

CHAPTER III

THEORY OF STRUCTURE FACTORS

III.1 The Elastic Scattering of X-Rays.

III.1.1 Electron as a scatterer of x-rays.

A free electron is the simplest type of scattering center. When an x-ray with an electric vector E traverses a free electron of charge e and mass m at rest at the origin (Fig. 3.1), the acceleration of the electron is

$$a = \frac{F}{m} = \frac{e E}{m}$$

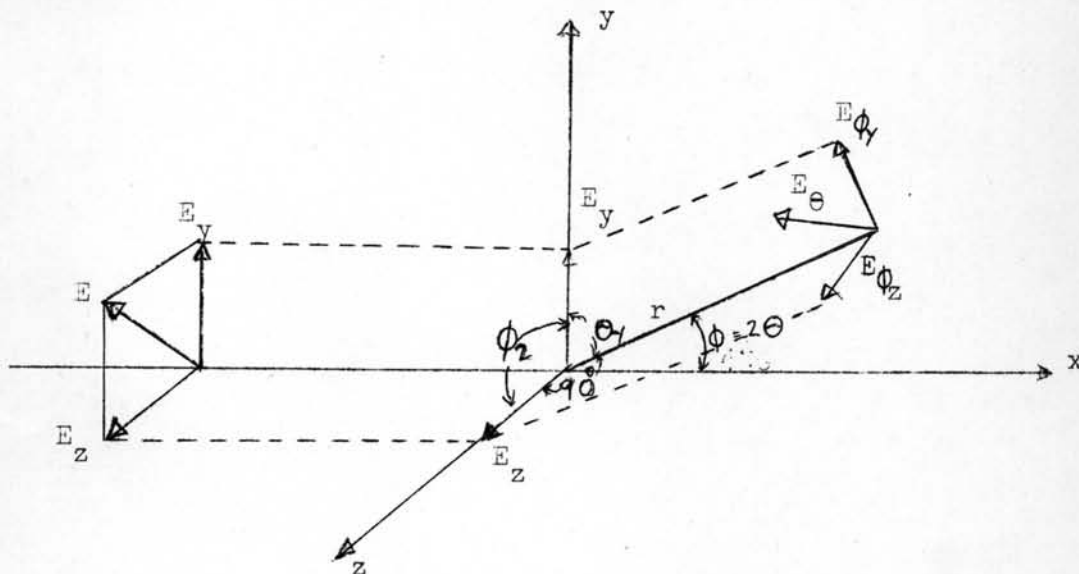


Fig. 3.1 An unpolarized ray travelling along the x-axis and measured at a point P in the xy -plane.

According to classical electromagnetic theory, an accelerated electron⁽⁷⁾ emits electromagnetic radiation whose electric vector at a distance r or at the point P is given by

$$\begin{aligned} E_{\theta} &= \frac{e \sin \theta}{rc^2} \cdot a \\ &= \left(\frac{E e}{m} \right) \cdot \frac{e \sin \theta}{r c^2} \\ &= \frac{E e^2 \sin \theta}{r m c^2} \dots\dots\dots (1) \end{aligned}$$

where θ is the angle between the electron's acceleration vector and the ray under consideration. Since the intensity of an electromagnetic wave is proportional to the square of the electric vector of that wave, the ratio of the scattered intensity and the initial intensity is

$$\frac{I_{\theta}}{I} = \frac{E_{\theta}^2}{E^2} = \frac{e^4 \sin^2 \theta}{r^2 m^2 c^4} \dots\dots\dots (2)$$

Since x-rays are unpolarized, the electric vector of the primary ray may be resolved into two plane polarized components, E_y and E_z , such that $E_y^2 + E_z^2 = E^2$. Thus the direction of E in the YOZ plane is random, and E_y is on the average equal to E . Therefore

$$E_y^2 = E_z^2 = \frac{1}{2} E^2.$$

Thus

$$I_y = I_z = \frac{1}{2} I \dots\dots\dots (3)$$

where I_y and I_z represent the intensities of the Y and Z components of the incident beam. Therefore the intensity I_{θ_y} of the scattered wave as contributed by the y component of the incident beam is, from eq. (2),

$$I_{\theta_y} = I_y \frac{e^4 \sin^2 \theta_y}{r^2 m^2 c^4},$$

and from eq. (3)

