SURESH
GYAN VIHAR
UNIVERSITY
Accredited by NAAC with 'A+' Grade

Bachelor of Science

(B.Sc.)

Atomic and Solid State Physics

Semester-II

Author- Dr. Priyanka Roy

SURESH GYAN VIHAR UNIVERSITY

Centre for Distance and Online Education
Mahal, Jagatpura, Jaipur-302017

EDITORIAL BOARD (CDOE, SGVU)

Dr (Prof.) T.K. Jain
Director, CDOE, SGVU

Dr. Dev Brat Gupta
Associate Professor (SILS) & Academic Head, CDOE, SGVU

Ms. Hemlalata Dharendra
Assistant Professor, CDOE, SGVU

Ms. Kapila Bishnoi
Assistant Professor, CDOE, SGVU

Dr. Manish Dwivedi
Associate Professor & Dy, Director, CDOE, SGVU

Mr. Manvendra Narayan Mishra
Assistant Professor (Deptt. of Mathematics) SGVU

Mr. Ashphaq Ahmad
Assistant Professor, CDOE, SGVU

Published by:
S. B. Prakashan Pvt. Ltd.
WZ-6, Lajwanti Garden, New Delhi: 110046
Tel.: (011) 28520627 | Ph.: 9205476295
Email: info@sbprakashan.com | Web.: www.sbprakashan.com

© SGVU
All rights reserved.

No part of this book may be reproduced or copied in any form or by any means (graphic, electronic or mechanical, including photocopying, recording, taping, or information retrieval system) or reproduced on any disc, tape, perforated media or other information storage device, etc., without the written permission of the publishers.

Every effort has been made to avoid errors or omissions in the publication. In spite of this, some errors might have crept in. Any mistake, error or discrepancy noted may be brought to our notice and it shall be taken care of in the next edition. It is notified that neither the publishers nor the author or seller will be responsible for any damage or loss of any kind, in any manner, therefrom.

For binding mistakes, misprints or for missing pages, etc., the publishers' liability is limited to replacement within one month of purchase by similar edition. All expenses in this connection are to be borne by the purchaser.

Designed & Graphic by : S. B. Prakashan Pvt. Ltd.

Printed at :

Introduction to Physics

Physics is the most fundamental of the sciences. Its goal is to learn how the Universe works at the most fundamental level—and to discover the basic laws by which it operates. *Theoretical physics* concentrates on developing the theory and mathematics of these laws, while *applied physics* focuses attention on the application of the principles of physics to practical problems. *Experimental physics* lies at the intersection of physics and engineering; experimental physicists have the theoretical knowledge of theoretical physicists, *and* they know how to build and work with scientific equipment.

Physics is divided into a number of sub-fields, and physicists are trained to have some expertise in all of them. This variety is what makes physics one of the most interesting of the sciences—and it makes people with physics training very versatile in their ability to do work in many different technical fields.

The major fields of physics are:

- *Classical mechanics* is the study the motion of bodies according to Newton's laws of motion, and is the subject of this course.
- *Electricity and magnetism* are two closely related phenomena that are together considered a single field of physics.
- *Quantum mechanics* describes the peculiar motion of very small bodies (atomic sizes and smaller).
- *Optics* is the study of light.
- *Acoustics* is the study of sound.
- *Thermodynamics* and *statistical mechanics* are closely related fields that study the nature of heat.
- *Solid-state physics* is the study of solids—most often crystalline metals.
- *Plasma physics* is the study of plasmas (ionized gases).
- *Nanoscience and Nanotechnology is the new emerging field of physics*
- *Atomic, nuclear, and particle physics* study of the atom, the atomic nucleus, and the particles that make up the atom.

- *Relativity* includes Albert Einstein's theories of special and general relativity. *Special relativity* describes the motion of bodies moving at very high speeds (near the speed of light), while *general relativity* is Einstein's theory of gravity.
- The fields of *cross-disciplinary physics* combine physics with other sciences. These include *astrophysics* (physics of astronomy), *geophysics* (physics of geology), *biophysics* (physics of biology), *chemical physics* (physics of chemistry), and *mathematical physics* (mathematical theories related to physics).

Besides acquiring knowledge of physics for its own sake, the study of physics will give you a broad technical background and set of problem-solving skills that you can apply to wide variety of other fields. Some students of physics go on to study more advanced physics, while others find ways to apply their knowledge of physics to such diverse subjects as mathematics, engineering, biology, medicine, and finance.

In this Book, there are five Blocks. Block I and II deals with Atomics physics and Atomic Spectra, Block III and IV deals with X-rays and Photo electric effect and, Block V deals with Crystal physics.

Syllabus

BPHY-31: ATOMIC AND SOLID STATE PHYSICS

BLOCK-I

Excitation of atoms – Critical Potential – Excitation Potential – Ionisation Potential – Experimental determination of critical potential – Frank and Hertz`s method – Sommerfield atom model – Qualitative treatment – Derivation of condition for the allowed elliptical orbits – Vector atom model - Quantum numbers associated with Vector atom model-Coupling schemes – L-S and J J coupling _ Pauli's exclusion principle and verification .

BLOCK -II

Magnetic dipole moments due to orbital and spin motion – Selection rule for electron transition – Intensity rules – Interval rule – Fine structure of D line – Zeeman effect – Normal and Anomalous (Experimental study and results) – Debye's theory of normal Zeeman effect – Lorentz theory of anomalous Zeeman effect - Stark Effect (definition only).

BLOCK-III

Origin of X-Rays – Polarization of x-rays-Absorption of X-Rays – Continuous, Characteristic X-Rays –Mosley's Law –Mosley's Law and its importance - Bragg's law – Bragg X-ray spectrometer –Powder crystal method –Rotating Crystal method-Compton Effect – Theory – Experimental Verification.

BLOCK-IV

Photo electric effect – laws of photoelectric emission -Einstein's photo electric equation- Richardson and Compton Experiment – Millikan's Experiment – verification of Einstein's equations –determination of Plank's constant-Photo electric cells - Photo Emissive, Photo Voltaic, Photo Conductive cells – Photo Multiplier – Applications of photo electric cells.

BLOCK-V

Types of solids – Crystalline and Amorphous solids - Space Lattice – The Basis and the crystal structure unit cell and Primitive lattice cell – Lattice parameter – Symmetry elements in a cubic crystals - Point groups – Bravais lattice in two dimension – Seven crystal systems – coordination number for SC, BCC and FCC - Miller Indices – Features of miller indices – Crystal Structure – Nacl, Diamond, Zinc Blende,KCl.

Contents

Block I

Atomic Physics

STRUCTURE

OVERVIEW

We will begin this Unit by describing Atomic physics, and in this context, we will distinguish between various atomic models. We will then touch LS and JJ coupling. In addition, study about Pauli's exclusion principle

LEARNING OBJECTIVES

After completing this Unit, you should be able to:

- differentiate between various atom models;
- Derive the condition for the allowed elliptical orbits in sommerfield atom model
- Derive the relation for LS and JJ coupling

1.1 Introduction

Speculations as to the structure of the atom date from the early years of the nineteenth century. But the first insight into it was provided much later, in the early part of the last century after the discovery of the positive rays and the electrons. However, the distribution of these charges was not properly understood at the time. To explain the accumulated spectral data, several atomic models, one after another, were proposed e.g., Thomson's plum-pudding model, Rutherford's nuclear model etc. The instability of the Rutherford's model gave the clue that finally led to a fairly successful model developed by Niels Bohr in 1913. While it helped to explain a good number of atomic phenomena, the model is not strictly valid from the standpoint of quantum mechanics. Essentially, we shall describe in this chapter the Bohr model in details the story of its success and failure.

Atomic spectra

Spectral lines emitted by individual atoms consist of a discrete set of wavelengths characteristic of the element concerned. This phenomenon has been utilized in the spectroscopic analysis and identification of elements. The spectra of atoms in general, however, are very complicated.

To build up the atom model, therefore, Bohr focussed his attention on the simplest element hydrogen. Its spectrum (Fig. 1) consists of lines that gradually crowd near UV-region and converge towards a short wavelength limit. This is a common feature of all atomic spectra. The position of the limit is only different for different types of atoms.

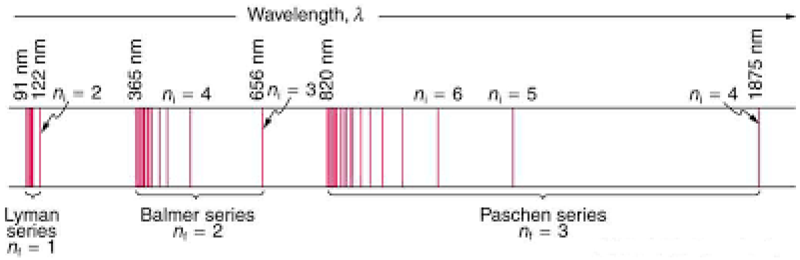


Fig 1

In an attempt to systematize the study of spectral line, Balmer (1885) showed purely empirically that the reciprocals of the wavelengths (not the wavelengths) of the series lines of hydrogen satisfy the following relation.

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) : n = 3, 4, 5, \dots$$

Where R_H is known as Rydberg cocstant for hydrogen, having a value 10967757 m^{-1}. The lines are successively called H_α, H_β, H_γ etc. lines. The above series is called the Balmer series.

Later other spectral series were found to exist and have been referred.

1.2 ATOM MODELS

Thomson's model

Thomson's atom model (1907), known as plum-pudding model, assumes that the entire positive charge is distributed over a sphere of radius equal to the atomic radius $\sim 10^{-10}$ m. In this homogeneous sphere of positive charge, the negatively charged point electrons are embedded in such a way, much like the plums in pudding (Fig.4.2) neutral. The electrons however are not at rest, but oscillate with definite frequencies about their mean positions.

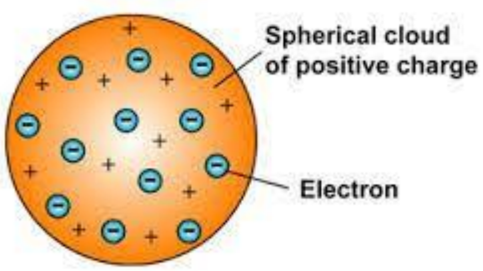


Fig.2

The model appeared plausible and obviously could explain the ionization process. But it suffered from a number of drawbacks. It failed to explain the observed frequencies of optical spectra and the results of α-ray scattering experiment of Geiger and Marsden. The model was therefore abandoned in favour of the now generally accepted Rutherford's planetary atom model.

Rutherford's nuclear atom model

Rutherford's nuclear model of the atom (1911) is an outcome of the scattering experiments of α-particles conducted by his colleagues Geiger and Marsden. Fast α-particles, doubly positively charge He^{++} ions, are emitted spontaneously from certain radioactive elements. Based on the scattering experiment, Rutherford proposed that the atom consists of a tiny but massive positively charged region, called the nucleus (nuclear radius $\sim$ 10^{-14} m) and cloud of negatively charged electrons surrounds the nucleus at a distance. The dimensions of the atom being 10^{-10}m, most of the space in the atom is empty. For neutral atoms, the charge on the extra nuclear electrons balances the positive charge of the nucleus.

Experiment in outline – The scattering experiment was conducted using thin foils of metals like gold. The α-particles were derived from a monoenergetic source of Po-214 placed behind a lead screen with a small hole in it. The narrow pencil of α-particles thus obtained was directed at a thin (6 x 10^{-7}m) gold foil. The scattered α – particles were detected by the flash in ZnS-screen S which was movable. A microscope M was used to observe and count the individual scintillations. The experimental set-up is sketched schematically in

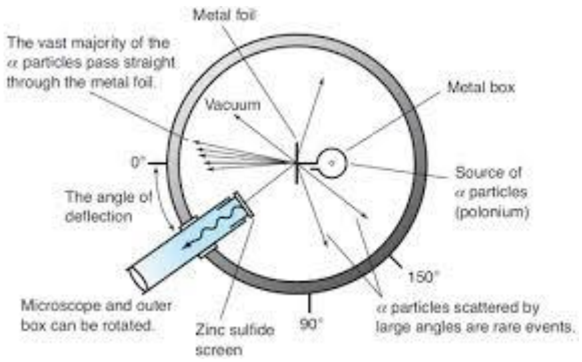


Fig.3.

Results – Most of the α-particles were scattered through small angles, that is, passed almost straight through the foil. The indicates that most of the space in an atom is empty. A small fraction of α-particles however was deviated through large angles, very few by even nearly 180°. The large angle scattering was startling for calculation on the basis of Thomson's model showed that the probability of scattering through angles as large as 90° was vanishingly small. Rutherford proposed that large angle scattering suggests that α-particles must have suffered much larger Coulomb force than what the distributed positive charge of Thomson model can bring forth. He concluded that within the atom there was small but massive core (over 99.9% mass of the atom) carrying positive charge and called it the nucleus. The electrons were assumed to be extra-nuclear, i.e., exist outside the nucleus. Rutherford's model is thus known as nuclear atom model.

To explain the stability of the atom, Rutherford assumed that electrons revolve round the nucleus, like planets revolving round the sun. The electrostatic attraction between the nucleus and the extra-nuclear electrons provided the necessary centripetal force. Mathematical derivation of Rutherored's α-ray scattering formula has been made in a subsequent chapter.

Limitation of the model- The serious drawback of the model is that the atom as a whole cannot be stable. To save the electron from being dragged into the nucleus due to electrostatic attraction, Rutherford assumed the circular motion of electrons, the centripetal force being provided by the electrostatic attraction. But, unfortunately, uniform rotation is an accelerated motion and an accelerated charge, according to classical e.m. theory, radiates energy. The consequent energy loss would make the electron spiral into the nucleus while emitting electromagnetic radiation of constantly increasing frequency. The time taken for the process is estimated to be about $10^{-8}8$. The Rutherford atom model cannot thus be stable. Further, the constantly increasing frequency of radiation contradicts the experimental result that gives only line spectra.

- It was at this stage that a yound Danish physicist, Niels Bohr, appeared in the Scene in 1913. The choice before him was to reject the Rutherford model or the classical electromagnetic theory. He rejected the latter by daringly introducing the revolutionary concept of stationary states of atom.

- Rutherford's nuclear atom model and his scattering formula have been discussed at length in chapter: Nuclear structure and General properties of nuclei.

Bohr's model of hydrogen atom

To understand the complex hyderogen spectrum and interpret it in terms of Rutherford's atom model, Bohr put forward a modified model, by (i) retaining the essential features of Rutherford's model for H-atom in which a single electron of mass m rotates around the nucleus of charge +e. and (ii) by drawing on the quantum ideas of Planck and Einstcin. This model is known as Bohr's atom model in developing which Bohr proposed a number of bold and daring postulates.

Bohr's postulates – The postulates of Bohr's atom model for H-atom are

1. The electron resolves round the nucleus, under the influence of Coulomb attraction, only in certain definite circular orbits without radiating energy. The possible discrete orbits are called the stationary states or quantized orbits of the atom.

2. The allowed stationary states are those for which the orbital angular momentum of the electron mvr is equal to an integral multiple of h(=h/2π), i.e.

$$mv_n r_n = nh, \quad n = 1, 2, 3, \ldots.$$

where r_n is the radius of the nth orbit.

3. Radiation of energy hv is either emitted or absorbed when transition of the electron between two stationary states m and n of energy E_m and E_n respectively occurs. When such a transition does take place, the energy conservation principle dictates

$$hv_{nm} = E_m \sim E_n$$

Equation (1) is called Bohr's quantum condition and equation (2) is referred to as Bohr's frequency rule.

Radil of orbits – The Coulomb attraction F between the charge of electron and the nucleus provides the centripetal force mv^2 / r required for circular motion.

$$\therefore F = \frac{c^2}{4\pi\varepsilon 0_n^2} = \frac{mv_n^2}{r_n}$$

where v_n is the velocity of the electron in its orbit of radius r_n

$$\text{or, } \frac{e^2}{4\pi\varepsilon 0rn} = mv_n^2$$

$$r_n = \frac{n^2h^2}{me^2}\, 4\pi\varepsilon_0 = \frac{n^2h^2\varepsilon_0}{\pi me^2} = n^2 \text{a0}; \; n = 1, 2, 3, \ldots$$

where a0 is the radius of the first orbit and is called the Bohr radius.

$$\text{a0} = \frac{h^2\varepsilon_0}{\pi me^2} = \mathbf{0.53 \times 10^{-10}\ m = 0.53\ A}$$

Velocity of electron , we get

$$v_n = \frac{nh}{mr_n}$$

Substituting the value of r_n from (4.5.5), we have

$$\hbar \quad v_n = \frac{\hbar}{ma0n} = \frac{e^2}{2\epsilon 0nh}$$

- Both the radius of the orbit and the velocity of electron depend on the n-value.

While r_n is proportional to n^2, the velocity is inversely proportional to n, implying that the electron in the innermost orbit has the highest velocity. Then n is known as quantum number, specifically the principal quantum number. In Bohr's model n = 0 in excluded for if n = 0,
r_n =0 and the electron would go through the nucleus.

Total energy of electron: Energy levels – In each allowed orbit, the electron will have a definite energy. The total energy E_n of the electron in its nth orbit is the sum of its kinetic and potential energy.

Kinetic energy, $T = \frac{1}{2}mv_n^2 = \frac{me^4}{32\pi^2n^2h^2\epsilon_0^2}$,

Potential energy, $V = \int_{\infty}^{Tn} \frac{e^2}{4\pi\epsilon 0r_n^2}\, dr_n = -\frac{e^2}{4\pi\epsilon_r r_n} = -\frac{me^4}{16\pi^2n^2h^2\epsilon_0^2}$, using

∴ Total energy, $E_n = T + V = \frac{me^4}{32\pi^2n^2h^2\epsilon_0^2} - \frac{me^4}{16\pi^2n^2h^2\epsilon_0^2} = \frac{me^4}{32\pi^2n^2h^2\epsilon_0^2}$

$$= -\frac{1}{n^2}, \frac{me^4}{32\pi^2n^2h^2\epsilon_0^2} = -\frac{1}{n^2}\frac{me^4}{n^2 8\epsilon_0^2h^2}$$

It is interesting to note that the potential energy V is – 2T.

The different energy levels are identified by the subscript n to E. If the values of the constants are substituted. (4.5.8) reduces to

$$E_n = \frac{-21.7\times10^{-19}}{n^2}\text{ J} = \frac{13.6}{n^2}\text{ Ev}$$

- The energy of the electron within the atom is also quantized, i.e., can take only certain discrete values. The quantization of angular momentum thus leads to the quantization of the total energy. The allowed energy values for a quantized system are often called energy levels or energy states. If these energy levels are plotted as horizontal lines separated by appropriate spacings, we get what is called energy-level diagram. The energy levels are represented schematically in Fig.. The negative sign to the total energy is due to the fact that the potential energy is taken to be zero when the electron is at infinity. It thus corresponds to a bound state implying that energy is required to remove the electron from the atom.

The lowest energy level is the one for which n = 1 and is called the ground state and
those corresponding to n = 2,3,4, … are the different excited states. Energy of some of the excited state are

E_1 = - 13.6Ev; E_2 = - 3.4 eV; E_3 = - 1.5 eV, …., E^{∞} = 0

Conventionally, the energy values are shown as horizontal lines in the energy level diagram. There is a continuum of energy states above E_∞ = 0 (shaded part in Fig..4.)

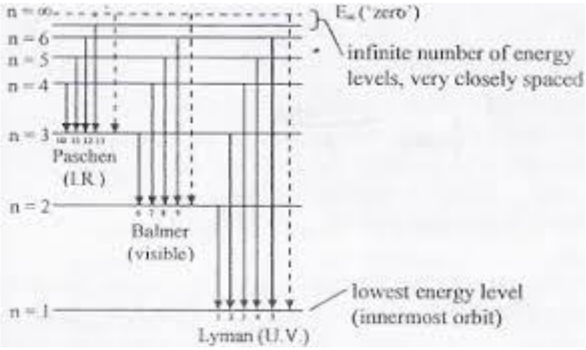


Fig 4

The level n = ∞ corresponds to the series limit and a state in which the electron is completely removed. The atom is said to be ionized. The enegyt $|E_1|$ required to remove the electron from the ground state, n = 1, of the atom is termed the ionization energy or the binding energy. If more energy is supplied to the electron, the excess over the binding energy will appear as the kinetic energy of the free electron.

Hydrogen Spectrum

At room temperature, almost all the H-atoms will be in the ground state. At higher temperature or during electric discharge, electrons may be in excited states. But their lifetime in the excited states is short so that they make transitions to lower energy states emitting electromagnetic radiations of definite frequency. There is no restriction on the change in n during the transition.

Let the electron make a transition from the initial state n_1 (upper state) of energy E_i to a final state n_f (lower state) of energy E_f, then by applying the Bohr's frequency rule, we obtain

$$V = \frac{E_i - E_f}{h} = \frac{me^4}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$

Substituting the values of E's.

In terms of wave number, $\bar{\nu}$ (defined by $\bar{\nu} = 1/\lambda = v/c$)

$$\frac{1}{\lambda} = \bar{\nu} = \frac{me^4}{8\epsilon_0^2 ch^3}\left(\frac{1}{n_f^2} - \frac{1}{n_f^2}\right)$$

$$= R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Where $R_\infty = \frac{me^4}{8\epsilon_0^2 ch^3}$ Rydberg constant for infinite nuclear mass.

Origin of spectral series ¯ Now, the origin of different spectral series of H-atom can be easily understood from Bohr's theory by substituting different values of n_i and n_f. We give below the different prominent spectral series.

1. **Lyman series** All transitions ending at $n_f = 1$ give rise to the ***Lyman series***. The wave number of different lines of the series may be obtained from relation .

$$\bar{v} = \frac{1}{\lambda} = R_\infty \left(\frac{1}{1^2} - \frac{1}{n_i^2} \right) ; n_i = 2, 3, 4, \ldots$$

The Lyman series is in the ultraviolet region of e.m. spectrum.

2. **Balmer series** All transitions ending at $n_f = 2$ give rise to the ***Balmer series***. The spectral lines of the series are given by

$$\bar{v} = \frac{1}{\lambda} = R_\infty \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right) ; n_i = 3, 4,5, \ldots$$

The Balmer series lines appear in the visible region.

The first ($n_i = 3$), the second ($n_i = 4$), the third ($n_i = 5$), etc. members of the series are called $H\alpha,\ H\beta,\ H\gamma,$ etc. respectively.

3. Paschen series $\bar{v} = \frac{1}{\lambda} = R_\infty \left(\frac{1}{3^2} - \frac{1}{n_i^2} \right) ; n_i = 4,5,6 \ldots$

4. Brackett series $\bar{v} = \frac{1}{\lambda} = R_\infty \left(\frac{1}{r^2} - \frac{1}{n_i^2} \right) ; n_i = 5,6,7 \ldots$

5. Pfund series $\bar{v} = \frac{1}{\lambda} = R_\infty \left(\frac{1}{5^2} - \frac{1}{n_i^2} \right) ; n_i = 6,7,8, \ldots$

The last three series are in the infrared region. Few series are illustrated in Fig.4.4.

- If the transition is caused from a lower energy level to a higher one by e.m. radiation of right energy, it will give rise to absorption spectrum, observed as dark lines of the same frequencies as emission lines.

Ritz combination principle

The Ritz combination principle states that certain frequencies in the emission spectrum can be summed to give other frequencies. Bohr's model is not only consistent with it but also provides a proper explanation for it.

If the electron is initially in an excited state, any n = 3, then it may transit downward from n=3 level to n=1 level directly. Alternatively, it may first transit from n=3 → n=2, and then from n = 2 3 → n=1. In the first case, the frequency v_{31} of the photon emitted is given by

$$hv_{31} = E_3 - E_1$$

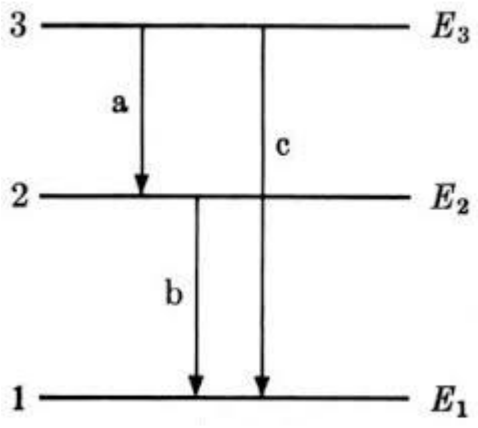


Fig.5

In the second case, two photons of frequency v_{32} and v_{21} would be emitted and

$$hv_{32} = E_3 - E_2; \;\; hv_{21} = E_2 - E_1$$

From Fig..5. it is quite apparent that $v_{31} = v_{32} + v_{21}$. The relation also follows

$$hv_{31} = E_3 - E_1 = (E_3 - E_2) + (E_2 - E_1) = hv_{32} + hv_{21}$$

or, $v_{31} = v_{32} + v_{21}$, and so on.

Generalising, we may write: $hv_{sm} = E_s - E_m$

$$= (E_s - E_n) + (E_n - E_m)$$

$$= h\nu_{sn} + h\nu_{nm}$$

Where s $>$ n, n $>$ m. But all the combinations predicted by the equation (4.7.3) are not actually observed and some selection rules are imposed to eliminate certain combinations.

Correction for finite nuclear mass

In the Bohr's model discussed, the nucleus is considered stationary, i.e., it is assumed to be infinitely massive compared to electron. However, a nucleus of finite mass cannot be at rest. To modify the model on this account is simple.

Both the electron of mass m and the nucleus of mass M move about the common centre of mass *0* of the electron nucleus composite system. Thus the kinetic energy must include an additional term for the motion of the nucleus.

As the total linear momentum of the atom is zero,

$$MV + mv = 0 \Rightarrow MV = -mv = p, \text{ say}$$

Kinetic energy of H-atom = $\frac{p^2}{2m} + \frac{p^2}{2M} = \frac{p^2}{2}\left(\frac{M+m}{Mm}\right)$

$= p^2 / 2\mu$

Where $\mu = \frac{mM}{m+M}$ = the reduced mass.

Hence, to take into account the motion of the nucleus, the electron mass m is to be replaced by the reduced mass μ.

$$\therefore E_n = \frac{\mu e^4}{32\pi^2 \epsilon_0^2 h^2 n^2}$$

The expression for Rydberg constant would now become

$$R_H = \frac{\mu e^4}{8\epsilon_0^2 ch^3} = \frac{R_\infty}{1+m/M}$$

Discovery of heavy hydrogen (deuterium)

The correction for the nuclear motion led to the discovery of heavy hydrogen or deuterium, an isotope of ordinary hydrogen having atomic mass almost double the mass the ordinary hydrogen ($M_p \simeq 2M_H$) by H.C. Urey in 1932.

While ordinary hydrogen (^{1}H) atom has only a proton in the nucleus, deuterium nucleus has a neutron in addition to proton. Since $M_D > M_H$, R_D is slightly greater than R_H,

$$R_H = \frac{R_\infty}{1+m/M_H} \quad R_D = = \frac{R_\infty}{1+m/M_D}$$

So, the spectral lines of ^{2}H will get slightly shifted to the shorter wavelength side compared to those of ^{1}H. Urey and co-workers observed faint companion lines on the shorter wavelength side of each of the hydrogen lines, whence they concluded that the fainter lines were due to a hitherto unknown isotope of hydrogen.

Computation of wavelength shift – we have

$$\frac{1}{\lambda H} = \bar{v}H = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right); \frac{1}{\lambda D} = \bar{v}_D = R_D\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\therefore \frac{\lambda D}{\lambda H} = \frac{R_H}{R_D} = \frac{R_\infty/(1+m/M_H)}{R_\infty/(1+m/M_D)} = \frac{1+m/M_D}{1+m/M_H}$$

$$\Rightarrow \quad \frac{\lambda H - \lambda D}{\lambda H} = \frac{m/M_H - m/M_D}{1+m/M_H} \simeq \frac{m}{M_H} - \frac{m}{2M_H} = \frac{m}{2M_H}$$

$$(\because M_D \simeq 2M_{H};\ m \ll M_{H};\ \text{so, } m/M_H \ll 1)$$

$$\therefore \Delta\lambda = \lambda_H - \lambda_D = \frac{m}{2M_H}\lambda_H = \frac{\lambda H}{3672} \ (\because m/M_H = 1/1836)$$

For H_β-line, λH = 4681 A and so $\Delta\lambda =$ (4681/3672) A = 1.28 A, the wavelength difference of H_β-lines for hydrogen and deuterium.

Hydrogenic atoms

Bohr's theory for H-atom can be used for any atom with a single electron such as singly ionized helium atom He^+, doubly ionised lithium, Li^{++} etc. These hydrogen –like atoms are called hydrogenic atoms.

Plainly, in hydrogenic atoms, the nucleus is of charge Ze, where Z is the atomic number. So, in hydrogenic atoms Ze^2 should be in place of e^2 in H-atom. With the change, the expressions for the energy and the radius of hydrogen like atoms become

$$E_n = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2h^2n^2} = -13.6\frac{Z^2}{n^2}\ \text{eV}$$

$r_n = n^2a_0/Z$

This shows that the orbits of atoms with higher Z-value are closer to the nucleus.

1.3 Excitation of atoms – (Critical Potential, Excitation Potential, Ionisation Potential)

As already stated, an atom is in its normal or ground state when it is in the lowest allowed state with n = 1. For emission of radiation, it must first transit to a state of higher energy. If in the process, it losses one or more electrons, it is ionised. If however it is raised to a higher energy state without ionization, it is said to be in an excited state.

The energy required to cause excitation may be supplied in a variety of ways and electron bombardment is the most convenient one. Electrons emitted from a hot filament (thermion) are imparted kinetic enegy $T = Ve$ by accelerating them across a potential V. Let E_m, E_n, … E_∞ be the sequence of possible energy states of the atom where E_m = energy in the ground state, E_n = energy of the first excited state etc.,

1. If $T < (E_n – E_m)$, the energy of bombarding electron is not sufficient to cause excitation. The elastic collision charges the kinetic energy of the atom as a whole without any change in the internal energy.

2. If $T = (E_n – E_m)$, the energy is just sufficient to excite the atom to the next higher state by energy transfer to one of the bound electrons. The collision is inelastic, the bombarding electron is left with zero kinetic energy and subsequently undergoes random thermal motion.

3. If $T = (E_n – E_m) = dT$, where $s > m$, the atom is excited to the higher state s as in 2 above, the excess kinetic energy dT being carried away by the free electron.

4. If $T > (E_\infty – E_m)$, the eleastic collision ionises the atom; a bound electron is freed and the excess kinetic energy, if any, is shared with the bombarding electron.

In this context, it is worthwhile to define the following important quantities.

Resonanace potential – A mihimum potential V is required to accelerate the bombarding electron to an energy *Ve* (in electron volt) in order that an atom may be excited from its ground state to the next higher state. This potential is called the resonance potential.

Excitation potentials – The various values of the potential required to impart the necessary energy to excite an atom to different higher states are known as excitation potentials.

Ionistion potential – The minimum potential necessary to supply the required energy to ionise an atom is called the ionization potential or the first ionization potential.

The resonance potential, the excitation potentials and the ionization potential are all included in the wider term eritical potentials.
Illustration – We illustrate the above definitions by taking H-atom.

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

So, the energy of the 1st, 2nd , 3rd , …. ∞th orbits are respectively – 13.6 eV, - 3.4eV, - 1.51 eV, …, 0 eV.

$\therefore$ Resonance potential = 13.6 – 3.4 = 10.2 eV
First excitation potential = resonance potential = 10.2 eV
Second excitation potential = 13.6 – 15.1 =12.09eV
Ionization potential = 13.6 – 0 =13.6eV

1.4 Measurements of critical potentials - Frank-Hertz experiment

Frank-Hertz experiment – The existence of discrete energy levels was confirmed by Franck and Hertz by conducting a series of experiments which we shall new describe.

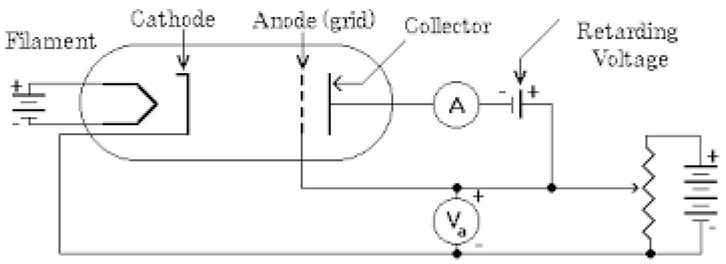


Fig. 4.10

Apparatus – It consists of a glass tube T (Fig.4.10) having a filament F, a wire grid G and a collecting plate P sealed into it. The atoms under study are taken into the tube in vapour-form (Franck and Hertz took Hg-vapour), at a low pressure. Electrons emitted from the filament F, when heated, are accelerated towards the grid G, kept at a positive potential V with respect of F. The idea is to bombard vapour atoms by these electrons of know energy eV. The collector P is kep at a slightly negative potential with respect to G. This small retarding potential Vo ($\ll$ V), allows only those electrons with energies greater than eV_0 to reach P to contribute to plate current recorded by milliameter *A*.

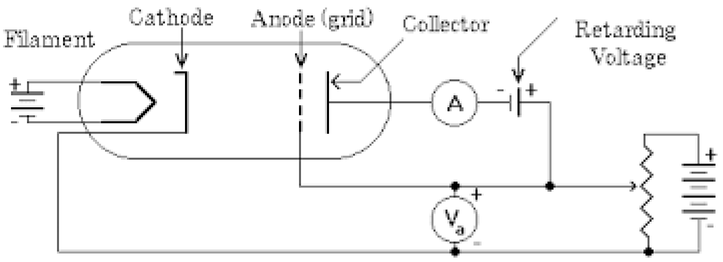
Method and observation – As V is increased gradually to resonanace potential V_r, more and more electrons reach the plate P and plate current i increases. Collisions of electrons with varpour-atoms are eleastic; energy transfer is negligible since atoms are much heavier than electrons. But whn V = Vr, the plate current sharply drops because electrons can now collide inelastically with vapour atoms; lose all the kinetic energy and cannot overcome V_0 to reach the collector P. A residual current is due to the elastic collisions of some electrons.

As V is increased further, the plate current rises again due to on-coming electrons gaining enough energy again to reach P overcoming V_0. This goes on till another abrupt drop in plate current occurs at $V = 2V_r$, and so on. A series of such potentials. V_r, $2V_r$, $3V_r$ etc. for a given atomic species is obtained. The different peaks are at potentials which are integral multiples of resonance potential. The difference in potentials between two consecutive peaks thus gives the resonance potential.

- The alternate rise and fall of current is explained thus. When p.d. between F and G is 2Vr, the electrons from F gain energy equal to the energy difference between two levels when half-way from F $\rightarrow$ G. If inelastic collision occurs at this point, the entire energy is lost. They start afresh with zero kinetic energy towards G and inelastic collision again would lead to a peak. Similarly for other peaks due to collision at different points in their path.

The importance of Franck and Hertz experiments is that provide a direct and independent evidence for the existence of atomic energy levels (quantization) and also confirm that these levels are the same as those suggested by the observations of the line spectra.

Ionization potential: A simplified apparatus for the determination of the ionization potential is described here.



.

It consists essentially of a sealed tube T containing a filament-heated cathode C, a plate P as anode and the experimental gas or vopour at a low pressure. As the plate voltage *V* is gradually increased from zero to some positive value, the plate current *i* increase according to the Child-Langmuir law:

$i = kV^{3/2}$

where k is a constant

The constant *k* is determined by the tube-geometry and the volume density of charge between the electrodes.

As *V* is increased, it is observed that at a certain $V = V_i$, the current suddenly begins to increase more rapidly. At this critical value V_i some electrons bump from the cathode to anode and acquire sufficient energy to knock off electrons from the gas atoms. The knocked off electrons contribute to the plate current and the positive ions annul some of the space charge. Due to this ionization the plate current shows a marked increase, as observed. The potential at which this occurs is the ionization potential. It is found to be 13.6 eV for hydrogen.

The thermions emitted from the filament have a certain initial velocity distribution and some of them can ionise the gas at relatively lower potentials than others. This fact explains the curved section joining the two lines in the graph (Fig.4.12.)

Merits and limitations of Bohr’s theory

The merits of Bohr’s theory can hardly be overestimated. It saved physics at a time when it was in the grip of severe crisis. But it has also its limitations.

Merits-It gives a convincing explanation and a simple and elegant picture of the origin of spectral lines. The theory predicted new undiscovered spectral series lines which were later observed.

The empirically determined value of Rydberg constant was evaluated by Bohr in terms of fundamental constants and the agreement was excellent.

The theory has been instrumental to the discovery of heavy hydrogen (deuterium) by Urey, and the general principle used by Bohr has been successfully applied to many phenomena such as excitation, ionization, X-ray spectra etc.

Limitations – There is an ad hoc nature in the assumptions of Bohr. The quantum idea of stationary orbits is mixed up with the classical idea of Coulomb force. The assumption of only circular orbits is also unjustified.

The spectral series, though agree excellently with H-atom, are at variance with the theory of multi-electron atomic systems. In these cases, it becomes necessary to introduce a magnetic quantum number.

Bohr’s theory can neither account for the origin of fine structure nor the multiplet structure of spectral lines like the doublet of sodium, triplets of magnesium etc.

The theory cannot also make calculations about the tranitions or the selection rules which apply to them.

In fact, the difficulty was with the atomic model itself. Even extension of Bohr's theory by Sommerfeld by introducing elliptic orbits could not save the situation except explaining the fine structure. The intensities or the polarization of lines remained unresolved. Every one was convinced that a more radical theory can only save the situation.

