1 CHAPTER

PHYSICAL PROPERTIES OF ELEMENTS

LEARNING OBJECTIVES

After studying this chapter, the student should be able to:

- Know and familiarize oneself with the atomic structure and models.
- Calculate electronic configurations.
- Classify materials on the basis of energy-band structures.
- Understand the effective mass and electron emission.

1.1 INTRODUCTION

Electronics has been defined as that branch of science and technology which relates to the conduction of electricity through vacuum by electrons alone or through gases by electrons and ions. Basically, it is a study of electron devices and their utilization. An electron device is that in which electrons flow through a vacuum or gas or semiconductor. In the beginning of the 20th century, electronics began to take technological shape and it has enjoyed an explosive development in the last four decades.

Electronics has a wide range of applications, such as rectification, amplification, power generation, industrial control, photo-electricity, communications, and so on. The electronic industry turns out a variety of items in the range of consumer electronics, control and industrial electronics, communication and broadcasting equipment, biomedical equipment, calculators, computers, microprocessors, aerospace, and defence equipment and components.

Initially, the discovery of electricity motivated research that has led to the present-day concept of an atom. Michael Faraday studied the passage of electricity through liquid solutions. The next step in the study of the electrical nature of matter was made by JJ Thomson. He focused his attention on the passage of electricity through gases. The studies by Thomson of the electrical discharge through gases at low pressure established that an atom is composed of charged particles—electrons and protons. Historically, the study of electrical discharge through gases and the discovery of cathode rays marked the beginning of a new branch of physics called *atomic physics*.

1.2 ATOMIC STRUCTURE

FLASH CARD

What You Learn Here
Define the atomic structure.

An atom is the smallest particle of a chemical element possessing the chemical properties of the element. The first model of an atom was given by JJ Thomson. His model explained an atom as a sphere of positively charged matter in which electrons were embedded. This model could not explain all features of optical spectra of hydrogen and other elements. In 1911, Rutherford established that an atom consists of a positively charged nucleus and a number of negatively charged electrons which revolve around the nucleus in various orbits. The nucleus consists of a number of neutral particles called *neutrons* and a number of positively charged particles called *protons*. The charge of the nucleus is positive and equal to the number of protons contained in it. The charge of a proton is 1.602×10^{-19} coulomb and that of an electron is -1.602×10^{-19} coulomb. Each atom is ordinarily electrically neutral. Hence, in a neutral atom the number of revolving electrons must equal the number of protons in the nucleus. The mass of an electron is 9.107×10^{-31} kg, while that of a proton or neutron is about 1836 times that of the electron. Thus, almost the entire mass of an atom is concentrated in the nucleus. The radius of an atom is of the order of 1 angstrom (10^{-10} m).

1.3 HYDROGEN ATOM

FLASH CARD

What You Learn Here
Recount the Rutherford model of the hydrogen atom.

The first modern picture of an atom was put forward by Rutherford in 1911. Such an atom has a central nucleus of small dimensions around which move a number of electrons. The electron orbits are of atomic dimensions, i.e., of the order of 10^{-8} cm. The nucleus carries a charge to counteract the combined charge of the electrons. Almost all of the mass of the atom resides in the nucleus. The Rutherford model of the hydrogen atom is shown in Fig. 1.1. The hydrogen atom consists of one proton and one electron revolving around the centre nucleus in a circular orbit of radius r.

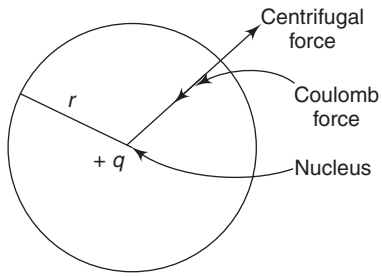

Fig. 1.1 *Rutherford model of hydrogen atom*

An electron in the circular orbit experiences a centripetal acceleration. According to electromagnetic theory, an accelerated electrical charge must radiate energy in the form of electromagnetic waves. The total energy of an electron in any orbit is the sum of its kinetic and potential energies. The potential energy of an electron is considered zero when it is at an infinite distance from the nucleus. The relation between the total energy possessed by an electron and the radius of the circular orbit r, is given below.

$$W = \text{potential energy} + \text{kinetic energy}$$

$$W = \frac{-Zq^2}{4\pi\varepsilon_0 r} + \frac{Zq^2}{8\pi\varepsilon_0 r} = \frac{-Zq^2}{8\pi\varepsilon_0 r} \tag{1.1}$$

where Z is the atomic number ($Z = 1$ for hydrogen); q, the charge of an electron = 1.602×10^{-19} coulomb; and ε_0, the permittivity of free space = 8.854×10^{-12} farad/m.

If the accelerated electron loses energy by radiation, the total energy of the electron continuously decreases and it must spiral down into the nucleus. Thus, the hydrogen atom cannot be stable. But most of the atoms are stable.

According to classical electromagnetic theory, an accelerating electron must radiate energy at a frequency equal to the mechanical frequency of the orbiting electron and hence proportional to the angular velocity of the electron. Therefore, as the electron spirals toward the nucleus, the angular velocity tends to infinity and hence, the frequency of the emitted energy will tend to infinity. This will result in a continuous spectrum with all possible wavelengths. But, many atoms like hydrogen emit line spectra of fixed wavelengths only.

The above two points are contradicting to what is normally happening in an atom. These two phenomena could not be explained using the Rutherford atomic model and are considered to be the main drawbacks of the Rutherford model of an atom.

1.4 BOHR ATOM MODEL

The Bohr atom model could successfully explain many of the atomic phenomena. Bohr took the Rutherford model of the atom and tried to overcome the defects of the model. Bohr proposed that the laws of classical mechanics and electromagnetics broke down within the atom. The basic postulates of Bohr's theory are a combination of the ideas of classical theory and Planck's quantum theory of radiation.

FLASH CARD

What You Learn Here

Recount the Bohr atomic model and list Bohr's postulates, define critical potentials, and spectral series of the hydrogen atom.

1.4.1 Bohr's Postulates

Bohr postulated three fundamental laws to overcome the inconsistency in the Rutherford model.

