ELEMENTS OF X-RAY DIFFRACTION AND STRUCTURE DETERMINATION

X-rays and X-ray Diffraction

X-rays were discovered in 1895 by the German physicist W.C. Röntgen and were so named because their nature was unknown at the time. It is known today that X-rays are electromagnetic radiation of exactly the same nature as light but of very much shorter wavelength. X-rays used in diffraction have wavelengths lying approximately in the range 0.5-2.5 Å, whereas the wavelength of visible light is of the order of 6000 Å, X-rays are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. Electrons are usually used for this purpose, the radiation being produced in an X-ray tube which contains an electron source and two metal electrodes. The high voltage maintained across these electrodes rapidly draws the electrons to the anode, or target, which they strike with very high velocity. X-rays are produced at the point of impact and radiate in all directions.
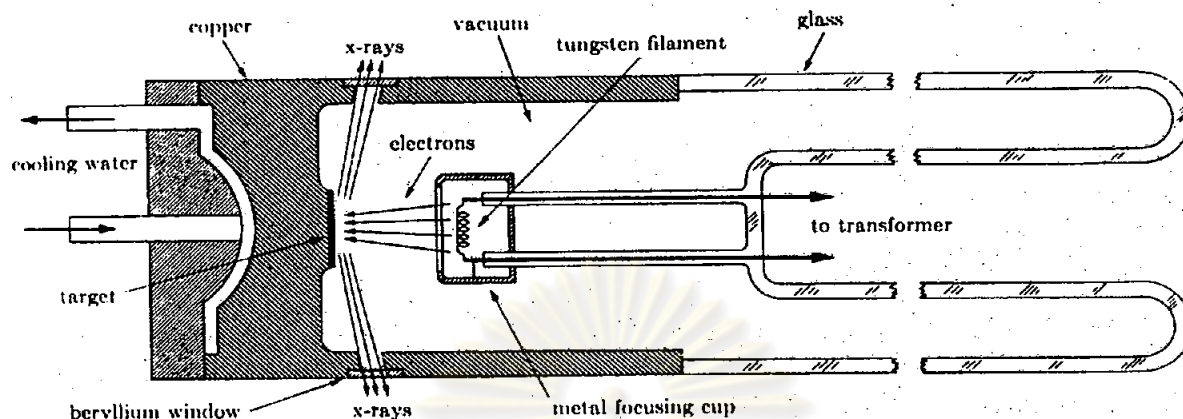
Fig.2.1   Cross section of x-ray tube

An electron in the path of an unpolarized X-ray beam vibrates with the frequency of the incident radiation , periodically absorbing energy and emitting it as X - radiation of the same frequency.   The original X - rays are unmodified in wavelength by the interaction but are radiated in all directions.   The electron has the effect of scattering the incident radiation and acts as a source of secondary X - rays.   The nucleus, because of its high mass, makes a negligible contribution to the radiation scattered by an atom.

An atom is not a point source of X-rays.   Its electrons occupy a space whose size is commensurable with the distances between adjacent atoms.   To develop the geometry of diffraction, it is permissible to adopt the simple picture that rays are scattered from different parts of the atom.

A crystal is an orderly arrangement of atoms.   All atoms in the path of an X-ray beam scatter X-rays simultaneously. 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.

The diffraction of X-rays by crystals was discovered by Max von Laue in 1912. He suggested that the periodic structure of a crystal might be used to diffract X-rays just as gratings are used to produce diffraction patterns with visible light.
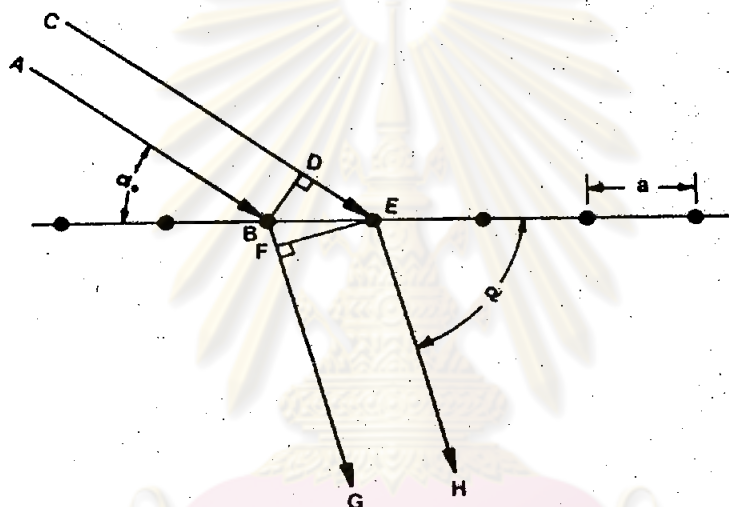

Fig. 2.2 Scattering of light by diffraction grating with the repeat distance "a"

In Fig. 2.2 the incident beam makes angle α_o with the diffraction grating. The incident ray CE travels farther than AB before reaching the grating, and the scattered ray BG travels farther than EH after passing the grating. The difference in path lengths of the beams CDEH and ABFG is DE-BF, and this difference must be equal to a whole number of wavelengths if the high intensity characteristic of constructive interference is to be observed at angle α. Therefore,

$$DE-BF = n\lambda \qquad \ldots\ldots\ldots\ldots\ldots 2.1$$

Where "λ" is the wavelenght of the light and "n" is an integer. By simple geometry

$$DE = a \cos \alpha_o \qquad \ldots\ldots\ldots\ldots\ldots 2.2$$

and

$$BF = a \cos \alpha \qquad \ldots\ldots\ldots\ldots\ldots 2.3$$

where a is the repeat distance, so

$$a (\cos \alpha_o - \cos \alpha) = n\lambda \qquad \ldots\ldots\ldots\ldots\ldots 2.4$$

This is the linear diffraction grating formula. Since crystals are periodic in three dimensions, three equations are required.

$$a (\cos \alpha_o - \cos \alpha) = h\lambda \qquad \ldots\ldots\ldots\ldots\ldots 2.5$$
$$b (\cos \beta_o - \cos \beta) = k\lambda \qquad \ldots\ldots\ldots\ldots\ldots 2.6$$
$$c (\cos \gamma_o - \cos \gamma) = l\lambda \qquad \ldots\ldots\ldots\ldots\ldots 2.7$$

These are called the Laue equations. The angles between the incident X-ray beam and the unit cell axes a,b,c are α_o, β_o, and γ_o and α, β, and γ are the corresponding angles for the diffracted beam. Constructive interference will occur only for values of these six angles for which h, k, and l in Eqs. (2.5) - (2.7) are integers.