$$\begin{aligned} I_{\theta} &= \frac{1}{2} I \frac{e^4 \sin^2 \theta}{r^2 m^2 c^4} \\ &= \frac{1}{2} I \frac{e^4 \cos^2 \phi}{r^2 m^2 c^4} \dots\dots\dots(4) \end{aligned}$$

where ϕ is the angle between the incident and the scattered beams. In a like manner, the contribution from the z component is

$$I_{\theta_z} = I_z \frac{e^4 \sin^2 \theta_z}{r^2 m^2 c^4}$$

but $\theta_z = \pi/2$, therefore

$$I_{\theta_z} = \frac{1}{2} I \frac{e^4}{r^2 m^2 c^4} \dots\dots\dots(5)$$

The total scattered intensity at point P due to an unpolarized x-ray beam of intensity I

$$\begin{aligned} I_e &= I_{\theta_y} + I_{\theta_z} \\ &= I \frac{e^4}{r^2 m^2 c^4} \left(\frac{1 + \cos^2 \phi}{2} \right) \dots\dots\dots(6) \end{aligned}$$

Eq.(6) is known as the Thomson equation for the scattering of an x-ray beam by a single electron. As in chapter II, the angle between incident and scattered rays is 2θ , therefore $\phi = 2\theta$ and eq. (6) becomes

$$I_e = I \frac{e^4}{r^2 m^2 c^4} \left(\frac{1 + \cos^2 2\theta}{2} \right) \dots\dots (7)$$

From which it follows that the intensity I_e depends on the angle of scattering and the inverse square of the distance. The factor $\left(\frac{1 + \cos^2 2\theta}{2} \right)$ is called the polarization factor since it reduces the true intensity of the primary beam I .



III.1.2 The atomic scattering factor f.

In describing a wave scattered by an atom we need to define the efficiency of scattering by an atom in a given direction as the atomic scattering factor $f^{(8)}$, which is expressed by the ratio

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

In order to determine the scattering of x-rays by an atom, it is necessary to consider the actual distribution of electron in an atom. Suppose each atom is consist of a spherically symmetrical distribution of charge density $\rho(r)$ and each volume element dv of the atom scattered wave. In summing all the volume elements, there appears a path difference for each point in the atom, so the phase factor must be taken into account in

relating the orientation of the incident and scattered beams, $(\hat{S} - \hat{S}_0)$, to the direction of the volume element dv . Consequently
 (1)
 the total atomic scattering factor is

$$f = \int df = \int f'(r) e^{\frac{2\pi i}{\lambda} (\hat{S} - \hat{S}_0) \cdot \bar{r}} dv \quad \dots\dots(8),$$

where \bar{r} is the vector from the origin to the volume element dv .
 Using spherical coordinates (Fig.3.2) integrated df , we found that

$$f = 4\pi \int_0^\infty \rho(r) \left(\frac{\sin kr}{kr} \right) r^2 dr \quad \dots\dots\dots (9)$$

where

$$k = \frac{4\pi \sin \theta}{\lambda} \quad \dots\dots\dots (10)$$

If $U(r)dr$ (15) is the probability that an electron lies between radii r and $r + dr$ (Fig.3.2), $U(r) = 4\pi \rho(r) r^2$, then the atomic scattering factor f is proved to be

$$f = \int_0^\infty \frac{\sin kr}{kr} U(r) dr \quad \dots\dots\dots (11)$$

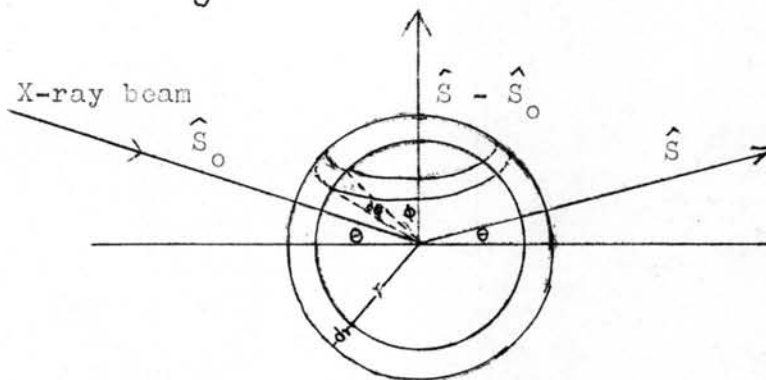


Fig. 3.2 The scattering of x-rays by a ring of electron within an atom.

