# UNIT 11 X-RAY SPECTRA

## Structure



## 11.1 INTRODUCTION

In Unit 10, you have studied the optical spectra of atoms. You know that optical spectra results when electrons in the outer open subshells make a transition from excited states to the ground state; the photons emitted in this process have wavelengths in the visible region. In this sense, observation of optical spectra supports the theory of atomic shell structure. But optical spectra are not the only source of information about the shell structure of atoms. As we have said in Unit 10, the transitions of electrons in inner shells result in X-ray spectra.

Therefore, in the last unit of the block we focus our attention on X-rays. Now, in order to generate X-rays an anticathode in a vacuum tube is bombarded by high energy electrons. Such a bombardment produces two types of X-rays. One of them has a continuous spectrum and is produced due to the deceleration of the charged electrons inside the anticathode. The highest frequency of such X-rays is given by $E/h$, where E is the kinetic energy of the bombarding electrons. The intensity distribution of these X-rays as a function of the frequency depends little on the material of the anticathode. This phenomenon is known as **Bremsstrahlung.**

Simultaneously, a second type of X-rays are also produced. Their frequencies are characteristic of the material of the anticathode. Hence they are known as **characteristic** X-rays. It is the study of characteristic X-rays that leads to the determination of the atomic structure. In this unit we are interested in **characteristic** X-rays which are discrete in nature and are produced by transitions involving the inner shells of atoms. You may know that the X-ray part of the electromagnetic spectrum extends from wavelengths of about $10^{-9}$ m to wavelengths about $6 \times 10^{-14}$ m corresponding to frequencies between about $3 \times 10^{17}$ Hz and $5 \times 10^{23}$ Hz. The energy of X-ray photons lies in the range of $1.2 \times 10^{3}$ eV to about $2.4 \times 10^{7}$ eV. These energies correspond to differences in inner shell electron energies. So, in Sec. 11.2 we shall discuss the atomic transitions responsible for X-ray spectra and the relevant selection rules.

Moseley used the shell model to analyze X-ray spectra of many elements and demonstrated the connection between the atomic number and the frequencies emitted. You will study this relationship known as Moseley's law in Sec. 11.3.

Finally, in the last section of this unit we present a brief discussion of the applications of X-rays, in medicine, materials science, astronomy and industry.

### Objectives

After studying this unit you should be able to

- determine X-ray terms and the allowed atomic transitions which produce characteristic X-rays,

- apply Moseley's law,
- discuss applications of X-rays.

## 11.2 X-RAY SPECTRA AND SELECTION RULES

X-ray spectra are associated with complex atoms containing many electrons. Characteristic X-rays (Fig. 11.1) are produced when electrons in the inner shells of the atoms **make transitions** from one state to another. In order to facilitate our study let us first learn the X-ray **terms.** In X-ray nomenclature, the inner-most shell of an **atom** ($n$ = 1) is known as the K shell. The next shell, **i.e.**, $n$ = 2 is termed the L shell. However, you know that for $n$ = 2, $l$ has two values **0** and **1** and therefore, for $s$ = 112, we have $j$ = **1/2** and 312. Thus we have three **terms** given by $2\,^2S_{1/2}$, $2\,^2P_{1/2}$ and $2\,^2P_{3/2}$. All the three terms have slightly different energies and in X-ray nomenclature they are known as $L_I$, $L_{II}$ and $L_{III}$ subshells. Similarly for $n$ = 3 shell, $l$ has three values 0, 1 and 2 and correspondingly $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. Thus, this shell has five subshells ($3\,^2S_{1/2}$, $3\,^2P_{1/2}$, $3\,^2P_{3/2}$, $3\,^2D_{3/2}$, $3\,^2D_{5/2}$) denoted by $M_I$ to $M_V$. You may like to determine certain X-ray terms yourself.

