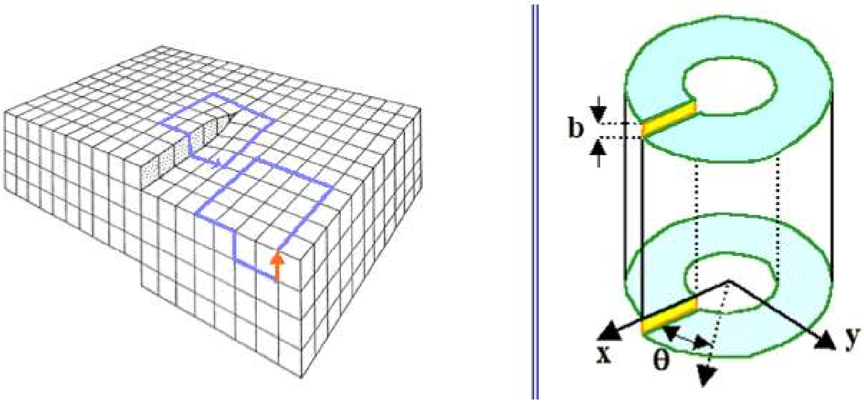


Fig 4.28 *Basic Geometry of Stress Field Dislocation*

A screw dislocation produces the deformation shown in the left hand picture. A radial slit was cut in the cylinder parallel to the z-axis, and the free surfaces displaced rigidly with respect to each other by the distance b, the magnitude of the Burgers vector of the screw dislocation, in the z-direction.

In the core region the strain is very large - atoms are displaced by about a lattice constant. Linear elasticity theory thus is not a valid approximation there, and we must exclude the core region.

In the z-direction, the displacement varies smoothly from 0 to b as the angle θ goes from 0 to 2π. This can be expressed as

$$u_z = \frac{b \cdot \theta}{2\pi} = \frac{b}{2\pi} \cdot \tan^{-1}(y/x) = \frac{b}{2\pi} \cdot \arctan(y/x)$$

Using the equation for the strain we obtain the strain field of a screw dislocation:

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon_{xy} = \varepsilon_{yx} = 0$$

$$\varepsilon_{xz} = \varepsilon_{zx} = -\frac{b}{4\pi} \cdot \frac{y}{x^2 + y^2} = -\frac{b}{4\pi} \cdot \frac{\sin\theta}{r}$$

$$\varepsilon_{yz} = \varepsilon_{zy} = \frac{b}{4\pi} \cdot \frac{x}{x^2 + y^2} = \frac{b}{4\pi} \cdot \frac{\cos\theta}{r}$$

The corresponding stress field is given by

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma_{xy} = \sigma_{yx} = 0$$

$$\sigma_{xz} = \sigma_{zx} = -\frac{G \cdot b}{2\pi} \cdot \frac{y}{x^2 + y^2} = -\frac{G \cdot b}{2\pi} \cdot \frac{\sin\theta}{r}$$

$$\sigma_{yz} = \sigma_{zy} = \frac{G \cdot b}{2\pi} \cdot \frac{x}{x^2 + y^2} = \frac{G \cdot b}{2\pi} \cdot \frac{\cos\theta}{r}$$

In cylindrical coordinates, the stress field is given below:

$$\sigma_{rz} = \sigma_{xy}\cos\theta + \sigma_{yz}\sin\theta$$

$$\sigma_{\theta z} = -\sigma_{xz}\sin\theta + \sigma_{yz}\cos\theta$$

The following figure and equations show the stress field of edge dislocation.

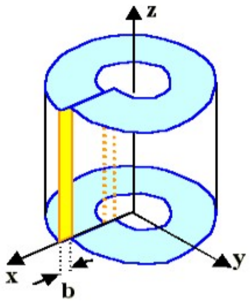


Fig 4.29 Stress Field of Edge Dislocation

$$\sigma_{xx} = -D \cdot y \frac{3x^2 + y^2}{(x^2 + y^2)^2}$$

$$\sigma_{yy} = D \cdot y \frac{x^2 - y^2}{(x^2 + y^2)^2}$$

$$\sigma_{xy} = \sigma_{yx} = D \cdot x \frac{x^2 - y^2}{(x^2 + y^2)^2}$$

$$\sigma_{zz} = \nu \cdot (\sigma_{xx} + \sigma_{yy})$$

$$\sigma_{zz} = \sigma_{zx} = \sigma_{yz} = \sigma_{zy} = 0$$

Check Your Progress

16. What do you mean by line defect?
17. What are the causes of dislocations?

4.11 GRAIN BOUNDARIES

NOTES

A Grain Boundary is a general planar defect that separates regions of different crystalline orientation (i.e., *grains*) within a polycrystalline solid.

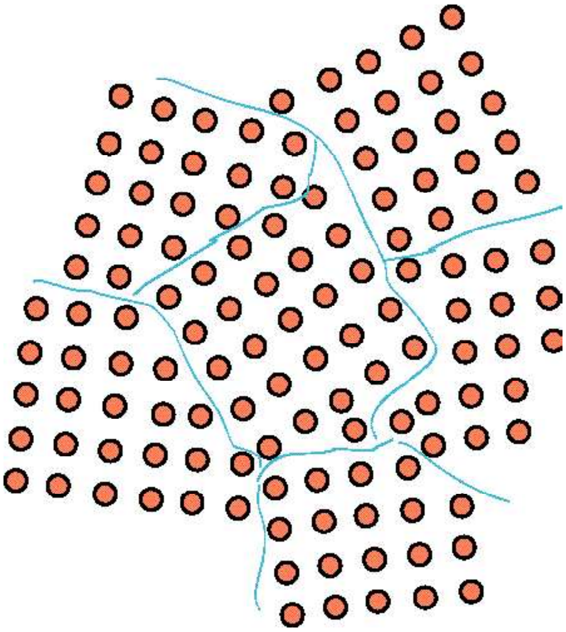


Fig 4.30 *Grain Boundaries*

The atoms in the grain boundary will not be in perfect crystalline arrangement. Grain boundaries are usually the result of uneven growth when the solid is crystallising. Grain sizes vary from *1 μm to 1 mm*.

(i) Tilt /Lineage Boundaries

It is boundary between two adjacent perfect regions in the same crystals that are slightly tilted with respect to each other.