Shortly after the discovery of X-ray diffraction, W.H. Bragg discovered that the geometry of the process is analogous to the reflection of light by a plane mirror. Because of the three dimen-sional periodicity of a crystal structure it is possible to construct sets of many planes that are parallel with each other, equally spaced, and contain identical atomic arrangements. If an incident X-ray beam makes an angle θ with such a set of planes, the reflected beam also

makes an angle θ with the planes, as in the case of optical reflec – tion. It follows that the angle between the incident and reflected rays is 2θ. Since there are large numbers of parallel planes involved in scattering X-rays, reflections from successive planes will inter- fere with each other, and there will be constructive interference only when the difference in path length between rays from successive planes is equal to a whole number of wavelengths.This is illustrated in Fig.2.3 where X-rays of wavelength λ are incident at angle θ on a set of planes with spacing d. The ray striking the second plane travels a distance AB+BC farther than the ray striking the first plane. These two rays will be in phase only
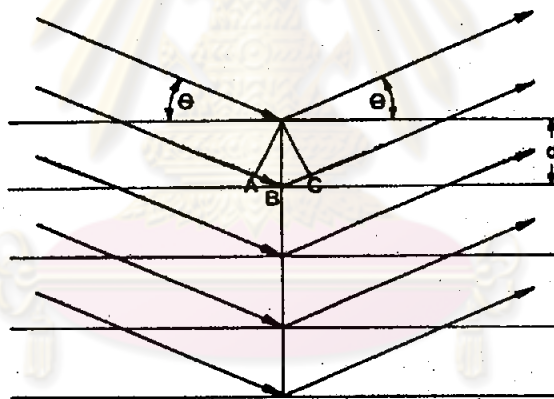

Fig.2.3 An X-ray beam makes angle θ with a set of planes with
   interplanar spacing d.

$$AB+BC = n\lambda \qquad \dots\dots\dots\dots\dots \text{'2.8}$$

where n is some integer. From elementary geometry

$$AB = BC = d \sin \theta \qquad \dots\dots\dots\dots 2.9$$

Therefore,

$$2d \sin \theta = n\lambda \qquad \dots\dots\dots\dots 2.10$$

and this is the well-known Bragg's law. Eq. (2.10) provides
no information other than that given by the Laue equations, but
the interpretation of X-ray diffraction patterns is frequently easier
in terms of Bragg's law since only one measured angle is required.

The structure Factor

The structure factor, F_{hkl} , is the resultant of j waves
scattered in the direction of the reflection hkl by the j atoms in
the unit cell. Each of these waves has an amplitude proportional
to f_j , the scattering factor of the atom, and a phase δ of the wave
scattered by the atom.

Scattering factor of the atom is expressed in term of the
scattering power of an equivalent number of electrons located at the
position of atomic nucleus and is calculated for an atom at rest.
Debye deduced on theoretical grounds in 1914 that the scattering
factor of an atom at ordinary temperatures (f) is related to its
scattering factor at rest (f_o) by the expression.

$$f = f_o e^{-B (\sin^2 \theta)/\lambda^2} \quad \dots\dots\dots\dots\dots\dots 2.11$$

where B incorporates the mean displacement of the atom from
its mean position and depends on the kind of the atom and the
orientation of the reflecting planes in the crystal, λ is the
wavelength of the incident beam and θ is the Bragg's angle. The
variation of the scattering factor of tungsten, vanadium and oxygen
with $\sin \theta/\lambda$ are shown in Fig.2.4 At $\sin \theta/\lambda = 0$ the value of the
scattering factor is always equal to the total numbers of electrons
in the atom. As $\sin \theta/\lambda$ increases, however, the scattering factor

decreases because X-rays scattered from an electron in one part of an atom will be, to an increasing extent, out of phase with those scattered in another part of the electron cloud.
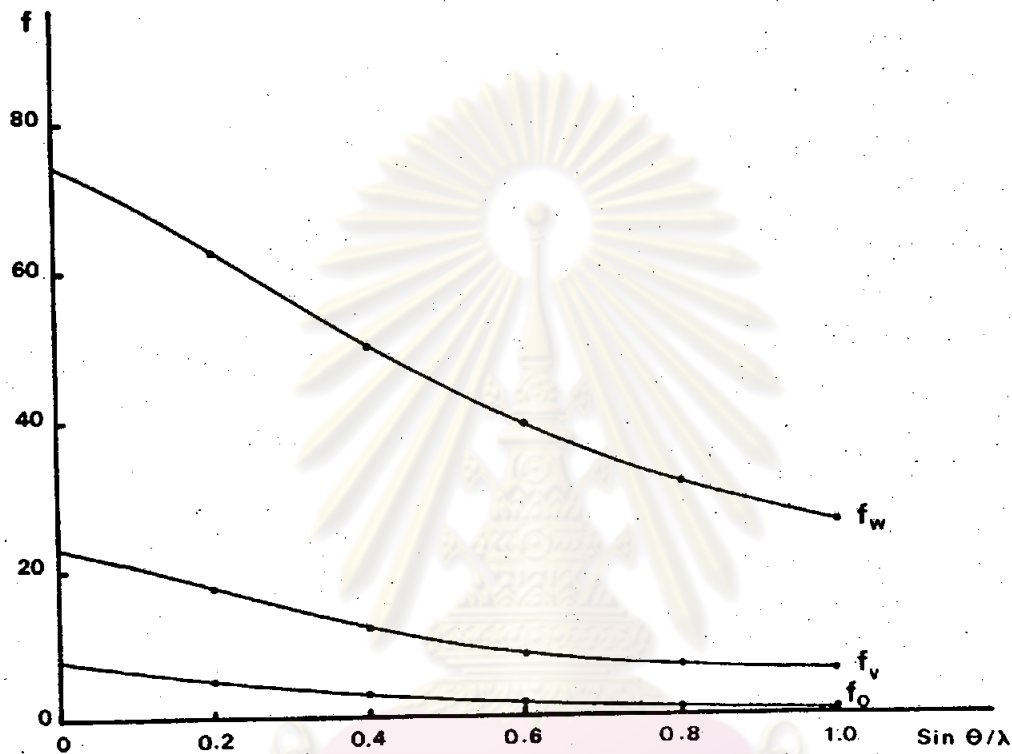