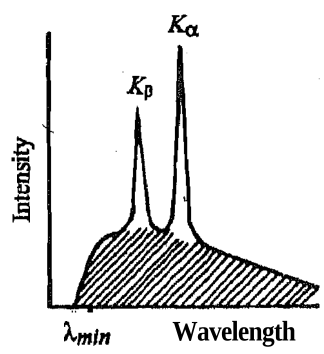


**Fig. 11.1:** X-ray **spectrum.**

### SAQ 1

*Spend 5 min*

Show that there will be seven subshells for $n$ = 4 shell and give all the spectroscopic tenns and their X-ray nomenclature.

We have listed some of the X-ray subshells with the **corresponding** values of $n$, 1 and **j** and spectroscopic terms in Table **11.1.**

**Table 11.1: X-ray terms**

| Subshell | $n$ | I | $j$ | Term |
|---|---|---|---|---|
| $K$ | 1 | 0 | 1/2 | $1\,^2S_{1/2}$ |
| $L_I$ | 2 | 0 | 1/2 | $2\,^2S_{1/2}$ |
| $L_{II}$ | 2 | 1 | 1/2 | $2\,^2P_{1/2}$ |
| $L_{III}$ | 2 | 1 | 3/2 | $2\,^2P_{3/2}$ |
| $M_I$ | 3 | 0 | 1/2 | $3\,^2S_{1/2}$ |
| $M_{II}$ | 3 | 1 | 1/2 | $3\,^2P_{1/2}$ |
| $M_{III}$ | 3 | 1 | 3/2 | $3\,^2P_{3/2}$ |
| $M_{IV}$ | 3 | 2 | 3/2 | $3\,^2D_{3/2}$ |
| $M_V$ | 3 | 2 | 5/2 | $3\,^2D_{5/2}$ |

The corresponding energy level diagram is shown in Fig. **11.2.** Study both Table 11.1 and Fig. 11.2 before proceeding further.

You may now **ask:** How are X-rays produced? Are all the transitions between the inner energy levels allowed or do there exist certain selection rules as in the case of optical spectra? Let us find the answer to these **questions.**

In its **normal** state an atom has two **electrons** in its K shell. Suppose one of the K shell electron is taken out of the atom by some process, such as the bombardment of the target in an X-ray tube. The collision causes the ejection of an atomic electron from the K shell. **The** atom is singly ionized and has one hole (vacancy) in its K shell. Such an ion is in a highly excited **state. The** ion **deexcites** when one of the remaining electrons makes a quantum jump from an outer energy state and fills the vacancy left by the

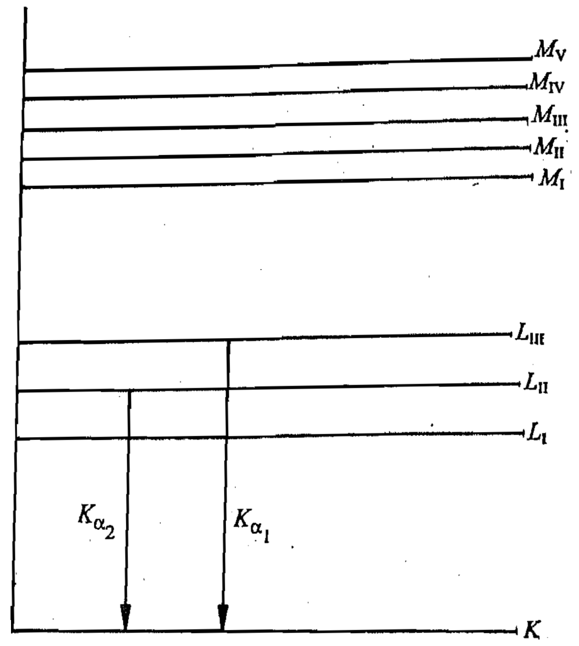


**Fig. 11.2: Some *X*-ray terms and $K_\alpha$ lines.**

ejected electron. In the process of stabilisation, a number of transitions of the atomic electrons from the upper (outer) states to lower (inner) states take place till the vacancy is transferred to the upper (outer) most level. Every transition produces characteristic emission lines and some of the lines lie in the *X*-ray region. Thus X-ray spectra is produced.