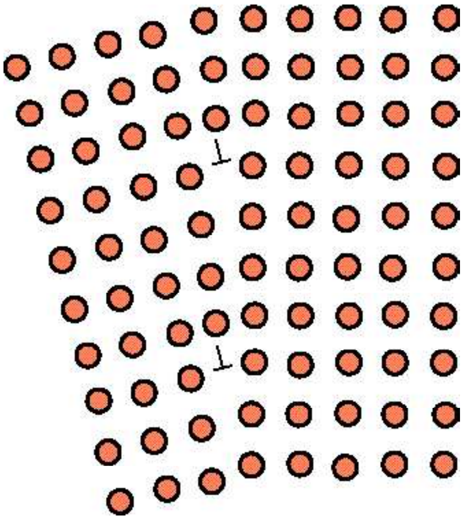
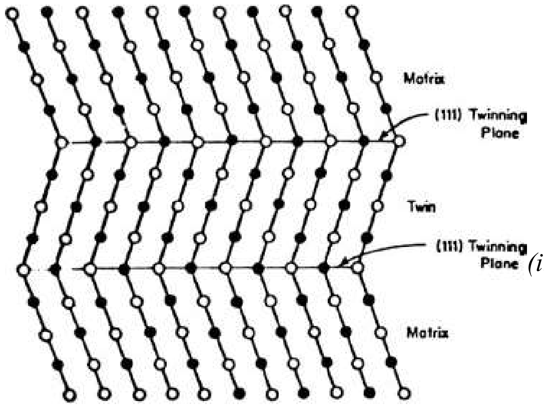


Fig 4.31 *Tilt Boundaries*



(ii) Twin Boundaries

Fig 4.32 (a) *Twin Boundaries*

A Twin Boundary happens when the crystals on either side of a plane are mirror images of each other.

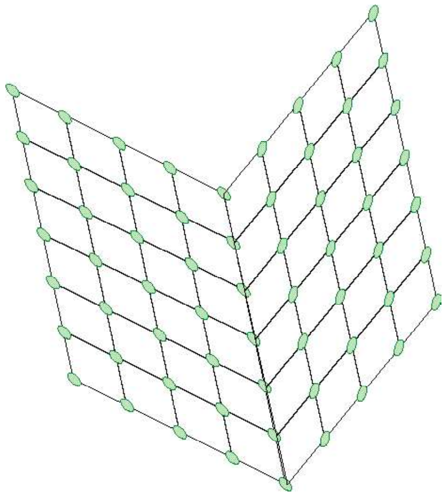


Fig 4.32 (b)

The boundary between the twinned crystals will be a single plane of atoms. There is no region of disorder and the boundary atoms can be viewed as belonging to the crystal structures of both twins.

Twins are either grown-in during crystallisation, or the result of mechanical or thermal work.

4.12 ETCHING AND ITS TYPES

Etching is the process of material being removed from a material's surface. The two major types of etching are wet etching and dry etching (e.g., plasma etching). The etching process that involves using liquid chemicals or etchants to take off the substrate material is called wet etching.

In the plasma etching process, also known as dry etching, plasmas or etchant gases are used to remove the substrate material. Dry etching produces gaseous products, and these products should diffuse into the bulk gas and be expelled through the vacuum system. There are three types of dry etching (e.g., plasma etching):

1. Chemical reactions (by using reactive plasma or gases)
2. Physical removal (generally by momentum transfer)
3. Combination of chemical reactions and physical removal

On the other hand, wet etching is only a chemical process.

Advantages and Disadvantages of Dry Etching (Plasma Etching) and Wet Etching

The advantages of wet etching processes are relatively fast with high etch rates. The simple equipment baths or spraying of wet chemistry can have high selectivity. The wet process typical etching agent are liquid solvents, corrosive leeches and acids. The process equipment is typically an immersion tank or spray system of the chemistry of choice. However, there are many disadvantages. Wet etching is generally isotropic, which results in the etchant chemicals removing substrate material under the masking material at the same rate as the bulk etch. Wet etching also requires large amounts of etchant chemicals because the substrate material has to be covered with the etchant chemical. Furthermore, the etchant chemicals have to be constantly replaced in order to keep the same initial etching rate as the etch chemistry loads with etched by-product. As a result, the chemical and disposal costs associated with wet etching are relatively high.

Some of the advantages of dry etching are its capability of automation, reduced material consumption, the ability to use different etch gases with very different process settings in the same tool with little to no hardware change over time. This process is also performed away from the operator in the vacuum chamber producing a condition of good industrial hygiene. Dry etching (e.g., plasma etching) chemistry disposal costs less and is easier to dispose of the by-products compared to wet etching. Some of the disadvantages of plasma etching: typically it is a batch process, and it is performed in a vacuum chamber.

Check Your Progress

18. What is grain boundary?
19. Define etching.

4.13 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The defects which take place due to imperfect packing of atoms during crystallisation are known as point defects.
2. When the thermal energy due to the vibration gets increased among atoms, it can result in a particular atom acquiring sufficient energy to escape, thereby creating a vacancy.

3. Atomic vibrations and vacancies allow atoms to move through a sold. This motion of matter through other matter is called diffusion.
4. The diffusion coefficient is affected by concentration, but this effect is generally small when compared to the effect of temperature.
5. If the solid is composed of a single element (pure copper for example), the movement of the atoms is called self-diffusion because the moving atom and the solid are the samse chemical element.
6. The electrical conductivity σ is defined as the rate of charge flow across a unit area in a conductor per unit potential (voltage) gradient.
7. Presence of vacancies in the crystal causes the absorption band to appear in the range of visible spectrum. When the vacancies capture electrons or holes, they are capable of absorbing light and since the crystal appears coloured because of absorption of light, these are called coloured centres.
8. 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.
9. Luminescence is the generic term for the emission of light which is not an effect of high temperature.
10. Fluorescence is a process where a substance emits light as an effect of the absorption of light of a shorter wavelength.
11. Any substance which is able to emit light of a distinct wavelength after excitation with another distinct wavelength is called a fluorochrome.
12. Tensile strength is a measurement of the force required to pull something, such as rope, wire, or a structural beam to the point where it breaks. The tensile strength of a material is the maximum amount of tensile stress that It can take before failure, for example breaking.
13. Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.
14. This type of deformation is not undone simply by removing the applied force. An object in the plastic deformation range, however, will first have undergone elastic deformation, which is undone simply be removing the applied force, so the object will return part way to its original shape.
15. Scratch hardness is the measure of how resistant a sample is to fracture or permanent plastic deformation due to friction from a sharp object. The principle is that an object made of a harder material will scratch an object made of a softer material when testing coatings, scratch hardness refers to the force necessary to cut through the film to the substrate. The most common

test is Mohs scale, which is used in mineralogy. One tool to make this measurement is the sclerometer.

16. The defects which take place due to dislocation or distortion of atoms along a line in some direction is called as line defect. Movement of dislocation is necessary for plastic deformation.
17. Dislocations arise in a crystal as a result of growth accidents, phase transformations, thermal stresses, external stresses causing plastic flow and segregation of solute atoms causing mismatches.
18. A Grain Boundary is a general planar defect that separates regions of different crystalline orientation (i.e., *grains*) within a polycrystalline solid.
19. Etching is the process of material being removed from a material's surface.

