

## On the Derivation of Integrated Reflected Energy Formulae

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### Abstract

A systematic procedure for deriving the equations of the integrated reflected X-ray energy is presented and conditions for the validity of the equations are formulated. Existing formulae are critically examined.

### Introduction

The concept of integrated reflected X-ray energy dates back to the early days of X-ray crystallography, and Lorentz factors have been calculated ever since. However, on going through the literature, the impression prevails that derivations of these factors for various experimental methods require different procedures, and that the reason for selecting a certain procedure in preference to others – equally feasible ones – is not always sufficiently justified; in particular, one fails to find definite guidelines on what to do when confronted with a new experimental situation.

This article attempts to present a systematic way of deriving the expressions for integrated reflected energies as measured by the different experimental techniques. Specifically this will be outlined for X-ray reflections from imperfect three-dimensional crystals, *i.e.* reflections belonging to the regime of the kinematic theory; the underlying reasoning is, however, quite generally applicable.

### General considerations

The starting point is the equation relating the intensity  $I$  scattered by the crystal in the direction  $\mathbf{s}_1$ , to the intensity  $I_0$  of the primary monochromatic beam, incident in the direction  $\mathbf{s}_0$  ( $\mathbf{s}_1$  and  $\mathbf{s}_0$  are unit vectors). Limiting the discussion to small, non-absorbing crystallites, or aggregates of small coherently reflecting domains, Laue (1960, chapter 14) derives the relation:

$$I(\mathbf{s}_1) = I_e F^2 G^2, \quad (1)$$

$$I_e = j_e I_0(\mathbf{s}_0)/r^2, \quad j_e = P \times 7.94 \times 10^{-30} \text{ m}^2,$$

$r$  is the distance from the crystal to the observation

point. The remaining symbols have their conventional meaning (see list of symbols).

This equation is valid in the kinematic approximation, *i.e.* under the assumption of negligible secondary and higher-order scattering processes within the scattering material. Hence it is applicable to situations where the total scattered power is weak compared with the power contained in the primary exciting beam.

Furthermore, (1) holds for a strictly monochromatic and perfectly parallel incident beam. For describing experimental conditions, this restriction must be relaxed. This is accomplished by introducing first the spectral intensity  $I'$ , customarily defined either with respect to the wavelength  $\lambda$  or with respect to the wave-number  $k$  ( $=1/\lambda$ ) as:

$$I'(\lambda) = \frac{dI}{d\lambda} \quad \text{or} \quad I'(k) = \frac{dI}{dk} \quad (2)$$

and by replacing the primary intensity  $I_0$  by the angular density of the spectral intensity  $i_0$

$$i_0(\lambda) = \frac{dI'(\lambda)}{d\Omega_0}, \quad i_0(k) = \frac{dI'(k)}{d\Omega_0}, \quad (3)$$

where  $\Omega_0$  refers to the (solid) angular opening of the primary beam. Equation (1) is thus written as

$$I = \iint j_e i_0(k) r^{-2} F^2 G^2 d\Omega_0 dk. \quad (4)$$

The reflected power through an element of area  $d\sigma$  about the point of observation is  $dH_r$ ;

$$dH_r = I d\sigma$$

and the energy reflected during time  $dt$  is  $dE_r$ ;

$$dE_r = I d\sigma dt.$$

Denoting the solid angle subtended by  $d\sigma$ , as seen from the crystal, by  $d\Omega_1$  the reflected energy is thus

$$E_r = \iiint j_e i_0(k) F^2 G^2 d\Omega_0 d\Omega_1 dk dt. \quad (5)$$

In general the reflected energy is due to different crystallites in various orientations (powder, mosaic crystal). Equation (5) for  $E_r$  must then be multiplied by the number of crystallites in or near the reflecting orientation. This is expressed by a distribution function  $U(\mathbf{b}_H)d\Gamma$ , giving the number of crystallites oriented so

that their reciprocal lattice vector  $\mathbf{b}_H$ , pertaining to the reflecting plane, lies within the solid angle  $d\mathcal{I}$ , thus

$$E_r = \iiint \iiint j_e i_0(k) F^2 G^2 U(\mathbf{b}_H) d\mathcal{I} d\Omega_0 d\Omega_1 dk dt. \quad (6)$$

There are eight integration variables in (6), their values are determined by the experimental conditions: the two solid angles  $\Omega_0$  and  $\Omega_1$  which are the angular divergence of the primary beam and the angular opening of the detecting device, respectively (each solid angle is described by two planar angles in mutually perpendicular planes), the two planar angles describing the directions  $\mathbf{b}_H$  of the reflecting crystallites, the wave-number  $k$  and the time  $t$ , which must be introduced to permit consideration of non-stationary situations.

Let these variables be denoted by  $x_1, x_2, \dots, x_8$  regardless of order. The factors of the integrand of (6) are functions of at least some of the  $x_i$ . Furthermore, each  $x_i$  varies over an interval which is determined by the experimental set up. The explicit relations will be discussed later.

The effect of crystal diffraction is described by the lattice factor  $G^2$ . This factor can be expressed in terms of three parameters  $Y_1, Y_2$  and  $Y_3$  which are related to the integration variables  $x_i$  through the diffraction vector  $\mathbf{L}$ :

$$\mathbf{L} = (\mathbf{s}_1 - \mathbf{s}_0)k, \quad (7)$$

$$Y_i = \mathbf{L} \cdot \mathbf{a}_i \pi, \quad i = 1, 2, 3, \quad (7a)$$

where  $\mathbf{a}_i$  are the three elementary lattice translations. Finally,

$$G^2 = \prod_{i=1}^3 \frac{\sin^2 N_i Y_i}{\sin^2 Y_i} \quad (8)$$

(Laue, 1960, chapter 14), where  $N_i$  is the number of elementary cells in the directions of  $\mathbf{a}_i$  in the reflecting crystallite. The numbers  $N_i$  are usually quite large ( $> 10^3$ ), yet should not exceed the limits set by the validity of the kinematic approximation.