The so called *K* and L series of X-rays result from all such electron transitions to the $n = 1$ and $n = 2$ inner shells of the singly ionized atom. A vacancy in *L* shell or *M* shell of heavy atoms also produces X-ray spectra Like optical spectra, the X-ray spectra is also subjected to the following selection rules.

$$\Delta l = \pm 1, \qquad \Delta j = 0, \pm 1 \tag{11.1}$$

Hence an $L_I$-shell electron cannot make a transition to *K* shell but $L_{II}$ to *K* and $L_{III}$ to *K* transitions are allowed. The above two transitions give rise to $K_{\alpha_1}$ and $K_{\alpha_2}$ lines. respectively. It is easy to see that the intensity ratio of $K_{\alpha_1}$ and $K_{\alpha_2}$ lines is 2:1. A measurement of the wavelengths of these lines can identify the atom. Similar transitionr between K and M shells or between *L* and *M* shells also produce characteristic X-ray lines.

You may now like to apply the selection rules to *X*-ray spectra.

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*Spend 5 min*

**SAQ 2**

Draw approximate energy levels for *L* and *M* shells and show all the allowed transitions.

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The first comprehensive study of characteristic *X*-rays was done by H.G.J. Moseley. He investigated the *K* and *L* spectra of many. elements in the periodic table. His survey of the elements revealed a pattern in the relationship between emitted frequencies and the atomic number of the atoms. These empirical observations are encapsulated in the form of Moseley's law. Let us now study this law.

## 11.3 MOSELEY'S LAW

As shown in Sec. 11.2, the energy of an X-ray subshell depends upon the quantum numbers n, 1, and $j$.

However, in a crude approximation we may represent the energy value of a shell by the hydrogenic formula after replacing the atomic number2 by $Z-\sigma$, where $\sigma$ is known as **screening constant.** Thus for $n$ shell we take

$$E_n = -\frac{R\,(Z-\sigma)^2}{n^2} \tag{11.2}$$

Now a transition between $n_2$ to $n_1$ will produce an X-ray line of frequency

$$\nu_{n_2,\,n_1} = \frac{E_{n_2}-E_{n_1}}{h}$$

$$= \frac{R}{h}\left[-\frac{(Z-\sigma_{n_2})^2}{n_2^2} + \frac{(Z-\sigma_{n_1})^2}{n_1^2}\right] \tag{11.3}$$

On the assumption that the screening constants $\sigma_{n_1}$ and $\sigma_{n_2}$ have the same value $\sigma$ we obtain

$$\nu_{n_2,\,n_1} = \frac{R}{h}(Z-\sigma)^2\left[-\frac{1}{n_2^2}+\frac{1}{n_1^2}\right] \tag{11.4}$$

The above equation shows that $\nu$ is directly proportional to the square of the atomic number Z. Such a relationship between the frequency $\nu$ and the atomic number Z is known as Moseley's law (Fig. 11.3). Moseley was able to change targets in his *X*-ray tube and observe the frequencies of X-rays for more than 40 elements between aluminium and gold in the periodic table. His experimental results were in agreement with Eq. (11.4). However, you should note that taking $\sigma$ to be independent of $n$ is not a good approximation, Hence Moseley's law has only a limited validity.