Learning activity - Illustrated Examples

Example 1. Show that the energy required to raise H-atom from the grond state (n – 1) to the first excited state (n = 2) is about 10 eV.

Solution. Let E_1 and E_2 be the energies of the electron in states n = 1 and n = 2 respectively.

$$\therefore E_1 \quad \frac{me^4}{32\pi^2 h^2 \epsilon_0^2}\ ; \quad E_1 = \frac{1}{4}\frac{me^4}{32\pi^2 h^2 \epsilon_0^2}$$

$\therefore$ Required energy, $E = E_1 - E_2 = \frac{3}{4}\frac{me^4}{32\pi^2 h^2 \epsilon_0^2}$

$$\therefore E = \frac{3 \times 9.1 \times 10^{-31} \times (1.60 \times 10^{-19})^4 \times 4\pi^2}{4 \times 32 \times \pi^2 \times (6.62 \times 10^{-34})^2 \times (8.85 \times 10^{-12})^2}\ \text{J} \simeq 10\ \text{eV}$$

Example 2. Given the Rydberg constant as 1.097 x 10^7 m^{-1}, calculate the wavelength of the first line of Balmer series in Angstrom unit.

Solution For the first line, i.e., H_α -line of the Balmer seres, $n_i = 3$, $n_f = 2$

$\therefore$ Wave number of H_α- line : $\bar{v} = R_H\left(\frac{1}{2^2} - \frac{1}{2^2}\right) = \frac{5}{36} R_H$

$\therefore$ Wavelength of H_α –line : $\lambda = \frac{1}{v} = \frac{36}{5R_H} = \frac{36}{5 \times 1.097 \times 10^7}$ m = 6563 A

Example 3. Calculate what will be the approximate quantum number n for an electron in an orbit of radius 0.1 nm.

Solution. The radius of Bohr orbit, in terms of Bohr radius a_0, is given by

$$r_n = n^2 a0 = 0.53n^2 \text{ A}$$

for $r_n = 0.1$ nm = 10^6 A, we therefore obtain from above

$$10^6 = 0.53_R{}^2 \Longrightarrow n^2 = 10^6 / 0.53 = 18.87 \times 10^5$$

$$\therefore n \simeq 1374$$

Example 4. What is the velocity of electron in the ground state of H-atom is terms of the speed of light? What is this called?

Solution. From the relation : $v_n = \frac{h}{m a_0 n}$, we have

$$v_1 = \frac{h}{m a_0} \ (n = 1)$$

In terms of the speed of light, the electron velocity is

$$\frac{h}{m a_0 n} = \frac{6.62 \times 10^{-34}}{9.1 \times 10^{-31} \times 0.53 \times 10^{-10} \times 3 \times 10^8} \simeq \frac{1}{137}$$

This is called the fine structure constant.

Example 5. Find the series limit of Balmer series, given $R_H = 1.097 \times 10^7 \, m^{-1}$

Solution. The wavelengths of spectral lines of the Balmer series are

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right) ; n = 3, 4, 5, \ldots$$

For the series limit, n = ∞. We thus obtain from above

$$\frac{1}{\lambda_\infty} = R_H \left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) = \frac{R_H}{4}$$

$$\therefore \lambda^{\infty} = \frac{4}{R_H} = \frac{4}{1.097 \times 10^7} = 3.646 \times 10^{-7} \text{m}$$

= 3646 A

Example 6. The first line of Balmer series of hydrogen has a wavelength 6563 A. Calculate the wavelength of the second line.

Solution. The wavelengths of the spectral lines Balmer series given by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) ; n = 3, 4, 5,$$

For the first line, n = 3; so the wavelength λ_1 is given by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{3R_H}{16}$$

For the second line, n = 4, So, the wavelength λ_2 is given by

$$\frac{1}{\lambda_2} = R_H\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3R_H}{16}$$

$$\therefore \frac{\lambda_1}{\lambda_2} = \frac{3R_H}{16} \times \frac{36}{5R_H} = \frac{27}{20}$$

$$\therefore \lambda_2 = \frac{\lambda_1 \times 20}{27} = \frac{6563 \times 20}{27}$$

= 4861 A

Example 7. The average life-time of an electron in an excited state of H-atom is about $10^{-8}{}_{8}$. How many revolutions does an electron in n = 2 state make before its transition to n = 1 state. The Rydberg constant for H-atom is 1.097 $\times 10^7$ m^{-1}

Solution. The frequency of revolution of the electron in an orbit is

$$f = \frac{electron\ speed}{orbital\ circumference} = \frac{v_n}{2\pi r_n}$$

But, $v_n = \frac{e^2}{2\varepsilon 0 nh}$ and $r_n = \frac{n^2h^2\epsilon_0}{\pi m 3^2}$

$$\therefore f = \frac{me^4}{8\varepsilon_0^2 h^3}\left(\frac{2}{n^3}\right) = \frac{2}{n^3} \text{ R}_{\text{Hc}}$$

For, n = 2, $f = \frac{2RHc}{8} = \frac{2\times 1.097\times 10^7 \times 3\times 10^8}{8} = 8.2 \times 10^{14} s^{-1}$

$\therefore$ No. of revolutions in $10^{-8} s$ is given by

$$N = f \times 10^{-8} = 8.2 \times 10^{14} \times 10^{-8} = 8.2 \times 10^6$$

Example 8. If the wavelength (mean) of sodium D-lines is 5893 A, estimate the minimum energy in electron volt of the bombarding electron for excitation of these lines.

Solution. Wavelength of D-lines : $\lambda = 5893 \times 10^{-10} m$

Frequency of D-lines : $v = c/\lambda = 3 \times 10^8 /(5893 \times 10^{-10})$Hz

$\therefore$ Energy of excitation of the D-lines is

$$hv = \frac{0.62 \times 10^{-34} \times 3 \times 10^8}{5893 \times 10^{-10}} \text{ J}$$

$$= \frac{0.62 \times 10^{-34} \times 3 \times 10^8}{5893 \times 10^{-10} \times 1.6 \times 10^{-15}} \text{ eV} = 2 \text{ Ev}$$

Example 9. Calculate the tonization potentials of (i) H-atom and (ii) He-atom in the ground state.

Solution. (i) We have, $E_n = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2}$ For ground state, n = 1.

$$\therefore E_1 = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2} = \frac{9.1 \times 10^{-31} \times (1.6 \times 10^{-19})}{8 \times (8.85 \times 10^{-12})^2} \text{ J}$$

$= 13.6$ eV

∴ Energy of the first orbit of H-atom = - 13.6 Ev

∴ Ionization potential of H-atom in ground state = 13.6 Ev

(ii) We have for hydrogen-like atom, $E_n = \frac{Z^2 me^4}{8\varepsilon_0^2 n^2 h^2}$

For He-atom, Z = 2 and for ground state n = 1

$$\therefore (E_1)\,He = -\frac{me^4}{8\varepsilon_0^2 h^2} \times 4 = +4\,(E_1)H$$

$$\therefore (E_1)\,He = +4 \times (-13.6) = -54.4 \text{ Ev}$$

∴ Ionization potential of He-atom in the ground state = 54.4 Ev.

Example 10. Find the wavelength separation of the first member of the Balmer series due to ^1H and ^2H (= ^2D).

Solution. We have : $\bar{v}H = R_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ . . . for ^1H

and $\bar{v}0 = R_D \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ . . . for ^2H (-^2D)

$$\therefore \frac{\bar{v}H}{\bar{v}D} = \frac{R_H}{R_D} = \frac{1 + m / MD}{1 + m / MH} = \frac{1 + m/2M_H}{1 + m/M_H}$$

$$\text{or, } \frac{\bar{v}H \sim \bar{v}D}{\bar{v}D} = \frac{1}{2\,(1 + M_H/m)} = \frac{1}{2(1840)} = \frac{1}{3680}$$

$$\therefore \frac{\Delta\bar{v}}{\bar{v}} = \frac{\Delta\lambda}{\lambda} = \frac{1}{3680}$$

∴ At λ = 656.3 nm, $\Delta\lambda$ = λ/3680 = 656.3/3680 = 0.178 nm.

Example 11. Show that the magnitude of the potential energy of an electron in the n th orbit of H-atom is half the magnitude of its kinetic energy in that orbit.

Solution. Potential energy of electron in nth orbit of H-atom is given by

$$V = -\frac{1}{4\pi\epsilon 0}\frac{e^2}{r_n} = \frac{1}{4\pi\epsilon 0}\frac{e^2}{n^2 a_0} \quad (\because r_n = n^2 a_0)$$

$$= -\frac{8.98\times10^{9}\times(1.6\times10^{-19})^2}{n^2\times 0.53\times10^{-10}}\ \text{J}$$

$$= -\frac{4.35\times10^{-18}}{n^2}\ \text{J} = -\frac{27.2}{n^2}\ \text{eV}$$

Kinetic energy, $T = E_n - V = -\frac{13.6}{n^2}\ \text{eV} + \frac{27.2}{n^2}\ \text{eV}$

Which is half of the potential energy in magnitude.

Example 12. A positronium atom is a system that consists of a positron and an electron. Calculate the reduced mass, the Rydberg constant and the wavelength of the first Balmer line for positronium. Given, m = 9.1 $\times 10^{-31}$ kg, R_H = 1.09737 $\times 10^{-3}$ A^{-1} and H_α= 6563 A.

Solution. The positron has the same mass m as that of the electron and has equal but positive charge.

$\therefore$ Reduced mass of positronium is

$$\mu_p = \frac{(m)(m)}{m+m} = \frac{1}{2}m = \frac{1}{2}\times 9.1\times10^{-31}\ \text{kg}$$

$= 4.55 \times 10^{-31}$ kg

Rydberg constant (= constant $\mu e^4 / 8\varepsilon_0^2 h^3 c$) for positronium is thus half that for hydrogen.

$$\therefore R_p = \frac{1}{2}R_H = \frac{1}{2}\times 1.09737\times 10^{-3}\ A^{-1}$$

$= 0.54868 \times 10^{-3}\ A^{-1}$

Wavelength of the first Balmer line, H_α in H-atom is given by

$$\frac{1}{\lambda H} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

While that in positronium is given by

$$\frac{1}{\lambda p} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\therefore \frac{\lambda p}{\lambda H} = \frac{R_H}{R_p} = 2$$

$$\therefore \lambda_p = 2\lambda_H = 2 \times 6563 \text{ A} = 13126 \text{ A}$$

Example 13. Show that the transitions from n = 3 → n = 2, n = 2 → n and n = 3 → n = 1 in Bohr atom model satisfy the following relation

$$v3 \rightarrow 2 + v2 \rightarrow 1 = v3 \rightarrow 1$$

Solution. We have : $v3 \rightarrow 2 = R^{\infty}c \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$; $v_2 \rightarrow 1 \; R^{\infty}c \left(\frac{1}{1^2} - \frac{1}{2^2}\right)$;

$$v3 \rightarrow 1 + v2 \rightarrow 1 = R^{\infty}c \left(\frac{1}{1^2} - \frac{1}{3^2}\right);$$

From the first two equations, we obtain

$$v3 \rightarrow 2 + v2 \rightarrow 1 = R^{\infty}c\left[\left(\frac{1}{2^2} - \frac{1}{3^2}\right) + \left(\frac{1}{1^2} - \frac{1}{2^2}\right)\right]$$

$$= R^{\infty}c \left(\frac{1}{1^2} - \frac{1}{3^2}\right) = v3 \rightarrow 1$$

$$\therefore v3 \rightarrow 2 + v2 \rightarrow 1 = v3 \rightarrow 1$$

Example 14. An electron circles a nucleus of charge Ze. Of the two orbits 1 and 2 of radii r_1 and r_2 respectively, it total energy is greater while in orbit 2 are greater than those in orbit 1.

Solution. Energy of electron,

$$E_n = \left(-\frac{Ze^2}{8\pi \varepsilon 0 rn}\right) = -\frac{1}{2}mv_n^2 \qquad (4.16.1)$$

Since $E_1 > E_2$, we have : $(E_1 - E_2) > 0$

or, $\left(-\frac{Ze^2}{8\pi\varepsilon 0r1} + \frac{Ze^2}{8\pi\varepsilon 0r2}\right) > 0$, using (4.16.1)

or, $\frac{Ze^2}{8\pi\varepsilon 0}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) > 0$

$\therefore r_1 > r_2$

From (i) again, $\frac{1}{2}\, m\,(v_2^2 - v_1^2) = \frac{Ze^2}{8\pi\varepsilon 0}\left(\frac{1}{r2} - \frac{1}{r1}\right)$

or, $(v_2^2 - v_1^2) > 0$ using (4.16.2) above.

$\therefore v_2 > v_1$

The acceleration of electron in circular orbit is the normal acceleration, $f = v^2/r$.

Since, $\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon 0r^2}$

$$\therefore fn = \frac{Ze^2}{4\pi m\varepsilon 0 r_n^2}$$

$$\therefore f2 - f1 = \frac{Ze^2}{4\pi m\varepsilon 0}\left(\frac{1}{r_2^2} - \frac{1}{r_1^2}\right)$$

Or, $(f2 - f1) > 0$ ($\because r_1 > r_2$)

$$\therefore f2 > f1$$

Example 15. Show that in a Bohr atom if the electron is considered as a wave travelling along the circular path, then the nth orbit will contain n complete de Broglie waves.

Solution. The radius r_n of the nth Bohr's circular orbit is given by

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2}$$

So, the circumference of the nth Bohr orbit is

$$2\pi r_n = -\frac{2n^2 h^2 \epsilon_0}{m e^2}$$

But the wavelength of the de Broglie wave (see later) is given by

$$\lambda = \frac{h}{mv} = \frac{h}{m}\left(\frac{2nh\varepsilon 0}{e^2}\right); (\because v_n = e^2/2nh\varepsilon 0)$$

∴ Number of complete de Broglie waves in nth orbit is

$$\frac{2n^2 h^2 \epsilon_0}{m e^2} \div \frac{h}{m}\left(\frac{2nh\varepsilon 0}{e^2}\right) = n$$

When we consider the differences between the spoken and written mediums, we find that most of them can be traced to two main sources *situational* and the *very nature of the two mediums*.

1.5 Sommerfeld's model

According to Bohr's theory, each spectral line of H-atom must be a single line, i.e., a single frequency. But Michelson and others observed each line to be considered of a small number of close components of slightly different frequencies. This is known as the fine structure of spectral lines, implying each energy level of a given n must be split into sub-levels of slightly different energies. But the phenomenon could not be explained on the basis of Bohr's theory.

To explain the fine structure, Sommerfeld extended Bohr's theory by introducing (i) general quantization rule and (ii) the idea of elliptic orbits for the electron.

The general quantization rule for any physical system proposed by Wilson and Sommerfeld runs as: For any physical system in which the coordinates are periodic functions of time, there exists a quantum condition for each coordinate given by

$$\oint p_q d_q = n_q h$$

Where q is one of the coordinates, p_q the corresponding momentum, n_q, a quantum number that takes integral values.

Elliptical orbits – According to Sommerfeld, the electron in the H-atom moves in an elliptical orbit around the nucleus as one focus (Fig.4.7).

The electron can now be located by two coordinates r and θ, the radial distance and the azimthal angle. Based on the general quantization rule, we now have two quantum condition – one for the radial momentum $p_r = m(dr/dt)$ and the other for the angular momentum, $p_o = mr^2 (d\theta / dt)$.

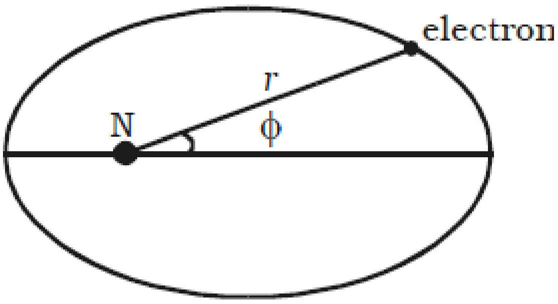


Fig.8

$\oint p_r dr = n_r h$ $n_r = 0,1,2, \ldots.,$

$\oint p_0 d\theta = k h$ $k = 1, 2, 3, \ldots,$

Where n_r is the radial quantum number and k, the azimuthal quantum number and the integration is over one complete period of motion. Since k = 0 corresponds to the motion of electron along a straight line through the nucleus, and has therefore been left out.

A complete analysis, which we shall not enter into, gives

$$N = k + n_{r,}\ \ n = 1,2,3, \ldots$$

$$\text{and } E_n = -\left(\frac{1}{n^2}\right)\frac{\mu Z^2 e^4}{32\pi^2 \epsilon_0^2 h^2}$$

where n is known as the total quantum number or principal quantum number. Also, from the analysis,

$$\frac{b}{a} = \frac{k}{n},$$

Where a and b are the sem-major and semi-major and semi-minor axis of the ellipse.

So, only those orbit are permitted for the electron for which the ratio of the major to minor axis is the ratio of two integers.

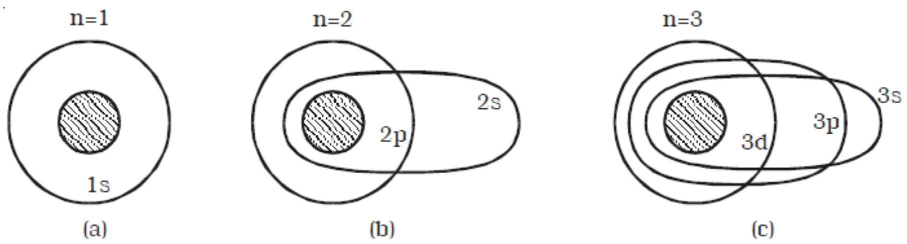


Fig 9

The energy expression (4.9.4) is identical to the one for circular orbits so that the mere introduction of elliptic orbits adds no new energy levels and hence does not explain the fine structure. Fig 4.8 illustrates the possible electron orbits in H-atom for n=1,2 and 3. The orbit is circular for n = 1, k = 1, n_r = 0.

The two orbits corresponding to n = 2 have the same energy and are said to be degenerate. The energy state n = 3 is three-fold degenerate.

Relativistic effects – Sommerfeld next considered the relativistic effects to remove the degeneracy (or the existence of multiple orbits of same energy) and explain the fine structure.

The speed of the electron in elliptic orbit changes with its position, speeding up when closer to the nucleus and slowing down when far away from it. Due to this variation in electron speed, there would be a variation in the mass of the electron according to the relativistic relation

$$m = \frac{m0}{\sqrt{1 + v^2/c^2}}$$

As a result of this mass-variation with velocity there is a slow precession of the major axis in the elliptic plane about an axis through one of the foci. The electron's path of motion in such a case, is a rosette as has been illustrated in Fig. .9. The precession rate however is different for different elliptical orbits.

Taken relativistic effects into consideration, the energy of hydrogen-like atom is given by

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 h^2 n^2}\left[1 + \frac{Z^2 \alpha^2}{n}\left(\frac{1}{k} - \frac{3}{4n}\right)\right]$$

Where μ is the reduced mass and α is the fine structure constant defined by

$$\alpha = \frac{e^2}{4\pi\epsilon 0ch} = \frac{1}{137}$$

A dimensionless universal constant.

For a given principal quantum number n, k can have n different values leading to different states with slightly different energies. So, we shall have a number of transitions in place of a single one of Bohr's theory. The lines thus generated are the fine structure. But all possible transitions are not allowed. Only those for which k changes by unity are allowed i.e.,

$$\Delta k = \pm 1$$

Which is the selection rule for an allowed transition. There is however no restriction on the change in n, i.e., Δn-value.

- Discrepancies however still remained. For instance, calculations show that the first line of Balmer series should have six-components, but in fact it has five. Selection rules reduced H_α -lines to three.
- Sommerfeld's theory included no consideration of electron spin, nor the exclusion principle of Pauli which are basic for an understanding of the complex atom. It is at present of historical interest only we have therefore not gone deep into it.
- A complete explanation of the fine structure of spectral lines can be provided only by the introduction of the concept of electron spin and quantum electrondynamics. In fact, the limitations of old quantum theory were overcome by quantum mechanics developed by Heisenberg, Schrodinger and extended by Dirac.

Bohr's correspondence principle

Bohr noted from the energy expression that as the quantum n becomes very large, the successive values of the allowed energy differ very little from each other, and appear almost continuous. Further, as the spectral lines tend to the series limit they crowd so much that the spectrum appears continuous. In this context, Bohr in 1923 enunciatted an important principle called the correspondence principle.

Statement-It states that the behaviour of an atomic system as predicted by quantum theory tends asymptotically (i.e., corresponds) to that expected in classical theory in transitions involving states of large quantum numbers.

Bohr's correspondence principle forms an important guideline in formulating the laws of atomic mechanics.

Let us apply this to the Bohr atom. Classically, an electric charge moving in a circular orbit radiates energy at a frequency equal to the frequency of rotation. The frequency of rotation,

$$\nu = \frac{\text{electron speed}}{\text{orbital circumference}} = \frac{v}{2\pi r}$$

Substituting the values of v and r from (4.5.5) and (4.5.7) and simplifying,

$$\nu_n = \frac{me^4}{32\pi^3\epsilon_0^2h^3}\,\frac{1}{n^3}$$

A radiated frequency in quantum theory, when the electron transits from state n to (n – 1) is, however

$$\nu_n = \frac{me^4}{64\pi^3\epsilon_0^2h^3}\left[\frac{1}{(n-1)^2} - \frac{1}{n^2}\right] = \frac{me^4}{64\pi^3\epsilon_0^2h^3}\,\frac{2n-1}{n^2(n-1)^2}$$

when n is very large, (2n – 1) $\simeq$ 2*n* and (n – 1) $\simeq$ *n*.

$$\therefore\ \nu_n = \frac{me^4}{32\pi^3\epsilon_0^2h^3n^3}$$

Which is identical with the classical frequency.

- The basic philosophy of the correspondence principle is that the Bohr model when applied to problems of the macroworld would give results identical to those obtained by the classical methods. Its applications however go beyond the Bohr atom. It implies that two theories must correspond whenever their regions of validity overlap.
- Bohr's quantum theory gives only the frequency of spectral line and states nothing about the state of polarisation, intensity etc. Bohr used the correspondence principle and utilized the classical theory for the purpose. He also deduced the selection rules in electron transitions with its help.

1.6 Vector atom model

The space quantization and the introduction of the concept of spin led to the vector model of the atom. First, we shall discuss the method how the two momenta combine and how that brings about changes in spectral characteristics of a one-electron atom.

The orbital angular momentum $\vec{L}$ and the spin angular momentum $\vec{S}$ of the electron in an atom combine to give a total angular momentum, $\vec{J}$. According to the vector model $\vec{J}$ is the vector sum of $\vec{L}$ and $\vec{S}$.

$$\therefore \vec{J} = \vec{L} + \vec{S}$$

The magnitude of $\vec{J}$, like those of $\vec{L}$ and $\vec{S}$, is given by

$$J = |\vec{J}| = \sqrt{j(j+1)}\, h$$

Where j is the total angular momentum quantum number.

We may write, in analogy with the components L_z and S_s, the possible J_z values:

$$J_z = m_j h$$

Where m_j can take up $(2j + 1)$ values from $-j$ to $+j$ in steps of unity.

i.e., $-j, -j + 1, \ldots, j - 1, j$

In adding $\vec{S}$ to $\vec{L}$, they can be added either parallel or anti parallel as shown in Fib.10.

The total angular momentum quantum number for single electron can have values.

$$j = l + s;\ j = l - s$$

$$\Rightarrow j = l + \frac{1}{2};\ j = l - \frac{1}{2}\ \left(\because s = \frac{1}{2}\right)$$

In case $l = 0$, j can have only the value $\frac{1}{2}$. If $l - 1$, $j = l \pm \frac{1}{2}$ i.e., $\frac{3}{2}$ or $\frac{1}{2}$

If $l = 2$, $j = 2 \pm \frac{1}{2}$ i.e., 5/2 or 3/2.

Since both $\vec{L}$ and $\vec{S}$ show quantization, J will also expectedly show space quantization. The internal magnetic field causes the $\vec{L}$ and the $\vec{S}$ to process about $\vec{J}$ (Fig.8.6a). In an external field $\vec{B}_e$, however, $\vec{J}$ will precess about $\vec{B}_e$ as shown in Fig.10b. The precession of $\vec{L}$ and $\vec{S}$ about the precessing $\vec{J}$ is rather very complicated.

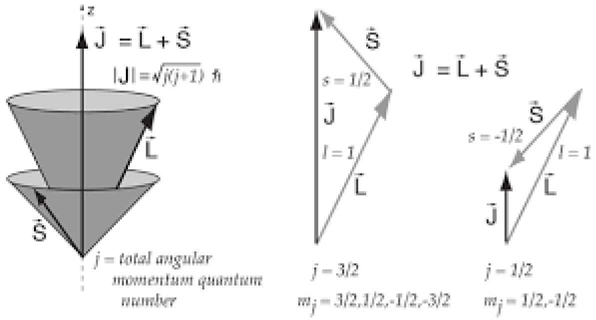


Fig. 10

Notiation – The notation used to describe the different atomic states is

nL_j

where n is the principal quantum number, j the total angular momentum quantum number and L refers to be orbital angular momentum quantum number.

Different L-values are represented by different symbols denoting the energy states.

L = 0 1 2 3 4 5 . . .

Symbol : S P D F G H . . .

Let us use the notation for representing the ground state of the H-atom. Plainly

$$n = 1,\ l = n - 1 = 0,\ s = \frac{1}{2} \text{ and } j = l \pm \frac{1}{2} = \frac{1}{2}$$

So, according to the notion, the state is given by $1S_{1/2}$

Similarly, for the first excited state,

$$n = 2,\ i = 0,\ s = \frac{1}{2},\ j = \frac{1}{2} \Longrightarrow 2S_{1/2}$$

$$n = 2,\ l = 1,\ s = \frac{1}{2},\ j = \frac{3}{2},\ \frac{1}{2} \Longrightarrow 2P_{3/2} \text{ and } 2P_{1/2} \text{ etc.}$$

All states except the S-state are doublet for n = 2.

Angles between $\vec{L}$ and $\vec{S}$ – We have: $\vec{J} = \vec{L} + \vec{S}$

$$\Rightarrow J^2 = (\vec{L} + \vec{S})(\vec{L} + \vec{S}) = L^2 + S^2 + 2\vec{L}.\vec{S}$$

$$= L^2 + S^2 + 2LS\cos\theta$$

$\therefore \cos\theta = \frac{J^2 - L^2 - S^2}{2LS}$

Where θ is the angle between the two vector $\vec{L}$ and $\vec{S}$.

Now, since we have $J^2 = j(j+1)h^2$, $L^2 = l(l+1)h^2$ and $S^2 = s(s+1)h^2$,

$$\cos\theta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}$$

Angle between $\vec{J}$ and the z-axis – Let $\emptyset$ be the angle between $\vec{J}$ and the z-axis.

$\therefore \cos\emptyset = \frac{J_z}{J} = \frac{m_j h}{\sqrt{j(j+1)}h} = \frac{m_j}{\sqrt{j(j+1)}}$

We have seen that the maximum value of m_j is j which is less than $\sqrt{j(j+1)}$. It thus follows that J can never align itself along the z-axis.

Spin-orbit interaction or splitting : Fine structure

The emission lines of H-spectrum show, as already stated, a doublet structure. But why? The reason behind this would now be investigated.

The electron in H-atom moves under a central potential V (r) due to the nucleus. The interaction between its orbital angular momentum $\vec{L}$ and spin angular momentum $\vec{S}$ is known as the **spin-orbit interaction or splitting**. The interaction is of the form $\vec{L}$, $\vec{S}$ and it makes the states $j = l - \frac{1}{2}$ to have a slightly lower energy than those with $j = l - \frac{1}{2}$. And this doublet levels constitute the fine structure of the H-atom spectrum.

For s-electrons, the orbital angular momentum is zero. So, spin-orbit interaction, does not occur.

The doublet separation decreases with increasing l. Further, the 2p doublet separation is greater than 3p doublet and so on. The energy levels of H-atom showing the splitting due to spin-orbit interaction is illustrated in Fig..

If spin-orbit interaction is 1s → 2p is a single line – the first line in the Lyman series of H-spectrum. It splits into two lines when the spin-orbit interaction is considered (Fig.8.7) The same is the story regarding the transitions 1s → 3p, 1s → 4 p and so on. Each line of the Lyman series, therefore, is a doublet and is often known as fine structure doublet. Fig.8.8 illustrates the transitions between 2p $\rightarrow$ 3d levels which give rise to three lines – the triplet. Spin-orbit coupling increases the complexity of H-spectrum.

The spin-orbit interaction-appears more prominent in case of heavy elements. This is because the spin-orbit energy is directly proportional to the fourth power of atomic number Z.

1.7 L-S and J J coupling

Total angular momentum in multi-electron atoms

Compared to an one-electron atom, the addition of orbital and spin angular moments makes the multi-electron atoms much more complicated and involved. In the later case, the active electrons that contribute to the angular momentum of the atom are those outside a closed shell-the valence electrons.

There are two coupling schemes for computing the total angular momentum $\vec{J}$ of a multi-electron system. The schemes are : (i) LS coupling or Russel Saunders coupling and (ii) the jj-coupling.

LS-coupling

In the LS-coupling, the orbital angular moments $\overrightarrow{L_1} + \overrightarrow{L_2} + \overrightarrow{L_3}$ … etc. of the electrons are vectorially added to produce the total orbital angular momentum $\vec{L}$. In a like manner, the spin angular moments S_1, S_2, S_3 … combine vectorially to form the total spin angular momentum, $\vec{S}$, Symbolically, therefore,

$$\vec{L} = \overrightarrow{L_1} + \overrightarrow{L_2} + \overrightarrow{L_2} + \ldots = \Sigma_i \overrightarrow{L_i}$$

and $$\vec{S} = \overrightarrow{S_1} + \overrightarrow{S_2} + \overrightarrow{S_3} + \cdots = \Sigma_i \overrightarrow{S_i}$$

Finally, the resultant momenta $\vec{L}$ and $\vec{S}$ combine vectorially to form the total angular momentum $\vec{J}$, so that we have

$$\vec{J} = \vec{L} + \vec{S}$$

This coupling scheme is valid only when the coupling between the individual $\overrightarrow{L_i}$ vectors and $\overrightarrow{S_i}$ vectors, i.e., between $\overrightarrow{L_1}$ and $\overrightarrow{S_2}$ etc. is weak. Then the individual $\overrightarrow{L_i}$'s would couple to give $\vec{L}$ and the individual $\overrightarrow{S_i}$'s will combine to give $\vec{S}$. It applies to a large number of elements, particularly the lighter ones. Due to its wide validity, this coupling scheme is the basis of the usual spectroscopic notation.

- Conventionally, capital letters L, S and J are used for the angular momentum quantum numbers of a multi-electron system and they are simply integers and half-integers. In expressing the magnitude of angular momentum vectors multiplication by h is to be made so that no confusion arises.

Now, if two orbital angular momenta of quantum numbers l_1 and l_2 combine to form L, the allowed values of L are

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \ldots |l_1 - l_2|$$

The allowed values of S and J can also be similarly calculated.

For a given L, the allowed J-values are similarly

$$J = (L + S), (L + S - 1), \ldots |L - S|$$

For L $>$ S, there are 2S + 1 values for J; for L $<$ S, the possible J-valuesare 2L + 1. The value of 2S + 1 is known as the **multiplicity** of the state.

The simplest multi-electron system is a two-electron system for which the spin quantum number ($S_1 = ½$, $S_2 = ½$) may be so set that they are both parallel and S = $\frac{1}{2} + \frac{1}{2}$ = 1; they could as well be oriented anti-parallel so that S = = $\frac{1}{2} + \frac{1}{2}$ = 0. When S = 0, 2S + 1 = multiplicity = 1. Such states are called the singlet states. When, however, S = 1, 2S + 1 = 3. These are known as the triplet states.

For an one-electron system our notation was nL_j. It now requires a change for representing the state symbol incorporating the multiplicity of the state. The state symbol is thus represented by

$N^{2S+1}L_J$

Where n stands for the principal quantum number,

2S + 1 represents the multiplicity of the state,

J the subscript, represents the total angular momentum quantum number and

L Stands for S,P,D, … etc. representing the oribital
Angular momentum quantum number.

This notation for describing the states is called the term symbol of the state.

If S = $\frac{1}{2}$, L = 1, J = $\frac{3}{2}$,$\frac{1}{2}$;the states will plainly be $^2P_{3/2}$, $^2P_{1/2}$ doublets.

For S = 1, L = 1, J = 2, 1,0; the states will be $^3P_2$, $^3P_1$, $^3P_0$ - triplet states.

The selection rules for LS-coupling scheme are:

$$\Delta L = \pm 1, \Delta S = 0$$

$$\Delta J = 0, \pm 1 \ (J = 0 \rightarrow J = 0 \text{ forbidden})$$

The selection rules $\Delta S = 0$ forbids the transition between the singlet and the triplet states.

jj – coupling

When the interaction between each $\vec{L_i}$ and $\vec{S_i}$ is strong, this type of coupling develop where the individual $\vec{L_i}$'s combine with the corresponding $\vec{S_i}$'s to form a $\vec{J_i}$, the total angular momentum of the *i*th electron. Then these $\vec{J_i}$'s couple to form $\vec{J}$, the total angular momentum of the atom. This coupling scheme is called jj-coupling which is, distinctly different from the LS-coupling. Symbolically, therefore,

$$\therefore \vec{J_i} = \vec{L_i} + \vec{S_1} ; \vec{J_2} = \vec{L_2} + \vec{S_2}; \ldots$$

$$\text{and } \vec{J} = \vec{J_i} + \vec{J_2} + \ldots = \Sigma_i \vec{J_i}$$

This type of coupling is applicable to heavy elements.

- Pure jj-coupling is rather rare. Many heavy elements have spectra requiring for their interpretation a coupling which is intermediate between the LS and *jj*.

Hund's rules

When the angular moments of a number of electrons combine, a number of possible L-values and S-values are obtained. There are two rules, known on Hund's rules, that govern which one of these values has the lowest energy, and the order in which the increase in energy occurs.

Rule 1. The total spin angular momentum $\vec{S}$ should be maximized according to Pauli's principle. Then

$S = M_s$,max

Rule 2. For the said S-values, L should be maximized according to Pauli's principle. Then

$L = M_{L,\,max}$

When the spin-orbit interaction splits the energy level corresponding to different J values the will be the lowest in energy.

1.8 Pauli's exclusion principle:

In the previous chapter, we studied quantum mechanically some simple systems by solving Schrodinger equation. But for a multi-electron system, the Schrodinger equation is not exactly solvable and no general expression for the energy levels can be obtained. The atomic spectra of the multi-electron atoms therefore are not as straightforward as those of one-electron system. Fortunately, a number of experimental results can be explained even without taking recourse to wave functions. We shall discuss here under the arrangement of electrons-electronic configuration-in multi-electron systems.

Shells and Sub-shells – As has been seen already, the quantum, state of an electron is completely specified by the set of four quantum numbers n, l, m_l and m_s. An equally valid set of quantum numbers gives n, l, j and m_j. In any atom, the electrons having the same quantum number n are said to be in the same shell is codified as follows.

$n = 1$, *K*-shell; $n = 2$, *L*-shell; $n = 3$, *M* – shell; $n = 4$, *N*-shell etc.

Again, for a given n, the electrons having the same l-value are said to be in the same sub-shell. Sub-shells are codified by nl values : 1s, 2s, 2p, 3s, 3p, 3d etc.

In any shell, as already shown, there could be n^2-different quantum states since, for a given l, the quantum number ml can take up (2l + 1) values.

Now, the question that arises is: how are the different electrons distributed among the shells and sub-shells? Could they be distributed in any manner we please or is there any restriction in regard to their occupancy of shells and sub-shells?

Pauli's exclusion principle – Pauli in 1925 enunciated his famous exclusion principle as a basic rule that determines how the electrons in multi-electron systems occupy the orbitals.

Statement- In any atom, no two electrons can have same set of quantum numbers (n, l, m_i, m_s) or (n, l, j, m_j).

If two electrons have all the quantum numbers the same, one of them is excluded in the formation of the atom. Hence the name exclusion principle. So, if two electrons in an atom have the same values for n, l and m_i, the fourth quantum number m_s = -1 for two electrons in an atom, then $m_s = +\frac{1}{2}$ for one and $m_s = -\frac{1}{2}$ for the other. Both of them cannot have $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$.

The principle also enunciates the indistinguishability or the equivalence of electrons. Hence sometimes it is also known as the equivalence principle. It applies to normal as well as excited states of the atom and has been extremely useful in explaining the atomic and spectral phenomena, particularly the periodicity of elements in the periodic table. In fact, it is one of the basic pillars of atomic physics and quantum mechanics.

Electronic configuration – A nucleus has a positive charge of Z units. Outside the nucleus, Z electrons are arranged so that the atom as a whole is neutral. Now, a system of particles is stable when its total energy is a minimum . So, the various electrons in a complex atom should occupy the lowest quantum state. But this is prevented by Pauli's principle which guides the arrangement of extra-nuclear electrons. We shall examine how these two basic rules: (i) the principle of minimum energy and (ii) the Pauli's principle determine the electron configuration.

Electrons of the same shell are, on the average, at roughly the same distance from the nucleus and so interact virtually with the same electric field and have similar energies. The energy of an electron in a particular shell depends to some extent on l-value, i.e., on the sub-shell, although the dependence is not so great as on n-value. The electrons in each shell increase, in general, in energy with increasing l. In a sub shell, however, the electrons have almost identical energies, since the dependence of electron – energy on m_l and m_s is minor.