The integration (6) should be carried out so that  $G^2$  is integrated over the intervals

$$\pi(H_i - \frac{1}{2}) < Y_i < \pi(H_i + \frac{1}{2}) \quad (i = 1, 2, 3), \quad (9)$$

where  $H_1, H_2$  and  $H_3$  are integers (the index of the reflection) (Laue, 1960, chapter 17). Such an interval contains one, and only one 'principal' maximum of  $G^2$ .

However, all practically non-vanishing values of  $G^2$  about any principal maximum are bunched within a region much smaller than that defined by (9). This region is bounded by three intervals  $\Delta' Y_i$  ( $i = 1, 2, 3$ ) defined as

$$H_i \pi - \beta_i/2 < Y_i < H_i \pi + \beta_i/2, \quad (9a)$$

where  $\beta_i$  equals a few times  $2\pi/N_i$ .

Hence the integral of  $G^2$  with respect to  $Y_i$  is practically a constant independent of the limits of integration, provided that each  $Y_i$  varies at least over the

minimum interval  $\Delta' Y_i$  defined by (9a) [and does not exceed the interval defined by (9)]:

$$\iiint_{\Delta Y_i} G^2 dY_1 dY_2 dY_3 = \pi^3 N_1 N_2 N_3 = \pi^3 V/V_0, \quad (10)$$

provided that each  $\Delta Y_i > \Delta' Y_i$ :  $V$  denotes the irradiated crystal volume and  $V_0$  the volume of the elementary cell.

In order to introduce integral (10) into the integration of (6), a transformation of variables is effected by substituting the parameters  $Y_1, Y_2$  and  $Y_3$  for three of the original eight integration variables;

$$E_r = \int dx_4 \dots \int dx_8 \int dY_1 \int dY_2 \int dY_3 j_e i_0(k) F^2 G^2 U \times \frac{\partial(x_1, x_2, x_3)}{\partial(Y_1, Y_2, Y_3)}. \quad (11)$$

The three substituted variables, denoted here by  $x_1, x_2, x_3$ , but not further specified so far, will henceforth be called 'inner variables', whilst the remaining five will be referred to as 'outer variables'.

The essential step in deriving the equations of the integrated reflected energy for different experimental situations is the proper selection of the appropriate inner variables.

It is proposed now to formulate the general rules governing this selection; they are based on the following consideration.

Under certain circumstances it is possible to express the reflected energy  $E_r$  (equation 11) as the product of two (or more) integrals, one of the factors being the definite integral over  $G^2$  (equation 10);

$$E_r = \{ \int dx_4 \dots \int dx_8 [j_e i_0(k) F^2 U J] \} (\pi^3 V/V_0), \quad (12)$$

where  $J$  is the Jacobian

$$J = \frac{\partial(x_1, x_2, x_3)}{\partial(Y_1, Y_2, Y_3)}. \quad (13)$$

If additional functions are used for the calculation of  $E_r$  (such as absorption, thermal correction *etc.*), they will be included as additional factors of the integrand in (12).

The quantity  $E_r$  of integral (11) will represent an integrated reflected energy if, and only if, the definite integral (10) can indeed be factored out of the integral for the reflected energy (11), in the manner of (12).

The inner variables must be chosen so as to allow such a separation of the integral (11). This will be possible if the following three criteria are met:

First, the inner variables must be such as to result in a finite and non-vanishing Jacobian,  $J$  (equation 13).

Second, the interval of variation of each inner variable must be sufficiently large, so that each parameter  $Y_i$  ranges at least over the minimum range defined by (9a), and this for every attainable value of every outer variable.

Third, no function appearing in the equation of reflected energy (6), except the lattice factor  $G^2$ , should depend significantly on any inner variable within its interval of variation.

If the experimental set up is such that these three requirements cannot be met for any choice of three inner variables, then the measurement of  $E_r$  will not result in an integrated reflected energy.

### Detailed calculations

A reflection from a plane corresponding to the reciprocal vector  $\mathbf{b}_H$  will be considered. The Bragg angle for a wavenumber  $k_H$  (contained in the primary spectrum) is denoted by  $\theta_H$ . The directions of the primary beam range over values  $\mathbf{s}_0$ , which contain at least one direction  $\mathbf{s}_0^H$  fulfilling the exact Bragg condition, at least at a certain time if the crystal rotates, or at least for one crystallite if polycrystalline material or a mosaic crystal is considered.

A Cartesian reference system  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  is set up as follows:  $\mathbf{i}$  is parallel to  $\mathbf{b}_H$ , while  $\mathbf{j}$  and  $\mathbf{k}$  are chosen so that  $\mathbf{s}_0^H$  lies in the  $\mathbf{ij}$  plane.