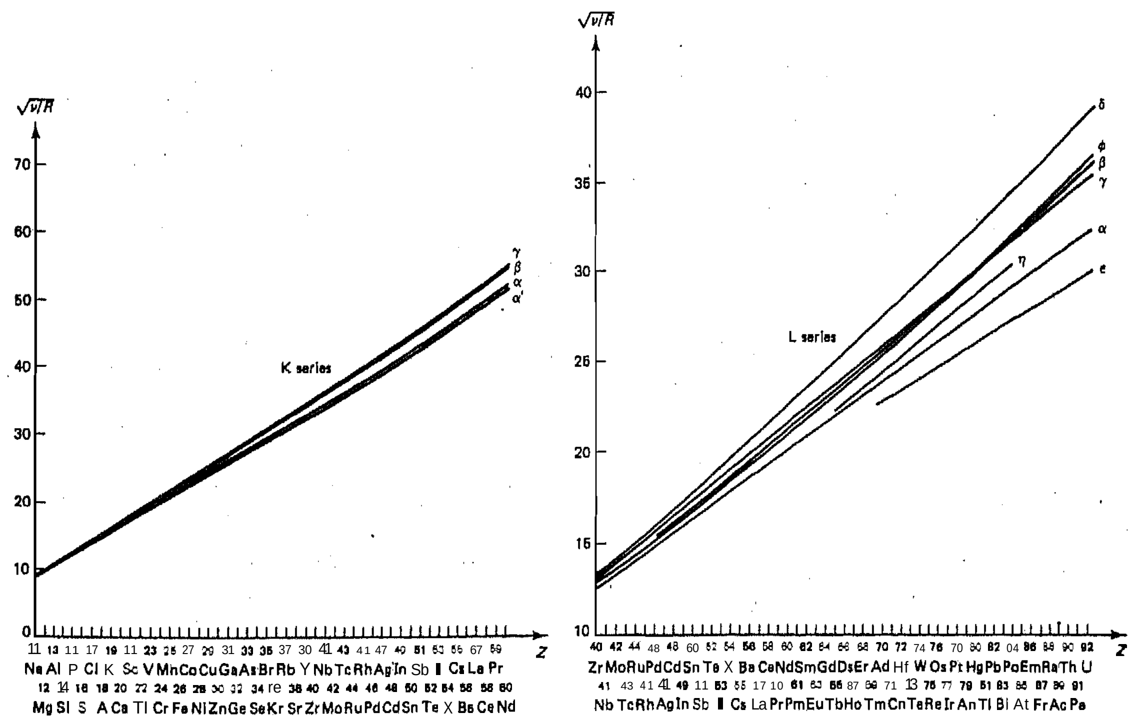


**Fig. 11.3** : Moseley's Law.

**SAQ 3**

*Spend 5 min*

Use Moseley's law to obtain the frequency of an *X*-ray line when an L to *K* transition takes place in a silver atom. Take $\sigma = 3$.

Let us now briefly consider some applications of X-rays, mainly in medicine, industry, materials science and astronomy.

## 11.4 APPLICATIONS OF X-RAYS

Due to their greater energy, X-rays ionize or dissociate the atoms and molecules of substances through which they pass. The phenomenon of *X*-ray absorption is an example of the familiar photoelectric effect — the absorption of an *X*-ray photon excites the atom above its ionization level and ejects a bound electron. A quantum mechanical probability can be introduced to describe the photon-atom interaction. And an absorption cross section can be defined to account for the behaviour of a beam of *X*-rays incident on the atoms in a sample of matter. We measure absorption in the laboratory by observing the attenuation of an X-ray beam in its passage through a thickness of material. The fractional decrease in intensity $-dI/I$ is related to the element of thickness $dx$ by the proportionality

$$-\frac{dI}{I} = \mu_x \, dx,$$

where the constant $\mu_x$ defines the absorption coefficient of the material. This expression is easily integrated to give the intensity as a function of distancex through the sample, starting with incident intensity $I_0$:

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_0^x \mu_x \, dx$$

or $$\ln \frac{I}{I_0} = -\mu_x x$$

or $$I = I_0 e^{-\mu_x x}$$

The absorption coefficient varies with the material and depends on the wavelength of the X-rays. We can use measurements of the attenuation to determine this dependence, and we can then infer the related behaviour of the absorption cross section for the given element.