4.14 SUMMARY

- The defects which take place due to imperfect packing of atoms during crystallisation are known as point defects.
- A vacancy is the simplest point defect in a crystal. This refers to a missing atom or a vacant atomic site.
- When the thermal energy due to the vibration gets increased among atoms, it can result in a particular atom acquiring sufficient energy to escape, thereby creating a vacancy.
- Whenever a pair of positive and negative ions are missing from a crystal the defect is known as Schottky defect. That is a pair of missing ion (one cation and one anion) vacancies is termed as Schottky defect.
- Frenkel defect occurs whenever a cation (positive ion) moves from a normal lattice point to an interstitial site.
- Atomic vibrations and vacancies allow atoms to move through a sold. This motion of matter through other matter is called diffusion. In other words diffusion is the shifting of atoms and molecules to new sites within a material resulting in the uniformity of composition as a result of thermal agitation.
- Vacancy mechanism for diffusion in (FCC, BCC, HCP) metals. Diffusion can occur by atoms moving into adjacent sites that are vacant.
- If the solid is composed of a single element (pure metal), the movement of atoms is called self diffusion because the moving atom and the solid are the same chemical-element. Copper and nickel are mutually soluble in all proportions in the solid state and form substitutional solid solutions e.g., plating of nickel on copper.
- Interstitial may occur when a solid is composed of two or more elements whose atomic radii differ significantly. The large atoms occupy lattice sites while the smaller ones fit into the voids created by the large atoms. These voids are called interstices.

NOTES

- The inequality of diffusion was first shown by Kirkendall. He used an α-brass/copper couple and showed that zinc atoms diffused out of brass into copper more rapidly than copper atoms diffused into brass. Voids can be observed in brass due to a net loss of Zn atoms.
- Ficks first law describes the rate at which diffusion occurs and allows the calculation of the instantaneous mass flow rate (flux) past any plane in a solid but gives no information about the time dependence of the concentration. The time dependence is contained in Fick's second law, which can be derived using Fick's first law and the law of conservation of mass.
- The diffusion coefficient is affected by concentration, but this effect is generally small when compared to the effect of temperature.
- If the solid is composed of a single element (pure copper for example), the movement of the atoms is called self-diffusion because the moving atom and the solid are the same chemical element.
- A diffusion couple consists of two solids of different compositions in contact with one another, so that each tries to diffuse into the other. This is called inter-diffusion and is responsible for diffusion welding.
- Case-hardening is a process in which one element (usually in gaseous form) is diffused into another (a solid), the diffusion being limited to a small region near the surface. The properties of this region are changed as a result.
- The electrical conductivity σ is defined as the rate of charge flow across a unit area in a conductor per unit potential (voltage) gradient.
- 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.
- Presence of vacancies in the crystal causes the absorption band to appear in the range of visible spectrum. When the vacancies capture electrons or holes, they are capable of absorbing light and since the crystal appears coloured because of absorption of light, these are called coloured centres.
- 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 in semiconducting materials can form when a material absorbs a photon of higher energy than its bandgap (hv is greater than Eg).

- Luminescence is an umbrella term for those kinds of events where light emission is not the result of high temperatures.
- Luminescence is the generic term for the emission of light which is not an effect of high temperature. So luminescence can be determined as an appearance of cold body radiation.
- Chemiluminescence is a light-emitting process based on a chemical reaction where the product has an excited intermediate. This intermediate emits light when falling into the ground state. Unlike fluorescence, electrons in chemiluminescent materials are excited by a chemical reaction and not by the absorption of photons.
- Tensile strength is a measurement of the force required to pull something, such as rope, wire, or a structural beam to the point where it breaks. The tensile strength of a material is the maximum amount of tensile stress that it can take before failure, for example breaking.
- Definition of material toughness is the amount of energy per unit volume that a material can absorb before rupturing. This measure of toughness is different from that used for fracture toughness, which describes load bearing capabilities of materials with flaws. It is also defined as a material's resistance to fracture when stressed.
- Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.
- Under tensile stress, plastic deformation is characterized by a strain hardening region and a necking region and finally, fracture (also called rupture). During strain hardening the material becomes stronger through the movement of atomic dislocations.
- Hardness is a measure of the resistance to localized plastic deformation induced by either mechanical indentation or abrasion. In general, different materials differ in their hardness, for example hard metals such as titanium and beryllium are harder than soft metals such as sodium and metallic tin, or wood and common plastics
- Indentation hardness measures the resistance of a sample to material deformation due to a constant compression load from a sharp object. Tests for indentation hardness are primarily used in engineering and metallurgy fields.
- Scratch hardness is the measure of how resistant a sample is to fracture or permanent plastic deformation due to friction from a sharp object. The principle is that an object made of a harder material will scratch an object made of a softer material when testing coatings, scratch hardness refers to the force necessary to cut through the film to the substrate. The most common test is Mohs scale, which is used in mineralogy.

- In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods and generally increases as they near their melting point.
- In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface. The crack will continue to grow until it reaches a critical size, which occurs when the stress intensity factor of the crack exceeds the fracture toughness of the material, producing rapid propagation and typically complete fracture of the structure.
- The defects which take place due to dislocation or distortion of atoms along a line in some direction is called as line defect. Movement of dislocation is necessary for plastic deformation.
- Edge dislocation is the defect which arise due to the insertion of an extra half plane of atoms.
- Burger’s circuit or loop is formed by taking integral lattice translations in each pair of parallel sides in the region of interest. Such a circuit would close itself in a perfect region of the crystal.
- Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of crystal forming a spiral ramp around the dislocation line.
- Etching is the process of material being removed from a material’s surface. The two major types of etching are wet etching and dry etching (e.g., plasma etching). The etching process that involves using liquid chemicals or etchants to take off the substrate material is called wet etching.

4.15 KEY TERMS

- **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.
- **Diffusion:** Diffusion is defined as the movement of individual molecules of a substance through a semipermeable barrier from an area of higher concentration to an area of lower concentration.
- **Tensile strength:** Tensile strength is a measurement of the force required to pull something, such as rope, wire, or a structural beam to the point where it breaks.
- **Elongation:** Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining

the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.

- **Creep:** In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses.
- **Fatigue:** In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface.

4.16 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. State the applications of diffusion.
2. What does the Fick's law say?
3. State the ways through which coloured centres are produced.
4. How is exciton formed?
5. What do you mean by the mechanical strength of crystal?
6. What do you understand by creep and fatigue?
7. How is the toughness measured?
8. What do you understand by hardness?
9. What are edge dislocation and screw dislocation?
10. What are tilt and twin grain boundaries?
11. What are the advantages and disadvantages of dry and wet etching?