Number of permitted electrons in a sub-shell and shell

For a given n, the quantum number l can have the following values:

$l = 0, 1, 2, 3, \ldots (n-1)$

For a given l, again, the quantum number m_l can take up the values:

$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l$

that is, $(2l + 1)$ different values. Hence the maximum number of electrons permitted in a sub-shell is $2(2l + 1)$, since m_s can have only two values: $m_s = \frac{1}{2}$ and $-\frac{1}{2}$.

The maximum number of electrons in a shell is therefore

$$N(n) = \sum_{l=0}^{n-1} 2(2l+1)$$

$$= 2(1 + 3 + 5 + \ldots + 2\overline{n-1}) = 2n^2$$

On this basis, the various sub-shells can have the following maximum number of electrons.

Sub-shell	l	Maximum electrons $2(2l + 1)$
s	0	2
p	1	6
d	2	10
f	3	14
⋮	⋮	⋮

Thus, an s-sub-shell can have, at best, 2 electrons; a p-sub-shell 6 electrons; a d-sub-shell 10 electrons and so on.

Let us now see the possible number of electrons and their distribution in a shell.

The innermost K-shell for which n = 1, the L value can only be l = 0; also $m_l = 0$ and $m_s = \pm\frac{1}{2}$. Thus, in K-shell there can only be 2-eletrons; since l = 0 for both, they are s-electrons in conformity with the results of table.

The next is L-shell for which n = 2; since n = 2, the possible l-values are l = 0, 1. For l = 0, there will be two s-electrons and for i = l, there will be six p-electrons, according to table. The set of quantum numbers that correspond to the above 8 electrons in shown in the table below.

n	l	m_l	m_s	Type
2	0	0	$\pm\frac{1}{2}$	s-electrons
2	1	1	$\pm\frac{1}{2}$	p-electons
		0	$\pm\frac{1}{2}$	
		-1	$\pm\frac{1}{2}$	

The third shell is M-shell for which n = 3; since n = 3, the L-values are l = 0,1 and 2. For l = 0, there are two s-electrons and for l = 1, there are six p-electrons, as mentioned earlier. When however l = 2, $m_l = -2, -1, 0, +1, +2$ and for each of the five values of m_l, $m_s = \pm\frac{1}{2}$ and there are thus ten electrons. These are all d-electrons, since they have l = 2. The following table gives the set of quantum numbers of the these ten electrons.

n	l	m_l	m_s	Type
3	2	2	$\pm\frac{1}{2}$	d-electrons
		1	$\pm\frac{1}{2}$	
		0	$\pm\frac{1}{2}$	
		-1	$\pm\frac{1}{2}$	
		-2	$\pm\frac{1}{2}$	

There can, therefore, be at best 18 (= 2 + 6 + 10) electrons in the M-shell of the atom. And so on.

The occupancy of different sub-shells is expressed by the following notion: the n-value followed by the symbol standing for l-value. The number of electrons in the sub-shell is indicated by a superscript after the symbol. For instance, the configuration of sodium is $1s^2 2s^2 2p^6 3s^1$. The configurations of some common elements are given in Table 8.1 in the next page.

Element	Configuration	Element	Configuration
H	$1s^1$	Zn	$[Ar]\ 4s^2 3d^{10}$
He	$1s^2$	Ga	$[Ar]\ 4s^2 3d^{10} 4p^1$
Li	$1s^2 2s^1$	Kr	$[Ar]\ 4s^2$
Be	$1s^2 2s^2$	Rb	$[Kr]\ 5s^1$
B	$1s^2 2s^2 2p^1$	Y	$[Kr]\ 5s^1 4d^1$
C	$1s^2 2s^2 2p^2$	Mo	$[Kr] 5s^2 4d^5$
N	$1s^2 2s^2 2p^3$	Ag	$[Kr] 5s^1 4d^{10}$
O	$1s^2 2s^2 2p^4$	Cd	$[Kr] 5s^2 4d^{10}$
F	$1s^2 2s^2 2p^5$	In	$[Kr] 5s^2 4d^{10} 5p^1$
Ne	$1s^2 2s^2 2p^6$	Xe	$[Kr] 5s^2 4d^{10} 5p^6$
Na	$[Ne] 3s^1$	Cs	$[Xe] 6s^1$
A1	$[Ne] 3s^2 3p^1$	La	$[Xe] 6s^2 5d^1$
Si	$[Ne] 3s^2 3p^2$	Ce	$[Xe] 6s^2 5d^1\ 4f^1$
Cl	$[Ne]\ 3s^2 3p^5$	Pr	$[Xe] 6s^2 4f^3$
Ar	$[Ne] 3s^2 3p^6$	Gd	$[Xe]\ 6s^2 5d^1\ 4f^7$
K	$[Ar] 4s^1$	Dy	$[Xe]\ 6s^2 4f^{10}$
Sc	$[Ar] 4s^2 3d^1$	Lu	$[Xe] 6s^1 5d^1 4f^{14}$
Cr	$[Ar] 4s^1 3d^5$	Au	$[Xe] 6s^1 5d^{10} 4f^{14}$
Mn	$[Ar] 4s^2 3d^5$	Tl	$[Xe]\ 6s^1 5d^{10} 4f^{14} 6p^1$
Cu	$[Ar] 3d^{10} 4s^1$	Rn	$[Xe]\ 6s^1 5d^{10} 4f^{14} 6^6$

* Symbol [ ] indicate that the atom has configuration of the previous inert gas plus additional electrons given.

Transition elements, Lanthanides and Actinides – In potassium (Z=19), the 19th electron goes into the 4s-sub-shell rather than in 3d; so does the 20th electro of calcium (Z = 20). The configurations of the next 10 elements, from Z = 21 (scandium) to Z = 30 (Zinc) differ only in the number of electrons in 3d sub-shell except however Cr (Z = 24) and copper (Z = 29) where there is only one 4s-electron each. The ten elements from scandium to zinc are known as transition elements. These are metals having similar chemical properties determined mainly by the valence electrons, but they hardly show any resemblance with elements in the major groups.

The lanthanides, comprising $_{58}$Ce to $_{71}$ Lu, have similar chemical properties since all have their outermost 6s^2 sub-shell completed while 4*f* sub-shell is being filled. They are called rate earths. Similar to lanthanides are the actinides, comprising $_{90}{}^{Th}$ to $_{103}$Lr, where the inner sub-shells are being filed while the outermost 7s^2 sub-shell is complete.

✍LEARNING ACTIVITY

1. **Discuss in detail about Somerfield model**
2. **Explain the Experimental determination of critical potential using Frank and Hertz`s method**
3. **Derive an expression for LS and JJ coupling**
4. **State and verify Pauli’s exclusion principle**

Note:

a) Write your answer in the space given below.

b) Check the answer with your academic counsellor.

SUMMARY

In this Unit, we said that various types of atom models and derive an expression for condition for the allowed elliptical orbits using somerfiels model and detail study about vector atom models and derivation for LS and JJ coupling. We also study about Pauli's exclusion principle and verification

Block II

Atomic Spectra

STRUCTURE

Overview

Learning Objectives

2.1 Introduction

2.2 Magnetic dipole moments due to orbital and spin motion –

2.3 Selection rule for electron transition – Intensity rules – Interval rule –

2.4 Fine structure of D line

2.5 Zeeman effect – Normal and Anomalous

2.6 Stark Effect (definition only)

Summary

OVERVIEW

In this chapter on `Atomic Physics', we shall study the spectra H-atom and atoms with more than one electron. While in Bohr's theory we came Across of only one quantum number w required as many as three such numbers in quantum mechanical system of one electron atom. A fourth quantum number, the spin quantum number, was soon needed to explain the spectral characteristics of atoms. Starting from hydrogen spectrum and the experiment of Stern and Gerlach that established the existence of spin, we shall switch over to electronic configurations of multi-electron atoms and the angular momentum coupling schemes. We shall also study the Zeeman splitting of spectral lines in a magnetic field and Stark effect of spectral lines in a electric field.

LEARNING OBJECTIVES

After completing this Unit, you should be able to:

- Theory of the spectra H-atom and atoms with more than one electron;
- Zeeman splitting of spectral lines in a magnetic field and Stark effect of spectral lines in an electric field.

2.1 Introduction

Atomic spectra

Spectral lines emitted by individual atoms consist of a discrete set of wavelengths characteristic of the element concerned. This phenomenon has been utilized in the spectroscopic analysis and identification of elements. The spectra of atoms in general, however, are very complicated.

To build up the atom model, therefore, Bohr focussed his attention on the simplest element hydrogen. Its spectrum consists of lines that gradually crowd near UV-region and converge towards a short wavelength limit. This is a common feature of all atomic spectra. The position of the limit is only different for different types of atoms.

In an attempt to systematize the study of spectral line, Balmer (1885) showed purely empirically that the reciprocals of the wavelengths (not the wavelengths) of the series lines of hydrogen satisfy the following relation.

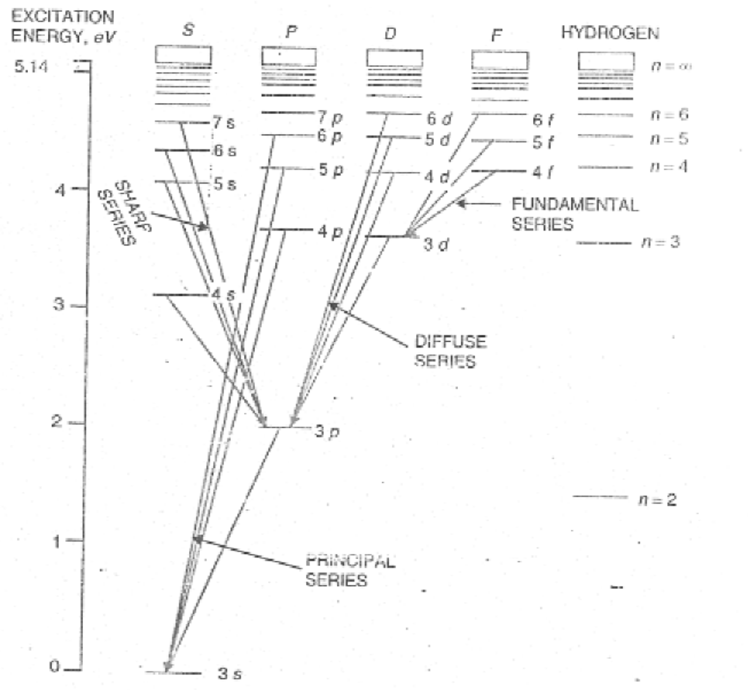
$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \; : n = 3, 4, 5, \ldots$$

Where R_H is known as Rydberg cocstant for hydrogen, having a value 10967757 m^{-1}. The lines are successively called H_α, H_β, H_γ etc. lines. The above series is called the Balmer series.

Later other spectral series were found to exist and have been referred.

2.2 Spectra of H-atom

Every state of the hydrogen atom is described by a distinct wave function which is specified by the three quantum numbers, n, l and m_1. The energy level diagram is illustrated in Fig. .The capital letters S,P.D, …



Describe the orbital angular momentum of atomic states, those for individual electrons are described by small letter s, p, d, . . . For a given n, the different *l* states have the same energy, but still we have shown them here separately.

Let us now see the spectral transitions. The transition of a system from one state to another under the influence of electromagnetic radiation depends on the interaction of the electronic field of radiation with the electric dipole moment of the atom (or molecule).

The transition from state m to state n is determined by the transition dipole moment μ_{mn} defined by

$$\mu_{mn} = \int \psi_m^* \, \mu \psi_n \, dr$$

Where ψ's are the wave functions of the corresponding state of the system and $\bar{\mu}$ the dipole moment operator. If μ_{mn} is finite then that transition is allowed, otherwise it is forbidden.

It can be shown from calculation that for the allowed transition the following rules, known as the selection rules, hold good.

$$\Delta n = \text{any value}; \ \Delta l = \pm 1;$$

$$\Delta ml = 0, \pm 1$$

Transitions in violation of the selection rules are forbidden as they are less probable. Some such allowed transitions are shown in Fig. Change in the state of the atom during transition implies that the photon must possess energy, linear momentum and angular momentum. For instance, $\Delta l = \pm 1$ suggests that the photon carries one unit, h, of angular momentum. A close scrutiny of the emission spectrum also shows that many spectral lines are not singlet, but closely spaced doublets.

Orbital magnetic moment of H-atom.

We may roughly consider an atom as an electron of charge –e circulating the nucleus with a speed v. It is equivalent to a circular current loop. The current i in the loop is the ratio of the charge to the period T of circulation.

$$\therefore I = -\frac{e}{T} = -\frac{e}{2\pi r/v} = \frac{ev}{2\pi r}$$

It would give rise to a magnetic dipole moment μ given by

μ = current × area of the loop

$$= i\,A = -\frac{ev}{2\pi r}\,\pi r^2, \text{ for a circular orbit,}$$

$$= \frac{e}{2m}\,mvr = -\frac{e}{2m}\,L$$

Where L = mvr, the magnitude of the orbital angular momentum.

But, the magnetic moment $\bar{\mu}$ and the angular momentum $\vec{L}$ are both vectors. So,

$$\boxed{\bar{\mu} = -\frac{e}{2m}\vec{L}}$$

Since $\vec{L}$ can have only certain quantized values, $\bar{\mu}$ also can have certain allowed values only. The implication of the negative sign is that $\bar{\mu}$ and $\vec{L}$ are oppositely directed.

$$\mu = -\frac{e}{2m}\sqrt{l(l+1)}\hbar$$

$$= -\frac{e\hbar}{2m}\sqrt{l(l+1)}$$

$$= -\mu B\sqrt{l(l+1)}$$

Where $\boxed{\mu B = e\hbar/2m}$

Is called Bohr magneton, the basic unit of atomic magnetic moment and has a magnitude 9.27 × 10^{-24} J / Tesla obtained by subsitutng the values of e, h and m.

From equation (8.2.3), we have

$$\mu_z = -\frac{e}{2m} L_z = -\frac{e}{2m} m_i h = -\mu B m_i$$

An important result follows from (8.2.4) and (8.2.5). Since $\sqrt{l(l+1)} > m_{i,}$ $|\mu| > \mu_z$. It implies that the magnetic moment μ cannot align itself along the *z*-direction.0

Magnetic dipole in a magnetic filed – Let a magnetic dipole of meoment $\bar{\mu}$ be placed in a magnetic field $\vec{B}$. Classically, it will experience a potential energy V, the energy of interaction between the magnetic moment and the magnetic field is given by

$$V = -\bar{\mu}\,\vec{B}.$$

If $\vec{B}$ is in the z-direction, then using equation

$$V = \mu_z B = \mu_B B_{ml}$$

Now, since *ml* is quantized, the potential energy V is also quantized. So, in a magnetic field, the atomic state of a given *l* splits into (2*l* + 1) different states according to the magnetic quantum number, $m_{l.}$

Larmor precession

If a dipole of magnetic moment $\bar{\mu}_l$ is placed in an external magnetic field $\vec{B}$, it acquires a potential energy V = $-\bar{\mu}_l\,\vec{B}$. Classically, it experiences a torque $\vec{T}$

$$\vec{T} = -\bar{\mu}_l \times \vec{B}.$$

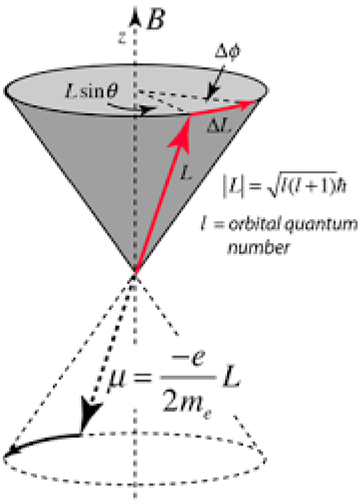
The torque's role is to align the dipole in the field direction. As $\vec{\mu}l$ and $\vec{L}$ are oriented antiparallel, $\vec{T}$ would be perpendicular to $\vec{\mu}l$, $\vec{L}$ and $\vec{B}$. But we have, from machanics,

$$\vec{T} = d\vec{L}/dt$$

So, $d\vec{L}/dt$ is also perpendicular to $\vec{\mu}l$, $\vec{L}$ and $\vec{B}$ implying that $d\vec{L}$, the change in angular momentum, is in the direction of $\vec{T}$. Since the magnetic of $\vec{L}$ remains the same, its direction most undergo a change to produce the change in $\vec{L}$. So, the change in angular momentum $d\vec{L}$ requires the precession of $\vec{L}$ about the magnetic field as shown in Fig.8.2. This is what is known as Larmor precession, the frequency of procession is logically termed Larmor frequency,

Now, $$\omega L = \frac{d\Phi}{dt} = \frac{1}{L\sin\theta}\frac{dL}{dt} = \frac{1}{L\sin 0}T$$

$$= \frac{1}{L\sin 0} = \mu l\, B\sin\theta = \frac{\mu l B}{L}$$



Substituting for L, we obtain

$$|\omega L| = \frac{e}{2m\mu l} = \mu l\, B = \frac{e^{B}}{2m}$$

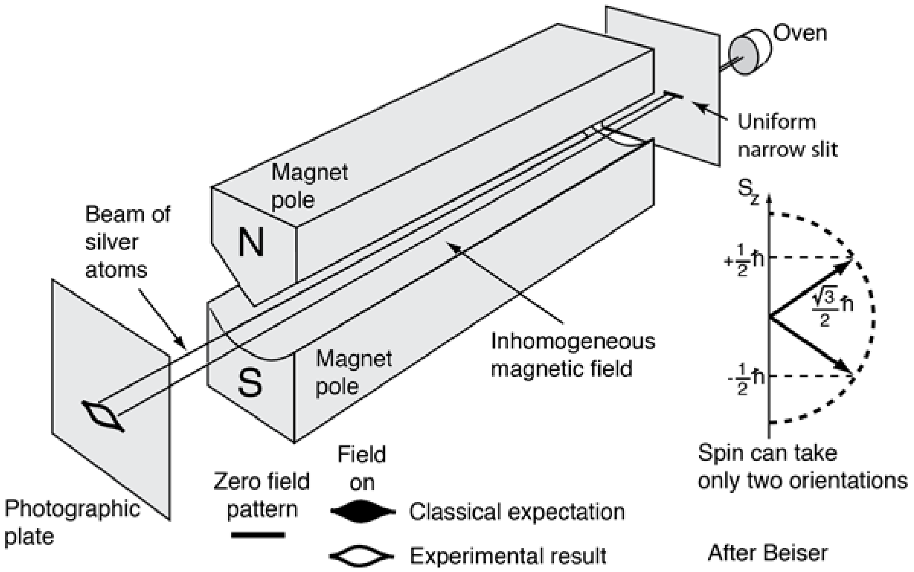
- The cause of precession is this: With the application of the field, $\vec{\mu}l$ tends to align along $\vec{B}$ for that corresponds to the minimum energy and this tendency of

$\vec{\mu}_l$ results in rotational energy which must be dissipated. But there is no available process of energy-dissipation and $\vec{\mu}_l$ in its tendency to align along $\vec{B}$ precesses about $\vec{B}$, keeping θ and energy constant.

Stern-Gerlach experiment

A direct demonstration of the existence of space quantization of angular momentum of the electron and the electron spin was made by the celebrated experiment conducted by two German scientists Otto stern and Walter Gerlach (1922).

Set-up – The experimental set-up is illustrated schematically in Fig.8.3. A beam of neutral silver atoms from an over O, that is, a neutral atomic beam of silver is directed after properly collimating it through a set of slits S_1, S_2 into an inhomogeneous magnetic field produced between the pole pieces SN. The S-piece is shaped as a knife edge while the N-piece is provided with a groove.



A photographic plate P is placed behind the field, perpendicular to the knife edge, to record the configuration of the atomic beam after its passage through the field. The whole arrangement is enclosed in an evacuated chamber to enable the silver atoms to traverse the field without collision.

Theory – If a magnetic dipole is placed in a homogeneous magnetic field, the forces on the poles are equal and opposite. So, no net force acts on the dipole. It experiences a torque and the result is a rotational motion of the dipole. In a non-homogeneous field, (here, along z-axis) however, the dipole experience a net resultant force (that varies with its orientation relative to the field) given by

$$F_z = -\frac{\partial V}{\partial z} \text{ where V = potential energy.}$$

Substituting the value of V from (8.2.6) in equation (8.4.1)

$$F_z = \mu_z \frac{dB}{dz} = \mu \cos\theta \frac{dB}{dz}$$

Where μ is the magnetic moment of the atom, μ_z the component of μ in z-direction, θ the angle $\vec{\mu}$ makes with z-axis and dB/dz the gradient of the magnetic field along the z-axis.

Due to the force F_z, the dipole makes a translational motion in the z-direction. As the net force on μ depends on the orientations of μ, the dipoles with different orientations will naturally be brought to different positions on the photographic plate.

Results and conclusion – The silver atom has only one valence electron. Its ground state $l = 0$ thus gives $L = 0$ and $\mu = 0$. So, the dipoles will experience no force along z-direction, and one would expect that the silver atoms would pass undefected to give only one line on the screen. But Stern and Gerlach found in their experiment two distinct lines – one above and other below the mean position. It follows that the magnetic moment of silver atom in the ground state is not zero. The pattern of splitting of the atomic beam on the photographic plate (Fig.8.3) confirms that the magnetic moment takes up to orientations in the inhomogeneous magnetic field corresponding to two m_s-values, $+\frac{1}{2}$ and $-\frac{1}{2}$

So, over and above the three quantum numbers n, l and m_l, a fourth quantum number m_s which can assume the values $+\frac{1}{2}$ and $-\frac{1}{2}$ only must be required to describe each atomic state. Stern-Gerlach experiment conclusively demonstrates the existence of an additional angular momentum vector which is quantized similar to the orbital angular momentum *L*.

The Splitting gives two short lines on the photographic plate and it is possible to determine from the distance between the lines (Illustrated Ex.15) the magnetic moment of silver atoms and hence the electronic magnetic moment.

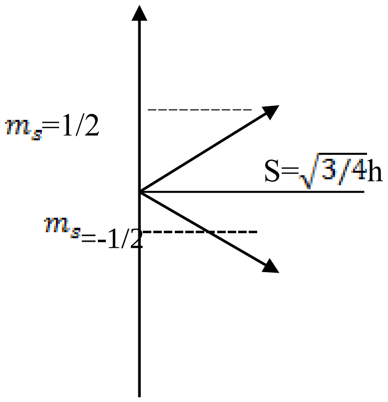
A question may however arise: Could the pattern be produced by spinning particles other than electrons – protons and neutrons in the nucleus? The magnitude of magnetic dipole is inversely proportional to the mass of the particle. So, for proton, it would be about 2000 limes smaller, Later, Frisch, Eastermann and Stern measured this small magnetic dipole to distinguish it from that of electron spin.

Electron spin

The idea of spinning electron was first introduced by Uhlenbeck and Goudsmit (1925). To explain the multiplet structure (fine structure) of spectral lines, they found it necessary to assume that electron must have another angular momentum, in addition to the orbital one, of value equal to $\frac{1}{2}$ $h / 2\pi$. This angular momentum is referred to as spin angular momentum or spin of the electron and is specified by the spin quantum number, s = $\frac{1}{2}$. They also proposed that the spin angular momentum vector $\vec{S}$ is similar to the orbital angular momentum vector $\vec{L}$ and can have (2s + 1) values + h/2 and –h/2. The magnetic spin quantum number m_s can thus have the values $\pm\frac{1}{2}$. The spin angular momentum vector $\vec{S}$ has the magnitude $|\vec{S}|$ = $\sqrt{s(s+1)}h$ = $(\sqrt{3}/2)h$.

The energy of the two atomic states corresponding, to m_s – values $\pm\frac{1}{2}$ will be degenerate. The atom, when placed in a magnetic field, say along z-direction, the states for $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ will spilt into two distinct states, illustrated in Fig.8.4. The $m_s = \frac{1}{2}$ state is known as the spin `up' state and the $m_s = -\frac{1}{2}$ state is known as the spin `down' state.

The magnetic moment associated with spin angular momentum $\vec{S}$ is given by



The quantization of S in an external magnetic field. The z-component of S=±

$$\vec{\mu}_s = -\frac{e}{m}\vec{S}$$

$$= -2\,\frac{eh}{2m},\,\frac{\dot{S}}{h} = -2\mu B\vec{S}/h$$

For orbital angular momentum $\vec{L}$ the corresponding relation is

$$\vec{\mu}l = -\mu_B\vec{L}/h$$

We now introduce a new quantity – the gyromagnetic ratio, g. The numerical factor that relates the magnetic moment in units of Bohr magneton to angular momentum vector in units of *h* is called the gyromagnetic ratio, g Corresponding to spin, we thus have g_s, and corresponding to the orbital angular momentum, we have g_l.

From (8.5.1) and (8.5.2) we get

$$\vec{\mu}_s = -2\mu_B\vec{S}/h = -g_s\mu_B\vec{S}/h$$

$$\vec{\mu}_l = -\mu_B\vec{L}/h = -g_{l}\mu_B\,\vec{L}/h$$

So that we have plainly $g_l = 1$ and $g_s = 2$

Pauli in 1920 first suggested the existence of the fourth quantum number over and above n, l and m_l without however any explanation for its significance. This was followed, in 1922 by Stern-Gerlach's experiment who demonstrated unambiguously the existence of another angular momentum in addition to the orbital one of the electron. The experiment is described already in Art. 8.4

The above values of μ_s and S may be obtained from the relativistic quantum mechanical theory of electron by Dirac.

2.3 Spectra of alkali metals (optical spectra):

The outer (valence) electrons of an atom determine the chemical and optical properties of their atoms. The electrons in the closed inner orbits do not take part in the emission of spectral lines.

Spectral terms:

Atoms are divided into two main categories, viz one electron and many electron systems.

(1) The alkali metals (such as lithium, sodium and potassium) have a single valence electron outside the completely filled sub shells. The valence electron in the alkali metals behaves like the orbiting electron in the hydrogen atom. Hence alkali metals have hydrogen-like spectra. Their spectrum is referred to one-electron spectra.

(2) In many electron system, the atoms have more than one valence or optical electron outside completely filled sub-shells. Hence they become effective in fixing the spectral properties. For example, the alkaline earths belonging to the two –electron system have spectra, which are similar among themselves.

Spectral notation:

The states of an atom, in which the values of its L vector are 0,1,2,3,4,5 are represented by the capital letters S, P, D, F G,H etc. The value of the total angular momentum of the atom J is written as a subscript at the lower right of the letter representing the particular L value of the atomic state. The multiplicity of the total spin (s) is written as a superscript at the upper left of the letter. If S is the total spin the multiplicity is equal to 2S+1.

For example,

(1) A state with L = 1, S = ½ and J = 3/2 would be written as ${}^2P_{3/2}$ and read “doublet P three halves”. (Since S=1/2 the multiplicity of the state = 2 X ½ + 1 = 2).

(2) A state with L = 2, S = 1 and J =2 would be written as ${}^3D_2$ and read “triplet –D two “ [Note J = L ± S]

Selection Rules:

An electron cannot jump from one energy level to all other energy levels. A transition of an electron between levels is possible only if certain rules called selection rules are satisfied. For the vector atom model three selection rules have been devised [L,S,J].

1) For L is $\Delta L \pm 1$ i.e., those lines are observed for which the value of L changes by ±1. For example, L can change from 0 to 1 ($\Delta L=1$) or from 1 to 0 ($\Delta L=-1$). L cannot change from 0 to 2 ($\Delta L=+2$) or from 2 to 0 ($\Delta L=-2$). This shows that the transition is possible between S and P levels ($\Delta L=\pm 1$), but not possible between S and D levels ($\Delta L=\pm 2$)

2) For J is $\Delta J=\pm 1$ or 0 ; but $0 \rightarrow 0$ is excluded.

3) For S is $\Delta S=0$

Intensity Rules:

Whether an allowed transition is weak or strong is determined using this. They are

1) Transition for which L and J changes in the same way (i.e., $\Delta J=\Delta L$) are strong. For other changes in J ($\Delta L \neq \Delta J$) we get weak transition.

2) Transitions for which L and J increase. (i.e., $L \rightarrow L+1$ and $J \rightarrow J+1$) are less intense than those for which L and J decreases (i.e., $L \rightarrow L-1$ and $J \rightarrow J-1$)

3) Transitions for which changes is L and J are opposite (i.e., $\Delta L=-\Delta J$) are forbidden.

Hence intensity rules are written as

$\Delta L=-1$	$\Delta J=-1$	Strongest
$\Delta L=-1$	$\Delta J=0$	Less intense
$\Delta L=+1$	$\Delta J=+1$	Weak
$\Delta L=+1$	$\Delta J=0$	very weak
$\Delta L=-1$	$\Delta J=+1$	Forbidden
$\Delta L=+1$	$\Delta J=-1$	Forbidden

The Interval Rule:

Lande has given a rule regarding the interval in frequency between the different levels constituting a multiplet. It states that the frequency interval between two levels with total angular momenta (J+1) and J respectively is proportional to (J+1).

2.4 Fine structure of sodium D-line:

Ten out of the eleven electrons of the normal sodium atom are interlocked in closed shells. They contribute nothing to the angular momentum of the atom. We have to consider only the states of eleventh optical electron for the spectrum.

The D-line belongs to principal series and it is the transitions form a P state to the S state. For the upper P state L=1, J= L ±S =3/2 or ½. Hence two possible terms are $^2P_{3/2}$ and $^2P_{1/2}$. For the lower S state L=0, J= ½, so that only one term $^2S_{½}$ is possible. The Fig. 1.1 shows two possible transitions between the two terms of the P-state and the single term of the S-state. They are (1) $^2P_{1/2} \rightarrow {}^2S_{½}$ which results in D_1 line of the wavelength 5896° A and (2) $^2P_{3/2} \rightarrow {}^2S_{½}$ giving the D_2 line of wavelength 5890°A.

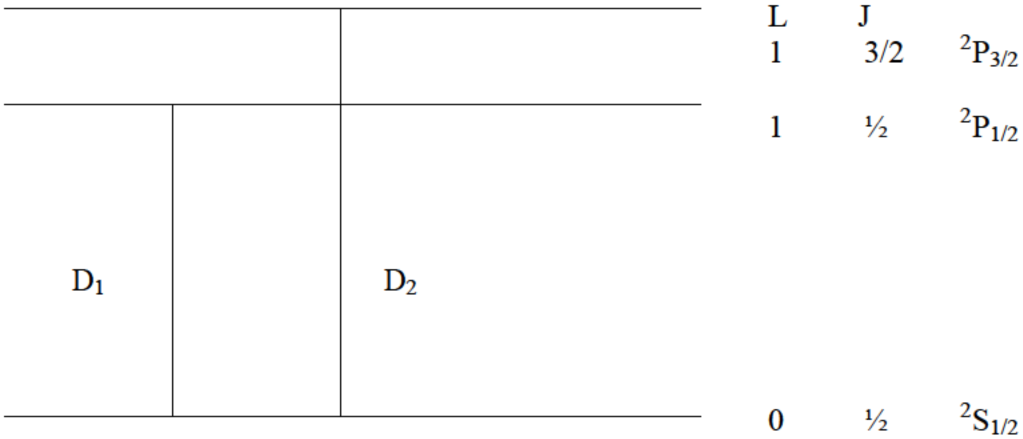


Fig. 1.1

Different series in Alkali Spectra : Main features

The alkali spectrum consists of spectral lines which can be classified into four series: principal series, sharp series, diffuse series and fundamental series. The principal series is the most prominent and can be observed in emission as well as in absorption spectrum. The other series are observed in emission spectrum only.

1. Principal Series:

The series arises from the transitions between various P-levels and lowest S-level. The lowest S-level has the lowest possible value for the energy and represents the ground state of the atom. The wave number of the series is given by the relation

$$\overline{\nu}_p = \frac{R}{(1+\mu_s)^2} - \frac{R}{(m+\mu_p)^2}, \quad m \geq 2$$

2. Sharp series.

This type of series comes from the transitions from S-levels (exclusive of the lowest) to the lowest of the P-levels.

$$\overline{\nu}_s = \frac{R}{(2+\mu_p)^2} - \frac{R}{(m+\mu_s)^2}, \quad m \geq 2$$

3. The diffuse series.

It arises from the transitions between the various D-levels and the P-level.
The wave number of the series is given by the relation

$$\overline{\nu}_D = \frac{R}{(2+\mu_p)^2} - \frac{R}{(m+\mu_D)^2}, \quad m \geq 3$$

4. Fundamental series or Bergmann Series.

The fundamental series arises from the transitions from various F-levels to the lowest D-level.

The wave number of the series is expressed by the relation

$$\overline{\nu}_F = \frac{R}{(3+\mu_D)^2} - \frac{R}{(m+\mu_F)^2}, \quad m \geq 4$$

Here μ_s , μ_p, μ_D and μ_F are the characteristic constants of sharp, principal, diffuse and fundamental series, respectively. The abbreviated forms for writing the wave number of each series are as follows:

1. $(1, \mu_s) \leftarrow (m, \mu_p)$ with $m \geq 2$ Principal series
2. $(2, \mu_p) \leftarrow (m, \mu_s)$ with $m \geq 2$ Sharp series

3. $(2, \mu_p) \leftarrow (m, \mu_D)$ with $m \geq 3$ Diffuse series
4. $(3, \mu_D) \leftarrow (m, \mu_F)$ with $m \geq 4$ Fundamental series

The other important features of the series are:

1. The sharp and diffuse series have a common limit.
2. The wavenumber interval between this common limit and the limit of the principal series is equal to that of first line of principal series.

Energy levels in Alkali Spectra and Quantum defect

The emission of alkali spectral lines can be fairly explained on the same lines as the Bohr-Sommerfeld theory for hydrogen atom. An atom has a number of discrete energy states. Each state is characterized by a total quantum number (n=1,2,3 ….∞).For each value of n, there are component levels labeled by an additional quantum number l,called the 'orbital' quantum number. l can take values 0,1,2………..(n-1). Thus n=1 state has only one level (l=0);n=2 state has two levels (l=0,1) and so on. The levels corresponding to l=0,1,2,3…….. are called s,p,d,f……….levels respectively. Thus n=1 state has a level called 1s; then n=2 state has two levelscalled 2s and 2p; the n=3 state has three levels called 3s, 3p and 3d; the n=4 state has four levels 4s, 4p, 4d, 4f and so on.

The energies of these levels are given by

$$E_{n,\ l} = -\frac{Rhc}{(n-\Delta)^2}$$

Here, Δ is called 'quantum defect' and depends on l. Thus the energies of levels with same n but different l are different.

Nonpenetrating and Penetrating Orbits

(i) Nonpenetrating Orbits. We assume that the charge due to the electrons in the closed core is distributed uniformly over a hollow sphere of radius ρ with the nucleus(N) at its centre (Fig.1.2). Suppose in the course of its motion round the nucleus, the elliptic orbit of the single optical electron in an alkali atom of atomic number Z does not penetrate the closed orbits or core of (Z-1) electrons. We expect the energy of the optical electron in the orbit to be nearly the same as that of the electron in the corresponding orbit in a hydrogen atom, on the Bohr-Sommerfeld model. It is found that the energies of the F states of the sodium atom agree to within one percent with the corresponding energy values of the hydrogen atom. Such orbits for which the energies are nearly the same as in hydrogen atoms are called nonpenetrating orbits.

Nonpenetrating orbits are defined as those orbits for which the observed energies are very nearly equal to those of the corresponding hydrogen- like orbits.

The f orbits in all of the alkali metals are good examples of non-penetrating orbits.

The resultant field under which the optical electron describes the orbit varies slowly as this electron moves in its orbit about the nucleus and the closed electron core. So the elliptic Bohr-Sommerfeld orbits in these cases precess slowly round the nucleus.

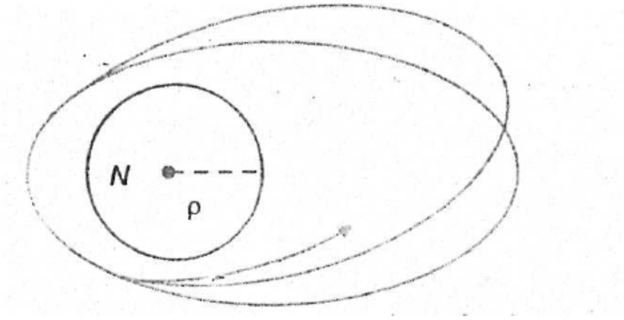


Fig. 1.2

(ii) Penetrating orbits.

If the optical electron orbit in an alkali atom penetrates the completed electron shells or subshells, more and more of the closed electron core is left behind as the optical electron moves in its orbit from aphelion to perihelion. This results in an increase in the field under which this electron traces its path as its distance from the nucleus goes from the maximum to minimum value [Fig.1.3]. So the electron traverses a path of increasing eccentricity. The increase in the force of attraction on the optical electron makes its energy in the orbit less than that for a corresponding Bohr-Sommerfeld state in a hydrogen atom. Thus the energies of the S and P states in the sodium atom are less than those of the corresponding states of the hydrogen atom. Such orbits for which the energies are considerably different from the corresponding values in the hydrogen atom are called penetrating orbits.

