

## 6.2. Trigonometric intensity factors

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### 6.2.1. Expressions for intensity of diffraction

The expressions for the intensity of diffraction of X-rays contain several trigonometrical factors. The earlier series of *International Tables* (Kasper & Lonsdale, 1959, 1972) gave extensive tables of these functions, but such tables are now unnecessary, as the functions are easily computed. In fact, many crystallographers can ignore the trigonometric factors entirely, as they are built into ‘black-box’ data-processing programs. The formulae for single-crystal reflections (*b*) and (*c*) of Table 6.2.1.1 in the previous edition (Lipson & Langford, 1998) list only the integrated reflection power ratio (*i.e.* integrated reflection) under the strong absorption case. The revised formulae given here include both the reflection power ratio and the integrated reflection power ratio for a crystal slab of finite thickness with any values of the ratio of the absorption to the diffraction cross sections and under all possible kinds of diffraction geometry.

A conspectus of the expressions for the intensity of diffraction as recorded by various techniques, including the fundamental constants as well as the trigonometric factors, is given in Table 6.2.1.1. Details of the techniques are given elsewhere in this volume (Chapters 2.1–2.3) and in textbooks, such as those of Arndt & Willis (1966) for single-crystal diffractometry and Klug & Alexander (1974) for powder techniques. Notes on individual factors follow.

### 6.2.2. The polarization factor

X-rays are an electromagnetic radiation, and the amplitude with which they are scattered is proportional to the sine of the angle between the direction of the electric vector of the incident radiation and the direction of scattering. Synchrotron radiation is practically plane-polarized, with the electric vector in the plane of the ring, but the radiation from an ordinary X-ray tube is unpolarized, and it may thus be regarded as consisting of two equal parts, half with the electric vector in the plane of scattering, and half with the electric vector perpendicular to this plane. For the latter, the relevant angle is  $\pi/2$ , and for the former it is  $(\pi/2) - 2\theta$ . The intensity is proportional to the square of the amplitude, so that the polarization factor – really the non-polarization factor – is

$$\begin{aligned} & \{\sin^2(\pi/2) + \sin^2[(\pi/2) - 2\theta]\}/2 \\ & = (1 + \cos^2 2\theta)/2. \end{aligned} \quad (6.2.2.1)$$

If the radiation has been ‘monochromatized’ by reflection from a crystal, it will be partially polarized, and the two parts of the beam will be of unequal intensity. The intensity of reflection then depends on the angular relations between the original, the reflected, and the scattered beams, but in the commonest arrangements all three are coplanar. The polarization factor then becomes

$$(1 + A \cos^2 2\theta)/(1 + A), \quad (6.2.2.2)$$

where

$$A = \cos^2 2\theta_M \quad (6.2.2.3)$$

and  $\theta_M$  is the Bragg angle of the monochromator crystal. The expression (6.2.2.2) may be substituted for (6.2.2.1) in Table 6.2.1.1 whenever appropriate.

### 6.2.3. The angular-velocity factor

In experiments where the crystal is rotated or oscillated, reflection of X-rays takes place as a reciprocal-lattice point moves through the surface of the sphere of reflection. The intensity is thus proportional to the time required for the transit of the point through the surface, and so is inversely proportional to the component of the velocity perpendicular to the surface. In most experimental arrangements – the precession camera (Buerger, 1944) is an exception – the crystals move with a constant angular velocity, and the perpendicular component of the velocity varies in an easily calculable way with the ‘latitude’ of the reciprocal-lattice point referred to the axis of rotation. If the reciprocal-lattice point lies in the equatorial plane and the radiation is monochromatic – the most important case in practice – the angular-velocity factor is

$$\operatorname{cosec} 2\theta. \quad (6.2.3.1)$$

If the latitude of the reciprocal-lattice point is  $\varphi$ , a somewhat more complex calculation shows that the factor becomes

$$\operatorname{cosec} \theta (\cos^2 \varphi - \sin^2 \theta)^{1/2}. \quad (6.2.3.2)$$

For  $\varphi = 0$ , the expression (6.2.3.2) reduces to (6.2.3.1). In some texts,  $\varphi$  is used for the co-latitude; this and various trigonometric identities can give superficially very different appearances to (6.2.3.2).

