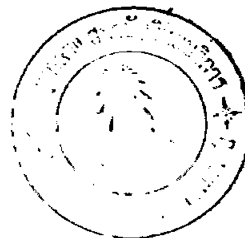

CHAPTER 2

A BRIEF ACCOUNT OF X-RAY CRYSTAL STRUCTURE DETERMINATION

2.1 X-ray diffraction

When a crystal is in the path of an X-ray beam, diffraction will occur only if certain conditions are satisfied.

A crystal is composed of atoms. An atom consists of a swarm of electrons about a positively charged nucleus. When X-rays pass through a crystal, an electron within the atom will vibrate with the frequency of the incident radiation, periodically absorbing energy and emitting it as X-radiation of the same frequency and wavelength as the incident beam. Then the electron is said to scatter the original X-ray waves and acts as a source of secondary X-rays. The nucleus may be neglected in connection with scattering because of its comparatively high mass. Each of the electron in the atom scatters X-rays and then combines to give the effect of a point source. Therefore, the atom as a whole scatters X-rays. All atoms in the path of an X-ray beam scatter X-rays simultaneously. The scattered X-rays 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[3,4,5].

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[6]. Scattering of light by a diffraction grating with repeat distance "a" is shown in Fig. 2.1.

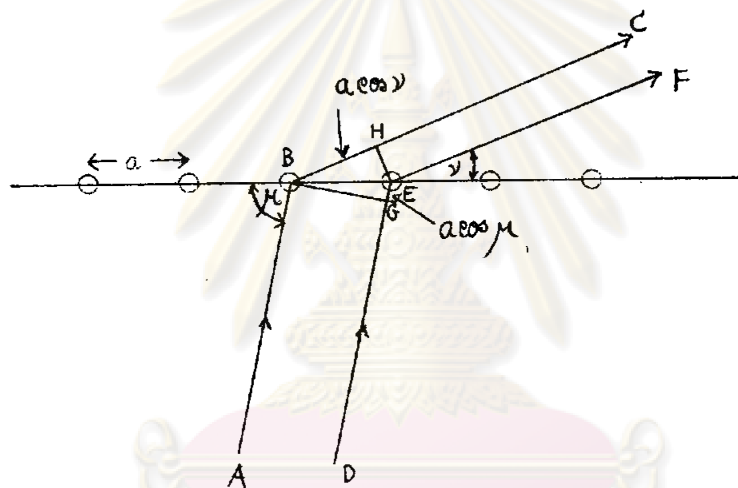

Fig. 2.1 Scattering of light by a diffraction grating.

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The incident beam makes an angle μ with the diffraction grating. The incident ray DE travels farther than AB before reaching the grating and the scattered ray BC travels farther than EF after passing the grating. The difference in path lengths of the beams ABHC and DGEF is BH-GE. The condition for a diffraction maximum is therefore;

$$BH - GE = n\lambda$$

where λ is the wavelength of the light, and n is an integer. By simple geometry BH = a cos ν and GE = a cos μ, where a is the repeat distance, so

$$a \cos \nu - a \cos \mu = n\lambda$$

Since crystals are periodic in three dimensions, three equations are required for the diffraction conditions

$$a \cos \nu_1 - a \cos \mu_1 = h\lambda \quad \text{.........} \quad 2.1\ a$$

$$b \cos \nu_2 - b \cos \mu_2 = k\lambda \quad \text{.........} \quad 2.1\ b$$

$$c \cos \nu_3 - c \cos \mu_3 = l\lambda \quad \text{.........} \quad 2.1\ c$$

where μ_1, μ_2 and μ_3 are the angles between the incident **X-ray beam** and the unit cell axes a,b,c respectively and ν_1, ν_2 and ν_3 are the corresponding angles for the diffracted beam, and h, k and l are integers. These equations are called the Laue equations.

Shortly after the discovery of X-ray diffraction, Bragg noted that the diffraction of X-rays by a crystal is analogous to the reflection of light by a plane mirror. He deduced a simple equation treating diffraction as "reflection" from planes in the lattice. To derive the equation, let an X-ray beam incidents on a pair of parallel planes with interplanar spacing "d" (Fig. 2.2). The parallel incident rays make an angle θ with these planes. The condition that the reflections from these planes be in phase is that the path difference of rays reflected from these planes be an integral number "n" of wavelengths; Fig. 2.2 shows that this path difference is 2d sin θ hence the condition is

$$2d \sin \theta = n\lambda \quad \text{........} \quad 2.2$$

This is Bragg's law.