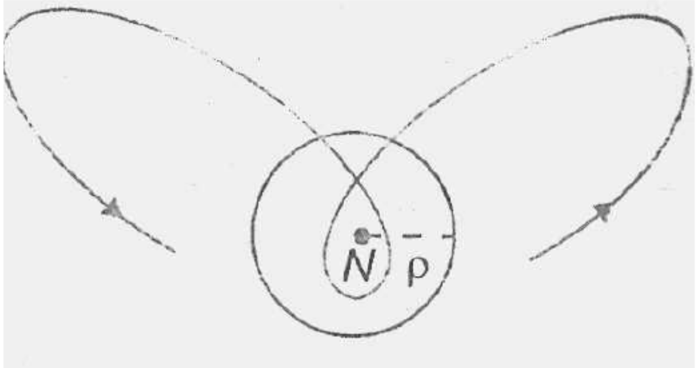


Fig 1.3

Explanation of Salient Features of Alkali Spectra

The electronic configuration of alkali metals is such that the core of an inert gas is surrounded by an s electron

$$\mathrm{Li} = [\mathrm{He}] + 2s^1$$
$$\mathrm{Na} = [\mathrm{Ne}] + 3s^1$$
$$\mathrm{K} = [\mathrm{Ar}] + 4s^1$$
$$\mathrm{Rb} = [\mathrm{K}] + 5s^1$$
$$\mathrm{Cs} = [\mathrm{Xe}] + 6s^1$$

The core electrons do not play any part in optical spectra. Only valence electrons, also called optical electrons determine the characteristics of optical spectra. The configuration is thus identical to hydrogen.

Let us discuss the characteristics of alkali spectra taking sodium as a typical example of an alkali element. The optical 3s electron of sodium when excited jumps to higher energy states, such as 3P, 4S, 3D, 4S, 5S, 4D………..etc. From the higher level the electron jumps back to the lower levels but only such that the l value changes by ± 1 i.e.,

$$\Delta l = \pm 1$$

This is called the 'selection rule'.

Fig.1.4 gives the energy level diagram of the sodium atom and shows the allowed transitions of the optical electron.

(i) When the electron jumps from any p-level to the lowest s-level (3s), it emits a line of principal series.

(ii) When the electron jumps from any s-level to the lowest p-level (3p), it emits a line of Sharp series.

(iii) When the electron jumps from any d-level to the lowest p-level (3p), it emits a line of diffuse series.

(iv)When the electron jumps from any f-level to the lowest d-level (3d), it emits a line of fundamental series.

Thus emission of all the spectral series is explained.

The different series in the spectrum arise from the following transistions of the optical electron.

Principal series	n	$^2P \rightarrow 3^2S$,	n= 3,4,5……..
Sharp series	n	$^2S \rightarrow 3^2P$,	n= 4,5,6……..
Diffuse series	n	$^2D \rightarrow 3^2P$,	n= 3,4,5……...
Fundamental series	n	$^2F \rightarrow 3^2D$,	n= 4,5,6……...

For a given set of values of the principal quantum number, we get several series here, unlike in the case of hydrogen.

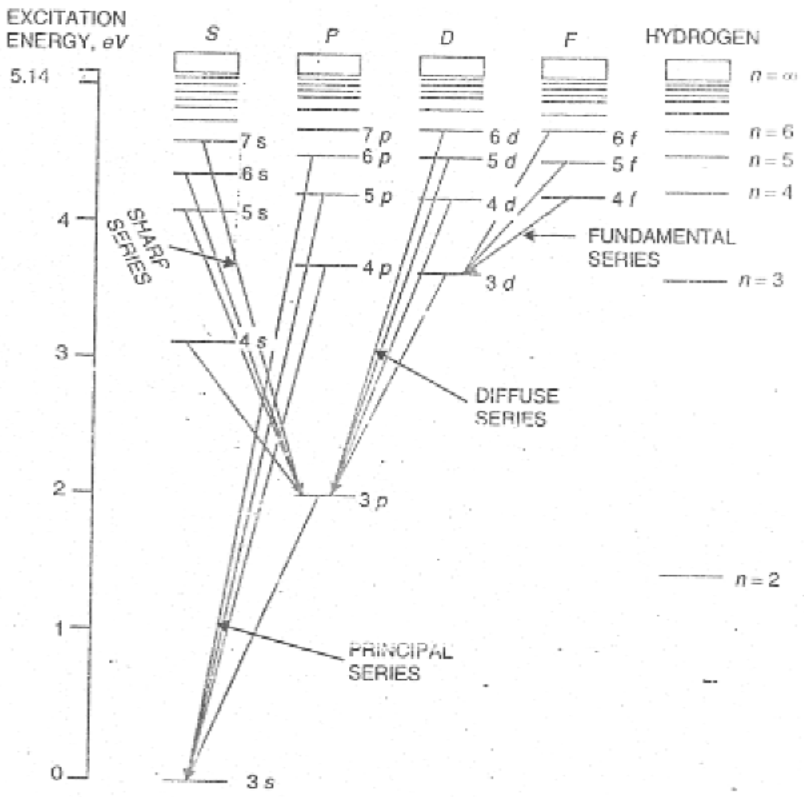


Fig. 1.4

According to the Bohr-Sommerfeld theory and quantum mechanical theory, all substates belonging to a given n in hydrogen have same value of energy. But this degeneracy is removed in a multi-electron system because of shield of nuclear charge and penetration of atomic core. The term value is written as

$$T = \frac{R \;\; Z_0^2}{n_{eff}^2}$$

Here Z_0 is effective nuclear charge outside the core, n_{eff}^2 is effective quantum number. As $Z_0 > 1$ and $n_{eff} < n$, the term value is increased. As a result energy levels in alkali atoms lie lower than the corresponding hydrogen levels. However for large n, Z_0, is equal to unity and $n_{eff} \rightarrow n$. The corresponding levels approach the hydrogen levels.

2.5 Zeeman Effect:

It is a magneto-optical phenomenon discovered by Zeeman in 1926

Principle:

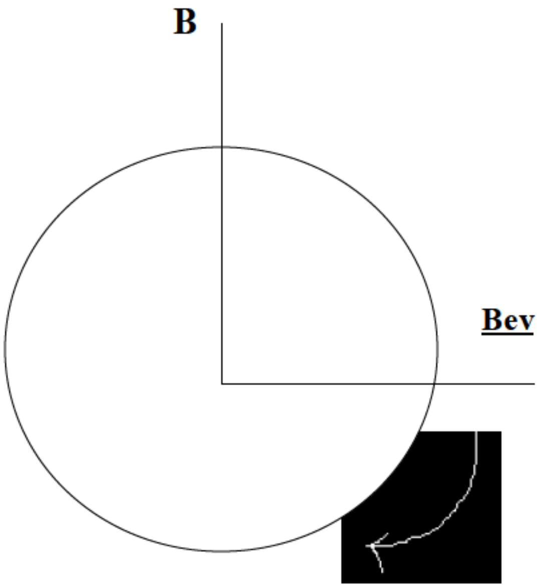
If a source of light producing line spectrum is placed in a magnetic field, the spectral lines are split up into components. When the splitting occurs into two or three lines, it is called normal Zeeman effect. The splitting of a spectral line into more than three components in weak magnetic field is called anomalous Zeeman effect. This cannot be explained by classical theory.

Expression for the Zeeman shift:

Consider an electron in the atom moving in a circular orbit of radius r with a linear velocity v and angular velocity ω. Let e be the charge of the electron and m its mass. The centripetal force on the electron towards the center in the absence of the magnetic field.

$$F = \frac{mv^2}{r} = m\omega^2 r \qquad (1)$$

Let an external magnetic field B be applied in a direction perpendicular to the plane of the orbits of the two circular components. Then an additional radial force of magnitude Bev acts on the electron. The direction of this force will be outwards from the center for clockwise motion and inwards towards the center for anticlockwise motion (Fig. 35). The resulting complex motion of the electron subjected to an additional force is called *Larmour precession*. This produces a change in the angular velocity without any change in the form the orbit.



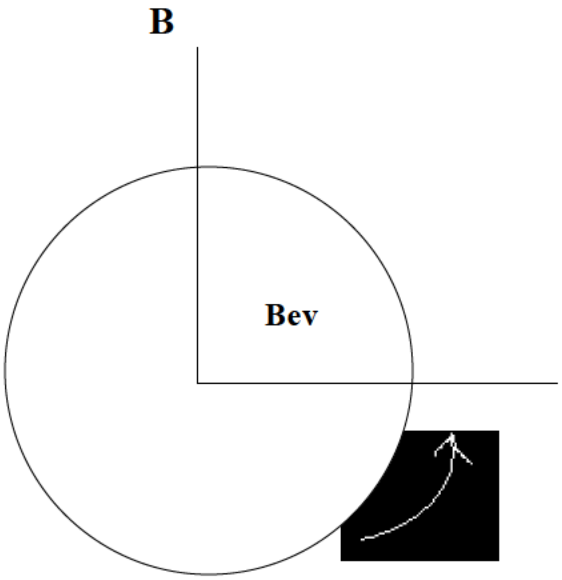


Fig. 1.5

Calculation:

Let $\delta\omega$ be the change in angular velocity caused by the field .For the clockwise direction, the additional radial force is directed away form the center. Hence

$$F - bev = m(\omega + \delta\omega)^2 r \qquad (2)$$

i.e., $m\omega^2 r - m(\omega + \delta\omega)^2 r = Be\omega r$, neglecting higher powers (i.e., $\delta\omega)^2$

we get

$$-2m\, r\, \omega\, \delta\omega = B\, e\, r\, \omega \qquad [v = r\,\omega]$$

$$\delta\omega = -Be / 2m \qquad (3)$$

For the circular motion in the anticlockwise direction, the additional force is directed towards the centre.

Hence $F + Bev = m(\omega + \delta\omega)^2 r$

Or $\delta\omega = +\dfrac{Be}{2m}$ (4)

From equation (3) and (4) we can write

$$\delta\omega = \pm\frac{Be}{2m} \qquad (5)$$

If ν is the frequency of vibration of the electron then

$\omega = 2\pi\nu$: $\delta\omega = 2\pi\delta\nu$ or $\delta\nu = \delta\omega / 2\pi$

$\therefore$ Change in frequency of the spectral line

$$\delta\nu = \pm\frac{Be}{4\pi m} \qquad (6)$$

If ν and λ are the frequency and wavelength of the original line, then

$$v = \frac{c}{\lambda} \qquad \text{or} \qquad \delta v = -\frac{c}{\lambda^2} d\lambda$$

$$\therefore \qquad \text{The Zeeman shift } d\lambda = \pm \frac{Be\lambda^2}{4\pi\, mc} \qquad (7)$$

Note: Taking the spectral line of wavelength λ, and applying a magnetic field B, the Zeeman shift dλ is measured. From the above equation (7),

$$\frac{e}{m} = \left(\frac{4\pi\, c}{B\lambda^2}\right) d\lambda \text{ can also be calculated.}$$

Experimental arrangement for the Normal Zeeman effect:

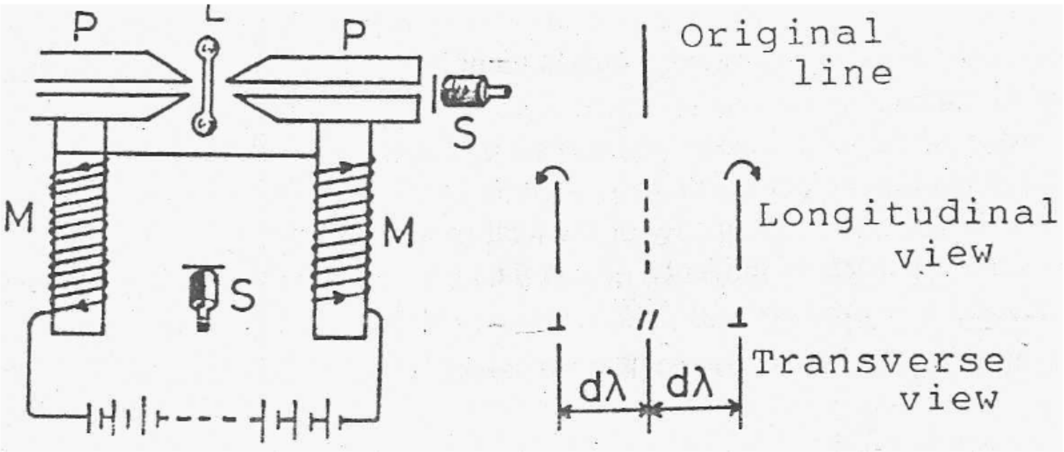


Fig. 1.6

In the above figure MM is an electromagnet capable of producing a very strong magnetic field. Longitudinal holes are drilled in the conical pole pieces (PP). A source of sodium light L emitting the spectrum is placed between the pole-pieces. The spectral lines are observed through a spectrograph (S) of high resolving power. The effect may be seen in two ways.

1) The position of the spectral line is noted without applying the magnetic field. The magnetic field is switched on and the spectral line is viewed longitudinally through the hole in the pole-pieces and it is parallel to the direction of the field. It is seen that the spectral line is split into two components one slightly shorter in wavelength and the other larger in wavelength than the original line. The original line is not present and the two components are found to be symmetrically situated about the position of the original line. Analyzing the two lines with a Nicol prism both the lines are found to be circularly polarized in opposite directions. This is called Normal longitudinal Zeeman effect.

2) When viewed transversely i.e., perpendicular to the direction of the magnetic field, a single spectral line is split up into three components. The central line has the same wavelength as the original line and is plane polarized with vibrations parallel to the field. The outer lines are symmetrically situated on either side of the central line. The displacement of either outer line from the central line is known as the Zeeman shift. The two outer lines are also plane polarized having vibrations in a direction perpendicular to the field and is called Normal Transverse Zeeman effect.

Explanation: (Lorentz classical theory)

The emission of light by gas is due to the vibratory motion of the electrons and it executes simple harmonic vibration about the centre of the atom. The frequency of the spectral line is given by the frequency of vibration of electron. Any linear motion of an electron can be resolved into three components namely a linear motion along the magnetic field and two opposite motions perpendicular to the field. The linear motion along the field is not affected and hence the frequency of this component is unchanged by the magnetic field. The other two circular components are affected by the magnetic field, one being retarded and other accelerated. Hence the frequency of one of these circular components is increased and that of the other is decreased by the same amount.

In the longitudinal view, the unaltered linear component along the field gives no light waves along the direction of observation due to the transverse nature of light vibrations. Hence the original line is not observed. The two components at right angles to the field produce circularly polarized light.

In the transverse, the unaffected linear component gives out vibrations parallel to the field and hence perpendicular to the direction of observation. This gives the central line of the triplet occupying the same position as the original line and plane polarized with vibrations parallel to the field. The two circular vibrations which are altered in frequency gives out vibrations perpendicular to the field and when viewed sideways appear as plane polarized vibrations in opposite sides.

Larmour Theorem: According to the theorem, the introduction of magnetic field modifies the classical motion of a set of electrons in the field of a nucleus with a uniform rotation at angular frequency (ω_l) were superposed upon their original motion. The angular momentum of the electrons about the axis parallel to B is slightly altered as a result of inductive action during the production of the field.This change is so small compared to the values of A_l due to the orbital motion.

For an electron in orbital motion, its orbital angular momentum A_l of magnitude $-2m\,\mu_l/e$ (μ_l is magnetic moment) will precess at the numerical rate $\omega_l = \frac{eB}{2m}$ where the angular frequency ω_l is known as the Larmour precessional frequency.

Statement: The effect of a magnetic field on an electron moving in an orbit is to superimpose on the orbital motion, the precessional motion of the entire orbit about the direction of magnetic field with angular velocity is given by

$$\omega_l = \frac{eB}{2m}$$

Quantum Mechanical explanation of the normal Zeeman effect:

Normal Zeeman effect without taking into account the concept of electron spin was explained by Debye. Neglecting the spin

The orbital angular momentum = $L = \frac{lh}{2\pi}$ (1)

And the magnetic moment = $\mu_l = \frac{lh}{2\pi} \times \frac{e}{2m} = \frac{2}{2m} L$ (2)

In the presence of a external magnetic field of flux density B, the vector precesses around the direction of magnetic field axis. It is known as Larmour precession and the frequency is

$$\omega = \frac{Be}{2m} \tag{3}$$

The additional energy of the electron due to this precession is given by

$$\Delta E = \mu_l B\cos\theta = \frac{e}{2m}\cdot\frac{lh}{2\pi}B\cos\theta \qquad \left[\because \mu_l = \frac{e}{2m}\frac{lh}{2\pi}\right]$$

$$= \frac{Be}{2m}\frac{h}{2\pi} l\cos\theta$$

But Be/2m = ω and l cosθ is the projection on B = m_l , then

$$\Delta E = m_l \frac{eh}{4\pi m} B = m_l \,\omega \frac{h}{2\pi} \qquad (4)$$

Now, m_l can have (2l + 1) values from +l to-l . It shows an external magnetic field will split a single energy level into (2l + 1) levels. Then d-state (l=2) is split into 5 sub-levels and p-state (l=1) is split into 3 sub-levels. (Fig. 37)

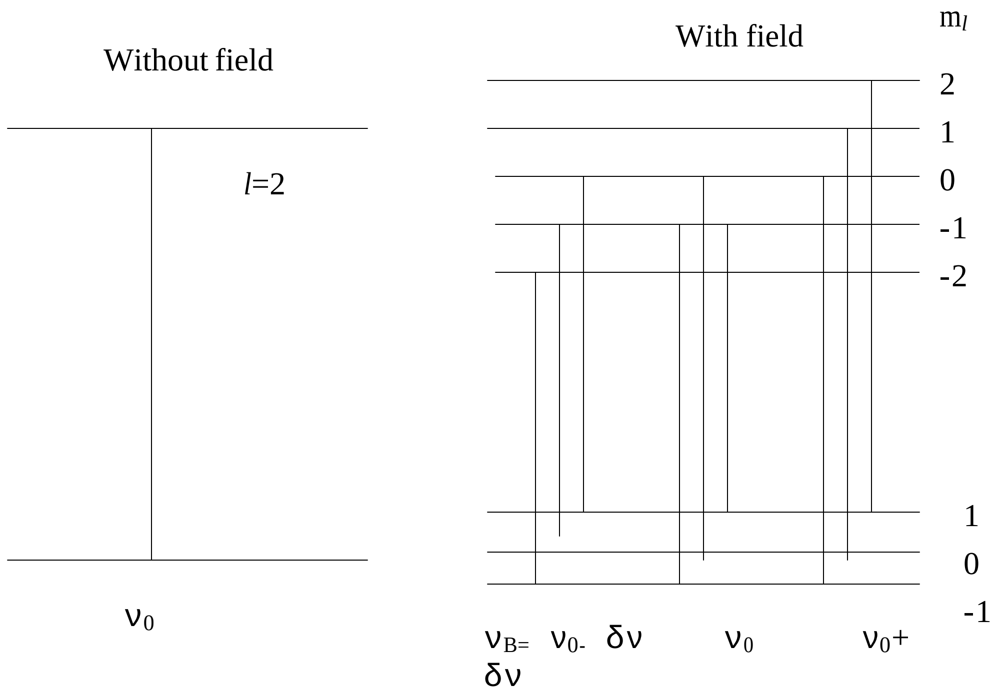


Fig. 1.7

Let E_0' represent the energy of the level l =1 in the absence of the magnetic field and E_B' represents the energy level in the presence of magnetic field. Then

$$E_B' = E_0' + \Delta E' = E_0' + m_l' \frac{eh}{4\pi\, m} .B \qquad (5)$$

Similarly if E_0'' *and* E_B'' represent the energies of the level, l=2 without and with magnetic field. Then,

$$E_B'' = E_0'' + \Delta E'' = E_0'' + m_l'' \frac{eh}{4\pi\, m} B \qquad (6)$$

Hence the quantity of energy radiated in the presence of magnetic field is

$$E''_B - E'_B = (E''_0 - E'_0) + (m''_e - m'_e)\frac{eh}{4\pi\, m}B$$

$$i.e.,\ h\nu = h\nu_0 + \Delta m_l \frac{eh}{4\pi\, m} \qquad [E = h\nu]$$

$$\text{or} \quad \nu = \nu_0 + \Delta m_l \frac{eB}{4\pi\, m} \tag{7}$$

where ν is the frequency of the radiation emitted with the magnetic field and ν_0 is the frequency of the radiation in the absence of the magnetic field.

The selection rule for $\Delta m_l = 0\ or\ \pm 1$

Form this, three possible lines are

$$\nu_1 = \nu_0 + \frac{eB}{4\pi\, m} \quad for\ \Delta m_l = 0 \tag{8}$$

$$\nu_2 = \nu_0 + \frac{eB}{4\pi\, m} \quad for\ \Delta m_l = +1 \tag{9}$$

$$\nu_3 = \nu_0 - \frac{eB}{4\pi\, m} \quad for\ \Delta m_l = -1 \tag{10}$$

Fig. 1.7 represents the normal Zeeman effect.

2.5 Anamalous Zeeman effect – Lande ‘g’ factor:

This effect can be explained only with the idea of spin and magnetic moment of the electron. With the introduction of spin, two angular momentum vectors L and S associated with each electron. The total angular momentum vector J = L + S. The magnetic moment due to orbital motion

$$\mu_l = L\frac{eh}{4\pi\, m} \tag{1}$$

μ_l is directed oppositely to L because of the negative charge of the electron.

Similarly, the magnetic moment due to the spin of the electron, $\mu_s = 2s\frac{eh}{4\pi\, m}$ (2)

μ_s is oppositely directed to S because of negative charge of the electron. The relationship between the magnetic moments and the angular momenta are shown in Fig. 1.8.

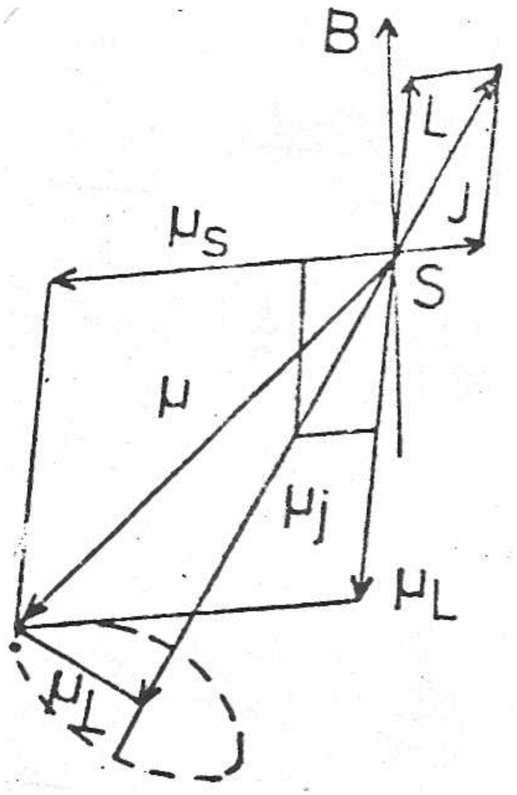


Fig 1.8

The resultant magnetic moment of the electron, each of these vectors μ_l and μ_s is resolved into two components, one along J and other perpendicular to it. The perpendicular component of each vector, averaged over a period of the motion is zero, since it is constantly changing direction. Hence the effective magnetic moment of the electron,

μ_l = component of μ_l along the direction of J + component of μ_s along the direction of J

$$= \frac{eh}{4\pi m} L\cos(L, J) + \frac{eh}{4\pi m} 2S\cos(S, J)$$

$$= \frac{eh}{4\pi m}\left[L\cos(L, J) + 2S\cos(S, J)\right]$$

According to Cosine law,

$$\cos(L,J) = \frac{L^2 + J^2 - S^2}{2LJ}$$

and $$\cos(S,J) = \frac{S^2 + J^2 - L^2}{2SJ}$$

Hence $$\mu_J = \frac{eh}{4\pi m}\left[\frac{L^2 + J^2 - S^2}{2J} + \frac{S^2 + J^2 - L^2}{J}\right]$$

$$\mu_J = \frac{eh}{4\pi m}\left[\frac{3J^2 + S^2 - L^2}{2J}\right]$$

$$= \frac{eh}{4\pi m} J\left[1 + \frac{L^2 + S^2 - L^2}{2J^2}\right]$$

Writing $J^2 = J(J+1)$ and so on, we get

$$\mu_J = \frac{eh}{4\pi m} J\left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right]$$

The quantity $1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$ = g and it is called Lande 'g' factor.

Hence $$\mu_J = \frac{eh}{4\pi m} g J \qquad (3)$$

If the atom is placed in a weak magnetic field, the total angular momentum vector J precess about the direction of the magnetic field axis. The additional energy Δ E due to the action of the magnetic field on this atomic magnet is

$$\Delta E = \mu_J.B \cos(J,B) = \frac{eh}{4\pi m} g J B \cos(J,B)$$

But $J\cos(J,B)$ is the projection of the vector J on the direction of the magnetic field m_J.

Hence $$\Delta E = \frac{eh}{4\pi m} Bg\ m_J$$

The quantity $\frac{eh}{4\pi m}$ B is called Lorentz unit. It is the unit of energy used for expressing the splitting of the energy levels in a magnetic field.

Since m_J has (2J+1) values, a given energy level is split up into (2J+1) sub-level with the application of magnetic field. When m_J is subjected to the selection rule $\Delta m_J=0$ or ± 1, we get transitions shown below for the sodium D-lines (Fig. 39)

The ground state $^2S_{1/2}$ splits into two sub levels. Here L=0: S=1/2: J=1/2 hence

$$g = 1 + \frac{\frac{1}{2}\times\frac{3}{2}+\frac{1}{2}\times\frac{3}{2}}{2\times\frac{1}{2}\times\frac{3}{2}} = 2$$

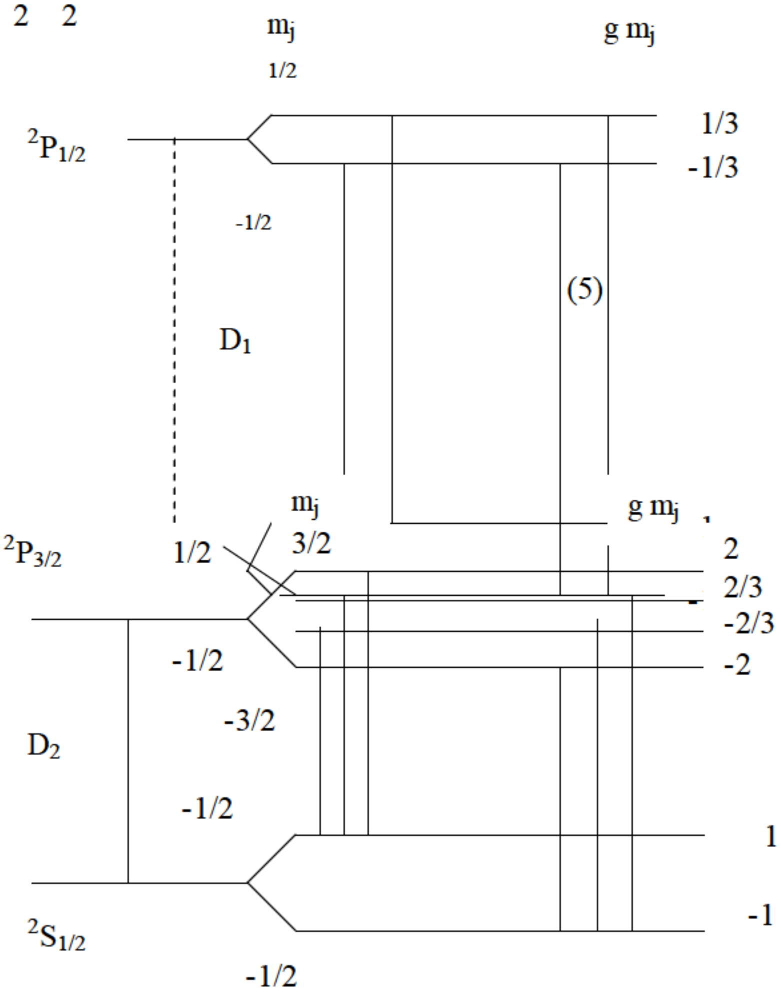


Fig. 1.9

Since m_J can have values ½ and -½, g m_J can have the values +1 and -1. The following Table gives the values for the quantum numbers necessary for the determination of splitting factor g m_J for each of the energy of sodium D-lines.

State	**L**	**S**	**J**	**g**	**m_J**	**m_J g**
$^2S_{1/2}$	0	½	½	2	½ , -1/2	1 , -1
$^2P_{1/2}$	1	½	½	2/3	½ , -1/2	1/3 , -1/3
$^2P_{3/2}$	1	½	3/2	4/3	3/2 ,1/2 -1/2 , -3/2	2 , 2/3 -2/3 ,-2

The longer wavelength component $^2P_{1/2}$ › $^2S_{1/2}$ splits into four lines. The shorter wavelength component $^2P_{1/2}$ › $^2S_{1/2}$ splits into six lines. Thus the introduction of electron spin has led to the complete agreement between experimental results and the theory of the anomalous Zeeman effect.

Note: In equation(3), the introduction of 2S, the factor 2 enters because of the anomalous gyrometric ratio for the intrinsic magnetic moment $\mu_S = \frac{eh}{4\pi\, mc}$ not associated with the orbital motion. The ratio of intrinsic magnetic moment to spin is $\frac{\mu_s}{S} = 2\frac{e}{2mc}$ which is twice the corresponding ratio for orbital motion.

Paschen – Back effect:

Paschen and Back found that whatever be the anomalous Zeeman pattern of a given line in a weak magnetic field, the pattern always approximates the normal Zeeman triplet as the field strength is progressively increased. The reduction may occur either through the coalescence of lines or through the disappearance of certain lines. This transition phenomenon is called Paschen-Back effect.

Explanation: In a strong magnetic field, the coupling between L and S breaks down and J loses significance. Also L and S are quantized and process separately about the external magnetic field B independent of each other. (Fig. 1.10). the energy change due to the presence of the field will be made up of two parts, one arising from the precession of L about B and the other from the precession of S about B.

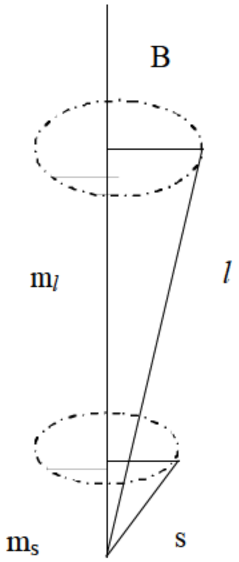


Fig. 1.10

Calculation of energy and frequency:

$$\Delta E = (\Delta E)_L + (\Delta E)_S$$
$$= B\frac{eh}{4\pi m}\left[L\cos(L,B) + 2S\cos(S.B)\right]$$
$$= \frac{eh}{4\pi m}B\left(m_L + 2m_S\right)$$

In terms of frequency change

$$\Delta\nu = \frac{eB}{4\pi m}\Delta\left(m_L + 2m_s\right)$$

The quantity ($m_L + 2m_S$) is known as the strong field quantum number and is an integer.

Now $\begin{aligned}&\Delta m_L = 0 \; or \; \pm 1, \Delta m_S = 0\\ &\Delta\left(m_L + 2m_S\right) = 0 \; or \; \pm 1\end{aligned}$

Hence in a strong magnetic field, a given spectral line will split into three components and is the characteristic of the Normal Zeeman effect.

Hyperfine Structure of spectral lines:

In 1891, Michelson and in 1897 Fabry and Perot studied the effects of hyperfine structure of the spectral lines. The hyperfine effect is because of the shifts of the electronic energy levels which are called fine structure. The hyperfine components of the spectral radiations are observed using a high resolution interferometer. The wavelength differences in the hyperfine structure of single isotopes are very much smaller than the electron spin fine structure. Pauli attributed the hyperfine structure to an angular momentum of the nucleus of the atom. The assumption of orbital and spin angular momentum of the electron could explain the fine structure of the spectral lines.The hyperfine structure is caused by the properties of the nucleus. The influence of the nucleus is mainly due to

1) The isotopic effect and 2) the nuclear spin (of which there will be an intrinsic angular momentum).

Isotopic Structure and Hyperfine Structure:

The ordinary fine structure is due to spin orbit interaction. After the discovery of isotopes,it was found that hyperfine pattern of lines was emitted by different isotope. According to Pauli this effect is due to that the nucleus has angular momentum and an associate magnetic moment. In light atoms the isotope shift-may arise due to simple differences in the nuclear motion. In the spectrum of heavy atom, isotope shift are found to be proportional to the differences in atomic mass.

2.6 Stark Effect

The stark effect is the electrical analogue of the Zeeman effect. The Stark effect is the splitting of spectral lines due to the action of an external lines due to the action of an external electric field on the radiating substance. Even very strong external electric fields are weak compared to the inter atomic fields. Hence the action of electric field on the motion of the atomic electrons can be regarded as small perturbations consequently the stark line splitting is very minute and can be observed only with instruments having a high resolving power. The lines are split into a series of components (satellites) located, in case of hydrogen, symmetrically on both sides of the original line.

Experimental study. Here the hydrogen atoms emitting spectral lines are subjected to a powerful electric field. The arrangement used by Stark is shown in the figure. The canal rays are produced in an ordinary glass discharge tube provided with a perforated cathode C. when the pressure in the tube is not very low, discharge takes place between the anode A and cathode C maintained at a suitable P.D. the canal rays stream through the perforations in the cathode and form behind the cathode narrow cylindrical bundles of luminous rays. An auxiliary electrode F is placed parallel and close to C at a distance of a few millimeters. A very strong electric field of several thousand volts per metre is maintained between F and C. The effect produced can be studied both transversely and longitudinally. Stark observed that the lines in the lines in the spectrum emitted by the canal rays of hydrogen were split up into numerous sharp components under the action of the electric field.

Results. The results obtained with the lines of the Balmer series of the hydrogen spectrum are given below:

(1) Every line is split up into a number of sharp components. All hydrogen lines form symmetrical patterns. The pattern depends

markedly on the quantum number n of the term involved. The number of lines and the total width of the pattern increases with n. thus, the number of components of H_β line is greater than that of the H_α line; similarly, the number of components of H_γ is greater than that of H_β .

(2) Observation perpendicular to the direction of the electric field (transverse view) shows that the components are polarized, some parallel to the direction of the field and other perpendicular to it.

(3) Upto fields of about 10^7 V/m, the resolution increases in proportion to the field strength (E) . In the region, we have linear or first order Stark effect. When E exceeds 10^7 V/m, there are shifts in the line patterns which are proportional to E^2 and we speak of the second order Stark effect.

Illustrated Examples

► **Example 1**. A spectrometer can resolve spectral lines in the region $\lambda \simeq$ 6000A, when separated by $\Delta\lambda =$ 0.1.A. Find the value of the external magnetic field required to confirm the normal Zeeman triplet.

Solution. The energy separation Δ E between two consecutive spectral lines is given by the relation

$$\Delta E = \mu_B B$$

Where *B* is the external magnetic field.

∴ Frequency separation Δv between them is

$$\Delta v = \mu_B B/h$$

$$\text{But,}\ \ \Delta v = \Delta\left(\frac{c}{\lambda}\right) = \frac{c\Delta\lambda}{\lambda^2}$$

From (8.17.2), using (8.17.3), the magnetic field is given by

$$B = \frac{hc.\Delta\lambda}{\mu_B \lambda^2}$$

$$\frac{6.62\ \times 10^{-34} \times 3 \times 10^8 \times 0.1 \times 10^{-10}}{9.3 \times 10^{-24} \times (6.0 \times 10^{-7})^2}$$

$$= \ 0.593\ \text{Wb/m}^2$$

► **Example 2,** Show that for a given principal quantum number n, there are n^2 possible states.

Solution. Every combination of the quantum numbers n, l and m_l defines a state of the atom. For a given n, the orbital quantum number l has the following values:

$$l = 0, 1, 2, \dots (n - 1).$$

For every *l*, again, there would be the following (2*l* + 1) values for the magnetic quantum number m_l.

$$m_l = 0, \pm 1, \pm 2, \dots \pm l$$

The total number of possible states of the atom is therefore

$$N(n,l,ml) = \sum_{l-0}^{n-1}(2l+1) = 1 + 3 + 5 + \dots + (2n - 1) = n^2$$

► **Example 3,** Using the vector atom model, determine the possible values of the total angular momentum of an f – electron.

Solution. An f-electron has the orbital quantum number, l = 3, Also, its spin quantum number s = 1/2.

∴ The total angular momentum quantum number, $j = l \pm s = 3 \pm \frac{1}{2} = \frac{7}{2}, \frac{5}{2}$

.

∴ The total angular momentum, $J = \sqrt{j\,(j+1)}\,\frac{h}{2\pi} = \frac{\sqrt[3]{7}}{2}\,,\frac{h}{2\pi}\,;\frac{\sqrt{35}}{2}\,\frac{h}{2\pi}$

► **Example 4,** An electron beam enters a uniform magnetic field of flux density 1.2 Wb/m^2. Find the energy difference in eV between electrons having spains parallel and anti-parallel to the field.

Solution. Energy of magnetic dipole in a field = $-\mu_B B\cos\theta$

When spin is parallel to the field, $\theta = 0 \Rightarrow$ energy, $E_1 = -\mu_B B$

When spin is antiparallel, $\theta = 180^o \Rightarrow$ energy, $E_2 = \mu_B B$

∴ Energy difference = $2\,\mu_B B = 2. \times 9.3 \times 10^{-24} \times 1.2 J$

$= 13.95 \times 10^{-5}$ Ev

► **Example 5.** An H-atom is placed in a magnetic field of 3T. Compute is energy difference between $m_{1} = -1$ components in 2p state.