### 6.2.4. The Lorentz factor

There has been some argument over the meaning to be attached to the term *Lorentz factor*, probably because Lorentz did not publish his results in the ordinary way; they appear in a note added in proof to a paper on temperature effects by Debye (1914). Ordinarily, *Lorentz factor* is used for the trigonometric part of the angular-velocity factor, or its equivalent, if the sample is stationary. (See below).

### 6.2.5. Special factors in the powder method

In the powder method, all rays diffracted through an angle  $2\theta$  lie on the surface of a cone, and in the absence of preferred orientation the diffracted intensity is uniformly distributed over the circumference of the cone. The amount effective in blackening film, or intercepted by the receiving slit of a diffractometer, is thus inversely proportional to the circumference of the cone, and directly proportional to the fraction of the crystallites in a position to reflect. When allowance is made for these geometrical factors, it is found that for the Debye–Scherrer and diffractometer arrangements the intensity is proportional to

$$p'' \operatorname{cosec} \theta, \quad (6.2.5.1)$$

where  $p''$  is the multiplicity factor (the number of permutations of *hkl* leading to the same value of  $\theta$ ). For the flat-plate front-reflection arrangement, the variation becomes

$$p'' \cos 2\theta \operatorname{cosec} \theta. \quad (6.2.5.2)$$

Combining the polarization, angular-velocity, and special factors gives a trigonometric variation of

$$p''(1 + \cos^2 2\theta) \sec \theta \operatorname{cosec}^2 \theta \quad (6.2.5.3)$$