- ***Postulate I*** Electrons cannot occupy states at all energy levels as given by classical mechanics; electrons can occupy states at only certain discrete energy levels. When an electron occupies a state at one of these discrete energy levels, the electron does not emit radiation and is said to be in stationary or non-radiating state.

- ***Postulate II*** When an electron moves one stationary state corresponding to the energy W_2 to another stationary state with lower energy W_1, there results emission of radiation at a frequency f given by

$$f = \frac{(W_2 - W_1)}{h} \tag{1.2}$$

where f is the frequency of radiation in hertz; h, the Planck's constant = 6.626×10^{-34} joule; and W_1 and W_2 are energies in joule.

- ***Postulate III*** Any stationary or non-radiating state is determined by the condition that the angular momentum of the electron in this state is quantized and must be an integral multiple of $h/2\pi$. Thus,

$$mvr = \frac{nh}{2\pi} \tag{1.3}$$

where n is an integer. The radii of the various stationary orbits is given by

$$r_n = \frac{\varepsilon_0 h^2 n^2}{\pi m q^2} \tag{1.4}$$

$$= 0.527 \times 10^{-10} n^2 \text{ m} \tag{1.5}$$

The total energy of an electron in stationary states in joule is given by

$$W_n = \frac{-mq^4}{8\varepsilon_0^2 h^2 n^2} \tag{1.6}$$

The total energy of an electron in stationary states in electronvolt is given by

$$W_n = \frac{-mq^3}{8\varepsilon_0^2 h^2 n^2} \tag{1.7}$$

$$= \frac{-13.6}{n^2} \text{ eV}$$

It should be noted that the energy is negative and, therefore, the energy of an electron in its orbit increases as n increases. The above expression for the energy of the electron suggests that to remove an electron from the first orbit ($n = 1$) of the hydrogen atom to the outside of the atom, that is to ionize the atom, the energy required is 13.6 eV. This is known as the *ionization energy* or the *ionization potential* of the atom.

1.4.2 Critical Potentials

The least energy, expressed in electronvolt, required to excite a free neutral atom from its ground state to a higher state is called critical potential of the atom. It is usual to distinguish two kinds of critical potentials, namely, excitation potential and ionization potential.

- ***Excitation Potential*** The energy in electronvolt required to raise an atom from its normal state into an excited state is called excitation potential of the state. It is also called radiation potential or resonance potential.

- ***Ionization Potential*** It is defined as the energy required to remove an electron from a given orbit to an infinite distance from the nucleus.

For example, the energy associated with an electron in the nth orbit of the hydrogen atom is $E_n = -13.6/n^2$ eV. Thus the energies of the first, second, third, ..., ∞ orbits are respectively –13.6, –3.4, –1.51, ..., 0 eV. The energy required to raise the atom from the ground state ($n = 1$) to the first excited state is (13.6 – 3.4) = 10.2 eV. The energy required to raise it to the second excited state is (13.6 – 1.51) = 12.09 eV, and so on. It is clear that 10.2 eV, 12.09 eV are excitation potentials, while 13.6 eV is the ionization potential of the hydrogen atom.

The number of ionization potential depends on the number of electrons in an atom. For hydrogen atom, there is only one ionization potential and several excitation potentials. The energy required for the removal of the outermost valence electrons is called the first ionization potential. The energy required for the removal of the second electron from the influence of the nucleus is called the second ionization potential and this will be higher than the first ionization potential.

EXAMPLE 1.1

Calculate the radii of the first, second, and third permitted electron orbits in a Bohr's hydrogen atom.

Solution Radius of the nth orbit for hydrogen, $r_n = \dfrac{\varepsilon_0 h^2 n^2}{\pi mq^2}$

$$= \frac{(8.854 \times 10^{-12})(6.62 \times 10^{-34})^2 n^2}{\pi (9.1 \times 10^{-31})(1.6 \times 10^{-19})^2}$$

Therefore, the radius of the first orbit is, $r_1 = 5.27 \times 10^{-11} \times 1^2$ m

$= 5.27 \times 10^{-11}$ m = 0.527 AU

The radius of the second orbit is, $r_2 = 5.27 \times 10^{-11} \times 2^2 = 2.108$ AU

The radius of the third orbit is, $r_3 = 5.27 \times 10^{-11} \times 3^2 = 4.743$ AU

1.4.3 Spectral Series of the Hydrogen Atom

When an electron jumps from higher orbits to lower orbits, radiation of energy takes place at particular frequencies. When an electron jumps from second, third, ... etc., orbits to the first orbit, the spectral lines are in the ultraviolet region. This is identified as *Lyman* series. When an electron jumps from outer orbits to the second orbit, the series is called *Balmer* series and lies in the visible region of the spectrum. When the transition of an electron is from outer orbits to the third orbit, the series is *Paschen* series and lie in the near infrared region. The transition from outer orbits to fourth and fifth orbits are respectively called *Brackett* series and *Pfund* series. The spectral lines for these two series lie in the very far infrared region of the hydrogen spectrum.

1.5 ATOMIC-ENERGY-LEVEL DIAGRAM

FLASH CARD

What You Learn Here
Illustrate the atomic energy levels.

In the energy-level diagram, the discrete energy states are represented by horizontal lines, and the height of the line represents the total energy E_n as calculated from Eq. (1.7). Figure 1.2 shows the energy-level diagram for hydrogen. The number immediately to the right of a line gives the value of integer n, while the number to the left of each line gives the energy to this level in electronvolt. The lowest energy level E_1 is called the normal or the ground state of the atom and the higher energy levels E_2, E_3, E_4, ..., are called the excited states. As n increases, the energy levels crowd and tend to form a continuum.

Sometimes, it is more convenient to specify the emitted radiation by its wavelength, λ in angstroms. Equation (1.2) can be rewritten as,

$$\lambda = \frac{12,400}{E_2 - E_1} \qquad (1.8)$$

where E_2 and E_1 are the energy levels in electronvolt.