Solution. The interaction energy between the magnetic moment of electron and the magnetic field B is

$$V = \mu_B B_{ml}$$

∴ Energy of $m_l = -1$-state is $V_1 = -\mu_B B$

Energy of $m_l = +1$-state is $V_2 = \mu_B B$

∴ Energy difference = $V_2 - V_1 = 2\,\mu_B B = 2(9.3 \times 10^{-24}) \times 3J$

$= 55.8 \times 10^{-23}$ J $= 3.48 \times 10^{-4}$ eV

► **Example 6.** Find the processional frequency of an electron orbit when placed in a magnetic field of 6T.

Solution. The frequency Δvl of Larmor precession is given by

$$\Delta vl = \frac{eB}{4\pi m}$$

Here, we have, B = 6T = 6Wb/m^2, e = 1.6×10^{-19} C and m = 9.1×10^{-21} kg.

$$\therefore\ \Delta vl = \frac{1.6\ \times 10^{-19} \times 6}{4 \times 3.14 \times 9.1 \times 10^{-31}}$$

$$= 8.4 \times\ 10^{10}\ Hz$$

► **Example 7.** An atomic state is denoted by $^4D_{5/2.}$ Give the values of L,S and J. What should be the minimum number of electrons involved for this state? Give a possible electronic configuration.

Solution. Atomic state is $^4D_{5/2.}$ So, 2S + 1 = 4 ⇒ S = 3/2; D indicates L = 2 and J = 5/2 (the subscript).

Since for each electron s = ½, the minimum number of electrons to give S = 3/2 is 3.

Possible combination for L = 2 with 3 electrons are:

$l_1 = 0,\ l_2 = 0,\ l_3 = 2;\quad l_1 = 0,\ l_2 = 0,\ l_3 = 1$

∴ Possible electronic configuration: s^2d^1 and $s^1p^{2.}$ The first configuration is rejected since the net spin = 1/2 . So, the possible configuration is $s^1\,p^2$.

► **Example 8.** In K, the longest wavelength lines in (n, 1) → (4,0) transitions have wavelengths 7699, 7665, 4047 and 4044A respectively. How will you construct the relevant part of energy level diagram? Find the splitting between the levels with same *n* and *l* but different *j*.

Solution. The first two lines arise from transitions between pair of levels: n = 4, l = 1, j = $\frac{3}{2},\frac{1}{2}$ to the ground state : n = 4, l = 0, j = $\frac{1}{2}$. The other two arise from transition from higher levels: n = 5, l = 1, j = $\frac{3}{2},\frac{1}{2}$ to the ground state. So, five levels are to be drawn on the energy level diagram: 2 pairs of levels with l = 1 and a single level (ground state) with l = 0.

Separation between the levels $\Delta E = he\left(\frac{1}{\lambda 1} - \frac{1}{\lambda 2}\right) = he\,\frac{\lambda 2 - \lambda 1}{\lambda 1 \lambda 2}$

∴ For n = 4, l = 1 for instance, the separation between the two levels is

$$\Delta E = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8} \times (7699 - 7665) \times 10^{-10}}{7699 \times 7655 \times 10^{-20}}\ \text{J}$$

$$= 7.12 \times 10^{-3} eV$$

► **Example 9.** Calculate the wavelength separation of the fine structure resulting from spin-orbit interaction within the hydrogen atom at λ = 4000A.

Solution. The magnetic field due to the orbital motion of the electron around proton is, by Biot-Savart law,

$$B = \frac{\mu 0}{4\pi} . \frac{2\pi i}{r} = \frac{\pi 0}{4\pi} . \frac{2\pi e f}{r}$$, with usual meanings of the symbols.

Here, r = 0.53A, f = c/λ = 0.75 × 10^{15}Hz. Substituting these values in above relation.

$$B = 10^{-7} \times \frac{2 \times 3.14 \times (1.6 \times 10^{-19}) \times (0.75 \times 10^{15})}{0.53 \times 10^{-10}} = 13.27\ \text{Wb/m}^2$$

∴ Energy separation between split-lines is given by

$$\Delta E = \frac{he.\Delta\lambda}{\lambda^2}\left(= \frac{hc}{\lambda} - \frac{hc}{\lambda'} = \frac{hc\Delta\lambda}{\lambda\lambda'} = \frac{hc\Delta\lambda}{\lambda^2}\right)$$

But $\Delta E = 2\mu_B B = 2 \times 9.3 \times 10^{-24} \times 13.27 \simeq 24.7 \times 10^{-23}$ J

$$\therefore \frac{hc\Delta\lambda}{\lambda^2} = 24.7 \times 10^{-23}$$

$$\therefore \Delta\lambda = \frac{24.7 \times 10^{-23}}{he}\lambda^2 = \frac{24.7 \times 10^{-23} \times (4 \times 10^{-7})^2}{6.62 \times 10^{-34} \times 3 \times 10^{8}}$$

$$= 1.90 \times 10^{-10}\ \text{m} = 1.99\text{A}$$

► **Example 10.** Find the critical voltage that must be applied to an X-ray tube to excite the K-series of copper. Given that the K-absorption limit is 1.380 A.

Solution. Here, $\lambda_{min} = 1.380 \times 10^{-10}$ m. From the relation $V_e = hc/\lambda$,

$$V = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{1.60 \times 10^{-19} \times 1.38 \times 10^{-10}}$$

= 8.98 kV

► **Example 11.** The K-absorption edge in tungsten is $\lambda_\infty = 0.178$ A and the average wavelengths of some lines in the K-series are $\lambda\alpha$ = 0.210A, $\lambda\beta$ = 0.184A, $\lambda\gamma$ = 0.179A. If a tungsten target is bombarded with electrons of 120keV, find the value of the maximum kinetic energies of electrons emitted from n = 1,2 and 3 levels.

Solution. The wavelength of the K-series lines are:

$$\frac{hc}{\lambda\alpha} = W_2 - W_1 \;;\; \frac{hc}{\lambda\beta} = W_3 - W_1$$

$$\frac{hc}{\lambda\gamma} = W_4 - W_1 \;;\; \frac{hc}{\lambda\infty} = W_\infty - W_1$$

But, by the very definition, $W_\infty = 0$. We thus have

$$W_1 = -\frac{hc}{\lambda\infty} = -\frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{0.178 \times 10^{-10} \times 1.6 \times 10^{-19}} \text{ eV} = -69.7\text{keV}$$

Energy of the next level is $W_2 = hc/\lambda\alpha + W_1$

$$\therefore\; W_2 = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{0.210 \times 10^{-10} \times 1.6 \times 10^{-19}} - 69.7 - (59.1 - 69.7) = -10.6\text{keV}$$

Similarly, for W_3 and W_4.

The maximum kinetic energy of the electrons from each level is

$$T_{max} = 120 - |W_n|$$

∴ Maximum kinetic energy of electron from n = 1 level is 120 – 69.7 = 50.3 keV, from n = 2 level is 120 – 10.6 = 109.4 keV. Similarly, for the other levels.

► **Example 12.** The K_α-line of an unknown material has an energy of 66 keV. Find the atomic number Z of the material.

Solution. The energy of K_α-line, hv = 66 keV = 66 x 10^3 eV.

$$\text{But, we have } h\nu = \frac{3hcR\infty(Z-1)^2}{4} \Rightarrow (Z-1)^2 = \frac{4h\nu}{3hcR\infty}$$

$$\therefore (Z-1)^2 = \frac{4 \times 66 \times 10^{3} \times 1.6 \times 10^{-19}}{3 \times 6.62 \times 10^{-34} \times 3 \times 10^{8} \times (1.097 \times 10^{7})} \simeq 6560$$

$$\therefore Z - 1 = \sqrt{6560} = 81 \Rightarrow Z = 82$$

► **Example 13.** Show that the Lande g-factor for pure orbital angular momentum and pure spin angular momentum are respectively 1 and 2. Also, evaluate the g-factor for the state $^3P_1$.

Solution. Pure orbital angular momentum implies $\vec{S}$ = 0. So, $\vec{J} = \vec{L} + \vec{S}$ $=\vec{L}$.

$$\therefore g = 1 + \frac{L\,(L+1) - L\,(L+1)}{2L\,(L+1)} = 1$$

Pure spin angular momentum implies $\vec{L}$ = 0. So, $\vec{J} = \vec{S}$

$$\therefore g = 1 + \frac{S\,(S+1) - S\,(S+1)}{2S\,(S+1)} = 2.$$

For the state $^3P_{1,}$ 2S + 1 = 3 ⇒ S = 1; P implies L = 1 and J = 1(subscript)

$$\therefore g = 1 + \frac{(1 \times 2) + (1 \times 2) - (1 \times 2)}{2\,(1 \times 2)} = 1 + \frac{1}{2} = \frac{3}{2}$$

► **Example 14.** Draw the Zeeman splittings of the D_2 and D_2 lines of sodium corresponding to the transition from the excited states $3^2P_{\frac{3}{2}}$ and $3^2P_{\frac{1}{2}}$ to the ground state $3^2S_{\frac{1}{2}}$.

Solution. For $3^2P_{\frac{1}{2}}$ level, J = $\frac{1}{2}$. So, it splits into two levels for which $m_J = \frac{1}{2}$ and $-\frac{1}{2}$. For $^2P_{\frac{1}{2}}$ level, J = $\frac{1}{2}$. So, it also splits into two levels, for which $m_J = \frac{1}{2}$ and $-\frac{1}{2}$. For $^2P_{\frac{3}{2}}$ level, J = $\frac{3}{2}$. So, it also splits into two levels, for which $m_J = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$.

So, the D_1 line which is singlet in field-free condition, splits into four lines and the D_2 line into six lines. The splitting and the allowed transitions are shown in Fig.8.14.

► **Example 15.** In a Stern-Gerlach type experiment, the magnetic field varies with distance in z-direction according to dB_z/dz = 1.4T/mm. Silver atoms travel a distance x = 3.5 cm through the magnet. The speed of atoms emerging from over is v = 750 m/s. Find the separation of the two beams as they leave the magnet. Mass of silver atom = 1.8 x 10^{-25}kg and its magnetic moment is 1 Bohr magneton.

Solution Potential energy of magnetic moment in the magnetic field is

$$V = -\vec{\mu}, \vec{B} = \mu_z B_z \quad (\because \text{Field has only z-component})$$

∴ Force on the atom, $F_z = \frac{dV}{dz} = \mu_z \frac{dB_z}{dz}$

Acceleration of a silver atom in passing through the magnet is

$$a = \frac{F_z}{m} = \frac{\mu_z (dB_z/dz)}{m}$$

∴ Vertical deflection Δz of either beam is $\Delta z = \frac{1}{2} at^2$, where t = time to traverse the magnet = *x/v*. So, the separation *d* of the beams as they leave the magnet is

$$d = \frac{\mu_z (dB_z/dz) x^2}{m v^2} = \frac{(9.27 \times 10^{-24} J/T \times (1.4 \times 10^3 \, T/m) \times (3.5 \times 10^{-2} m)^2}{1.8 \times 10^{-25} kg) \, (750 \, m/s)^2}$$

$$= 1.6 \text{ x } 10^{-4} \text{m} = 0.16 \text{ nm}$$

LEARNING ACTIVITY

1. **Discuss in detail about normal Zeeman effect**
2. **Explain the Experimental determination of Anomalous Zeeman Effect.**
3. **What is stark effect**
4. **Explain the fine structure of D line.**
5. **What is Paschen – Back effect**

Note:

a) Write your answer in the space given below.

b) Check the answer with your academic counsellor.

SUMMARY

In this chapter, we studied the spectra H-atom and atoms with more than one electron. While in Bohr's theory we came Across of only one quantum number w required as many as three such numbers in quantum mechanical system of one electron atom. A fourth quantum number, the spin quantum number, was soon needed to explain the spectral characteristics of atoms. And also detail studied about the experiment of Stern and Gerlach that established the existence of spin, We also detail studied about the Zeeman splitting of spectral lines in a magnetic field and Stark effect of spectral lines in a electric field.

Block III

X- Rays

STRUCTURE

OVERVIEW

In this chapter on `Atomic Physics', we shall study the X ray spectra and its types. We shall also study the diffraction of x rays and detail study about Compton effect and its verification

LEARNING OBJECTIVES

After completing this Unit, you should be able to:

- Origin of the X ray spectra and its types
- Diffraction of X rays and bragg law and its applications.
- Compton effect and its experimental verification

3.1 Introduction

A German scientist, Wilhelm Roentgen, in 1895, discovered X–rays when he was studying the phenomenon of discharge of electricity through gases.

After performing a series of experiments, Roentgen concluded that when a beam of fast moving electrons strike a solid target, an invisible penetrating radiation is produced. Due to the unknown

nature of the radiation, Roentgen called these radiations as X – rays.

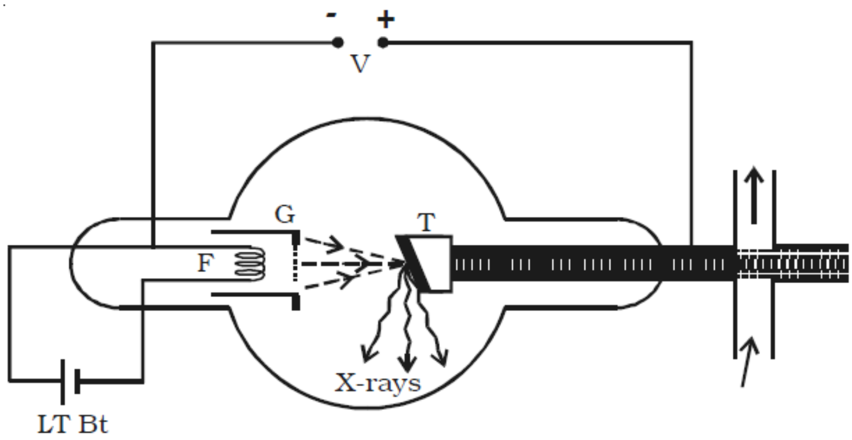
X-rays are electromagnetic waves of short wavelength in the range of 0.5 Å to 10 Å. Roentgen was awarded Nobel prize in 1901 for the discovery of X–rays.

3.2 Origin of X-Rays

Production of X–rays – Modern Coolidge tube

X–rays are produced, when fast moving electrons strike a metal target of suitable material. The basic requirement for the production of X–rays are: (i) a source of electrons, (ii) effective means of accelerating the electrons and (iii) a target of suitable material of high atomic weight.

The modern type of X-ray tube designed by Coolidge is shown in Fig 6.16. It consists of a highly evacuated hard glass bulb containing a cathode and an anode target. The pressure inside the tube is 10-6 mm of mercury. The cathode is a tungsten filament F and is heated by passing a current through it from a low tension battery. The electrons are emitted by the process of thermionic emission from the cathode. The filament is surrounded by a molybdenum cylinder G kept at a negative potential to the filament. Hence, the electrons emitted from the filament are collimated into a fine pencil of electron beam.



Goolidge tube

The target T consists of a copper block in which a piece of tungsten or molybdenum is fixed. The anode should have the following characteristics :

(i) high atomic weight – to produce hard X-rays

(ii) high melting point – so that it is not melted due to the bombardment of fast moving electrons, which cause lot of heat generation.

(iii) high thermal conductivity – to carry away the heat generated.

The face of the copper anode is sloped at about 45^{o} to the electron beam. Being good conductor of heat, copper helps to conduct the heat efficiently to the water cooling system. A high potential of about 20 kV is applied between filament F and the target T. Due to this high potential difference, the electrons emitted from the filament are accelerated. When these accelerated electrons strike the target, they give up their kinetic energy and thereby produce X–rays.

The intensity of X-rays depends upon the number of electrons striking the target. i.e. the rate of emission of electrons from the filament. This can be controlled by varying the filament current.

Soft X–rays and Hard X–rays

X–rays are of two types : (i) Soft X–rays and (ii) Hard X–rays

(i) Soft X–rays

X–rays having wavelength of 4Å or above, have lesser frequency and hence lesser energy. They are called soft X – rays due to their low penetrating power. They are produced at comparatively low potential difference.

(ii) Hard X–rays

X–rays having low wavelength of the order of 1Å have high frequency and hence high energy. Their penetrating power is high, therefore they are called hard X–rays. They are produced at comparatively high potential difference.

The wavelength of X–rays depends upon the kinetic energy of the electrons producing them and this kinetic energy depends upon the potential difference between the filament and the target.

Properties of X–rays

(i) X–rays are electromagnetic waves of very short wave length. They travel in straight lines with the velocity of light. They are invisible to eyes.

(ii) They undergo reflection, refraction, interference, diffraction and polarisation.

(iii) They are not deflected by electric and magnetic fields. This indicates that X-rays do not have charged particles.

(iv) They ionize the gas through which they pass.

(v) They affect photographic plates.

(vi) X–rays can penetrate through the substances which are opaque to ordinary light e.g. wood, flesh, thick paper, thin sheets of metals.

(vii) When X–rays fall on certain metals, they liberate photo electrons (Photo electric effect).

(viii) X-rays have destructive effect on living tissue. When the human body is exposed to X-rays, it causes redness of the skin, sores and serious injuries to the tissues and glands. They destroy the white corpuscles of the blood.

(ix) X–rays do not pass through heavy metals such as lead and bones. If such objects are placed in their path, they cast their shadow.

Detection of X–rays

The basic properties which are generally used for the detection of X-rays are : (i) blackening of a photographic plate and (ii) the ionization produced by X–rays in a gas or vapour. An ionization chamber, which utilizes the property of ionization, is generally used to detect and measure the intensity of X-rays.

Absorption of X–rays

When X–rays pass through any material, a part of the X-ray energy is absorbed by the material. If a beam of X-rays of intensity I passes through a length dx of any material, its intensity is decreased by dI. For any given material, the amount of absorbed intensity is $\mu I dx$

where μ is called the absorption co-efficient. i.e., $dI = -\mu I dx$

3.3 Characteristic X-Ray spectrum

X–ray spectra – continuous and characteristic X–ray spectra.

The spectrum from an X-ray tube contains two distinct parts :

(i) Continuous X–ray spectra

It consists of radiations of all possible wavelengths, from a certain lower limit to higher values continuously, as in the case of visible light.

Origin – Continuous X–ray spectra

X-rays are produced, when high velocity electrons strike the target material of high atomic number. It has also been mentioned in the production of X-rays, that most of the energy of the electrons goes into the heating of the target material.

A few fast moving electrons penetrate deep into the interior of the atoms of the target material and are attracted towards the nuclei by the attractive forces of their nuclei. Due to these forces, the electrons get deflected from their original path. As a result of this, the electrons are decelerated, and hence energy of the electron decreases continuously.

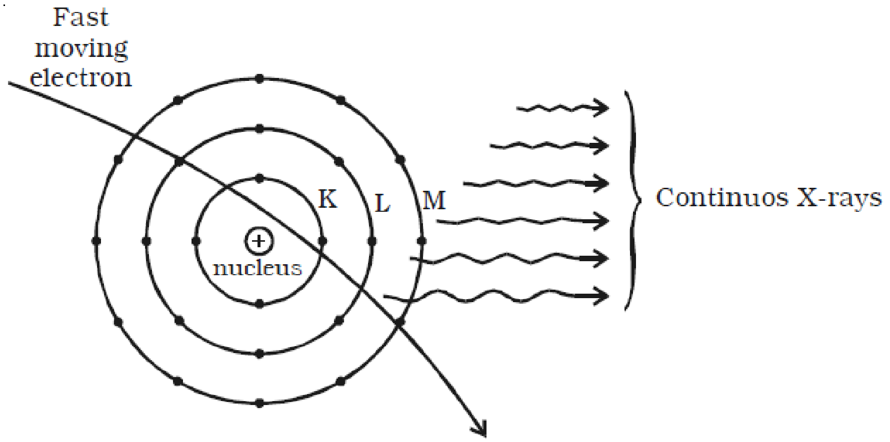


Fig continuous of x ray

This loss of energy during retardation is given off in the form of X-rays of continuously varying wavelength. The X – rays consist of continuous range of frequencies upto a maximum frequency νmax or minimum wave length λmin. This is called as continuous X – rays. The minimum wave length depends on the anode voltage. If V is the potential difference between the anode and the cathode

$$eV = h\nu_{\max} = \frac{hc}{\lambda_{\min}} \quad [\because \nu = \frac{c}{\lambda}]$$

The minimum wavelength of the given radiation

$$\lambda_{\min} = \frac{hc}{eV}$$

where h is Planck's constant, c is the velocity of light and e, the charge of the electron. Substituting the known values in the above equation.

$$\lambda_{\min} = \frac{6.626\times10^{-34}\times3\times10^{8}}{1.6\times10^{-19}\times V} = \frac{12400}{V} \text{ Å}$$

For the given operating voltage, the minimum wave length is same for all metals.

(ii) Characteristic X–ray spectra

It consists of definite, well defined wavelengths superimposed on the continuous spectrum. These spectral lines generally occur in the form of small groups and are characteristic of the material of the target.

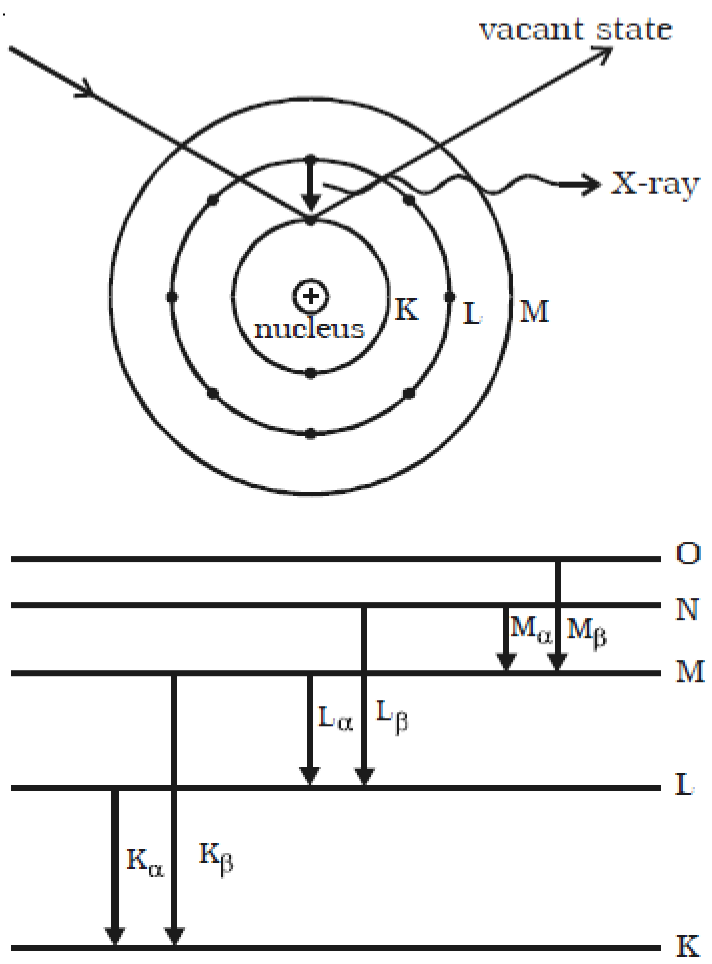


Fig. Characteristic X-ray Spectra

Origin – Characteristic X–ray spectra

Few of the fast moving electrons having velocity of about (1/10)th of the velocity of light may penetrate the surface atoms of the target materials and knock out the tightly bound electrons even from the inner most shells (like K, L shells) of the atom. Fig 6.22a shows the case, when the fast moving electrons knock off one electron from KShell and the vacancy is filled by the nearby electron from the L shell. During this transition, the energy difference is radiated in the form of X-rays of very small wave length. This corresponds to Kα – line of the series. The frequency ν1 of this line is given by the relation (EK – EL) = hν1. Suppose, the electron from M shell jumps to the K shell, it gives out Kβ line and so on. If an electron jumps from the MShell to the vacant state in L-Shell, it contributes Lα line and if the vacancy in L-Shell is filled up by an electron of N shell, it contributes Lβ and so on (Fig 6.22b).

The frequency of radiation depends upon the target material. The X-ray spectra consists of sharp lines and is the characteristic of target material. Hence this spectra is known as characteristic spectra.

3.4 Moseley's law

A comprehensive investigation of characteristic X-ray spectra was made by Moseley (1913) who used nearly 40 elements from aluminium to gold as targets in X-ray tube. The radiation from each target was analysed by single crystal X-ray spectrograph, using a thin crystal of potassium ferrocyanide. The spectrum was recorded on a photographic plate and the entire arrangement was placed in a vacuum chamber to avoid the absorption of long wavelength X-rays in air.

The photographic plate, on development, showed traces of dark lines of varying intensities, each corresponding to a characteristic line of the given element. The characteristic spectra could be easily divided into two distinct groups- a short wavelength group, generally less than 1 nm (K-series) and a long wavelength group, greater than 1 nm (L-series). The wavelength of the L-series were roughly ten times as great as those of the K-series. Subsequent investigations confirmed the existence of two other series line (M-series and N-series) of longer wavelengths in heavier atomic species (Z > 66).

Moseley demonstrated that, unlike the optical spectra., the characteristic spectra are much simpler in character consisting, as they are, of comparatively fewer lines. Further they are of the same type, irrespective of the element, except that the frequencies of the corresponding lines increase with increasing atomic weight. The K-series spectra of different elements are shown in Fig.

Moseley's law – Moseley from his investigation deduced the following relation between the frequency v of any particular line emitted by an element and its atomic number Z.

$$\boxed{\sqrt{V} = a(Z - b)}$$

Where *a* and *b* are constants characteristic of the element.

This is known as the general form of Moseley's law.

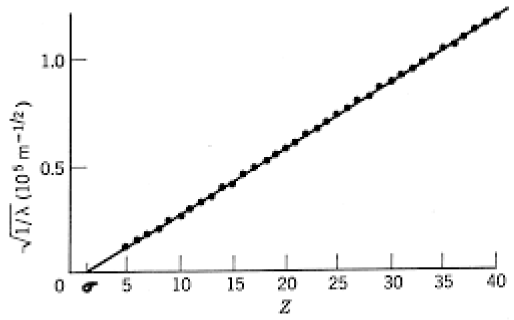


Fig.1 Moseley law

By plotting the square root of the frequency ν of K_α-line against the atomic number Z of the element concerned, Moseley obtained the curve A of Fig.1 – *a* straight line given by the above equation. The same linear relation was found to hold good for any X-ray line in any series, of course with different slopes. The plot of $\sqrt{V}$ vs. Z is known as Moseley's plot or Moseley's diagram. The curve B in Fig.1 is a plot of $\sqrt{V}$ against atomic weight. It is apparent from the two curves that in so far as the frequency of the characteristic line is concerned, the atomic number is more fundamental than the atomic weight. That is to say, the chemical identity of an element depends on the atomic number Z and not on the atomic weight or the mass number *A*.

Derivation of Moseley's law The general form of Mosely's law can be easily derived from Bohr's theory.

Let a transition occur from state n_1 to state n_2. So, the energy of the emitted X-ray photon is

$$h\nu = RchZ^2(1/n_1^2 - 1/n_2^2)$$

$$\Rightarrow \nu = RcZ^2(1/n_1^2 - 1/n_2^2) = a^2Z^2$$

Where R = Rydberg constant, a^2 = Rc $(1/n_1^2 - 1/n_2^2)$ and c is the velocity of light in free space.

$$\therefore \sqrt{V} = aZ$$

For K_α-line, n1 = 1, $n2$ = 2, so that $a^2 = \frac{3}{4}$ Rc.

The present of the constant b in Moseley's equation, as deduced from experimental data, has been interpreted as the shielding effect of nucleus by the remaining electrons in the lower level and b is known as the screening constant. For instance, for K_α-emission one of the two K-electrons is first emitted leaving a single electron is K-shell. The negative charge of this residual electron partially screens the nuclear charge +Ze of the atom. The effective Coulomb force on the L-electron is thus due approximately to a net positive charge + (Z – 1)e. So, instead of Z^2 in (8.15.2), we should rather write $(Z – 1)^2$,

$$\text{i.e., } v = \frac{3}{4} Rc (Z – 1)^2$$

$$\text{or, } \sqrt{v} = a (Z-1)$$

where $a^2 = \frac{3}{4}$ Re, as before, and b = 1.

With this interpretation, we have the general form of Moseley's law.

$$\sqrt{v} = a(Z - b)$$

Importance of Moseley's work Moseley's investigation showed for the first time that it would be more logical to arrange elements in the Periodic table in order of increasing atomic number instead of atomic weight. When this was done certain anomalies of the old periodic table were removed. For example, cobalt (Z – 27, A – 58.9) should precede nickel (Z – 28, A = 58.7) though the atomic weight of Co is higher than that of Ni. Other such examples are argon-potassium and tellurium-iodine.

Moseley's work also helped (i) in the discovery of new elements in the missing gaps of Z-values 21, 43, 61, 72 and 75 in the old Periodic table and (ii) in the determination of atomic numbers of rare-earth elements and fixing their positions in the Periodic table.

Moseley investigated systematically, the characteristic radiations emitted by different targets. Based on his experiments, he has concluded that the frequency of the spectral line in the characteristic X-ray spectrum is directly proportional to the square of the atomic number (Z) of the element considered. This is known as Moseley's law.

$$\nu \propto Z^2 \quad \text{or} \quad \sqrt{\nu} = a(Z-b)$$

where *a* and *b* are constants depending upon the particular spectral line.

Applications of Moseley's law

(i) Any discrepancy in the order of the elements in the periodic table can be removed by Moseley's law by arranging the elements according to the atomic numbers and not according to the atomic weights.

(ii) Moseley's law has led to the discovery of new elements like hafnium (72), technetium (43), rhenium (75) etc.

(iii) This law has been helpful in determining the atomic number of rare earths, thereby fixing their position in the periodic table.

Applications of X–rays

X–rays have a number of applications. Some of them are listed below:

Medical applications

(i) X–rays are being widely used for detecting fractures, tumours, the presence of foreign matter like bullet etc., in the human body.

(ii) X–rays are also used for the diagnosis of tuberculosis, stones in kidneys, gall bladder etc.

(iii) Many types of skin diseases, malignant sores, cancer and tumours have been cured by controlled exposure of X-rays of suitable quality.

(iv) Hard X–rays are used to destroy tumours very deep inside the body.

Industrial applications

(i) X–rays are used to detect the defects or flaws within a material

(ii) X–rays can be used for testing the homogeneity of welded joints, insulating materials etc.

(iii) X-rays are used to analyse the structure of alloys and the other composite bodies.

(iv) X–rays are also used to study the structure of materials like rubber, cellulose, plastic fibres etc.

Scientific research

(i) X–rays are used for studying the structure of crystalline solids and alloys.

(ii) X–rays are used for the identification of chemical elements including determination of their atomic numbers.

(iii) X–rays can be used for analyzing the structure of complex molecules by examining their X–ray diffraction pattern.

3.5 Diffraction of X–rays

Soon after the discovery of X-rays, Schuster pointed out that X-rays behave as electromagnetic waves of wavelength much shorter than that of visible light. Attempts were made to measure the wave length of X-rays by means of diffraction gratings which proved unsuccessful, as the grating failed to disperse X–rays on account of their very small wavelength. Obviously, diffraction effects can only be observed if the spacing between the lines ruled on the grating is of the order of magnitude of wavelength of the wave used. Thus, in order to diffract X–rays, grating with much finer rulings, having distance between rulings comparable to the wave length of X–rays are required. It is impossible to construct a grating of such fine dimensions artificially.

In a crystal, the atoms or molecules are arranged symmetrically in a three dimensional space. Any plane containing an arrangement of atoms is known as lattice plane or cleavage plane. The spacing between the atoms is of the order of 10-10 m, comparable to the wavelength of X-rays. It was suggested that the regular arrangement of atoms or molecules in the cleavage planes of a crystal might provide a grating element suitable to diffract X–rays. The crystal might serve as a three dimensional grating, whereas optical grating is a two dimensional one.

Laue experiment

Von Laue, in 1913, suggested that a crystal can act as a three dimensional grating for an X-ray beam. The experimental arrangement used to produce diffraction in X–rays by Laue is shown in Fig 6.17(a).

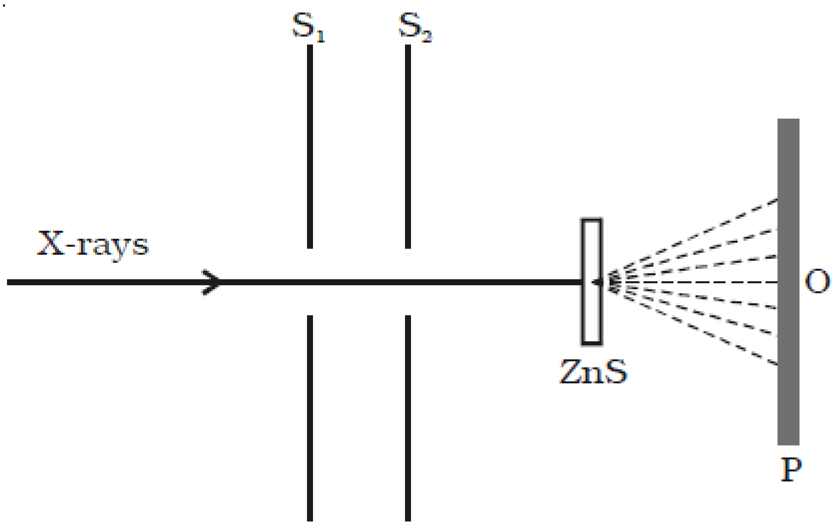


Fig. Laue experiment setup

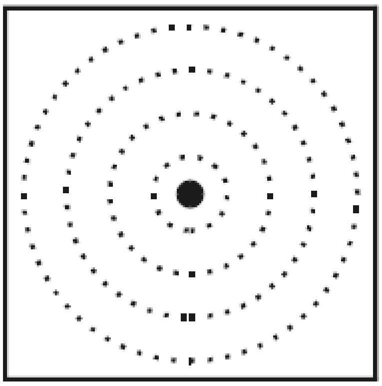


Fig. Laue spot

X–rays from the X–ray tube is collimated into a fine beam by two slits S1 and S2. The beam is now allowed to pass through a zinc sulphide (*ZnS*) crystal. The emergent rays are made to fall on a photographic plate P. The diffraction patten so obtained consists of a central spot at O and a series of spots arranged in a definite pattern about O as shown in Fig b. The central spot is due to the direct beam, whereas the regularly arranged spots are due to the diffraction pattern from the atoms of the various crystal planes. These spots are known as Laue spots. The Laue experiment has established following two important facts :

(i) X–rays are electro magnetic waves of extremely short wave length.

(ii) The atoms in a crystal are arranged in a regular three dimensional lattice.

Bragg's law for X-ray diffraction

W.L. Bragg and W.H. Bragg studied the diffraction of X–rays in detail and used a crystal of rock salt to diffract X–rays and succeeded in measuring the wavelength of X–rays.

Consider homogeneous X–rays of wave length λ incident on a crystal at a glancing angle θ. The incident rays AB and DE after reflection from the lattice planes Y and Z travel along BC and EF respectively as shown in Fig 6.18.

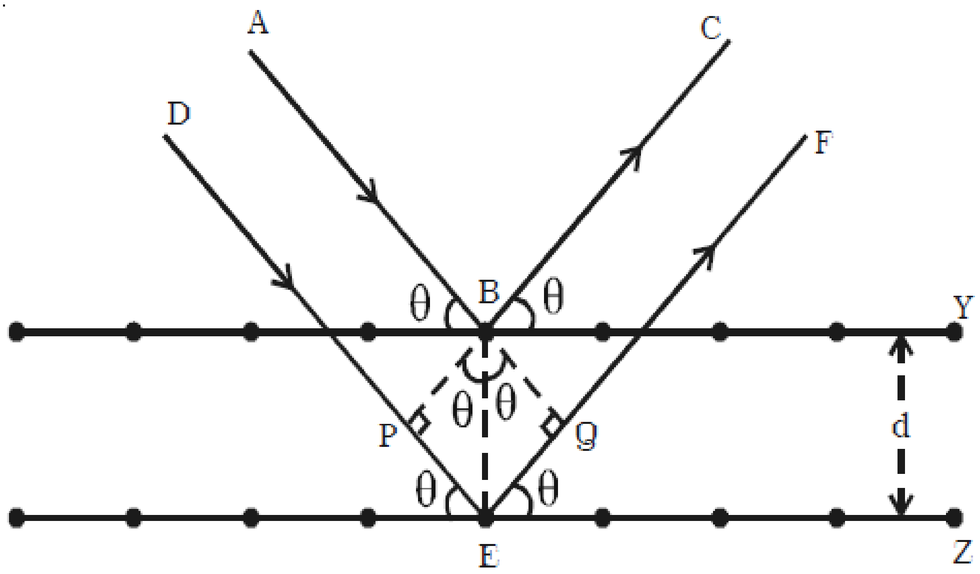


Fig. Braggs Law

Let the crystal lattice spacing between the planes be *d*. BP and BQ are perpendiculars drawn from *B* on *DE* and *EF* respectively. Therefore, the path difference between the two waves ABC and DEF is equal to $PE + EQ$.

In the ΔPBE, $\sin\theta = PE / BE$ (or) $PE = BE \sin\theta = d \sin\theta$

In the ΔQBE, $\sin\theta = EQ/BE$ (or) $EQ = BE \sin\theta = d \sin\theta$

$\therefore$ Path difference $= PE + EQ = d \sin\theta + d \sin\theta = 2d \sin\theta$

If this path difference $2d \sin\theta$ is equal to integral multiple of wavelength of X-ray i.e. $n\lambda$, then constructive interference will occur between the reflected beams and they will reinforce with each other. Therefore the intensity of the reflected beam is maximum.

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

where, $n = 1, 2, 3 \ldots$ etc.

This is known as Bragg's law.

