

## The (*hkl*) Dependence of Diffraction-Line Broadening Caused by Strain and Size for all Laue Groups in Rietveld Refinement

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### Abstract

Models are presented which are compatible with the Rietveld method for the anisotropic broadening of the diffracted peaks produced by crystallite size and microstrain. The models, derived from general crystallographic considerations, are different for different Laue groups.

### 1. Introduction

In the actual state-of-the-art Rietveld refinement method, two approaches are used for dealing with the anisotropic broadening produced by the strain and crystallite size. The first approach (see Delhez *et al.*, 1993) has two stages. In the first stage, pattern decomposition is used to obtain line shape parameters for individual peaks. The dependence of these parameters on Miller indices *h*, *k*, *l* is then modelled using empirical expressions. These models are used in the second stage, the Rietveld refinement process itself. Additionally, in the first stage, it is easy to obtain qualitative and quantitative information about the crystal imperfections, by using the procedures described by de Keijser *et al.* (1982) and (1983). Hence, with this approach, Langford *et al.* (1993) found that anisotropic broadening of the diffraction peaks on zinc oxide is mainly caused by stacking faults.

In the second approach, analytical expressions in *h*, *k*, *l* for the line shape parameters are used directly in the refinement process. Many authors, like Lartigue *et al.* (1987) or David & Jorgensen (1993), use positive-definite quadratic forms for both average crystallite radius and strain dispersion. As these are macroscopic quantities, the quadratic forms must be invariant to the Laue-group operations (Friedel law is valid). This condition reduces the number of independent parameters from six to one for cubic symmetry, two for hexagonal, trigonal and tetragonal, three for orthorhombic and four for monoclinic. The ellipsoids represented by the quadratic forms become spheres in the cubic symmetry and rotation ellipsoids for hexagonal, trigonal and tetragonal, with the rotation axis along the *n*-fold axis. Hence, this

representation excludes anisotropy in a plane normal to the *n*-fold axis for hexagonal, trigonal and tetragonal symmetry, and entirely for cubic. These restrictions are not physically justified, being only the consequence of an inadequate model for the strain-size anisotropy. In fact, in the Rietveld refinement of tetragonal zirconium oxide and zirconium cerium oxide, Lutterotti & Scardi (1990) found significant values for the coefficients of the terms *hk* and *l(h + k)*, their presence in the quadratic form violating the condition of invariance. The model, used empirically, could sometimes give a good fit of the diffraction pattern, but in this case the parameters have no physical meaning.

We can also explain intuitively the inadequacy of this model. Let us suppose that the average crystallite is reasonably approximated by an ellipsoid. Supposing no strain, the width of a given diffraction peak on this crystallite is given by the radius of the ellipsoid in the direction of the reciprocal-lattice vector **H**. As the sample is a polycrystal, all crystallites obtained from this crystallite by applying the operations of the Laue group give diffraction peaks in the same place. However, these peaks have different widths, as the ellipsoid radii along the equivalents of **H** are different. The width of the resulting peak is given by the mean value of these radii. We can imagine, in place of this aggregate of crystallites related by symmetry, a unique crystallite giving the same diffraction peak. Let us call this 'the composite crystallite'. Obviously, the surface of the composite crystallite is invariant to the operations of the Laue group and cannot be represented by an ellipsoid, even if the individual crystallites are ellipsoids.

The quadratic form in *h*, *k*, *l* is also incorrect for the strain dispersion. Thompson *et al.* (1987) have used, for this quantity, a model based on a quartic instead of a quadratic form. As will be shown below, such a model is correct; however, their formula for hexagonal symmetry is erroneous. It contains four refinable parameters, in reality only three, and is not invariant to the Laue-group operations. In the present paper, models for the dispersion of strain and radius of average composite crystallite are derived using this invariance condition.

