

## Chapter three: The intensities of diffracted beams

### 3.1 Scattering by an electron

The x-rays are emitted because of the rapid deceleration of the electrons striking the target. Similarly, an electron will oscillate during its motion and therefore emits an electromagnetic wave. In this sense, an electron is said to *scatter x-rays*, the scattered beam being simply the beam radiated by the electron under the action of the incident beam.

The intensity of the scattered beam depends on the angle of scattering ( $\alpha$ ), in a way which was first worked out by J. J. Thomson. He found that the intensity of the beam scattered by a single electron of charge  $e$  and mass  $m$ , at a distance  $r$  from the electron, is given by:

$$I = I_o \frac{e^4}{r^2 m^2 c^4} \sin^2 \alpha$$

Where  $I_o$  =intensity of the incident beam and  $c$  = velocity of light.

From the following Figure

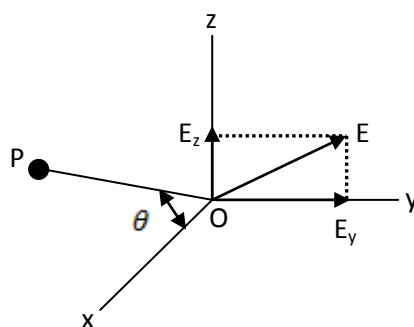


Fig. 1

Suppose that  $Ox$  = the incident beam is travelling and encounters an electron at  $O$ .

$P$  = the scattering intensity in the  $xz$  plane and  $2\theta$  =the angle between  $OP$  and  $Ox$ .

An unpolarized incident beam has its electric vector  $E$  in a random direction in the  $yz$  plane. This beam may be resolved into two plane polarized components, having electric vectors  $E_y$  and  $E_z$  where

$$E^2 = E_y^2 + E_z^2$$

Since  $E_y = E_z$ , therefore,  $E_y^2 = E_z^2 = \frac{1}{2} E^2$

The intensity of these two components of the incident beam is proportional to the square of their electric vectors, since  $E$  measures the amplitude of the wave and the intensity of a wave is proportional to the square of its amplitude. Therefore,

$$I_{Oy} = I_{Oz} = \frac{1}{2} I_0$$

Since the scattered beam whose intensity at  $P$ , so that

$$I_{Py} = I_{Oy} \frac{e^4}{r^2 m^2 c^4}$$

Where  $\alpha = \pi/2$ . Similarly, the intensity of the scattered  $z$  component is given by

$$I_{Pz} = I_{Oz} \frac{e^4}{r^2 m^2 c^4} \cos^2 2\theta$$

Where  $\alpha = \frac{\pi}{2} - 2\theta$ . The total scattered intensity at  $P$  is

$$I_P = I_{Py} + I_{Pz}$$

$$I_P = I_0 \frac{e^4}{r^2 m^2 c^4} \left( \frac{1 + \cos^2 2\theta}{2} \right)$$

This is the **Thomson equation** for the scattering of an x-ray beam by a single electron.  $\left( \frac{1 + \cos^2 2\theta}{2} \right)$  is

called the **polarization factor**.  $\frac{e^4}{m^2 c^4}$  is constant and equal to  $7.94 \times 10^{-26} \text{ cm}^2$ . If  $r$  few cm:

$$\frac{I_P}{I_0} \approx 10^{-26}$$

Another way for electron to scatter is manifested in *Compton effect*, where a stream of x-ray quanta or photons, each of energy  $h\nu_1$ , strikes an electron, the collision is an elastic one like that of two billiard balls. The electron is knocked aside and the photon is deviated through an angle  $2\theta$ . Since some of the energy of the incident photon is used in providing kinetic energy for the electron, the energy  $h\nu_2$  of the photon after impact is less than its energy  $h\nu_1$  before impact. The wavelength  $\lambda_2$  of the scattered radiation is thus slightly greater than the wavelength  $\lambda_1$  of the incident beam, the magnitude of the change being given by the equation:

$$\Delta\lambda(\text{\AA}) = \lambda_2 - \lambda_1 = 0.0243(1 - \cos 2\theta)$$

The increase in wavelength depends only on the scattering angle  $2\theta$ , and it varies from zero in the forward direction ( $2\theta = 0$ ) to  $0.05\text{\AA}$  in the extreme backward direction ( $2\theta = 180$ ).

