Chapter 2

Crystal Diffraction

In this chapter we shall describe concisely the fundamental features of Laue x-ray diffraction by a crystal. Readers interested in detailed discussions are referred to References [1]–[5].

Two kinds of radiation must distinguished in crystallographic investigations by x-rays:

1. The characteristic radiation of the target element emitted in the form of sharp spectral lines due to the inelastic excitation of the target atoms.
2. The continuous radiation emitted in the form of a broad spectrum generated by the deceleration of electrons in the target.

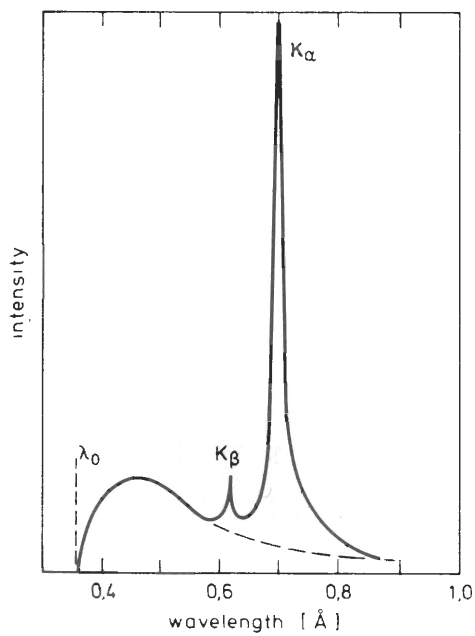

Figure 2.1:
X-ray spectrum of a Mo target obtained with an acceleration voltage of 30 keV.

The shortest (threshold-) wavelength λ_0 of this continuous spectrum is related to the maximum energy E of the exciting electrons through the well known formula:

$$(2.1) \qquad E = hc/\lambda_0 \quad \text{or} \quad E[\text{keV}] = \frac{12.345}{\lambda_0\,[\text{Å}]} \ ,$$

where h is Planck's constant and c the velocity of light. For example Fig. 2.1 shows the x-ray spectrum of a Mo target obtained with electrons accelerated to 30 keV. In addition to this continuous spectrum the characteristic x-ray lines of the K_α and K_β excitations can be seen. In order to make proper use of the x-ray diffraction patterns of crystals for our purposes we have to know two essential features of x-ray diffraction:

(i) what are the directions of the diffracted beams
and
(ii) what are the intensities in the spots produced by these beams on the receiving film?

2.1 Bragg's Law

X-ray diffraction is an elastic scattering process in which a large number of atoms cooperate. Because of the periodic arrangement of the atoms in the lattice, the waves scattered by the atoms have definite phase relations among them. As known from optical diffraction theory constructive interference occurs if the phase difference or the path differences between successive wave fronts is $n\lambda$, n being an integer and λ the wavelength of the incident x-rays. This holds if the Bragg law:

$$(2.2) \qquad 2d\sin\theta = n\lambda$$

is fulfilled, where d is the distance of adjacent parallel planes

in the crystal and θ is the angle between the incident wave and the reflection plane as shown in Fig. 2.2. Bragg's law shows that reflection is possible only for $\lambda \leq 2d$.

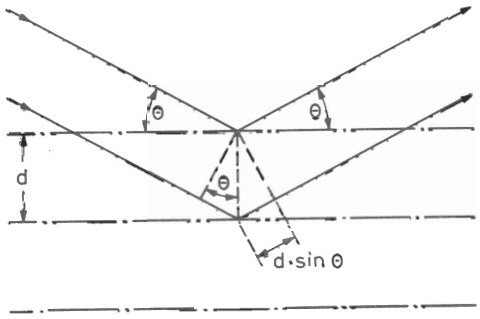

Figure 2.2:
Diffraction of x-rays by a crystal.

2.2 Laue Method

The Laue method is the most convenient one for the determination of orientation and symmetry of crystals. In this method a parallel beam of x-rays with a continuous wavelength distribution is directed onto the surface of a fixed single crystal. Each reflecting plane in the crystal selects from the incident beam a wavelength satisfying Bragg's law (2.2). The diffracted beams, all together forming the diffraction pattern, reproduce therefore structural properties of the crystal. This pattern is recorded by a flat film receiving either the transmitted or reflected diffraction beams. Fig. 2.3 is a schematic drawing of the arrangement. The sample is mounted on the top of the adjustable goniometer. After passing a collimator the incident x-ray beam strikes the sample. A Laue reflection pattern can be detected on film A, whereas a film in position B can show the transmission pattern. The Laue pattern of a (100) oriented tungsten single crystal taken with the back-reflection technique is shown in Fig. 2.4. This pattern is invariant under a rotation of $2\pi/4$ in view of the four-fold symmetry of a body centred cubic crystal about a cubic axis. Fig. 2.5 shows the technical details of a real Laue back reflection camera.