## 6.2. TRIGONOMETRIC INTENSITY FACTORS

Table 6.2.1.1. Summary of formulae for integrated powers of reflection

<p>(a) Crystal element</p> $\rho = Q\delta V$ $Q = \frac{N^2 e^4 \lambda^3}{2m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta}  F ^2 \quad \text{for non-polarized X-rays}$ $Q = \frac{N^2 \lambda^3}{\sin 2\theta}  F ^2 \quad \text{for neutrons}$	$P_H/P_0 = (1 - \tan \theta \tan \varphi) \{1 - \exp[-\sec(\theta + \varphi)\sigma t - \sec(\theta - \varphi)\sigma t]\} / 2$ <p style="text-align: right;">for <math>\mu = 0</math></p> <p>Define <math>u = [(1 - b)^2(\xi + 1)^2 + 4b]^{1/2}</math> and <math>w = (1 + b)(\xi + 1)</math></p> $\frac{P_H}{P_0} = \{\exp[-(w - u)\tau/2] - \exp[-(w + u)\tau/2]\} / u$ <p style="text-align: right;">for <math>\mu \geq 0</math></p>
<p>(b) Reflection from a crystal slab of thickness <math>t</math></p> $\sigma = QW(\Delta\theta_0)$ $\xi = \mu/\sigma$ <p>1. Symmetrical Bragg geometry</p> $P_H/P_0 = (\sigma t \operatorname{cosec} \theta) / (1 + \sigma t \operatorname{cosec} \theta) \quad \text{for } \mu = 0$ $P_H/P_0 = \{1 - \exp[-2(\xi^2 + 2\xi)^{1/2} \sigma t \operatorname{cosec} \theta]\} \{(\xi^2 + 2\xi)^{1/2} + \xi + 1 + [(\xi^2 + 2\xi)^{1/2} - (\xi + 1)] \times \exp[-2(\xi^2 + 2\xi)^{1/2} \sigma t \operatorname{cosec} \theta]\}^{-1} \quad \text{for } \mu \neq 0$ $\rho' = \frac{Q[1 - \exp(-2\mu t \operatorname{cosec} \theta)]}{2\mu} \quad \text{for } \mu/\sigma_0 \gg 1$ <p>2. Asymmetrical Bragg geometry, when the reflecting planes are inclined at an angle <math>\varphi</math> to the crystal surface, and the surface normal is in the plane of the incident and reflected beams.</p> $\tau = \sigma t \operatorname{cosec}(\theta + \varphi)$ $b = -\sin(\theta + \varphi) / \sin(\theta - \varphi)$ <p>angle of incidence <math>(\theta + \varphi)</math> and angle of emergence <math>(\theta - \varphi)</math> to the crystal surface</p> $\frac{P_H}{P_0} = \frac{1 - \exp[- 1 + b  \operatorname{cosec}(\theta + \varphi)\sigma t]}{1 -  b  \exp[- 1 + b  \operatorname{cosec}(\theta + \varphi)\sigma t]}$ <p style="text-align: right;">for <math> b  &lt; 1, \varphi &lt; 0^\circ</math> and <math>\mu = 0</math></p> $\frac{P_H}{P_0} = \frac{1 - \exp[- 1 + b  \operatorname{cosec}(\theta + \varphi)\sigma t]}{ b  - \exp[- 1 + b  \operatorname{cosec}(\theta + \varphi)\sigma t]}$ <p style="text-align: right;">for <math> b  &gt; 1, \varphi &gt; 0^\circ</math> and <math>\mu = 0</math></p> <p>Define <math>u = [(1 - b)^2(\xi + 1)^2 + 4b]^{1/2}</math> and <math>v = (1 - b)(\xi + 1)</math>:</p> $\frac{P_H}{P_0} = \frac{2[1 - \exp(-u\tau)]}{(u + v) + (u - v) \exp(-u\tau)} \quad \text{for } \mu \geq 0$ $\rho' = Q\{1 - \exp[-(1 - b)\mu t \operatorname{cosec}(\theta + \varphi)]\} [(1 - b)\mu]^{-1}$ $= \frac{Q}{2\mu} (1 - \cot \theta \tan \varphi) \left\{ 1 - \exp \left[ -\frac{2\mu t \operatorname{cosec}(\theta + \varphi)}{1 - \cot \theta \tan \varphi} \right] \right\}$ <p style="text-align: right;">for <math>\mu/\sigma_0 \gg 1</math></p>	$\rho' = \frac{Q}{(1 - b)\mu} \{\exp[-\mu t \sec(\theta + \varphi)] - \exp[-\mu t \sec(\theta - \varphi)]\}$ $= \frac{Q}{\left[1 - \frac{\sec(\theta + \varphi)}{\sec(\theta - \varphi)}\right] \mu} \{\exp[-\mu t \sec(\theta + \varphi)] - \exp[-\mu t \sec(\theta - \varphi)]\}$ <p style="text-align: right;">for <math>\mu/\sigma_0 \gg 1</math></p>
<p>(c) Transmission from a crystal slab of thickness <math>t</math></p> <p>1. Symmetrical Laue geometry</p> $P_H/P_0 = \exp(-\xi \sigma t \sec \theta) [1 - \exp(-2\sigma t \sec \theta)] / 2 \quad \text{for } \mu \geq 0$ $\rho' = Q t \sec \theta \exp(-\mu t \sec \theta) \quad \text{for } \mu/\sigma_0 \gg 1$ <p>2. Asymmetrical Laue geometry, when the reflecting planes are at <math>\pi/2 - \varphi</math> to the crystal surface, with the normal in the plane of the incident and reflected beams.</p> $\tau = \sigma t \sec(\theta - \varphi)$ $b = \sec(\theta + \varphi) / \sec(\theta - \varphi)$ <p>angle of incidence <math>(\theta + \varphi)</math> and angle of emergence <math>(\theta - \varphi)</math> to the normal to the crystal surface</p>	<p>(d) Powder halo: no absorption correction included</p> $\frac{P}{I_0} = \frac{Q p'' V \cos \theta}{2} = \frac{N^2 e^4 \lambda^3 V}{8m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin \theta} p''  F ^2,$ <p>where <math>P</math> is the diffracted power.</p> <p>(e) Debye-Scherrer lines on cylindrical film: no absorption correction included</p> $\frac{P_l}{I_0} = \frac{Q p'' l V}{8\pi r \sin \theta} = \frac{N^2 e^4 \lambda^3 l V}{32\pi m^2 c^4 r} \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} p''  F ^2,$ <p>where <math>l</math> is the length of line measured and <math>r</math> is the radius of the camera. <math>P_l</math> is the power reflected into length <math>l</math>.</p> <p>(f) Reflection from a thick block of powdered crystal of negligible transmission</p> $\frac{P_l}{I_0} = \frac{Q p'' l}{16\pi \mu r \sin \theta} = \frac{N^2 e^4 \lambda^3 l}{64\pi m^2 c^4 \mu r} \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} p''  F ^2$ <p>(g) Transmission through block of powdered crystal of thickness <math>t</math></p> $\frac{P}{I_0} = \frac{Q p'' t}{4\pi r \sin 2\theta} \frac{\delta'}{\delta}$ $= \frac{N^2 e^4 \lambda^3}{8\pi m^2 c^4 r} \frac{t \delta'}{\delta} \frac{1 + \cos^2 2\theta}{\sin^2 2\theta} p''  F ^2,$ <p>where <math>\delta', \delta</math> are the densities of the block of powder and of the crystal in bulk, respectively.</p> <p>(h) Rotation photograph of small crystal, volume <math>V</math></p> <p>1. Beam normal to axis</p> $\rho = \frac{Q V p'}{2\pi(\cos^2 \varphi - \sin^2 \theta)^{1/2}}$ $= \frac{N^2 e^4 \lambda^3 V}{4\pi m^2 c^4} \frac{1 + \cos^2 \theta}{\sin 2\theta} \frac{\cos \theta}{(\cos^2 \varphi - \sin^2 \theta)^{1/2}} p'  F ^2$ <p>2. Equi-inclination Weissenberg photograph</p> $\rho = \frac{Q V}{2\pi \xi \cos \theta} \frac{N^2 e^4 \lambda^3 V}{4\pi m^2 c^4} \frac{1 + \cos^2 2\theta}{\xi \cos \theta}  F ^2$
Absorption is neglected in both (g) and (h)	
<b>Symbols</b>	
$Q$ $\delta V$ $e, m$	Integrated reflection from a crystal of unit volume Volume of crystal element Electronic charge and mass

