CHAPTER 2

THEORY OF X-RAY DIFFRACTION AND STRUCTURE DETERMINATION

2.1 Scattering of X-rays by atoms

X-rays are short waves consisting of electromagnetic pulses. Their wavelengths are of the order 1 A^{o}. They are produced when electrons, travelling at high speeds, collide with atoms.

Atoms in a crystal are arranged in a pattern which is repeated regularly in three dimensions, and so they act as a diffraction grating for penetrating X-rays. X-rays are scattered from these atoms.

We will consider how X-rays are scattered by a single electron. If an electron is located in the path of an unpolarized X-ray beam, it is forced into oscillation by the electromagnetic field of the incident radiation.

In Fig.2.1.1, the incident beam is supposed to be travelling in the X-direction, an electron is at a point O, P is a point at a distance r from the electron in XZ plane where OP is inclined at an angle ϕ to the incident beam.

The intensity of the scattered radiation at a distance r from the electron is

$$I = I_o \left(\frac{e^4}{m^2c^4r^2}\right)\left(\frac{1+\cos^2\phi}{2}\right) \quad \ldots (2.1.1)$$

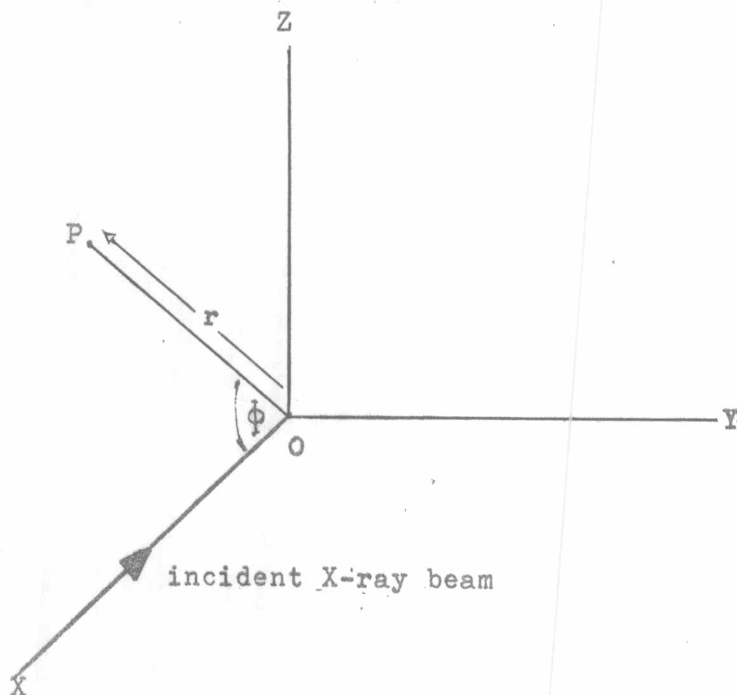


Fig.2.1.1 Coherent scattering of X-rays by a single electron.

where I_o is the intensity of the incident beam,

c is the velocity of light,

e and m are the charge and mass of the electron respectively,

and ϕ is the angle between the direction of scattering of the electron and the undeviated beam direction.

This equation is called Thomson equation for the scattering of an X-ray beam by a single electron. It shows that the scattered intensity decreases as the inverse square of the distance from the

scattering electron. The value in the second bracket in the Eq. (2.1.1) is called the polarization factor.

The electron occupies a finite volume and each atom has a specific number of electrons. Hence the amplitude of the scattered wave from the whole atom increases as the number of electrons in the atom.

An atomic scattering factor, f , is the efficiency of scattering by an atom in a particular direction and it is expressed by the ratio

$$f = \frac{A_{atom}}{A_{electron}} \qquad \ldots (2.1.2)$$

where A_{atom} is the amplitude scattered by an atom that can be written as the sum of the amplitude of the scattering by its individual electrons, $A_{electron}$.

The curve of scattering factor against $\frac{\sin\theta}{\lambda}$ is called the scattering factor curve . It is shown in Fig.2.1.2. The curves have their maximum values when $\frac{\sin\theta}{\lambda} = 0$, corresponding to $\theta = 0$, the value of f is equal to Z , the number of electrons in the atom.

The value of f depends on the type of atom and the Bragg angle θ . Fig.2.1.2 shows that the amplitude scattered by an atom decreases with an increase in θ . The scattering factors for the various atoms are different and they are difficult to calculate. They are tabulated in vol.III of the International Tables of Crystallography.