There are differences between the transmission and reflection methods. In order to detect the diffracted beam in transmission the absorption of the x-rays in the sample must be small: this means that the crystal has to be thin. On the other hand, it must not be too thin since the intensity of the diffracted beam is proportional to the volume of the diffracting material. Fig. 2.6 demonstrates the formation of the Laue pattern and the location of Laue spots on hyperbolas or straight lines in back-reflection and on ellipses, hyperbolas, straight lines or parabolas in transmission. In both cases the spots lie on the lines of intersection of a cone with the film plane. Each such cone is formed by all diffracted beams arising from revolving reflection planes about a common axis, the

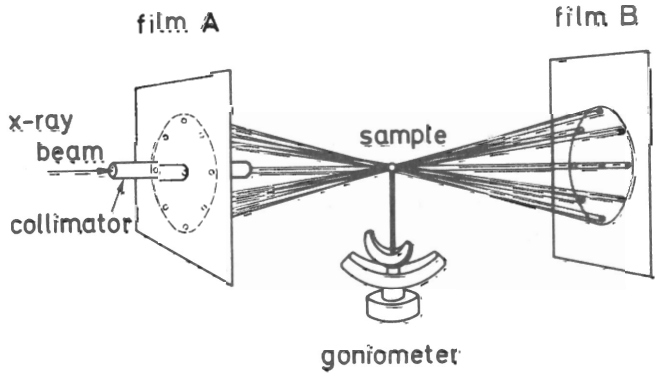

Figure 2.3:
Schematic drawing of an experimental setup for taking either back-reflection or transmission patterns.

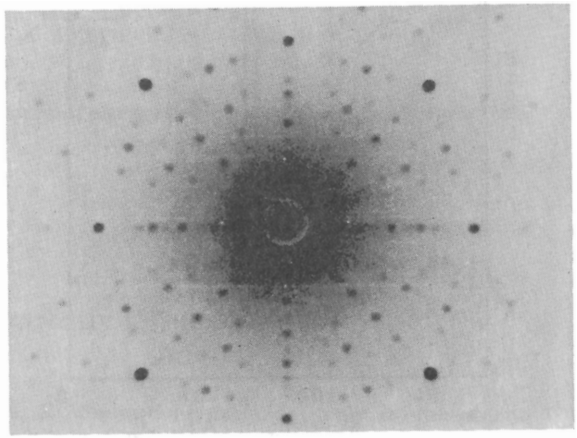

Figure 2.4:
Laue pattern of a (100) tungsten surface taken with the back-reflection technique.

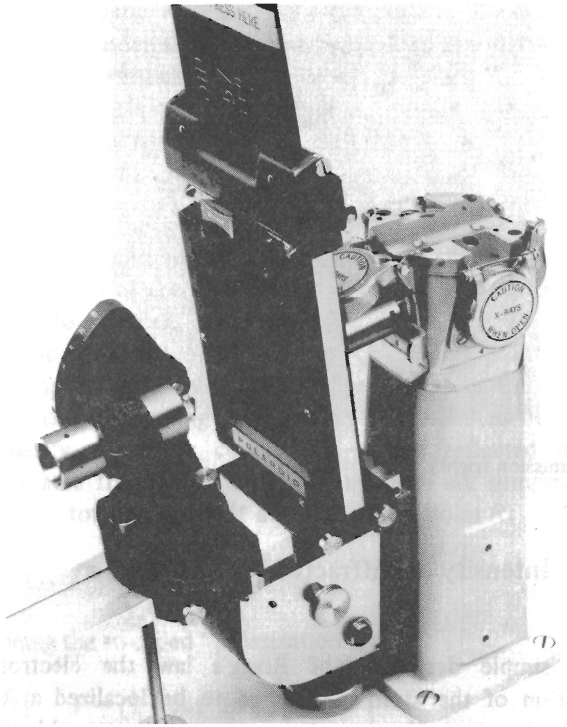

Figure 2.5:
Laue back-reflection camera (Courtesy of Polaroid Company).

so-called "zone axis", which is perpendicular to their normals. The corresponding Laue spots form a "zone".