Fig.2.4   Atomic scattering factor of tungsten, vanadium and oxygen as a function of sin θ/λ

To express the phase factors in the structure amplitude equation in terms of the positions of the atoms in the unit cell. Consider a two-dimensional structure (Fig.2.5) with black atoms at the corners of the cell and a white atom γ with coordinates $x_γ$ and $y_γ$ (these symbols refer to fractional parts of the cell edges a and b). Assume a set of (hk) "planes" reflecting in the first order. The closest (hk) plane to the origin has intercepts $\frac{1}{h}$. a and $\frac{1}{k}$. b on the cell

edges. From Bragg's law these distances are equivalent to 2π phase changes in the a and b directions, respectively. The atom γ is displaced from the origin at o by the components x_γ. a along a and y_γ. b along b. The distance x_γ . a is equivalent to a phase component

$$\frac{x_\gamma \cdot a \, 2\pi}{a/h} = hx_\gamma \cdot 2\pi = \delta_{\gamma a} \qquad \cdots\cdots\cdots\cdots 2.12$$

along a for the γ atom. Similarly, y_γ. b is equivalent to the plase component

$$\frac{y_\gamma \cdot b \, 2\pi}{b/k} = ky_\gamma \cdot 2\pi = \delta_{\gamma b}$$

along b. The phase factor for the γ atom is the sum of the two component phase factors and therefore

$$\delta_\gamma = \delta_{\gamma a} + \delta_{\gamma b}$$

$$= 2\pi \, (hx_\gamma + ky_\gamma) \qquad \cdots\cdots\cdots\cdots 2.13$$

It can be shown that for a three-dimensional structure

$$\delta_\gamma = 2\pi \, (hx_\gamma + ky_\gamma + lz_\gamma) \qquad \cdots\cdots\cdots\cdots 2.14$$
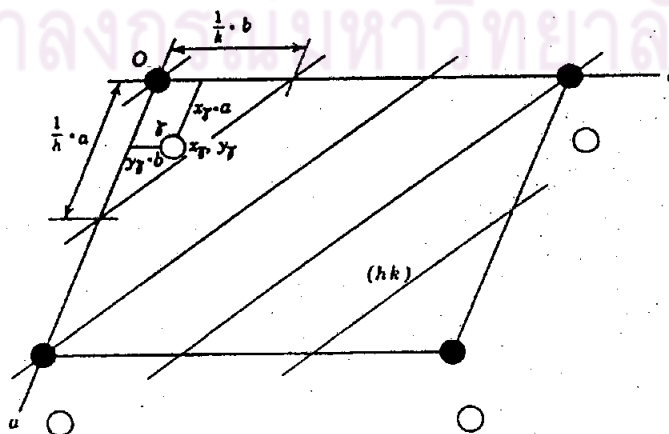

Fig.2.5　A two-dimensional structure

$|F_{(hkl)}|$ is known as the structure amplitude and is the ratio of the amplitude of the wave scattered by all atoms in the cell to the amplitude of the wave scattered by one electron.
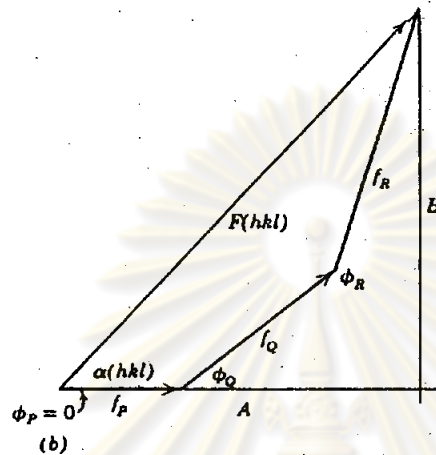

Fig.2.6   Vector representation of waves with different amplitudes

and phases

From Fig.2.6

$$|F_{(hkl)}|^2 = |A^2 + B^2|^{1/2}$$

$$= |(F_{\cos\alpha})^2 + (F_{\sin\alpha})^2|^{1/2} \qquad \dots 2.16$$

where

$$(F_{\cos\alpha})^2 = (f_P \cos\delta_P + f_Q \cos\delta_Q + f_R \cos\delta_R)^2 \dots 2.17$$

$$(F_{\sin\alpha})^2 = (f_P \sin\delta_P + f_Q \sin\delta_Q + f_R \sin\delta_R)^2 \dots 2.18$$

Then for a unit cell with j atoms

$$|F_{(hkl)}| = [(\Sigma f_{o,j} \cos\delta\gamma)^2 + (\Sigma f_{o,j} \sin\delta\gamma)^2]^{1/2} \dots 2.19$$

where f_j and δ_j refer, respectively, to the atomic scattering factor and the phase factor of the j th atom.

Substituting $\delta_j = 2\pi (hx_j + ky_j + lz_j)$ into Eq. (2.19) we obtain

$$|F_{(hkl)}|^2 = [\sum_j f_j \cos 2\pi (hx_j + ky_j + lz_j)]^2 +$$

$$[\sum_j f_j \sin 2\pi (hx_j + ky_j + lz_j)]^2 \dots 2.20$$

The function cos x, sin x and e^x may be expressed by the series

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \dots 2.21$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \dots 2.22$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots 2.23$$

Substituting $x = i\delta$ and multiplying both sides of the Eq. (2.23) by f we have

$$fe^{i\delta} = f(1 + i\delta - \frac{\delta^2}{2!} - \frac{i\delta^3}{3!} + \frac{\delta^4}{4!} - \dots)$$

$$= f[(1 - \frac{\delta^2}{2!} + \frac{\delta^4}{4!} - \dots) + i(\delta - \frac{\delta^3}{3!} + \frac{\delta^5}{5!} - \dots)]$$

$$= f(\cos \delta + i \sin \delta) \dots 2.24$$

Since the right side of the Eq. (2.24) is a complex number which represent a wave with amplitude f and phase angle δ, the left side of this equation will also represent the same meaning. Therefore, the structure factor which is the sum of the waves scattered by the n atoms is

$$F_{(hkl)} = \sum_{j} f_j e^{i\delta_j} \quad \dots\dots\dots\dots\dots 2.25$$

Substituting δ as given in Eq. (2.14) into Eq. (2.25) we have

$$F_{(hkl)} = \sum_{j} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \quad \dots\dots\dots\dots\dots 2.26$$

The structure factor may be considered as the sum of the wavelets scattered from all the infinitesimal elements of electron density in a unit cell. Since electron density ρ is defined as the number of electrons per unit volume, it follows that the number of electrons in any volume element dv is

$$\rho (x,y,z) \, dv$$

In the exponential form the wavelet scattered by this element is

$$\rho (x,y,z) e^{2\pi i (hx + ky + lz)} \, dv$$

The resultant is the sum of all the elements in the unit cell, i.e., the integral over its volume

$$F_{(hkl)} = \int_{v} \rho (x,y,z) e^{2\pi i (hx + ky + lz)} \, dv \quad \dots\dots 2.27$$

The observed intensities of the beam of x-rays diffracted in any given direction from a crystal of any shape or size are related to the structure factor by the following equation

$$\left| F_{o \,(hkl)} \right| = \sqrt{\frac{KI_{(hkl)}}{LpA}} \quad \dots\dots\dots\dots\dots 2.28$$

$|F_{o(hkl)}|$ is the modulus of the observed structure factor , therefore only $|F_{o(hkl)}|$ can be obtained experimentally.