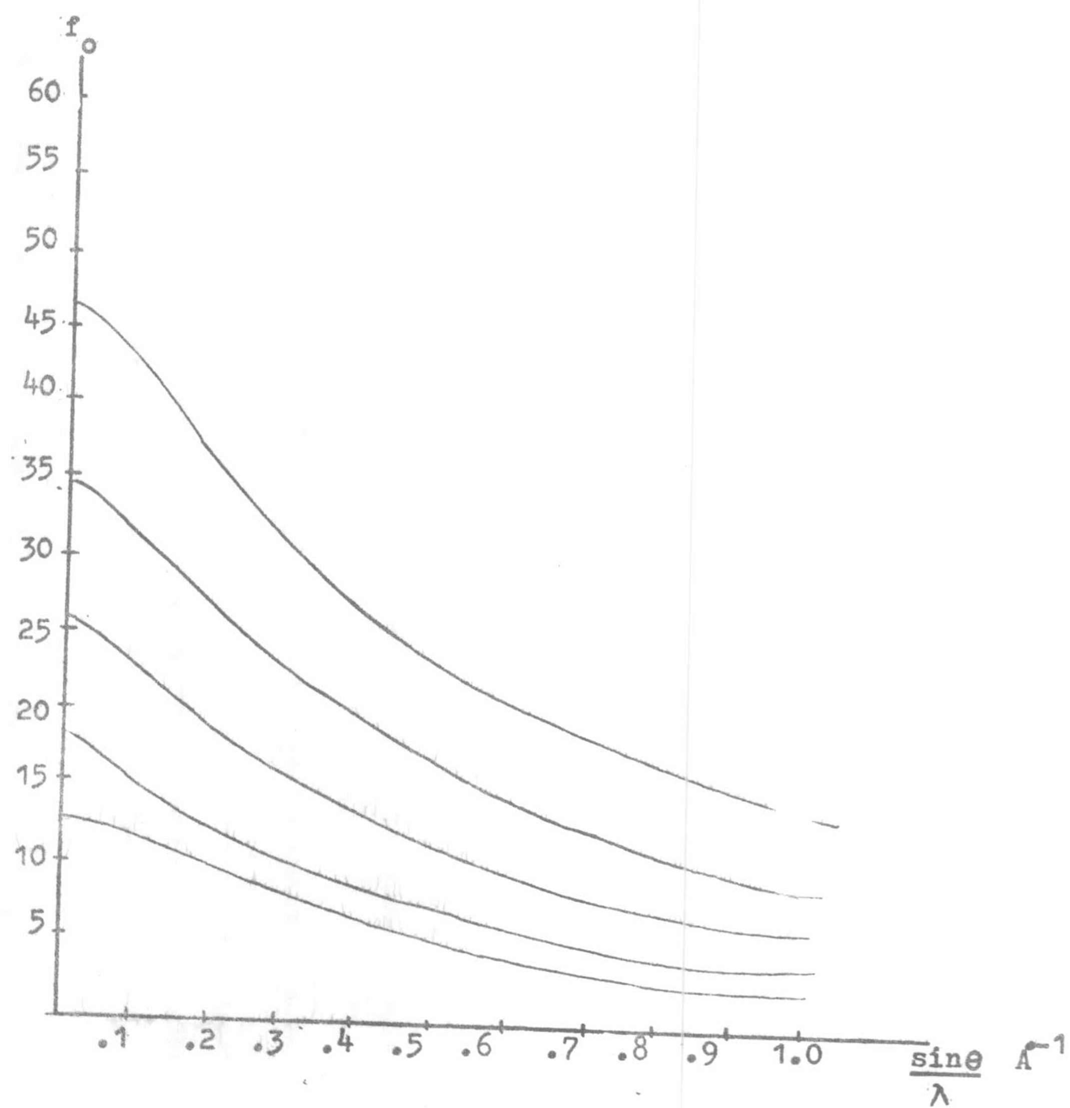


Fig.2.1.2 The variation of the scattering factor of each atom is a function of $\frac{\sin\theta}{\lambda}$.

2.2 Diffraction from a crystal

Diffraction is essentially a scattering phenomenon. Incident X-rays are scattered simultaneously by atoms of a crystal in the path of an X-ray beam. In general, the scattered waves interfere with and destroy one another, but in certain specific directions they combine to form new wave fronts. This cooperative scattering is known as diffraction.

Consider first the effect when a beam of monochromatic X-rays is incident on a single row of equally spaced identical atoms. The condition for diffraction by a row of atoms is shown in Fig.2.2.1 a. Two rays of an X-ray beam strike the row, of periodicity a, at an angle of incidence μ_1. The diffracted rays are in phase only if

$$\vec{a}.\vec{s} - (-\vec{a}.-\vec{i}) = \vec{a}.(\vec{s} - \vec{i})$$

$$= h\lambda \qquad \ldots (2.2.1)$$

where $\vec{a}$ is the repeat translation vector in the lattice,

$\vec{s}$ and $\vec{i}$ are the scattering and incident beam vectors,

h is an integer,

and λ is the wavelength of the monochromatic X-rays beam.

In terms of angles

$$a \cos\nu_1 - a \cos\mu_1 = h\lambda$$

where the angle of diffraction ν_1 is measured from the positive end of the row.

The condition for diffraction is not only in the direction $(a.\cos\nu_1)$ but in all directions that make an angle of ν_1 with the row. The diffracted beams will lie on the surfaces of concentric cones, coaxial with the row and with half-apex angles equal to ν_1 (Fig. 2.2.1 b).

In two-dimensional lattice, a plane lattice array of atoms may be defined by two translation periods a and b in the rows OA and OB, and the angle γ, Fig.2.2.2 a, we have the condition

$$\vec{b}.\vec{s} - \vec{b}.\vec{i} = \vec{b}.(\vec{s} - \vec{i})$$

$$= k\lambda \qquad \ldots (2.2.2)$$

or $$b.\cos\nu_2 - b.\cos\mu_2 = k\lambda$$

Diffraction occurs if the two equations, Eq.2.2.1 and Eq. 2.2.2 , are simultaneously satisfied. The beam meets the plane at such an angle that the cone about OA intersects the cone about OB along OX and OY. The angle between OA and OX is ν_1 , and that between OB and OY is ν_2 , in Fig.2.2.2 b.

The diffraction directions for a three-dimensional array of atoms are shown by three sets of diffraction cones coaxial with three reference rows. We will have the condition for the $\vec{c}$,

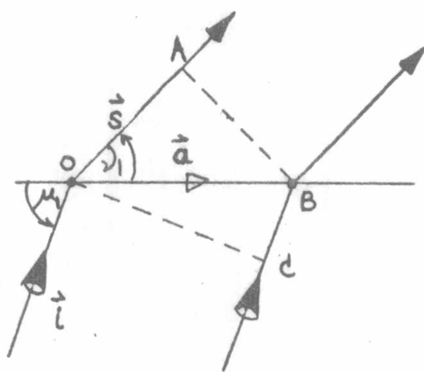
$$\vec{c}.\vec{s} - \vec{c}.\vec{i} = \vec{c}.(\vec{s} - \vec{i})$$

$$= l\lambda \qquad \ldots (2.2.3)$$

or $$c.\cos\nu_3 - c.\cos\mu_3 = l\lambda$$

if $\vec{c}$ is the third vector defining the lattice.

Fig.2.2.3 shows the intersecting cones of scattering directions for a three-dimensional lattice. When three cones intersect, each cone will make two intersections with each



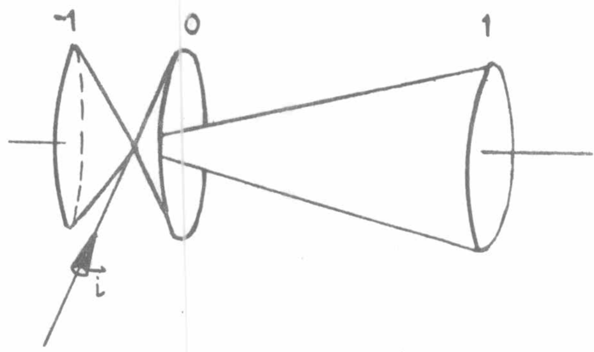
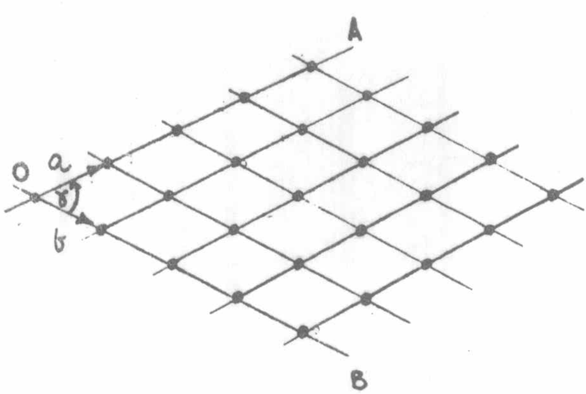


Fig.2.2.1(a) Scattering from a row of atoms. (b) Cones of diffracted rays from a row of atoms.