In the transmission method the intersection of the primary beam with the film plane is a common point to all zones. In the back-reflection technique the incident beam is not contained in the spots of a zone unless the zone axis is perpendicular to the incident beam. In that case the "zone" (hyperbola) on the film degenerates into a straight line passing through the primary beam. Laue patterns obtained by both techniques (with drawn-in lines connecting the spots of a particular "zone") are shown on Fig. 2.7.

The shortest wavelength of the incident beam, λ_0, has a decisive effect on the occurence of a transmission pattern. This shortest wavelength satisfies the Bragg equation in first order for small glancing angles corresponding to spots close to the centre of the Laue transmission pattern. However, such spots do not necessarily correspond to short wavelengths, but can also arise from crystal planes with a smaller spacing. If the tube voltage is low the Laue spots corresponding to short wavelengths do not appear.

This is illustrated by the transmission pattern for the (111) plane of tungsten shown in Fig. 2.7 which contains no spots near the centre of the pattern.

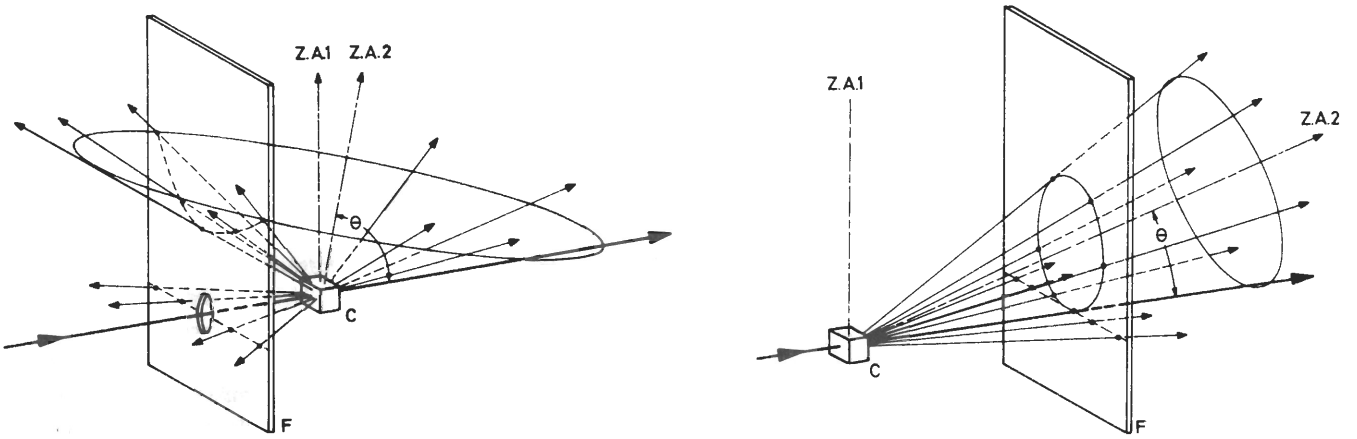

Figure 2.6:
Formation of Laue spots belonging to a particular zone in back-reflection (left) and transmission (right). The Laue spots belonging to the zone with zone axis *Z. A.* 1 lie on a straight line.

