

## Diffraction Profiles from Small Crystallites

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### Abstract

The diffraction profile for a small crystallite has been obtained as the orientational average of the diffraction intensity given by Ino & Minami [*Acta Cryst.* (1979), A35, 163–170]. The formula obtained is a type of Debye interference function modified by a function  $\mathcal{V}(\mathbf{r})$  (the self-convolution of a crystal shape function) and is expressed as a sum over all the atomic distance vectors in the crystal structure. Since the set of the vectors has Laue symmetry (the order of the group:  $L$ ), the summation can be simplified to a sum over a reduced range corresponding to  $1/L$  of the original range, while the  $\mathcal{V}(\mathbf{r})$  is changed to  $\bar{v}(\mathbf{r}) = \sum_{p=1}^L \mathcal{V}(R_p \mathbf{r}) / (LV)$  ( $V$ : volume of the crystal;  $R_1, \dots, R_L$ : element of Laue symmetry group). Once the  $\bar{v}$  function is determined, the profile for a complicated crystal of any size and any crystal system can be systematically and efficiently calculated.

### Introduction

The X-ray intensity formula for a powder specimen composed of very small crystallites can be given by the interference function

$$I(b) = \sum_i \sum_j f_i(b) f_j(b) j_0(2\pi b r_{ij}), \quad (1)$$

where  $j_0(x) = \sin(x)/x$ ,  $b = (2/\lambda) \sin\theta$ ,  $\lambda$  is the X-ray wavelength,  $\theta$  is the scattering angle,  $f_i$  and  $f_j$  are the atomic scattering factors of the  $i$ th and  $j$ th atoms in the crystallite, and  $r_{ij}$  is the atomic distance between them. The summation is to be taken over all atoms in the crystallite. For monatomic substances, equation (1) reduces to

$$I(b) = f^2(b) \sum_r A(r) j_0(2\pi b r), \quad (2)$$

where  $A(r)$  is the frequency of occurrence of an atomic distance  $r$  and the summation is to be taken over all possible  $r$ .

For nearly spherical crystallites (diameter  $D$ ) of a monatomic face-centered cubic structure, Germer & White (1941) calculated the intensity profile using  $A(r) = Nn(r)\varepsilon(r/D)$  ( $N$ : total number of atoms),  $r = a(m/2)^{1/2}$  ( $m$ : positive integer;  $a$ : lattice constant),  $\varepsilon(x) = 1 - (\frac{3}{2})x + (\frac{1}{2})x^3$ , where  $n(r)$  is the number of atoms at a distance  $r$  from any particular atom in an infinite f.c.c. crystal. For simple monatomic parallelepiped crystallites with edges  $N_x|a_x|$ ,  $N_y|a_y|$ ,  $N_z|a_z|$  ( $N_x, N_y, N_z$ : integers) parallel to the crystal axes  $a_x, a_y, a_z$ , James (1948) derived

$$A(r) = (N_x - |m_x|)(N_y - |m_y|)(N_z - |m_z|),$$

$$r = |m_x a_x + m_y a_y + m_z a_z|,$$

where  $m_x, m_y, m_z$  are integers from  $-(N_x - 1)$ ,  $-(N_y - 1)$ ,  $-(N_z - 1)$  to  $(N_x - 1)$ ,  $(N_y - 1)$ ,  $(N_z - 1)$  respectively.

For a monatomic b.c.c. crystal of cubic shape with the cube edges parallel to the crystal axes, Morozumi & Ritter (1953) classified the atomic distance  $r$  into three kinds and gave  $A(r)$ 's for each kind of  $r$ . Intensities from cubic diamond crystallites containing 27 and 1000 unit cells were computed by Tiensuu, Ergun & Alexander (1964), although  $A(r)$  was not well defined. Ergun (1970) calculated the intensity for a spherical diamond crystallite using the function  $A(r) = Nn(r)\varepsilon(r/D)$ , where  $r = a(p^2 + q^2 + s^2)^{1/2}/4$  ( $p, q, s$ : integers),  $n(r)$  is the number of like distances from any particular atom in an infinite diamond lattice, and  $\varepsilon(r/D)$  is the same function as that derived by Germer & White.