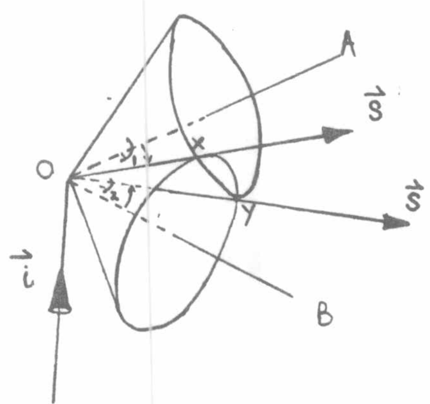


Fig.2.2.2(a) A two-dimensional lattice. (b) Intersecting cones for two-dimensional lattice.

of the other two cones. The three rows will scatter in phase only along a direction that is the intersection of three cones.

The equations (2.2.1) , (2.2.2) and (2.2.3) are called the Laue conditions.

The Bragg Law consider a beam of parallel X-rays of wavelength λ falling on parallel planes of spacing d. Both the incident and reflected X-ray beams make an angle θ with the set of planes, hkl, as shown in Fig.2.2.4.

Since there are large numbers of parallel planes, reflection from these planes will interfere with each other and reinforcement will occur when the rays are in phase with one another, i.e., where the path difference is an integral number of wavelengths,

$$AB + BC = n\lambda$$

where n is an integer.

From geometry,

$$AB = BC = d.\sin\theta$$

therefore

$$n\lambda = 2d.\sin\theta \qquad \ldots (2.2.4)$$

This is known as "Bragg's Law".

From Eq.(2.2.4) we can write

$$\sin\theta = \frac{\lambda/2}{d_{hkl}} = \frac{1/d_{hkl}}{2/\lambda} \qquad \ldots (2.2.5)$$

if

$$\frac{1}{d_{hkl}} = \sigma_{hkl}$$

$$\sin\theta = \frac{\sigma_{hkl}}{2/\lambda}$$

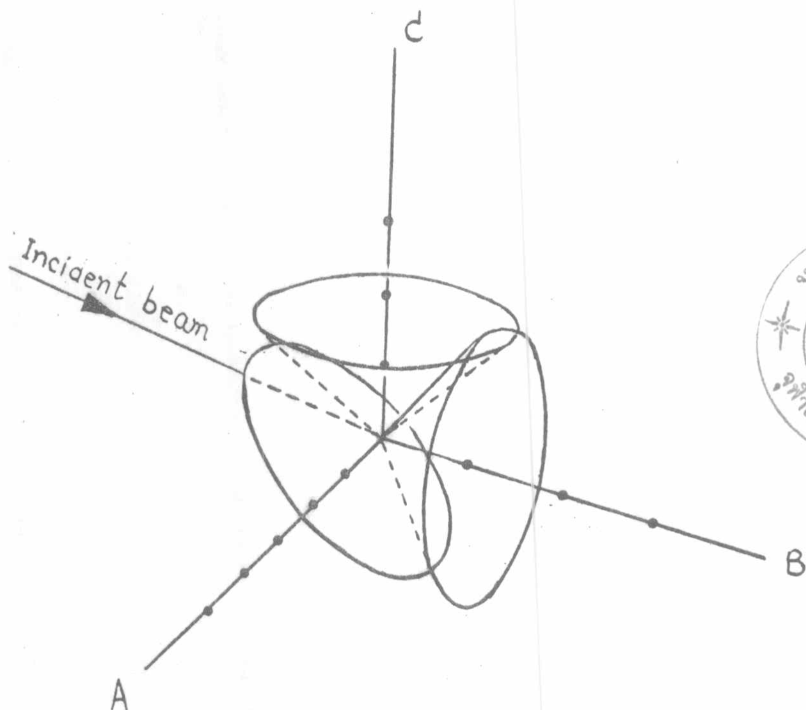


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Fig.2.2.3 Cones on three axes defining possible diffraction direction.

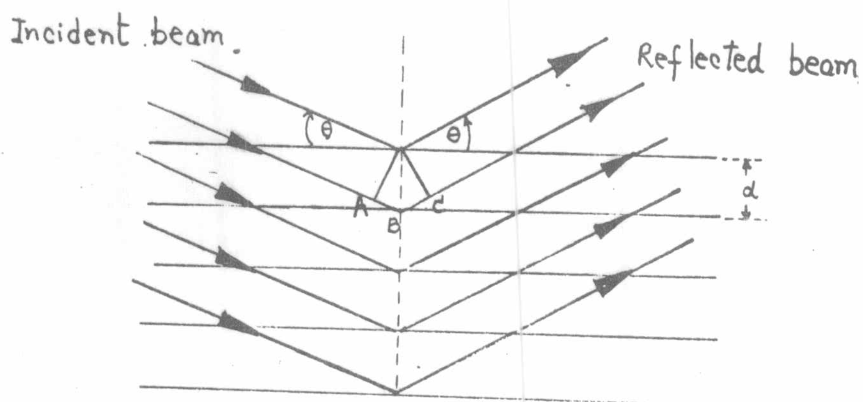

Fig.2.2.4 An X-ray beam at an angleθ with a set of planes with interplanar spacing d.

In Fig.2.2.5 , the crystal plane hkl is set on the center of the sphere of radius $\frac{1}{\lambda}$. The point O is called the origin of the reciprocal lattice, and the sphere is called the Ewald sphere or the sphere of reflection.