Long-Answer Questions

1. Discuss the most common point defects in a crystal.
2. Explain the diffusion mechanisms.
3. Describe the types of colour centres.
4. Discuss the classification of exciton.
5. Explain the general idea of luminescence.
6. Elaborate on the tensile strength
7. Discuss about the toughness.
8. Explain plastic deformation with examples.
9. Elaborate on the stress field of dislocation.

NOTES

4.17 FURTHER READING

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UNIT 5 ELEMENTS OF THIN FILM

NOTES

Structure

5.0 INTRODUCTION

Thin Film Deposition is a well-known technique to deposit a thin film of sample material that ranges from a few nanometres to about 100 micrometres, or in other words the thickness of atomic dimension onto a 'Substrate', or on a previously deposited film layer. Thin Film Deposition techniques are an essential need have today's semiconductor and electronics industry like solar panels, CDs, disk drives, and optical devices industries. Thin Film Deposition can be divided into two broad categories - Chemical deposition method and Physical vapour deposition Coating method. Physical vapour deposition is used in a wide range of technologies applications where the sample material is vapourised from a source boat and deposited on a substrate using any of one from mechanical, electromechanical, or thermodynamic processes. Nowadays two most commonly used deposition techniques for physical vapour deposition are the Thermal Evaporation Technique and Sputtering Technique. Physical evaporation is one of the basic and oldest methods used for depositing metal films. Metals like Aluminum, gold, and other metals are heated using current elements in a boat to the point of vaporisation and then freed to evaporate to form a thin film covering the surface of the substrate. All film deposition needs an under a vacuum or very carefully controlled atmosphere. Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface. After leaving the source material surface these free atoms travel through the vacuum chamber and got coated on a substrate positioned above the evaporating material. In this unit, you will study about thin films, their deposition by thermal evaporation, thickness measurement, multiple-beam interferometry, size effects in thin films and Fuchs-Sondheimer Model.

5.1 OBJECTIVES

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

- Discuss the concept of thin films by thermal evaporation
- Explain the meaning of cathode sputtering and evaporation at reduce
- Describe the thickness measurement by quartz crystal method
- Discuss the four probe method and multiple-beam interferometry
- Explain the size effects in thin films and Fuchs-Sondheimer Model

5.2 CONCEPT OF THIN FILM AND ELECTRICAL CONDUCTION

A thin film is a layer of material which has thickness in the range of fractions of a nanometer (monolayer) to several micrometers. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. A familiar example is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently the metal layer is deposited using techniques such as sputtering.

Electrical Conduction in Thin Films

The conductivity of a thin metal film forming an island structure can be defined in terms of the island size and spacing, and of the properties of the substrate and the film material. The potential barrier heights for electron tunnelling between particles of gold, particles of platinum, and particles of silver through soda and barium aluminosilicate glass have been determined.

Thin-film nanocomposites, consisting of silver nanoparticles embedded in a dielectric Teflon AF matrix, are synthesized using vapor phase co-deposition. The electrical conductivity of these composites is measured in-situ as a function of film thickness at various metal concentrations. At low metal concentrations (90%), fragmented fractal nanoclusters are able to further interconnect to achieve the percolation process and eventually evolve into a metallic continuum with dielectric polymer inclusions.

5.2.1 Deposition of Thin Films by Thermal Evaporation

The thermal Evaporation Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film. This evaporated material in a vacuum chamber now creates a vapor stream that travels through the vacuum without reacting or scattering against other atoms or walls of the chamber. It traverses the chamber and hits the substrate, sticking to it as a coating or thin-film substrate. Two primary methods used for heating the source material during the process of Thermal Evaporation. One includes Filament Evaporation, as it is achieved with a simple electrical heating element or filament inside a boat. The other heat method used electron beam or E-Beam Evaporation where an electron beam is focused at the source material to evaporate it and convert it into the gas phase. The main advantages of thin Film Evaporation systems including high deposition rates, real-time deposition and thickness control, and (with suitable physical configuration) good evaporant stream directional control for processes such as Lift Off to achieve directly patterned coatings.

NOTES

Basic Principle: Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface. After leaving the source material surface these free atoms travel through the vacuum chamber and got coated on a substrate positioned above the evaporating material.

Procedure: In thermal evaporation techniques, depending on the availability of tools and types of source and substrate materials used for deposition different methods can be applied to heat the source material. The instrument available in the laboratory utilised either resistance heating or electron beam heating, usually several KeV, from an electron beam gun (electron beam heating).

5.2.2 Cathode Sputtering

As we know, the destruction of the negative electrode in a gas discharge is caused by the impact of positive ions. In a larger aspect, destruction of a solid through bombardment by charged or neutral particles is called sputtering.

On the one hand, cathode sputtering is an undesirable phenomenon that shortens the life of electronic devices; on the other hand, it is of practical use for cleaning surfaces, revealing the structure of a substance (ionic etching), depositing thin films, and producing directional molecular beams. The bombarding ions that penetrate the target produce displacement of its atoms. New displacement is produced due to these displaced atoms. Few of the atoms reach the surface and pass out of it. Under certain conditions, particles may leave the target's surface in the form of ions. In single crystals, conditions are most favorable for particle emission in direction in which the atomic packing density is the greatest.

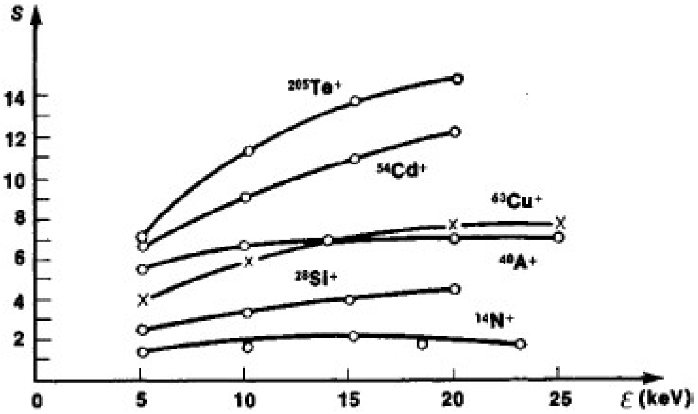

Fig 5.1 *Dependence of Sputtering Coefficient S for a Copper Target on Energy ε of Bombarding ions*

When the energy of ions å is greater than å$_o$ cathode sputtering occurs which is called cathode sputtering threshold. The value of ε_0 ranges from a few to several dozen electron volts. It is characterized quantitatively by the sputtering coefficient S, which is equal to the number of at oms dislodged by one ion. Near the threshold S is very small (10^{-s} atoms per ion), but under optimum conditions it may be as high as several dozen. Its value is independent of gas pressure at pressures $p < 13.3$ newtons per sq m (N/m^2), or 0.1 mm of mercury, but when $p > 13.3$ N/m^2, *S* is affected both by the characteristics of the bombarding ions, such as their energy y £ (Figure 5.1), their mass M (Figure 5.2), and their angle of incidence a on the target (Figure 5.3), and by the properties of the substance being sputtered, such as the cleanliness of the surface, temperature, crystal structure and mass of the target's atoms.