As described in the previous paper (Ino & Minami, 1979), the diffraction intensity for a bounded crystal can be calculated by either the direct-lattice sum or the reciprocal-lattice sum; the former is more convenient for a very small crystal. In this paper, the intensity profile will be derived from the direct-lattice-sum expression, and it will be shown that the computation of the intensity profile can be simplified by symmetry considerations of the atomic vector set in the crystal concerned.

### Formula of intensity profile from crystallites

Let us consider the diffraction intensity from a small crystal with a particular size and shape, and designate the position vector and the atomic scattering factor of the  $\alpha$ th atom in a unit cell as  $\mathbf{r}_\alpha$  and  $f_\alpha$  respectively. Using a formula derived by Ino & Minami (1979) for a very small crystal, the intensity of scattered X-rays is expressed as:

$$I(\mathbf{b}) = (1/V_c) \sum_{\mathbf{m}} \sum_{\alpha} \sum_{\beta} f_{\alpha}(\mathbf{b}) f_{\beta}(\mathbf{b}) \mathcal{V}(\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta) \times \exp[2\pi i \mathbf{b}(\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta)], \quad (3)$$

where  $\mathbf{b}$  is the scattering vector,  $\mathbf{m}$  is the position vector of the Bravais-lattice point,  $V_c$  is the unit-cell volume and  $\mathcal{V}(\mathbf{r})$  is the self-convolution of the shape function  $s(\mathbf{r})$ , i.e.

$$\mathcal{V}(\mathbf{r}) = \int s(\mathbf{r}') s(\mathbf{r}' + \mathbf{r}) d\mathbf{r}', \quad (4)$$

$$s(\mathbf{r}) = \begin{cases} 1 & \text{(inside the crystal boundary),} \\ 0 & \text{(outside the crystal boundary).} \end{cases} \quad (5)$$

If a polycrystalline sample consists of small crystals oriented completely at random, the intensity from the sample is given as the average of equation (3) over all directions of the scattering vector  $\mathbf{b}$ . As the atomic scattering factors can be regarded as spherically symmetric, the intensity from the polycrystal is given by

$$I(b) = (1/V_c) \sum_{\mathbf{m}} \sum_{\alpha} \sum_{\beta} f_{\alpha}(b) f_{\beta}(b) \mathcal{V}(\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta) \times \int_0^{2\pi} b |\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta|, \quad (6)$$

where the summation is to be taken over all the set of the atomic distance vectors  $\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta$ . The summation procedure can be simplified by virtue of the crystal symmetry.

If the crystal possesses the symmetry of a space group  $\mathbf{G}$ , the set of points occupied by atoms can be classified into subsets  $P_1, P_2, \dots$ , such that elements of each subset can be transformed one to another by the operation of the symmetry group  $\mathbf{G}$  and they are thus *equivalent with respect to the symmetry of  $\mathbf{G}$* . Then the  $P_i$  set can be expressed, in terms of the position vector, as

$$P_i = \{\mathbf{m} + \mathbf{r}_i^{(t)} | \mathbf{m} \in \Omega, t = 1, 2, \dots, N_i\}, \quad (7)$$

where  $\mathbf{r}_i^{(t)}$  and  $N_i$  are the equivalent position vector and its number in a unit cell, respectively, and  $\mathbf{m} \in \Omega$  means that  $\mathbf{m}$  belongs to the whole direct space  $\Omega$ . Since the atomic distance vectors  $\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta$  in equation (6)

belong to the so-called 'vector set' (Buerger, 1950), the set of the distance vectors has the symmetry of a space group  $\bar{\mathbf{G}}$  determined by the direct product of  $\mathbf{G}$  and the inversion group, and the rotational part of the space group is a Laue group, which is denoted by  $\mathbf{R}$ . Then the set of distance vectors joining the points in the set  $P_j$  to those in the set  $P_i$  can be classified into subsets  $D_{ij1}, D_{ij2}, \dots$ , such that elements in each vector set are equivalent with respect to the symmetry of  $\bar{\mathbf{G}}$ , and the subset can be expressed as