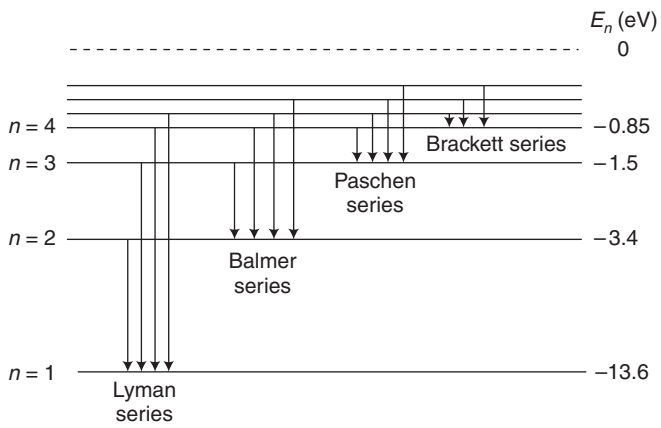

Fig. 1.2 *Energy-level diagram of hydrogen*

EXAMPLE 1.2

Find the wavelength of the photon emitted when a hydrogen atom goes from $n = 10$ state to the ground state.

Solution The wavelength in angstrom units is given by, $\lambda = \dfrac{12,400}{E_2 - E_1}$

Since the hydrogen atom goes from $n = 10$ state to the ground state, $\lambda = \dfrac{12,400}{E_{10} - E_1}$

The energy of the 10^{th} state is $E_{10} = \dfrac{-13.6}{10^2} = -0.136$ eV.

The energy in the ground state is $E_1 = -13.6$ eV.

Thus, the wavelength of the emitted photon = $\dfrac{12,400}{-0.136 - (-13.6)} = 920.97$ Å

EXAMPLE 1.3

Calculate the wavelength of the Balmer-series limit.

Solution When an electron jumps from outer orbits to the second orbit, the series is called Balmer-series. Using Eq. (1.8), the wavelength limit for the Balmer-series can be found by calculating the wavelength of the radiation due to the transition of electron from the infinite orbit to the second orbit.

Wavelength of the Balmer-series limit = $\dfrac{12,400}{E_\infty - E_2}$

Energy of the electron at the infinite orbit, $E_\infty = \dfrac{-13.6}{\infty^2} = 0$

Energy of the electron at the second orbit, $E_2 = \dfrac{-13.6}{2^2} = -3.4$

Therefore, the wavelength limit = $\dfrac{12,400}{E_\infty - E_2} = \dfrac{12,400}{3.4} = 3647$ AU

1.6 ELECTRONIC CONFIGURATIONS OF ELEMENTS

FLASH CARD

What You Learn Here
Categorize the location and energy of each electron through "quantum number" representations.

In order to understand the location and energy of each electron in an atom, four quantum numbers are required. The four quantum numbers are identified as follows:

- ***Principal Quantum Number (n)*** This number characterizes the average distance of an electron from the nucleus and corresponds to the principal energy level in which the electron resides. It gives some idea about the position of the electron around the nucleus. The allowed values of this quantum number n are

positive integers starting from 1. Thus, n can have values 1, 2, 3, ... The principal energy levels or shells having different values of n are also represented by the letters K, L, M, N, and so on. The maximum number of electrons that can reside in a shell corresponding to the principal quantum number n is equal to $2n^2$.

▪ ***Azimuthal Quantum Number (l)*** This quantum number is also called the *orbital angular momentum quantum number.* The quantum number l gives a measure of the angular momentum of an electron in this orbit. Physically, this number indicates the shape of the classical orbit. For a given value of n, the azimuthal quantum number l can take all positive integral values from 0 to $(n - l)$. The particular 1 value defines the subshell. The subshells with $l = 0, 1, 2$ ... are designated s, p, d, f, g, h, k, ..., respectively.

For a given principal quantum number, the energies of the various subshells are in the order s < p < d < f .... Thus, an electron in the s subshell has lower energy than that in the p subshell with the same principal quantum number. The magnitude of this angular momentum is $h\sqrt{l(l+1)}/2\pi$.

▪ ***Magnetic Quantum Number (m_l)*** This is also called *orbital magnetic number*. The magnetic moment of an electron due to its orbital motion gives rise to a magnetic field which can interact with an external magnetic field. Under the influence of the external magnetic field, the electrons orient themselves in certain preferred region of space around the nucleus. The magnetic quantum number m_l determines the preferred orientation of the orbitals in space with respect to an applied magnetic field.

For a given value of l, the magnetic quantum number can take integral values between –1 to +1 including 0. For a given value of l, the total allowed values of m_l are $(2l + 1)$. The magnitude of the component of angular momentum along the direction of the magnetic field is $m_l(h/2\pi)$.

▪ ***Spin Quantum Number (m_s)*** This number is concerned with the spinning of the electron about its own axis. This spin produces a spin magnetic moment, which can be either parallel or antiparallel to the surrounding magnetic field. Thus, there are two spin states for an electron. Hence, the spin quantum number can take only two possible values, $+\frac{1}{2}$ or $-\frac{1}{2}$.

The position of an electron in an atom is completely described by these four quantum numbers. *Pauli's exclusion principle* states that in an atom, no two electrons can exist in the same quantum state. In other words, there cannot be two electrons in an atom with the same value of all the four quantum numbers. Using Pauli's exclusion principle, the configuration of electrons can be written. All the electrons with the same value of n constitute a shell and a shell can have a maximum of $2n^2$ electrons.

The energy-state capacity of different shells and subshells are considered hereunder:

K-shell corresponds to $n = 1$ and has only one subshell, namely, 1s. The 1s subshell corresponds to $n = 1$, $l = 0$, $m_l = 0$, $m_s = \pm 1/2$ and has 2 states.

L-shell corresponds to $n = 2$ and has two subshells, namely, 2s and 2p. The 2s subshell corresponds to $n = 2$, $l = 0$, $m_l = 0$, and has 2 states. The 2p subshell corresponds to $n = 2$, $l = 1$, $m_l = 0, \pm 1$, and has 6 states.

FLASH CARD

What You Learn Here
Define energy capacities of different shells and subshells.

M-shell corresponds to $n = 3$ and has three subshells, namely, 3s, 3p and 3d. The 3s subshell corresponds to $n = 3$, $l = 0$, $m_l = 0$, and has 2 states. The 3p subshell corresponds to $n = 3$, $l = 1$, $m_l = 0, \pm 1$, and has 6 states. The 3d subshell corresponds to $n = 3$, $l = 2$, $m_l = 0, \pm 1, \pm 2$, and has 10 states.