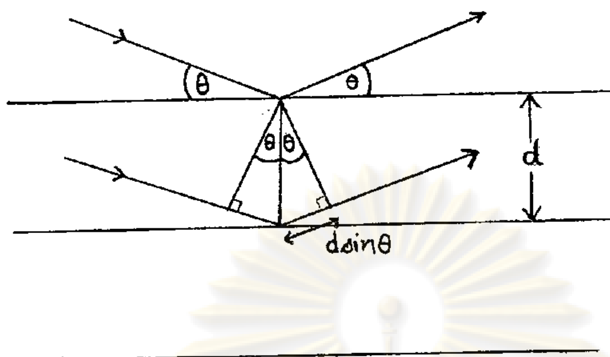

Fig. 2.2 Construction showing conditions for diffraction.

2.2 The structure factor

The structure factor, F(hkl), is the resultant wave due to the combined scattering of all the atoms in the unit cell. In order to calculate the structure factor, it is necessary to know the scattering factor of the atom and the phase of the wave scattered by the atom.

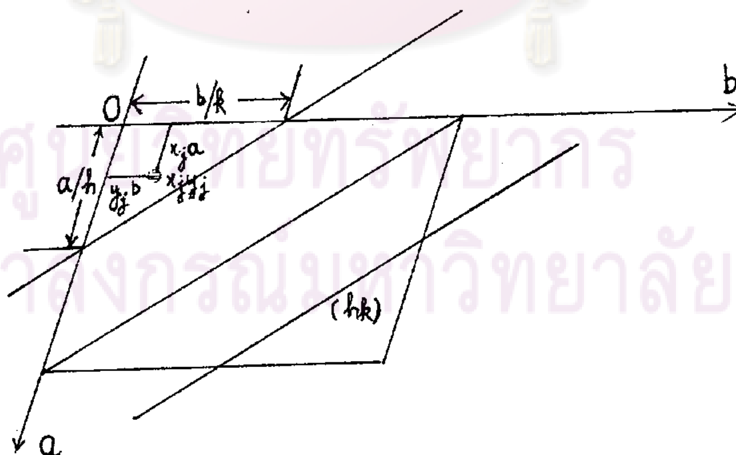

Fig. 2.3 Construction showing a set of (hk) planes in a two-dimensional structure with an atom j having fractional coordinates $x_j y_j$.

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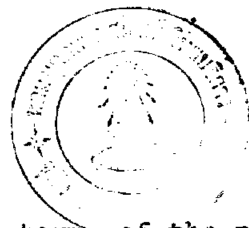

To express a phase in terms of the position of the atom, let us consider a set of (hk) planes in a two-dimensional structure with an atom j having fractional coordinates $x_j y_j$, as shown in Fig. 2.3. The closest (hk) plane to the origin has intercepts a/h and b/k on the cell edges. From Bragg's law, a path difference between reflection from successive planes of any given set hkl is equal to $2\pi n$. Accordingly, the distance a/h is equivalent to phase difference 2π if n = 1 and then the distance ax_j will be equivalent to phase difference $2\pi a x_j \times \frac{h}{a} = 2\pi h x_j$. Similarly the distance by_j is equivalent to the phase difference $2\pi k y_j$. Therefore, the phase difference of a wave scattered by an atom whose fractional coordinates $x_j y_j$ is

$$\delta_j = 2\pi(hx_j + ky_j) \quad \ldots\ldots 2.3$$

The corresponding expression for the three dimensions is

$$\delta_j = 2\pi(hx_j + ky_j + lz_j) \quad \ldots\ldots 2.4$$

The scattering factor of the atom, f_o, is a function only of the atom type and of $\sin\theta/\lambda$ where θ is the Bragg's angle and λ is the wavelength of the incident beam. It is also independent of the position of the atom in the cell. The variation of the scattering factor of tungsten, cobalt and oxygen with $\sin\theta/\lambda$ are shown in Fig. 2.4

When $\sin\theta/\lambda = 0$ all waves are in phase, so the value of f_o is equal to the total number of electrons in the atom. As $\sin\theta/\lambda$ increases, f_o 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.