K is a scale factor necessary to place I on an absolute basis and depending on crystal size, beam intensity, and a number of fundamental constants.

P is the polarization factor which is given by

$$P = \frac{1 + \cos^2 2\theta}{2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 2.29$$

The Lorentz factor, L depends on the precise measurement technique used. For the equi - inclination Weissenberg it is given by

$$L = \frac{\sin \theta}{\sin 2\theta \sqrt{\sin^2\theta - \sin^2\mu}} \qquad \ldots\ldots\ldots\ 2.30$$

where μ is the equi - inclination setting angle. A is an absorption correction.

Electron Density

Atoms are positions of relatively high electron density in the crystal. Thus the electron density varies throughout the crystal, reaching maximum values at locations of atom centers, lower values at chemical bonds, and falling virtually to zero elsewhere in the structure. If the electron density could be mapped throughout the unit cell, and each atom gave a recognizable peak on the map, the structure could be easily deduced and then proved by a comparison of intensities calculated for the tentative structure with the intensities measured on the crystal. The first step in the implementing such a

procedure is to adopt a method of evaluating the electron density. Atoms are arranged in a periodic fashion in space and therefore the electron density also varies periodically throughout the crystal. They are described by periodic function, known as Fourier series.

One form of a general one - dimensional Fourier series may be written as follows :

$$f_{(x)} = a_o + \sum_1^n (a_h \cos 2\pi hx + b_h \sin 2\pi hx) \quad \ldots\ldots\ldots\ldots \quad 2.31$$

where the h's are integers, a_h and b_h are constants, and x is a fraction of a period.

It is often convenient to represent the Fourier series in terms of complex notation.

$$f_{(x)} = \sum_{-n}^n C_h e^{2\pi i\ hx} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.32$$

where we define $C_h = (a_h - ib_h)/2$, $C_{\bar{h}} = (a_h + ib_h)/2$, and $C_o = a_o$

The three-dimensional periodic electron density in a crystal can be represented by a three - dimensional Fourier series similar to Eq. (2.32)

$$\rho\ (x,y,z) = \sum_{h'}\sum_{k'}\sum_{l'} C_{h'k'l'}\ e^{2\pi i(h'x+k'y+l'z)}, \quad \ldots\ldots\ldots \quad 2.33$$

where h',k',l' an integers between $-\infty$ and ∞.

Substitution of Eq. (2.33) into Eq. (2.27) gives

$$F_{(hkl)} = \int_v \sum_{h'}\sum_{k'}\sum_{l'} C_{h'k'l'}\ e^{2\pi i(h'x+k'y+l'z)}\ e^{2\pi i(hx+ky+lz)}\ dv$$

$$F_{(hkl)} = \int_v \sum_{h'} \sum_{k'} \sum_{l'} C_{h'k'l'} \ e^{2\pi i \ [(h+h')x+(k+k')y+(l+l')z]} dv \qquad \ldots\ldots 2.34$$

If $h' = -h$, $k' = -k$, $l' = -l$, the Eq. (2.34) becomes

$$F_{(hkl)} = \int_v C_{\overline{hkl}} \ dv = V C_{\overline{hkl}}$$

$$C_{\overline{hkl}} = \frac{1}{v} F_{(hkl)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 2.35$$

In Eq. (2.33) substitution of $\overline{h}$, $\overline{k}$, $\overline{l}$ for h',k',l' and of $C_{\overline{hkl}}$

from Eq. (2.35) gives the required series :

$$\rho \ (x,y.z) = \frac{1}{v} \sum_h \sum_k \sum_l F_{hkl} \ e^{-2\pi i \ (hx+ky+lz)} \qquad \ldots\ldots\ldots 2.36$$

The comparison of the expression for the electron density, Eq. (2.36), with that for the structure factor, Eq. (2.27), shows that the electron density is the Fourier transform of the structure factors and in turn the structure factors are the Fourier transform of electron density.

The structure factor can be written in the form

$$F_{(hkl)} = \left| F_{(hkl)} \right| \ e^{2\pi i \ \alpha'_{hkl}} = \left| F_{(hkl)} \right| \ e^{i\alpha_{hkl}} \qquad \ldots\ldots 2.37$$

where $2\pi \ \alpha'_{hkl}$ is the phase angle.

Substitution in Eq. (2.36) gives

$$\rho \ (x,y.z) = \frac{1}{V} \sum_h \sum_k \sum_l \left| F_{(hkl)} \right| \ e^{-2\pi i \ (hx+ky+lz-\alpha'_{hkl})} \qquad \ldots\ldots 2.38$$

This form of the three - dimensional Fourier series is advantageous because the phase angle $2\pi\alpha'_{hkl}$ for each coefficient appears explicitly.

Patterson Function

The lack of knowledge of the phases of structure factor prevents us from directly computing an electron-density map and so showing the positions of the atoms in the unit cell. A.L. Patterson approached this problem in a way that he used the squares of the moduli as Fourier coefficients; these quantities are directly related to the observed intensities and so they can always be measured. The function he derived is now known as Patterson function.

