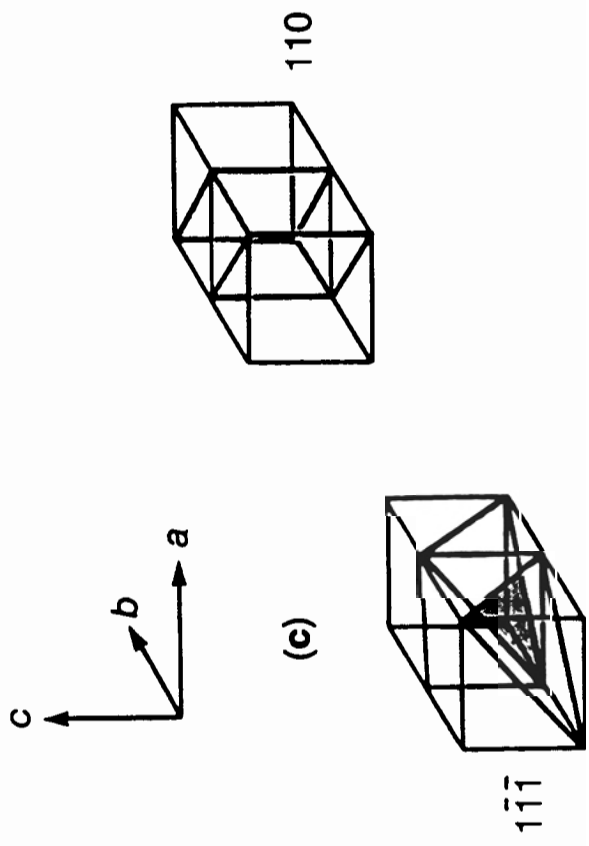
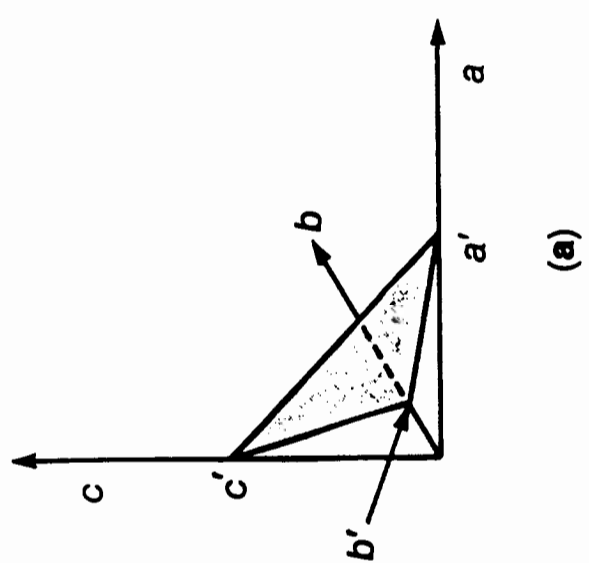


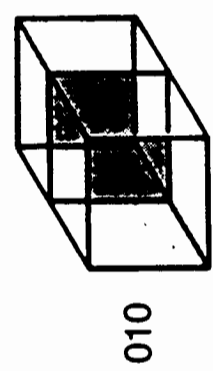
(b)



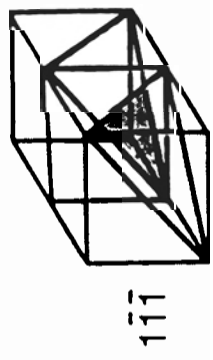
(c)



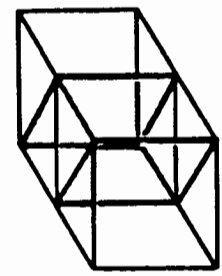
(a)