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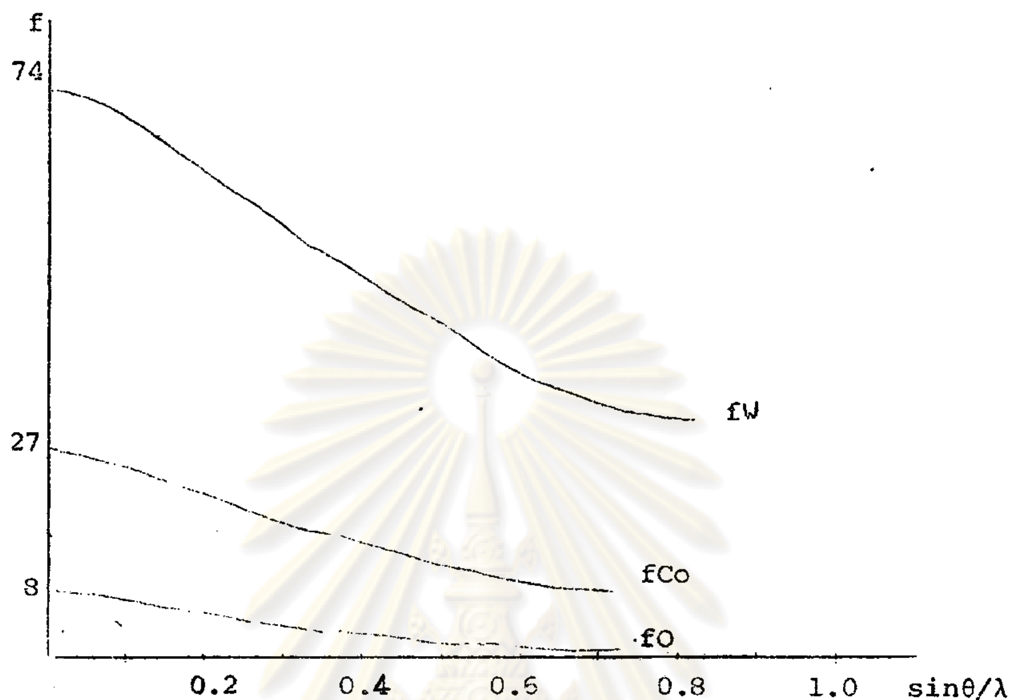

Fig. 2.4 Atomic scattering factor of tungsten, cobalt and oxygen as a function of $\sin\theta/\lambda$.

Atomic scattering factors, f_o, are calculated for atoms at rest, but, in fact, at ordinary temperatures the atoms are always vibrating about their rest points. The magnitude of vibration depends on the temperature, the mass of the atom, and the type of bonds in the crystal. The scattering factor of an atom at ordinary temperatures (f) is related to its scattering factor at rest (f_o) by the expression[5]

$$f = f_o e^{-B\sin^2\theta/\lambda^2} \qquad \text{.......... 2.5}$$

where B is the Debye factor which is related to 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.

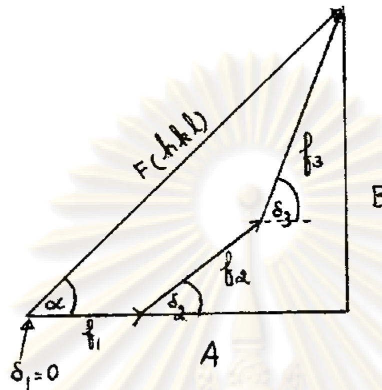

Fig. 2.5 Vectors representation of scattered waves of different amplitudes and phases.

From Fig. 2.5

$$|F(hkl)|^2 = A^2 + B^2$$

$$= [(F \cos \alpha)^2 + (F \sin\alpha)^2].. \quad 2.6$$

where $A = F \cos \alpha = f_1 \cos \delta_1 + f_2 \cos \delta_2 + f_3 \cos \delta_3$

$$= \sum_j f_j \cos \delta_j \quad .... \; 2.7$$

and $B = F \sin \alpha = f_1 \sin \delta_1 + f_2 \sin \delta_2 + f_3 \sin \delta_3$

$$= \sum_j f_j \sin \delta_j \quad .... \; 2.8$$

where f_j and δ_j are the scattering factor and phase of the jth atom

$$\alpha(hkl) = \tan^{-1} \frac{B}{A}$$

$$= \tan^{-1} \frac{\sum_j f_j \sin\delta_j}{\sum_j f_j \cos\delta_j} \quad .... \; 2.9$$