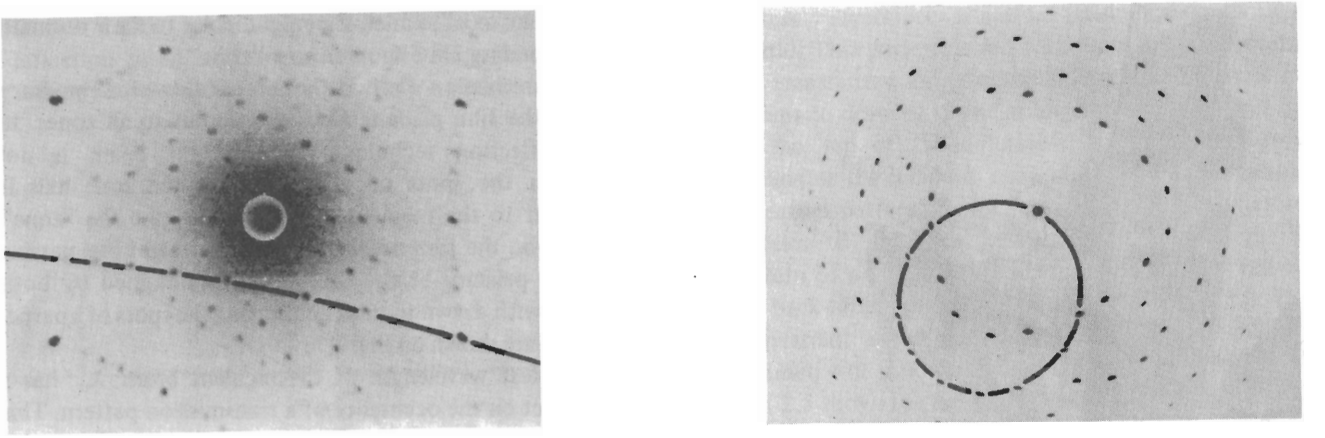

Figure 2.7: Laue patterns of the (111) tungsten surface in back-reflection (left) and transmission (right).

The exposure time for a transmission pattern can be much shorter than that for a reflection pattern. This is due to the fact that the atomic scattering factor f, defined in Section 2.4.2 and, consequently, the intensity of the spots decreases with increasing $(\sin\theta)/\lambda$ or θ/λ respectively (cf. Fig. 2.9). Further, as shown in Section 2.4.8, the Compton effect, which makes an important contribution to the background, is smaller in the transmission case. Therefore the contrast in transmission is greater than in back-reflection.

However, taking into consideration the significant absorption of probes commonly at one's disposal, the back-reflection technique is favoured in most cases.

The determination of the diffraction angle, given by the Bragg condition, is relative simple, whereas the calculation of the intensity and the identification of a spot is much more difficult. There are generally several wavelengths $n\lambda$ $(n = 1, 2, \ldots)$ in a broad x-ray spectrum which fulfill the Bragg condition. Thus, the intensity of a given Laue spot may be due to the superposition of the intensities of diffraction spots of different order. Moreover, the intensities of the incident x-rays depend on their wavelengths (see Fig. 2.1). In particular, if the wavelength of a characteristic x-ray line of the incident beam satisfies the Bragg condition, the corresponding spot is much more intense than all other ones. With some experience it is possible to distinguish this special case, but in view of this ambiguity the Laue method is in most cases only used in determining the orientation of crystals, and not in crystal structure investigations.

2.3 Intensity of Diffracted Waves

In the simple derivation of Bragg's law the electronic distribution of the atom is assumed to be localized at the centre of the atom. However, x-rays are only scattered by the atomic electrons, because the nuclei are too heavy to respond significantly to an x-ray photon. Therefore, the relative intensities of the different reflections depend on the number, position and distribution of the electrons in the unit cell.

The intensities of the diffracted waves can be calculated step by step; first we consider the scattering of x-rays by a single electron, then by an atom and finally by all atoms in the unit cell. At last the influence of the "Lorentz factor", of absorption, of geometric factors, of the Compton effect and of the temperature factor on the intensity are discussed.

2.3.1 *Scattering by a Free Electron*

The electric field of an x-ray wave exerts a force on an electron which induces an oscillatory motion about its mean position. An electromagnetic wave is emitted as a result of the acceleration and deceleration of the electron. This describes the scattering process. The wavelength and frequency of the scattered wave are equal to those of the incident wave (elastic scattering). Thomson first calculated the scattering of an

electromagnetic wave by a charged particle. According to his theory the intensity of the scattered wave at a distance r from an electron with charge e and mass m is

$$(2.3) \qquad I^* = I_0 \frac{e^4 \sin^2 \alpha}{(rmc^2)^2} \quad ,$$

where I_0 is the intensity of a polarized incident beam, c the velocity of light and α the angle between the direction of the acceleration of the electron and that of the scattered wave. In order to calculate the intensity of the scattered beam the electric field vector of the unpolarized incident beam is decomposed into its components perpendicular and parallel to the plane containing the incident and reflected beams. The intensity of either component in the reflected beam is calculated from Equation (2.3) and both are summed up to give the total intensity I^* at the arbitrary point R:

$$(2.4) \qquad I^* = I_0 P e^4 / (rmc^2)^2 \quad ,$$

P being the so-called "polarization factor":