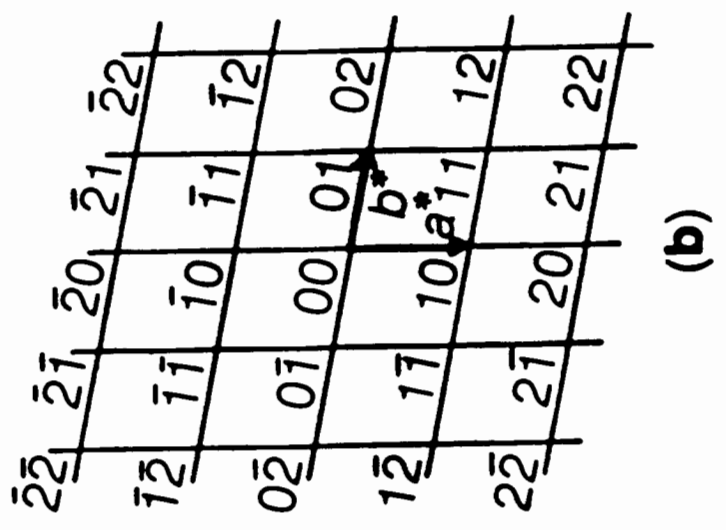
010



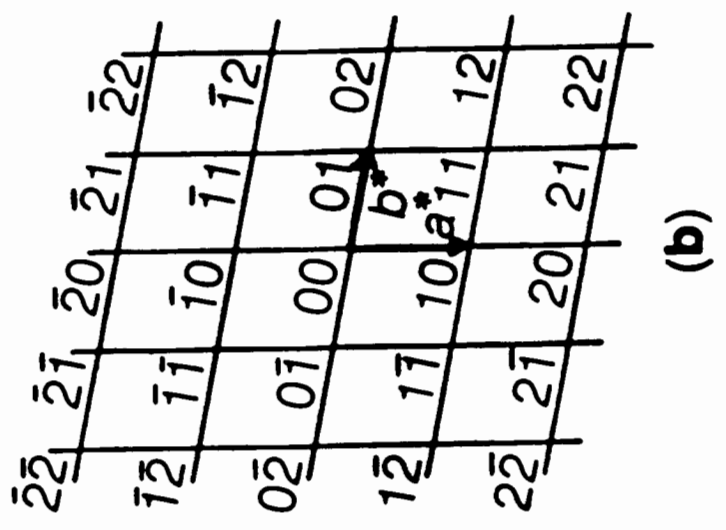
$\bar{1}\bar{1}\bar{1}$



110

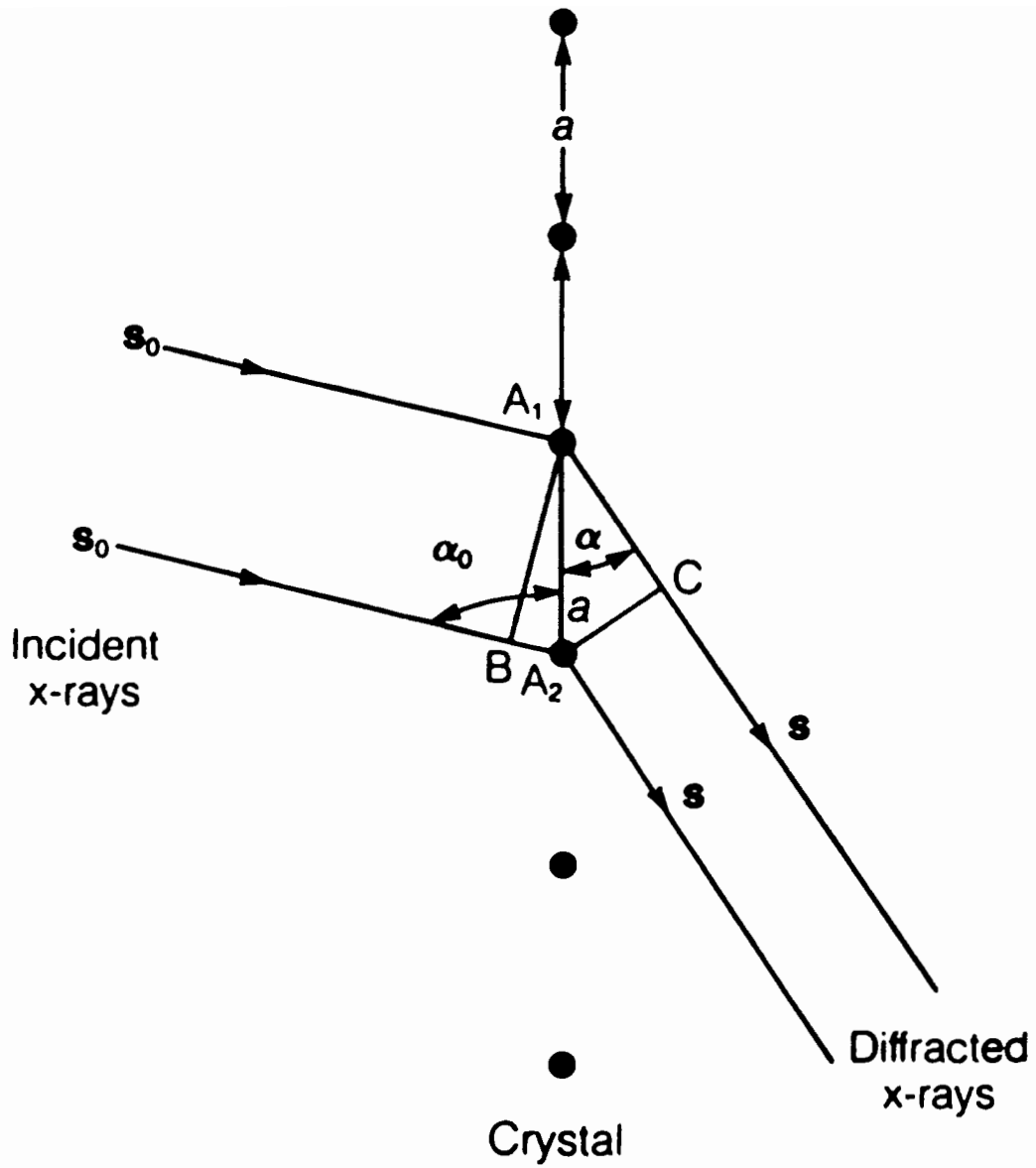


(a)

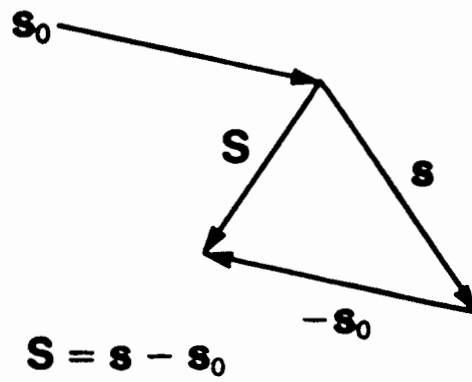


(b)

FIGURE 17 - 9 Relationship between (a) the direct (crystal) lattice, and (b) the reciprocal lattices.



(a)



(b)

If γ is the angle between the direction of the scattered radiation and the row of scatterers, this condition is given by

$$l\lambda = c \cos \gamma \quad (6.6)$$

where l is an integer and c is the spacing between points (or the length of the unit cell along \mathbf{c}). If the row of points is very long, complete annihilation of the scattered waves will occur at all other angles. Then, from such a row, radiation will be scattered only along the surfaces of cones, with the conical axis lying coincident with the crystallographic \mathbf{c} -axis. This is illustrated in Figure 6.12, where the distance to the point of observation is large compared to the size of the crystal and the crystal serves as the point of origin for the scattered X-rays.

If the incident radiation makes an angle γ_0 other than 90° with the row of scatterers, Eq. 6.6 must be modified to be

$$l\lambda = c(\cos \gamma - \cos \gamma_0) \quad (6.7)$$

If we expand this to a two-dimensional array, with spacing a and c along the \mathbf{a} and \mathbf{c} axes, Eqs. 6.7 and 6.8 must be satisfied simultaneously,

$$h\lambda = a(\cos \alpha - \cos \alpha_0) \quad (6.8)$$

Equation 6.8 describes a second set of cones that is now coincident with the crystallographic \mathbf{a} -axis. We see that reinforcement will occur only where the two sets of cones intersect, which is a line. For a three-dimensional array, such as an orthorhombic crystal with spacings a , b , and c , a third condition must be simultaneously satisfied.

$$k\lambda = b(\cos \beta - \cos \beta_0) \quad (6.9)$$

Equations 6.7 to 6.9 are called the von Laue conditions for diffraction. The three resulting cones will intersect at points that are the points of reflection.

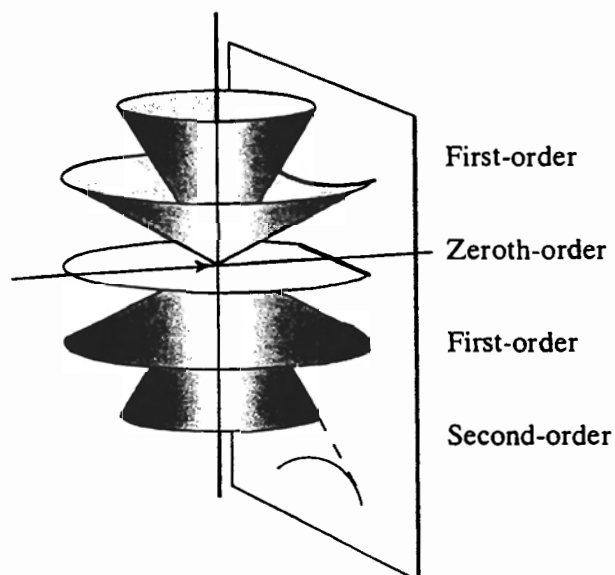


Figure 6.12 An incident beam of X-rays causes a set of scattering cones from a one-dimensional crystal aligned along the vertical axis. Each cone makes an angle 2θ relative to the incident beam to conform to the von Laue conditions for diffraction. The intersection of each cone with a piece of flat photographic film is an arc. Each arc is a layer line representing the order of the reflection, the integer index l in Eq. 6.6. In a three-dimensional crystal, each axis of the unit cell generates a set of concentric cones, with the conical axes aligned parallel with the crystallographic axes.