N-shell corresponds to $n = 4$ and has four subshells, namely, 4s, 4p, 4d and 4f. The 4s subshell corresponds to $n = 4$, $l = 0$, $m_l = 0$, and has 2 states. The 4p subshell corresponds to $n = 4$, $l = 1$, $m_l = 0, \pm 1$, and has 6 states.

The 4d subshell corresponds to $n = 4$, $l = 2$, $m_l = 0, \pm1, \pm2$, and has 10 states. The 4f subshell corresponds to $n = 4$, $l = 3$, $m_l = 0, \pm1, \pm2, \pm3$ and has 14 states.

Table 1.1 gives the electronic configuration in an atom taking into consideration the Pauli's exclusion principle. Actually, seven shells are required to account for all the chemical elements, but only the first four are indicated in the table.

Table 1.1 *Electron distribution in subshells*

Shell	K	L			M			N		
n	1	2			3			4		
l	0	0	1	0	1	2	0	1	2	3
Subshell	s	s	p	s	p	d	s	p	d	f
No. of electrons	2	2	6	2	6	10	2	6	10	14

The electrons in the innermost shells are very strongly attached to the atom and cannot be easily separated, i.e., the electrons that are very near to the nucleus are most tightly bound and, hence, have the lowest energy. The atoms that have electrons in the closed shells will have very stable configurations.

The atomic number Z gives the number of electrons orbiting about the nucleus. Superscripts are used to designate the number of electrons in a particular subshell. For silicon, the atomic number Z is 14 and it has an electronic configuration designated by $1s^2 2s^2 2p^6 3s^2 3p^2$. Note that silicon has only two electrons in the outermost subshell which can actually accommodate 6 electrons. Hence, the silicon atom needs four more electrons to have a completely filled outermost subshell. Silicon is classified as a tetravalent element, i.e., it has a valency of 4. This property is also possessed by carbon (C), germanium (Ge), tin (Sn) and lead (Pb) whose electronic configuration is given in Table 1.2. This accounts for the fact that these elements are in the same group (IVA) in the periodic table. However, carbon in crystalline form is an insulator, silicon and germanium are semiconductors, and tin and lead are metals. The reason for this behaviour can be understood from the study of energy-band theory of crystals.

FLASH CARD

What You Learn Here
Calculate the electronic configuration of some elements.

Table 1.2 *Electronic configurations of some group IVA elements*

Element	Atomic number	Electronic configuration
C	6	$1s^2 2s^2 2p^2$
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Ge	32	$1s^2 2s^2 2p^6\ 3s^2\ 3p^6 3d^{10} 4s^2 4p^2$
Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$
Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$

1.7 ENERGY-BAND THEORY OF CRYSTALS

FLASH CARD

What You Learn Here
Recount how energy bands are formed in a crystal.

The crystalline structure is common among most of the metals and semiconductors. Any crystal is made up of a space array of atoms of molecules in regular repetition in three dimensions of some fundamental building block. For a gaseous element, the electronic energy levels are the same as for a single free atom because the individual atoms in a gas are well apart and has negligible influence on each other. However, in a crystal, the individual atoms are so closely packed that the resulting energy levels are modified due to interaction between the atoms. When atoms form crystals, the energy levels of the inner-shell electrons are not appreciably affected, however, the levels of the outer-shell electrons are considerably altered as these electrons are shared by the adjacent atoms in the crystal. As a result of this interaction between the outer-shell electrons, the energy levels spread up to form a band of energy as shown in Fig. 1.3.

In order to understand the formation of energy bands in a crystal, let us consider a silicon crystal made up of N atoms. We shall also assume that the interatomic spacing can be varied without affecting the fundamental crystal structure. For very large interatomic spacing, say 'a' in Fig. 1.3, the interaction between adjacent atoms is negligible, and the energy levels are same as that of isolated atoms. In silicon, the outermost subshells, namely, 3s and 3p contain 2 electrons each. Hence, in a silicon crystal consisting of N atoms, the outermost subshells 3s and 3p consist of $2N$ electrons each. Thus, the 3s subshell has $2N$ electrons completely occupying the available $2N$ states, and the 3p subshell has only $2N$ electrons partially occupying the available $6N$ states, all at the same energy level.

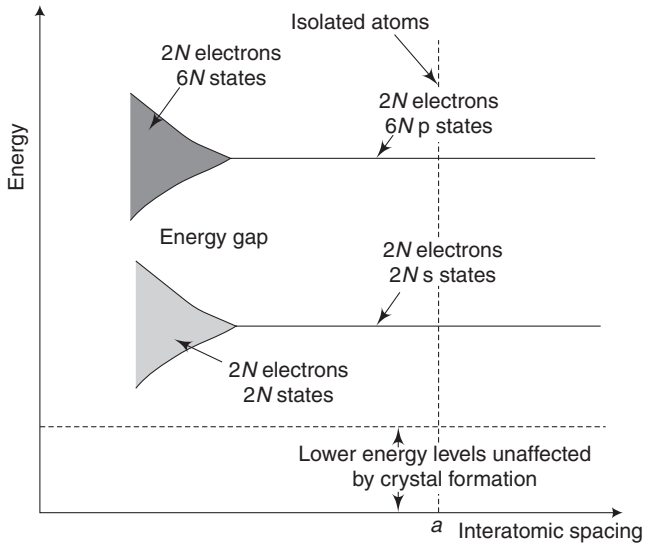

Fig. 1.3 *Formation of energy band in a crystal*

If the interatomic spacing is gradually decreased, i.e., moving from right to left in Fig. 1.3, there will be a gradual increase in the interaction between the neighbouring atoms. Due to this interaction, the atomic wave functions overlap, and the crystal becomes an electronic system which should obey the Pauli's exclusion principle. Hence, the $2N$s states spread out to form a band of energy. Actually, the separation between levels is small but since N is very large, of the order of 10^{23} cm^{-3}, the total spread between the minimum and maximum energy levels becomes large. This spread will have several electronvolt of energy and is referred to as energy band and is indicated by the lower shaded region in Fig. 1.3. The $2N$ states in this band are completely filled with $2N$ electrons.