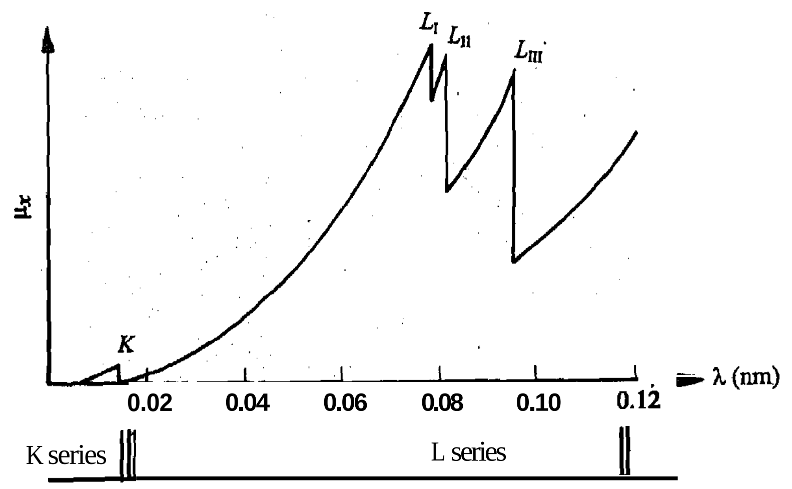


**Fig. 11.4: K and L absorption edges of lead. The wavelength thresholds occur where the *X*-ray photon energy becomes insufficient to eject a *K* or L shell electron. Emission lines of lead in the *K* and L series are also shown.**

Fig. 11.4 shows a typical graph of $\mu_x$ as a function of the wavelength $\lambda$. We observe zero absorption in the limit $\lambda \to 0$. This observation tells us that the absorbing medium is transparent to X-rays' when the beam energy is very large. We then observe a steady growth in absorption as the photon energy decreases from large values and as $\lambda$ increases from zero, until we reach a sharp value of $\lambda$ where the medium suddenly becomes transparent again. This feature of the graph is called an absorption edge, the first of several to appear with increasing $\lambda$ in the figure. The indicated $K$ absorption edge occurs at wavelength $\lambda_K$, where the photon energy is the minimum needed to ionize the atom and leave a vacancy in the $K$ shell. When $\lambda$ becomes larger than $\lambda_K$, the X-ray photon energy becomes too small to free a K-shell electron but remains large enough to eject an electron from an L (or higher) shell. We again observe a steady growth in absorption as the wavelength continues to increase until we reach one of the indicated L absorption edges. The various absorption thresholds along with the characteristic X-ray emission lines provide a signature of the particular atom, and both give an indication of the energy levels of the system. We include the emission lines of the $K$ and L series in the figure so that we can note the positions of these spectral lines relative to the absorption edges.

**Medicine**

The property of penetration of materials by X-rays makes them very useful for various applications, particularly in medical diagnosis. The relatively greater absorption of X-radiation by bones as compared with tissue results in a fairly 'well-defined' photograph of the bone structure. You must surely have seen such X-ray plates. X-rays are also used for treatment of cancer since they seem to have a tendency to destroy diseased tissue more readily than healthy tissue. But you must remember that X-radiation (in any amount, small or large) does destroy some good tissue. Hence, extreme care must be taken to protect oneself when handling X-rays or during exposure to X-rays.

X-rays are used to produce a photographic image of an opaque specimen and provide information about the gross internal structure of any object that they can penetrate. This technique called radiography is widely used in diverse areas ranging from medicine to industry. Whether it is to examine the chest of a patient for evidence of tuberculosis, silicosis, heart pathology or embedded foreign objects, of bones in cases of fractures or of arthritis or other bone diseases, X-rays, as you know, are the most handy tool used in medical applications.