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Substituting $\delta_j = 2\pi(hx_j + ky_j + lz_j)$ into eq. (2.6), we obtain

$$|F(hkl)|^2 = [\sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)]^2$$
$$+ [\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)]^2 \quad \ldots\ldots\ 2.10$$

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

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \ldots \quad \ldots\ldots\ 2.11$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \ldots \quad \ldots\ldots\ 2.12$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots \quad \ldots\ldots\ 2.13$$

Substituting $x = i\delta$ and multiplying both sides of the eq. (2.13) by f we have

$$fe^{i\delta} = f(1 + i\delta - \frac{\delta^2}{2!} - i\frac{\delta^3}{3!} + \frac{\delta^4}{4!} \ldots)$$
$$= f[(1 - \frac{\delta^2}{2!} + \frac{\delta^4}{4!} - \ldots) + i(\delta - \frac{\delta^3}{3!} + \frac{\delta^5}{5!} - \ldots)]$$
$$= f(\cos\delta + i\sin\delta) \quad \ldots\ldots\ 2.14$$

Since the right side of the eq.(2.14) 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

$$F = \sum_j f_j e^{i\delta_j} \quad \ldots\ldots\ldots\ 2.15$$

Substituting δ as given in eq. (2.4) into eq. (2.15) we have

$$F(hkl) = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad \ldots\ldots\ldots\ 2.16$$

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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. The electron density, $\rho(x,y,z)$, is the number of electrons per unit volume, so the number of electrons in any volume element dv is

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

The wavelet scattered by the electron in volume element is

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

and the structure factor will be equal to the sum of all of the volume elements in the unit cell, i.e. the integral over its volume

$$F(hkl) = \int_V \rho(x,y,z)e^{2\pi i(hx+ky+lz)}dv \quad \ldots\ldots 2.17$$

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 relation[7]

$$|F_o(hkl)| \quad \propto \quad \sqrt{I(hkl)} \quad \ldots\ldots\ldots\ldots 2.18$$

where $|F_o(hkl)|$ is the modulus of the observed structure factor, therefore only $|F_o(hkl)|$ can be obtained experimentally.

There are various factors that can affect the observed intensities, namely the polarization of X-rays, the absorption of X-rays by the crystal, the length of time that the plane is in a scattering position and the apparatus used in measurement of the intensities. The value of $|F_o(hkl)|$, therefore, requires corrections for these factors. The eq. (2.18) will be rewritten as

$$|F_o(hkl)| = \sqrt{\frac{KI_{hkl}}{LpA}} \quad \ldots\ldots\ldots\ldots 2.19$$

where 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

$$p = \frac{1 + \cos^2 2\theta}{2} \qquad \text{......... 2.20}$$

and is a function of 2θ only. The Lorentz factor , L, depends on the precise measurement technique used. For the equi-inclination Weissenberg it is given by

$$L = \frac{\sin\theta}{\sin 2\theta \sqrt{\sin^2\theta - \sin^2\mu}} \qquad \text{......... 2.21}$$

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

If the proposed structure of the crystal is correct, the value of the observed structure factor and the calculated one will be theoretically equal.

2.3 Electron density

Since X-rays are scattered by the electrons of the atoms, a crystal property suitable for our mathematical treatment is the electron density.

When a function is periodic, it is frequently useful to express that function by means of a Fourier series. A general one-dimensional Fourier series may be written as

$$f(x) = a_o + \sum_{1}^{n} (a_h \cos 2\pi hx + b_h \sin 2\pi hx) \qquad \text{......... 2.22}$$

or

$$f(x) = \sum_{-n}^{n} C_h e^{2\pi ihx} \qquad \text{......... 2.23}$$

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Since crystals are periodic structure, they can be described by periodic functions. The three-dimensional periodic electron density in a crystal can be represented by a three-dimensional Fourier series similar to eq.(2.23)

$$\rho(x,y,z) = \sum_{h'}\sum_{k'}\sum_{l'} C_{h'k'l'} e^{2\pi i(h'x+k'y+l'z)} \quad ....2.24$$

where h´, k´ and l´ are integers between $-\infty$ and ∞.