When two atoms occur at locations $x_1 \, y_1 \, z_1$ and $x_2 \, y_2 \, z_2$, there arises a peak in the Patterson function at location uvw such that

$$u = x_2 - x_1$$
$$v = y_2 - y_1$$
$$w = z_2 - z_1$$

Patterson defined a function P (uvw) of the form

$$P_{(uvw)} = V \int_0^1 \int_0^1 \int_0^1 \rho_{(xyz)} \, \rho \, (x+u, y+v, z+w) \, dxdydz \quad \dots\dots \ 2.39$$

If we substitute in this expression the values for the electron densities given by Eq. (2.36) we arrive at the equation

$$P_{(uvw)} = \frac{1}{v} \int_0^1 \int_0^1 \int_0^1 \underset{h \ k \ 1 \ h'k'1'=-\infty}{\Sigma \ \Sigma \ \Sigma \ \Sigma \ \Sigma^\infty} F_{(hk1)} \exp \, \{-2\pi i (hx+ky+1z)\}$$

$$x \ F_{(h'k'1')} \ \exp \ \{-2\pi i (h'x+k'y+1'z)\}$$

$$\exp \, \{-2\pi i (h'u+k'v+1'w)\} \, dx \, dy \, dz \quad \dots\dots\dots \ 2.40$$

The right - hand side is zero unless h=-h', k=-k', 1=-1', when this condition applies,

$$P_{(u,v,w)} = \frac{1}{v} \underset{h}{\Sigma} \underset{k}{\Sigma} \underset{l=-\infty}{\Sigma^{\infty}} F_{(hkl)} F_{(\bar{h}\bar{k}\bar{l})} \exp \{2\pi i \ (hu+kv+lw)\}$$

$$\ldots\ldots\ldots\ldots 2.41$$

From Friedel's law, $I_{(hkl)} = I_{(\bar{h}\bar{k}\bar{l})}$ the relationship between

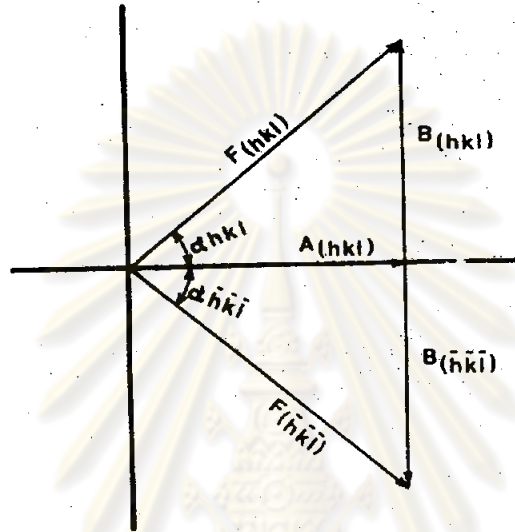F (hkl) and F $(\bar{h}\bar{k}\bar{l})$ is obtained.

Fig.2.7   Vector representation of $F_{(hkl)}$ and $F_{(\bar{h}\bar{k}\bar{l})}$

$$F_{(hkl)} = A_{(hkl)} + i \ B_{(hkl)} \qquad \ldots\ldots\ldots\ldots 2.42$$

$$F_{(\bar{h}\bar{k}\bar{l})} = \bar{F}_{(hkl)} = A_{(hkl)} - i \ B_{(hkl)} \qquad \ldots\ldots\ldots\ldots 2.43$$

$$F_{(hkl)} \ F_{(\bar{h}\bar{k}\bar{l})} = A^2_{(hkl)} + B^2_{(hkl)}$$

According to the Pythagorean theorem

$$A^2_{(hkl)} + B^2_{(hkl)} = |F_{(hkl)}|^2 \qquad \ldots\ldots\ldots\ldots 2.44$$

Thus

$$F_{(hkl)} \ F_{(\bar{h}\bar{k}\bar{l})} = |F_{(hkl)}|^2 \qquad \ldots\ldots\ldots\ldots 2.45$$

Substitute in Eq. (2.41) we get

$$P(uvw) = \frac{1}{v} \underset{h\ k\ l}{\Sigma\ \Sigma\ \Sigma} |F_{(hkl)}|^2 e^{2\pi i\ (hu+kv+lw)} \quad \ldots\ldots\ldots\ 2.46$$

The exponential in Eq. (2.46) can be expressed in the form of its real and imaginary components according to the well-known Eulerian relation

$$e^{i\phi} = \cos\phi + i\sin\phi \quad \ldots\ldots\ldots\ldots\ 2.47$$

When this is substituted for the exponential in Eq. (2.47), the Fourier representation of Patterson's function can be written

$$P(uvw) = \frac{1}{v} \underset{h\ k\ l}{\Sigma\ \Sigma\ \Sigma} |F_{(hkl)}|^2 [\cos 2\pi\ (hu+kv+lw) +$$

$$i\ \sin 2\pi\ (hu+kv+lw)] \quad \ldots\ldots\ldots\ldots\ 2.48$$

According to Friedel's law, $F_{(hkl)}$ and $F_{(\bar{h}\bar{k}\bar{l})}$ have equal magnitudes but opposite phases. Therefore $|F_{(hkl)}|^2$ and $|F_{(\bar{h}\bar{k}\bar{l})}|^2$ have equal magnitudes. There occur the following terms for positive and negative values of h,k,l :

$$|F_{(hkl)}|^2 \cos 2\pi\ (hu+kv+lw)$$

$$|F_{(hkl)}|^2 \cos 2\pi\ (\bar{h}u + \bar{k}v + \bar{l}w) = |F_{hkl}|^2 \cos 2\pi\ (hu+kv+lw)$$

$$|F_{(hkl)}|^2 i\sin 2\pi\ (hu + kv + lw)$$

$$|F_{(\bar{h}\bar{k}\bar{l})}|^2 i\sin 2\pi\ (\bar{h}u+\bar{k}v+\bar{l}w) = -|F_{(hkl)}|^2 i\sin 2\pi\ (hu+kv+lw)$$

It will be observed that the sine terms are equal and opposite. They therefore cancel one another in pairs, and Eq. (2.48) assumes the simple form

$$P(uvw) = \frac{1}{v} \sum_h \sum_k \sum_l |F_{(hkl)}|^2 \cos 2\pi (hu+kv+lw) \cdots\cdots\cdots 2.49$$

This function is centrosymmetrical because it has identical values for positive and negative values of the parameters uvw.

The labor of computing a full three – dimensional Patterson Fourier synthesis for a crystal is very great. It is much more usual to compute the projections of this synthesis. In making projections of the three-dimensional Patterson Fourier synthesis, the projections on planes normal to axes of a crystal for $P_{(xyz)}$ are $P_{(xy)}$, i.e., the coordinate z vanishes when projected along c. Coefficients for $P_{(xy)}$ are $|F_{(hko)}|^2$, obtainable from a single c-axis Weissenberg or precession photograph.