How do Bragg's law and the von Laue conditions relate? To find the relationship, we need only ask what the reflecting planes are and what the Bragg angle θ represents. Figure 6.11 compares the von Laue row of scatterers for a one-dimensional crystal to the Bragg reflecting planes, which by definition form equal angles with both the incident and the scattered beams. The diffraction angle can now be defined relative to the direction of incident beam. Since the incident beam is fixed, this is a more convenient reference than the scattering plane, which is variable. We readily see that the angle of scattered beam relative to the incident beam is twice the Bragg's angle, 2θ . In practice, this is the angle we measure, called the diffraction or scattering angle. Thus, for each value l in Eq. 6.6, equivalent to n in Eq. 6.5, there is a series of planes that generate a continuous set of scattered beams. For each value of l , the scattered beams form a set of cones in which the angle of the cone relative to the incident beam is the diffraction angle 2θ , and the axis of the cone lies parallel to the direction of the one-dimensional crystal. We notice that $l = 0$ conforms to the conditions for diffraction, and yields a plane of scattered X-rays, with $2\theta = 0$. Under the von Laue equation, h , k , and l , which are called the *Miller indices*, define the integer number of wavelengths that result in an observed reflection from a three-dimensional crystal. Thus for a given set of Miller indices h , k , and l , Bragg's law and the von Laue equation are equal.

$$\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{1/2} = \frac{2 \sin \theta}{\lambda} = \frac{n}{d}$$

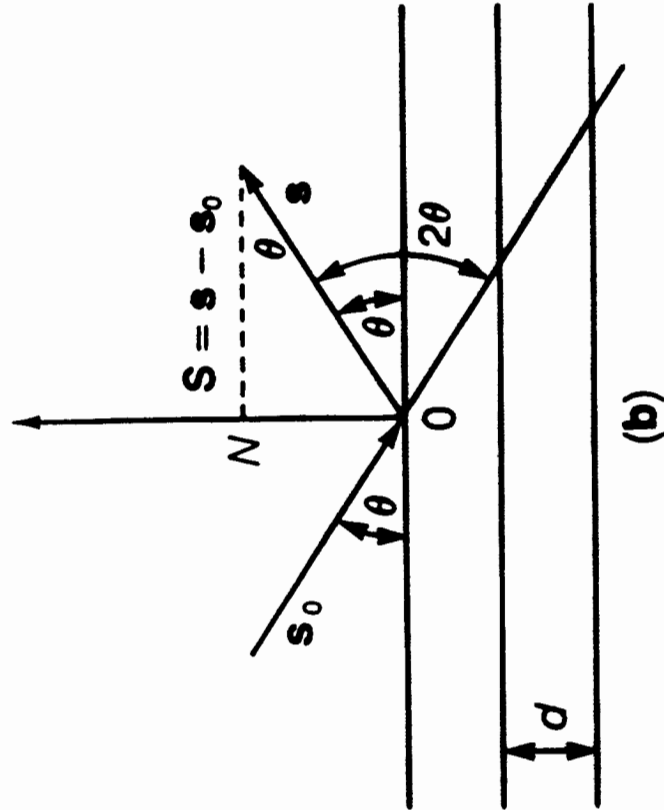
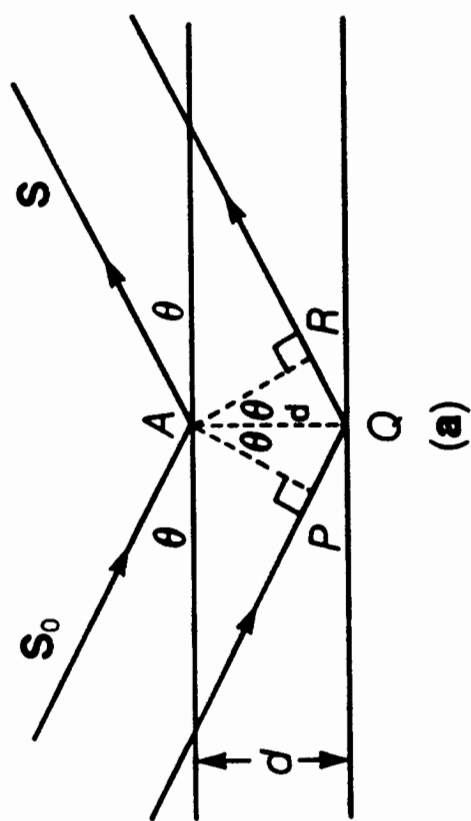


FIGURE 17 - 8
Bragg's law of x-ray reflection. (a) X-rays being "reflected" from the $hk\ell$ set of lattice planes at the angle θ . **(b)** The diffraction vector \mathbf{S} is perpendicular to the lattice planes that are reflecting x-rays.