Substituting $\rho(x,y,z)$ from eq.(2.24) in eq.(2.17) we have

$$F(hkl) = \int_v \sum_{h'}\sum_{k'}\sum_{l'} C_{h'k'l'} e^{2\pi i(h'x+k'y+l'z)} e^{2\pi i(hx+ky+lz)} dv \quad .... 2.25$$

$$F(hkl) = \int_v \sum_{h'}\sum_{k'}\sum_{l'} C_{h'k'l'} e^{2\pi i\left[(h+h')x+(k+k')y+(l+l')z\right]} dv \quad .... 2.26$$

If h´ = -h, k´ = -k, l´ = -l, the eq.(2.26) becomes

$$F(hkl) = \int_v C_{\bar{h}\bar{k}\bar{l}} dv = VC_{\bar{h}\bar{k}\bar{l}} \quad .... 2.27$$

$$C_{\bar{h}\bar{k}\bar{l}} = \frac{1}{V}F(hkl) \quad .... 2.28$$

Substitution of $\bar{h}$, $\bar{k}$, $\bar{l}$ for h´, k´, l´ and of $C_{\bar{h}\bar{k}\bar{l}}$ from eq. 2.28 in eq.(2.24) gives

$$\rho(x,y,z) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{l} F(hkl) e^{-2\pi i(hx+ky+lz)} \quad .... 2.29$$

The expression for the structure factor, eq.(2.16), and the electron density, eq.(2.29), are similar but the exponential terms are opposite in sign because these quantities are Fourier transform of each other.

The structure factor can be written in the form

$$F(hkl) = |F(hkl)| e^{2\pi i\alpha'_{hkl}} = |F(hkl)| e^{i\alpha_{hkl}} \quad .... 2.30$$

where $2\pi\alpha'_{hkl}$ is the phase angle. Then the eq.(2.29) can be rewritten

$$\rho(x,y,z) = \frac{1}{V}\sum\sum\sum_{hkl}|F(hkl)|e^{-2\pi i(hx+ky+lz-\alpha'_{hkl})} \quad \ldots\ldots\ldots 2.31$$

Hence the electron density in the cell can be calculated if the phase angles are known.

2.4 Patterson function

As we have seen in section 2.2 that only the modulus of the structure factors can be derived from the observed intensities, so it is impossible to directly deduce the actual positions of the atoms in the cell. However, it is theoretically possible to deduce the vectors between every pair of atoms in a crystal. In 1934, A.L. Patterson showed that a Fourier series using values of $|F(hkl)|^2$ as coefficients in stead of F(hkl) could produce this useful information. This series is called the Patterson function. A peak at the point uvw in a Patterson map indicates that there exist atoms at x_1,y_1,z_1 and x_2,y_2,z_2 in the crystal such that

$$u = x_1-x_2$$

$$v = y_1-y_2$$

$$w = z_1-z_2$$

Patterson defined a function P(uvw) of the form

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\rho(x+u,y+v,z+w)\,dxdydz \quad \ldots\ldots 2.32$$

Substituting the values of electron density from eq.(2.29) we obtain

$$P(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_l\sum_{h'}\sum_{k'}\sum_{l'} F(hkl)e^{-2\pi i(hx+ky+lz)}$$

$$\times F(h'k'l')e^{-2\pi i(h'x+k'y+l'z)-2\pi i(h'u+k'v+l'w)}dxdydz$$

$$\ldots\ldots\ldots 2.33$$

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The right-hand side will be zero unless $h' = -h$, $k' = -k$, $l' = -l$.

When this condition applies,

$$P(uvw) = \frac{1}{V}\sum_h \sum_k \sum_l F(hkl)F(\bar{h}\bar{k}\bar{l})e^{2\pi i(hu+kv+lw)} \quad \text{..... 2.34}$$

By using Friedel's law $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$, the relationship between $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ can be obtained.

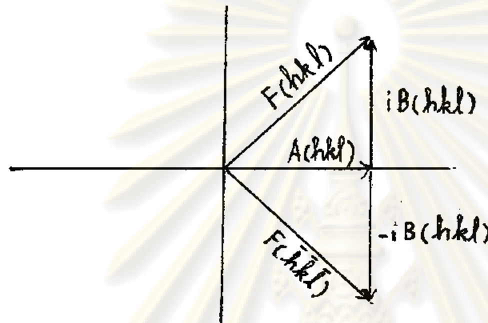

Fig. 2.6 Vector representation of $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$.