Among the disadvantages of working with Patterson projections is that the resolution of peaks is much poorer than in the full Patterson synthesis, and in moderately complicated crystals, it may be so poor that the Patterson projection is nearly or quite useless. Harker pointed out the advantages of certain two-dimensional sections and one-dimensional lines through the full three-dimensional Patterson function. Such sections do not suffer from overlap of peaks as do projections. They can be chosen so that they contain peaks due to pairs of symmetry equivalent atoms. For example, in monoclinic space group there is a mirror plane perpendicular to the b axis (Fig. 2.8) and thus for every atom with coordinates x, y, z there is another x, $\bar{y}$, z. The vectors between these atoms all have the coordinates o, 2y, o,i.e.) are concentrated on the Harker line which is the v axis in the Patterson.
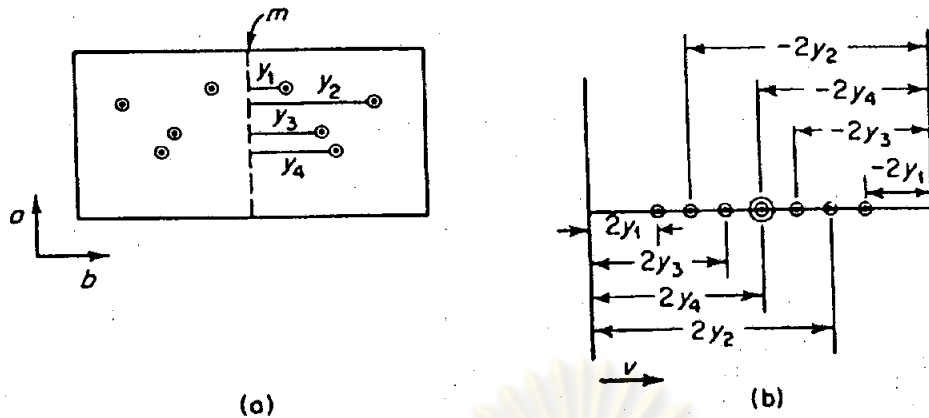
Fig.2.8   (a) Projection of a structure in space group Pm on the ab

face. (b) Harker peaks produced along the v axis by the

atoms in (a)

Difference Synthesis

Another extremely valuable approach to finding atoms lies in

the ΔF or difference synthesis. This is a Fourier synthesis which may

be expressed in the form

$$\Delta\rho = \frac{1}{v} \sum_{h} \sum_{k} \sum_{l} (|F_o| - |F_c|) e^{-\alpha_c} e^{-2\pi i(hx+ky+lz)}$$

where α_c is the phase of F_c

The difference synthesis has two major virtues. First, if

the phases α_c are correct, it provides a direct measure of the errors

between the model used and the true structure implied by the $|F_o|$'s.

This property is highly useful for refinement. Second, it permits

the selection and use of a partial set of data for which the probabi-

lities are especially high that the assigned phases are correct.

Furthermore, this partial set proves to be particularly rich in

useful information, which cannot be extracted by an F_o synthesis. The

second case is considered only in detail. The fundamental arguments

behind these assertions may be seen by considering three limiting cases of $|F_o|$'s and $|F_c|$'s. In the first $|F_o| \approx |F_c|$. If the phasing model is a suitable one, there is a high probability that α_c is approximately that corresponding to the true phase of F_o. If α_c differs from the true value, a large $|F_o|$ can introduce serious errors into the resulting synthesis. The use of these reflections offers at this stage relatively little gain, and the possible risk of large distortions so these reflections are automatically eliminated.

If $|F_o| \gg |F_c|$, the probability of correspondence between α_c and α_o is small and diminishes as $|F_c|$ approaches zero. In the difference synthesis, $|F_o| - |F_c|$ will be large and contribute to the summation, but the phase uncertainty is still present and can provide grounds for rejection.

The third and most interesting case is $|F_c| \gg |F_o|$. These reflections carry informations about the disagreement between the model and the true structure which cannot be obtained by a F_o synthesis because they are too weak to have much effect on the summation. $||F_o| - |F_c||$ will be large and a significant contributor to difference synthesis. Furthermore, it can be shown that these terms will be more or less correctly phased regardless of differences between α_c and α_o. The truth of preceding statement can be seen from Fig.2.9.
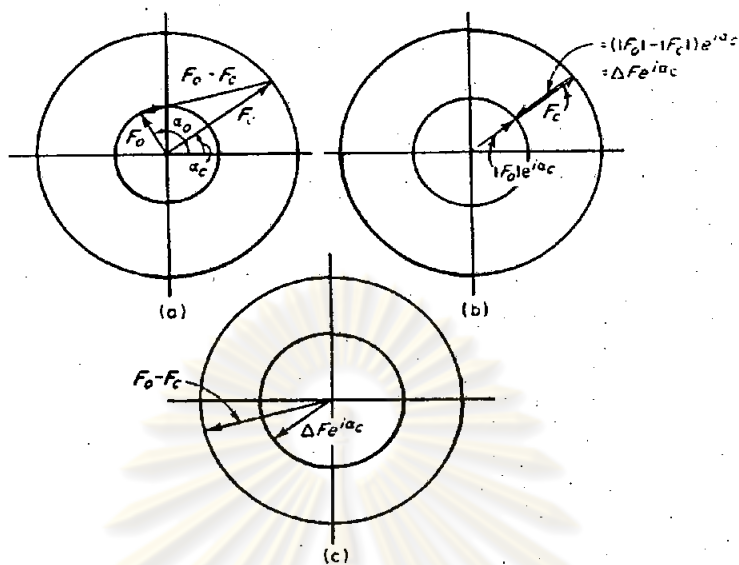
Fig.2.9　(a) Vectors for the case $|F_c| > |F_o|$.

(b) Vectors for the same case if α_o is taken as equal to α_c.

(c) Comparison for vectors $F_o - F_c$ and $\Delta Fe^{i\alpha_c}$.