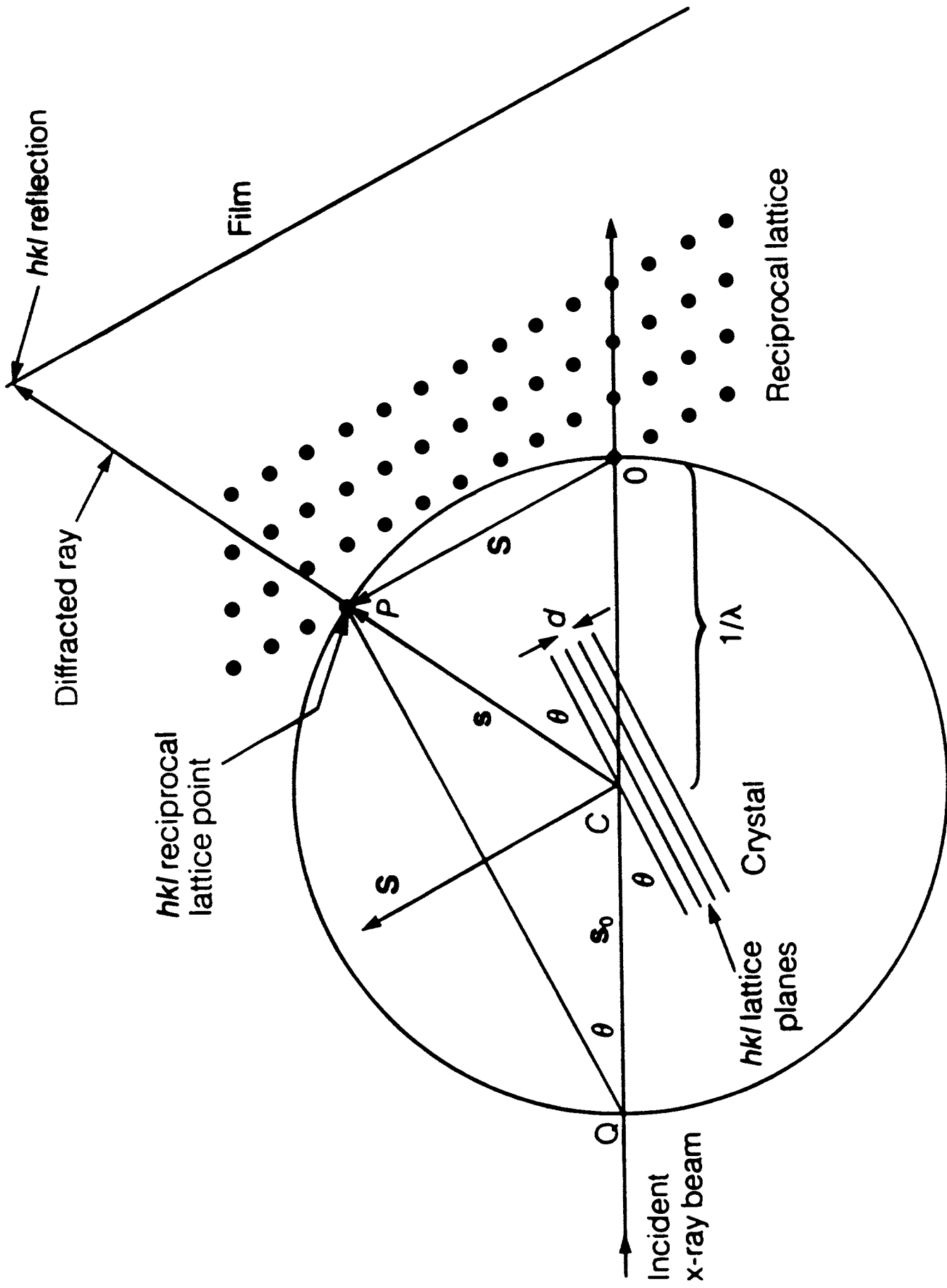


FIGURE 17 - 10
 The sphere of reflection, a geometrical illustration of Bragg's law

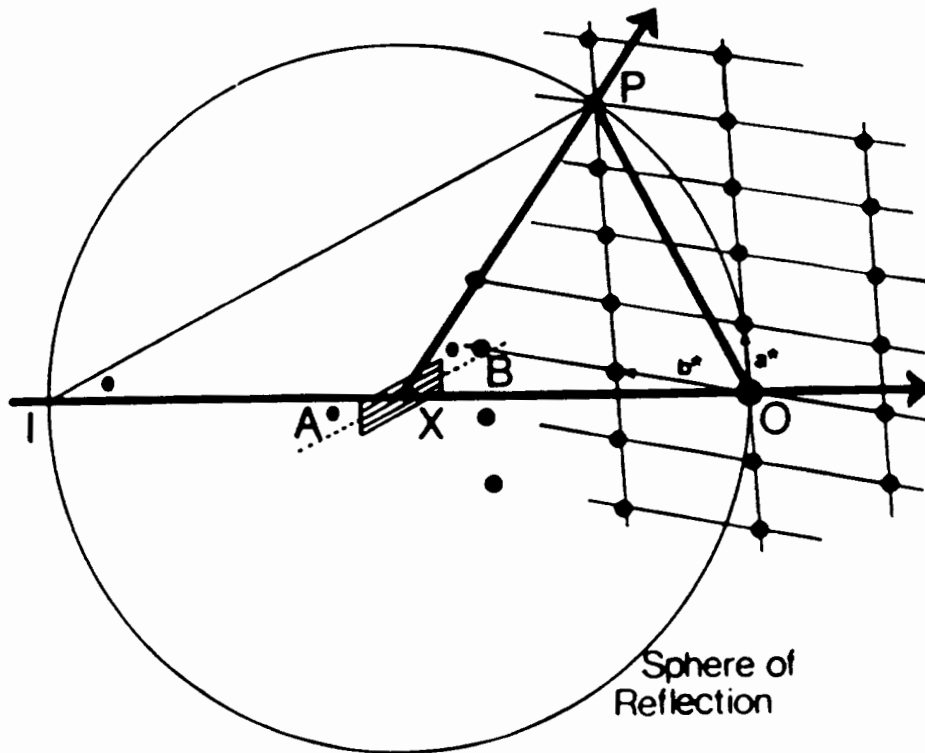


Figure 5. The Ewald construction. For clarity, this is shown as a planar diagram but IXO is the diameter of a sphere of radius $1/\lambda$.

To help understand diffraction from a crystal, there is a construction introduced by Ewald and shown in *Figure 5*. As we move the crystal, the reciprocal lattice also moves about a fixed origin. With the crystal, X, as centre, a sphere is drawn of radius $1/\lambda$, and the origin, O, of the reciprocal lattice is taken as the point where the X-ray beam leaves the sphere after passing through the crystal. As the crystal is rotated about the z-axis (perpendicular to the page) the reciprocal lattice rotates until the point P lies on the surface of the sphere. The point P is the 410 reflection arising from the planes of spacing d_{410} . The angles at IX and XP, i.e. IXA and BXP, are equal to θ so that $\text{OXP} = 2\theta$ and OP is perpendicular to the crystal planes AXB. Now $OP = 2 \times XO \times \sin \theta = 2 \times (1/\lambda) \times \sin \theta$. However, $OP = 1/d_{410}$ and so $1/d_{410} = (2/\lambda) \times \sin \theta$ which is Bragg's Law! Thus, the Ewald sphere gives a readily understandable way of relating the orientation of the crystal to the diffraction pattern observed. In order to collect a set of X-ray data, it is necessary to move the crystal (and detector) in such a way that every reciprocal lattice point passes through the sphere of reflection.