From Fig. 2.6

$$F(hkl) = A(hkl) + iB(hkl)$$

$$F(\bar{h}\bar{k}\bar{l}) = A(hkl) - iB(hkl)$$

If these are multiplied together, the result is

$$\begin{aligned} F(hkl)F(\bar{h}\bar{k}\bar{l}) &= [A(hkl) + iB(hkl)][A(hkl) - iB(hkl)] \\ &= A^2(hkl) + B^2(hkl) \\ &= |F(hkl)|^2 \end{aligned} \quad \text{........ 2.35}$$

Substitue in eq.(2.34) we get

$$P(uvw) = \frac{1}{V}\sum_h \sum_k \sum_l |F(hkl)|^2 e^{2\pi i(hu+kv+lw)}$$

.... 2.36

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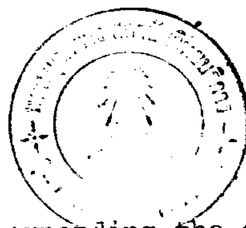

This result can be simplified by expanding the exponential with the aid of the relation

$$e^{i\phi} = \cos\phi + i\sin\phi \quad \ldots\ldots\ 2.37$$

This expression changes eq. (2.36) to

$$P(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2 \left[\cos 2\pi(hu+kv+lw) + i\sin 2\pi(hu+kv+lw)\right] \quad \ldots\ldots\ 2.38$$

Since $|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2$, the summation gives rise to pair terms in hkl and $\bar{h}\bar{k}\bar{l}$:

$$|F(hkl)|^2 i\sin 2\pi(hu+kv+lw)$$

and

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

These terms cancel each other in the summation, leaving

$$P(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2 \cos 2\pi(hu+kv+lw) \quad \ldots\ldots\ 2.39$$

This function has the same value for uvw and $\bar{u}\bar{v}\bar{w}$, consequently it is centrosymmetrical at the origin. This means that all Patterson functions have a center of symmetry.

2.5 Difference synthesis

The second Fourier function of importance is the so-called difference synthesis or error synthesis which the coefficients are the quantities $(F_o - F_c)$ or ΔF. The difference synthesis corresponds to point-by-point subtraction of an F_c Fourier from an F_o Fourier calculated with the same phases[7].

$$\rho_o(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l F_{ohkl}\, e^{-2\pi i(hx+ky+lz)} \quad \ldots\ 2.40$$

$$\rho_c(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l F_{chkl}\, e^{-2\pi i(hx+ky+lz)} \quad \ldots\ldots\ 2.41$$

If eq.(2.41) is subtracted from eq.(2.40), the difference synthesis will be given as

$$\rho_o(x,y,z)-\rho_c(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l (F_o-F_c)_{hkl}\, e^{-2\pi i(hx+ky+lz)} \quad \ldots\ldots\ 2.42$$

or

$$\Delta\rho = \frac{1}{V}\sum_h\sum_k\sum_l (|F_o|-|F_c|)\, e^{i\alpha_c -2\pi i(hx+ky+lz)} \quad \ldots\ldots\ 2.43$$

The difference synthesis has two major virtues. First, if the model matched the actual structure exactly, the difference density map should be zero everywhere, except that random errors in measuring $|F_o|$ should produce a small random fluctuation in the function. Therefore, if the phases α_c are correct, it provides a direct measure of the errors between the model used and the true structure. This property is very useful for refinement. Second, it permits the selection and use of a partial set of data for which the probabilities are especially high that the assigned phases are correct. Furthermore, this partial set can provide useful information which is difficult or impossible to obtain from the F_o synthesis. Only the second case is considered in detail.

To see how to select the data for the difference synthesis let us consider three limiting cases of $|F_o|$'s and $|F_c|$'s. First, the reflections for which $|F_o| \simeq |F_c|$. These reflections tend merely to reproduce the model and add little new information. Furthermore, if α_c differs from the true value, a large $|F_o|$ can introduce serious errors into the resulting synthesis. So in the dif-

ference synthesis $|F_o| - |F_c| \simeq 0$, these reflections are rejected. Second, those for which $|F_o| \neq |F_c|$. If $|F_o| >> |F_c|$, these reflections are theoretically useful because $|F_o|$ will make a significant contribution to the F_o Fourier and should provide useful information, but 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 so these reflections are also eliminated. The third which is the most interesting case is $|F_o| << |F_c|$. These reflections carry information about the disagreement between the model and the true structure. The value $|F_o| - |F_c|$ will be large and contribute to the summation in the difference synthesis. Furthermore, when $|F_o|$ becomes smaller than $|F_c|$, the approximation that α_Δ is nearly equal to α_c becomes more and more reliable, where α_Δ is the phase of ΔF.