## 2. The strain and size peak profile

Let us denote  $\mathbf{h}$  the unit vector of  $\mathbf{H}$ ,  $\varepsilon_{hh} = -\Delta H/H$  the relative change of the corresponding interplanar distance produced by stress and  $R_h$  the crystallite radius along  $\mathbf{h}$ . All polycrystal averages (over the orientations of crystallites, dimension distribution and the mean over the equivalents of  $\mathbf{H}$ ) are denoted by  $\langle \cdot \rangle$ . The quantity  $\langle \varepsilon_{hh} \rangle$  represents the  $(h, k, l)$ -dependent macroscopic strain, producing a peak shift. Ferrari & Lutteroti (1994) have discussed its determination from X-ray diffraction, simultaneously with the texture. In this paper, we hypothesize that there is no macroscopic strain in the sample; the dispersion of  $\Delta H/H$  will then be  $\langle \varepsilon_{hh}^2 \rangle$ . Denoting by  $\mathbf{Q}$  the wavevector transfer, the normalized size-strain peak profile in the reciprocal space is given by the following Voigt function:

$$V_H(Q) = \int d(\Delta H) L_H(Q + 2\pi\Delta H) G_H(\Delta H) \quad (1)$$

$$L_H(Q) = (3\langle R_h \rangle / 4\pi) [1 + 9\langle R_h \rangle^2 (Q - 2\pi H)^2 / 16]^{-1} \quad (2)$$

$$G_H(\Delta H) = (2\pi \langle \varepsilon_{hh}^2 \rangle)^{-1/2} H^{-1} \exp[-(\Delta H)^2 / (2H^2 \langle \varepsilon_{hh}^2 \rangle)] \quad (3)$$

The quantity  $\langle R_h \rangle$  is the radius of the average composite crystallite defined in §1. The factor  $3/4$  in  $L_H$  ensures the conservation of integral breadth when the exact expression for a sphere is approximated by a Lorentzian function. Both  $\langle R_h \rangle$  and  $\langle \varepsilon_{hh}^2 \rangle$  are invariant to the rotations of the Laue group. The formulae (1), (2) and (3) can be transposed in both constant-wavelength and energy-dispersive diffraction methods, by using the Bragg law and the definition of  $Q$ :  $H = 2 \sin \theta_H / \lambda_H$ ,  $Q = 4\pi \sin \theta / \lambda$ . Details are given in the Appendix.

## 3. Dependence of the strain on $(h, k, l)$

In this section we derive the dependence of  $\langle \varepsilon_{hh}^2 \rangle$  on  $h, k, l$ . Firstly, we will find the strain as a function of  $h, k, l$  in a given monocrystallite. Denoting by  $\mathbf{h}'$  the vector obtained by strain from the unit vector  $\mathbf{h}$ , and taking into account that  $|\mathbf{h}' - \mathbf{h}| \ll 1$ , we can write  $\varepsilon_{hh} = |\mathbf{h}'| - 1 \simeq \mathbf{h}(\mathbf{h}' - \mathbf{h})$ . On the other hand, if we define an orthogonal coordinate system  $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$  in the unstrained crystallite, we can write  $\mathbf{h} = \sum_i A_i \mathbf{x}_i$  and also  $\mathbf{h}' = \sum_i A_i \mathbf{x}'_i$ . The system  $(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3)$  is obtained from  $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$  using the strain tensor  $e_{ij} = \partial u_j / \partial x_i$  ( $\mathbf{u}$  is the deformation vector):  $\mathbf{x}'_i = \sum_j (\delta_{ij} + e_{ij}) \mathbf{x}_j$ . If we choose  $\mathbf{x}_1 = \mathbf{a}/a$ ,  $\mathbf{x}_3 = \mathbf{c}^*/c^*$  and  $\mathbf{x}_2 = \mathbf{x}_3 \times \mathbf{x}_1$ , then the direction cosines of  $\mathbf{h}$  become  $A_i = (Ha)^{-1} \sum_j B_{ij} h_j$ . Here  $(h_1, h_2, h_3)$  is an alternative notation for  $(h, k, l)$  and the matrix  $\mathbf{B}$  is as follows:  $B_{11} = 1$ ,  $B_{21} = -\cot \gamma$ ,  $B_{22} = a/(b \sin \gamma)$ ,  $B_{31} = aa^* \cos \beta^*$ ,  $B_{32} = ab^* \cos \alpha^*$ ,  $B_{33} = ac^*$ ,  $B_{ij} = 0$  for  $j > i$ . The standard notations are