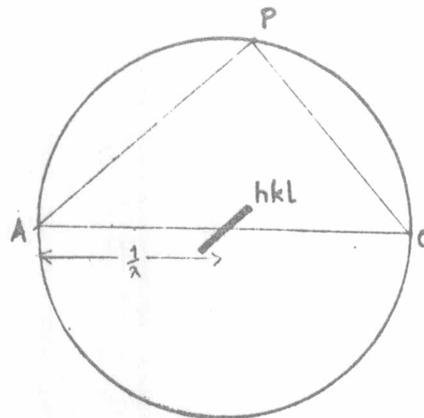

Fig.2.2.5 Geometrical construction of a reflection sphere.

Consider the reciprocal lattice vector ;

$$\vec{R} = p.\vec{a^*} + q.\vec{b^*} + r.\vec{c^*} \quad \ldots (2.2.6)$$

The three coefficient p, q, r may have any integral values.

$$\vec{a}.\vec{R} = \vec{a}.(p\vec{a^*} + q\vec{b^*} + r\vec{c^*})$$

$$= p$$

similarly $\vec{b}.\vec{R} = q$ ... (2.2.7)

and $\vec{c}.\vec{R} = r$

a^* , b^* and c^* are the reciprocal axes, and we have the conditions

$$\vec{a^*}.\vec{a} = \lambda \quad \ldots (2.2.8\ a)$$

$$\vec{b}^{*} \cdot \vec{b} = \lambda \qquad \ldots (2.2.8\text{ b})$$

$$\vec{c}^{*} \cdot \vec{c} = \lambda \qquad \ldots (2.2.8\text{ c})$$

The reciprocal lattice vector, $\vec{R}$, can be written in the form of unit vectors s and i as

$$\vec{R} = \frac{\vec{s} - \vec{i}}{\lambda} \qquad \ldots (2.2.9)$$

Substitute the vector $\vec{R}$ in the equation (2.2.7), then compare them with the Laue equations (2.2.1), (2.2.2) and (2.2.3), we will have

$$p = \vec{a} \cdot \left(\frac{\vec{s} - \vec{i}}{\lambda}\right) = h$$

$$q = \vec{b} \cdot \left(\frac{\vec{s} - \vec{i}}{\lambda}\right) = k$$

$$r = \vec{c} \cdot \left(\frac{\vec{s} - \vec{i}}{\lambda}\right) = l$$

or we may substitute $\vec{R}$ in the equation (2.2.6), and get

$$\frac{\vec{s} - \vec{i}}{\lambda} = h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}$$

If σ_{hkl} is the reciprocal lattice vector and defined by

$$\sigma_{hkl} = \frac{1}{d_{hkl}} = h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}$$

we can get

$$\frac{\vec{s} - \vec{i}}{\lambda} = \sigma_{hkl}$$

In Fig.2.2.6, the incident beam $\frac{\vec{i}}{\lambda}$ and the reflected beam $\frac{\vec{s}}{\lambda}$ form the same angle θ with the hkl plane.

Fig.2.2.6 Condition of reflection based on a reflection sphere.

$$\frac{1}{\lambda}|\vec{s} - \vec{i}| = |\sigma_{hkl}|$$

and

$$\sin\theta = \left|\frac{\vec{s} - \vec{i}}{2}\right|$$

$$\therefore \quad 2\sin\theta = |\vec{s} - \vec{i}|$$

$$= \lambda\,\sigma_{hkl}$$

$$\sigma_{hkl} = \frac{1}{d_{hkl}},$$

therefore

$$2d_{hkl}\sin\theta = \lambda \qquad \ldots (2.2.10)$$

which is the Bragg's law. Thus it is obvious that the three Laue conditions are equivalent to the Bragg condition and both can be related to the reciprocal lattice concept.

2.3 The Fourier transform of the structure factor and the electron density

A crystal is periodic in three dimensions, it can be represented by a three-dimensional lattice of atoms in a unit cell.

The structure factor equation can be written in terms of indices of reflection hkl and fractional co-ordinates within the unit cell (X,Y,Z), as

$$F_{hkl} = V \int_{X=0}^{1} \int_{Y=0}^{1} \int_{Z=0}^{1} \rho(XYZ) \exp\{2\pi i(hX+kY+lZ)\}\, dX dY dZ \qquad \ldots (2.3.1)$$

where $\rho(XYZ)$ is the electron density.

The structure with j atoms in the unit cell at the position (x_j, y_j, z_j) has a Fourier transform which is the resultant of j waves scattered in the direction of the reflection hkl by the j atoms, and can be written as

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp\{2\pi i(hx_j+ky_j+lz_j)\} \qquad \ldots (2.3.2)$$

The structure factor, F_{hkl}, is related to the atomic position x_j, y_j, z_j of an atom j and its scattering factor f_j, thus

$$F_{hkl} = A_{hkl} + i B_{hkl} \qquad \ldots (2.3.3)$$

where $$A_{hkl} = \sum_{j}^{N} f_j \cos 2\pi (hx_j+ky_j+lz_j)$$

and $$B_{hkl} = \sum_{j}^{N} f_j \sin 2\pi (hx_j+ky_j+lz_j) \qquad \ldots (2.3.4)$$

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The phase angle, α_{hkl}, associated with each structure factor, is given by

$$\alpha_{hkl} = \tan^{-1}\left(\frac{B_{hkl}}{A_{hkl}}\right) \qquad \ldots (2.3.5)$$

The value of $|F_{hkl}|$, the modulus of the structure factor, is expressed in terms of A_{hkl} and B_{hkl} as follows,

$$|F_{hkl}| = \sqrt{A^2_{hkl} + B^2_{hkl}} \qquad \ldots (2.3.6)$$

From Eq.(2.3.4) , we find

$$F_{hkl} = |F_{hkl}| \exp \{i\alpha_{hkl}\} \qquad \ldots (2.3.7)$$

These equations, (2.3.1),(2.3.2) and (2.3.3), can lead to the determination of crystal structures. The structure amplitudes, the $|F|$'s, can be derived from the observed intensities of X-ray reflections, but the phase angles α_{hkl} cannot be directly determined. If the phases of the structure factors are known, then the crystal structure is known.