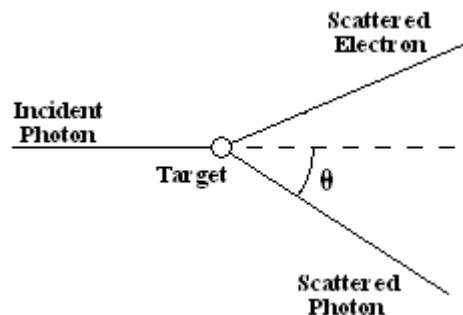


Fig. 2

### 3.2 Scattering by an atom

When an x-ray beam encounters an atom, each electron in it scatters in accordance with the Thomson equation. For simplicity, the electrons are shown as points arranged around the central nucleus. The waves scattered in the forward direction by electrons A and B are exactly in phase on a wave front such as  $XX'$ , because each wave has travelled the same distance before and after scattering. The other scattered waves have a path difference equal to  $(CB-AD)$  and are thus somewhat out of phase along a wave front such as  $YY'$ , the path difference being less than one wavelength.

Partial interference occurs between the waves scattered by A and B, with the result that the net amplitude of the wave scattered in this direction is less than that of the wave scattered by the same electrons in the forward direction.

A quantity  $f$  is the atomic scattering factor, is used to describe the "efficiency" of scattering of a given atom in a given direction. It is defined as a ratio of amplitudes:

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

$f = Z$  for any atom scattering in the forward direction. As  $\theta$  increases, however, the waves scattered by individual electrons become more and more out of phase and  $f$  decreases.

To summarize, *when a monochromatic beam of x-rays strikes an atom, two scattering processes occur. Tightly bound electrons are set into oscillation and radiate x-rays of the same wavelength as that of the incident beam.*

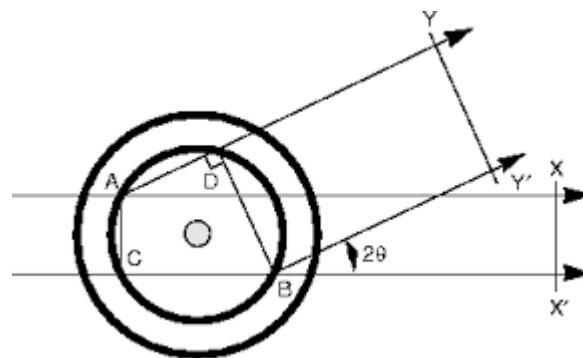


Fig. 3

### 3.3 Scattering by a unit cell

In unit cell, assuming that the Bragg law is satisfied, we wish to find the intensity of the beam diffracted by the crystal as a function of atom position. The phase differences occur in the waves scattered by the individual electrons, for any direction of scattering except the extreme forward direction. Similarly, the waves scattered by the individual atoms of a unit

cell are not necessarily in phase except in the forward direction, and we must now determine how the phase difference depends on the arrangement of the atoms.

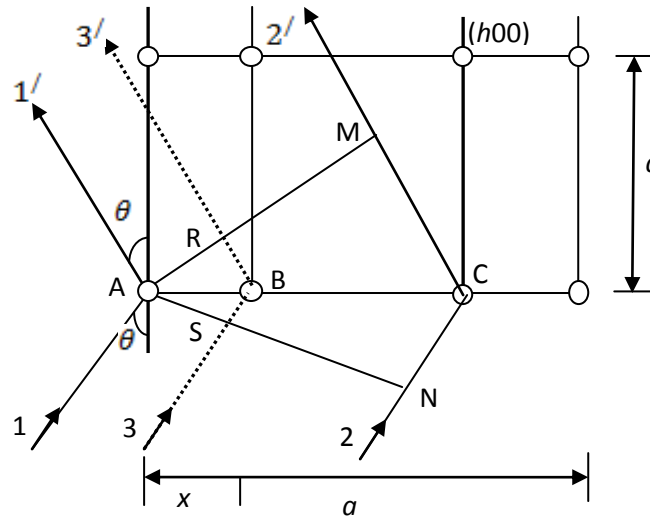


Fig. 4.