## 6. INTERPRETATION OF DIFFRACTED INTENSITIES

Table 6.2.1.1. *Summary of formulae for integrated powers of reflection (cont.)*

Symbols	
$c$	Speed of light
$\lambda$	Wavelength of radiation
$\mu$	Linear absorption coefficient for X-rays or total attenuation coefficient for neutrons
$2\theta$	Angle between incident and diffracted beams
$\varphi$	In (b) and (c), as defined; in (h), latitude of reciprocal-lattice point relative to axis of rotation
$V$	Volume of crystal, or of irradiated part of powder sample
$N$	Number of unit cells per unit volume
$\xi$	In (b) and (c), as defined; in (h), radial coordinate $x_i$ used in interpreting Weissenberg photographs
$I_0$	Energy of radiation falling normally on unit area per second
$hkl$	Indices of reflection
$F$	Structure factor of $hkl$ reflection
$W(\Delta\theta_0)$	Distribution function of the mosaic blocks at angular deviation $\Delta\theta_0$ from the average reflecting plane
$\sigma$	Diffraction cross section per unit volume
$\sigma_0$	Diffraction cross section per unit volume at $\Delta\theta_0 = 0$
$b$	Asymmetry parameter
$\tau$	Reduced thickness of the crystal slab
$P_H/P_0$	Reflection power ratio, <i>i.e.</i> the ratio of diffracted power to the incident power
$\rho$	Integrated reflection power ratio from a crystal element
$\rho'$	Integrated reflection power ratio, angular integration of reflection power ratio
$p'$	Multiplicity factor for single-crystal methods
$p''$	Multiplicity factor for powder methods