The electron density must be computed first, and sub - sequently the atomic centers are located at the electron density peaks. In the unit cell the value of the electron density is nil except where there are atoms. Where there is an atom j the electron density may be represented by the f_j value which is the Fourier transform of the structure factors, and vice versa, as shown in Eq.(2.3.2). The relationship of the structure factor, F_{hkl}, and the electron density at a position X,Y,Z in the unit cell, $\rho(XYZ)$, is shown thus

$$\rho(XYZ) = \frac{1}{V}\sum_h \sum_k \sum_l F_{hkl} \exp\{-2\pi i(hX+kY+lZ)\} \quad \ldots (2.3.8)$$

The electron density equation can take different forms depending on the space group of the crystal structure. The electron density equations are given for each of the 230 space groups in the International Tables for X-ray Crystallography, Vol.I. In the particular instance, the space group of Nb_3As is $P4_2/n$ and the electron density is expressed as

$$\rho(XYZ) = \frac{4}{V_c}\Bigg[\sum_0^\infty \sum_0^\infty \sum_0^\infty{}^{h+k=2n} \{F(hkl)\cos 2\pi(hX+kY)+F(\bar{h}kl)\cos 2\pi(hX-kY)\} \cos 2\pi lZ$$

$$- \sum_0^\infty \sum_0^\infty \sum_0^\infty{}^{h+k=2n+1} \{F(hkl)\sin 2\pi(hX+kY)-F(\bar{h}kl)\sin 2\pi(hX-kY)\} \sin 2\pi lZ\Bigg]$$

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2.4 Diffraction data collection

X-ray diffraction data are collected from the various types of diffraction pattern that are obtained from single-crystal cameras and powder cameras. The diffraction patterns are related to the distribution of electrons in the unit cell. The size, shape and symmetry of the reciprocal and direct lattices can be calculated from the geometry of diffraction.

From a powder photograph, the indices of a diffraction line can be determined. It is used for determining unit cell parameters accurately for a crystal structure. The line diffraction pattern is obtained when a collimated beam of monochromatic X-rays falls on the specimen.

The other crystallographic data can be obtained from single-crystal cameras. The simplest type of single-crystal camera in common use is the oscillation camera. The crystal is glued to a fine glass fibre and this is attached to a rotating goniometer head. The X-ray beam is collimated and is perpendicular to the axis of rotation of the crystal. As the crystal rotates so the X-ray reflections are produced one by one and are recorded by the film. The diffraction spots on the oscillation photograph, in Fig.2.4.1, are found to lie on a series of straight lines, called layer lines. From the distances between these layer lines, the length of the rotation axis of the unit cell can be found.

There is a disadvantage of this method, because the

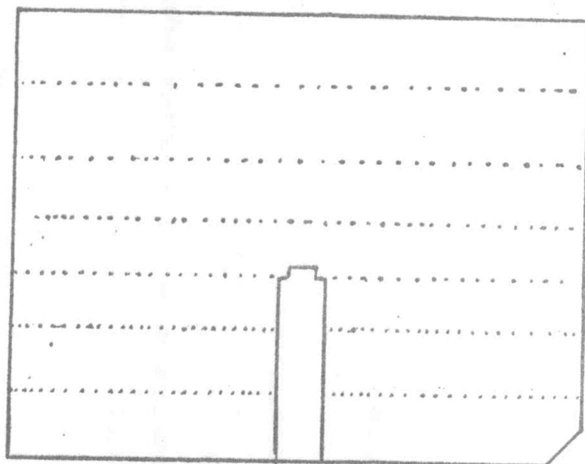

Fig.2.4.1 Oscillation photograph.

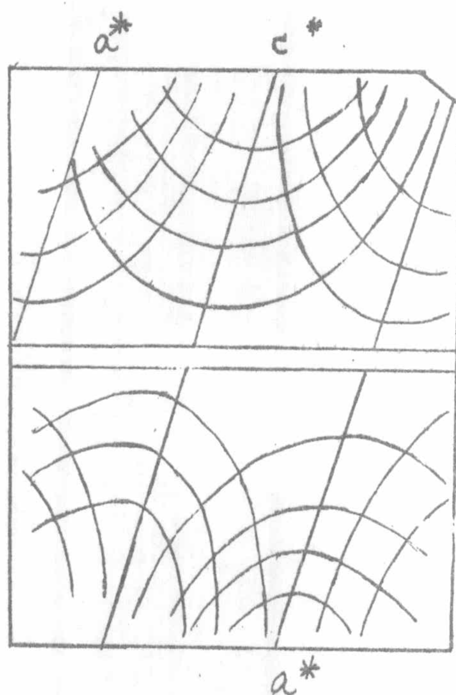

Fig.2.4.2 Weissenberg photograph with a^* and c^* axial lines.

information is contained in a two-dimensional reciprocal lattice plane that is condensed into an one-dimensional layer line. It is rarely used for the collection of intensity data but is more often used for the preliminary examination of crystals, the determination of unit cell dimensions and the crystal system. It is difficult to index reflections and many films are necessary to avoid the possible overlapping of spots.

Weissenberg photographs give a view of an entire reciprocal lattice level, the whole layer of information to be collected at one time without difficulty caused by overlapping.

From a Weissenberg photograph in Fig.2.4.2, a family of lines parallel to a reciprocal axis, a set of similar nonintersecting curves, called festoons, are produced at increasing distances from the center of the film.

The Weissenberg photograph is a map of the reciprocal lattice layer. By measuring the reciprocal lattice constants and converting them into the direct lattice ones, the cell constants are obtained. The diffraction spots in Weissenberg photographs can provide almost any information about that reciprocal lattice level. The systematic absences of certain types of reflections in the Weissenberg photograph will show the symmetry of the crystal structure.

In the diffraction photographs, the important information is obtained from the intensities of the diffraction spots. There are two general methods for obtaining the intensities of diffracted beam, such as diffractometric and photographic methods.

Diffractometer can provide more precise intensity data than do photographic methods.

The intensity measurement of the X-ray diffraction photographs involves the systematic comparison of the observed reflection against a calibrated density scale. If the spots on the film are similar to one another in appearance then one can produce an intensity scale by exposing one reflection along a strip of film for various lengths of time with the X-rays running under the same conditions. The relative intensities of the diffraction spots can be determined by comparison with various reference spots in the intensity scale. The value is then assigned as the observed intensity on an arbitrary scale.