As shown in Fig.4, from atoms A and C:

The path difference between ray 2' and ray 1', is given by:

$$\delta_{2'/1'} = MCN = 2d_{h00} \sin \theta = \lambda$$

where  $d_{h00} = AC = \frac{a}{h}$

From atoms A and B:

$$\delta_{3'/1'} = RBS = \frac{AB}{AC} (\lambda) = \frac{x}{a/h} (\lambda)$$

Therefore, the phase difference  $\emptyset$

$$\emptyset = \frac{\delta}{\lambda} 2\pi$$

where  $2\pi$  in radians,  $\phi$  between the wave scattered by atom B and that scattered by atom A at the origin is given by:

$$\phi_{3/1'} = \frac{\delta_{3/1'}}{\lambda} 2\pi = \frac{2\pi hx}{a}$$

If atom B position:  $u=x/a$

$$\phi_{3/1'} = \frac{2\pi hx}{a} = 2\pi hu$$

For 3-dimension  $\phi = 2\pi(hu + kv + lw)$

This relation is general and applicable to a unit cell of any shape. The phase of each wave is given by above equation in terms of the  $hkl$  reflection considered and the  $uvw$  coordinates of the atom. Using our previous relations, we can then express any scattered wave in the complex exponential form:

$$Ae^{i\phi} = f e^{2\pi i(hu + kv + lw)}$$

The resultant wave scattered by all the atoms of the unit cell is called the *structure factor* and is designated by the symbol  $F$ . It is obtained by simply adding together all the waves scattered by the individual atoms. If a unit cell contains atoms 1, 2, 3, ...,  $N$ , with fractional coordinates  $u_1v_1w_1$ ,  $u_2v_2w_2$ ,  $u_3v_3w_3$ , ... and atomic scattering factors  $f_1$ ,  $f_2$ ,  $f_3$ , ..., then the structure factor for the  $hkl$  reflection is given by:

$$F = f_1 e^{2\pi i(hu_1 + kv_1 + lw_1)} + f_2 e^{2\pi i(hu_2 + kv_2 + lw_2)} + f_3 e^{2\pi i(hu_3 + kv_3 + lw_3)} + \dots$$

This equation may be written more compactly as

$$F_{hkl} = \sum_{n=1}^N f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

$F$  is, in general, a complex number, and it expresses both the amplitude and phase of the resultant wave. Its absolute value  $|F|$  gives the amplitude of the resultant wave in terms of the

amplitude of the wave scattered by a single electron. Like the atomic scattering factor  $f$ ,  $|F|$  defined as ratio of amplitudes:

$$|F| = \frac{\text{amplitude of the wave scattered by all the atoms of a unit cell}}{\text{amplitude of the wave scattered by one electron}}$$

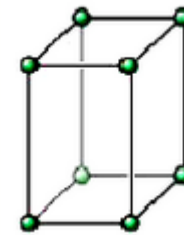
The intensity of the beam diffracted by all the atoms of the unit cell is given by the following:

$$I = |F_{hkl}|^2$$

### 3.4 Structure-factor calculation:

**1-Unit cell has one atom at the origin**

$$F = f e^{2\pi i 0} = f$$



In this case the structure factor is independent of  $h$ ,  $k$  and  $l$ ; it will decrease with  $f$ .