$$(2.5) \qquad P = (1 + \cos^2 2\theta)/2 \quad ,$$

where θ is related to α by

$$(2.6) \qquad \alpha = 90^\circ - 2\theta \, .$$

2.3.2 *Scattering by an Atom*

According to the Thomson equation, the scattered intensity is inversely proportional to the square of the mass of the scattering particle. This implies that nuclei are too heavy to give a significant contribution to the scattering so that the x-rays are scattered only by electrons. Each electron of an atom scatters part of the radiation coherently in accordance with the Thomson equation. The distribution of electrons around the nucleus results in phase differences between the waves scattered by different electrons. These scattered waves are in phase only in forward direction ($2\theta = 0$). If 2θ is not equal to zero, the resulting phase differences give rise to partial intereference (see Fig. 2.8). Thus, the net amplitude is less than that in forward direction.

The scattering power or "form" factor f of an atom is defined as the ratio of the amplitudes:

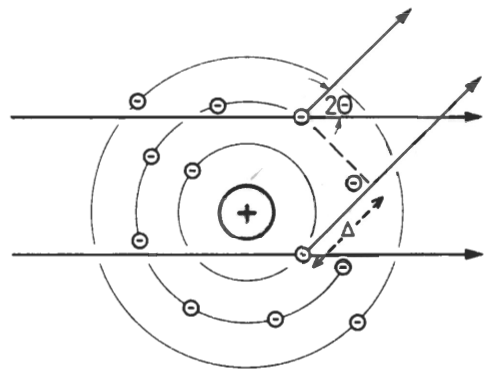

Figure 2.8:
Origin of phase differences depending on the diffraction angle in the scattering on an x-ray wave by different electrons of an atom.

$$f = \frac{\text{amplitude of the wave scattered by all electrons of an atom}}{\text{amplitude of the wave scattered by a free electron}}$$

For scattering in the forward direction, when all electrons scatter in phase, f is equal to Z (Z being the atomic number equal to the number of electrons of an atom). The phase differences giving rise to interferences do not only depend on the scattering angle but also on the wavelength of the x-rays. At a fixed value of θ, f will be the smaller the shorter the wavelength. Theory shows that f must be a function of $(\sin\theta)/\lambda$ as shown in Fig. 2.9 for copper and silver.

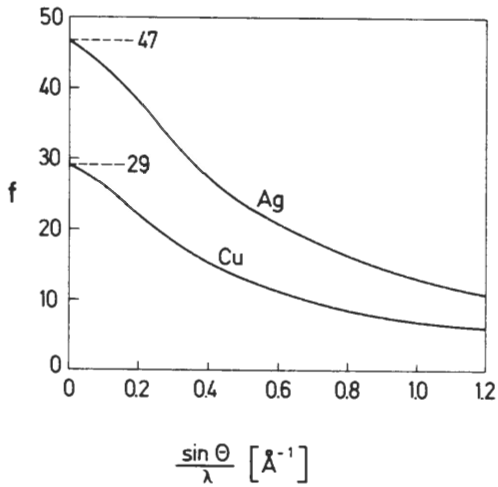

Figure 2.9:
Atomic scattering factor f of copper and silver as a function of $(\sin\theta)/\lambda$.

2.3.3 *Scattering by a Single Crystal*

Finally, we have to determine the intensity of the beam scattered by a unit cell. Possible scattering directions are given by Bragg's law. As in the case of scattering from several electrons of an atom, phase differences resulting from the spatial arrangement of atoms in the unit cell determine the interference process. The problem of scattering from a unit cell can be reduced to a phase coherent superposition of waves with different phases and amplitudes. Using the conventional formalism we find the resultant wave scattered by all atoms of the unit cell by summing the contributions from all N atoms in the unit cell. The resultant expression is called the structure factor F_{hkl}:

$$(2.7) \qquad F_{hkl} = \sum_{n=1}^{N} f_n \cdot \exp\left[2\pi i (h u_n + k v_n + l w_n)\right]$$

The absolute value $|F|$ gives the amplitude of the resultant wave which is defined as:

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

The intensity of a wave is proportional to the square of its amplitude:

$$(2.8) \qquad |F|^2 = F_{hkl} \cdot F^*_{hkl} ,$$

where F^*_{hkl} is complex conjugate to F_{hkl}. To illustrate the calculation of structure factors we give two examples:

Example 1:
Simple cubic structure with one atom at the origin in the unit cell (α-polonium). The fractional coordinates u_1, v_1, w_1 of this atom are: 000. From (2.7) we get in this case:

$$F = f \cdot \exp\left[2\pi i (0h + 0k + 0l)\right] = f$$
$$F^2 = f^2 .$$

Thus F^2 does not depend on h, k, l and all reflections give the same contribution to the intensity.