**Industry**

X-ray radiography is also used in detecting internal flaws in metal casting or welded joints. A defective casting or welded joints inserted into a bridge or a building can lead to disastrous results. Such metal parts and welds in a pipe are routinely examined by X-rays to observe cracks, inclusions and voids before they are used. X-ray radiography also helps in detecting any crack in the body of ships, cars and aeroplanes. Industrial radiography enables detection of internal physical imperfections in materials such as flaws, segregations, porosities etc. It is often used to visualize inaccessible internal parts of industrial systems to check their location or condition, e.g., in the foundry industry to guarantee the soundness of castings; in the welding of pressure vessels, pipelines, ships and reactor components to guarantee the soundness of welds; in the manufacture of fuel elements for reactors to guarantee their size and soundness; in the solid-propellant and high explosives industry to guarantee the purity of the material being used; in the automotive, aircraft, nuclear, space, oceanic and guided-missile industries, whenever internal soundness is required.

Among the many objects now examined by radiography are coal, minerals, rubber tyres, golf balls, fabricated objects with internal seals, electrical equipment, printed circuits, fibers, plastics, containers of all kinds, grain, fruit, meats, battery, plates, suitcases, postal packages, and paintings.

Computerized tomography (CT) scan use X-rays to produce images of internal organs of the body and has made a strong impact on medical diagnosis and industrial inspection.

**Materials Science**

X-rays also find application in materials science. You have briefly studied Bragg's diffraction law in the context of wave-particle duality. It was first discovered for diffraction of X-rays from the surface layers of a crystal. With a known crystal of lattice spacing $d$, we can measure the wavelength of the radiation; and with a known wavelength we can measure the lattice spacing $d$. X-ray diffraction has been developed into a standard technique for analysing crystal structure and its defects. X-ray diffraction and crystallography has led to extensive study of crystal structures, their atomic arrangements and electron distribution, etc. Chemical elemental analysis of solids, liquids and thin films uses X-rays as a non-destructive physical method. X-ray microscopy is used to obtain quantitative chemical information about samples as small

Astronomy

X-rays are being widely used in astronomy for exploring the universe. All types of astronomical objects, from stars to galaxies and quasars emit X-rays which can be detected by specially designed X-ray ***telescopes*** placed in rockets, satellites and space probes above the Earth's atmosphere. These have led to the discovery of new stellar objects and yielded information about the distribution of stellar objects in the sky, time-evolution of galaxies and supernova remnants, and later stages of a star's life when it metamorphoses into a collapsed object like a white dwarf, neutron star or black hole.

With this brief discussion of X-ray applications, we come to the end of this unit. Let us now summarise what you have studied in this unit.

## 11.5 SUMMARY

- X-rays are produced in two ways

  (i) when high speed electrons penetrate atoms, they decelerate as they pass close to the atomic nuclei and produce continuous X-radiation spect um. This is often referred to as "Bremsstrahlung".

  (ii) In another process, these electrons remove electrons from the inner shells by collision. The transitions of atomic electrons from outer shells to vacant inner shells result in characteristic X-rays.

- The selection rules for atomic transitions that yield a characteristic X-ray spectrum are

  $$\Delta l = \pm 1, \Delta j = 0, \pm 1$$

- The relationship between the characteristic X-ray frequencies emitted by an atom and its atomic number are given by Moseley's law.

- X-rays find several applications in medicine, industry, astronomy and materials science.

## 11.6 TERMINAL QUESTIONS

**Spend 15 *min*.**

1. At what potential difference must an X-ray tube operate to produce x-rays with a minimum wavelength of 1Å?

2. X-rays from a certain cobalt target tube are composed of the strong K-series of cobalt and weak $K$ lines due to impurities. The wavelengths of the $K_\alpha$ lines are 1.785 Å for cobalt and 1.537 Å and 2.285 Å for the impurities, Using Moseley's law, calculate the atomic numbers of the impurities and identify the elements.

## 11.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. For $n = 4$, $l = 0, 1, 2, 3$, and $s = 1/2$

   Thus for $l = 0$, $j = 1/2$

   $l = 1$, $j = 1/2, 3/2$

   $l = 2$, $j = 3/2, 5/2$

   $l = 3$, $j = 5/2, 7/2$

Hence for $n = 4$, the **subshells** and corresponding terms are

| | | | | | | |
|---|---|---|---|---|---|---|
| $N_I$ | $N_{II}$ | $N_{III}$ | $N_{IV}$ | $N_V$ | $N_{VI}$ | $N_{VII}$ |
| $4\,^2S_{1/2}$ | $4\,^2P_{1/2}$ | $4\,^2P_{3/2}$ | $4\,^2D_{3/2}$ | $4\,^2D_{5/2}$ | $4\,^2F_{5/2}$ | $4\,^2F_{7/2}$ |

2. *See* **Fig.** 11.5.