The coefficients for the difference synthesis are

$$\Delta F = F_o - F_c \quad \ldots\ldots\ldots \quad 2.44$$

$$|\Delta F|e^{i\alpha_\Delta} = |F_o|e^{i\alpha_o} - |F_c|e^{i\alpha_c} \quad \ldots\ldots\ldots \quad 2.45$$

Since α_o is unknown, we assume that $\alpha_o \simeq \alpha_c$ then

$$|\Delta F|e^{i\alpha_\Delta} \simeq |F_o|e^{i\alpha_c} - |F_c|e^{i\alpha_c} \quad \ldots\ldots\ldots \quad 2.46$$

$$|\Delta F|e^{i\alpha_\Delta} \simeq (|F_o| - |F_c|)e^{i\alpha_c} \quad \ldots\ldots\ldots \quad 2.47$$

$$|\Delta F|e^{i\alpha_\Delta} \simeq \Delta F e^{i\alpha_c} \quad \ldots\ldots\ldots \quad 2.48$$

ΔF is always negative because $|F_o| << |F_c|$, then

$$|\Delta F|e^{i\alpha_\Delta} \simeq -|\Delta F|_c e^{i\alpha_c} \quad \ldots\ldots\ldots \quad 2.49$$

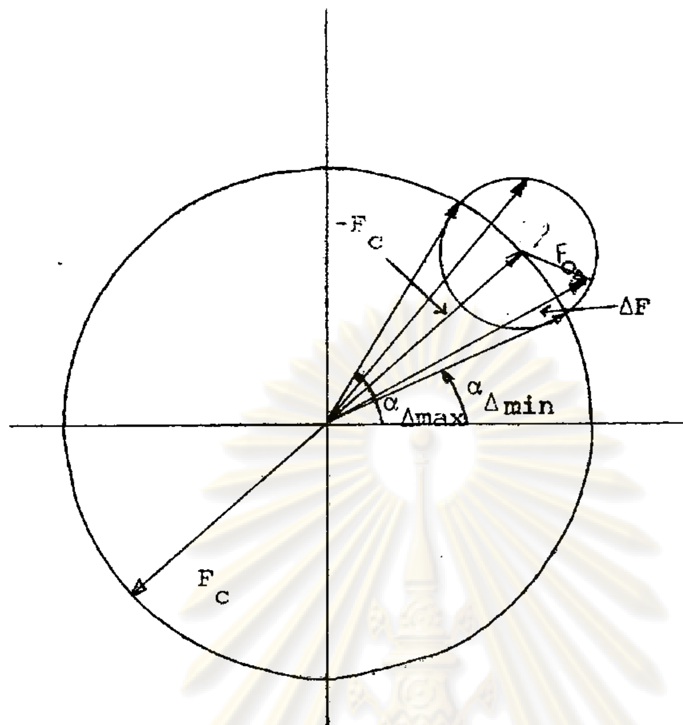

Fig. 2.7 Construction showing range of α_{Δ}.

From Fig. 2.7, the radius of the big circle is equal to $|F_c|$ and the radius of the small one is equal to $|F_o|$. It can be seen that the end of ΔF must always lie on the small circle, and as the small 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.

With the reasons described above, the most valuable reflections for use in the difference synthesis are those for which $|F_o|$ is very small and $|F_c|$ is very large.

The difference synthesis also has other very useful applications. First, difference density maps are nearly free from series termination errors because these errors are about the same for both

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ρ_o and ρ_c. Second, when a crystal contains atoms having a wide range of atomic numbers, it is very difficult or impossible to find very light atoms in an ordinary Fourier synthesis of the electron density because the peak heights of the light atoms are nearly equal to the background fluctuations. However the background fluctuations occurring in ρ_o and ρ_c are nearly the same, they tend to cancel in the difference density leaving as a residue any real difference in the electron densities of the structure and model.