2.5 Intensity data correction

Intensity data collected as described in Section 2.4 , is obtained from physical measurements on the crystal, the calculation of a structure will depend on the skilful extraction of the information from the observed intensities. From the intensity measuring for the various indexed reflection can be correlated, they must be multiplied by a Lorentz factor relating to the velocity and polarization factor $(Lp)^{-1}$, and by the absorption factor A^* for each reflection.

2.5.1 Lorentz and polarization correction factor$(Lp)^{-1}$

The usual X-ray beam is unpolarized, i.e., the electric vectors can point in any direction normal to the direction of propagation. Consider the component of these vectors that are shown in Fig.2.5.1 in two directions, one parallel to the surface of the reflecting plane, and the other at right angle to the first, and the sums of these two components will be equal.

Under the influence of a polarized wave of a given amplitude, if the electric vector is perpendicular to the plane containing the incident and scattered beams, an amplitude of a coherent wave that is scattered at a distance r is $\frac{e^2}{rmc^2}$ where e and m are the charge and mass of electron respectively, c is the velocity of light. If the electric vector is parallel to

the plane of the incident and scattered beams, the amplitude of the scattered radiation is $\frac{e^2}{rmc^2}\cos 2\theta$, where 2θ is the reflection angle.

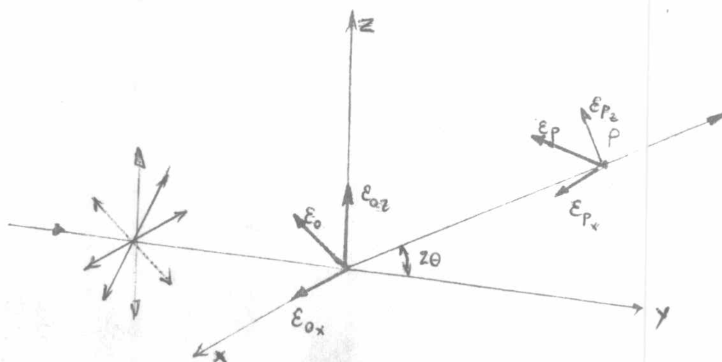

Fig.2.5.1 Unpolarized X-ray beam with electric vectors.

If the radiation is unpolarized, the mean amplitude of the scattered wave is $\frac{e^2}{rmc^2}\left\{\frac{1+\cos^2 2\theta}{2}\right\}^{1/2}$, and the term $\left\{\frac{1+\cos^2 2\theta}{2}\right\}$ is called the polarization factor.

The other trigonometric factor $\frac{1}{\sin^2\theta}$ called the Lorentz factor, L , arises because the time required for a reciprocal lattice point to pass through the sphere of reflection is not constant but varies with its position in reciprocal space and the direction in which it approaches the sphere. So the Lorentz factor depends on the way in which the reciprocal lattice point (hkl) passes through the reflecting sphere and also on the precise measurement technique used.

As the Lorentz factor, L, and the polarization factor, p, always occur together, it is in practice convenient to be able to correct them simultaneously.

As the quantity of the structure amplitudes $|F_{hkl}|$ is related to the intensities

$$|F_{hkl}| \propto \sqrt{I_{hkl}} \qquad \text{... (2.5.1)}$$

for correcting data with Lorentz-factor and polarization factor the equation can be written as

$$|F_{hkl}| = \sqrt{\frac{K}{Lp} \quad I_{hkl}} \qquad \ldots (2.5.2)$$

The Lorentz and polarization factors, combined and referred to as the Lp factor, are tabulated for various diffraction geometries in Vol. II of the International Tables for X-ray Crystallography.

2.5.2 Absorption correction factor (A^*)

A rough measurment is made of the dimensions of the crystal from which the diameter of the equivalent cylinder is estimated, and treated as a perfect cylinder . The absorption correction factor A^* will be calculated to correct the absorption error. After an X-ray beam of intensity I_o passes through a thickness t of crystal, the original beam is reduced by a factor $e^{-\mu t}$. Consequently

$$I = I_o \, e^{-\mu t} \qquad \ldots (2.5.3)$$

where I is the intensity of the beam which has traversed a thickness t,

μ is the linear absorption coefficient of the crystal.

For the crystal shown in Fig.2.5.2, assumed ideally imperfect, the small volume dv will contribute to the diffracted beam, an intensity proportional to $e^{-\mu(x+x')}dv$. The total intensity is reduced by absorption, then the fraction is given by

$$A = \left\{ \int_{V_x} e^{-\mu(x+x')} dv \right\} \Big/ \left\{ \int_{V_x} dv \right\}$$

$$= \frac{1}{V_x} \int_{V_x} e^{-\mu(x+x')} dv$$

The atomic absorption coefficient, μ_a, depends on the element and it is a function of the wavelength of the X-radiation. If a slab of material contains dn atoms and thickness dx, then the total mass of material is $A_t \frac{dn}{N_A}$ where A_t is the atomic weight and N_A is Avogadro's number. The density of the material is given by

$$\rho = \frac{A_t}{N_A} \frac{dn}{dx} \qquad \ldots (2.5.4)$$

$$dn = \frac{\rho N_A}{A_t} dx$$

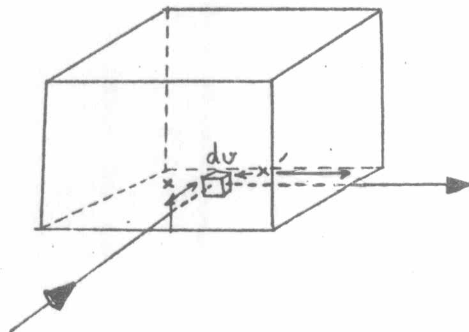

Fig.2.5.2 The diffracted beam from a small volume dv is reduced by absorption.

For the attenuation of a beam going through such material one may write

$$\frac{dI}{I} = -\mu_a dn$$

Because $\frac{dI}{I}$ is equal to $-\mu dx$, so we can write

$$\mu_a dn = \mu\, dx$$

and

$$\mu_a = \frac{\mu}{\rho}\frac{A_t}{N_A}$$

$$= \mu_m \frac{A_t}{N_A} \qquad \ldots (2.5.5)$$

where $\mu_m = \frac{\mu}{\rho}$ is called the mass absorption coefficient, which is used for mixed materials or compounds.

The linear absorption coefficients of mixtures of elements or compounds can be determined by using the relationship.

$$\mu_{compound} = \Sigma\, \mu_{element}$$

$$= \Sigma\, \mu_m \rho_p$$

where ρ_p is the partial density of the element within the compound and the summations are taken overall the elements in the compound.