Similarly, at the same value of interatomic spacing at p-level, $6N$ p states spread up to form a band. This band is shown as the upper shaded region in Fig. 1.3. Though a total of $6N$ states are available in this band, only $2N$ states are occupied and $4N$ states remain unoccupied.

An energy gap exists between the two energy bands. This energy gap is called the *forbidden energy gap*, as no electrons can occupy states in this gap. This forbidden energy gap decreases as the atomic spacing is decreased and becomes zero with further reduction in the interatomic spacing, say at '*b*', as shown in Fig. 1.4. That is, the two energy bands will overlap when the interatomic spacing is small enough. Under such circumstances, the 6*N* p states in the upper band merge with the 2*N* s states in the lower band, giving a total of 8*N* states. Half of these 8*N* states are occupied by the 4*N* available electrons. These 4*N* electrons now no longer belong to either the p subshell or the s subshell but belong to the crystal as a whole. Thus, at this interatomic spacing, each atom in the crystal can contribute 4 electrons to the crystal. The band occupied by these contributed electrons is called the *valence band*.

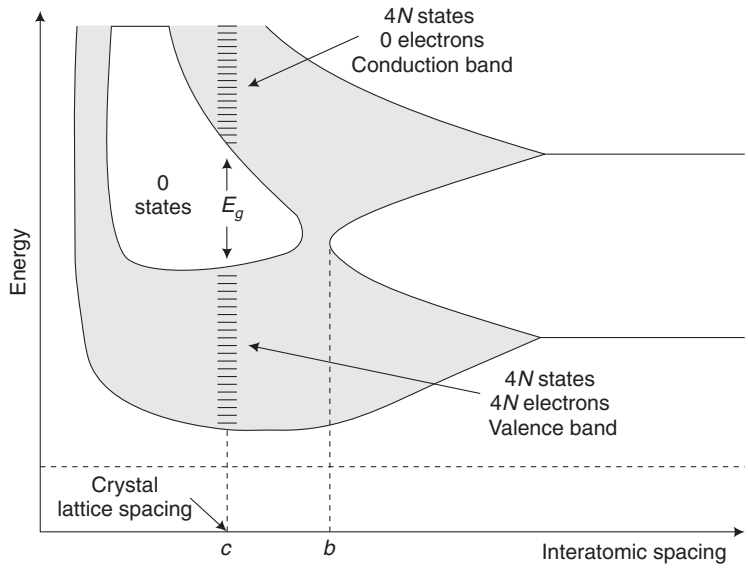

Fig. 1.4 *Energy band in a crystal as a function of interatomic spacing*

If the interatomic spacing is reduced further, say '*c*' as shown in Fig. 1.4, the interaction between the atoms becomes extremely large, and the energy-band structure assumes the shape shown in Fig. 1.4. The exact energy-band structure depends upon (i) the orientation of the atoms relative to one another in space, and (ii) the atomic number of the atom, and may be obtained from solution of Schrodinger's wave equation. For spacing '*c*', 4*N* states in the valence band are completely filled by 4*N* electrons and this valence band is separated from the upper unfilled or empty band by a forbidden energy gap E_g. The forbidden energy gap contains no allowed states. The upper band has 4*N* unfilled states and is referred to as the *conduction band*.

1.8 ENERGY-BAND STRUCTURES AND CONDUCTION IN INSULATORS, SEMICONDUCTORS, AND METALS

FLASH CARD

What You Learn Here
Distinguish between insulators, metals and semiconductors through energy-band structures.

A very poor conductor of electricity is called an insulator; an excellent conductor is a metal; and a material whose conductivity lies between these two extremes is a semiconductor. A material may be classified as one of these three depending upon its energy-band structure.

1.8.1 Insulator

PROBE

Explain why diamond is considered a good insulator.

An insulator is a material having extremely poor electrical conductivity. The energy-band structure of Fig. 1.4 at the normal lattice spacing is indicated schematically in Fig. 1.5(a). The forbidden energy gap is large; for diamond, the gap energy is about 6 eV. If additional energy is given to an electron in the upper level of valence band, this electron attempts to cross the forbidden energy gap and enter the conduction band. However, in an insulator, the additional energy which may ordinarily be given to an electron is, in general, much smaller than this high value of forbidden energy gap. Hence, no electrical conduction is possible. The number of free electrons in an insulator is very small, roughly about 10^7 electrons/m^3.

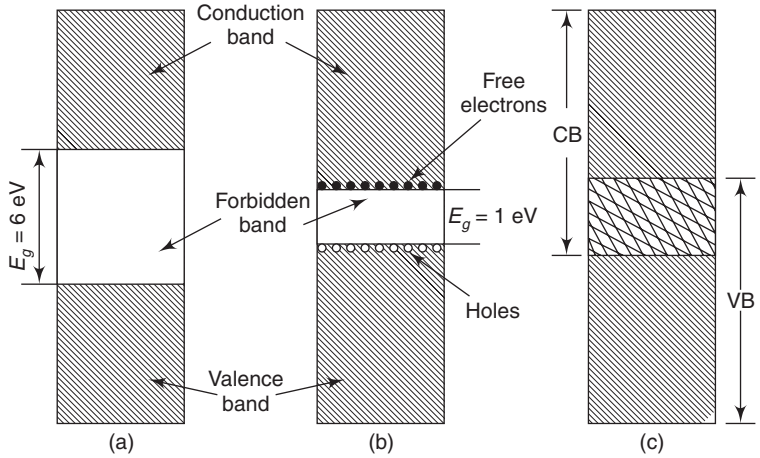

Fig. 1.5 *Energy-band gap in (a) insulators, (b) semiconductors, and (c) metals*

1.8.2 Metal

PROBE

Copper is considered a good conductor of electricity—analyze why.

Conduction in metals is only due to the electrons. A metal has overlapping valence and conduction bands. The valence band is only partially filled and the conduction band extends beyond the upper end of filled valence band. The outer electrons of an atom are as much associated with one ion as with another, so that the electron attachment to any individual atom is almost zero. The band occupied by the valence electrons may not be completely filled and that there are no forbidden levels at higher energies. Depending upon the metal, at least one, and sometimes two or three, electrons per atom are free to move throughout the interior of the metal under the action of applied fields. When an electric field is applied, few electrons may acquire enough additional energy and move to higher energy within the conduction band. Thus, the electrons become mobile. Since the additional energy required for transfer of electrons from valence band to conduction band is extremely small, the conductivity of a metal is excellent.