Bragg's X-ray spectrometer

Bragg's spectrometer used to determine the wavelength of X – rays is shown in Fig . Bragg's spectrometer is similar in construction to an ordinary optical spectrometer.

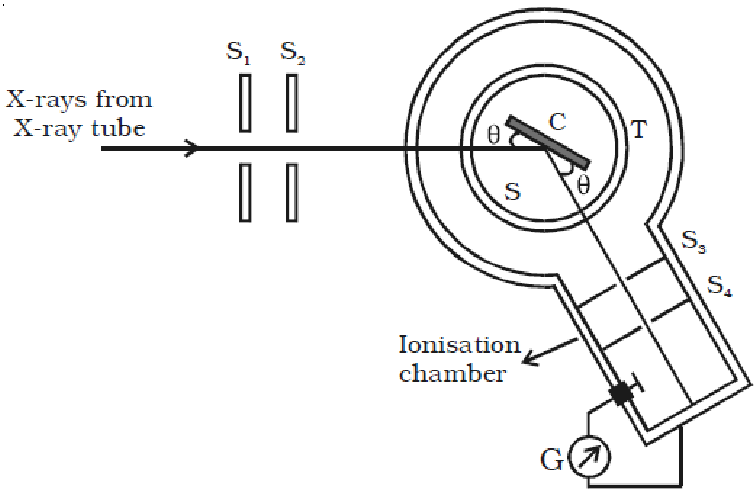


Fig. Bragg's spectrometer

X–rays from an X-ray tube are made to pass through two fine slits S1 and S2 which collimate it into a fine pencil. This fine X-ray beam is then made to fall upon the crystal 'C' (usually sodium chloride crystal) mounted on the spectrometer table. This table is capable of rotation about a vertical axis and its rotation can be read on a circular graduated scale S. The reflected beam after passing through the slits S3 and S4 enters the ionization chamber. The X-rays entering the ionization chamber ionize the gas which causes a current to flow between the electrodes and the current can be measured by galvanometer G. The ionization current is a measure of the intensity of X-rays reflected by the crystal.

The ionization current is measured for different values of glancing angle θ. A graph is drawn

between the glancing angle θ and ionization current (Fig 6.20).

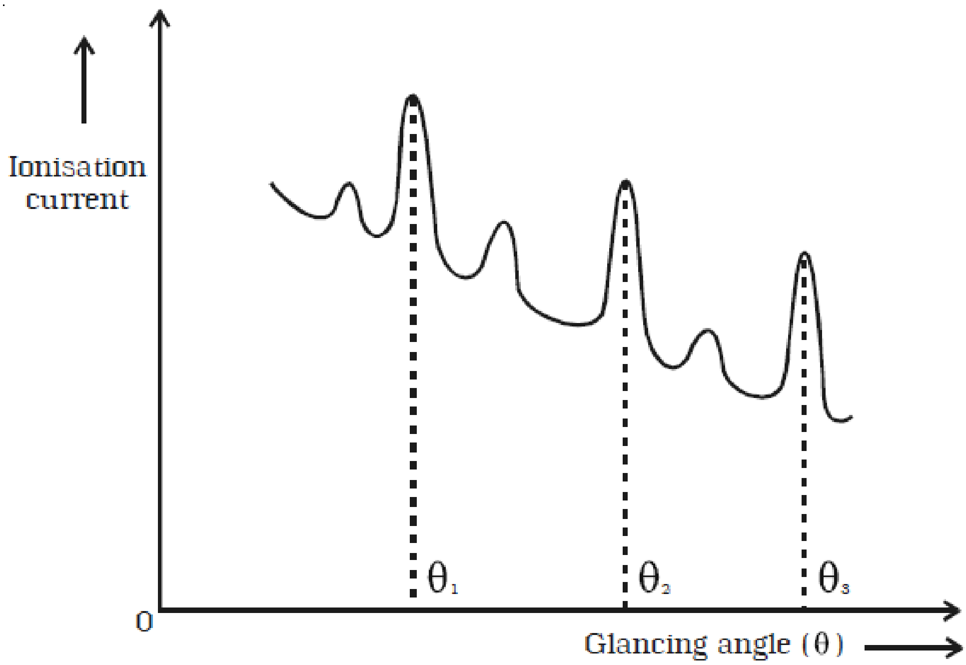


Fig. Plot of glancing angle and ionization current

For certain values of glancing angle, the ionization current increases abruptly. The first peak corresponds to first order, the second peak to second order and so on. From the graph, the glancing angles for different orders of reflection can be measured. Knowing the angle θ and the spacing *d* for the crystal, wavelength of X–rays can be determined.

3. 6 THE POWDER CRYSTAL METHOD

If a powdered specimen is used, instead of a single crystal, then there is no need to rotate the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample. This method is useful for samples that are difficult to obtain in single crystal form.

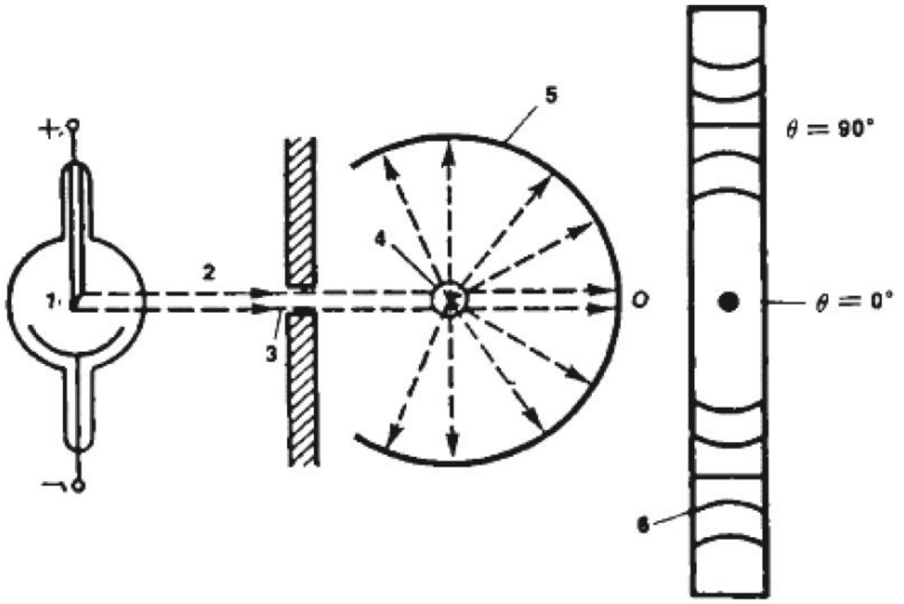


Fig. Experimental arrangement in powder method

The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors a, b and c which define the unit cell for the crystal. For every set of crystal planes, by chance, one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

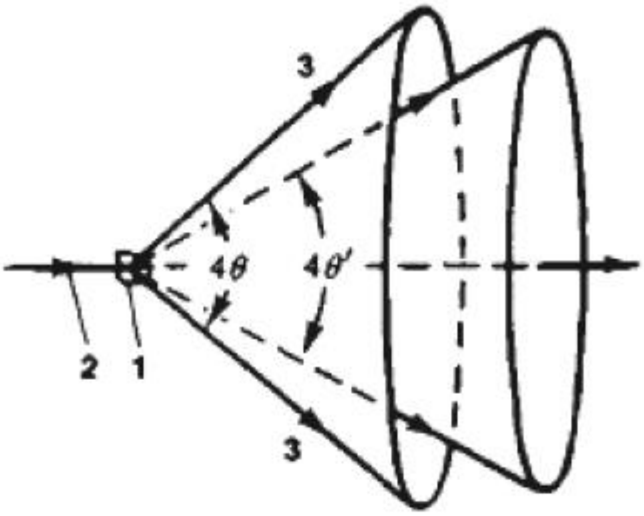


Fig. Cones of Diffracted Beams of X ray

A sample of some hundreds of crystals)i.e. a powdered sample(show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film. A very small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract x-rays. The specimen is placed in the Debye Scherrer camera and is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator. The powder diffracts the x-rays in accordance with Braggs law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.

When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams. Application of XRD 1. Differentiation between crystalline and amorphous materials; 2. Determination of the structure of crystalline materials; 3. Determination of electron distribution within the atoms, and throughout the unit cell; 4. Determination of the orientation of single crystals; 5. Determination of the texture of polygrained materials; 6. Measurement of strain and small grain size…..etc Advantages

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward
- X-ray is the cheapest, the most convenient and widely used method.
- X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

Disadvantage

- Homogeneous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacings, *hkl*)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample

3.7 ROTATING CRYSTAL METHOD

In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis.

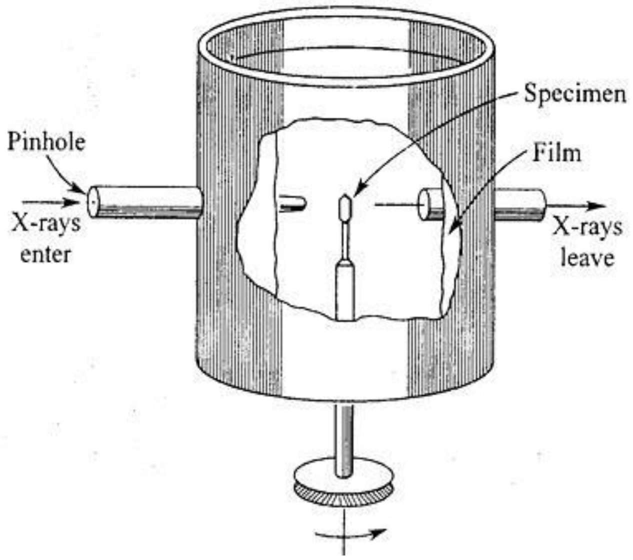


Fig. Schematic representation of Rotating Crystal Technique

As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed. Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle θ at which a $d_{h,k,l}$ reflection occurs is known, can be determined.

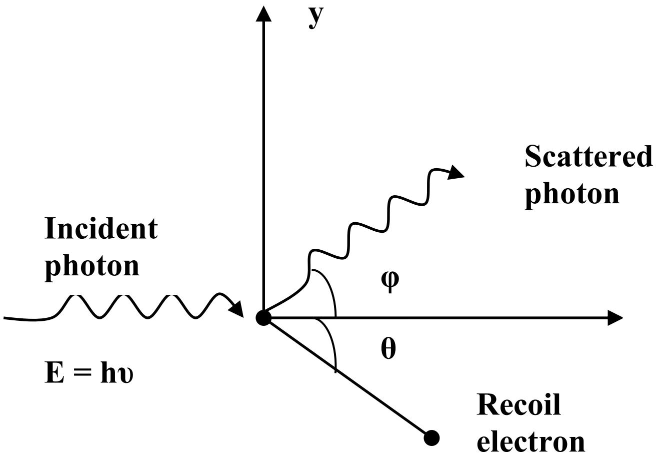
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns)both angles and intensities(for various crystal orientations, one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.

3.8 Compton Effect

When a monochromatic beam of X-rays are scattered by a material of low atomic number (paraffin or graphite), then the scattered ray consists of two components, one component having the same wavelength as the incident X-rays and the other with a higher wavelength. This effect is known as **Compton Effect.**

Theory of Compton Effect



Let us consider a photon of energy ‘hν’ and momentum ‘hν/c’ strikes an electron at rest. The initial momentum of the electron is zero and only rest mass energy m_0c^2. During the collision, the X-ray photon gives some energy to the free electron. Due to this energy transfer, the electron recoil out with energy ‘mc^2’ and momentum ‘mv’ and moves out at an angle ‘θ’ to the x-axis. The scattered photon comes out with lesser energy hν’ and momentum hν’/c inclined at an angle φ from the original direction.

Let us calculate the total energy before and after collision.

Energy before and after collision

Initial energy of photon	=	$h\nu$
Final energy of photon	=	$h\nu'$
Initial energy of electron	=	m_0c^2
Final energy of electron	=	mc^2
Total initial energy	=	$h\nu + m_0c^2$
Total final energy	=	$h\nu' + mc^2$

According to the principle of conservation of energy

$$h\nu + m_0c^2 = h\nu' + mc^2 \text{ ------------------ (1)}$$

Momentum before and after collision along x-axis

Initial momentum of photon	=	$h\nu/c$
Final momentum of photon	=	$(h\nu'/c)\cos\varphi$
Initial momentum of electron	=	0
Final momentum of electron	=	$mv\cos\theta$

Total initial momentum = $h\nu/c + 0$

Total final momentum = $(h\nu'/c)\cos\varphi + mv\cos\theta$

According to the principle of conservation of momentum

$$h\nu/c + 0 = (h\nu'/c)\cos\varphi + mv\cos\theta \text{ ------------------ } (2)$$

Momentum before and after collision along y-axis

Initial momentum of photon = 0

Final momentum of photon = $(h\nu'/c)\sin\varphi$

Initial momentum of electron = 0

Final momentum of electron = $- mv\sin\theta$

Total initial momentum = 0

Total final momentum = $(h\nu'/c)\sin\varphi - mv\sin\theta$

According to the principle of conservation of momentum

$$0 = (h\nu'/c)\sin\varphi - mv\sin\theta \text{ ------------- } (3)$$

From eqn (2) $mvc\cos\theta = h(\nu-\nu'\cos\varphi)$ ------------------ (4)

From eqn (3) $mvc\sin\theta = h\nu'\sin\varphi$ ------------------ (5)

Squaring and adding eqns (4) and (5)

$$m^2v^2c^2 = h^2(\nu^2 - 2\,\nu\,\nu'\cos\varphi + \nu'^2\cos^2\varphi) + h^2\,\nu'^2\sin^2\varphi$$

$$m^2v^2c^2 = h^2(\nu^2 - 2\,\nu\,\nu'\cos\varphi + \nu'^2) \text{ ------------------ } (6)$$

from eqn (1)

$$mc^2 = h\,\nu - h\,\nu' + m_0c^2$$

$$= h\,(\nu - \nu') + m_0c^2$$

Squaring

$$m^2c^4 = [h\,(\nu - \nu') + m_0c^2\,]^2$$

$$m^2c^4 = [h(\nu - \nu')\,]^2 + 2h(\nu - \nu')\,m_0c^2 + [m_0c^2]^2$$

$$m^2c^4 = h^2(\nu^2 - 2\,\nu\,\nu\; + \nu'^2\,) + 2h(\nu - \nu')\,m_0c^2 + m_0^2c^4 \text{ ------------ } (7)$$

Subtracting (6) from (7)

$$m^2c^4 - m^2v^2c^2 = h^2(\nu^2 - 2\,\nu\,\nu\; + \nu'^2\,) + 2h(\nu - \nu')\,m_0c^2 + m_0^2c^4$$

$$- \quad h^2\nu^2 + 2h^2\,\nu\,\nu'\cos\varphi - h^2\,\nu'^2)$$

$$m^2c^2\,(c^2 - v^2) = -\,2\,h^2\,\nu\,\nu'(1 - \cos\varphi) + 2h(\nu - \nu')\,m_0c^2 + m_0^2c^4 \text{ ----- } (8)$$

According to the theory of relativity, we have,

$$m = \frac{m_0}{\sqrt{1 - \left(\dfrac{v^2}{c^2}\right)}}$$

Squaring

$$m^2 = \frac{m_0^2}{\left(1-\frac{v^2}{c^2}\right)} = \frac{m_0^2}{\left(\frac{c^2-v^2}{c^2}\right)}$$

$$= \frac{m_0^2 c^2}{c^2 - v^2}$$

$$m^2\left(c^2 - v^2\right) = m_0^2 c^2$$

Multiply both sides by c^2

$$m^2 c^2\left(c^2 - v^2\right) = m_0^2 c^4 \quad \text{--------------------------- (9)}$$

From equations (8) and (9)

$$m_0^2 c^4 = -2h^2 \nu\nu'(1-\cos\varphi) + 2h(\nu-\nu')m_0 c^2 + m_0^2 c^4$$

$$2h(\nu-\nu')m_0 c^2 = 2h^2 \nu\nu'(1-\cos\varphi)$$

$$\frac{(\nu-\nu')}{\nu\nu'} = \frac{h}{m_0 c^2}(1-\cos\varphi)$$

$$\left(\frac{1}{\nu'}\right) - \left(\frac{1}{\nu}\right) = \frac{h}{m_0 c^2}(1-\cos\varphi)$$

$$\left(\frac{\lambda'}{c}\right) - \left(\frac{\lambda}{c}\right) = \frac{h}{m_0 c^2}(1-\cos\varphi)$$

$$\lambda' - \lambda = \frac{h}{m_0 c}(1-\cos\varphi)$$

$$\because \nu = \frac{c}{\lambda}$$

i.e., change in wavelength (or) Compton shift is given by,

$$\boxed{d\lambda = \frac{h}{m_0 c}(1 - \cos\varphi)} \text{---------} (10)$$

Here, dλ is independent of wavelength of incident radiation as well as the nature of the scattering substance.

Thus the change in wavelength (or) Compton Shift purely depends on the angle of scattering.

Special Cases

Case (i) When $\varphi = 0$, $\cos\varphi = 1$ hence $d\lambda = 0$

Case (ii) When $\varphi = 90°$, $\cos\varphi = 0$, $d\lambda = \frac{h}{m_0 c}$

$$d\lambda = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^{8}}$$

$$d\lambda = 0.0243 \text{ A°}$$

This is known as **Compton wavelength.**

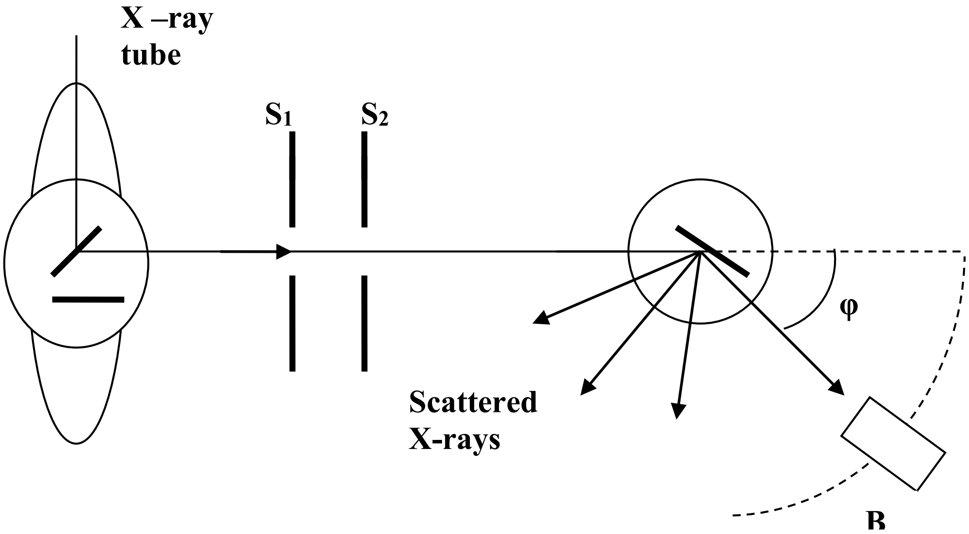
Case (iii) When φ = 180° , cos φ = -1 , $d\lambda = \frac{2h}{m_0 c}$

$$d\lambda = 0.0485 \text{ A}^\circ$$

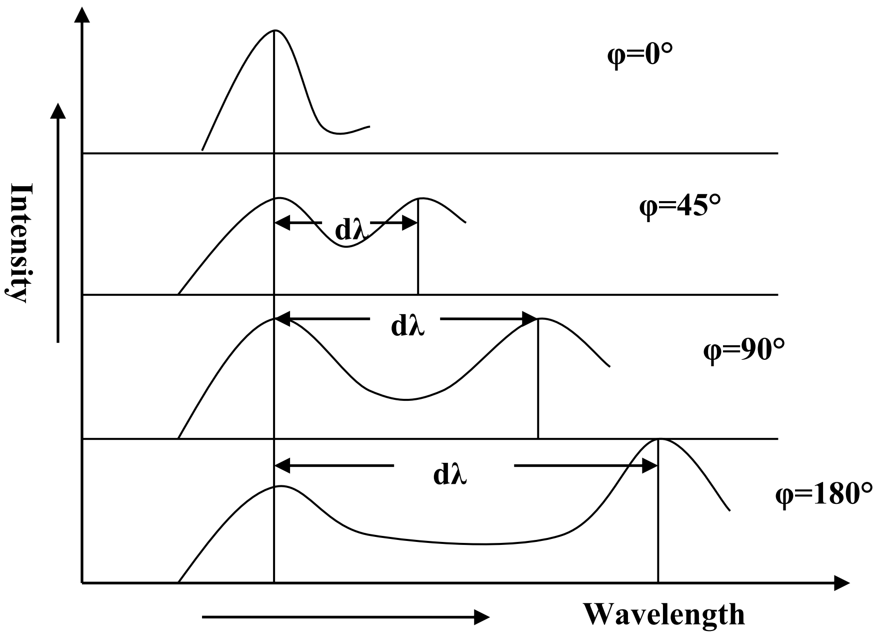
Hence dλ has maximum value when φ = 180°

Experimental verification of Compton effect

A monochromatic beam of x-rays of wavelength 'λ' is allowed to fall on a scattering material (a small carbon block C). A Bragg's spectrometer 'B' which can move freely about an arc is used to find the wavelength of the scattered x-ray.The wavelength is measured for different values of scattering angle.



A graph between intensity and wavelength for various scattering angles is shown in the figure.



The Compton shift is found to vary with the angle according to the relation

$$d\lambda = (h/m_0c)(1 - \cos\varphi).$$

From the graph, when φ = 90°, dλ = 0.0243 A° which agrees with Compton formula. Thus Compton effect is experimentally verified.

✍**LEARNING ACTIVITY**

1. **Discuss in detail about characteristic of X ray spectrum.**
2. **State and Explain Bragg's law.**
3. **What are the applications of Moseley's law**
4. **Explain the Powder crystal method in detail.**
5. **What is Compton effect? Derive an expression for Compton shift.**

Note:

a) Write your answer in the space given below.

b) Check the answer with your academic counsellor.

SUMMARY

In this chapter, we studied the X ray spectra and its types also detail study about production, absorption and continues x rays. We detail studied about diffraction of xarys and various application including Compton effect.

Block IV

Photoelectric effect

STRUCTURE

OVERVIEW

In this chapter on `Atomic Physics', we shall study the photo electric effect and laws of photo electric emission . We shall also study the Einstein's photo electric equation and its verification. We shall study about various types of photo electric cells and its applications.

LEARNING OBJECTIVES

After completing this Unit, you should be able to:

- Photo electri effect and its applications
- Einstein's photo electric equation and its verification.
- various types of photo electric cells and its applications

4.1 Introduction

Whenever light or electromagnetic radiations (such as X-rays, ultraviolet rays) fall on metal surface, it emits electrons. This process of emission of electrons from a metal plate, when illuminated by light of suitable wavelength, is called the photoelectric effect. The electrons emitted are known as the photoelectrons. In the case of alkali metals, photoelectric emission occurs even under the action of visible light. Zinc, cadmium etc. are sensitive to only ultraviolet light.

4.2 Photo electric effect

Photoelectric emission is the phenomena by which a good number of substances, chiefly metals, emit electrons under the influence of radiation such as γ rays, X-rays, ultraviolet and even visible light. This effect was discovered by Heinrich Hertz in 1887 while working with resonance electrical circuits. A year later, Hallwachs, Elster and Geitel investigated the phenomenon with a simple experimental arrangement.

Hallwachs Experiment

Hallwachs experimental set-up to study the photo electric effect is shown in Fig 7.1. It consists of an evacuated quartz bulb with two zinc plates cathode C and anode A. The plates are connected to a battery and a sensitive galvanometer. In the absence of any radiation incident on the plates, there is no flow of current and hence there is no deflection in the galvanometer. But, when an electro magnetic radiation like ultraviolet radiation is allowed to fall on the plate C which is connected to the negative terminal of the battery, a current begins to flow, indicated by the deflection in the galvanometer (G). But, when ultraviolet radiation is made to fall on A, there is no deflection in the galvanometer. These observations reveal that the particles emitted by the plate C due to the photoelectric effect are negatively charged. These particles were found to be electrons. The observed current known as the photoelectric current is due to the flow of electrons.

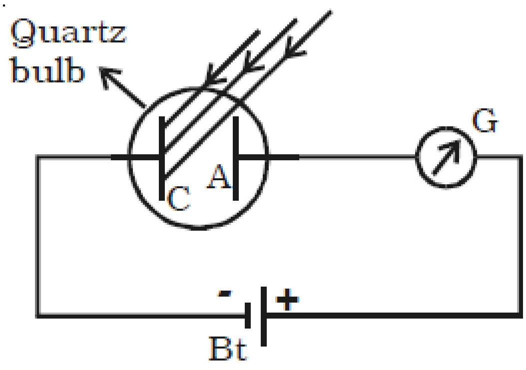


Fig Photo electric effect

After the study of photoelectric effect by Hallwachs, scientists J.J.Thomson, Lenard, Richardson, Compton did a series of experiments to study the relationship between photoelectric current, intensity of incident radiation, velocity and the kinetic energy of the photo electrons, and their dependence on the wave length of incident radiation used.

Lenard's method to determine e/m for photoelectrons

The apparatus used is shown in the figure. It consists of a glass tube G which can be evacuated through the side tube T. ultraviolet light passes through a quartz window W and falls on an aluminium cathode C enclosed in G. an earthed metal screen A with a small central hole forms the anode. The cathode (C) can be maintained at a desired potential, positive or negative relative to the anode A. P_1 and P_2 are small metal electrodes connected to electrometers E_1 and E_2.

When C is raised to a negative potential and illuminated, negatively charged particles are produced and accelerated towards the anode. A few particles pass through the hole in A and proceed with uniform velocity to P_1. Their arrival at P_1 is indicated by E_1. By applying a uniform magnetic field B(represented by the dotted circle) perpendicular to the plane of the figure and directed toward the reader, the photoelectrons can be deflected towards P_2. Their arrival at P_2 is indicated by the deflection they produce in E_2.

Lenard first studied the relation between current and the potential applied to C. when the cathode potential was several volts positive, the current was zero. When Vwas +2 volts, there was a feeble current showing that a few particles possessed enough velocity to overcome the retrading potential of 2 volts. When the potential was further decreased, the current increased and reached a saturation value for -20 volts. Figure shows the variation of photoelectric current with cathode potential.

After this preliminary investigation, Lenard applied to C a negative potential V, very large compared to the potential of 2 volts. The velocity imparted by the accelerating potential is so large that the velocity of the particles in the act of emission is negligible in comparison to it. Let V be the accelerating potential and v the velocity acquired by the photoelectrons. Then,

$$\frac{1}{2}mv^2=eV \qquad \text{……………………….(1)}$$

Where e is the charge and m the mass of the photoelectron.

Let R be the radius of the circular path described by the photoelectrons in the region of uniform magnetic field of strength B.

Then $\frac{mv^2}{R}$ = Bev.

Therefore, v = $\frac{BeR}{m}$ ………………………..(2)

Substituting this value of v in equation (1) $\frac{1}{2}m\left(\frac{BeR}{m}\right)^2 = eV$

Therefore, $\frac{e}{m} = \frac{2V}{B^2R^2}$ …………………………………..(3)

Knowing V, B and R, e/m is calculated. Lenard found the value of e/m to be the same as that for electrons. This clearly shows that the photoparticles are nothing but electrons.

4.3 Richardson and Compton experiment

The apparatus used by them is shown in the figure. The emitter of photoelectrons (C) is a small strip of the metal under study and is kept at the centre of a spherical glass bulb B. B is silvered on the inner side and can be evacuated through the tube T. the silver coating on the inside of the bulb serves as the anode A and is connected to an electrometer E which measures the photoelectric current. Monochromatic light L is made to pass through a quartz window W and fall on C. C can be maintained at any desired potential V relative to A and this potential can be read with a voltmeter.

Effect of intensity of incident radiation on photo electric current

Keeping the frequency of the incident radiation and the potential difference between the cathode and the anode at constant values, the intensity of incident radiation is varied. The corresponding photoelectric current is measured in the microammeter.

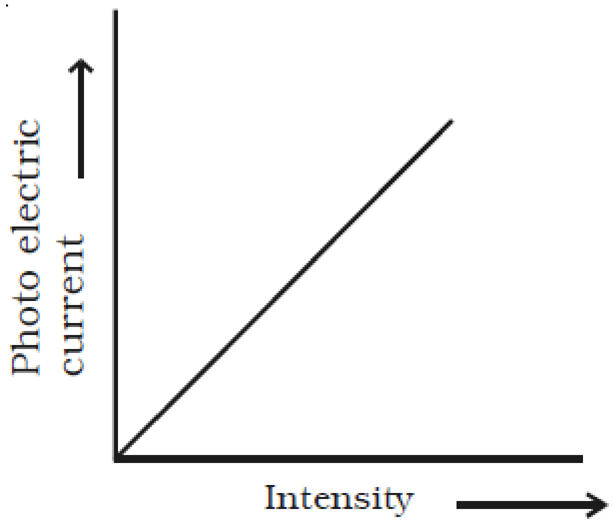


Fig. *Variation of photoelectric current with intensity of incident radiation.*

It is found that the photo electric current increases linearly with the intensity of incident radiation (Fig 7.2). Since the photoelectric current is directly proportional to the number of photoelectrons emitted per second, it implies that the number of photoelectrons emitted per second is proportional to the intensity of incident radiation.

Effect of potential difference on the photoelectric current

For a given metallic surface C, keeping the intensity *(I1)* and frequency of the incident radiation constant, the effect of potential difference between the plates on the photoelectric current can be studied. Fig 7.3

shows the variation of photo electric current with the potential difference V between the two plates. When the positive potential of A is increased, the photoelectric current is also increased.

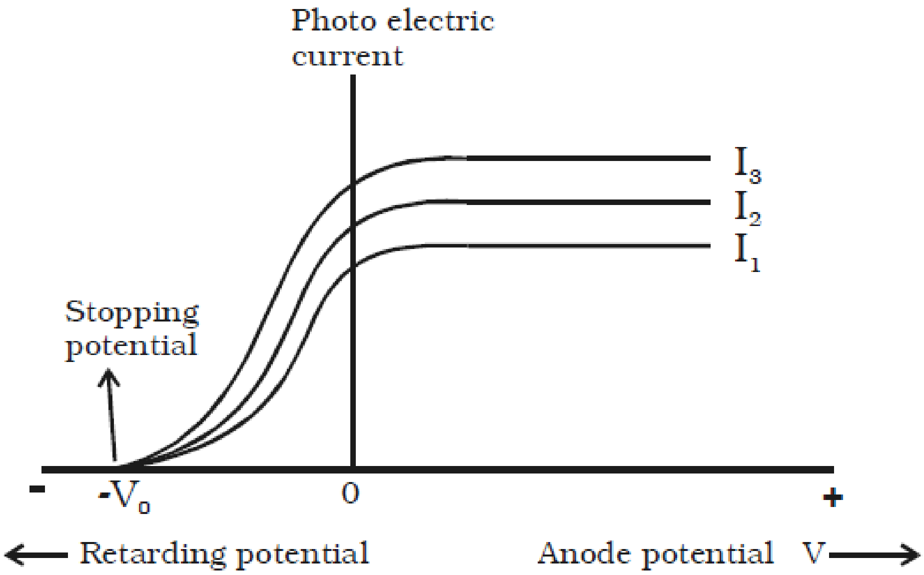


Fig. *Variation of photo electric current with potential difference*

However, if the positive potential is further increased such that it is large enough to collect all the photo electrons emitted from the plate C, the photoelectric current reaches a certain maximum value and this current is known as saturation current. If the potential of the plate A is made negative, the photocurrent does not immediately drop to zero but flows in the same direction as for positive potential. This shows that the photo electrons are emitted from the plate C with finite velocity. If the negative or retarding potential is further increased, the photo current decreases and finally becomes zero at a particular value. Thus, the minimum negative (retarding) potential given to the anode for which the photo electric current becomes zero is called the cut-off or stopping potential.

If m is the mass of the photo electron emitted with a velocity v_{max} then the kinetic energy associated with it is $\frac{1}{2} mv^2_{\mathrm{max}}$.

Since at the stopping potential V_o, the fastest electron is just prevented from reaching the plate A, workdone in bringing the fastest electron to rest = kinetic energy of the fastest electron.

$eVo = \frac{1}{2} mv^2_{\mathrm{max}}$

The above equation indicates that the stopping potential depends upon the velocity of the fastest electron. The experiment is repeated with the incident radiation of same frequency, but of higher intensities $I2$ and $I3$. It is found from the graph, the saturation currents are proportional to the intensities of the radiation. But, the stopping potential remains the same for all the intensities. Thus, for a given frequency of incident radiation, the stopping potential is independent of its intensity.

Effect of frequency of incident radiation on stopping potential

Keeping the photosensitive plate (C) and intensity of incident radiation a constant, the effect of frequency of the incident radiations on stopping potential is studied. Fig 7.4 shows the variation of the photo electric current with the applied potential difference V for three different frequencies. From the graph, it is found that higher the frequency of the incident radiation, higher is the value of stopping potential Vo. For frequencies $\nu 3 > \nu 2 > \nu 1$, the corresponding stopping potentials are in the same order $(Vo)3 > (Vo)2 > (Vo)1$.

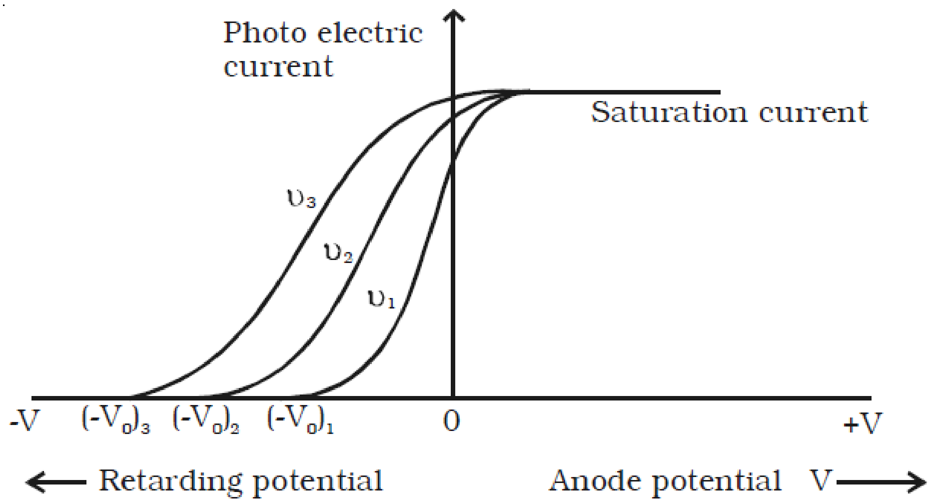


Fig. Variation of photoelectric current with applied potential difference for different frequency of incident radiation

It is concluded from the graph that, the maximum kinetic energy of the photoelectrons varies linearly with the frequency of incident radiation but is independent of its intensity. If the frequency of the incident radiation is plotted against the corresponding stopping potential, a straight line is obtained as shown in Fig 7.5.

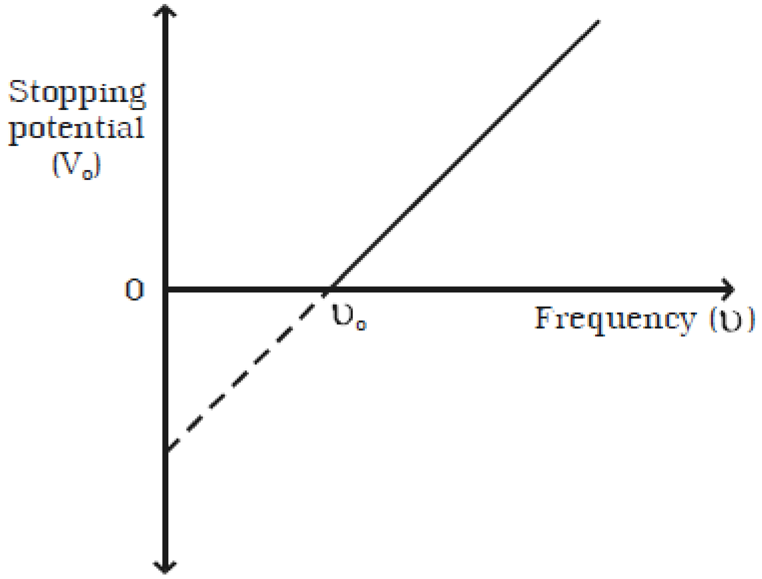


Fig. *Variation of stopping potential with frequency of incident radiation.*

From this graph, it is found that at a frequency ν o, the value of the stopping potential is zero. This frequency is known as the threshold frequency for the photo metal used. The photoelectric effect occurs above this frequency and ceases below it. Therefore, threshold frequency is defined as the minimum frequency of incident radiation below which the photoelectric emission is not possible completely, however high the intensity of incident radiation may be. The threshold frequency is different for different metals.

4.4 Laws of photoelectric emission

The experimental observations on photoelectric effect may be summarized as follows, which are known as the fundamental laws of photoelectric emission.

(i) For a given photo sensitive material, there is a minimum frequency called the threshold frequency, below which emission of photoelectrons stops completely, however great the intensity may be.

(ii) For a given photosensitive material, the photo electric current is directly proportional to the intensity of the incident radiation, provided the frequency is greater than the threshold frequency.

(iii) The photoelectric emission is an instantaneous process. i.e. there is no time lag between the incidence of radiation and the emission of photo electrons.

(iv) The maximum kinetic energy of the photo electrons is directly proportional to the frequency of incident radiation, but is independent of its intensity.