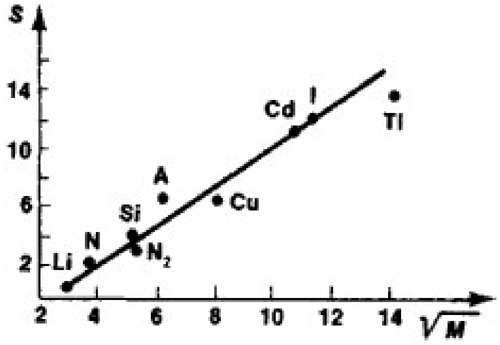

Fig 5.2 *Dependence of Sputtering Coefficient S mass,* M *of the Bombarding lons (ε = 400ev)*

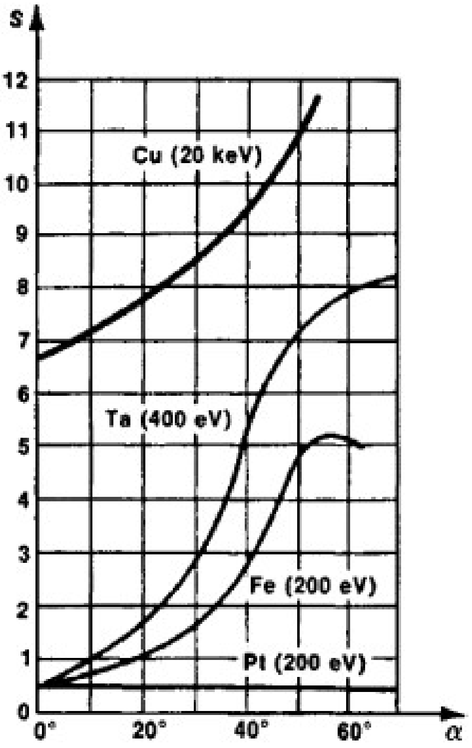

Fig 5.3 *Dependence of Sputtering Coefficient S on Angle of Incidence a of ions Bombarding the surface of Cu, Ta, Fe, and Pt (the numbers indicate the energy of the ions)*

Anisotropic is the distribution of particles escaping from the sputtered surface. It depends on the energy of the ions, and for single crystals, it also depends on the type of crystal lattice and structure of the facet being sputtered. The substance being sputtered is deposited on the screen in the form of individual spots with a symmetry pattern identical to that of the facet being sputtered and of the etch figures formed on the sputtered face as a result of the cathode sputtering. The energy of the sputtered particles varies from fractions of an electron volt up to values of the order of the energy in the primary ions. Sputtered particles average energy is usually dozens of electron volts and depends on the properties of the target material and the characteristics of the ion beam.

5.2.3 Evaporation At Reduce

In Algeria, water resources are scarce and renewable due to low annual precipitation. The extremely high rate of evaporation from water surfaces in arid and semi-arid areas greatly reduces optimal utilization of water reservoirs. In order to reduce evaporation rates, dams with a capacity of 7.4 billion m3 were constructed. One of the biggest problems with these dams in Algeria is the huge amount of water loss through evaporation due to high evaporation rate. Therefore, applying techniques to reduce evaporation are greatly needed. The most applicable techniques for reducing evaporation is the application of a thin chemical film on the surface of the water. Some methods of practical importance are mentioned below:

1. By Keeping Free Water Surface Area Minimum

The water bodies with large surface area are reservoirs of lakes.

It is possible to reduce the surface area by adopting following measures:

(a) The reservoir site may be selected in such a way that area to storage ratio is minimum.

(b) To avoid water loss water could be stored below ground.

(c) When there are more than one reservoirs on one river the water may be stored in one large reservoir when possible rather than in several small reservoirs.

2. By Spreading Surface Films on the Reservoirs and Lakes

Scientists have come up with a new method of conserving water. They took small amounts of oil and spread them over the surface of water. The amount was just enough to make a thin layer over the surface, which covered it completely. This is called "oiling" the water.

Experiments have shown that a compound called hexadeconal or cetryl alcohol derived from tallow, sperm oil or coconut oil is capable of forming monomolecular film on the water surface. This material is white, waxy, crystalline and solid, and is generally available in flakes or powder form.

It is relatively tasteless and odorless. It is pervious to oxygen and carbon dioxide. It is also nontoxic to living being and polar compound in which one end of the molecule is hydrophilic and therefore, shows great affinity for water whereas the other end is hydrophobic and repels water.

Due to this property it forms a monomolecular film on the water surface.

The film so formed is only about 15 x 10^{-4} mm thick but it is tight enough to prevent water molecule from escaping the water body. It is flexible and moves with the motion of water surface without breaking. The film is penetrable by rain drops but the film again closes after allowing rain drops to enter.

It is estimated that such a film may reduce evaporation by one-third. Theoretically only 25 gm of hexadeconal is sufficient to spread a mono-molecular film on one hectare of water surface. In practice, however, due to working problems as much as 100 times of theoretically required quantity may be necessary. Even then it is quite economical and promising. Combination of hexadeconal and octadeconal was also used for better results.

3. By Providing Mulch on the Land Surfaces:

The mulch is a protective blanket made from some waste material used to cover the land. By "mulch" one generally understands a mixture of straw, leaves etc. It restricts air movement, maintains high water vapour pressure near the soil surface and shields the sun's energy to reduce evaporation. There are many types of mulches including compost, manure,

Check Your Progress

1. What is the basic principle of working of thermal evaporation technique?
2. Define cathode sputtering.
3. What is mulch?

5.3 THICKNESS MEASUREMENT

It has been well known that the film deposition and their structure of vacuum are highly dependent on the deposition parameters like a vacuum, distance between source and substrate. Since the thin film formation and the resulting structure of the films decide to a large extent the physical properties. since these properties highly dependent on the same deposition parameters hence it becomes important that as many of these parameters must be under close control as possible during the deposition of thin-film if vacuum deposited thin films are to be made reproducible in every respect.