The directions  $\mathbf{s}_0$  and  $\mathbf{s}_1$  pertinent to this reflection are expressed in this system by the angles  $\theta_0 = \theta_H + \delta\theta_0$  and  $\varepsilon_0$ , and  $\theta_1 = \theta_H + \delta\theta_1$  and  $\varepsilon_1$ , respectively:

$$\mathbf{s}_0 = (-\sin \theta_H - \cos \theta_H \delta\theta_0)\mathbf{i} + (\cos \theta_H - \sin \theta_H \delta\theta_0)\mathbf{j} + \varepsilon_0 \mathbf{k}, \quad (14)$$

$$\mathbf{s}_1 = (\sin \theta_H + \cos \theta_H \delta\theta_1)\mathbf{i} + (\cos \theta_H - \sin \theta_H \delta\theta_1)\mathbf{j} + \varepsilon_1 \mathbf{k}.$$

The angular displacements,  $\delta\theta_0$  etc., are small. The elementary translations of the reflecting crystallite  $\mathbf{a}_i$  are represented in the reference system by

$$\mathbf{a}_i = \alpha_{i1} \mathbf{i} + \alpha_{i2} \mathbf{j} + \alpha_{i3} \mathbf{k}. \quad (15)$$

The value of the determinant ( $\alpha$ ), composed of the elements  $\alpha_{ij}$  is  $V_0$ .

If the crystallite is tilted from the exact reflecting position by small angular amounts  $\tau, \nu, \mu$  about the  $\mathbf{i}, \mathbf{j}$  and  $\mathbf{k}$  axes respectively, this displacement is described by the matrix ( $\Delta$ )

$$(\Delta) = \begin{pmatrix} 1 & \mu & \nu \\ -\mu & 1 & \tau \\ -\nu & -\tau & 1 \end{pmatrix}. \quad (16)$$

Denoting its elements by  $\Delta_{ij}$ , the elementary translations of the misoriented crystallite are

$$\mathbf{a}'_i = \alpha'_{i1} \mathbf{i} + \alpha'_{i2} \mathbf{j} + \alpha'_{i3} \mathbf{k}, \quad (17)$$

with

$$\alpha'_{ij} = \sum_k \alpha_{ik} \Delta_{kj}.$$

If the crystal rotates with constant angular velocity  $\omega$  about an axis  $\mathbf{u}$ ;

$$\mathbf{u} = \sin \psi \cos \varphi \mathbf{i} + \sin \psi \sin \varphi \mathbf{j} + \cos \psi \mathbf{k}, \quad (18)$$

the elements  $\Delta_{ij}$  become time dependent:

$$\begin{aligned} \mu &= \omega t \cos \psi + \mu_0, \\ \nu &= \omega t \sin \psi \sin \varphi + \nu_0, \end{aligned} \quad (19)$$

$$\tau = \omega t \sin \psi \cos \varphi + \tau_0.$$

The vectors  $\mathbf{a}'_i$  are introduced into the equation for the reflected energy through the parameters  $Y_i$  of (7a), which become

$$Y_i = \mathbf{L} \cdot \mathbf{a}'_i \pi. \quad (20)$$

Defining the vector  $\mathbf{L}'$  by

$$\mathbf{L}'_i = \sum_k L_k \Delta_{ki}, \quad (20a)$$

where  $\mathbf{L}'_i$  and  $L_i$  are the components of  $\mathbf{L}'$  and  $\mathbf{L}$  respectively, it is immediately seen from (17) and (20) that

$$Y_i = \mathbf{L}' \cdot \mathbf{a}_i \pi. \quad (20b)$$

The explicit expressions for these components are obtained from (20a), (16), (17) and (14). With  $k = k_H + \delta k$ , and disregarding higher powers of the small quantities:

$$\begin{aligned} L'_1 &= 2k_H \sin \theta_H + k_H \cos \theta_H (\delta\theta_0 + \delta\theta_1) + 2 \sin \theta_H \delta k, \\ L'_2 &= k_H \sin \theta_H (\delta\theta_0 - \delta\theta_1 - 2\mu), \\ L'_3 &= k_H (\varepsilon_1 - \varepsilon_0 + 2 \sin \theta_H \nu). \end{aligned} \quad (21)$$

On substituting these components in (8), by means of (20b),  $G^2$  is expressed as an explicit function of the integration variables. These variables are:  $\delta\theta_0, \varepsilon_0, \delta\theta_1, \varepsilon_1$  [the angles  $\delta\theta_0 + \theta_H$  and  $\varepsilon_0$  determine the direction of the primary ray, the angles  $\delta\theta_1 + \theta_H$  and  $\varepsilon_1$  that of the reflected ray, see (14)]; the angles  $\mu$  and  $\nu$  describing the misorientation of the reflecting crystallite, (16); the wavenumber  $\delta k$  (with  $k = \delta k + k_H$ ) and the time  $t$ , which becomes a non-trivial variable if the crystal rotates, and enters calculations through (19). It should be noted that (21) and (14) assume that these angular variables as well as  $\delta k/k_H$  are small, less than about 0.1 rad.

Some of the functions of the first factor of (12) may also depend on these variables; the distribution  $U$  is a function of  $\mu$  and  $\nu$ . However, for a randomly oriented powder,  $U(\mu, \nu)$  is constant

$$U_{\text{powder}} = \frac{U_T}{4\pi} M_H, \quad (22)$$

where  $U_T$  is the number of irradiated crystallites and  $M_H$  the multiplicity of the reflecting plane.

For a mosaic crystal,  $U$  is more or less sharply peaked, depending on the mosaic spread  $\sigma$ . In this case we have

$$\int_{\Delta\mu} \int_{\Delta\nu} U(\mu, \nu) d\mu d\nu = U_T, \quad (22a)$$

provided that  $\Delta\mu, \Delta\nu > \sigma$ . For a single crystallite,  $U$  is a delta type function ( $\sigma = 0$ ).

The primary spectral intensity density is in general a function of  $\theta_0$ ,  $\varepsilon_0$  and  $k$ . For an isotropic X-ray source,  $i_0(k)$  is constant for any  $k$ , within the angular opening of the primary beam  $\Delta\theta_0$  and  $\Delta\varepsilon_0$ , and zero otherwise. Its  $k$  dependence is determined by whether mono- or polychromatic radiation is used.