In *electron-gas theory* description of a metal, the metal is visualized as a region containing a periodic three-dimensional array of heavy, tightly bound ions permeated with a swarm of electrons that may move about quite freely. According to this theory, the electrons in a metal are continuously moving and the direction of flight changes whenever the electron collides with other electrons. The average distance travelled by an

electron between successive collisions is called *mean-free-path* of an electron. In the absence of any applied potential, the average current in a metal is zero because the number of electrons passing through unit area in any direction is almost same as the number of electrons passing through the same unit area in the opposite direction. This can be attributed to the random nature of motion of electrons.

When a constant electric field E (volt per metre) is applied to a metal, the electrons would be accelerated and the velocity would increase indefinitely with time. However, because of collision of electrons, electrons lose energy and a steady-state condition is reached where a finite value of drift velocity v_d is attained. The drift velocity, v_d is in the direction opposite to that of the electric field and its magnitude is proportional to E. Thus,

$$v_d = \mu E \tag{1.9}$$

where μ = mobility of the electron, m^2/volt-second. Due to the applied field, a steady-state drift velocity has been superimposed upon the random thermal motion of the electrons. Such a directed flow of electrons constitutes a current. If the concentration of free electrons is n (electrons per cubic meter), the current density J (ampere per square metre) is

$$J = nqv_d = nq\mu E = \sigma E \tag{1.10}$$

where
$$\sigma = nq\mu \tag{1.11}$$

σ is the *conductivity* of the metal in (ohm-metre)$^{-1}$. For a good conductor, n is very large, approximately, 10^{28} electrons/m^3. Equation (1.10) can be recognized as Ohm's law which states that the conduction current density is proportional to the applied electric field. The energy acquired by the electrons from the applied field is given to the lattice ions as a result of collisions. Hence, power is dissipated within the metal by the electrons, and the power density (joule heat) is given by

$$JE = \sigma E^2 \text{ watt/metre}^3 \tag{1.12}$$

1.8.3 Semiconductor

PROBE

Categorize germanium either as a conductor or a semiconductor or an insulator. Give reasons for your response.

The conductivity of a material is proportional to the concentration of free electrons. The number of free electrons in a semiconductor lies between 10^7 and 10^{28} electrons/m^3. Thus, a semiconductor has conductivity much greater than that of an insulator but much smaller than that of a metal. Typically, a semiconductor has a forbidden energy gap of about 1 eV. The most important practical semiconductor materials are germanium and silicon, which have values of E_g of 0.785 and 1.21 eV, respectively, at 0 degree Kelvin. Energies of this magnitude normally cannot be acquired from an applied field. At low temperatures the valence band remains full, the conduction band empty, and these materials are insulators at low temperatures. The conductivity of these materials increases with temperature and hence, these materials are called as intrinsic semiconductors. As the temperature is increased, some of the electrons in the valence band acquire thermal energy greater than the gap energy and move into the conduction band. These electrons are now free to move about under the influence of even a small applied field. These free electrons, also called *conduction electrons*, constitute for conduction and the material becomes slightly conducting. The current density due to the motion of electrons is given by

$$J_n = n\mu_n qE = \sigma_n E \tag{1.13}$$

where, μ_n is the electron mobility, and the suffix 'n' represents that the respective terms are due to motion of electrons. The absence of an electron in the valence band is represented by a small circle and is called a hole.

The hole may serve as a carrier of electricity whose effectiveness is comparable with the free electron. The hole conduction current density is given by

$$J_p = p\mu_p qE = \sigma_p E \tag{1.14}$$

where μ_p is the hole mobility and p is the hole concentration.

Hence, the total current density J in a semiconductor is given by

$$J = (n\mu_n + p\mu_p)qE = \sigma E \tag{1.15}$$

where $\sigma = (n\mu_n + p\mu_p)q$ is the total conductivity of a semiconductor. For a pure semiconductor (intrinsic semiconductor), the number of free electrons is exactly same as the number of holes. Thus, the total current density is

$$J = n_i(\mu_n + \mu_p)\, qE \tag{1.16}$$

where $n_i = n = p$ is the intrinsic concentration of a semiconductor.

The conductivity of an intrinsic semiconductor can be increased by introducing certain impurity atoms into the crystal. This results in allowable energy states which lie in the forbidden energy gap and these impurity levels also contribute to the conduction. Such a semiconductor material is called an extrinsic semiconductor.

▪ ***Effective Mass*** An electron travelling through a crystal under the influence of an externally applied field hardly notices the electrostatic field of the ions making up the lattice, i.e., it behaves as if the applied field were the only one present. This is the basis of the electron-gas approximation and the assumption will now be looked at a little more closely. If the electrons were to experience only the applied field, E, then immediately after a collision it would accelerate in the direction of the field with an acceleration a, proportional to the applied force, i.e.,

FLASH CARD

What You Learn Here
Effective mass as an important parameter of semiconductor technology.

$$qE = ma \tag{1.17}$$

where the constant of proportionality is the electron mass, m. When quantum theory is applied to the problem of an electron moving through a crystal lattice, it predicts that under the action of an applied field, the electron acceleration will indeed be proportional to the field, but that the constant of proportionality will be different from the normal mass of an electron:

$$qE = m_n a \tag{1.18}$$

The field due to the lattice ions can, therefore, be ignored providing we treat the electrons inside the crystal as if they had a slightly different mass to the real electron mass or, to put it another way, the effect of the lattice ions on an electron is to make it behave as if it had a different mass. This new mass is called the effective mass of the electron, m_n, and the effective mass of a hole, m_p, can be similarly defined. In general, m_n and m_p are not the same. Usually, m_n is of the same order as m; in germanium, for instance, $m_n = 0.2$ m and in silicon, $m_n = 0.4$ m.

The value of effective mass is an important parameter for any semiconductor, especially from the device point of view. Certain semiconductors, for instance, have low electron effective mass and hence, high electron mobility. This makes them very suitable for high-frequency devices. The III-V semiconductor GaAs comes into this category and some of the best microwave transistors are made from this material.