$$D_{ijk} = \{\mathbf{m} + \mathbf{r}_{ijk}^{(s)} | \mathbf{m} \in \Omega, s = 1, 2, \dots, n_{ijk}\}, \quad (8)$$

where  $\mathbf{r}_{ijk}^{(s)}$  and  $n_{ijk}$  are the equivalent distance vectors and their number in a unit cell, respectively. Combination of the  $N_i$  points in the  $P_i$  set with the  $N_j$  points in the  $P_j$  set yields  $2N_i N_j$  distance vectors. However, since only  $n_{ijk}$  vectors are different, the set  $D_{ijk}$  involves some multiplicity. Thus, there is the following relation between  $N_i, N_j, n_{ijk}$  and the multiplicity weight  $w_{ijk}$ :

$$\sum_k w_{ijk} n_{ijk} = 2N_i N_j \quad (i \neq j). \quad (9)$$

Another relation for the combination of the  $N_i$  points in the  $P_i$  set can also be derived as follows:

$$\sum_k w_{ii} n_{iik} = N_i^2. \quad (10)$$

Thus the summation over the vector  $\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta$  in equation (6) can be transformed into

$$I(b) = \sum_{i \geq j} f_i(b) f_j(b) \sum_k \mathcal{V}_{ijk}(b), \quad (11)$$

$$\mathcal{V}_{ijk}(b) = (V_i/V_c) w_{ijk} \sum_{\mathbf{m}} \sum_{s=1}^{n_{ijk}} v[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}] j_0[2\pi b |\mathbf{m} + \mathbf{r}_{ijk}^{(s)}|], \quad (12)$$

where

$$v(\mathbf{r}) = \mathcal{V}(\mathbf{r})/V_i \quad (V_i: \text{the volume of the crystal}). \quad (13)$$

Since the whole Bravais lattice  $\{\mathbf{m}\}$  and the  $D_{ijk}$  set are invariant under the operation of any elements  $R_p$  ( $p = 1, 2, \dots, L$ ) included in  $\mathbf{R}$ , the  $D_{ijk}$  set can be generated by the operation of the Laue group from the particular atomic distance vectors located inside a subspace  $\Omega_0$  whose volume is  $1/L$  times that of  $\Omega$ ; that is,

$$D_{ijk} = \{R_p[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}] | \mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0, R_p \in \mathbf{R} \quad (s = 1, 2, \dots, n_{ijk})\}. \quad (14)$$

$\Omega_0$  for 11 Laue groups is listed in Table 1. If the number of different vectors of  $R_p[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}]$  ( $p = 1, 2, \dots, L$ ) is  $n[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}]$ , the frequency of occurrence of the same vector in  $R_p[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}]$  ( $p = 1, 2, \dots, L$ ) is given by

Table 1. Sectorial subspace  $\Omega_0$  for 11 Laue groups

Laue group	$\Omega_0$ (conventional cell)
$\bar{1}$	$z \geq 0$ (Triclinic)
$2/m$	$x \geq 0, y \geq 0$ (Monoclinic; 2nd setting)
$mmm$	$x \geq 0, y \geq 0, z \geq 0$ (Orthorhombic)
$4/m$	$x \geq 0, y \geq 0, z \geq 0$
$4/mmm$	$x \geq 2y \geq 0, z \geq 0$
$m\bar{3}$	$x \geq y \geq 0, x \geq z \geq 0$
$m\bar{3}m$	$x \geq y \geq z \geq 0$
$\bar{3}$	$x \geq y \geq 0$
$\bar{3}m$	$x \geq 2y \geq 0$
$6/m$	$x \geq y \geq 0, z \geq 0$
$6/mmm$	$x \geq 2y \geq 0, z \geq 0$