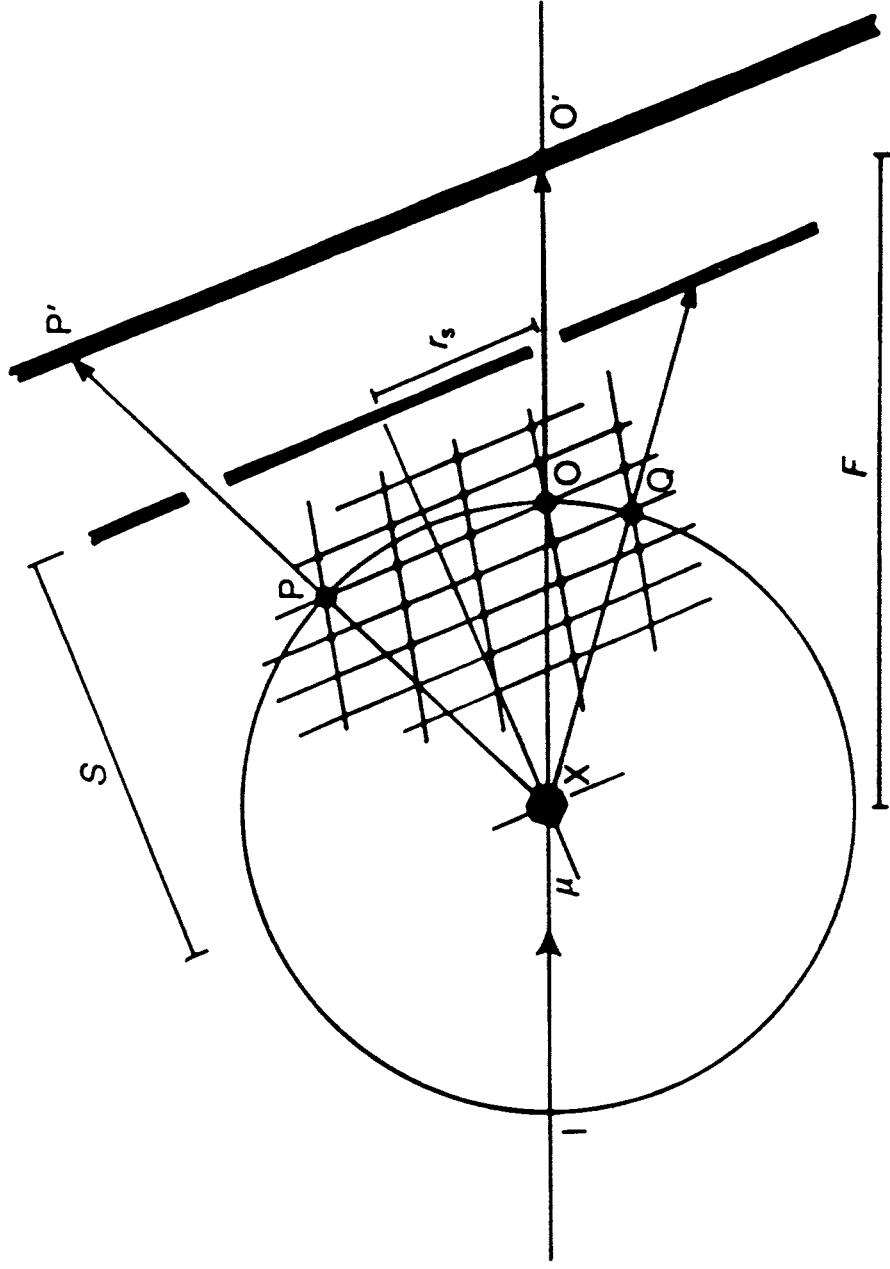


Figure 9. Schematic representation of the precession camera. The crystal is aligned so that the X-ray beam is perpendicular to reciprocal lattice plane OP . It is then offset by the precession angle μ . A screen with an annular hole of radius r_s is placed at distance S from the crystal. Screen, film (at $O'P'$, distance F from X), and reciprocal lattice plane OP are parallel. The crystal precesses causing the normal to OP to move in a circle around IXO which in turn makes all of the reciprocal lattice points on the plane OP within a radius OP of O , pass through the Ewald sphere and the annular screen to be recorded on the film.