4.6 *Einstein's photoelectric equation*

In 1905, Albert Einstein, successfully applied quantum theory of radiation to photoelectric effect.

According to Einstein, the emission of photo electron is the result of the interaction between a single photon of the incident radiation and an electron in the metal. When a photon of energy $h\nu$ is incident on a metal surface, its energy is used up in two ways :

(i) A part of the energy of the photon is used in extracting the electron from the surface of metal, since the electrons in the metal are bound to the nucleus. This energy W spent in releasing the photo electron is known as photoelectric work function of the metal. The work function of a photo metal is defined as the minimum amount of energy required to liberate an electron from the metal surface.

(ii) The remaining energy of the photon is used to impart kinetic energy to the liberated electron. If m is the mass of an electron and v, its velocity then

Energy of the incident photon = Work function + Kinetic energy of the electron

$h\nu = W + 1/2\, mv^2$ ...(1)

If the electron does not lose energy by internal collisions, as it escapes from the metal, the entire energy $(h\nu - W)$ will be exhibited as the kinetic energy of the electron. Thus, $(h\nu - W)$ represents the maximum kinetic energy of the ejected photo electron. If v_{max} is the maximum velocity with which the photoelectron can be ejected, then

$h\nu = W + 1/2\, mv^2_{max}$ …(2)

This equation is known as Einstein's photoelectric equation.

When the frequency (ν) of the incident radiation is equal to the threshold frequency (ν_o) of the metal surface, kinetic energy of the electron is zero. Then equation (2) becomes,

$h\nu_o = W$ …(3)

Substituting the value of W in equation (2) we get,

$h\nu - h\nu_o = 1/2\, mv^2_{max}$ (or) $h(\nu - \nu_o) = 1/2\, mv^2_{max}$

This is another form of Einstein's photoelectric equation.

verification of Einstein's photoelectric equation

Einstein's photoelectric equation is, $\frac{1}{2} mv^2 = h(\nu - \nu_o)$

…(1)

If V_o is the stopping potential and e, the electronic charge, then

$\frac{1}{2} mv^2 = eV_o$

…(2)

From equations (1) and (2),

$eV_o = h(\nu - \nu_o)$

or

$$V_o = \left(\frac{h}{e}\right)\nu - \left(\frac{h}{e}\right)\nu_o$$

This is an equation of a straight line. Millikan verified the above equation experimentally and found that it is in harmony with the observed facts.

Experimental verification of Einstein's Photoelectric equation – Millikan's experiment.

Theory. Milikan's experiment is based on what is k now as the "stopping potential ". The stopping potential is the necessary retarding potential difference required in order to just half the most energetic photoelectron emitted.

$$\left.\begin{matrix} The\ K.E\ of\ a\ photoelectron\ leaving\ the\ surface \\ of\ a\ metal\ irradiate\ with\ light\ of\ frequency\ v \end{matrix}\right\} = \frac{1}{2} m v^2_{max} = h\nu - \phi.$$

Let V be the P.D. which is applied between the emitter and a collecting electrode in order to prevent the photoelectron from just leaving the emitter, the emitter being maintained at a positive potential with respect to the collector. Then, $eV=\frac{1}{2}mv_{max}^{2}$.

Therefore, $eV=hv-\phi$

or $V=\frac{h}{e}v - \frac{\phi}{e}$ ………………………….(1)

ϕ is constant for a given metal; h and e are also constants.

Hence, equation (1) represents a straight ling. V is measured for different values of v. A graph is then plotted between the stopping potential (V) taken along the Y-axis and the frequency of light (v) taken along the X-axis. The graph is a straight line. The slope of the straight line

$$\tan\theta = \frac{h}{e}$$

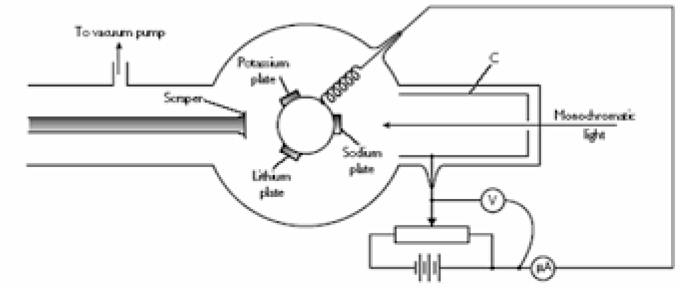
Therefore,

$h = e\tan\theta$ …………………………………………(2)

Hence the value of h.(Plank's constant) can be calculated. The intercept on the X-axis gives the threshold frequency v_0 for the given emitter. From this, photoelectric work function = ϕ =hv_0 can be calculated.

Experiment : Milikan's apparatus is shown in the figure. Alkali metals are employed as emitters, since they readily exhibit photoelectric emission even with visible light. Cylindrical blocks (C) of sodium, postassium or lithium are mounted on a spindle S at the centre of the glass flask G. the flask is evacuated to a very high vacuum to free the metals from all absorbed gases and to prevent their oxidation. The spindle can be rotated from outside by an electromagnet. As each metal block passes by the adjustable sharp edge K, a thin layer of it is removed, thus exposing a fresh surface of the metal to the irradiating light entering the flask through a quartz window W. monochromatic light provided by a spectroscope is used to illuminate the fresh metal surfaces. The photoeelctrons are collected by a Faraday cylinder F. The Faraday cylinder is made of copper oxide which is not photosensitive.

The photocurrent is measured by an electrometer connected to the Faraday cylinder.



The stopping potential of the liberated photoelectrons is measured by raising the emitter surface to a positive potential, just sufficient to prevent any of the electrons from reaching the collector (F). The stopping potential is the positive potential applied to the emitter, which corresponds to zero current in the electrometer. The stopping potential (V) is determined for different wavelengths of the incident light. The value of V should be corrected for any contact potential between the metal (C) and Faraday cylinder (F). On plotting V against v, we get a straight line. Measuring the slope of the straight line, the value of h/e is obtained. Then substituting the known value of e, h is calculated. The value of h calculated in this way agrees fairly well with the value obtained by other methods. Thus the Einstein's equation can be verified experimentally.

4.6 Photoelectric cells

Photoelectric cell is an arrangement to convert light energy into electrical energy. There are three types of photocells, photoemissive, photovoltaic and photoconductive.

(i) **Photo-emissive Cell**. This consists of a glass or quartz bubl(B) according as it is to be used with visible or ultraviolet light. C is the silver cathode in the form of a semi-cylinderical plate. The anode (A) is a rod mounted vertically at the centre of the bulb and parallel to its axis. A positive potential of about 100 volts is applied to the anode, the negative being connected to the cathode through a galvanometer G. when light falls on the cathode C, electrons are ejected from the cathode

. A small current flows through the cell and can be measured by the galvanometer. The photoemissive cell is used for reproduction of sound from photo-films.

(ii) **Photo-voltaic cell**. It consist of a layer of semiconductor material spread over a metallic surface by heat treatment. In one type of the photovoltaic cell, the metal plate is made of copper and the semiconductor is cuprous oxide (Cu_2O). On the other side of the semiconductor, there is a very thin layer of a translucent deposit which allows the semiconductor to be illuminated by radiations. Light falling on the surface film (of gold or silver) penetrates into it and ejects photoelectrons from the semiconductor layer. These electrons travel in a direction opposite to the direction of incident light. The conventional current, therefore, flows in the direction of the incident light. For small values of the resistance of the galvanometer, the current is directly proportional to the intensity of light. No external battery is required to operate a photovoltaic cell as the cell itself generates an e.m.f.

(iii) **Photoconductive Cell**: These cells are based on the principle that the electrical resistance of a semiconductor material, like selenium, decreases with the increase of intensity of radiation incident upon it and conductivity is increased. A film of selenium is deposited on one side of an iron plate and a P.D. of 100 volts is applied between iron and selenium from an external battery. A galvanometer is included in the electric circuit. When a beam of light falls on the selenium film, a delfection will be observed in the galvanometer. As the intensity of the incident light is varied, the resistance of selenium also varies accordingly and the current in the circuit undergoes corresponding variations. The solar battery consists of several thousands photoconductive cells, which produce several kilowatt power.

4.7 Applications of Photoelectric cells:

(i) Exposure meters in photography. An exposure meter is a device to calculate the correct time of exposure. The photoelectric cell in the instrument produces a current proportional to the light falling on it. The current operates a galvanometer, the scale of which is calibrated to read the time of exposure.

(ii) Photo-multiplier: It is based on the principle of secondary emission. When light strikes the surface of photosensitive metal plate C, it causes the ejection of photoelectrons from it. These electrons are then attraced to a metal surface called a dynode, by setting a P.D. between the cathode C and the dynode 1. High energy electrons striking a metal surface can cause the ejection of one or more secondary electrons from the surface. Suppose that a photoelectron striking dynode 1 produces x electrons by secondary emission. These electrons are then directed towards dynode 2 by making its potential higher than that of dynode 1. Suppose x electrons are again ejected by secondary emission for each incident electron. Then, for each electron emitted by the photosensitive plate, there are now x^2 electrons and so on. If there are several dynode, each at a potential higher than the preceding one, an avalanche of electrons reaches the collector plate A. A strong current then flows in the outer circuit. This device is used to amplify very weak light signals.

(iii) Photoelectric cells are used to compare the illuminating powers of two light sources. They are also used in the measurement of the intensity of illumination of a light source.

(iv) Sound reproduction in films. The film is provided with a sound track at on edge. Light passing through the sound track of the film falls on a photocell. Current is produced, which fluctuates correspondingly with the intensity of sound recorded in the sound track. The current impulses are converted to sound by speakers.

(v) Automatic operation of street lights. A photoelectric cell, located in a street light circuit, switches off the street light when sunlight is incident on the cell. When sunlight fades and it becomes dark, the photoelectric cell switches on the street lights.

✍**LEARNING ACTIVITY**

1. **What is Photo electric effect.**
2. **State Laws of photo electric emission.**
3. **What are the applications of Photo electric cells**
4. **Derive an expression for Einstein’s Photo electric equation.**

Note:

a) Write your answer in the space given below.

b) Check the answer with your academic counsellor.

SUMMARY

In this chapter, we studied the Photoelectric effect and its applications. Also detail studied about laws of photo electric emission and photo electric cells and its applications..

Block V

CRYSTAL PHYSICS

STRUCTURE

OVERVIEW

In this Chapter the general static properties of crystals, as well as possibilities to observe crystal structures, are reviewed. We emphasize basic principles of the crystal structure description. More detailed information can be obtained.

LEARNING OBJECTIVES

After completing this Unit, you should be able to:

- Classification of solids
- Seven types of crystal structure and its types.
- various types of defects in crystals

5.1 Introduction

Crystal Physics*' or '*Crystallography' is a branch of physics that deals with the study of all possible types of crystals and the physical properties of crystalline solids by the determination of their actual structure by using X-rays,neutron beams and electron beams. Solids can broadly be classified into two types based on the arrangement of units of matter. The units of matter may be atoms, molecules or ions.

5.2 Types of Solids

They are,

(i) Crystalline solids and (ii) Non-crystalline (or) Amorphous solids

CRYSTALLINE SOLIDS

A crystalline material can either be a single (mono) crystal or a polycrystal. A single crystal consists of only one crystal, whereas the polycrystalline material consists of many crystals separated by well-defined boundaries. Examples Metallic crystals – Cu, Ag, Al, Mg etc, Nonmetallic crystals – Carbon, Silicon, Germanium

NON CRYSTALLINE SOLIDS

In amorphous solids, particles are arranged in an orderly manner. They are randomly distributed. They do not have directional properties and so they are called as `isotropic' substances. They have wide range of melting point and do not possess a regular shape. Examples: Glass, Plastics, Rubber etc.

SINGLE CRYSTALS

Single crystals have a periodic atomic structure across its whole volume. At long range length scales, each atom is related to every other equivalent atom in the structure by translational or rotational symmetry

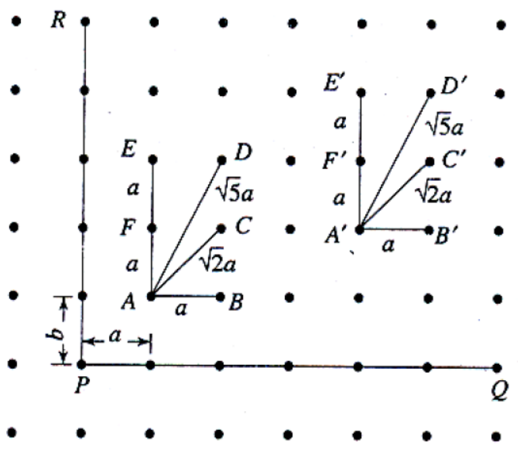
POLYCRYSTALLINE SOLIDS

Polycrystalline materials are made up of an aggregate of **many small single crystals.** They have a high degree of order over many atomic or molecular dimensions. **Grains** are separated by **grain boundaries.** The atomic order can vary from one domain to the next**.** The grains are usually **100 nm - 100 microns in diameter**. Poly crystals with grains less than 10 nm in diameter are **nanocrystalline**

5.3 Space Lattice

A lattice is a regular and periodic arrangement of points in three dimension.It is defined as an infinite array of points in three dimension in which every point has surroundings identical to that of every other point in the array. The Space lattice is otherwise called the Crystal lattice

TWO DIMENSIONAL SPACE LATTICE



BASIS

A crystal structure is formed by associating every lattice point with an unit assembly of atoms or molecules identical in composition, arrangement and orientation.

This unit assembly is called the `***basis***’. When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure. The crystal structure is real, while the lattice is imaginary.

UNIT CELL

A unit cell is defined as a fundamental building block of a crystal structure, which can generate the complete crystal by repeating its own dimensions in various directions.

LATTICE PARAMETERS

The three interfacial angles and their corresponding intercepts are essential. These six parameters are said to be ***lattice parameters***.

Similarly the angles between X and Y and Z axes are denoted by α, β and γ respectively as shown in the above figure. These angles α, β and γ are called as ***interaxial angles or interfacial angles***.

5.4 Crystal systems

The seven systems are,

Cubic

Tetragonal

Orthorhombic

Trigonal (Rhombohedral)

Hexagonal

Monoclinic and

Triclinic

Primitive lattice: It has lattice points only at the corners of the unit cell.

Body centred lattice: It has lattice points at the corners as well as at the body centre of the unit cell.

Face centred lattice : It has lattice points at the corners as well as at the face centres of the unit cell.

Base centred lattice: It has lattice points at the corners as well as at the top and bottom base centres of the unit cell.

THE SEVEN CRYSTAL SYSTEMS WITH ITS LATTICE PARAMETERS.

S.No	**Crystal Systems**	**Lattice Parameters**	**Types of lattice**	**Examples**
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma$	P I F	Po Na, Fe Ag, Au, Cu
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P I	TiO_2 KH_2PO_4
3	Orthohombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P I F C	$C_{15}H_{20}O_2$ $BaSO_4$ KSO_4 α - s
4	Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^\circ\ \gamma \neq 90^\circ$	P C	$CaSO_4\ 2H_2O$ $K_2MgSO_4\ 6H_2O$
5	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	P	$K_2Cr_2\ O_7$
6	Trigonal	$a = b = c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$ (But less than 120°)	P	Calcite
7	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ\ \ \gamma = 120^\circ$	P	Quartz

BRAVIAS LATTICES

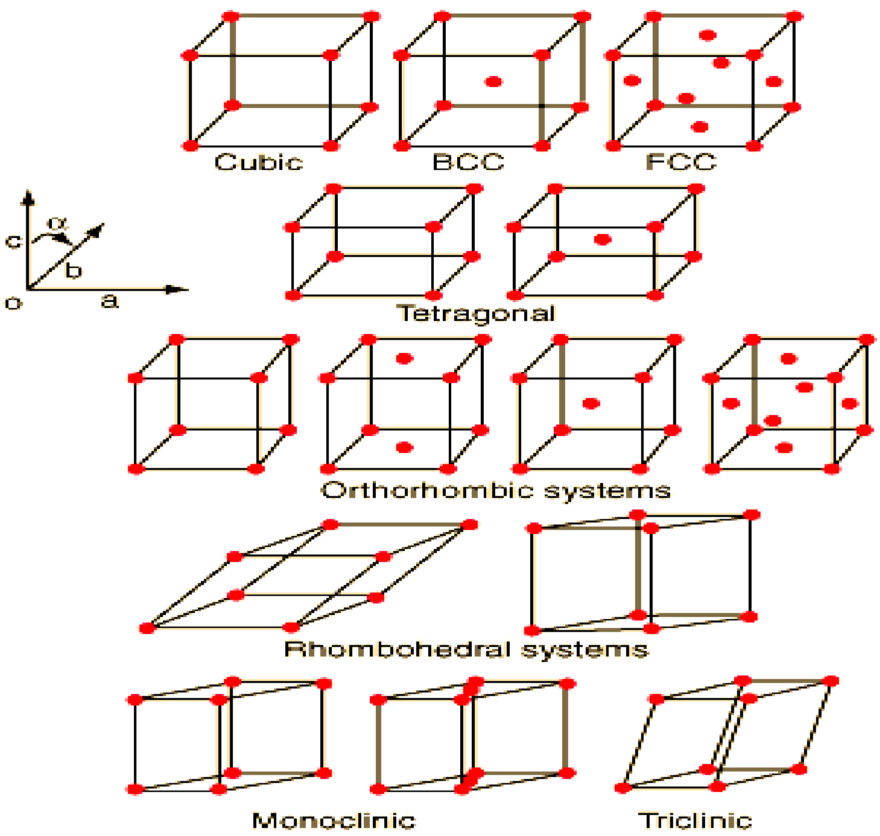
It is found that the point symmetry of crystal lattice can lead to 14 different types of lattices in three dimensional spaces. These 14 different types of arrangement are called Bravais lattices. Each type of this arrangement can be represented by a unit cell. The Bravais lattices formed by unit cells are marked by the following symbols:

Primitive Lattice - P
Body Cenetred Lattice - I
Face Cenetred Lattice - F
Base Cenetred Lattice - C

The 14 Bravais lattices are illustrated in the fig.

The occurrences of the 14 Bravais lattices are given in the following table.

S.No.	**System**	**No.of Bravais lattices**	**Bravais Lattice**
1.	Cubic	3	Simple (or) Primitive, Face centered and Bodycentered
2.	Monoclinic	2	Simple (or) Primitive, Base Centered
3.	Orthorhombic	4	Simple (or) Primitive, Base Centered, Face centered and Body centered
4.	Tetragonal	2	Simple (or) Primitive and Body Centered
5.	Hexagonal	1	Simple (or) Primitive
6.	Trigonal (Rhombohedral)	1	Simple (or) Primitive
7.	Triclinic	1	Simple (or) Primitive
	Total	14	



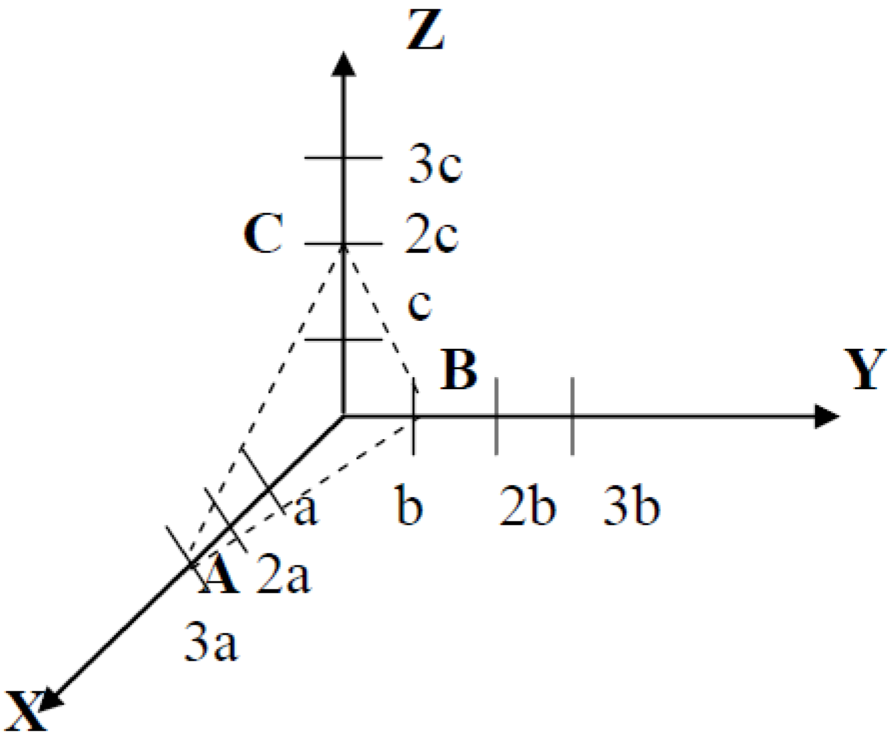
5.5 Miller Indicies

A set of three numbers which is used to designate a plane in a crystal is known as Miller indices.

Steps for finding Miller indices

The steps in determining the Miller indices of a plane are illustrated below.

Let us consider a plane ABC which cuts 3 units along the x – axis, 1 unit along the y – axis and 2 units along the z – axis.



Step 1

Find the intercepts made by the plane ABC along the three axes and express the intercepts interms of multiples of axial lengths. i.e.,

OA : OB : OC = pa : qb : rc

From fig. p = 3, q = 1, and r = 2

$\therefore$ The intercepts are 3a : 1b : 2c

Step 2

Find the coefficients of the intercepts i.e., 3, 1, 2

Step 3

Find the reciprocal of these numbers $\frac{1}{p}:\frac{1}{q}:\frac{1}{r}\, i.e., \frac{1}{3}:\frac{1}{1}:\frac{1}{2}$

Step 4

Convert these reciprocals into whole numbers by multiplying each and every reciprocal with their least common multiplier (LCM).

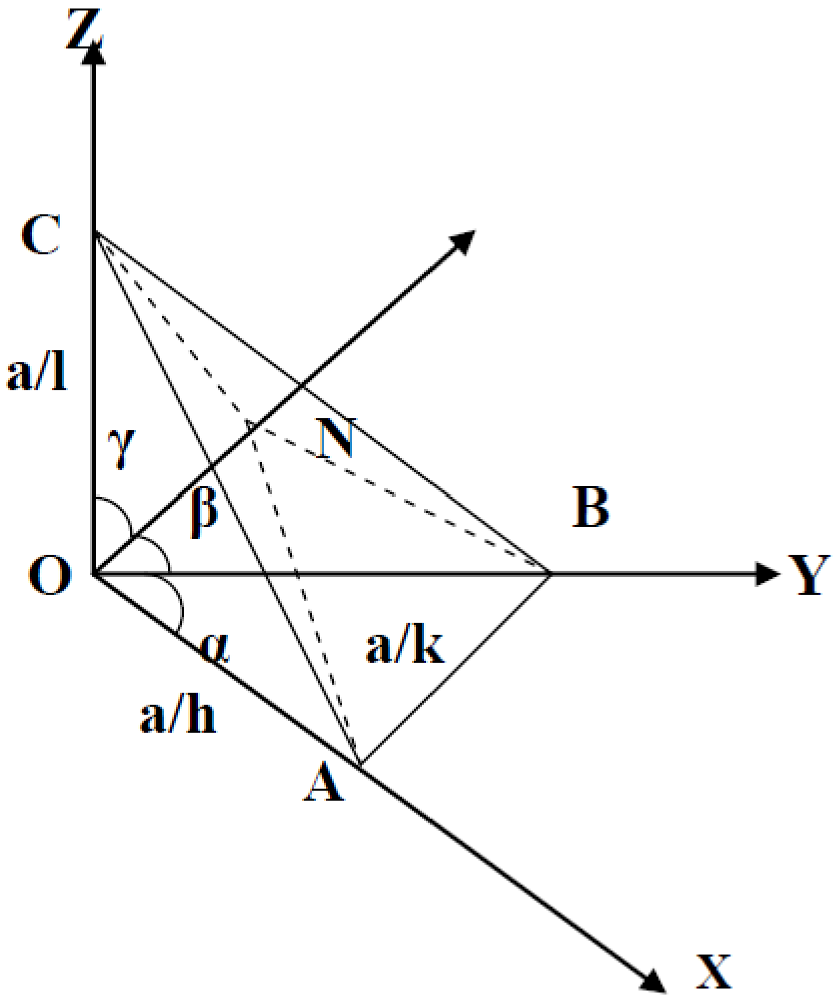
Since 6 is the LCM in this case, we get $6\times\frac{1}{3}\quad 6\times\frac{1}{1}\quad 6\times\frac{1}{2}$

$\therefore$ We have $= 2 \quad 6 \quad 3$

Step 5

Enclose these numbers in a bracket like this ( ) i.e., (2 6 3). This represents the indices of the given plane and is called the Miller indices of the plane.

d spacing in cubic lattice



Let us consider the plane ABC. The plane ABC belongs to a family of planes whose Miller indices are (h k l). Let ON = d i.e., the perpendicular distance to the plane from the origin. Let OA, OB, and OC be the intercepts made by the plane on X, Y and Z axis respectively. Let α, β, γ represents the angle between ON and X, Y and Z axis respectively.

Then the intercepts of the plane on the three axes are,

$$OA = \frac{a}{h}; OB = \frac{a}{k}; OC = \frac{a}{l}$$

Where 'a' is the length of the cube edge.

From Δ ONA,

$$\cos\alpha = \frac{ON}{OA} = \frac{d}{a/h} = \frac{dh}{a}$$

From Δ ONB,

$$\cos\beta = \frac{ON}{OB} = \frac{d}{a/k} = \frac{dk}{a}$$

From Δ ONC,

$$\cos\gamma = \frac{ON}{OC} = \frac{d}{a/l} = \frac{dl}{a}$$

From the law of direction cosines, $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$.

$$\therefore \left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$$

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

$$d^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

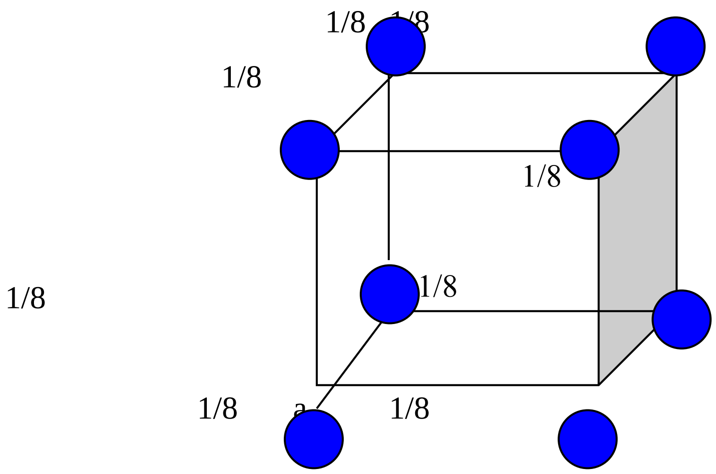
$$\therefore d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

5.6 Crystal Structure

Simple Cubic crystal structure (SC)

1. **Number of atoms per unit cell**

The diagram shows the unit cell of SC structure. In this structure the atoms are only at the corners of the cube.



To form full crystal structure each corner atom is shared by 8 adjoining unit cells. Hence 1/8th part of an atom is present in every corner of the cube. Since there are eight corners,

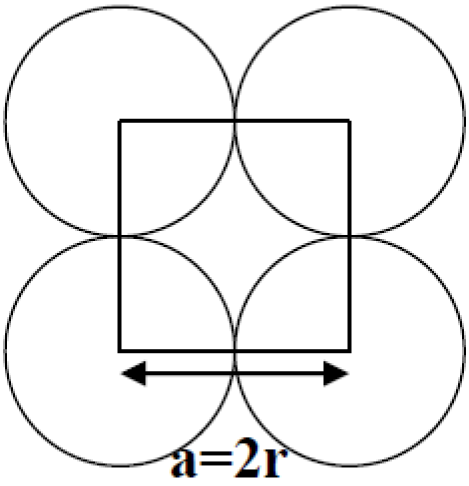
∴total no of atoms $= \frac{1}{8} \times 8 = 1$ atom.

2. Co-ordination Number

Consider one corner atom in a SC structure. This atom is surrounded by 4 nearest neighboring atoms in the same plane and one vertically above the atom and one exactly below the atom.

Hence the coordination number is 4 + 1 + 1 = 6.

3. Atomic Radius



Each corner atom touches each other along the edges of the cube. If ‘r’ is the atomic radius and ‘a’ is the side of the cube, then from the fig.

$a = 2r$

$r = a/2$

4. Packing Factor

$$\text{Packing Factor} = \frac{\text{Volume of all the atoms in the unit cell(v)}}{\text{Volume of the unit cell(V)}}$$

$$\text{Packing Factor} = \frac{\text{number of atoms present in a unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell(V)}}$$

No. of atoms present in the unit cell (SC) = 1

Volume of one atom = $\frac{4}{3}\pi r^3$

Volume of unit cell = a^3 (where 'a' is the side of the cube)

PF = $$\frac{1 \times \frac{4}{3}\pi r^3}{a^3}$$

We know a = 2r. Substitute the value of 'a' in the above equation, we get

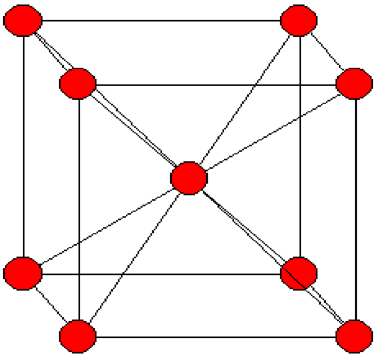
PF = $$\frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} = 0.5236$$

Thus, packing fraction is about 52% and hence this structure is a loosely packed one.

Example: **Polonium**

Body Centred cubic structure (BCC)

1. Number of atoms per unit cell



The diagram shows the unit cell of BCC structure. In this structure the atoms are at the corners of the cube and there is one atom at the centre of the cube. To form full crystal structure each corner atom is shared by 8 adjoining unit cells. Hence 1/8th part of an atom is present in every corner of the cube. Therefore,

Contribution of corner atoms $= \frac{1}{8}\times 8 = 1$ atom.

Contribution of centre atoms $= \frac{1}{2}\times 6 = 3$ atoms.

Total number of atoms / unit cell = 1+3 = 4 atoms.

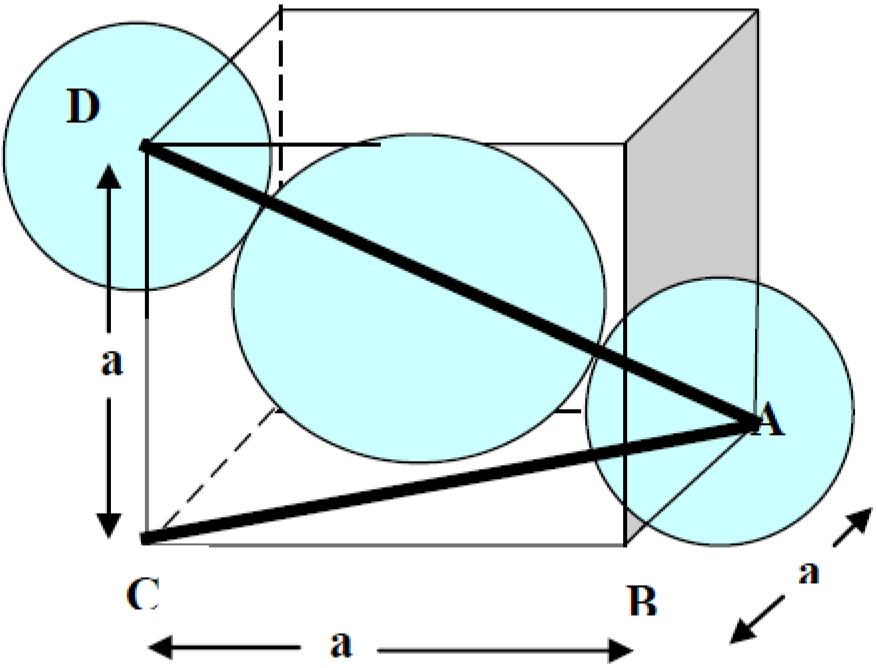
2. Co-ordination Number

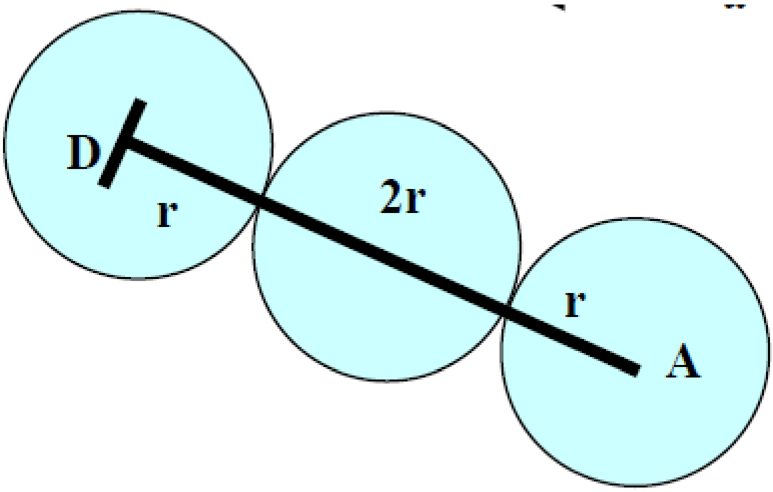
Consider the body centre atom in a BCC structure. This atom is surrounded by the corner atoms only. So the nearest neighbor for a body centre atom is the 8 corner atoms.

Hence the coordination number = 8

3. Atomic Radius

In this structure the unit cell has 8 atoms at the corners of the cube and 1 atom at the centre of the cube. Here the corner atoms do not touch each other, but each corner atom touches the central atom. If ‘r’ is the atomic radius and ‘a’ is the side of the cube, then from the fig.





In triangle ΔADC,

$$AD^2 = AC^2 + DC^2$$

$$= AB^2 + BA^2 + DC^2 \quad \text{(from } \Delta ABC\text{)}$$

$$(4r)^2 = a^2 + a^2 + a^2$$

$$16r^2 = 3a^2$$

$$r^2 = \frac{3a^2}{16}$$

$$\therefore \text{ atomic radius } r = \frac{\sqrt{3}}{4}a$$

4. Packing Factor

$$\text{Packing Factor} = \frac{\text{Volume of all the atoms in the unit cell(v)}}{\text{Volume of the unit cell(V)}}$$

No. of atoms present in the unit cell (BCC) = 2

Volume of one atom = $\frac{4}{3}\pi r^3$

Volume of unit cell = a^3

(where ‘a’ is the side of the cube)

PF = $$\frac{2\times\frac{4}{3}\pi r^3}{a^3}$$

We know $r = \frac{\sqrt{3}}{4}a$

Substitute the value of ‘r’ in the above equation, we get

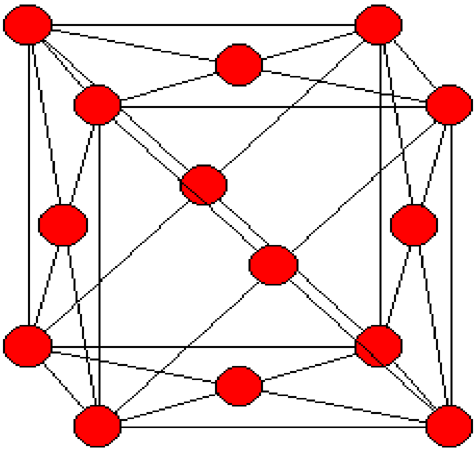
PF = $$\frac{\frac{8}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}}{8}\pi = 0.68$$

Thus, packing fraction is about 68% and hence this structure is not a closely packed one.

Examples: **Tungsten, sodium, iron, and chromium.**

Face Centred Cubic Structure (FCC)

1. Number of atoms per unit cell



The diagram shows the unit cell of FCC structure. In this structure the atoms are at the corners of the cube and there are six atoms at the face centers of the cube. To form full crystal structure each corner atom is shared by 8 adjoining unit cells. Hence 1/8th part of an atom is present in every corner of the cube. Along with this each face centered atom is shared by 2 adjoining unit cells. Therefore,

Contribution of corner atoms $= \frac{1}{8} \times 8 = 1$ atom.

Contribution of face centered atoms $= \frac{1}{2} \times 6 = 3$ atoms.

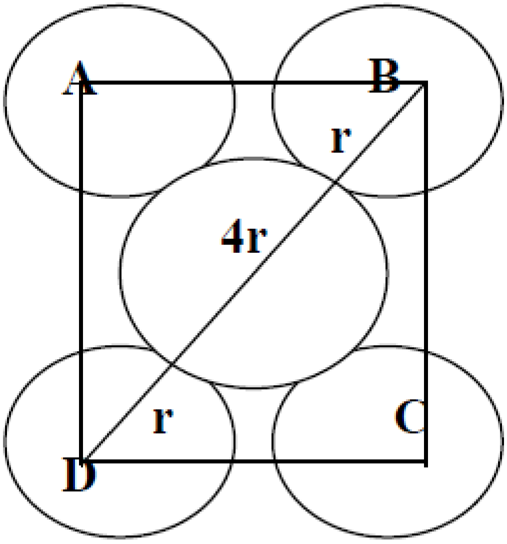
Total number of atoms / unit cell = 1+3 = 4 atoms.

2. Co-ordination Number

In this structure the nearest neighbors of any corner atom are the face centered atoms of the surrounding unit cells. Any corners atom has four such atoms in its own plane, four in the plane above it and four in the plane below it.