Each of the eight integration variables ranges over an interval of 'attainable' values, *i.e.* values for which none of the functions of the first factor in (12) vanishes. They are determined, at least partly, by the experimental conditions.

The remaining functions in the first factor of (12), namely  $F^2$ ,  $J$  and  $j_e$  (which contains the polarization factor), will be assumed to be constant within the relevant intervals.

If  $E_r$  is to represent an integrated energy, the ranges of the parameters  $Y_i$  must exceed the interval  $\Delta'Y_i$  defined by (9a) (criterion II).

The corresponding intervals of the parameters  $L'_i$  of (21) are  $\beta'_i$  and are related to the intervals through (20b) and (20a),

$$\beta_i = \pi \sum \beta'_j A_{ji} a_i. \quad (23)$$

The magnitude of each  $\beta'_i$  is of the order  $1/(N_i V_0^{1/3})$ . For simplicity all three values  $\beta'_i$  will be assumed to be equal and denoted by  $\beta'$ .

### Specific derivations

A remark regarding notation: in the following discussion the pairs of the angular parameters  $\theta_0$ - $\theta_1$  and  $\varepsilon_0$ - $\varepsilon_1$  will often be distinguished according to the size of their respective intervals of variation. Of the two parameters  $\theta_0$  and  $\theta_1$ , the one ranging over the larger interval will be denoted by  $\theta_L$ , whilst the other will be denoted by  $\theta_S$ . Similarly,  $\varepsilon_L$  ( $\varepsilon_S$ ) denotes that of the two parameters  $\varepsilon_0$  and  $\varepsilon_1$  which varies over the larger (smaller) interval.

The equations for the integrated reflected energy for specific cases are derived from (12). For each case the triplet of inner variables must be selected, the conditions under which this selection holds be established and the appropriate Jacobian be calculated. The selection is based on the three criteria formulated above for calculating  $J$  of (13). The relation

$$J = J'/\pi^3 V_0, \quad (24)$$

with

$$J' = \frac{\partial(x_1, x_2, x_3)}{\partial(L'_1, L'_2, L'_3)},$$

will be used, which follows from (20b) and (13).  $J'$  (or  $1/J'$ ) is evaluated from (21) once the inner variables  $x_i$  are selected.

### I. Polychromatic radiation

This technique employs primary radiation of a wide spectral range, so that the wavenumber  $k$  fulfils the requirement of criterion (II). On the other hand the effective interval  $\Delta k$  will usually be so small that the primary spectral density  $i_0(k)$  may be regarded as constant within  $\Delta k$  (criterion III) and thus  $k$  may be selected as an inner variable.

In the preceding and following equations the spectral intensity with respect to wavenumber, and its angular density  $i_0(k)$  is used [(2) and (3)]. The angular density of the spectral intensity with respect to the wavelength  $i_0(\lambda)$  can be used equally well, by substituting  $|i_0(k) dk| = |i_0(\lambda) \lambda^2 d\lambda|$ . In the integrated equations the substitution is effected by replacing  $i_0(k)$  by  $i_0(\lambda) \lambda^2$ .

(A) *Single stationary crystal.* The crystal is assumed to be in reflecting orientation, *i.e.*  $\theta_0 = \theta_1$ , the primary radiation is assumed to contain the appropriate wavenumber  $k_H$ . We may set  $\mu = \nu = 0$ .

On inspecting (21) it is immediately seen that the Jacobian  $J'$  (24), (or its reciprocal) will be finite – see criterion (I) – if the three inner variables are any two of the variables  $k$ ,  $\theta_0$  and  $\theta_1$ , and either  $\varepsilon_0$  or  $\varepsilon_1$ .

Applying now the second criterion, the choice becomes unique. In order to ensure the proper interval for  $L'_3$  of (21), namely  $-\beta'/2 < L'_3 < +\beta'/2$ ,  $\varepsilon_L$  must be selected as an inner variable. Furthermore the interval  $\Delta\varepsilon_L$  must exceed the interval  $\Delta\varepsilon_S$  by at least  $\beta'/k_H$ .

Similarly, considering the required variation of  $L'_2$ , it is seen that  $\Delta\theta_L$  must be selected as the second internal variable; again  $\Delta\theta_L$  must exceed  $\Delta\theta_S$  by at least  $\beta'/k_H \sin \theta_H$  (equation 21).

The third inner variable is  $k$ . The proper interval for  $L'_1$  is assured if  $\Delta k$  exceeds  $\frac{1}{2} \cot(\Delta\theta_0 + \Delta\theta_1) k$  by more than  $\beta'$ , which may certainly be assumed to hold in all practical cases.

The three inner variables are therefore:  $k$ ,  $\theta_L$  and  $\varepsilon_L$ . Hence the Jacobian  $J'$  (equation 24) is evaluated from (21):

$$\frac{1}{J'} = \frac{\partial(L'_1, L'_2, L'_3)}{\partial(k, \theta_L, \varepsilon_L)} = 2k_H^2 \sin^2 \theta_H \quad (25)$$

and from (12),

$$E_r = j_e i_0(k) F^2 V (2V_0^2 k_H^2 \sin^2 \theta_H)^{-1} \Delta\theta_S \Delta\varepsilon_S \Delta t \quad (26)$$

( $\Delta t$  is the duration of the measurement), with the provisions  $\Delta\varepsilon_L > \Delta\varepsilon_S + \beta'/k_H$  and  $\Delta\theta_L > \Delta\theta_S + \beta'/k_H \sin \theta_H$ . If one or both of these provisions do not hold, some additional considerations are required. If, for example,  $\Delta\varepsilon_L$  does not exceed  $\Delta\varepsilon_S$  by  $\beta'/k_H$  but is itself larger than  $\beta'/k_H$ , then  $\Delta\varepsilon_S$  in (26) must be replaced by  $\Delta'\varepsilon_S$ , which will be intermediate between  $(\Delta\varepsilon_L - \beta'/k_H)$

and  $\Delta\epsilon_S$ . Clearly, the difference between  $\Delta\epsilon_S$  and  $\Delta'\epsilon_S$  will be negligible if  $\Delta\epsilon_L$  (and therefore, in this case, also  $\Delta\epsilon_S$ ) is considerably larger than  $\beta'/k_H$ .