for the Debye–Scherrer and diffractometer arrangements, and

$$p''(1 + \cos^2 2\theta) \tan 2\theta \operatorname{cosec} \theta \quad (6.2.5.4)$$

for the flat-plate front-reflection arrangement.

Nowadays, angle-dispersive experiments are normally carried out by stepping the sample and detector in small angular increments, both being stationary while the intensity at each step is recorded. The Lorentz factor for a random powder sample is then of the form  $p''(\cos \theta \sin^2 \theta)^{-1}$ . The factor  $\cos \theta$  arises from the fact that spherical shells of diffracted intensity in reciprocal space intersect the Ewald sphere at an angle that depends on  $\theta$ ,

and the surface area of the shells increases as  $d^{*2}$ , which is embodied in the factor  $\sin^2 \theta$ . It turns out that this factor is equivalent to a combination of the polarization factor (6.2.2.1), the angular-velocity factor (6.2.3.1) and (6.2.5.1), and the form of (6.2.5.3) is thus unchanged.

### 6.2.6. Some remarks about the integrated reflection power ratio formulae for single-crystal slabs

The transfer equations for intensity may be rewritten in the form of one-dimensional power transfer equations (Hu & Fang, 1993). The  $P_H/P_0$  in (b) and (c) for a mosaic crystal slab under symmetrical and unsymmetrical Bragg and Laue geometries are the general solutions of power transfer equations employing three dimensionless parameters  $b$ ,  $\xi$  and  $\tau$ . For a crystal slab with a rectangular mosaic distribution, considering multiple reflection, the integrated reflection power ratio,  $\rho'$ , can be obtained by substituting  $\sigma_0$  for  $\sigma$  in the formulae for  $P_H/P_0$  and multiplying the result by the mosaic width. However, for crystals with other kinds of mosaic distribution, the corresponding  $\rho'$  can be obtained only by integrating the expression for  $P_H(\Delta\theta_0)/P_0$  over the whole range of  $\Delta\theta_0$ . Formulae (1)–(3) listed in Table 6.3.3.1, *i.e.* the transmission coefficient  $A$  multiplied by  $Q$ ,  $QA$ , are identical to those of (b) and (c) for the case of  $\mu/\sigma_0 \gg 1$ , which is the integrated reflection power ratio for a crystal slab based on the kinematic approximation without consideration of multiple reflection.

The secondary extinction factor for X-ray or neutron diffraction in a mosaic crystal slab can be obtained as  $\rho'/(QA)$ , in which the integrated reflection power ratio with consideration of multiple reflections can be obtained as described above.

Both the transmission power ratio  $P_T/P_0$  and the absorption power ratio  $P_A/P_0$  can also be obtained by solving the power transfer equations. For details, see Hu (1997a,b), Werner & Arrott (1965) and Werner, Arrott, King & Kendrick (1966).

### 6.2.7. Other factors

The various expressions in Table 6.2.1.1 contain  $|F|^2$ , the square of the modulus of the structure factor. The relation of  $F$  to the atomic scattering factors, the atomic positional coordinates, and the temperature is treated in Chapter 6.1.

For the factors relevant for the precession method (Buerger, 1944), see Waser (1951a,b), Burbank (1952), and Grenville-Wells & Abrahams (1952). For the de Jong–Bouman method, see Bouman & de Jong (1938) and Buerger (1940). For the retigraph, see Mackay (1960).