Example 2:
Body centred cubic structure with two atoms in the cubic unit cell located at 000 and $^1/_2\ ^1/_2\ ^1/_2$ (W-type). In that case we get from (2.7):

$$F = f \cdot \exp\left[2\pi i (0h + 0k + 0l)\right] + f \cdot \exp\left[2\pi i (h/2 + k/2 + l/2)\right]$$
$$= f \cdot \{1 + \exp\left[\pi i (h + k + l)\right]\} .$$

From this expression we conclude:

$$F = 2f \quad \text{when } h + k + l \text{ is even}$$
$$F = 0 \quad \text{when } h + k + l \text{ is odd} .$$

The second example illustrates the influence of an additional atomic plane in the case of the bcc-structure. The interference conditions are changed in such a way, that reflections possible on account of Bragg's law in the first example, are in fact missing in the second one.

Such rules specifying the presence or absence of particular reflections are of decisive importance for the recognition of diffraction patterns. The structure factors for different crystal structures are given in Chapters 3, 4 and 5.

2.3.4 *Lorentz Factor*

The so-called "Lorentz factor" influencing the intensity of Bragg reflections arises from the fact that the x-ray beam striking the crystal is not perfectly parallel and monochromatic. Radiation with glancing angles $\theta + \Delta\theta$ in the vicinity of the direction θ satisfying the Bragg condition exactly, contribute with a small intensity to the reflected beam. The small angular divergence $\Delta\theta$ results from the finite aperture angle of the incident beam. Furthermore, in the Laue method, continuous x-rays are used. In view of the finite width of the reflection maximum wavelength $\lambda \pm \Delta\lambda$ also contribute to the intensity. According to theory (see M. v. Laue [1]) the corresponding correction factor for the intensity is given by

$$(2.9) \qquad L \sim N\lambda^2/(2V\sin^2\theta) ,$$

where $V = [\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)]$

is the volume of the unit cell expressed by the unit vectors $\vec{a}_i$ of the crystal axes and N the number of the unit cells in the volume of the diffracting material. The angular function $1/\sin^2\theta$ is called the "white Lorentz factor" since this

dependence is valid for continuous radiation alone, as in the Laue method.

2.3.5 *Absorption Correction*

Absorption of the incident and reflected waves or of the transmitted beam is taken into account by absorption corrections.

Reflection

The incident x-ray beam will in general be reflected from crystal planes as shown in Fig. 2.10. From this figure we deduce the path length z of an x-ray beam reflected at a penetration depth x to be

$$(2.10) \quad z = x + x/\cos 2\sigma \quad ,$$

where $\sigma = 90^\circ - \theta$.

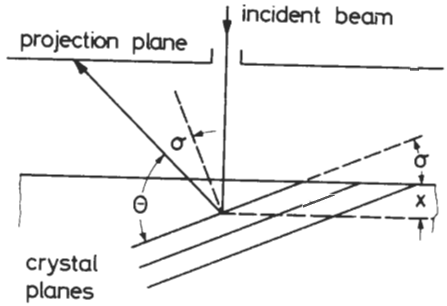

Figure 2.10:
Reflection of an x-ray beam at a penetration depth x.

The corresponding differential intensity dI for x-rays reflected at a depth between x and $x + dx$ and striking the projection plane is given by

$$(2.11) \quad dI \approx \bar{I} \exp(-\mu z)\, dx \, ,$$

$\bar{I}$ being the intensity of the incident beam influenced by all factors mentioned before and μ the absorption coefficient. Assuming negligible transmission and integrating over all depths x we obtain for the intensity of the reflected beam:

$$(2.12) \quad I \approx \bar{I} \int_0^\infty \exp[-\mu x\,(1 + 1/\cos 2\sigma)] \cdot dx$$

$$= \bar{I}\,(1 - \cot^2\theta)/2\,\mu \, .$$

Transmission

In order to calculate the absorption correction in the case of transmission we consider the special case of a thin crystal plate (see Fig. 2.11). In this case we get

$$(2.13) \quad z = x + (D - x)\cos 2\theta \, ,$$

D being the thickness of the sample. Proceeding as before we get the intensity

$$(2.14) \quad I \approx \bar{I} \int_0^D \exp\{-\mu[x + (D - x)/\cos 2\theta]\}\, dx$$

$$= \frac{\bar{I}[\exp(-\mu D/\cos 2\theta) - \exp(-\mu D)]}{\mu\,(1 - 1/\cos 2\theta)}$$