used for the unit-cell parameters. Finally, by setting  $\varepsilon_{mn} = \frac{1}{2} \sum_{i=m}^3 \sum_{j=n}^3 (e_{ij} + e_{ji}) B_{im} B_{jn}$ , one obtains

$$\varepsilon_{hh} = (\varepsilon_{11} h^2 + \varepsilon_{22} k^2 + \varepsilon_{33} l^2 + 2\varepsilon_{12} hk + 2\varepsilon_{13} hl + 2\varepsilon_{23} kl) \times (E_H^2)^{-1}, \quad (4)$$

where

$$E_H = aH. \quad (5)$$

This formula is identical to (A1) from Thompson *et al.* (1987) for cubic symmetry only.

The next step consists in squaring (4) and averaging for randomly oriented crystallites. For the quantity  $\langle \varepsilon_{hh}^2 \rangle E_H^4$  we obtain a quartic form in  $h, k, l$  with 15 terms, given below by formula (6). The coefficients  $E_1, \dots, E_{15}$  are linear combinations of terms like  $\langle \varepsilon_{ij} \varepsilon_{mn} \rangle$ . If  $(h, k, l)$  are changed into  $-(h, k, l)$ , formula (6) remains unchanged; this then gives just the anisotropic strain model for the triclinic group  $\bar{1}$ . For other groups we must set the invariance conditions for all  $n$ -fold axes. In the group  $6/m$ , for example,  $(h, k, l) \rightarrow (-k, h+k, l)$  by the sixfold axis. The invariance condition of  $\langle \varepsilon_{hh}^2 \rangle E_H^4$  to this transformation gives the following relations for the coefficients:  $E_2 = E_1$ ,  $E_4 = 3E_1/2$ ,  $E_5 = E_6 = 2E_{15}$ ,  $E_7 = E_9 = E_1/2$  and  $E_8 = E_{10} = E_{11} = E_{12} = E_{13} = E_{14} = 0$ . In the group  $6/mmm$ , the twofold axis gives no supplementary condition. Then, redefining the coefficients, we obtain a model with three refinable parameters for all hexagonal groups. The anisotropic strain models for all Laue groups are listed below in formulae (6) to (17). The character  $R$  after the symbol of the trigonal groups refers to the rhombohedral setting. For the monoclinic group the model is given only for the first setting; for the second setting  $k$  and  $l$  must be permuted:

The  $(h, k, l)$ -dependent strain models for all Laue groups are as follows:

$$\begin{aligned} \bar{1} \\ \langle \varepsilon_{hh}^2 \rangle E_H^4 = & E_1 h^4 + E_2 k^4 + E_3 l^4 + 2E_4 h^2 k^2 + 2E_5 k^2 l^2 \\ & + 2E_6 h^2 l^2 + 4E_7 h^3 k + 4E_8 h^3 l + 4E_9 k^3 h \\ & + 4E_{10} k^3 l + 4E_{11} l^3 h + 4E_{12} l^3 k + 4E_{13} h^2 kl \\ & + 4E_{14} k^2 hl + 4E_{15} l^2 hk \end{aligned} \quad (6)$$

$$\begin{aligned} 2/m \\ \langle \varepsilon_{hh}^2 \rangle E_H^4 = & E_1 h^4 + E_2 k^4 + E_3 l^4 + 2E_4 h^2 k^2 + 2E_5 k^2 l^2 \\ & + 2E_6 h^2 l^2 + 4E_7 h^3 k + 4E_8 h k^3 + 4E_9 h k l^2 \end{aligned} \quad (7)$$

$$\begin{aligned} 2/mmm \\ \langle \varepsilon_{hh}^2 \rangle E_H^4 = & E_1 h^4 + E_2 k^4 + E_3 l^4 + 2E_4 h^2 k^2 + 2E_5 k^2 l^2 \\ & + 2E_6 h^2 l^2 \end{aligned} \quad (8)$$

$$4/m$$

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^4 + k^4) + E_2l^4 + 2E_3h^2k^2 + 2E_4l^2(h^2 + k^2) + 4E_5hk(h^2 - k^2) \quad (9)$$