The coefficients which are actually desired for the difference synthesis are

$$\Delta F = F_o - F_c$$

$$|\Delta F| \, e^{i\alpha\Delta} = |F_o| \, e^{i\alpha_o} - F_c \, e^{i\alpha_c}$$

These expressions correspond to Fig. 2.9a and merely state that the coefficients are the vectors required to correct the current F_c to the true F_o. As usual, α_o is unknown, so the assumption is made (Fig. 2.9b) that

$$\alpha_o \approx \alpha_c$$

$$|\Delta F| \, e^{i\alpha\Delta} \approx |F_o| \, e^{i\alpha_c} - |F_c| \, e^{i\alpha_c}$$

$$|\Delta F| \, e^{i\alpha\Delta} \approx (|F_o| - |F_c|) \, e^{i\alpha_c}$$

$$|\Delta F| \, e^{i\alpha\Delta} \approx \Delta F \, e^{i\alpha_c}$$

Since we are considering at present only the reflections for which ΔF is negative, the approximation actually used is

$$\Delta F \, e^{i\alpha\Delta} \approx -|\Delta F| \, e^{i\alpha_c}$$

From Fig. 2.10, the end of ΔF must always be on a smaller circle of radius $|F_o|$. It can be seen that as the smaller circle is smaller and smaller, the range over which α_Δ will vary as α_o changed is smaller too. Therefore, the approximation that α_Δ is nearly equal to α_c becomes more and more reliable.

It should be clear from these arguments that the most valuable reflections for use in difference synthesis are those for which $|F_o|$ is very small and $|F_c|$ very large.
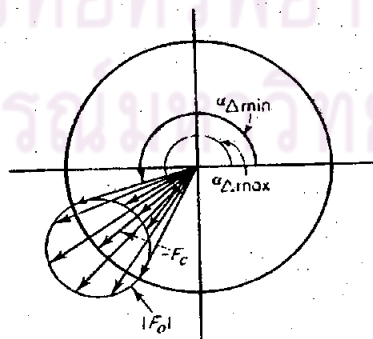

Fig.2.10   Construction showing range of $\alpha\Delta$

In addition to the useful applications have been mentioned above, difference density maps have another useful application. When a crystal contains atoms having a wide range of atomic numbers, very light atoms are difficult to notice in an ordinary synthesis of electron density, because the peaks of light atoms are about the same heights as the background fluctuations. But since the background fluctuations occuring in ρ_{obs} and ρ_{cal} are nearly the same, they cancel in the difference density, leaving as a residue and real difference in the electron densities of the structure and model.

The difference synthesis corresponds to a point – by – point subtraction of an F_c Fourier from an F_o Fourier calculated with the same phases. Correctly placed atoms will not appear in the synthesis, incorrectly placed ones will be in holes, and missing ones will appear as peaks. Thus it can be used as a guide to the removal of atoms which are incorrectly placed. The appearance of such holes should not lead automatically to the conclusion that the particular atoms or the whole structure, is incorrect. There are various reasons. The most common is failure to include a ΔF_{ooo} term in synthesis for which the model is less than the whole structure. Another is the use of weighting or cutoff functions which reduce the contributions from reflections for which $|F_c| < |F_o|$. The effect of these functions is to make the effective average value of $|F_c|$ too large and the corresponding calculated electron density too high. Physical reasons for the appearance of atoms in holes are the use of too small temperature factors, which increases the calculated peak density over what it should be, and the misidentification of atom types.
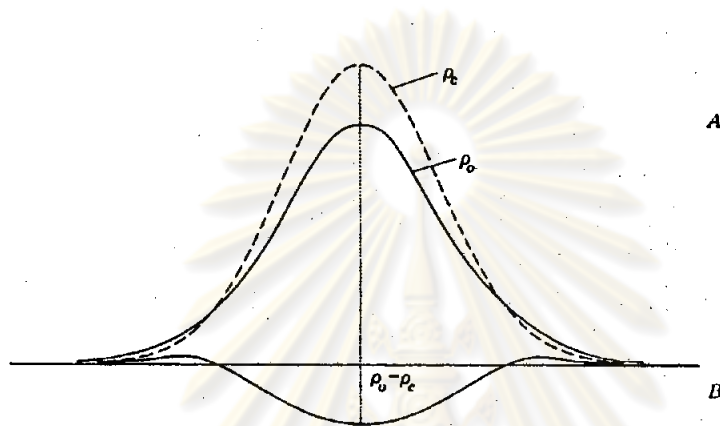
Fig.2.11   Difference electron density resulting from overestimation

of temperature motion

Refinement

The chief obstacle to overcome in the analysis of a crystal structure is the determination of the rough structure. It is a routine matter to refine this roughly known structure to any precision which the data permit. The degree to which a structure has been improved is commonly measured by a discrepancy index

$$R = \frac{\Sigma \mid \mid F_{obs} \mid - \mid F_{cal} \mid \mid}{\Sigma \mid F_{obs} \mid} \qquad \ldots\ldots\ldots\ldots\ldots 2.50$$

This is a crude measure of how much the model departs from the actual structure, as expressed by the differences in their diffraction amplitudes. The value of this index is limited by the quality of the data, and may be as small as 2 percent. Well-refined structures commonly have R in the neighborhood of 5 to 6 percent. For a completely wrong structure the expected value of R is 82.8 percent if the crystal is centrosymmetrical, or 58.6 percent, if noncentrosymmetrical. Model with R values of 45 percent or lower are worth trying to improve by refinement.

An analytical method of refinement of great power and generality is that based on the principle of least squares. Consider a linear function with n variable x_1, x_2...x_n. These variables can be thought at as defining a space whose value af any point is determined both by the location x_1, x_2...x_n and by independent parameters p_1, p_2, ..., p_n which define the function. Thus

$$f = p_1 x_1 + p_2 x_2 + p_3 x_3 + \ldots\ldots + p_n x_n \qquad \ldots\ldots\ldots\ldots\ldots 2.51$$

If the values of the function are measured at m different points with m > n, the principle of least squares state that the best values for the parameters P_1, P_2 ..., P_n are those which minimize the sums of the squares of the properly weighted differences between the observed and calculated values of the function for all the observational points. Thus the quantity to be minimized is given by

$$D = \sum_{r=1}^{m} W_r (f_{or} - f_{cr})^2 \quad \ldots\ldots\ldots\ldots\ldots 2.52$$

where f_{or} is one of the m observed values of the function, f_{cr} is the corresponding calculate value and W, the weight to be assigned an observation, is equal to the reciprocal of the variance of that observation.

In X-ray diffraction, the quantity most commonly minimized is

$$D = \sum_{hkl} W_{hkl} (|F_o| - |k F_c|)^2 \quad \ldots\ldots\ldots\ldots 2.53$$

where $\sum_{hkl}$ indicates summation over all the observed reflections and W_{hkl} is the weight of the observation.