Expanding the exponential functions in the limit $\mu D \ll 1$ Eq. (2.14) approximately reduces to

$$(2.15) \quad I \approx \frac{\bar{I}\mu D\,(1 - 1/\cos 2\theta)}{\mu(1 - 1/\cos 2\theta)} = \bar{I} D$$

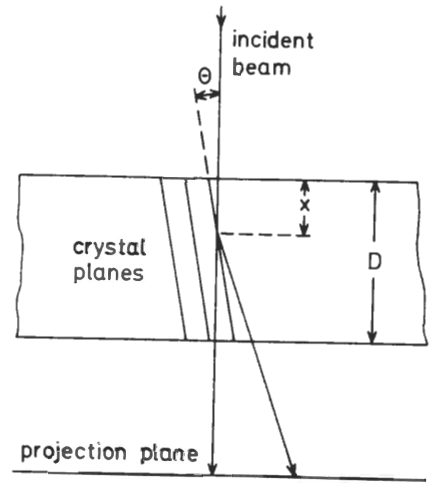

Figure 2.11:
Transmission of an x-ray beam through a thin crystal plate of thickness D.

2.3.6 *Geometrical Relations*

Finally, in using the Laue method, we have to consider some special geometrical relationships. That is, we have to take into consideration that the film plane forms an angle of $(90^\circ - 2\sigma)$ with the reflected beam. Therefore, the intensity of the reflected beam in the film plane is given by

$$(2.16) \quad I_{film}/I = \cos 2\sigma .$$

Correspondingly we find for the transmission case

$$(2.17) \quad I_{film}/I = \cos 2\theta .$$

The divergence of the incident beam is disregarded in these geometrical relations. In the transmission technique this divergence may eventually result in a focusing of the transmitted beam in the film plane.

2.3.7 *Final Formulae for the Intensity*

Gathering all factors influencing the intensity [Eqs. (2.4), (2.7), (2.9), (2.12), (2.14), (2.15), (2.16) and (2.17)] and replacing r in formula (2.4) by

$$(2.18) \quad r = a/\cos 2\sigma \quad \text{in the reflection case}$$

and by

$$(2.19) \quad r = a/\cos 2\theta \quad \text{in the transmission case,}$$

a being the distance between the film and the crystal, one finds that the intensity for a reflected beam is given by:

$$(2.20) \quad I_{refl} \sim \frac{I_0 e^4 \lambda^2 N|F|^2}{8\, Va^2\, \mu(mc^2)^2} \cdot \frac{(1 - \cos^2 2\theta)\,(1 - \cot^2\theta)\,\cos^3 2\sigma}{\sin^2\theta}$$

Analogously, the intensity of a transmitted beam is

$$(2.21) \quad I_{trans} \sim \frac{I_0 e^4 \lambda^2 N|F|^2}{4\, Va^2\, \mu(mc^2)^2} \cdot \frac{(1 + \cos^2 2\theta)\cos^4 2\theta}{(\cos 2\theta - 1)\sin^2\theta} \cdot [\exp(-\mu D/\cos 2\theta) - \exp(-\mu D)] ,$$

which reduces for $\mu D \ll 1$ to

$$(2.22) \quad I_{trans} \sim \frac{I_0 e^4 \lambda^2 N|F|^2 D\,(1 + \cos^2 2\theta)\cos^3 2\theta}{4\, Va^2\, (mc^2)^2 \sin^2\theta} .$$

2.3.8 *Note on Compton Effect*

In Section 2.3.1 no mention was made of the inelastic scattering of x-rays by electrons, the so-called Compton effect. This process can be best understood by considering the incident beam not as a wave but as a stream of x-ray quanta or photons, each with an energy $h\nu$. The inelastic collision of a photon and an electron results in an energy loss of the photon i.e. a shift to longer wavelengths. Therefore, no interference can occur. Compton scattering has the undesirable effect of increasing the background on which the diffraction pattern is superposed. Since Compton scattering is due to collisions of quanta with loosely bound electrons, its intensity relative to that of the elastic scattering increases with increasing proportion of loosely to tightly bound electrons. This means that Compton scattering increases with decreasing atomic number Z. For that reason, it is difficult to obtain good diffraction patterns from organic materials. The wavelength of the Compton scattered wave λ_2 is slightly greater than that of the incident wave λ_1. The difference