4/*mmm*

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^4 + k^4) + E_2l^4 + 2E_3h^2k^2 + 2E_4l^2(h^2 + k^2) \quad (10)$$

$\bar{3}$

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^2 + k^2 + hk)^2 + 2E_2l^2(h^2 + k^2 + hk) + E_3l^4 + (4/3)E_4l(h^3 - k^3 + 3h^2k) + (4/3)E_5l(-h^3 + k^3 + 3hk^2) \quad (11)$$

$\bar{3}R$

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^4 + k^4 + l^4) + 2E_2(h^2k^2 + k^2l^2 + l^2h^2) + 4E_3hkl(h + k + l) + 4E_4(h^3k + k^3l + l^3h) + 4E_5(hk^3 + kl^3 + lh^3) \quad (12)$$

$\bar{3}m1$

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^2 + k^2 + hk)^2 + 2E_2l^2(h^2 + k^2 + hk) + E_3l^4 + (4/3)E_4l(2h^3 - 2k^3 + 3h^2k - 3hk^2) \quad (13)$$

$\bar{3}m1R$

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^4 + k^4 + l^4) + 2E_2(h^2k^2 + k^2l^2 + l^2h^2) + 4E_3hkl(h + k + l) + 4E_4[hk(h^2 + k^2) + kl(k^2 + l^2) + lh(l^2 + h^2)] \quad (14)$$

$\bar{3}1m$

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^2 + k^2 + hk)^2 + 2E_2l^2(h^2 + k^2 + hk) + E_3l^4 + (4/3)E_4l(3h^2k + 3hk^2) \quad (15)$$

Hexagonal

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^2 + k^2 + hk)^2 + 2E_2l^2(h^2 + k^2 + hk) + E_3l^4 \quad (16)$$

Cubic

$$\langle \varepsilon_{hh}^2 \rangle E_H^4 = E_1(h^4 + k^4 + l^4) + 2E_2(h^2k^2 + k^2l^2 + l^2h^2). \quad (17)$$

For the isotropic case, the right side of equations (6) to (17) must be proportional to  $E_H^4$ . In this case, we must correlate some parameters and set the rest to zero. For example, in group  $\bar{3}$  we must set  $E_1 = (16/9)E_0$ ,  $E_2 = (4a^2/3c^2)E_0$ ,  $E_3 = (a^4/c^4)E_0$  and  $E_4 = E_5 = 0$ ,  $E_0$  being the unique refinable parameter. In a computer

program, it is advisable to write (6) to (17) with the scaling factors included. In group  $\bar{3}$  this means  $(16/9)E_1$  instead of  $E_1$ , etc., then for the isotropic case we have, simply,  $E_1 = E_2 = E_3 = E_0$ ,  $E_4 = E_5 = 0$ . These could also be the starting values of parameters for the anisotropic refinement. In this paper we preferred the actual form of (6) to (17) for space-saving and aesthetic reasons.

#### 4. The direction-dependent crystallite size

In principle, starting from explicit models for the crystallite surface and for the crystallite dimension distribution, it is possible to find expressions for the radius of the average composite crystallite. In practice, however, the analytical calculation is possible only for a very small number of cases (sphere, for example, is an uninteresting case). Even if analytical calculations were possible, the result would be of limited validity, being strongly dependent on the chosen models. There is a very large variety of crystallite surface models and dimension distributions, and it is impossible to find a generally valid, closed analytical expression for  $\langle R_h \rangle$ . However,  $\langle R_h \rangle$  can always be developed in a convergent series (an open expression) of symmetrized spherical harmonics, the coefficients being refinable parameters. The symmetrized spherical harmonics are the functions  $P_{2l}^m(x) \cos m\varphi$  or  $P_{2l}^m(x) \sin m\varphi$ , or, for the cubic groups, certain linear combinations of the first type. The numbers denoted by  $l, m$  fulfil some selection rules summarized in the paper by Popa (1992). We have denoted by  $P_l^m(x)$  of argument  $x = \cos \Phi$  the normalized Legendre functions

$$P_l^m(x) = [(l+m)!/(l-m)!]^{1/2} (l+1/2)^{1/2} (-1)^{l-m} (2^l l!)^{-1} \times (1-x^2)^{-m/2} d^l \cdot m (1-x^2)^l / dx^{l-m} \quad (18)$$