Similar considerations will apply for the equations derived below.

(B) *Stationary mosaic crystal.* The orientation of the crystallites is described by the distribution function  $U(\mu, \nu)$ , (22a), which decreases to zero outside the interval  $|\Delta\mu| > \sigma/2$  and  $|\Delta\nu| > \sigma/2$ . As  $\sigma$  may be comparable with  $\beta'/k$ , neither  $\mu$  nor  $\nu$  can serve as an inner variable (criterion III). The inner variables are thus the same as for the case of the stationary single crystal, namely  $k$ ,  $\theta_L$  and  $\epsilon_L$ , provided, however, that  $\Delta\theta_L$  and  $\Delta\epsilon_L$  exceed the values of  $\Delta\theta_S$  and  $\Delta\epsilon_S$  by  $\sin\theta_H \gamma$  or  $\gamma$ , respectively, where the angular diffraction broadening  $\gamma$  is defined by

$$\gamma = \sigma + \beta'/k_H \sin\theta_H. \quad (27)$$

Thus  $J'$  and  $E_r$  are also in this case given by (25) and (26), respectively; the only difference is in the provisions regarding  $\Delta\epsilon_L$  and  $\Delta\theta_L$ .

(C) *Rotating crystal.* The crystal rotates about the axis  $\mathbf{u}$ , described by (18), and the time dependent expressions for  $\mu$  and  $\nu$  (19) are used in (21). If a mosaic crystal is under consideration, it must be remembered that the distribution function  $U$  is defined in a coordinate system rotating with the crystal. The number of appropriately oriented crystallites is therefore  $U(\mu_0, \nu_0) d\mu_0 d\nu_0$ .

The selection of the inner variables is again accomplished by the three criteria and (21), remembering that  $\mu$  and  $\nu$  are time dependent;  $k$  and  $t$  can be selected so

that they satisfy the three criteria. As to the third variable,  $\mu_0$  and  $\nu_0$  are disqualified because  $U$  depends on them (criterion III). Of the four remaining angular variables,  $\epsilon_L$  or  $\theta_L$  can be chosen only if either of the following two inequalities holds (criterion II).

Case (I):

$$(\Delta\epsilon_L - \Delta\epsilon_S)/\sin\theta_H > (\Delta\theta_1 + \Delta\theta_0) \sin\psi \sin\phi/\cos\psi + \gamma(1 + \sin\psi \sin\phi/\cos\psi) \quad (28)$$

or case (II):

$$\Delta\theta_L - \Delta\theta_S > (\Delta\epsilon_1 + \Delta\epsilon_0) \cos\psi/\sin\theta_H \sin\psi \sin\phi + \gamma(1 + \cos\psi/\sin\psi \sin\phi). \quad (29)$$

The inner variables are  $t$ ,  $k$  and  $\epsilon_L$  for case (I) and  $t$ ,  $k$  and  $\theta_L$  for case (II).

The Jacobian  $J'$  and integrated reflected energy  $E_r$  are now directly obtained from (21) and (12); the results are given in Table 1.

If both  $\cos\psi$  and  $\sin\phi$  vanish,  $t$  cannot be an inner variable. In this case the rotation axis is normal to the reflecting plane, and the geometry is that of a stationary crystal.

(D) *Powder method.* For a randomly oriented stationary powder, the distribution function  $U(\mu, \nu)$  is constant, (22), and thus  $\mu$  and  $\beta$  can be selected as inner variables without violating criterion (III). The third inner variable is again  $k$ . It is directly seen (equation 21) that this set satisfies the three criteria for any value of the other variables. The resulting expressions for  $J'$  and  $E_r$  are shown in Table 1.