The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardised to measure thickness after removed from the deposition chamber. Only a few measurement methods are suitable for real-time monitoring of film thickness during thin film growth on the substrate. The very useful and accurate gravimetric technique to determine both thin film deposition rate and thickness of thin-film utilised a quartz crystal oscillator. It is based on the fact of using the thickness-shear mode of piezoelectric quartz crystal. A change in the resonant frequency of the crystal oscillator during the process of thin-film deposition varies linearly with the deposited mass on the electrode of the crystal. If the crystal sensor is made to place near the substrate during the process of deposition the as the coating on the crystal increases its mass will lower its resonant frequency. Here we discuss the application of quartz-crystal monitors in a thin film deposition chamber of ultrahigh vacuum pressure setup. Inside this kind of chamber, there are two holders for quartz oscillators. The mass deposited from the source material and its evaporation rate is controlled during deposition by a monitoring quartz sensor mounted and from the side of the substrate holder and so the crystal does not receive the same deposition rate as the substrate.

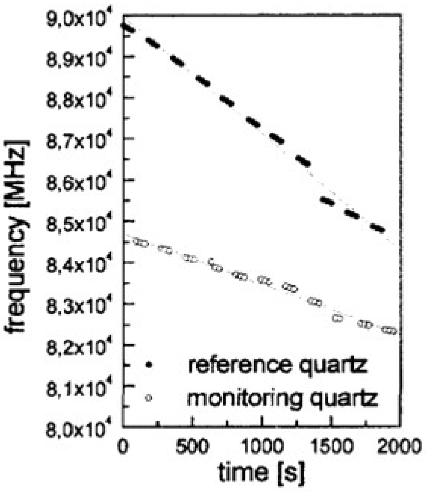

Fig. 5.4 *The Frequency changes of Reference and Monitoring Quartz Crystals as a Function of Evaporation Time. Solid Lines Represent Linear Fit Results*

There is no direct correlation between the mass of the crystal and the resonant frequency, therefore a tooling factor correction has to be determined. For this purpose, a reference quartz oscillator is mounted on the backside of a rotatable thin film substrate holder. The determination of tooling factor is performed by source material evaporation in one process on both, monitoring and reference, quartz crystals. The calibration of quartz crystal monitors is done by silver evaporation with the evaporator. The frequency was sampled every 30 s during 30 min of evaporation. Registered changes of frequency are shown in Figure 5.4. The tooling factor between reference and monitoring quartz determined as a ratio of slopes of fitted lines were equal to 2.2(2). In the next step, silver was evaporated on a glass substrate with a deposition rate of about 9 A/min. The observed frequency change corresponds to the deposition of 20.8 mg of silver. Assuming the uniform film thickness and its density as for bulk system it is equivalent to a thickness of 198 A. This result is in very good agreement with a thickness measured by X-ray reflectometry.

5.3.1 Four Probe Method

The resistance, R of a conductor is proportional to its length L and inversely proportional to its area of cross section A, at a constant temperature.

$$R = \rho \frac{L}{A} \qquad \ldots 5.1$$

where ρ is the resistivity of the conductor and its unit is ohmmeter.

NOTES

Semiconductor can be described as electrical conductivity intermediate between a conductor and insulator. Semiconductors have the characteristic property that their electrical resistivity decreases with increasing temperature.

Further as per band theory, the energy levels of semiconductors can be grouped into two bands, valence band and the conduction band. In the presence of an external electric field it is electrons in the valence band that can move freely, thereby responsible for the electrical conductivity of semiconductors. In case of intrinsic semiconductors, the Fermi level lies in between the conduction band minimum and valence band maximum. Since conduction band lies above the Fermi level at 0K, when no thermal excitations are available, the conduction band remains unoccupied. So conduction is not possible at 0K, and resistance is infinite. As temperature increases, the occupancy of conduction band goes up, thereby resulting in decrease of electrical resistivity of semiconductor.

The resistivity of semiconductor by four probe method are as follows:

(1) The resistivity of material is uniform in the area of measurement.

(2) If there is a minority carrier injection into the semiconductor by the current-carrying electrodes most of the carriers recombine near electrodes so that their effect on conductivity is negligible.

(3) The surface on which the probes rest is flat with no surface leakage.

(4) The four probes used for resistivity measurement contact surface at points that lie in a straight line.

(5) The diameter of the contact between metallic probes and the semiconductor should be small compared to the distance between the probes.

(6) The boundary between the current carrying electrodes and the bulk material is hemispherical and small in diameter.

(7) The surface of semiconductor material may be either conducting and non-conducting. A conducting boundary is one on which material of much lower resistivity than semiconductor has been plated. When the surface of the semiconductor is in contact with insulator, a non-conducting boundary is produced.

$$\rho = \frac{\rho_0}{f\left(\frac{w}{s}\right)} \qquad \ldots 5.2$$

Where in equation (5.2) function, f(w/S) is a divisor for computing resistivity which depends on the value of w and S

We assume that the size of the metal tip is infinitesimal and sample thickness is greater than the distance between the probes,

$$\rho = \frac{V}{I} \times 2\pi S \qquad \ldots 5.3$$

Where equation (5.3) V – the potential difference between inner probes in volts. I – Current through the outer pair of probes in ampere.

S – Spacing between the probes in meter.

Temperature dependence of resistivity of semiconductor

Total electrical conductivity of a semiconductor is the sum of the conductivities of the valence band and conduction band carriers. Resistivity is the reciprocal of conductivity and its temperature dependence is given by

$$\rho = A \exp \frac{E_g}{2KT} \qquad \ldots 5.4$$

Where E_g – band gap of the material T – Temperature in kelvin

K – Boltzmann constant, K – 8.6×10^{-5} eV/K

The resistivity of a semiconductor rises exponentially on decreasing the temperature.

5.3.2 Multiple-Beam Interferometry

A technique called multiple-beam interferometry is used to measure surface roughness or defects. The technique is based upon placing two highly reflective surfaces close together and then directing beams of light through a lens onto the surfaces.

Characteristics of Multiple-Beam Interference Patterns

Multiple-beam interferometry has an advantage in that the breadth of the fringes becomes extremely narrow. When the optimal conditions are satisfied, the breadth of the fringes in multiple-beam interferometry is on the order of 1/50 of the corresponding breadth in two-beam method, and hence precision improves by a factor of 50. The limit of measurement in multiple-beam interferometry is therefore in the order of 0.5 nanometer (5 Angstroms).

As in the case of two-beam interferometry, successive interference fringes appear localized at every level change of half a wavelength. However, because the fringes are narrow, information concerning the regions between the fringes is likely to be unavailable.

Practical Applications of Multiple-Beam Interferometry

When surface topography is measured by multiple-beam interferometry, the specimen and the reference plate make contact at some point. Hence, this method is not appropriate for specimens that are sensitive to contamination or for very soft specimens. Moreover, specimens which for some reason cannot be coated with silver are not suitable.

As previously explained in the discussion of conditions for sharpness of interference fringes, the closest possible proximity of the specimen and the reference plate is essential. In order to realize this, the specimen and reference flat are clamped in a jig having three screws that must be adjusted while observing the interference fringes through the microscope. As in the case of two-beam interferometry, the pattern must be adjusted so that the fringes appear perpendicular to the step to be measured, and the dispersion of the fringes is also adjusted. Measurement can be performed if at least three fringes appear in the view field.