The linear absorption coefficients can be determined when the atomic mass absorption coefficients and the density and composition of the material are known. Mass absorption coefficients are listed in Vol. III of the International Tables for X-ray Crystallography. From the calculated value of μ, μr is found where r is the estimated radius of the crystal that is shaped by grinding into a sphere or a cylinder. Then absorption factors at various inclination angles of the beam to the crystal can be expressed in the form of tables and these are given in Vol. II of the International Tables for X-ray Crystallography.

2.5.3 The temperature factor

A crystal is consisted of atoms bound together in a periodic pattern. Every atom in a crystal structure is bound to the other atoms by bonding forces of various types. The position of the atom is that corresponding to the minimum potential energy. All the atoms are vibrating about their mean positions with various amplitudes which increase as does the temperature of the solid. These vibrations will affect the relative co-ordinates of the atoms and the diffraction pattern.

When we assume that the thermal vibration are isotropic, the values of the temperature factor, B , are the same for all atoms, then we have the structure factor as modified by the isotropic thermal vibration,

$$\{F_{hkl}\}_T = F_{hkl} \exp\left\{\frac{-B\sin^2\theta}{\lambda^2}\right\}$$

or the intensities

$$\{I_{hkl}\}_T = I_{hkl} \exp\left\{\frac{-2B\sin^2\theta}{\lambda^2}\right\}$$

The observed intensities are reduced by thermal vibration with the factor $\exp\left\{\frac{-2B\sin^2\theta}{\lambda^2}\right\}$ which is known as the Debye-Waller factor.

2.6 The determination of space groups

There are seven three-dimensional co-ordinate systems which are the basis for their classification and useful in describing crystals. The crystal system is composed of 32 point groups that are the combination of the possible symmetry elements. Then the 32 point groups are combined with the 14 Bravais space lattices to obtain all possible space groups which describe the only way that identical objects may be arranged in an infinite lattice. A space group is designated by a capital letter identifying the lattice type (P,C,etc.) followed by the point-group symbol modified by the introduction of translational symmetry elements if needed.

The list of 230 space groups is given in the International Table for X-ray Crystallography, Vol.I.

Space group determination is one of the preliminary stages of a crystal-structure analysis. They can be determined from the various types of the diffraction pattern.

Laue photographs are one type of X-ray diffraction photographs. They are made by diffracting white X-rays from a stationary crystal. They are suited to detecting symmetry axis if the incident X-ray beam is directed along the symmetry axis.

From other kinds of X-ray photographs, sets of equivalent reflections give information about symmetry elements in the crystal. If such an oscillation photograph is taken about an axis perpendicular to a mirror plane then the photograph will have the zero

layer as a line of mirror symmetry. When an oscillation photograph shows a mirror line then it is the space group of monoclinic system and if mirror lines are located about two different axis the symmetry must be orthorhombic.

The information obtained from Laue and other types of photographs should make possible the correct and unique assignment of the crystal system and even the crystal class. The space group is determined when sufficient information is obtained from the X-ray diffraction data.

Systematic absences are the disappearance of certain reflections in the reciprocal lattice as found in Weissenberg photographs. Systematic absences such as a row extinction can be detected when photographs of successive levels are superimposed. Systematic absences of reflection caused by translation symmetry elements are given in Table 2.6.1, where n is an integer so 2n and 2n+1 are general representations for the set of even and odd numbers.

From the condition of systematic absences in the photograph, we shall know the symmetry element of the crystal and this leads to the right space group.

Table 2.6.1 Some translational symmetry elements and their systematic absence condition

Symmetry element	Affected reflection	Systematic absence condition
Body-centered lattice(I)	hkl	h+k+l = 2n+1
Face-centered lattice(F)	hkl	h+k = 2n+1 i.e,h,k,l h+l = 2n+1 not all even k+l = 2n+1 or all odd
A-centered lattice	hkl	k+l = 2n+1
B-centered lattice	hkl	h+l = 2n+1
C-centered lattice	hkl	h+k = 2n+1
n glide perpendicular to a	0kl	k+l = 2n+1
d glide perpendicular to a	0kl	k+l = 4n+1, 2 or 3
b glide perpendicular to a	0kl	k = 2n+1
c glide perpendicular to a	0kl	l = 2n+1
n glide perpendicular to b	h0l	h+l = 2n+1
d glide perpendicular to b	h0l	h+l = 4n+1, 2 or 3
c glide perpendicular to b	h0l	l = 2n+1
a glide perpendicular to b	h0l	h = 2n+1
n glide perpendicular to c	hk0	h+k = 2n+1
d glide perpendicular to c	hk0	h+k = 4n+1, 2 or 3
a glide perpendicular to c	hk0	h = 2n+1
b glide perpendicular to c	hk0	k = 2n+1
2-fold screw along a	h00	h = 2n+1
2-fold screw along b	0k0	k = 2n+1
2-fold screw along c	00l	l = 2n+1

2.7 The determination of crystal structures

The intensity of X-ray beam scattered in any one diffracted direction depends upon the atomic arrangement and the positions of the atomic centers. A crystal is considered as a continuous distribution of electron density, reaching the maximum at the center of atom and falling off to zero in the space between atoms. Because the phases of structure factors are not directly known, therefore the Patterson function , which is related to the electron density, and includes no phase angle, is very useful in the structure determination of heavy-atom crystal. The electron density at any point can be put in Patterson's function P(UVW), that is expressed as

$$P(UVW) = V \int_0^1 \int_0^1 \int_0^1 \rho(XYZ)\ \rho(X+U,\ Y+V,\ Z+W)\ dX\ dY\ dZ \quad \ldots (2.7.1)$$

where an electron density distribution,

$$\rho\,(XYZ) = \frac{1}{V} \sum_{hkl} F_{hkl}\ \exp.(-2\ \pi i)(hX+kY+lZ)$$

The Patterson function can be represented by the Fourier series.

$$P(UVW) = \frac{1}{V} \sum_{hkl} |F_{hkl}|^2\ \exp.(-2\ \pi i)(hU+kV+lW) \quad \ldots (2.7.2)$$

Physical interpretation of the function P(UVW) is given in terms of interatomic vector. From any point (x,y) in the unit cell , that is shown in Fig.2.7.1, draw a vector with

components $\vec{U}$ and $\vec{V}$ that represent vectors joining two atoms. Atomic positions are derivable from the complete knowledge of interatomic vectors.