Table 1. *Integrated reflected energy  $E_r$  for various methods*

$$E_r = (j_e F^2 V/V_0^2) J' D.$$

Method	Inner variables	$(J')^{-1}$	$D$	Provisions
Polychromatic radiation				
(I-1) Stationary	$k, \theta_L, \epsilon_L$	$2k_H^2 \sin^2 \theta_H$	$\Delta\theta_S \Delta\epsilon_S \Delta t i_0(k)$	$\Delta\theta_L > \Delta\theta_S + \gamma; \Delta\epsilon_L > \Delta\epsilon_S + \gamma.$
(I-2) Rotating	$t, k, \epsilon_L$	$4k_H^2 \sin^2 \theta_H \cos\psi\omega$	$\Delta\epsilon_S \Delta\theta_0 \Delta\theta_1 i_0(k)$	$(\Delta\epsilon_L - \Delta\epsilon_S)/\sin\theta_H > (\Delta\theta_0 + \Delta\theta_1) \sin\psi \sin\phi/\cos\psi + \gamma(1 + \sin\psi \sin\phi/\cos\psi).$
(I-3) Rotating	$t, k, \theta_L$	$4k_H^2 \sin^3 \theta_H \sin\psi \sin\phi\omega$	$\Delta\theta_S \Delta\epsilon_0 \Delta\epsilon_1 i_0(k)$	$\Delta\theta_L - \Delta\theta_S > (\Delta\epsilon_0 + \Delta\epsilon_1) \cos\psi/\sin\theta_H \sin\psi \sin\phi + \gamma(1 + \cos\psi/\sin\psi \sin\phi).$
(I-4) Powder	$k, \mu, \nu$	$8k_H^2 \sin^3 \theta_H$	$\Delta\theta_0 \Delta\theta_1 \Delta\epsilon_0 \Delta\epsilon_1 \Delta t M_H i_0(k)/4\pi$	None
Monochromatic radiation				
(I-5) Stationary	$\theta_0, \theta_1, \epsilon_L$	$k_H^3 \sin 2\theta_H$	$\Delta\epsilon_S \Delta t i_0^*$	$\Delta\theta_0 > \gamma; \Delta\theta_1 > \gamma; \Delta\epsilon_L > \Delta\epsilon_S + \gamma.$
(I-6) Rotating	$t, \theta_L, \epsilon_L$	$k_H^3 \sin 2\theta_H \cos\psi\omega$	$\Delta\theta_S \Delta\epsilon_S t_0^*$	$(\Delta\epsilon_L - \Delta\epsilon_S)/\sin\theta_H > (2\Delta\theta_S + \beta'/2k_H \cos\theta_H) \sin\psi \sin\phi/\cos\psi + \gamma(1 + \sin\psi \sin\phi/\cos\psi).$
(I-7) Rotating	$t, \theta_0, \theta_1$	$2k_H^3 \sin 2\theta_H \sin\theta_H \sin\psi \sin\phi\omega$	$\Delta\epsilon_0 \Delta\epsilon_1 t_0^*$	$2\Delta\theta_S > (\Delta\epsilon_0 + \Delta\epsilon_1) \cos\psi/\sin\psi \sin\phi \sin\theta_H + \gamma(1 + \cos\psi/\sin\psi \sin\phi) + \beta'/2k_H \cos\theta_H.$
(I-8) Powder	$\theta_L, \mu, \nu$	$2k_H^3 \sin 2\theta_H \sin\theta_H$	$\Delta\theta_S \Delta\epsilon_0 \Delta\epsilon_1 \Delta t M_H t_0^*/4\pi$	$\Delta\theta_L > \Delta\theta_S + \gamma.$

II. Monochromatic radiation

If the primary radiation is monochromatic, the spectral intensity is sharply peaked about  $k_H$ , and therefore (criterion III) the wavenumber  $k$  cannot serve as an inner variable. The range of  $\Delta k/k$  values is, however, small and we may assume that

$$\Delta k \sin \theta_H \ll \beta'$$

[otherwise the  $\Delta k/k$  must be included in the angle  $\gamma$  of (27)]. Denoting the angular density of the primary (monochromatic) intensity by  $i_0^*$ , we have:

$$i_0^* = \int_{\Delta k} i_0(k) dk. \tag{30}$$

With this property, the selection of inner variables, evaluation of  $J'$ , (24) through (21), and of  $E_r$ , (12), proceed in a manner analogous to the previous considerations. The results for the various techniques are collected in Table 1.

Discussion

Equations for the integrated reflected energy (or power) have been customarily expressed in terms of the incident intensity  $I_0 = i_0^* \Delta\theta_0 \Delta\epsilon_0$  or the incident spectral intensity  $I'(k) = i_0(k) \Delta\theta_0 \Delta\epsilon_0$  [or  $I'(\lambda) = i_0(\lambda) \Delta\theta_0 \Delta\epsilon_0$ ]. This presupposes that the angular opening of the detecting device is always sufficiently large to collect the entire reflected power. However, this is not necessarily a condition for obtaining the integrated reflected energy (see column 'provisions' in Table 1). Furthermore, whilst a large detecting aperture is certainly present if photographic methods are employed, this may not be so if counters and associated slit systems are used. Finally, the absolute reflected energy depends often on the size of the detecting aperture. For these reasons it seems to be better justified to express the integrated reflected energy in

terms of the angular density of the primary intensity or of the primary spectral intensity, in conjunction with the appropriate angular openings, i.e. in terms of the factor  $D$  of Table 1.

The Lorentz factor is defined (Laue, 1960, chapter 17) as that factor which results on introducing the integration

$$\int G^2 dV_r,$$

into the intensity equation ( $dV_r$  is the element of reciprocal space). Hence the Lorentz factor is, in the notation of this paper, equal to  $J'V/V_0^2$ ,  $J'\omega V/V_0^2$  or  $J'V/4\pi V_0^2$  for stationary or rotating crystal or (randomly oriented) powder methods respectively (the expressions for  $J'$  are given in Table 1). The definition implies that the integral of  $G^2$  over the reciprocal volume can indeed be factored out, in the manner of (12), which in turn can be done provided that criterion (III) holds. It must be noted, however, that the equations are valid only if, in addition, the experimental set up is such that the corresponding provisions – last column of Table 1 – hold true.

To facilitate comparison with equations appearing in the literature, Table 2 shows equations (I-1) to (I-8) expressed in the 'conventional' way, with the primary intensity  $I_0 (=i_0^* \Delta\theta_0 \Delta\epsilon_0)$  for monochromatic radiation or the primary spectral intensity  $I'(k) [=i_0(k) \Delta\theta_0 \Delta\epsilon_0]$  for polychromatic radiation, and by assuming the angular opening of the detecting device to be sufficiently large. The Lorentz factor contained in each equation is placed in square brackets. For the stationary methods, equations are written for the reflected power  $P_r = E_r/\Delta t$ . The polarization factor is contained in the factor  $j_e$  [see (1)]. The last column of Table 2 shows the provisions required for the corresponding equation to hold; these provisions are in addition to the condition of having large detector aperture.