1.9 PRACTICAL SEMICONDUCTOR MATERIALS

FLASH CARD

What You Learn Here
Compare germanium, silicon, and gallium arsenide on parameters that make them practical semiconductors.

All semiconductors have crystalline structure. The most commonly used semiconductor materials, germanium, silicon, and gallium arsenide have practical applications in Electronics. The most frequently used semiconductors are germanium and silicon because the energy required to break their covalent bonds and release a free electron from their valence bands is lesser than that required for gallium arsenide. The energy required for releasing an electron from the valence band is 0.66 eV for germanium, 1.08 eV for silicon, and 1.58 eV for gallium arsenide.

Germanium can be purified relatively well and crystallized easily. Germanium is an earth element and it is obtained from the ash of the certain coals or from the flue dust of the zinc smelters. The recovered germanium is in the form of germanium dioxide powder which is then reduced to pure germanium. Germanium diodes are used as infrared detectors in fibre-optic communication system because of narrower energy gap.

Silicon is an element found in most of the common rocks. Sand is silicon dioxide which is then reduced to 100% pure silicon. Silicon dioxide is a natural insulator which is useful in the fabrication of semiconductor devices and integrated circuits. Silicon is largely preferred to germanium because of its large gap energy, which produces improved device properties at high temperatures. Silicon is a better thermal conductor and is required to remove unavoidable heat developed in the device.

Gallium arsenide has higher electron mobility, μ_n which leads to faster switching capabilities. It has high-temperature operating capabilities because of its larger energy gap.

1.10 ELECTRON EMISSION FROM METALS

FLASH CARD

What You Learn Here
Explain "electron emission from metals" and classify the types of emissions.

Electron emission from metals is important to analyze electron energy and energy distribution. Electron emission is the process by which the free electrons escape from the surface of a substance. Metals are used for electron emission because a metal is made up of atoms bound in crystal lattices, of electrons bound to the atoms, and of many free electrons which are not bound to any particular location in the metal. The free electrons are always in motion and travel more or less freely throughout the body of the metal. However, these electrons are free only to the extent that they may transfer from one atom to another within the metal but they cannot leave the metal surface. If a certain amount of external energy is given to a free electron, its kinetic energy is increased and thus electron will cross over the surface barrier to escape from the metal. This amount of kinetic energy required at absolute zero temperature is known as *work function* of that metal. It is denoted by E_w, and expressed in electronvolt (eV). One eV, equal to 1.602×10^{-19} joule, is the amount of energy acquired by an electron when it is accelerated through a potential difference of one volt (1 V).

The work function of pure metals varies approximately from 2 to 6 eV. The metal used for electron emission should have low work function so that a small amount of external energy is required to cause emission of electrons. Work function of a metal is principally determined by the spacing between its atoms. Wider spacing usually give lower values of work function. The work functions of some common metals are given in Table 1.3.

Table 1.3 *Work functions of some common metals*

Metal	Work function in eV	Metal	Work function in eV
Ag	4.60	K	1.90
Al	3.00	Li	2.21
Ba	2.52	Na	2.00
Ca	3.00	Ni	5.00
Cs	1.67	Rb	1.82
Cu	4.30	Th	3.50
Fe	4.74	Zn	3.44

Types of Electron Emission

The four basic methods of obtaining electron emission from the surface of a metal are classified according to the type of additional energy (equal to the work function of the metal) supplied from the sources such as heat energy, energy stored in electric field, light energy, and kinetic energy of the electric charges bombarding the metal surface, as discussed below:

- ***Thermionic Emission*** When a metal is heated to sufficient temperature, enough thermal energy is imparted to electrons to enable them to escape from the metal surface. The higher the temperature, the greater is the emission of electrons. This method is known as *thermionic emission* and is employed in vacuum tubes.

Richardson, and later on Dushman, on the thermodynamic basis, derived the equation for thermionic emission at a certain temperature, T. This equation is given by

$$I_{th} = SA_oT^2\, e^{-E_w/kT} \tag{1.19}$$

where I_{th} = thermionic emission current in ampere
S = area of filament in m^2
A_o = constant
T = absolute temperature, K
k = Boltzmann constant, eV/K
E_w = work function, eV

At high temperatures, the electrons are literally being 'boiled' from the metal surface. This is analogous to the boiling of water.

The commonly used thermionic emitters with low E_w, as given in Table 1.4, are tungsten in high voltage (kV) tubes, thoriated tungsten in high power (KW) tubes, and oxide-coated metals in low power electron tubes and Cathode Ray Tubes (CRT).

Table 1.4 *Properties of commonly used thermionic emitters*

Thermionic emitter	Work function in eV	Range of operating temperature in K	Emission efficiency in mA/W
Tungsten	4.52	2500–2600	2–10
Thoriated tungsten	2.63	1900–2000	50–100
Oxide-coated	1.10	900–1100	100–1000

▪ ***Field Emission*** When the potential difference between two electrodes is extremely high, electrons are emitted from the negative electrode, even at ordinary temperatures. If the electric field at the metallic surface of the negative electrode is of the order of 10^6 volt per metre, electrons are quite easily pulled out from the surface. This process of electron emission is known as *field emission*. Field emission does not depend on the temperature of the surface. This type of emission is employed in cold cathode devices and mercury and rectifier tubes.

▪ ***Photo-electric Emissions*** When the surface of certain metals are illuminated by a beam of light, electrons are ejected out of the metal by the light photons incident on the metal surface. Such an electron emission is known as *photo-electric emission* and is used in a photo-electric cell. The greater the intensity of light beam falling on the metal surface, the greater is the photo-electric emission.

▪ ***Secondary Emission*** When a beam of high-velocity electrons strike a metal surface, the free electrons are ejected out of the metal. This process is known as *secondary emission*.