[In Popa (1992) the factor  $(l+1/2)^{1/2}$  was omitted erroneously]. The angles  $\Phi$  and  $\varphi$  are the polar and azimuthal angles in an orthogonal coordinate system ( $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ ) with  $\mathbf{x}_3$  a unit vector along the  $n$ -fold axis and  $\mathbf{x}_1$  along a twofold axis, if these exist. Then we have

$$x = \cos \Phi = A_3 = H^{-1}(ha^* \cos \beta^* + kb^* \cos \alpha^* + lc^*) \quad (19)$$

$$\tan \varphi = A_2/A_1 = (ka/b - h \cos \gamma)/(h \sin \gamma) \quad (20)$$

for all Laue groups, except for  $\bar{3}R$ ,  $\bar{3}m1R$  and  $\bar{3}1m$ . For the groups  $\bar{3}R$ ,  $\bar{3}m1R$  we have

$$x = \cos \Phi = (Ha)^{-1}[3(1+2 \cos \alpha)]^{-1/2}(h+k+l) \quad (21)$$

$$\tan \varphi = (h+k-2l)/[3^{1/2}(h-k)]. \quad (22)$$

For  $\bar{3}1m$  [this group was omitted in Popa (1992)] only  $\tan \varphi$  is different from that given by (20). One has therefore

$$\tan \varphi = 3^{1/2}k/(2h + k). \quad (23)$$

The series of  $\langle R_h \rangle$  is truncated at a number of terms depending on the magnitude of the anisotropy, the first term being just the average radius of the composite crystallite. Below, in the formulae (24) to (34), we do not give all the significant terms, because there isn't a method for working out their numbers beforehand, but only the terms that differentiate one Laue group from another. For more terms see Table 3 in the paper by Popa (1992).

The list of the direction-dependent size models for all Laue groups is as follows.

1

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_2^1(x) \cos \varphi + R_3 P_2^1(x) \sin \varphi + R_4 P_2^2(x) \cos 2\varphi + R_5 P_2^2(x) \sin 2\varphi + \dots \quad (24)$$

2/m

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_2^2(x) \cos 2\varphi + R_3 P_2^2(x) \sin 2\varphi + \dots \quad (25)$$

2/mmm

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_2^2(x) \cos 2\varphi + \dots \quad (26)$$

4/m

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_4^0(x) + R_3 P_4^4(x) \cos 4\varphi + R_4 P_4^4(x) \sin 4\varphi + \dots \quad (27)$$

4/mmm

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_4^0(x) + R_3 P_4^4(x) \cos 4\varphi + \dots \quad (28)$$

$\bar{3}$

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_4^0(x) + R_3 P_4^3(x) \sin 3\varphi + R_4 P_4^3(x) \cos 3\varphi + \dots \quad (29)$$

$\bar{3}m$

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_4^0(x) + R_3 P_4^3(x) \sin 3\varphi + \dots \quad (30)$$

6/m

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_4^0(x) + R_3 P_6^0(x) + R_4 P_6^6(x) \cos 6\varphi + R_5 P_6^6(x) \sin 6\varphi + \dots \quad (31)$$

6/mmm

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_4^0(x) + R_3 P_6^0(x) + R_4 P_6^6(x) \cos 6\varphi + \dots \quad (32)$$

$m\bar{3}$

$$\langle R_h \rangle = R_0 + R_1 K_4^1(x, \varphi) + R_2 K_6^1(x, \varphi) + R_3 K_6^2(x, \varphi) + \dots \quad (33)$$

$m\bar{3}m$

$$\langle R_h \rangle = R_0 + R_1 K_4^1(x, \varphi) + R_2 K_6^1(x, \varphi) + \dots \quad (34)$$