Errors of measurement tend to be related to the actual value of $|F_o|$. One of weighting scheme suggested by Cruickshank is

$$W = (a + |F_o| + c |F_o|^2)^{-1} \quad \ldots\ldots\ldots\ldots 2.54$$

where $a \approx 2 |F_o \text{ min}|$

$c \approx 2 / |F_o \text{ max}|$

To obtain the best fit, it will be necessary to consider the parameters p as variables which may be adjusted to minimize D. Minimization is achieved by taking the derivative with respect to each of the parameters and equating to zero. This leads to the n normal equations

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

$$= 0 \quad (j = 1, 2, \ldots, n) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ 2.55$$

If the normal equations are not linear, they may be made linear by opproximating the function as a Taylor series,

$$f(p_1, p_2, \ldots, p_n) = f(a_1, a_2, \ldots, a_n) + \frac{\partial f(a_1, a_2, \ldots, a_n)}{\partial p_1}(p_1 - a_1) +$$

$$+ \frac{\partial f(a_1, a_2, \ldots, a_n)}{\partial p_n}(p_n - a_n) \quad \ldots\ldots\ldots \ 2.56$$

$$f(p_1, p_2, \ldots, p_n) = f(a_1, a_2, \ldots, a_n) + \frac{\partial f(a_1, a_2, \ldots, a_n)}{\partial p_1} \Delta p_1 +$$

$$+ \frac{\partial f(a_1, a_2, \ldots, a_n)}{\partial p_n} \Delta p_n \quad \ldots\ldots\ldots \ 2.57$$

where terms in Δp_j of powers higher than the first have been neglected. The a_j are approximate values of p_j, and $f(a_1, a_2, \ldots, a_n)$, $\partial f(a_1, a_2, \ldots, a_n) / \partial p_1 \ldots \partial f(a_1, a_2, \ldots, a_n) / \partial p_n$ are the function and its derivatives evaluated at these approximate values. If the a_j are sufficiently good approximations, application of a least-squares process to the linear equations (2.57) will give values for the quantities Δp_j such that the a_j''s given by

$$a_j' = a_j + \Delta p_j \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\ 2.58$$

are better approximation than the initial a_j's. Because of neglecting second and higher powers in the Δp_j's, the calculations must be repeated using as approximate values for each repetition of the results derived from the preceding calculation. The iterative process is complete when there is no significant change in the parameters are required and the solution of the normal equations gives their values without iteration.

The function $|F_c|$ in Eq. (2.55) is expressed as a Taylor series. Second and higher powers are neglected so that

$$|kF_c(p_1,\dots,p_n)| = |kF_c(a_1,\dots,a_n)| + \frac{\partial|kF_c|}{\partial p_1}\Delta p_1 + \dots\dots\dots$$

$$+ \frac{\partial|kF_c|}{\partial p_n}\Delta p_n \qquad \dots\dots\dots\dots\dots\dots\ 2.59$$

where $p_1,\dots,p_n$ may be any of the scale, positional, or thermal parameters and $\Delta p_j = p_j - a_j$. Substituting Eq. (2.59) in (2.55) gives

$$\sum_{hkl} W_{hkl}\left(|F_o| - |kF_c(a_1,\dots,a_n)| - \frac{\partial|kF_c|}{\partial p_1}\Delta p_1 \dots \frac{\partial|kF_c|}{\partial p_n}\Delta p_n\right) \times$$

$$\frac{\partial|kF_c|}{\partial p_j} = 0 \qquad (j = 1,2,\dots,n) \qquad \dots\dots\dots\dots\ 2.60$$

or

$$\sum_{hkl} W_{hkl}\left(\Delta F - \frac{\partial|kF_c|}{\partial p_1}\Delta p_1 \dots \frac{\partial|kF_c|}{\partial p_n}\Delta p_n\right) \frac{\partial|kF_c|}{\partial p_j} = 0$$

$$(j = 1,2,\dots,n) \qquad \dots\dots\dots\dots\dots\ 2.61$$

Expansion and rearrangement of Eq.(2.61)leads to the following set
of equations

$$\Sigma_{r=1}^{m} w_r \left(\frac{\partial |kF_{cr}|^2}{\partial P_1}\right) \Delta P_1 + \Sigma_{r=1}^{m} w_r \frac{\partial |kF_{cr}|}{\partial P_1} \frac{\partial |kF_{cr}|}{\partial P_2} \Delta P_2 +$$

$$+ \Sigma_{r=1}^{m} w_r \frac{\partial |kF_{cr}|}{\partial P_1} \frac{\partial |kF_{cr}|}{\partial P_n} \Delta P_n = \Sigma_{r=1}^{m} w_r \Delta F_r \frac{\partial |kF_{cr}|}{\partial P_1}$$

$$\Sigma_{r=1}^{m} w_r \frac{\partial |kF_{cr}|}{\partial P_2} \frac{\partial |kF_{cr}|}{\partial P_1} \Delta P_1 + \Sigma_{r=1}^{m} w_r \left(\frac{\partial |kF_{cr}|}{\partial P_2}\right) \Delta P_2 +$$

$$+ \Sigma_{r=1}^{m} w_r \frac{\partial |kF_{cr}|}{\partial P_2} \frac{\partial |kF_{cr}|}{\partial P_n} \Delta P_n = \Sigma_{r=1}^{m} w_r \Delta F_r \frac{\partial |kF_{cr}|}{\partial P_2}$$

$$\Sigma_{r=1}^{m} w_r \frac{\partial |kF_{cr}|}{\partial P_n} \frac{\partial |kF_{cr}|}{\partial P_1} \Delta P_1 + \Sigma_{r=1}^{m} w_r \frac{\partial |kF_{cr}|}{\partial P_n} \frac{\partial |kF_{cr}|}{\partial P_2} \Delta P_2 +$$

$$+ \Sigma_{r=1}^{m} w_r \left(\frac{\partial |kF_{cr}|}{\partial P_n}\right)^2 \Delta P_n = \Sigma_{r=1}^{m} w_r \Delta F_r \frac{\partial |kF_{cr}|}{\partial P_n}$$

These equations are linear in the Δp_j's and solvable for
them. Combination of these with the initial approximation, the $a_j's$,
gives better. These may be used to repeat the process until conver-
gence is obtained , and successive cycles produce no further changes.

With the development and improvement of high-speed electronic
computers, it is now common practive to refine structures by the
method of least squares because it seeks the best values of the
variable parameters for each atom to fit the observed intensities.
It is used not only to find the best coordinate of each atom but
also to find the thermal parameters of each atom.