Since 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, it may occur that correctly placed atoms will not appear in the synthesis, incorrectly placed ones will be in holes and missing ones will appear as peaks. Therefore, the difference synthesis can be used as a guide in the removal of atoms which are incorrectly placed. However, the appearance of holes in the difference map should not lead automatically to the conclusion that the particular atoms or the whole structure is incorrect. These holes appear for various reasons. First, the failure to include a ΔF_{000} term in the synthesis for which the model is less than the whole structure. Second, the application of weighting or cutoff function $w<1$ for $|F_c|<|F_o|$ which makes the effective average value of $|F_c|$ too large and the corresponding calculated electron density too high, then this excess density becomes a hole in the difference map. Furthermore, the physical reasons for the appearance of atoms in holes are the use of too small thermal parameters (Fig. 2.8) which

increases the calculated peak density over what it should be, and the misidentification of atom types.

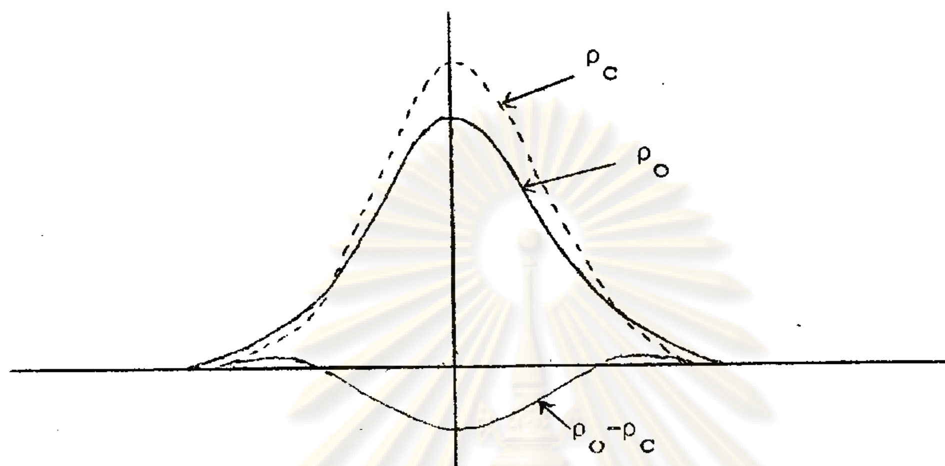

Fig. 2.8 Difference electron density resulting from using too small values of thermal parameters.

2.6 Refinement

After completing the structure, the refinement stage will be taken to improve the precision and details of the structure. The degree to which a structure has been improved is commonly measured by a residual index

$$R = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|} \quad \ldots\ldots\ldots \quad 2.50$$

There is no single value of the R factor which can be taken as assuring the correctness of a placing model. With modern techniques, any well-behaved structure should be capable of refinement to an R below 0.2 and most to below 0.1. For a completely wrong structure the expected value of R is 0.83 if the crystal is cen-

trosymmetrical, or 0.59 if noncentrosymmetrical. Models with R values of 0.45 or lower are worth trying to improve by refinement[3].

An analytical method of refinement of great power and generality is the method of least squares. The basis of this method can most easily be understood by considering a linear function with n variables $x_1, x_2, \ldots x_n$

$$f = p_1x_1 + p_2x_2 + p_3x_3 + \ldots p_nx_n \quad \ldots\ldots 2.51$$

where $p_1, p_2, \ldots p_n$ are independent parameters. If the values of the function are measured at m different points with $m>n$, the principle of least squares states that the best values for the parameters $p_1, p_2 \ldots p_n$ 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

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

where w_r is the weight to be assigned an observation, f_{or} is one of the m observed values of the function, and f_{cr} is the corresponding calculated value.

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

$$D = \sum_{hkl} w_{hkl}(|F_o| - |kF_c|)^2 \quad \ldots\ldots\ldots 2.53$$

where $\sum_{hkl}$ indicates summation over all the observed reflections and w_{hkl} is the weight of the observation. Usually in crystallography only relative weights can be estimated. Cruickshank[8] suggested that

$$w = 1/(c_1 + |F_o| + c_2|F_o|^2) \quad .... \ 2.54$$

where c_1 and c_2 are about $2|F_{o\ min}|$ and $2/|F_{o\ max}|$ respectively.

It is now a common practice to refine structures by the method of least squares because of the development and improvement of the high-speed electronic computers. Furthermore, this method is used not only to find the best coordinates of each atom but also to find the best thermal parameter of the corresponding atom.

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