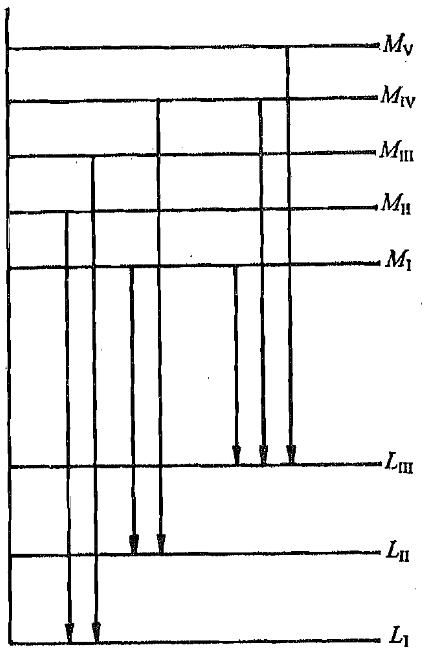


**Fig.11.5: Energy levels for *L* and *M* shells, and allowed transitions between L and *M* shells.**

3. $$\nu = \frac{13.6 \times 1.602 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{Js}} \times (47-3)^2 \left(-\frac{1}{4} + 1\right) \quad (\because \text{ for silver } Z = 47) \quad n_1 = 1 \text{ and } n_2 = 2$$

$$= 4.7 \times 10^{18}\ \text{Hz}$$

**Terminal Questions**

1. The energy is given by

$$E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34}\ \text{Js} \times 3 \times 10^8\ \text{m s}^{-1}}{10^{-10}\ \text{m}}$$

$$= 2.0 \times 10^{-15}\ \text{J}$$

And the potential difference is

$$V = \frac{E}{e} = \frac{2.0 \times 10^{-15}\ \text{J}}{1.6 \times 10^{-19}\ \text{C}}$$

$$= 1.25 \times 10^4\ \text{V}$$

2, Using Moseley's law we can write

$$\nu = \frac{c}{\lambda} = \frac{R}{h}(Z-\sigma)^2 \left(-\frac{1}{n_2^2} + \frac{1}{n_1^2}\right)$$

For K series $n_1 = 1$, $n_2 = 2$. For cobalt $Z = 27$ and applying Moseley's law we can write

$$\frac{3 \times 10^8 \text{ ms}^{-1}}{1.785 \times 10^{-10} \text{ m}} = \frac{13.6 \times 1.6 \times 10^{-19} \text{J}}{6.626 \times 10^{-34} \text{ Js}} \times (27 - \sigma)^2 \times \left(1 - \frac{1}{4}\right)$$

or

$$(27 - \sigma)^2 = \frac{3 \times 10^8 \times 6.626 \times 10^{-34} \times 4}{1.785 \times 10^{-10} \times 13.6 \times 1.6 \times 10^{-19} \times 3}$$

$$= 680$$

or

$$(27 - \sigma) \simeq 26$$

$$\therefore \sigma = 1$$

(i) Now for the first impurity, $\lambda = 1.537$ Å. Therefore, from Moseley's law we have

$$\frac{3 \times 10^8 \text{ ms}^{-1}}{1.537 \times 10^{-10} \text{ m}} = \frac{13.6 \times 1.602 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} (Z - 1)^2 \times \frac{3}{4}$$

or

$$(Z - 1)^2 = 790$$

**or**

$$(Z - 1) \simeq 28$$

and

$Z = 29$, so the impurity is copper.