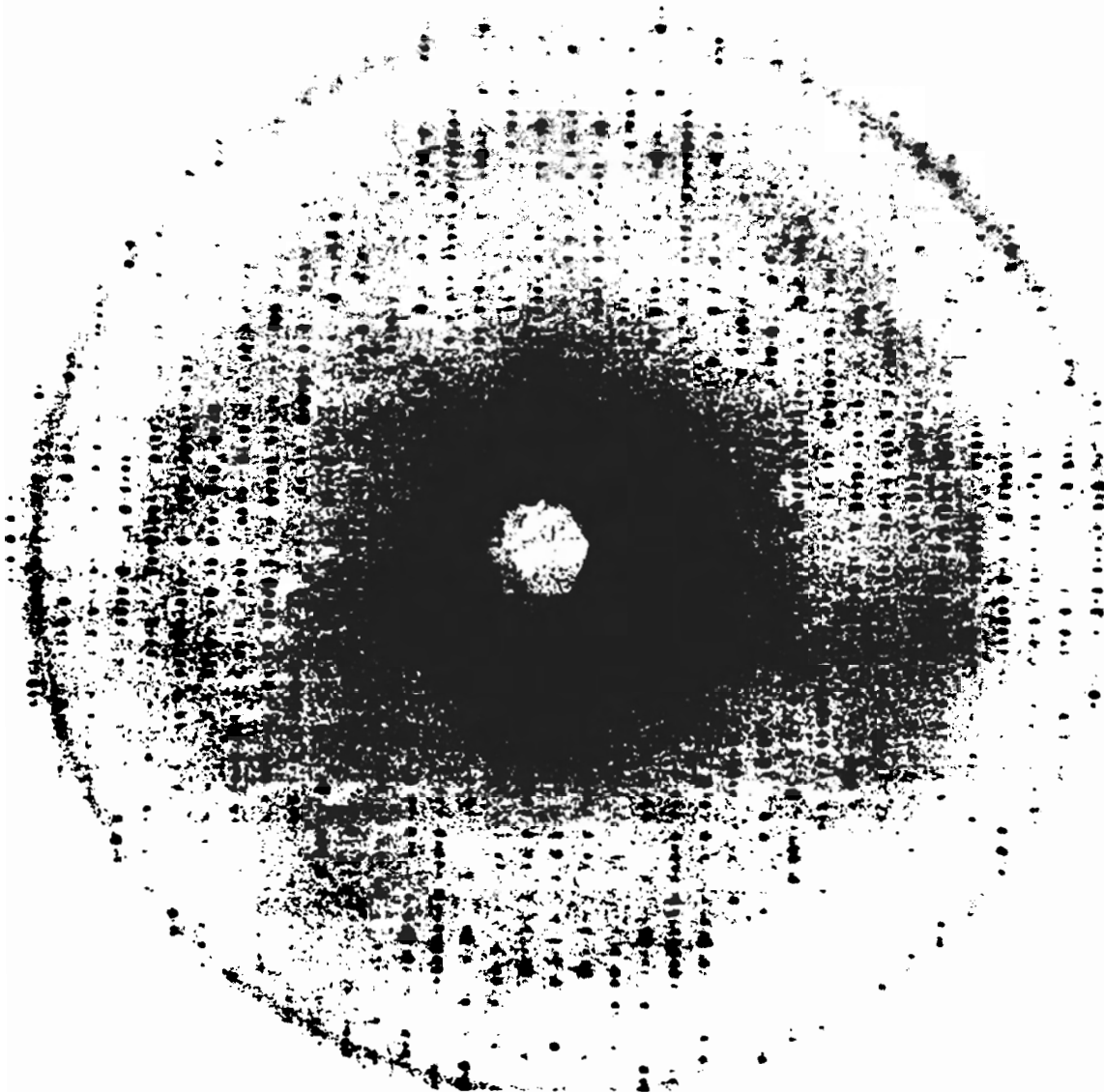
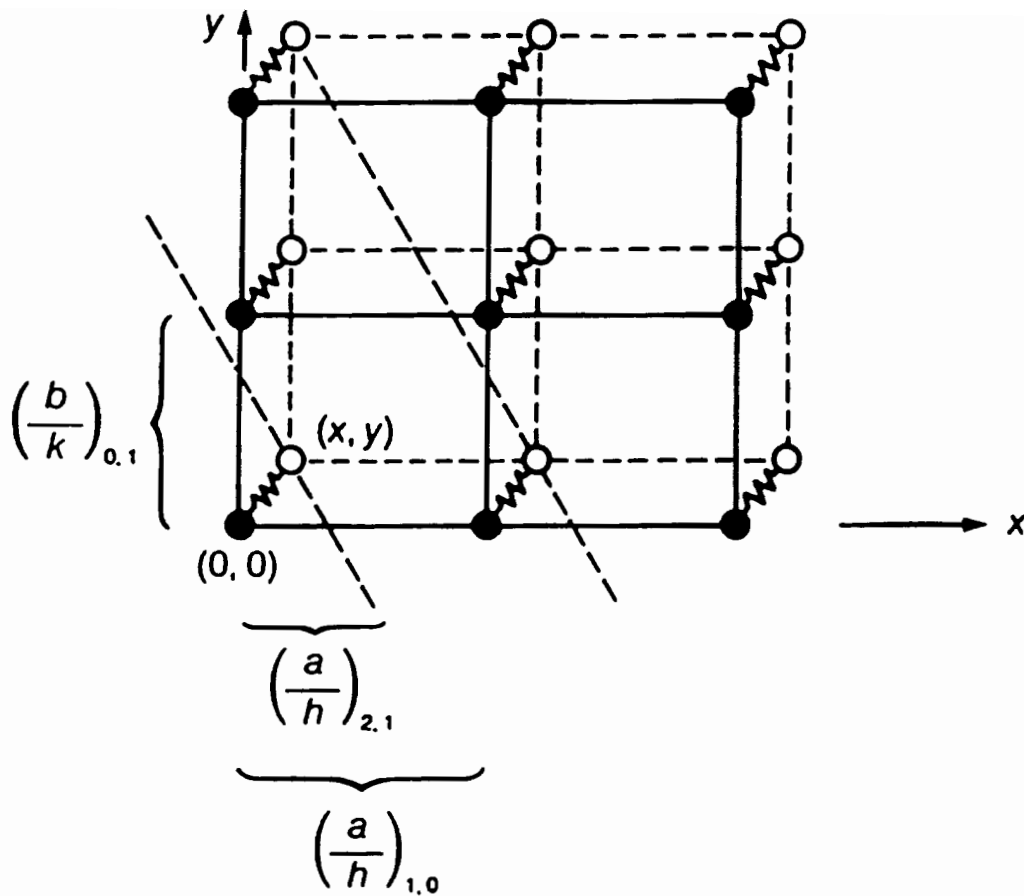
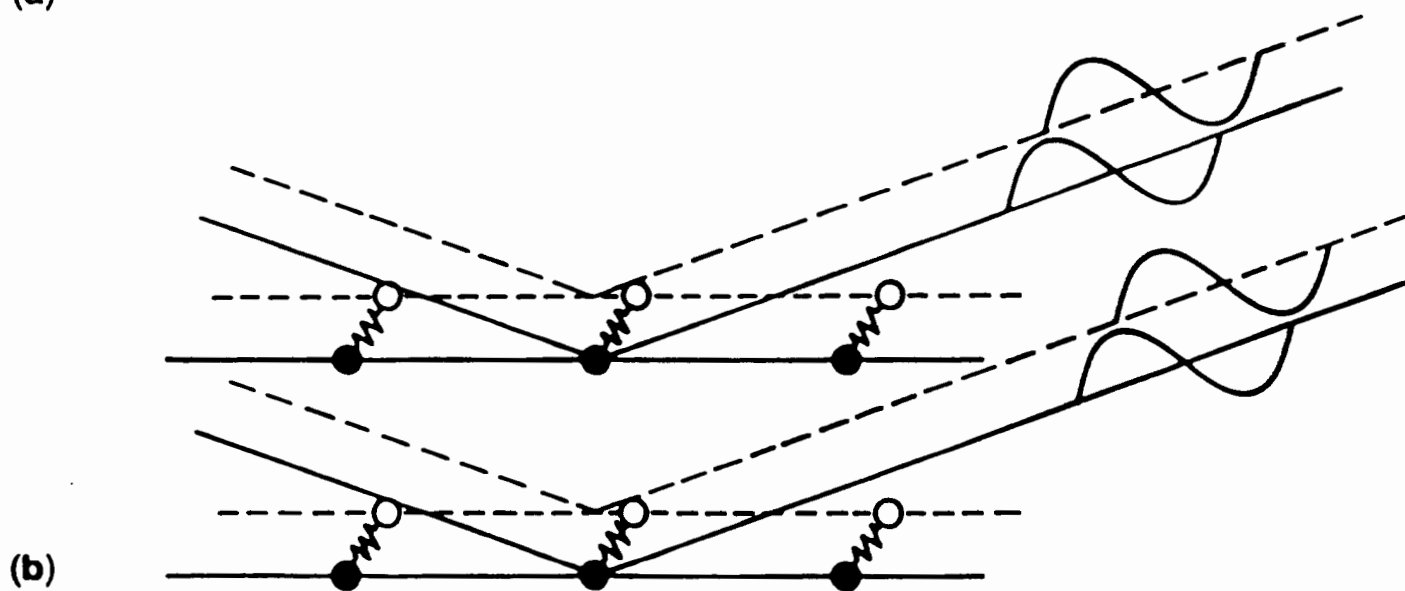