It is seen that the equations for the Laue, monochromatic rotation and monochromatic powder methods [equations (II-5), (II-6) and (II-8)] are

Table 2. Integrated reflected energy  $E_r$  or integrated reflected power  $P_r$  in conventional notation

Method		Provisions (additional to large detecting aperture)
Polychromatic radiation		
(II-1) Stationary	$P_r = j_e F^2 I'(k) [V/2k_H^2 \sin^2 \theta_H V_0^2]$	None.
(II-2) Rotating	$E_r = j_e F^2 I'(k) \Delta\theta_1 / \omega [V/4k_H^2 \sin^2 \theta_H \cos \psi V_0^2]$	Same as for (I-2), Table 1.
(II-3) Rotating	$E_r = j_e F^2 I'(k) \Delta\epsilon_1 / \omega [V/4k_H^2 \sin^3 \theta_H \sin \psi \sin \phi V_0^2]$	Same as for (I-3), Table 1.
(II-4) Powder	$P_r = j_e F^2 I'(k) M_H \Delta\theta_1 \Delta\epsilon_1 [V/32\pi k_H^2 \sin^3 \theta_H V_0^2]$	None.
Monochromatic radiation		
(II-5) Stationary	$P_r = j_e F^2 I_0 / \Delta\theta_0 [V/k_H^3 \sin 2\theta_H V_0^2]$	$\Delta\theta_0 > \gamma$ .
(II-6) Rotating	$E_r = j_e F^2 I_0 / \omega [V/k_H^3 \sin 2\theta_H \cos \psi V_0^2]$	None.
(II-7) Rotating	Not applicable if detecting aperture is large	
(II-8) Powder	$P_r = j_e F^2 I_0 M_H \Delta\epsilon_1 [V/8\pi k_H^3 \sin 2\theta_H \sin \theta_H V_0^2]$	None.

identical to the customary expressions *e.g.* as given by Laue [1960, chapter 17, equations (18.19), (18.33)\* and (18.30)].

Equations for integrated intensities for polychromatic rotation and powder methods have also been published (Buras & Gerward, 1975). These expressions do not, however, take into account the dependence on the aperture of the detecting device; it is for this reason that the Lorentz factors included in these equations differ from those of Table 2 – (II-2) and (II-4) – by a constant factor.

For the case of a stationary crystal with monochromatic radiation, (I-5), no expression seems to have been derived so far. This method is indeed not normally employed for intensity measurements; however, instances may occur where this equation is applicable, *e.g.* for intensity evaluation of the kinematic image in topographs obtained with monochromatic radiation.

Likewise (I-3) and (I-7) of Table 1 have no counterpart in existing literature. Although the relevant geometry is hardly encountered, the existence of this possibility should not be ignored.

With polychromatic radiation, different expressions for the Lorentz factor are obtained for a given method, depending on whether primary spectral intensity is expressed with respect to  $k$  or with respect to  $\lambda$ . (Indeed spectral intensity may be defined with respect to other parameters which are functions of  $k$ .) The appropriate parameter should therefore be denoted, in these cases, in conjunction with the Lorentz factor.

The procedure for deriving the integrated energy equation proposed in this paper can be adapted to other instances, such as for perfect crystals, one- or two-dimensional crystals, multiple reflections *etc.*, once the appropriate lattice factor or its equivalent has been derived.

Any such lattice factor must be characterized by the fact that it is non-vanishing in a limited region, the region of reflection. The number of coordinates required to specify a point in this region will be equal to the number of inner variables required for the later integration. After writing the initial equation for the reflected energy – in analogy to (6) – the range of attainable values of all the variables appearing there are established; these ranges are determined by the experimental set up. The next step is the selection of the inner variables in accordance with the three criteria formulated above [following (12)]. These criteria hold quite generally, and only if the required number of inner variables can be found without violating them will the experimental measurement result in an integrated

energy. Formally this quantity will be given by an equation analogous to (12), obtained by factoring out the integrated lattice factor and introducing the corresponding Jacobian. Integrating this equation over the outer variables will give the explicit expression for the integrated energy.

### List of symbols

$\mathbf{a}_i, \mathbf{a}'_i$	Elementary lattice translations of crystal in or near reflecting orientation.
$\mathbf{b}_H$	Reciprocal vector of reflecting plane.
$E_r$	Reflected X-ray energy.
$F$	Absolute value of structure factor.
$G^2$	Lattice factor.
$I_0, I$	Primary and scattered intensity.
$I'(k), I'(\lambda)$	Spectral intensity with respect to $k, \lambda$ .
$i_0(k)$	Spectral intensity with respect to $k$ per unit solid angle.
$i_0^*$	Intensity per unit solid angle.
$J_e$	The classical electron radius times the polarization factor.
$J, J'$	Jacobian [(13) and (14)].
$k$	Wavenumber.
$\mathbf{L}, L_i$	Diffraction vector and its components (equation 7).
$\mathbf{L}', L'_i$	Modified diffraction vector and components ( $\mathbf{L}' \cdot \mathbf{a}_i = \mathbf{L} \cdot \mathbf{a}'_i$ ).
$M_H$	Multiplicity factor for powder method.
$N_i$	Number of unit cells in direction of $\mathbf{a}_i$ .
$P$	Polarization factor.
$P_r$	Reflected X-ray power.
$\mathbf{s}_0, \mathbf{s}_1$	Unit vectors in directions of primary and scattered beam.
$\mathbf{u}$	Axis of crystal rotation.
$U(\mu, \nu)$	Orientation distribution function of crystallites.
$V$	Irradiated crystalline volume.
$V_0$	Volume of unit cell.
$x_i$	( $i = 1$ to 8) Notation for integration variables.
$x_1, x_2, x_3$	Notation for inner variables.
$Y_j$	$= \mathbf{L} \cdot \mathbf{a}'_j \pi$ .
$\alpha_{ij}, \alpha'_{ij}$	( $j = 1, 2, 3$ ). Components of $\mathbf{a}_i, \mathbf{a}'_i$ .
$\beta_i$	Range of values $Y_j$ resulting in non-vanishing $G^2$ .
$\beta'_i, \beta'$	Range of values $L'_i$ resulting in non-vanishing $G^2$ (equation 23).
$\gamma$	Angular diffraction broadening (equation 27).
$(\Delta), \Delta_{ij}$	Matrix, components of matrix describing misorientation of crystallites (equation 17).
$\epsilon_0, \theta_0, \epsilon_1, \theta_1$	Angles describing directions of $\mathbf{s}_0$ and $\mathbf{s}_1$ .
$\Delta\epsilon_0, \Delta\epsilon_1$	Angular opening of primary beam and detecting device in the direction normal to the plane containing $\mathbf{s}_0$ and $\mathbf{s}_1$ .