**2-Unit cell is base-centered**

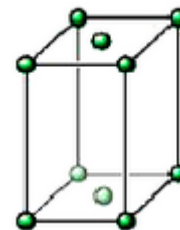
$$F = f e^{2\pi i 0} + f e^{2\pi i \left(\frac{h}{2} + \frac{k}{2}\right)} = f(1 + e^{\pi i(h+k)})$$

$$F = 2f \text{ if } h + k = \text{even}$$

$$F = 0 \text{ if } h + k = \text{odd}$$

$$(200), (400), (220), \dots \implies |F_{hkl}|^2 = 4f^2$$

$$(100), (121), (300), \dots \implies |F_{hkl}|^2 = 0$$



**3- Unit cell is body-centered cell**

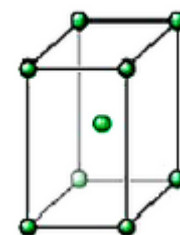
$$F = f e^{2\pi i 0} + f e^{2\pi i \left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}\right)} = f(1 + e^{\pi i(h+k+l)})$$

$$F = 2f \text{ if } h + k + l = \text{even}$$

$$F = 0 \text{ if } h + k + l = \text{odd}$$

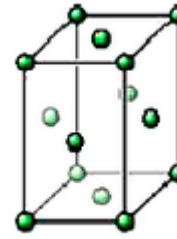
$$(200), (400), (220), \dots \implies |F_{hkl}|^2 = 4f^2$$

$$(100), (111), (300), \dots \implies |F_{hkl}|^2 = 0$$



#### 4- For face centered unit cell

The fcc crystal structure has atoms at 000,  $\frac{1}{2}\frac{1}{2}0$ ,  $\frac{1}{2}0\frac{1}{2}$  and  $0\frac{1}{2}\frac{1}{2}$ :



$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} = f(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)})$$

If  $h$ ,  $k$ , and  $l$  are unmixed, then all three sums  $(h + k)$ ,  $(h + l)$ , and  $(k+l)$  are even integers, and each term in the above equation has the value 1  $\Rightarrow F = 4f$

If  $h$ ,  $k$ , and  $l$  are mixed, then the sum of the three exponentials is 1, whether two of the indices are odd and one even, or two even and one odd  $\Rightarrow F = 0$

$$|F_{hkl}|^2 = \begin{cases} 16f^2 & h, k \text{ and } l \text{ unmixed even and odd} \\ 0 & h, k \text{ and } l \text{ mixed even and odd} \end{cases}$$

Thus, reflections will occur for such planes as (111), (200), and (220) but not for the planes (100), (210), (112), etc.

#### 5- For body centered cell with different atoms:

For NaCl, this crystal has cubic lattice with 4 Na and 4 Cl atoms per unit cell, located as follows

$$\text{Na} = 000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$$

$$\text{Cl} = \frac{1}{2}\frac{1}{2}\frac{1}{2}, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00$$

$$F = [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}][f_{\text{Na}} + f_{\text{Cl}}e^{\pi i(h+k+l)}]$$

This shows at once that NaCl has a face-centered lattice and that

$$F = 0 \quad \text{for mixed indices;}$$

$$F^2 = 0$$

For unmixed indices,

$$F = 4[f_{\text{Na}} + f_{\text{Cl}}e^{\pi i(h+k+l)}]$$



$F = 4(f_{Na} + f_{Cl})$  if  $(h + k + l)$  is even such as (200), (400), (220), etc.;

$$F^2 = 16(f_{Na} + f_{Cl})^2$$

$F = 4(f_{Na} - f_{Cl})$  if  $(h + k + l)$  is odd such as (100), (111), (300), etc.;

$$F^2 = 16(f_{Na} - f_{Cl})^2$$

### 3.5 The factors that affect the relative intensity of the diffraction lines on a powder pattern

- (1) polarization factor
- (2) structure factor
- (3) multiplicity factor
- (4) Lorentz factor
- (5) absorption factor
- (6) temperature factor

**3.5.1 Polarization factor & 3.5.2 Structure factor** have already been described, and the others will be discussed in the following sections.

#### 3.5.3 Multiplicity factor

- 1- The multiplicity factor arises from the fact that in general there will be several sets of  $hkl$ -planes having different orientations in a crystal but with the same  $d_{hkl}$  and  $F^2$  values.
- 2- Evaluated by finding the number of variations in position and sign in  $\pm h$ ,  $\pm k$  and  $\pm l$
- 3- The value depends on  $hkl$  and crystal system

From above, **the multiplicity factor ( $p$ )** can be defined as the number of different planes in a form having the same spacing.