Using eq. (10) in eq. (11)

$$f = \int_0^{\infty} \frac{\sin \left(\frac{4 \pi \sin \theta r}{\lambda} \right)}{\frac{4 \pi \sin \theta r}{\lambda}} U(r) dr \quad \dots \dots \dots (12)$$

The scattering factor (f) is a function of $\frac{\sin \theta}{\lambda}$ ⁽⁹⁾ where θ is the Bragg angle and λ is the wavelength of the primary beam. The f factor decreases as $\frac{\sin \theta}{\lambda}$ increase. For a fixed wavelength λ , f depends only on the angle θ . For $\theta = 0$, i.e. forward scattering, all waves are in phase, so f is equal to the number of electrons z , i.e. the exponential term in eq.(8) becomes unity so f deduces to the integral of $\rho(r)$ over the atom. Then as θ approaches zero, f approaches z . As θ increases, f decreases because there is a partial interference, i.e. there is a path difference. The greater the angle θ , the less the scattering factor f becomes. And for a fixed θ , the shorter the wavelength the smaller f becomes. Fig.3.3 illustrates, the f of carbon as a function of $\frac{\sin \theta}{\lambda}$ as calculated in tables of atomic scattering factors ⁴

⁴ B.D. Cullity, Elements of X-Ray Diffraction (Mass.: Addison-Wesley Publishing Co. Inc., 1956) pp. 474.

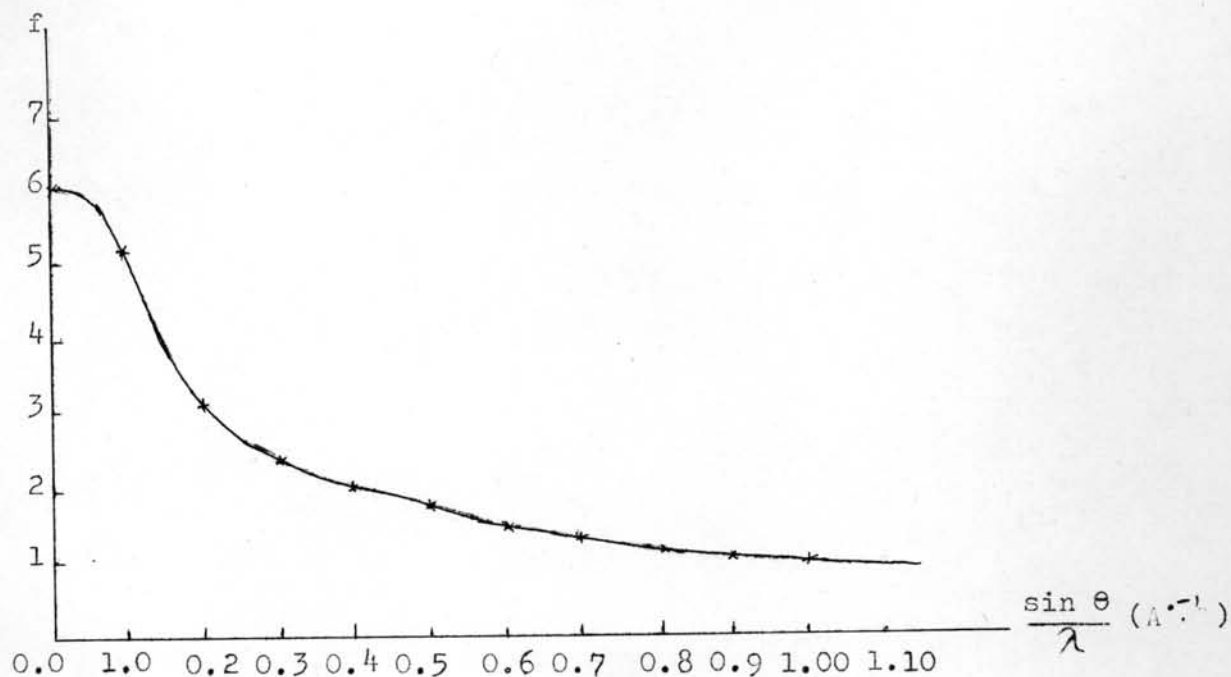


Fig. 3.3 Scattering factor f for the carbon atom.