\* Equation (18.33) of Laue (1960, chapter 17) relates to rotation about an axis normal to the primary beam. In this equation the term  $\cos \chi$  appears instead of  $\sin 2\theta_H \cos \psi$  of (II-6), where  $\chi$  is the angle between  $\mathbf{s}_1$  and the normal to both  $\mathbf{s}_0$  and  $\mathbf{u}$ . Hence  $\cos \chi = \mathbf{s}_1 \cdot (\mathbf{s}_0 \times \mathbf{u})$ , which in turn can be seen, by means of (14) and (18), to be equal to  $\sin 2\theta_H \cos \psi$ .

$\Delta\varepsilon_L(\Delta\varepsilon_S)$	The larger (the smaller) of $\Delta\varepsilon_0$ and $\Delta\varepsilon_1$ .	$\varphi, \psi$	Angles defining direction of the axis of rotation (equation 18).
$\varepsilon_L(\varepsilon_S)$	The angle $\varepsilon_0$ or $\varepsilon_1$ associated with $\Delta\varepsilon_L(\Delta\varepsilon_S)$ .	$\omega$	Angular velocity of rotating crystal.
$\theta_H$	Bragg angle corresponding to $\mathbf{b}_H$ and wavenumber $k_H$ .	$\Omega_0, \Omega_1$	Solid angular opening of primary beam and detecting device ( $\Omega_0 = \Delta\theta_0 \Delta\varepsilon_0$ , $\Omega_1 = \Delta\theta_1 \Delta\varepsilon_1$ ).
$\Delta\theta_0 \Delta\theta_1$	Angular opening of primary beam and detecting device in the plane containing $\mathbf{s}_0$ and $\mathbf{s}_1$ .		
$\Delta\theta_L(\Delta\theta_S)$	The larger (the smaller) of $\Delta\theta_0$ and $\Delta\theta_1$ .		
$\theta_L(\theta_S)$	The angle $\theta_0$ or $\theta_1$ associated with $\Delta\theta_L(\Delta\theta_S)$ .		
$\mu, \nu, \tau$	Angles defining misorientation of crystal-lite.		
$\sigma$	Mosaic spread.		

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## 'Polar Flattening': Non-Spherical Effective Shapes of Atoms in Crystals

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### Abstract

An examination of the nearest non-bonded interatomic distances found in crystals shows that where the two atoms are each covalently bound to only one other atom they exhibit non-spherical effective shapes. Such atoms behave as if flattened at their poles. Despite the large number of crystal structures now known in detail, various factors can militate against discovering effective atomic shapes. Possible causes of flattening are briefly discussed.

### Introduction

In his review of van der Waals radii, Bondi (1964, p. 442) states '... all atoms have been treated as spheres and sphere segments, although it is well known that many are more nearly pear-shaped'. Bondi cites no references to this 'well known' fact and it is not absolutely clear what is implied by 'pear-shaped'. However, we believe there is now sufficient structural evidence, albeit not as extensive as we might hope, indicating that, for singly bound atoms at least, effective atomic shapes in crystals do deviate from spherical. In their more recent reviews of van der Waals radii, Zefirov & Zorkii (1976) have found considerable variabilities for certain atoms and this might in some cases be due to non-sphericity.

Currently, much effort is being devoted to formulating atom-atom potential energies which, it is hoped, will explain the packing and non-bonded interatomic distances found in crystals. Such an approach is clearly more fundamental, based as it is on the potential energy approximation to the free energy, instead of on the geometric concept of hard spheres.

Although the potential energy between two molecules must have a complicated and specific dependence on the six molecule orientation defining variables, the atom-atom approximation has led to sufficient success for it to be regarded as a useful empirical approximation to this energy. In virtually all cases the atom-atom potential is regarded as being spherical about the nucleus, *i.e.* it has the same functional dependence on distance irrespective of the mutual orientation of the molecules. However, the potential energy between two non-bonded atoms in different molecules can be regarded as composed of an attractive (dispersive) and a repulsive term. To regard both as spherical about the nuclei is to ignore the non-spherically disposed electrons. Thus it is not *whether* atoms in molecules behave as spheres in their non-bonding interactions with other atoms but to what *extent* they are non-spherical.\*

\* Bondi and others use 'anisometric' which should probably be avoided in view of 'isometric' being commonly used for the cubic system. 'Aspherical' is a possible alternative but is usually restricted to slight deviations from spherical.