Fig. 12.10 Diffraction pattern for a crystal of yeast phenylalanine transfer RNA. The x-ray beam from a Cu K_{α} source ($\lambda = 1.54 \text{ \AA}$) is incident perpendicular to the film. A hole is cut in the film to reduce the overexposure caused by the very intense incident beam compared to the diffracted beams. The crystal has been rotated to produce what is technically labeled as a 15° precession photograph. The size of the unit cell is $a = 33 \text{ \AA}$, $b = 56 \text{ \AA}$, $c = 161 \text{ \AA}$. (The photograph was kindly supplied by Prof. Sung-Hou Kim, University of California, Berkeley.)



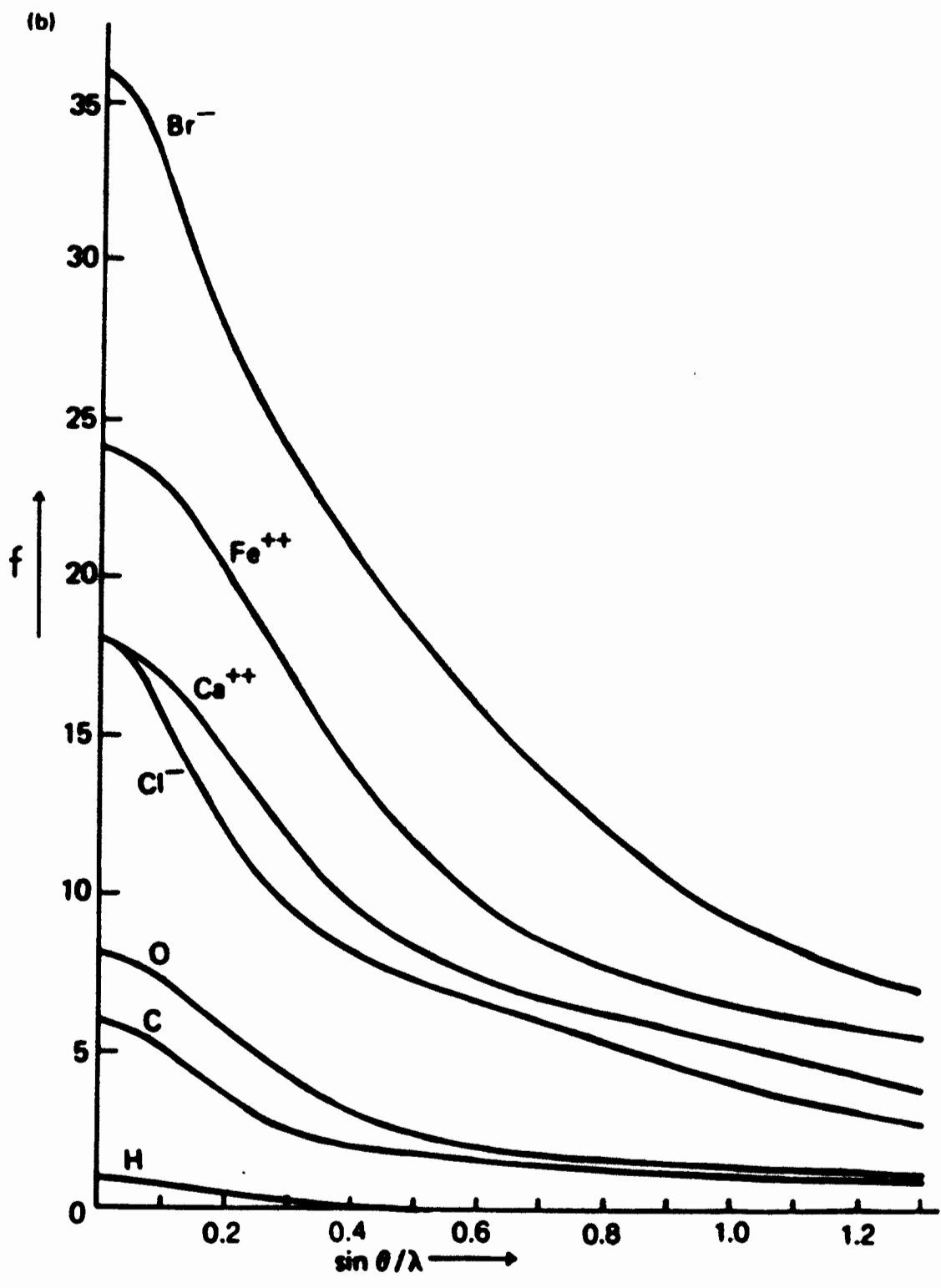
(a)



(b)

FIGURE 17-13

(a) A two-dimensional crystal containing a "diatomic molecule," represented by $\bullet\text{---}\circ$, showing that different reflections differ in intensity (see text). (b) Waves scattered from the lattice of dark atoms are in phase with each other, as are waves scattered from the lattice of light atoms. However, the waves from the two lattices are not in phase with one another.