III.1.3 Scattering by a unit cell

A crystal can be considered as a repetition of its unit cell and each unit cell represents a group of atoms. These atoms contribute their scattered waves each having an amplitude proportional to the value of the atomic scattering factor f for that atom with a phase that is determined by the position of the atom in the unit cell. Thus we are dealing with the adding of scattered waves of the same wavelength but of different amplitudes and phases in a similar way to the scattering from an atom. The phase of a scattered wave from the given

atom is related to the position of the atom within the unit cell. The resultant wave which is the summation of the scattered waves from all atoms in the unit cell, gives the result called the structure factor F . The structure factor (F) expresses both the amplitude and the phase of the resultant wave. The absolute value of the structure factor, like the atomic scattering factor f , is defined as a ratio :

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

To find the amplitude of the resultant wave scattered by all the atoms in a unit cell, we must first find the phase of the waves scattered by each atom in relation to that particular atom's configuration within the cell. As with the scattering from each electron within an atom phase differences appear in the waves scattered by each atom within the unit cell, for any direction except the forward one. To find the phase we must determine the path difference, and to simplify the problem, let us consider an orthogonal unit cell, one of the sections of which is shown in Fig. 3.4

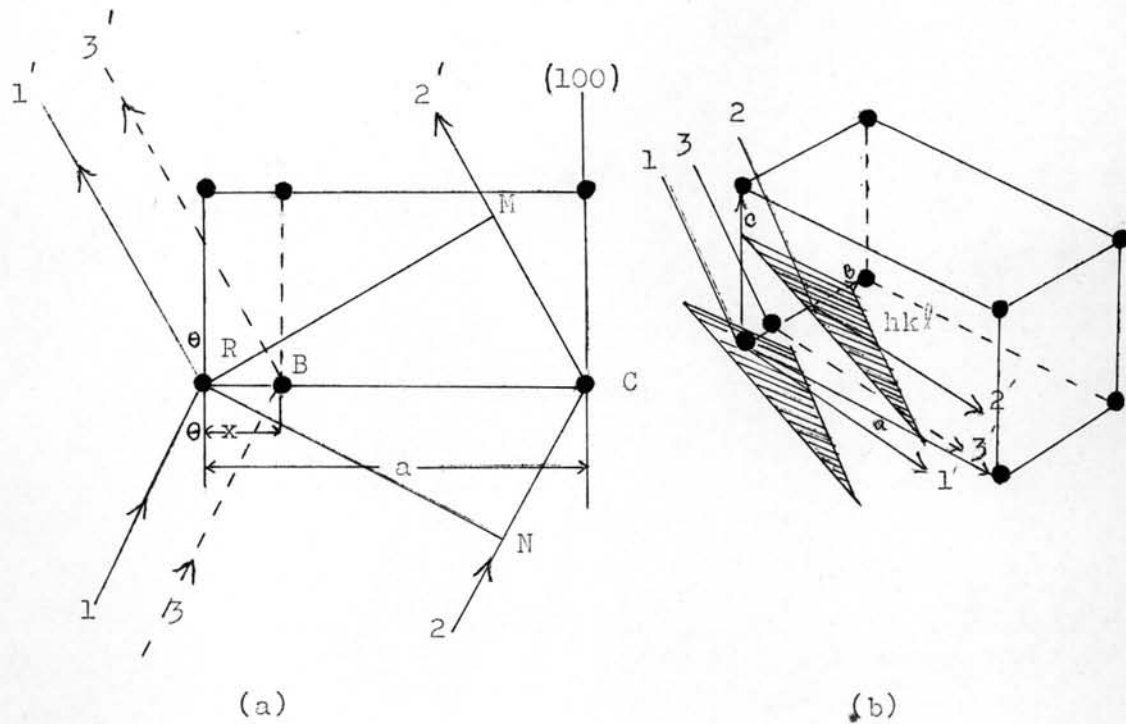


Fig. 3.4

- (a) The effect of atom position on the phase difference between diffracted rays.
- (b) The three dimensional analogue of (a)