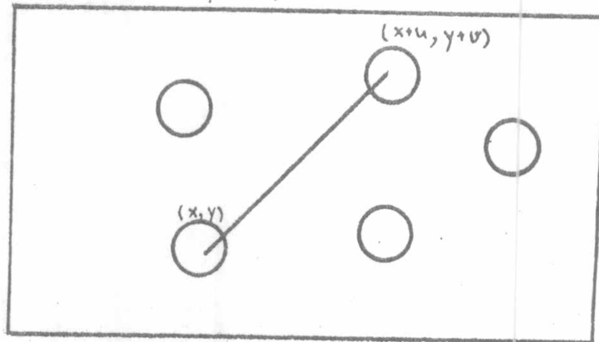

Fig.2.7.1 A crystal structure projected on to (x,y) plane and the electron density being finite within the circles.

Suppose the unit cell of the crystal containing N point atoms, each of which is repeated on an infinite lattice , so the Patterson function consists of N^2 Patterson peaks repeated in the same way. The Patterson function will be a superposition of peaks derived from all of pairs of atoms in the unit cell. It gives the vector distance between every pair of atoms, and is related to the electron density if a Fourier series is summed with the squares of the structure amplitudes as coefficients as in Eq.(2.7.2). The quantity $|F_{hkl}|^2$ are directly derivable from the measured X-ray intensities and so the series in Eq.(2.7.2) can be summed. It is possible to determine the features of a crystal-structure from its Patterson function.

2.8 Accuracy and refinement process

When a crystal structure is solved, the solution will appear as a set of fractional co-ordinates. The accurate positional parameters for the atoms can be determined from F_o synthesis.

More accurate determination is obtained by using Booth's method which yields good results. Co-ordinates of a maximum electron density value are located roughly by inspection or graphical interpolation. An example is given here.

Choose the electron density at 3x3 grid of points surrounding the peak maxima and tabulate it in the form of Table 2.8.1 and 2.8.2 where $\rho_1 > \rho_2 > 0$

Table 2.8.1 $\Delta\rho$ as a function of x-coordinate

x	0	1	2
$\Delta\rho$	0	ρ_1	ρ_2

Table 2.8.2 $\Delta\rho$ as a function of y-coordinate

y	0	1	2
$\Delta\rho$	0	ρ_1	ρ_2

The electron density is given by

$$\rho = ax^2 + bx \qquad \ldots (2.8.1)$$

where the values of a and b are given by substituting the values of ρ_1 and ρ_2 from Table 2.8.1 and 2.8.2. in the Eq.(2.8.1) which gives

$$a = \frac{\rho_2 - 2\rho_1}{2}$$

$$b = \frac{-\rho_2 - 4\rho_1}{2}$$

From these equations, the maxima X_m and Y_m are expressed as

$$X_m = \frac{-b}{2a}$$

$$= \frac{(\rho_2/\rho_1) - 4}{(2\rho_2/\rho_1) - 4} \quad \ldots (2.8.2)$$

and

$$Y_m = \frac{(\rho_2/\rho_1) - 4}{(2\rho_2/\rho_1) - 4}$$

So the accurate positions of atoms in the crystal are obtained.

Least-squares method

A set of the observed structure factor, $|F_o|$, and the calculated structure factor, $|F_c|$, are obtained as function of the co-ordinates x_j, y_j, z_j and the temperature factor, B_j for the jth atom. The correct parameters can be expressed as ($x_j + \Delta x_j$, $y_j + \Delta y_j$, $z_j + \Delta z_j$, $B_j + \Delta B_j$)

The method of least-squares, as applied to structure refinement, involves varying the atomic parameters so as to

minimize the quantity

$$D = \sum_{hkl} W_{hkl} \left(|F_o| - |K F_c| \right)^2 \quad \ldots (2.8.3)$$

where W_{hkl} is the weight of the observation.

Many weighting schemes have been proposed based on the value of $|F_o|$ One such scheme suggested by Cruickshank et al. (1961) is

$$W = 1/(a + |F_o| + c\,|F_o|^2) \quad \ldots (2.8.4)$$

where a and c are about $2F_{min}$ and $2/F_{max}$ respectively , F_{min} and F_{max} are the minimum and maximum observed structure factors.

As previously mentioned the calculated structure factor,

$$(F_c)_{hkl} = \sum_{j=1}^{n} f_j \exp\{2\pi i(hx_j + ky_j + lz_j)\}$$

where f_j is the scattering factor for the jth atom in the unit cell.

The parameters, x_j , y_j, z_j, B_j and the scale factors, K , are considered as variables which may be adjusted to minimize D.

The right side of Eq.(2.8.3) is differentiated with respect to each of the parameters and setting the derivative equal to zero. Therefore

$$\sum_{hkl} W_{hkl} \left(|F_o| - |KF_c(p_1,p_2,\ldots,p_n)| \right) \frac{\partial}{\partial p_j} |KF_c(p_1,p_2,\ldots,p_n)| = 0$$

where p_j is any of the scale, positional, and thermal parameters.

Assume that , $\Delta p_j = p_j - a_j$,

where a_j is the initial approximation value of the parameters,

then express the function $|F_c|$ as a Taylor series and neglect second and higher powers of the series. This gives

$$\sum_{hkl} W_{hkl}\left(|F_o| - |KF_c(a_j)| - \frac{\partial}{\partial p_1}|KF_c|\,\Delta p_1 - \cdots - \frac{\partial}{\partial p_n}|KF_c|\,\Delta p_n\right)\frac{\partial}{\partial p_j}|KF_c|$$

$$= 0 \qquad \ldots (2.8.5)$$

The partial derivatives $\frac{\partial}{\partial p_j}|KF_c|$'s are taken for each of the m reflections, where $m > n$.

From the set of Eq.(2.8.5), the quantities Δp_j are solved. The combination of these values with the initial approximation, the a_j's, as in $a_j' = a_j + \Delta p_j$, gives better values for the various parameters.

These may be used to repeat the process until the residual value R, that is defined as

$$R = \frac{\sum\left(|F_o| - |F_c|\right)}{\sum |F_o|} \qquad \ldots (2.8.6)$$

will be decreased to the minimum. When the R drops to the minimum, the crystal structure is more accurate by this refinement.