Applications: Fabry-Parot Interferometer

Resolving power of spectrum is the intensity interference pattern of two beams, either due to split of wave front or amplitude.

In general $I = 4I_0 \cos^2 \frac{\delta}{2}$

$$\delta = \frac{2\pi}{\lambda}\Delta$$

δ = phase diffarance Δ = optical path difference

If one beam has abrupt phase change of π, due to reflex

$$I = 4I_0\ sin^2\frac{\delta}{2}$$

In the case of multiple beam interference

$$I < 0\frac{1}{i + F\ sin^2\frac{\delta}{2}}$$

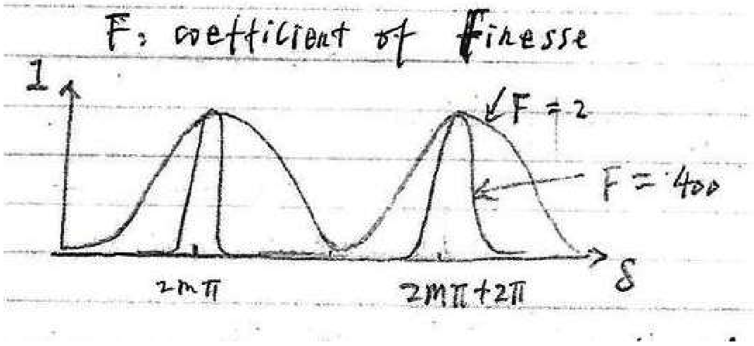

Fig 5.5 *Pattern of Fabry-Parot Interferometer*

The higher the F, the more concord ratio of the light is.

F ⇒ reduce to two beams

F ⇒ sinusoidar vartiation of fringe

Multiple beam interference from A plane parallel film

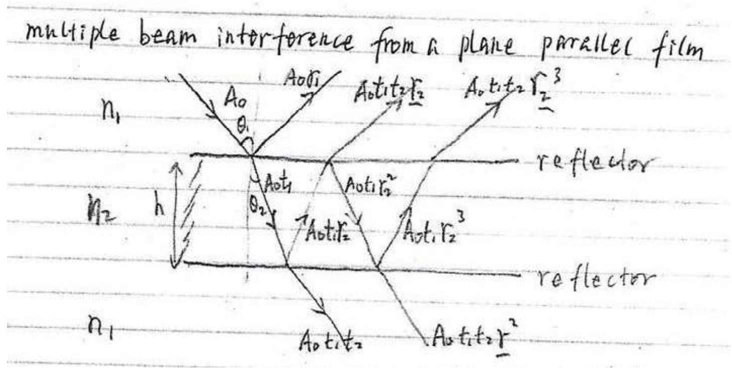

Fig 5.6 *Mutiple Beam Interference from a Plane Parallel Film*

The reflected wave

Ist $= A_0 r_1$

2nd $= A_0 t_1 t_2 r_2, e^{18}$

3rd : $A_0 t_1 t_2 r_2^3 e^{128}$

4th : $A_0 t_1 t_2 r_2^4. e^{135}$

5.4 SIZE EFFECTS IN THIN FILMS

An enhancement of the critical field of V3Ge, Nb, and Ta is achieved by reducing the effective coherence length of these materials. This change in the coherence length is obtained in Nb and Ta by changing the grain size and therefore, the mean free path of the bulk material. Thin films of V3Ge, Nb, and Ta have been obtained in thicknesses ranging from 200 000 to 100 Å. The V3Ge films were produced by the hydrogen reduction of the mixed chlorides and by a new method called getter sputtering. The Nb and Ta films were sputtered. In all cases, MgO wafers were used as substrates. The critical temperatures of the films were approximately that of the bulk, although the thinner films always displayed slightly lower critical temperatures. The transition field of the films, measured by a resistance technique, was found to increase as the thickness of the films decreased. In conjunction with the transition field increase, a corresponding increase in the residual resistivity was observed, which implies a reduction in the mean free path. The departure of the transition magnetic field from the bulk value occurred at such large thicknesses (a few 10 000 Å) that such a size effect cannot be explained in terms of the film thickness becoming comparable with the coherence length. This effect can be interpreted in terms of the very small grain size produced by sputtering films which, in turn, leads to a mean free path well below 100 Å. The presence of a sufficiently small grain size provides a means to produce negative surface energy superconductors with decreasing mean free path and consequently increasing κ (the Ginzburg-Landau parameter), without the addition of alloying elements.

5.5 FUCHS-SONDHEIMER MODEL

Over many decades, the effect of surfaces on electron transport in thin films has attracted great interest, both for its technological importance and the underlying physics of mesoscopic systems. The Fuchs-Sondheimer (FS) model, first proposed in 1938 and extended by various researchers, is still the best known and most widely used analytical approach to describe the resistivity due to electron specularity parameter *p* which represents the probability for specular (rather than diffuse) electron reflection from a surface.

Due to its simplicity and versatility, the FS model has been widely used to fit measured thin film resistivity data. However, the use of the single parameter *p* to describe the electron surface scattering has resulted in ambiguity, as the understanding regarding the physical parameters that determine *p* is limited. More specifically, some studies indicate that *p* is affected by the surface chemistry, reporting that the surface scattering specularity of Cu(001) decreases during oxidation or when adding metal- lic cap layers, including Ta, Ni, or Ti. Some specularity is retained for insulating cap layers, which is attributed to the low surface density of states. Other studies have attributed the changes in p to the surface morphology, e.g., adatoms and surface vacancies. These disturb the smooth surface potential and increase the resistivity corresponding to a scattering specularity *p* 0.34 from measurements on evaporated silver thin films, and *p* 0.29 from first principles simulations. The clusters may exhibit atomically smooth surface potentials and therefore do not alter the specularity, but nevertheless increase the resistivity by causing deviations in the thickness and scattering at discrete atomic-height surface steps. Consequently, many recent studies describe the effects of surface chemistry and atomic roughness with p within the framework of the FS model, while the scattering from larger scale undulation.

The surface roughness of narrow conductors contributes to the resistivity increase associated with electron scattering. This may be the cause for the incorrect resistivity prediction by FS model for narrow conductors. More specifically, the reported measured resistivity of thin films <20 nm is consistently higher than the prediction from FS model, suggesting that a single parameter p may be insufficient to correctly describe. As a consequence, multiple models have been developed which explicitly treat surface roughness as a contributor to the resistivity.