Take atom A as the origin and suppose atom C at the 100 position scatters one wavelength out of phase compare with the wave scattered at the origin A when the first order reflection is satisfied by Bragg's law. The path difference between rays 2' and 1' is given by

$$\Delta_{2'1'} = MCN = 2 d_{h00} \sin \theta = \lambda \dots\dots\dots(13)$$

and the phase difference,

$$\phi_{2'1'} = \frac{\int_{2'1'}}{\lambda} (2\pi) = \frac{\lambda}{\lambda} (2\pi) = 2\pi \dots (14)$$

If atom B is at a distance x from atom A along AC, the path difference between ray 3' and ray 1' will be less than λ by simple proportion

$$\int_{3'1'} = \text{RBS} = \frac{AB}{AC} (\lambda) \dots (15)$$

But by the definition of Miller indices, plane(hoc) cuts a into h parts, therefore

$$AC = \frac{a}{h} \dots (16)$$

thus

$$\int_{3'1'} = \frac{x}{a/h} (\lambda) = \frac{x}{a} h (\lambda) \dots (17)$$

and the phase of the h order wave scattered by atom B is

$$\phi_{3'1'} = \frac{\int_{3'1'}}{\lambda} (2\pi) = 2\pi h \frac{x}{a} = 2\pi hu \dots (18)$$

where u is a fraction of the unit cell edge along the $[100]$ direction, $u = \frac{x}{a}$.

Similarly in three dimensions as in Fig. 3.4(b), any atom with the general fractional coordinates uvw (atom B in the figure) will contribute to the hkl reflection, the phase difference ϕ between this atom, say atom B and atom A, is

$$\phi = 2\pi (hu + kv + lw) \dots (19)$$

where $h, k,$ and l are all integers. This relation will hold for any crystal in any crystal system.

From the atomic scattering factor f , we know that waves may differ not only in phase, but also in amplitude if they are not scattered from the same kind of atom. Thus the structure factor F is the sum of waves of amplitude $f_1, f_2, f_3, \dots, f_N$, and phase $\phi_1, \phi_2, \phi_3, \dots, \phi_N$, from atom $A_1, A_2, A_3, \dots, A_N$, situated at points $u_1v_1w_1, u_2v_2w_2, u_3v_3w_3, \dots, u_Nv_Nw_N$ in the unit cell. The waves scattered by all the atoms of the unit cell must be added. The most convenient way of doing this summation is by expressing each amplitude by the length of a vector, and the phase by the direction of the vector. The resultant scattered beam is then represented by the vector sum of the waves, (Fig. 3.5(a)). In Fig. 3.5 (b) the wave for the j^{th} atom may be resolved into a horizontal and a vertical component $f_j \cos \phi_j$, and $f_j \sin \phi_j$ respectively.

These components when added give two sides of a right angled triangle whose hypotenuse is \bar{F} . Thus

$$|\bar{F}|^2 = \left[\sum_j f_j \cos 2\pi (hu_j + kv_j + lw_j) \right]^2 + \left[\sum_j f_j \sin 2\pi (hu_j + kv_j + lw_j) \right]^2, \dots \dots (20)$$

where the summations are taken over all the atoms in the unit cell.