(iii) for the second impurity, we have $\lambda = 2.285$ Å. Thus

$$(Z - 1)^2 = \frac{3 \times 10^8 \text{ ms}^{-1} \times 6.626 \times 10^{-34} \text{ Js}}{2.285 \times 10^{-10} \times 13.6 \times 1.6 \times 10^{-19} \text{ J}} \times \frac{4}{3}$$

$$= 530$$

or

$$(Z - 1) = 23$$

**and**

$Z = \mathbf{24}$, so the impurity is chromium.

## Table of fundamental constants

| *Quantity* | *Symbol* | *Value* |
|---|---|---|
| Planck's constant | $h$ | $6.62618 \times 10^{-34}$ J s |
| | $\hbar = \frac{h}{2\pi}$ | $1.05459 \times 10^{-34}$ J s |
| Velocity of light in vacuum | $c$ | $2.99792 \times 10^{8}$ m s$^{-1}$ |
| Elementary charge (absolute value of electron charge) | $e$ | $1.60219 \times 10^{-19}$ C |
| Permeability of free space | $\mu_0$ | $4\pi \times 10^{-7}$ H m$^{-1}$ = $1.256\,64 \times 10^{-6}$ H m$^{-1}$ |
| Permittivity of free space | $\varepsilon_0 = \frac{1}{\mu_0 c^2}$ | $8.854\,19 \times 10^{-12}$ F m$^{-1}$ |
| Gravitational constant | $G$ | $6.672 \times 10^{-11}$ N m$^2$ kg$^{-2}$ |
| Fine structure constant | $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$ | $\frac{1}{137.036} = 7.297\,35 \times 10^{-3}$ |
| Avogadro's number | $N_A$ | $6.022\,05 \times 10^{23}$ mol$^{-1}$ |
| Faraday's constant | $F = N_A e$ | $9.648\,46 \times 10^{4}$ C mol$^{-1}$ |
| Boltzmann's constant | $k$ | $1.380\,66 \times 10^{-23}$ J K$^{-1}$ |
| Gas constant | $R = N_A k$ | $8.314\,41$ J mol$^{-1}$ K$^{-1}$ |
| Atomic mass unit | a.m.u. $= \frac{1}{12} M_{^{12}C}$ | $1.660\,57 \times 10^{-27}$ kg |
| Electron mass | $m$ or $m_e$ | $9.109\,53 \times 10^{-31}$ kg = $5.485\,80 \times 10^{-4}$ a.m.u. |
| Proton mass | $M_p$ | $1.672\,65 \times 10^{-27}$ kg = $1.007\,276$ a.m.u. |
| Neutron mass | $M_n$ | $1.674\,92 \times 10^{-27}$ kg = $1.008\,665$ a.m.u. |
| Ratio of proton to electron mass | $M_p/m_e$ | 1836.15 |
| Electron charge to mass ratio | $\lvert e \rvert / m_e$ | $1.758\,80 \times 10^{11}$ C kg$^{-1}$ |
| Classical radius of electron | $r_0 = \frac{e^4}{4\pi\varepsilon_0 mc^2}$ | $2.817\,84 \times 10^{-15}$ m |
| Bohr radius for atomic hydrogen (with infinite nuclear mass) | $a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$ | $5.29177 \times 10^{-11}$ m |
| Rydberg's constant for infinite nuclear mass | $R_\infty = \frac{me^2}{8\varepsilon_0^2 h^3 c} = \frac{\alpha}{4\pi a_0}$ | $1.097\,37 \times 10^{7}$ m$^{-1}$ |
| Rydberg's constant for atomic hydrogen | $R_H$ | $1.096\,78 \times 10^{7}$ m$^{-1}$ |
| Bohr magneton | $y = \frac{eA}{2m}$ | $9.27408 \times 10^{-24}$ J T$^{-1}$ |
| Nuclear magneton | $\mu_N = \frac{eA}{2M_p}$ | $5.05082 \times 10^{-27}$ J T$^{-1}$ |