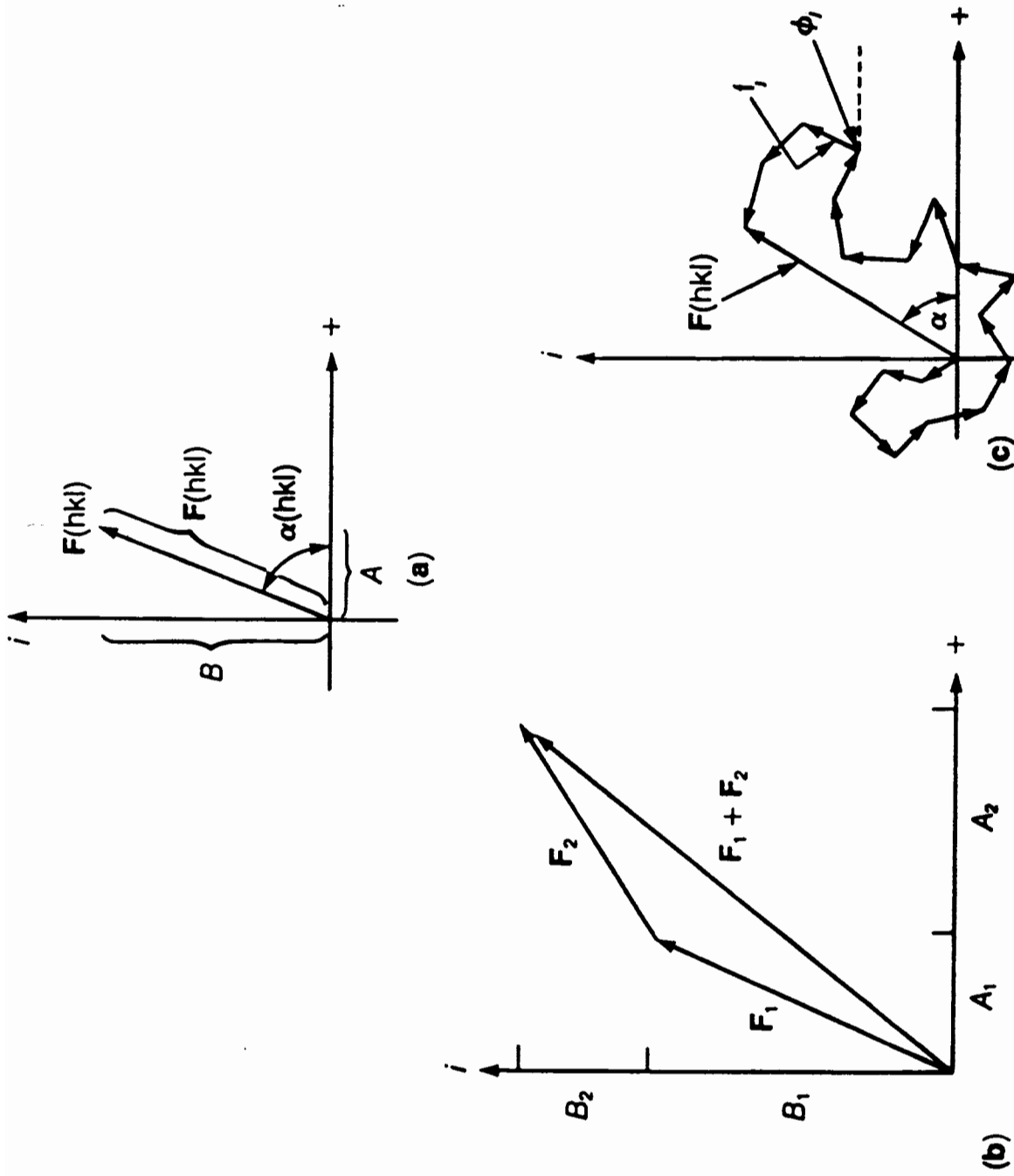


FIGURE 17-12

Representation of structure factors by vectors in the complex plane. (a) The structure factor magnitude $F(hkl)$ is represented by the length of a vector in the complex plane. The phase angle $\alpha(hkl)$ is given by the angle, measured counterclockwise, between the positive real axis and the vector F . (b) Complex numbers can be added by adding their real and complex components. (c) The structure factor for a reflection may be thought of as the vector sum of the x-ray scattering contributions from many atoms. Each of the j contributions may be represented as a vector in the complex plane, with amplitude f_j and phase ϕ_j .

Systematic Absences:

Consider space group $P2_1$ in which there is a 2-fold screw axis parallel to the b axis of the unit cell. The equivalent positions due to this screw axis are (x,y,z) and $(-x,y+0.5,-z)$. Thus for every atom j at fractional coordinates (x,y,z) there is a symmetry-related atom j' at $(-x,y+0.5,-z)$.

Then the structure factor for reflections F_{0k0} is:

$$F_{0k0} = \sum f_j e^{2\pi i(ky_j)}$$

Separating the contributions of atoms j from those of the symmetry-related atoms j' gives:

$$F_{0k0} = \sum f_j e^{2\pi i(ky_j)} + \sum f_{j'} e^{2\pi i(ky_{j'})}$$

Because atoms j and j' are identical, we can substitute the atomic scattering factor f_j for $f_{j'}$ and factor the result:

$$F_{0k0} = \sum f_j \left(\sum e^{2\pi iky_j} + \sum e^{2\pi iky_{j'}} \right)$$

If the y coordinate of atom j is y , then the y coordinate of atom j' is $y+0.5$. Making these substitutions for y_j and $y_{j'}$ gives:

$$F_{0k0} = \sum f_j \left(\sum \left[e^{2\pi iky} + e^{2\pi ik(y+0.5)} \right] \right)$$

Since the f_j scattering factors are nonzero, the F_{0k0} reflection will be absent only if the inner summation above is equal to zero. Thus F_{0k0} is absent when:

$$e^{2\pi iky} + e^{2\pi ik(y+0.5)} = e^{2\pi iky} (1 + e^{\pi ik}) = 0$$

Remembering that $e^{\pi ik} = \cos(k\pi) + i \sin(k\pi)$, this expression is equal to zero whenever k is an odd number, *ie*, $k = 1, 3, 5, \dots$

$$\vec{F}(hkl) = \sum_{atoms} \vec{f}_i(hkl)$$

$$= \sum |f_i| \cdot e^{i\phi_i(hkl)}$$

$$= |F(hkl)| \cdot e^{i\alpha(hkl)}$$

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)| \cdot e^{i\alpha(hkl)} \cdot e^{-2\pi i(hx+ky+lz)}$$

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

$$R = \frac{\sum^{hkl} ||F_{obs}| - |F_{calc}||}{\sum^{hkl} |F_{obs}|}$$

Fast Fourier Transform:

Starting in the 1960's it became widely recognized that it is possible to greatly speed the Fourier Transform process by suitably separating terms in the summation. Consider a Fourier series of the following form:

$$\rho(x) = \sum_0^H F_h e^{2\pi i h x}$$

This can be factored into two summations over alternating terms in even and odd values of h .

$$\rho(x) = \sum_0^{H/2} F_{2h} e^{2\pi i (2h)x} + \sum_0^{H/2} F_{2h+1} e^{2\pi i (2h+1)x}$$

Removing the common term from the odd summation gives:

$$\rho(x) = \sum_0^{H/2} F_{2h} e^{2\pi i (2h)x} + e^{2\pi i x} \sum_0^{H/2} F_{2h+1} e^{2\pi i (2h)x}$$

In this last equation, the exponential terms are the same in both summations, and so can be calculated only once and used twice. This corresponds to separating the data into two similar lots with a constant phase shift of $e^{2\pi i x}$ between them, carrying out the summation with different coefficients (F 's) on each, and then combining them with the aid of the phase shift.

This splitting into equal equal summations and factoring, leading to reuseable coefficients can be applied repeatedly. The resulting method reduces the work required to form the original summation from n^2 to $n \log_2(n)$. The algorithm is referred to as the Cooley–Tukey Fast Fourier Transform.