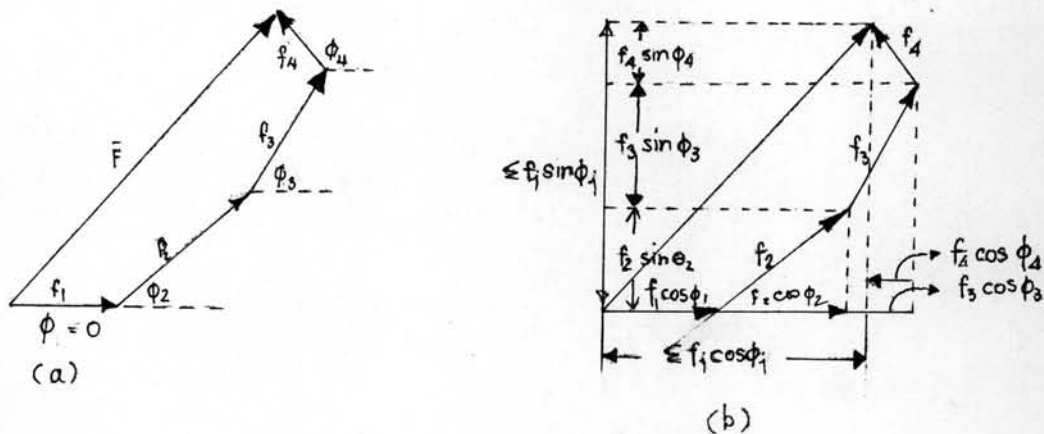


Fig. 3.5 Vector addition of diffracted rays from individual atoms.

Using complex numbers such as $E = A + iB$, where A and B are real and $i = \sqrt{-1}$ is imaginary then

$$|\bar{E}|^2 = (A - iB)(A + iB) = A^2 + B^2 \quad \dots \dots \dots (21)$$

Comparing (20) and (21) we see that

$$A_{hkl} = \sum_j f_j \cos 2\pi (hu_j + kv_j + lw_j), \quad \dots \dots \dots (22)$$

$$B_{hkl} = \sum_j f_j \sin 2\pi (hu_j + kv_j + lw_j) \quad \dots \dots \dots (23)$$

and the structure factor can be written

$$F_{hkl} = A_{hkl} + i B_{hkl}, \quad \dots \dots \dots (24)$$

where the phase of the resultant wave is

Consequently, F can be written in the exponential form

$$F = \sum_{n=1}^N f_n \exp(2\pi i (hu_n + kv_n + lw_n)) \dots\dots\dots(26)$$

Since by definition intensity is the square of amplitude, thus

$$I_{hkl} \propto |F_{hkl}|^2 \dots\dots\dots(27)$$

This relation permits a calculation of the intensity of any hkl reflection from a knowledge of the atomic position. In theory $F_{hkl}^{(15)}$ is a function of f_j of the atom and of the position of the atoms in the unit cell if we make the following assumptions:

1. the atoms are stationary;
2. the crystal diffracts the x-rays only once as they pass through the crystal;
3. the beam is parallel;
4. the crystal does not absorb the x-rays.

However, a number of corrections must be added to relate the observed intensity with theory. Firstly we must add the polarization factor $\frac{1 + \cos^2 2\theta}{2}$ as in eq.(7). Since the polarization of x-rays causes the intensity of a reflection to be a function of the polarization factor p ,

$$p = \frac{1 + \cos^2 2\theta}{2} \dots\dots\dots(28)$$

Secondly, there is the factor relating the direction of reflection and the direction of the beam with respect to the crystal itself, namely the Lorentz factor L .⁽¹⁶⁾ Reflections in Weissenberg photographs should be modified by this factor, which is

$$L = \frac{\sin \theta}{\sin 2\theta \sqrt{\cos^2 \mu - \cos^2 \theta}}, \dots\dots\dots(29)$$

where μ is the inclination angle of a certain layer.

If the crystal used in the experiment is relatively large, the absorption is also large. The absorption factor A ⁽¹⁵⁾ involves the exponential term $e^{-\mu t}$ and must be taken into account when considering intensity of each reflection. μ is the absorption coefficient of the crystal, and t is the x-ray path length in the crystal.

During the exposure the energy associated with the x-ray beam will raise the temperature of the crystal. Therefore the temperature factor^(4,16) should be considered because the increased thermal agitation will decrease the intensity of the diffraction beam. Debye has shown the relation of the scattering factor in the following way

$$f = f_0 e^{-\frac{B \sin^2 \theta}{\lambda^2}}, \dots\dots\dots(30)$$

where f_0 is the scattering factor of the stationary atom while f is of the vibrating atom, and B is a constant characterized by the atom. Therefore the temperature factor $T^{(4)}$ may be written as

$$T = e^{-\frac{B \sin^2 \theta}{\lambda^2}}, \dots\dots\dots(31)$$

Thus after taking these factors into account, more correct expression for the intensity of a reflection is

$$I \propto |F|^2 L p A T, \dots\dots\dots(32)$$

where $|F|$ is the absolute structure factor, L is the Lorentz factor, p is the polarization factor, A the absorption factor, and T the temperature factor.