Hence the coordination number = 4 + 4 + 4 =12

3. Atomic Radius



In Δ BCD,

$$BD^2 = BC^2 + DC^2$$

$$(4r)^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$r^2 = \frac{2a^2}{16}$$

$$\therefore \text{atomic radius } r = \frac{\sqrt{2}}{4}a$$

4. Packing Factor

$$\text{Packing Factor} = \frac{\text{Volume of all the atoms in the unit cell(v)}}{\text{Volume of the unit cell(V)}}$$

No. of atoms present in the unit cell (FCC) = 4

Volume of one atom = $\frac{4}{3}\pi r^3$

Volume of unit cell = a^3

(where ‘a’ is the side of the cube)

PF = $$\frac{4\times\frac{4}{3}\pi r^3}{a^3}$$

We know $a=\frac{4r}{\sqrt{2}}$. Substitute the value of ‘a’ in the above equation, we get

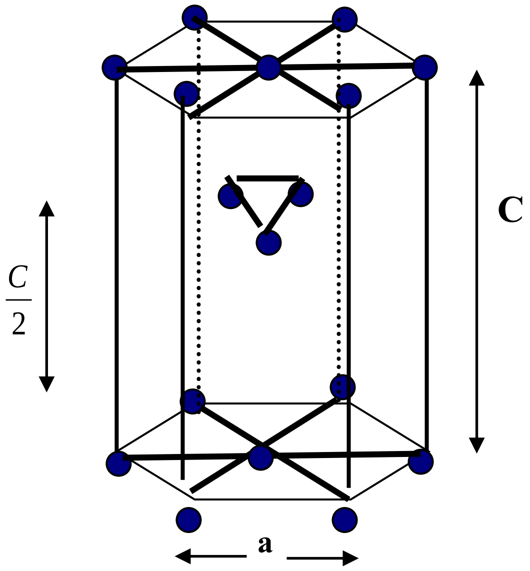
PF = $$\frac{\frac{16}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3}=\frac{\sqrt{2}}{6}\pi=0.74$$

Thus, packing fraction is about 74% and hence this structure has high packing fraction.

<u>Examples:</u> **copper, aluminum, and silver**

Hexagonal Closed Packed Structure (HCP)

1. Number of atoms per unit cell



The diagram shows the unit cell of HCP structure. In this structure there are three layers of atoms in a unit cell. The bottom layer has six corner atom and one face centered atom. Similarly the top layer has same atomic arrangement as the bottom layer. At c/2 distance from the bottom layer there is a middle layer containing three atoms.

Atoms at the top layer = 7

Atoms at the bottom layer = 7

Contribution of corner atoms $= \frac{1}{6} \times 6 = 1$ atom.

Contribution of base atoms $= \frac{1}{2} \times 1 = \frac{1}{2}$ atom

Atoms at the centre of the unit cell = 3 full atoms

Total no. of atoms in an unit cell = top layer + Bottom layer + Centre

$$= \left[1 + \frac{1}{2}\right] + \left[1 + \frac{1}{2}\right] + 3$$

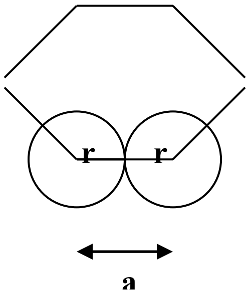
$$\text{Total no. of atoms in an unit cell} = \frac{3}{2} + \frac{3}{2} + 3 = 6\text{atoms}$$

2. Co-ordination Number

Consider the face centered atom in the bottom layer. It is surrounded by six corner atoms. Above the face centered atom there is a layer containing 3 atoms. Similarly below the face centered atom there is a layer containing 3 atoms. So the number of atoms surrounding a given particular atom is 6 + 3 + 3 =12.

Hence the coordination number = 12.

3. Atomic Radius

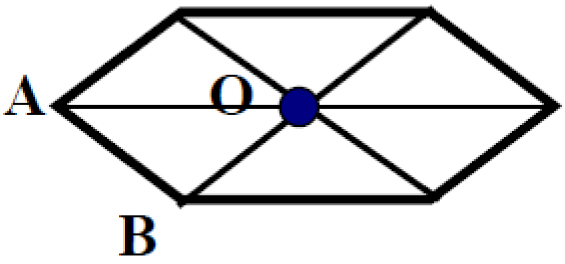


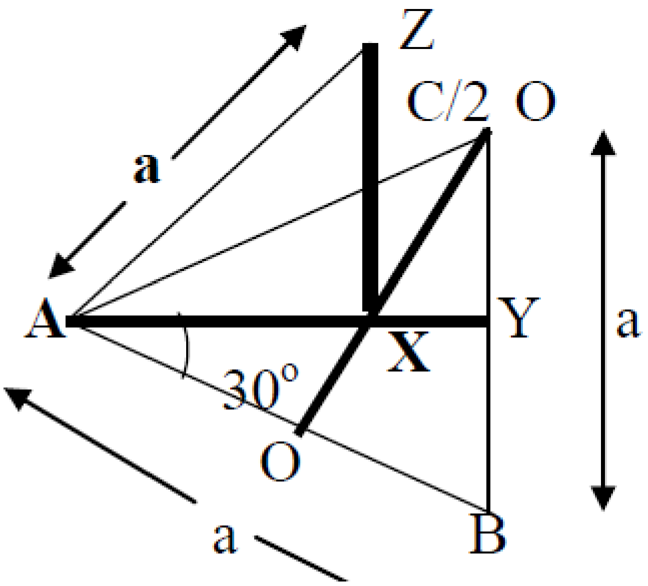
In this structure the atoms touch each other along the edges of hexagon and the face centered atom touches all the corner atoms. If ‘r’ radius of atom and ‘a’ is the side of the hexagon then we can write,

2r = a (or) r = a/2

4. Packing Factor

For calculating packing fraction first we have to calculate (c/a) ratio. Let ‘C’ be the height of the unit cell and ‘a ‘be the Distance between two atoms.





In triangle ABY, $\quad \cos 30^{o} = \dfrac{AY}{AB}$

$$AY = AB \cos 30^{o}$$

$$AY = AB\,\frac{\sqrt{3}}{2}$$

$$AY = a\,\frac{\sqrt{3}}{2} \qquad \text{---------} \ (1)$$

In triangle AXZ,

$$(AZ)\,2 = (AX)\,2 + (XZ)\,2 \qquad \text{---------} \ (2)$$

$$a2 = (AX)\,2 + \left(\frac{C}{2}\right)^2$$

$$a2 = (AX)\,2 + \left(\frac{C^2}{4}\right) \qquad \text{---------} \ (3)$$

$$\text{But} \quad AX = \frac{2}{3}\,AY \quad \text{(from the figure)}$$

$$AX = \frac{2}{3}\,a\,\frac{\sqrt{3}}{2}$$

$$AX = \frac{a}{\sqrt{3}} \qquad \text{----------} \ (4)$$

□□□Substitute equation (4) in equation (3)

$$a2 = \left[\frac{a}{\sqrt{3}}\right]^2 + \left(\frac{C^2}{4}\right)$$

$$a2 = \frac{a^2}{3} + \left(\frac{C^2}{4}\right)$$

$$\left(\frac{C^2}{4}\right) = a^2 - \left(\frac{a^2}{3}\right)$$

$$\left(\frac{C^2}{4}\right) = a^2 \left(1 - \left[\frac{1}{3}\right]\right)$$

$$\frac{C^2}{a^2} = \frac{8}{3}$$

$$\boxed{\frac{C}{a} = \sqrt{\frac{8}{3}}} \quad \text{or} \quad \boxed{\frac{C}{a} = \mathbf{1.63}} \quad -\ (\ 5\ )$$

4. Packing Factor

$$\text{Packing Factor} = \frac{\text{Volume of all the atoms in the unit cell(v)}}{\text{Volume of the unit cell(V)}}$$

No. of atoms present in the unit cell (HCP) = 6

Volume of one atom = $\frac{4}{3}\pi r^3$

Volume of unit cell = Area of the base x height

= 6 X area of triangle ABO **X** height of unit cell (bottom area of hexagon is divided into six triangles)

V = 6 x $\frac{1}{2}$ x BO x AY x height of unit cell

= 6 x $\frac{1}{2}$ x a x a $\frac{\sqrt{3}}{2}$ x C (BO = a,AY= a $\frac{\sqrt{3}}{2}$ &height of unit cell = C)

□□Volume (V) of the HCP unit cell = 3a2 $\frac{\sqrt{3}}{2}$ C

□ Packing factor (APF) = $\dfrac{6 \times \frac{4}{3}\pi r^3}{3a^2 \frac{\sqrt{3}}{2} C}$

Put r = a / 2, $$= \frac{6 \times \frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{3a^2 \frac{\sqrt{3}}{2} C}$$

PF $$= \frac{\frac{8\pi a^3}{8}}{\frac{3a^2\sqrt{3}C}{2}}$$

But C = a $\sqrt{\frac{8}{3}}$, $\therefore$ PF $$= \frac{2\pi a^3}{3\sqrt{3}a^2 a\sqrt{8/3}}$$

PF $$= \frac{2\pi}{3\sqrt{8}}$$

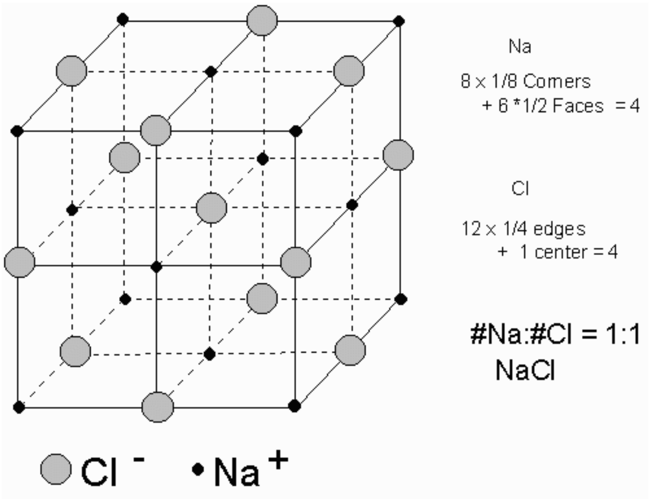
PF = 0.74 = 74%

Thus packing factor for HCP is 74%. Hence it is closely packed structure.

Examples: Zinc, Cadmium, Zirconium, Magnesium, Titanium, Berylium

Sodium Chloride Structure (NaCl)

Sodium chloride is an ionic crystal. It has **FCC structure** with a basis of one Na^+ ion and one Cl^- ion in an alternate fashion. Most of the alkali halides and sulphides exhibit this type of structure.



Structure Composition

The Cl^- ions are situated at the corners as well as at the centers of the faces of the cube. The Na^+ **ions** are situated exactly at the midpoint of the axial length of the unit cell along each axis. Thus, NaCl crystal can be thought to be composed of two FCC sub lattices. One of Cl^- ion having the origin of (0, 0, 0) and the other of Na^+ **ion** having the origin (1/2, 0, 0).

Let us discuss the important parameters of the NaCl crystal.

Number of Atoms per Unit Cell

In this NaCl structure, we have two types of ions namely Na^+ and Cl^-. Let us find the number of sodium ions and chlorine ions separately.

(i) Number of Na^+ ions per unit cell

Here we have two types of Na^+ ions, namely,

(a) Midpoint Na^+ ions

(b) Body centered Na^+ ion

(a) Each Na^+ ions situated at the mid point of the axial length is shared by 4 unit cells. Similarly, we have 12 midpoint Na^+ ions.

∴ Number of midpoint Na^+ ions per unit cell $= \frac{1}{4}\times 12 = 3$ ions.

(b) Each body centered Na^+ ion is shared by that particular unit cell alone.

$\therefore$ Number of body centered Na^+ ion per unit cell $= \frac{1}{1} \times 1 = 1$ ion.

$\therefore$ Total number of Na^+ ions per unit cell = 3 + 1 = 4 ions.

(ii) Number of Cl^- ions per unit cell

Here, we have two types of Cl^- ion namely,

(a) Corner Cl^- ions

(b) Face centered Cl^- ions

(a) Each corner Cl^- ions is shared by 8 unit cells. Similarly, we have 8 such corner ions.

$\therefore$ Number of corner Cl^- ions per unit cell $= \frac{1}{8} \times 8 = 1$ ion.

(b) Each face centered Cl^- ions is shared by 2 unit cells. Similarly, we have 6 face centered Cl^- ions.

$\therefore$ Number of face centered Cl^- ions per unit cell $= \frac{1}{2} \times 6 = 3$ ions.

$\therefore$ Total number of Cl^- ions per unit cell = 3 + 1 = 4 ions.

Thus, there are 4 Na^+ ions and 4 Cl^- ions per unit cell in a NaCl crystal.

<u>**Coordination number**</u>

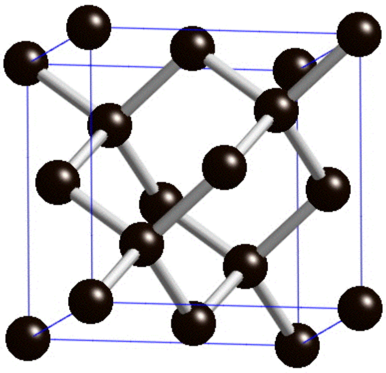
Each Cl^- ions has 6 Na^+ ions as nearest neighbors. Similarly, each Na^+ ion has 6 Cl^- ions as nearest neighbors. Hence, the coordination number of NAACO for opposite kind of ions is 6.

Atomic radius

The distance between any two nearest neighbors is a/2.

***Examples*: KCl, KBr, CaO, etc.**

Diamond structure



Diamond structure is formed due to the combination of two interpenetrating FCC sub lattices, having the origin (0, 0, 0) and (1/4, 1/4, 1/4) along the body diagonal.

Let us discuss the important parameters of the diamond structure.

Number of Atoms per Unit Cell

In diamond we have 3 types of atoms viz.,

(i) Corner atoms, represented by ‘c

(ii) Face centered atoms represented by ‘F’

(iii) Four atoms present inside the unit cell represented as 1, 2, 3, and 4.

(i) Number of corner atoms per unit cell

Each corner atom is shared by 8 unit cells. Similarly, we have 8 corners atoms in an unit cell.

∴ Number of corner atoms per unit cell $= \frac{1}{8} \times 8 = 1$ atom.

(ii) Number of face centered atoms per unit cell

Each face centered atom is shared by 2 unit cell. Similarly, we have 6 face centered atoms.

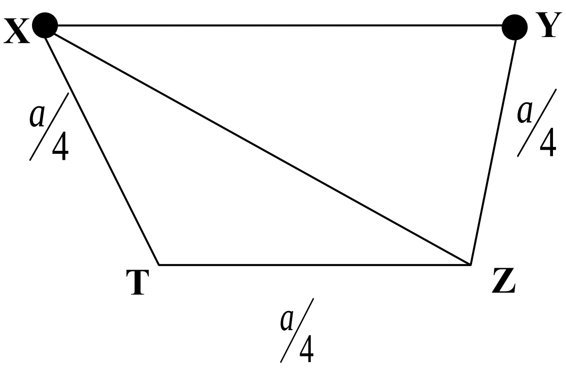
$\therefore$ Number of face centered atoms per unit cell $= \frac{1}{2} \times 6 = 3$ atoms.

(iii) Number of atoms inside the unit cell

Inside the unit cell we have 4 atoms, represented by 1, 2, 3, 4 which is shared by that particular unit cell alone.

$\therefore$ **Total number of atoms per unit cell = 1 + 3 + 4 = 8 atoms.**

Atomic radius



Here, the corner atoms do not have contact with each other and the face centered atoms also do not have contact with the corner atoms. But both the face centered atoms and the corner atoms has contact with the 4 atoms (1, 2, 3, 4) situated inside the unit cell.

From the diagram,

$$XY^2 = XZ^2 + ZY^2$$

$$= XT^2 + TZ^2 + ZY^2$$

$$XY^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2$$

$$XY^2 = \frac{3a^2}{16}$$

Since XY = 2r, we can write,

$$(2r)^2 = \frac{3a^2}{16}$$

$$4r^2 = \frac{3a^2}{16}$$

$$r^2 = \frac{3a^2}{64}$$

$$r = \frac{a\sqrt{3}}{8}$$

Coordination number

Coordination number of diamond is 4.

Packing factor

$$\text{Packing Factor} = \frac{\text{Volume of all the atoms in the unit cell(v)}}{\text{Volume of the unit cell(V)}}$$

No. of atoms present in the unit cell = 8

Volume of one atom = $\frac{4}{3}\pi r^3$

Volume of unit cell = a^3 (where ‘a’ is the side of the cube)

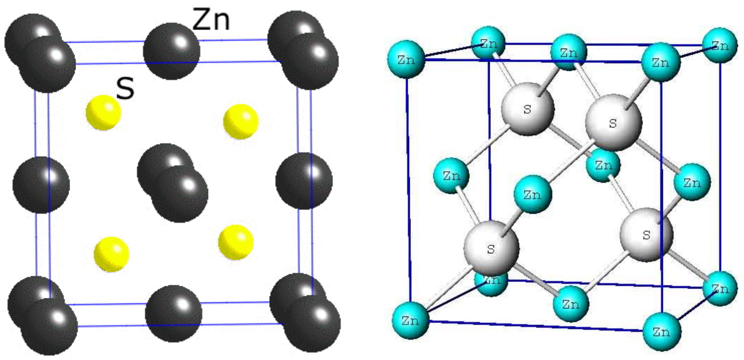
$$\text{PF} = \frac{8\times\frac{4}{3}\pi r^3}{a^3}$$

We know $a = \frac{8r}{\sqrt{3}}$, so the above equation becomes,

$$\text{PF} = \frac{32\pi r^3 3\sqrt{3}}{3(8r)^3} = 0.34 = 34\%$$

Since the packing factor is very low, it is termed as diamond has very loosely packed structure.

Zinc Sulphide Structure

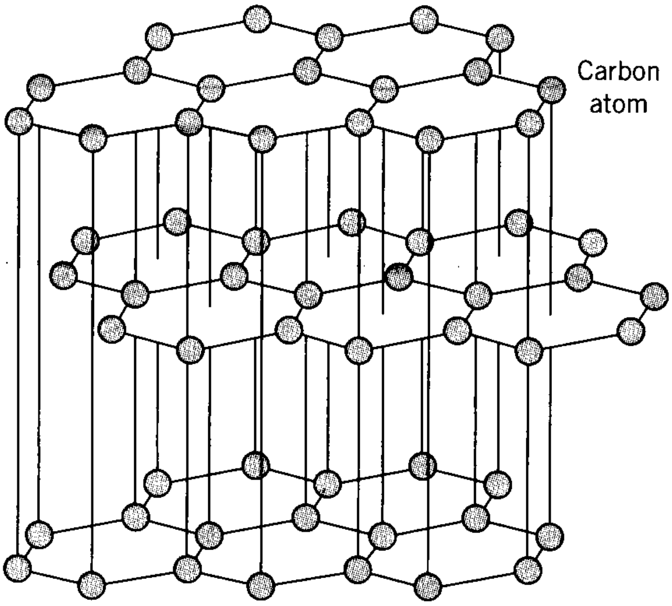


The zinc sulphide structure has a similar structure to that of a diamond. We know that the diamond structure is made by carbon atoms (corner + face centered + 4 atoms inside the unit cell). In the diamond structure if the corner and face centered atoms are replaced by sulphur (S^-) atoms and the four atoms present inside the unit cell are replaced by zinc (Zn^+) atoms, then we get zinc sulphide structure. It also has the coordination number as 4.

Graphite Structure

The above diagram shows the graphite structure. In the case of graphite, carbon atoms are arranged in regular hexagons in flat parallel layers such that each atom is linked by the neighbouring atoms.

However there is no strong bonding between different layers which are therefore easily separable from each other. This is the cause of softness and lubricating action of graphite.



Meanwhile in each hexagonal layer, the carbon atoms are united by covalent bonds or by metallic bonds by loosing one valence electron. Due to the presence of metallic bonds, the graphite acts as a good electrical conductor.

The carbon atoms are arranged in layer or sheet molecular structure. Graphite is formed when carbon atoms use only three of their possible covalent bonds. Thus they leave one valence electron per atom and that electro helps to form metallic type bond which holds the sheets together with a spacing of about 3.4 A^o. But the carbon atoms in the layer are covalent bonded and spacing between the atoms in the layer is about 1.42 A^o.

POLYMORPHISM AND ALLOTROPY.

Polymorphism

Definition

A substance that can exist in two or more forms in the same state is called polymorphism. (or) The ability of a material to have more than one structure is called polymorphism.

Explanation

Mercury II iodide can be found in either red or yellow form. The two types of crystal are polymorphs. So, Mercury II iodide exhibits polymorphism.

The red form is energetically stable below 126ºC; the yellow form is energetically stable above 126 ºC. At 126 ºC the two forms can change into one another. This temperature is the transition temperature.

Examples

S.No.	**Substances**	**Form – I**	**Form – II**	**Transition temperature**
1.	MercuryII iodide	HgI_2 (s) Red	HgI_2 (s) yellow	126 ºC
2.	Ammonium Chloride	NH_4Cl (s) Cesium Chloride structure	NH_4Cl (s) Sodium Chloride structure	184 ºC

Allotropy

Definition

An element that can exist in two or more forms in the same state is called allotropy. (or) If the change in structure is reversible, then the polymorphic change is known as allotropy.

Explanation

Sulphur has two allotropes, called rhombic and monoclinic sulphur. They can be distinguished by the shape of their crystals or by measuring their densities.

Rhombic sulphur is energetically stable below 95.5ºC and monoclinic sulphur is energetically stable above this temperature. Therefore sulphur is an element that shows **enantiotropy.**

Examples

S.No.	**Element**	**Form – I**	**Form – II**	**Transition temperature**
1.	Sulphur	S_8(s) rhombic	S_8(s) monoclinic	95.5 ºC
2.	Carbon	C (s) graphite	Cl (s) diamond	-
3.	Tin	Stable Sn (s) grey	Metastable Sn (s) white	13.2 ºC

Crystal defects

In an ideal crystal, the atomic arrangement is perfectly regular and continuous throughout. But real crystals are never perfect; lattice distortion and various imperfections, irregularities or defects generally present in them. The mechanical, electrical and magnetic properties of engineering crystalline solids, particularly metals and alloys, are affected by the imperfections in the crystals.

If atoms in the solid are not arranged in a perfectly regular manner, it is called defects in crystals.

The various types of structural imperfections or defects in crystals are classified as follows:

1. Point defects (or) Zero dimensional defects
    a. Vacancies
        i. Schottky defect
        ii. Frenkel defect
    b. Interstitial atoms
    c. Impurities
        i. Substitutional Impurity
        ii. Interstitial Impurity

2. Line defects (or) One dimensional defects
    a. Edge dislocation
    b. Screw dislocation

3. Surface defects (or) Place defects (or) two dimensional defects
    a. Grain boundaries
    b. Tilt boundaries
    c. Twin boundaries
    d. Stacking faults

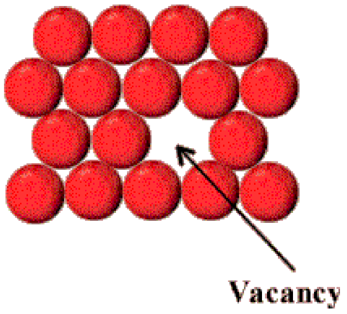
1. ***Point defects***

Point defect is also called zero dimensional imperfections. In a crystal lattice, point defect is one which is completely local in its effect, e.g. a vacant lattice site. The introduction of point defect into a crystal increases its internal energy as compared to that of the perfect crystal. They change the electrical resistance of a crystal.

Point defects are created during crystal growth and application of thermal energy, mechanical stress or electric field. Further they are created by irradiating the crystal by x-ray, microwaves and light.

Different types of point defects are described below.

a. Vacancies



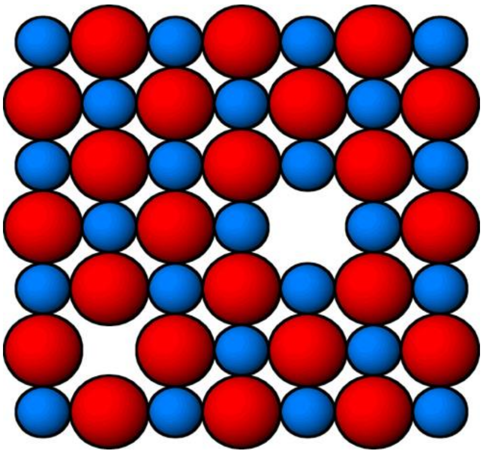
A vacancy is the simplest point defect in a crystal. This refers to a missing atom (or) a vacant atomic site. Such defects may arise either from imperfect packing density crystallization process or from thermal vibration of atoms at high temperature.
Vacancy may also occur if an atom leaves its own site and dissolved interstitially into the structures. The vacancies may be single or deviancies or trivacancies and so on.

Vacancies are classified into two types as follows.

(i) Schottky defect

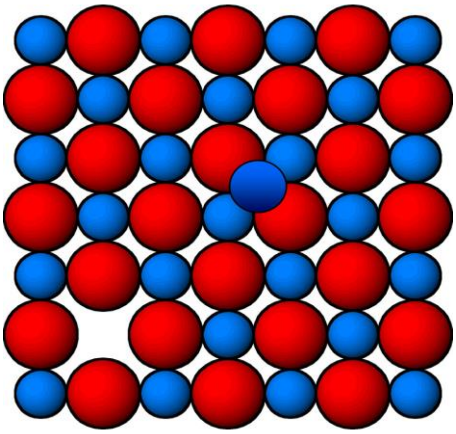
(ii) Frenkel defect

(i) Schottky defect



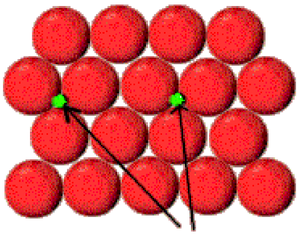
Schottky vacancies refer to the missing of anion and cation. In general the missing of pair of ions in ionic crystal is called schottky defect. This defect is the combination of one action vacancy and one anion vacancy. The concentration of Schottky defect decreases the density of the crystal. This type of point defect is dominant in alkali halides.

(ii) Frenkel defect

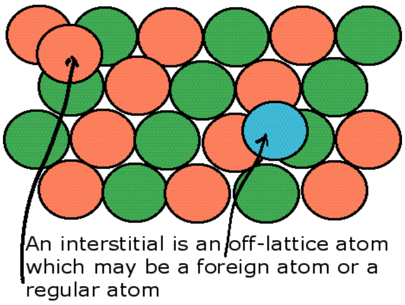


Frenkel vacancies refer to the shift of cation from the regular site to interstitial site. As cations are generally the smaller ions, it is possible for them to get displaced into the void space present in the lattice. The concentration of Frenkel defects does not change the density of the crystal and the overall electrical neutrality of the crystal. The point defect in silver halides and calcium fluoride are of the Frenkel type.

b.Interstitial atoms



Interstitial Atoms



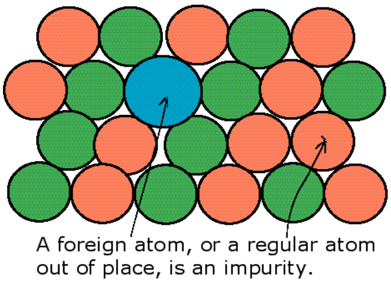
This is an extra atom inserted into the voids between the regularly occupied sites. Thus such an atom does not occupy regular lattice sites. This extra tom may be an impurity atom or an atom of the same types as on the regular lattice sites.

C. Impurities

This is a defect in which a foreign atom occupies a regular lattice site. Foreign atoms generally have atomic radii and electronic structures differing from those of the host atoms and therefore act as centers of distortion.

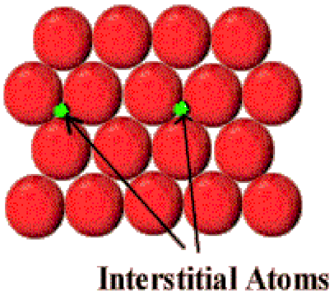
Basically there are two types of impurity defects.

i. **Subtitutional impurity** refers to a foreign atom substitutes or replaces a parent atom in the lattice.



Example: In the case of semiconductor technology, Aluminum and phosphorus doped in silicon are substitutional impurities in the crystal.

ii. Interstitial impurity is a small sized atom occupying the void space in the parent crystal, without dislodging any of the parent atoms from their sites. An atom can enter the interstitial or void space only when it is substantially smaller than the parent atom.



Example: Presence of carbon in iron

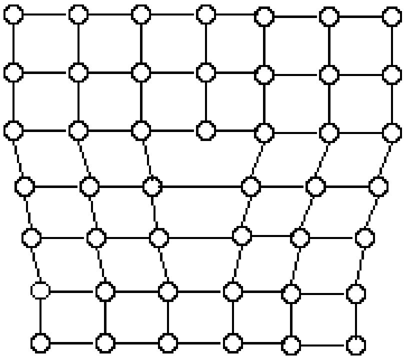
2. *Line defects*

Line defects are called dislocations. A dislocation may be defined as a disturbed region between two substantially perfect parts of a crystal. It is a line defect in a crystal structure whereby a part-plane of atoms is displaced from its symmetrically stable positions in the array. Dislocation is the region of localized lattice disturbance separating the slipped and unslipped regions of a crystal. Movement of dislocation is necessary for plastic deformation.

The two basic types of dislocations are:

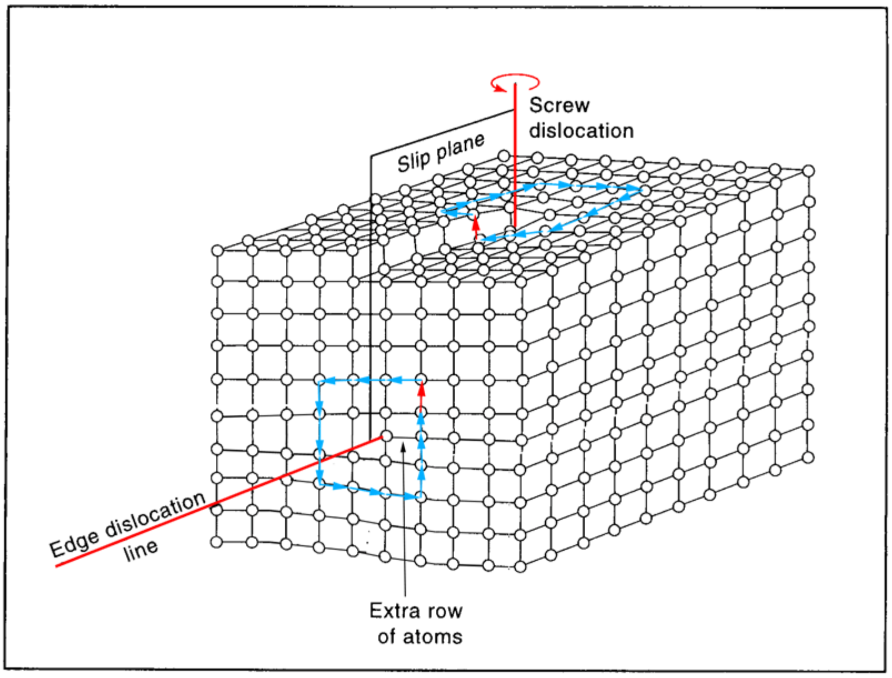
a) Edge dislocation
b) Screw dislocation

a) Edge dislocation



An edge dislocation is a defect where an extra half-plane of atoms is introduced mid way through the crystal, distorting nearby planes of atoms. When enough force is applied from one side of the crystal structure, this extra plane passes through planes of atoms breaking and joining bonds with them until it reaches the grain boundary.

b) Screw dislocation



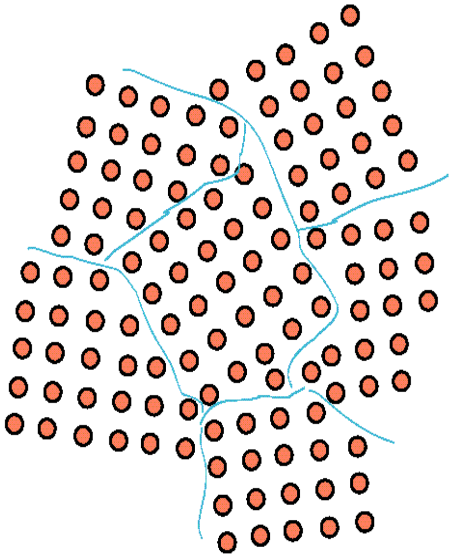
Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line. When the atoms are displaced in two separate planes perpendicular to each other, the imperfection produced is called screw dislocation.

The diagram shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminates within the crystal. The row of atoms marking the termination of the displacement is the screw dislocation.

3. ***Surface Defects***

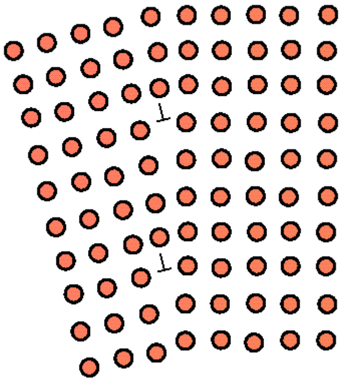
The defects, which take place on the surface of a material, are known as surface defects or plane defects. The surface defects take place either due to imperfect packing of atoms during crystallization or defective orientation of the surface.

a. Grain Boundary



It is a general planar defect that separates regions of different crystalline orientation (i.e., grains) within a polycrystalline solid. The atoms in the grain boundary will not be in perfect crystalline arrangement. Grain boundaries are observed during the solidification of polycrystalline material. Grain boundary area depends on the grain size of the material and increases with decrease in grain size and vice versa.

b. Tilt Boundaries



It is also called as a small angle boundary as the orientation of grains in two neighboring crystals differs by only a few degrees. By rotation of an axis in the boundary it is possible to bring the axis of two ordering grains into coincidence, i.e, a tilt boundary, in which case

Tan θ = b/h (or) θ = b/h

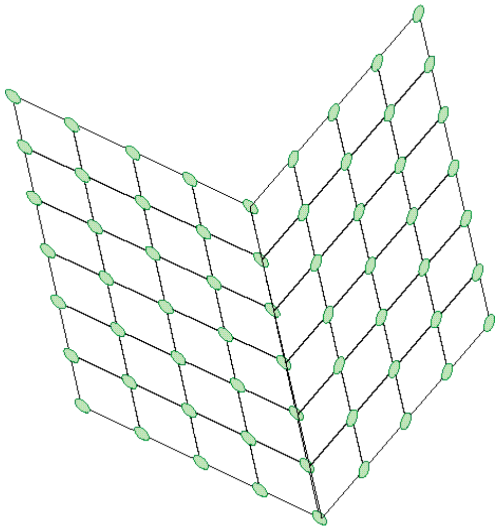
Where, b is the length of the Burgers vector

h is the vertical spacing between two neighbouring edge dislocations.

θ is the angle of tilt

These defects affect the deformation behavior, mechanical properties and recrystallisation temperature of materials. They also have an influence on electrical properties and corrosion resistance.

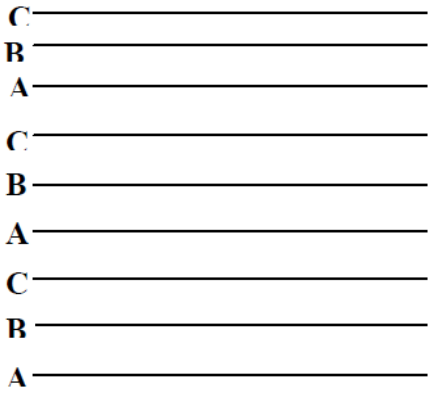
c. Twin boundaries

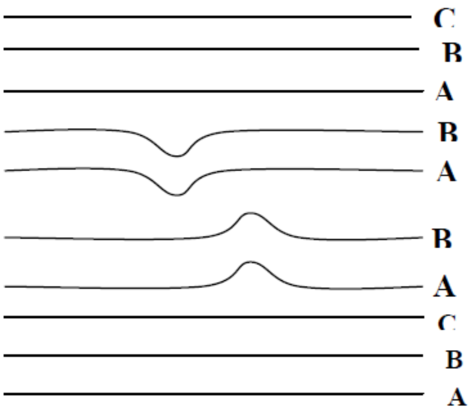


A ‘twin’ is an area defect wherein a mirror image of the regular lattice is formed during the growth of the silicon ingot, usually caused by a perturbation. The twin boundary is the mirror plane of the twin formation.

d. Stacking faults

A defect in a face – centered cubic or hexagonal close – packed crystal in which there is a change from the regular sequence of positions of atomic planes is called **stacking fault**.





For example in the case of closed packed FCC structure the stacking sequence can be written as ABC ABC ….. In that sequence, it is possible in one atom layer ‘A’ the atoms are not positioned properly in a small region and hence deviates from the sequence, relative to the atoms of the layers above and below giving a defect, since now there is sequence of ABAB… which belongs to HCP structure instead of ABC ABC….

The above diagram shows the stacking fault in FCC metal. So stacking fault arise when there is only small dissimilarity between the stacking sequences of closed planes in FCC and HCP metals. Stacking faults are more frequently found in deformed metals than in annealed metals.

✍**LEARNING ACTIVITY**

1. **What is crystalline solids.**
2. **What is braves lattice.**
3. **Derive the expression for co ordination number for /Sc and FCC structure.**
4. **Derive an expression for packing factor of HCP structure.**

Note:

a) Write your answer in the space given below.

b) Check the answer with your academic counsellor.

SUMMARY

In this chapter, we studied the types of solids with examples. Also detail studied about crystal structure of various compounds.