$$(2.23) \quad \Delta\lambda = \lambda_2 - \lambda_1 = 0.024\,(1 - \cos 2\theta)\,[\text{Å}] .$$

as well as the Compton scattering intensity reaches its maximum value in the back-reflection region ($2\theta \approx 180^\circ$). Moreover, since the scattering factor f decreases with increasing $(\sin\theta)/\lambda$, transmission patterns show a greater contrast than back-reflection patterns (see Fig. 2.7).

The atomic scattering factor f was calculated by assuming the atoms to be located at fixed points in the lattice. Actually, the atoms oscillate about their mean positions due to their thermal vibrations even at the absolute zero of temperature, and the amplitudes of these vibrations increase as the temperature increases. These thermal vibrations decrease the intensity of a diffracted beam and increase the background intensity because they have the effect of smearing out the lattice planes. Atoms can no longer be regarded as lying at fixed points but rather in platelike regions. Thus the reinforcement of waves scattered at the Bragg angle by adjacent planes is not as perfect as it is for a crystal with fixed atoms, because the path difference deviates now somewhat from the required integral number of wavelengths. The reinforcement becomes more imperfect as the relative displacement increases, i.e., as the temperature increases, or as the angle of incidence increases, since reflections belonging to high angles of incidence involve planes with low lattice distances d.

It should be noted here that the temperature effect does not cause any broadening of the diffraction spots. The diffraction spots remain sharp up to the melting point of the crystal, but the intensity of the spots decreases by an exponential function, the so-called Debye-Waller factor or temperature factor, as theoretical calculations show. Thus the temperature factor has no influence on the specific rules given by the structure factor for the presence or absence of reflections. Since this temperature effect depends on the kinds of atoms which make up the lattice and the interactions between them, calculations of the Debye-Waller factor become quite difficult in all but the simplest cases. We have therefore neglected the temperature factor in the intensity calculations of our plot programme. To include such effects would in any case have involved considerable complications. Apart from other quantities, the Debye-Waller factor depends on the melting point of the crystal. Since we plot only one representative for each structure type it would have been necessary to take an average value for the melting points of the different elements or compounds exhibiting that structure. Such a procedure is somewhat meaningless. Our simplified procedure for interpreting the Laue back-reflection patterns is insensitive to the relative intensity of the spots but only on their symmetry. There is therefore nothing to be gained by including Debye-Waller effects.

2.4 Intensity Calculations Used in the Programme

The starting point for intensity calculations in the computer programme is Equation (2.20). Because only the relative intensities of the spots are important for the plots, all constants can be omitted.

The atomic factor f is taken from tabulated values [6]. For different elements with a given crystal structure an average value of Z is taken for the atomic factor f (see Chapter 6).

The absorption coefficient μ is approximately proportional to the third power of the x-ray wavelength [7]:

$$\mu = C\,\lambda^3. \quad (C = \text{const.}) \tag{2.24}$$

The wavelength dependence of the primary intensity of the radiation from the x-ray tube, I_0, can be presented by an expression given by Kramers [8]:

$$I_0 = K\,(\lambda/\lambda_0 - 1)/\lambda^2. \tag{2.25}$$

K is proportional to the current in the x-ray tube and to the atomic number of its anode material.

Thus the explicit λ and θ dependence of the reflected or transmitted intensity in the film plane is known. Equation (2.20) and (2.22) take on the following forms:

$$I_{refl} \sim \frac{(1+\cos^2 2\theta)\,|F|^2\,(\lambda/\lambda_0 - 1)}{\sin^2\theta} \cdot \frac{(1+\cot^2\theta)\,(\sin^2\theta - \cos^2\theta)^3}{\lambda^3} \tag{2.26}$$

$$I_{trans} \sim \frac{(1+\cos^2 2\theta)\,|F|^2\,(\cos 2\theta)^3\,(\lambda/\lambda_0 - 1)}{\sin^2\theta} \tag{2.27}$$

In Chapters 8 through 10 only Laue diffraction patterns for back-reflection are reproduced; therefore only Equation (2.26) was used in the plot programme. Equation (2.27) is given here for the sake of completeness and convenience.

References for Chapter 2

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