For cubic system of 100 reflection,

(100), (010), (001), ( $\bar{1}00$ ), ( $0\bar{1}0$ ), ( $00\bar{1}$ ), therefore,  $p_{100}=6$

For cubic system of 110 reflection,

(110), (101), (011), ( $\bar{1}10$ ), ( $1\bar{1}0$ ), ( $\bar{1}\bar{1}0$ ), ( $\bar{1}01$ ), ( $10\bar{1}$ ), ( $\bar{1}0\bar{1}$ ), ( $0\bar{1}1$ ), ( $01\bar{1}$ ), ( $0\bar{1}\bar{1}$ ),

therefore,  $p_{110}=12$

### 3.5.4 Lorentz factor

The *Lorentz factor* ( $L$ ) depends on the diffractometer data obtained by the usual  $\theta - 2\theta$ , and it can be written as:

$$L = \left(\frac{1}{\sin 2\theta}\right) (\cos \theta) \left(\frac{1}{\sin 2\theta}\right) = \frac{\cos \theta}{\sin^2 2\theta} = \frac{1}{4\sin^2 \theta \cos \theta}$$

This in turn is combined with the polarization factor ( $\frac{1+\cos^2 2\theta}{2}$ ) to give the Lorentz–polarization factor ( $LP$ ), which can be given by:

$$LP = \frac{1+\cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

The effect of the LP factor is to decrease the intensity at intermediate angles and increase the intensity in the forward and backwards directions, as shown in the following Figure:

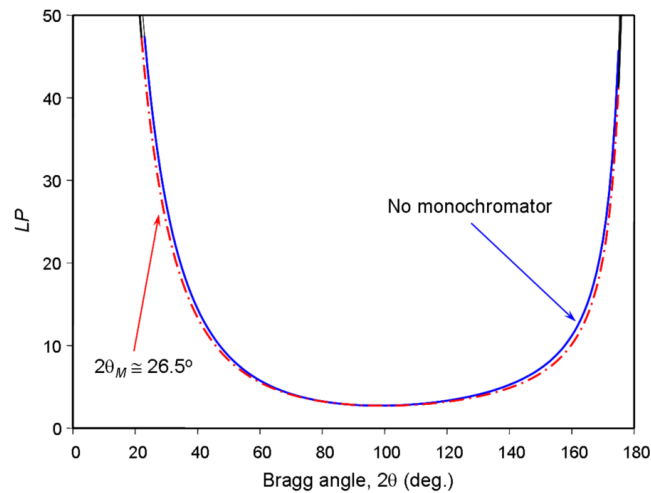


Fig. 5.

### 3.5.5 Absorption factor

Angle-dependent absorption within the sample itself will modify the observed intensity.

Absorption factor ( $A$ ) for infinite thickness specimen is:

$$A = \frac{\mu}{2}$$

Whereas, absorption factor for thin specimens is given by:

$$A = 1 - e^{(-2\mu t / \sin \theta)}$$

where  $\mu$  is the absorption coefficient and  $t$  is the total thickness of the film.

### 3.5.6 Temperature factor

So far we have considered a crystal as a collection of atoms located at fixed points in the lattice. Actually, the atoms undergo thermal vibration about their mean positions even at the absolute zero of temperature, and the amplitude of this vibration increases as the temperature increases. The temperature factor ( $T$ ) is given by:

$$T = e^{-B \sin^2 \theta / \lambda^2}$$

where  $B$  is the thermal factor and can be given by:

$$B = 8\pi^2 \times u^2$$

where  $u$  is the average displacement of an atom from its mean position and is incorporated into the atomic scattering factor  $f$ .

### 3.5 Intensities of powder pattern lines

The relative intensity of powder pattern lines is given by:

$$I = |F|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)$$

Where  $I$  = relative *integrated intensity* (arbitrary units),  $F$  = structure factor,  $p$  = multiplicity factor, and  $\theta$  = Bragg angle.