Namba has considered the resistivity increase due to the variation of the film thickness around its mean and derived an expression that describes the resistivity as a function of the experimentally measurable root-mean-square (RMS) surface roughness x. However, this roughness effect is secondary and the model typically underestimates the measured resistivity increase. When applying these FS based models to fit experimental data, the adjustable parameters raise concerns, as it is not evident whether the improved fit is the result of the correct physics or due to the larger fitting flexibility. Alternatively, multiple quantum mechanical and quasi- classical models have been developed that describe the thin film resistivity as a function of surface morphology, abandoning any adjustable parameters. These models do not include surface chemistry effects and therefore cannot completely replace the phenomenological FS model. Nevertheless, they make significant achievements towards an emerging parameter-free surface scattering model. For example, one major discovery is a $1/d^2$ dependence in the resistivity due to surface roughness without bulk scattering, which completely contradicts the zero resistivity prediction by the FS model. These quantum mechanical approaches describe the semi two-dimensional electron transport sandwiched between flat surfaces with perturbations, where the perturbations are in principle a function of the complete description of the surface structure which, however, in practice is approximated using Gaussian or Delta functions. The surface roughness is accounted for as a perturbation to the smooth film. This roughness is assumed to be small, that is, the surface root-mean-square roughness x is small in comparison to the film thickness and lateral correlation length n. Mathematically these quantum mechanical models describe the effect due to atomic-level roughness while neglecting larger. The current literature is divided over the issue of whether or not there is a correlation between surface roughness and resistivity. Some researchers have found that this relationship does exist, but others have found no correlation at all. The reason for this discrepancy is still unclear, but it has been suggested that the difference in results could be due to the size scale of surface roughness used.

Check Your Progress

4. What are the two primary methods for heating the source material?
5. What is the significant parameter of thickness measurement?
6. What is multiple-beam interferometry?

5.6 ANSWERS TO ‘CHECK YOUR PROGRESS’

1. Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface.
2. Cathode sputtering is an undesirable phenomenon that shortens the life of electronic devices; on the other hand, it is of practical use for cleaning surfaces, revealing the structure of a substance (ionic etching), depositing thin films, and producing directional molecular beams.
3. The mulch is a protective blanket made from some waste material used to cover the land. By “mulch” one generally understands a mixture of straw, leaves etc. It restricts air movement, maintains high water vapour pressure near the soil surface and shields the sun's energy to reduce evaporation.
4. Two primary methods used for heating the source material during the process of Thermal Evaporation. One includes Filament Evaporation, as it is achieved with a simple electrical heating element or filament inside a boat.
5. The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardized to measure thickness after removed from the deposition chamber.

6. A technique called multiple-beam interferometry is used to measure surface roughness or defects. The technique is based upon placing two highly reflective surfaces close together and then directing beams of light through a lens onto the surfaces.

NOTES

5.7 SUMMARY

- The thermal Evaporation Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film.
- Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface.
- Cathode sputtering is an undesirable phenomenon that shortens the life of electronic devices; on the other hand, it is of practical use for cleaning surfaces, revealing the structure of a substance (ionic etching), depositing thin films, and producing directional molecular beams.
- The energy of the sputtered particles varies from fractions of an electron volt up to values of the order of the energy in the primary ions. Sputtered particles average energy is usually dozens of electron volts and depends on the properties of the target material and the characteristics of the ion beam.
- The mulch is a protective blanket made from some waste material used to cover the land. By “mulch” one generally understands a mixture of straw, leaves etc. It restricts air movement, maintains high water vapour pressure near the soil surface and shields the sun's energy to reduce evaporation.
- Two primary methods used for heating the source material during the process of Thermal Evaporation. One includes Filament Evaporation, as it is achieved with a simple electrical heating element or filament inside a boat. The other heat method used electron beam or E-Beam Evaporation where an electron beam is focused at the source material to evaporate it and convert it into the gas phase.
- The main advantages of thin Film Evaporation systems including high deposition rates, real-time deposition and thickness control, and (with suitable physical configuration) good evaporant stream directional control for processes such as Lift Off to achieve directly patterned coatings.
- In thermal evaporation techniques, depending on the availability of tools and types of source and substrate materials used for deposition different methods can be applied to heat the source material. The instrument available in the laboratory utilised either resistance heating or electron beam heating, usually several KeV, from an electron beam gun (electron beam heating).
- The thin film formation and the resulting structure of the films decide to a large extent the physical properties. since these properties highly dependent on the same deposition parameters hence it becomes important that as

many of these parameters must be under close control as possible during the deposition of thin-film if vacuum deposited thin films are to be made reproducible in every respect.

- The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardized to measure thickness after removed from the deposition chamber.
- A change in the resonant frequency of the crystal oscillator during the process of thin-film deposition varies linearly with the deposited mass on the electrode of the crystal. If the crystal sensor is made to place near the substrate during the process of deposition the as the coating on the crystal increases its mass will lower its resonant frequency.
- The application of quartz-crystal monitors in a thin film deposition chamber of ultrahigh vacuum pressure setup.
- The mass deposited from the source material and its evaporation rate is controlled during deposition by a monitoring quartz sensor mounted and from the side of the substrate holder and so the crystal does not receive the same deposition rate as the substrate.
- There is no direct correlation between the mass of the crystal and the resonant frequency, therefore a tooling factor correction has to be determined. For this purpose, a reference quartz oscillator is mounted on the backside of a rotatable thin film substrate holder.
- The determination of tooling factor is performed by source material evaporation in one process on both, monitoring and reference, quartz crystals. The calibration of quartz crystal monitors is done by silver evaporation with the evaporator.
- The resistance, R of a conductor is proportional to its length L and inversely proportional to its area of cross section A, at a constant temperature.
- A technique called multiple-beam interferometry is used to measure surface roughness or defects. The technique is based upon placing two highly reflective surfaces close together and then directing beams of light through a lens onto the surfaces.
- The presence of a sufficiently small grain size provides a means to produce negative surface energy superconductors with decreasing mean free path and consequently increasing κ (the Ginzburg-Landau parameter), without the addition of alloying elements.

5.8 KEY TERMS

- **Thermal evaporation:** Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film.

NOTES

- **Basic principle:** Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface. After leaving the source material surface these free atoms travel through the vacuum chamber and got coated on a substrate positioned above the evaporating material.
- **Thickness measurement:** The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardized to measure thickness after removed from the deposition chamber.

5.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What do you mean by the evaporation at reduce?
2. Write the procedure of thermal evaporation technique.
3. Mention the uses of thickness measurement.
4. State the practical applications of multiple-beam interferometry.

Long-Answer Questions

1. Explain the thermal evaporation technique.
2. Discuss in detail about the thickness measurement by quartz crystal method.
3. Describe the resistivity of semiconductor by four probe method.
4. Explain the characteristics of multiple-beam interferometry.
5. Describe the Fuchs-Sondheimer (FS) model.

5.10 FURTHER READING

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