Key Terms

Azimuthal quantum number
Balmer series
Bohr's Postulates
Brackett series
Conduction band
Conductivity
Effective mass
Excitation potential
Field Emission
Ionization energy
Ionization potential
Lyman series
Magnetic quantum number
Mean-free-path
Neutrons
Orbital angular momentum quantum number
Orbital magnetic number
Paschen series
Pauli's exclusion principle
Pfund series
Photo-electric emissions
Principal quantum number
Protons
Rutherford model
Secondary emission
Spin quantum number
Thermionic emission
Work function

Review Questions

1. Define the term 'electronics'. ○○●
2. List the major areas of applications of electronics. ○○●
3. Give the order of radius of an electron and an atom. ○○●
4. Describe Rutherford's model of the atom and what are the drawbacks of this model? ○●●
5. State the postulates of Bohr regarding his atom model. Obtain expressions for the radius and electron-energy of the nth orbit. ○○●
6. Calculate the energy of the electron in the nth orbit in the hydrogen atom. [*Ans.* $E_n = -13.6/n^2$ eV] ○●●
7. What is meant by the term *ground state of an atom*? ○○●
8. What are the wavelengths of the first three lines of the Paschen series? ○●●
[*Ans.* $\lambda_1 = 18750$ Å, $\lambda_2 = 12810$ Å and $\lambda_3 = 10930$ Å]
9. Draw and discuss the energy-level diagram of hydrogen atom. ○●●
10. What is meant by ionization potential of an atom? ○○●
11. Calculate (i) ionization potential, and (ii) first excitation potential of the hydrogen atom. ○●●
[*Ans.* 13.6 eV, 10.2 eV]
12. What are the four quantum numbers? ○○●

13. State and explain Pauli's exclusion principle. ○●●
14. What is meant by the terms *electronic shell* and *sub-shell*? ○○●
15. Give the electronic configuration of Si, Ge, Sn, and Pb. ○●●
16. Explain why the energy levels in a crystal split up to form energy bands. ●●●
17. Describe the energy-band theory of a crystal. ●●●
18. What is meant by forbidden energy gap? ○○●
19. Describe the energy-band structures of an insulator, a metal, and a semiconductor. ○●●
20. Define mean-free-path of an electron. ○○●
21. Define drift velocity of an electron. ○○●
22. What is meant by effective mass of an electron? Explain. ○○●
23. What are the three commonly used semiconductors? ○●●
24. What are the band gap energies of germanium, silicon, and gallium arsenide? ○●●
25. Explain how electrons are emitted from metals. ●●●
26. Explain the term *work function*. ○●●
27. Discuss briefly the different types of electron emission. ○●●
28. Give the Richardson–Dushman equation and explain the effect of various factors in it. ○●●

Note: ○○● Level 1 & Level 2 category
○●● Level 3 & Level 4 category
●●● Level 5 & Level 6 category

Objective-Type Questions

1. One of the following is not a semiconductor:
(a) Gallium arsenide (b) Indium (c) Germanium (d) Silicon

2. Referring to energy-level diagram of semiconductor materials, the width of the forbidden band-gap is about
(a) 10 eV (b) 100 eV (c) 1 eV (d) 0.1 eV

3. The electron mobility of the following semiconductor material is higher:
(a) Germanium (b) Silicon (c) Gallium arsenide (d) Indium

4. When a beam of high-velocity electrons strike a metal surface, the free electrons are ejected out of the metal. This process is known as
(a) field emission (b) photoelectric emission
(c) secondary emission (d) all the above

5. The energy required for relegating an electron from the valence bond for germanium is
(a) 0.66 eV (b) 1.08 eV (c) 1.58 eV (d) 1.88 eV

6. The unit of mobility is
(a) $m^2V^{-1}s^{-1}$ (b) $mV^{-1}s^{-1}$ (c) Vsm^{-1} (d) Vms^{-1}

7. Which model comes up with solution for quantum mechanics?
(a) Bohr's model (b) Rutherford model
(c) Schrodinger model (d) J J Thomson model

8. Power density (Joule beat) in metal is given by
(a) J watt (b) JE $\frac{\text{watt}}{\text{metre}^3}$ (c) $\sigma E^2 \frac{\text{watt}}{\text{metre}^3}$ (d) both b and c

9. The conductivity of a semiconductor crystal due to any current carrier is NOT proportional to
(a) mobility of the carrier (b) effective density of state in conduction band
(c) electronic charge (d) surface states in the semiconductor

10. A long specimen of *P*-type semiconductor
(a) is positively charged (b) is electrically neutral
(c) has an electric field along its length (d) acts as a dipole

11. In order to understand the location *K* energy of each electron in an atom, what do we need?
(a) *n, l, ml* (b) *l, ml, ms* (c) *n, ml, ms* (d) *n, l, ml, ms*

n = Principle quantum number *l* = Azimuthal quantum number
ml = Magnetic quantum number *ms* = Spin quantum number

12. When copper is added to silver in small quantity so as to form an alloy, the resistivity of such on alloy is
(a) equal to the resistivity of copper (b) equal to the resistivity of silver
(c) greater than the resistivity of copper (d) in between the resistivity of silver and copper **[IES 2002]**

13. Piezoelectric quartz crystal resonators find application where
(a) signal amplification is required (b) rectification of the signal is required
(c) signal frequency control is required (d) modulation of signal is required **[IES 2002]**

14. Which material among the following possesses as excellent dielectric properties and good reliability for use in making capacitors?
(a) Silicon monoxide (b) Silicon dioxide
(c) Tin oxide (d) Chromium oxide **[IES 2002]**

15. In a degenerate semiconductor, the majority carriers are controlled by
(a) Fermi-Dirac statistics (b) Maxwell-Boltzman statistics
(c) Bose-Einstein (B-E) statistics (d) Pauli's exclusion principle **[IES 2002]**

16. Fermions are the particles, which obey
(a) Maxwell-Boltzman's statistics (b) Bose-Einstein's statistics
(c) Heisenberg's uncertainty principle (d) Pauli's exclusion principle **[IES 2002]**

17. The unit of mobility is
(a) $m^2V^{-1}s^{-1}$ (b) $mV^{-1}s^{-1}$ (c) Vsm^{-1} (d) Vms^{-1} **[IES 2003]**

18. Which of the following materials are piezoelectric?
(a) Mica and quartz (b) Mica, barium titanate, and quartz
(c) Mica and diamond. (d) Barium titanate and quartz **[IES 2003]**

19. The material which has the property of becoming electrically polarized in response to an applied mechanical stress is termed
(a) ferroelectric (b) piezoelectric (c) optoelectronic (d) superconducting **[IES 2003]**