In (33) and (34) the symmetrized harmonics for the cubic groups  $K_{2l}^\mu(x, \varphi)$  are

$$K_4^1(x, \varphi) = 0.3046972 P_4^0(x) + 0.3641828 P_4^4(x) \cos 4\varphi \quad (35)$$

$$K_6^1(x, \varphi) = -0.1410474 P_6^0(x) + 0.527751 P_6^4(x) \cos 4\varphi \quad (36)$$

$$K_6^2(x, \varphi) = -0.4678013 P_6^2(x) \cos 2\varphi + 0.3153915 P_6^6(x) \times \cos 6\varphi. \quad (37)$$

The number of terms that must be used in formulae (24) to (34) can be determined by successive refinements starting from the isotropic case  $\langle R_h \rangle = R_0$ . Terms are then added one by one until the corresponding fitted coefficient becomes insignificant.

In principle, the models (24) to (34) for  $(h, k, l)$ -dependent size hold even if there is a contribution to the peak broadening from the stacking faults, but this is not separable from the size broadening. We believe it would be possible to separate the two effects if  $\langle R_h \rangle$  in (2) is replaced by an effective radius

$$\langle R_h \rangle_{\text{eff}}^{-1} = \langle R_h \rangle^{-1} + 2p_f P_h. \quad (38)$$

Here  $p_f$  is the faulting probability, which must be a refinable parameter, and  $P_h$  is a determined function of  $h, k, l$  which can be found in Warren (1969) only for face-centred cubic, body-centred cubic and hexagonal close-packed metals. It would be desirable to find  $P_h$  for any symmetry, but this is not the aim of this paper.

## APPENDIX A

### Strain and size in the diffraction pattern

The diffraction pattern can be written as follows

$$I(z_i) = B(z_i) + s \sum_H c_H \int d(\Delta z) R(\Delta z) V_H(z_i - z_H + \Delta z)$$

where  $z$  is one of the variables  $2\theta$  or  $\lambda$ , as the diffraction method is constant wavelength or energy dispersive (time-of-flight for neutrons),  $s$  is the scale factor,  $B(z_i)$  is the background and  $R(\Delta z)$  is the instrumental resolu-

tion, normalized to unit area. The factor  $c_H$  also depends on the diffraction method. In the normalized Voigt profile

$$V_H(z) = \int d(\Delta z') G_H(\Delta z') L_H(z + \Delta z')$$

the Gaussian component  $G_H$  represents the strain effect, and the Lorentzian component  $L_H$  the size effect. In terms of the integral breadths  $\beta_{GH}$ ,  $\beta_{LH}$ , these functions are

$$G_H(z) = \beta_{GH}^{-1} \exp(-\pi z^2 / \beta_{GH}^2),$$

$$L_H(z) = \beta_{LH}^{-1} (1 + \pi^2 z^2 / \beta_{LH}^2)^{-1}.$$

For the constant-wavelength diffraction method,  $z = 2\theta$  and the quantities  $c_H$ ,  $\beta_{GH}$ ,  $\beta_{LH}$  are as follows

$$c_H = \lambda^3 k_H n_H F_H^2 / (v_c^2 \sin \theta_H \sin 2\theta_H),$$

$$\beta_{GH} = 2 \tan \theta_H (2\pi \langle \varepsilon_{hh}^2 \rangle)^{1/2},$$

$$\beta_{LH} = 2\lambda / (3 \langle R_h \rangle \cos \theta_H),$$

where  $v_c$  is the unit-cell volume,  $n_H$  the multiplicity factor,  $F_H$  the structure factor and  $k_H$  a factor containing polarization, texture and sample transmission.

For the energy-dispersive diffraction method,  $z = \lambda$  (or alternatively  $d$ -spacing or time-of-flight) and  $c_H$ ,  $\beta_{GH}$ ,  $\beta_{LH}$  are

$$c_H = i(\lambda_H) \lambda_H^4 k_H n_H F_H^2 / (v_c^2 \sin^3 \theta),$$

$$\beta_{GH} = \lambda_H (2\pi \langle \varepsilon_{hh}^2 \rangle)^{1/2},$$

$$\beta_{LH} = \lambda_H^2 / (3 \langle R_h \rangle \sin \theta).$$

Here  $i(\lambda)$  is the wavelength-dependent flux incident on the sample.

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