$L/n[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}]$ . Thus equation (12) can be transformed as

$$\mathcal{J}_{ijk}(b) = \left( \frac{V_t}{V_c} \right) w_{ijk} \sum_{s=1}^{n_{ijk}} \sum_{\mathbf{m}} n[\mathbf{m} + \mathbf{r}_{ijs}^{(s)}] \bar{v}[\mathbf{m} + \mathbf{r}_{ijk}^{(s)}] \times j_0 [2\pi b |\mathbf{m} + \mathbf{r}_{ijk}^{(s)}|] \quad (15)$$

where

$$\bar{v}(\mathbf{r}) = (1/L) \sum_{p=1}^L v(R_p \mathbf{r}); \quad (16)$$

$[\mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0]$  means the summation conditions of  $\mathbf{m}$ . If  $\mathbf{r}_{ijk}$  is selected as a representative of the vectors  $\mathbf{r}_{ijs}^{(s)}$  ( $s = 1, 2, \dots, n_{ijk}$ ), an operator  $R_{ijk}^{(s)}$  can be determined for an  $\mathbf{r}_{ijk}^{(s)}$  such that

$$\mathbf{r}_{ijk}^{(s)} = R_{ijk}^{(s)} \mathbf{r}_{ijk} + \mathbf{m}^{(s)} \quad [\mathbf{m}^{(s)}: \text{a lattice vector}]. \quad (17)$$

Using the  $r_{ijk}$  and the  $R_{ijk}^{(s)}$  one can change the summation condition from  $[\mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0]$  to  $[\mathbf{m} + \mathbf{r}_{ijk} \in [R_{ijk}^{(s)}]^{-1} \Omega_0]$ . As the function  $n(\mathbf{r})\bar{v}(\mathbf{r})$   $j_0(2\pi b|\mathbf{r}|)$  is invariant under the operation of  $\mathbf{R}$ , one can finally obtain:

$$I(b) = \sum_{i \geq j} \sum f_i(b) f_j(b) \sum_k \mathcal{J}_{ijk}(b), \quad (18)$$

$$\mathcal{J}_{ijk}(b) = \left( \frac{V_t}{V_c} \right) w_{ijk} \sum_{\mathbf{m}} n(\mathbf{M} + \mathbf{r}_{ijk}) \bar{v}(\mathbf{m} + \mathbf{r}_{ijk}) \times j_0(2\pi b |\mathbf{m} + \mathbf{r}_{ijk}|),$$

where  $\Omega_{ijk}$  is the subspace specified by the point symmetry of the position  $\mathbf{r}_{ijk}$  such that

$$\Omega_{ijk} = \bigcup_{s=1}^{n_{ijk}} [R_{ijk}^{(s)}]^{-1} \Omega_0. \quad (19)$$

The function  $\bar{v}(\mathbf{r})$  in equation (16) can be rewritten as

$$\bar{v}(\mathbf{r}) = (2/L) \sum_{p=1}^{L/2} v(R_p^0 \mathbf{r}) \quad (20)$$

( $R_p^0$ : proper rotation belonging to Laue group  $\mathbf{R}$ ) because  $\mathcal{V}(\mathbf{r})$  has centrosymmetry and its calculation may be simplified if the crystal shape has some symmetry. For example, it turns out to be simply  $\mathcal{V}(\mathbf{r})/V_t$  if  $\mathcal{V}(\mathbf{r})$  has spherical symmetry or has some symmetry not lower than that of  $\mathbf{R}$ .

Vectors  $\mathbf{r}_{ijk}^{(s)}$  can be obtained by Buerger's procedures in § 2.1.12.5 of *International Tables for X-ray Crystallography (IT)* (1959) (Buerger, 1959); hence operators  $R_{ijk}^{(s)}$  ( $s = 1, 2, \dots, n_{ijk}$ ) and  $\mathbf{r}_{ijk}$  can be obtained from the column 'coordinates of equivalent positions' in § 4.3 of *IT* (1952).  $w_{ijk}$  can be obtained by Buerger's procedures or from equations (9) and (10). The condition for  $\mathbf{m}$  is given for five types of lattice in Table 2. The  $n(\mathbf{r})$  of a direct vector  $\mathbf{r}$  can be obtained on referring to 'general multiplicity factor of  $\{hkl\}$ ' in § 3.5 of *IT* (1952). Thus, the intensity profiles for small crystals of any crystal symmetry and any shape can be systematically and efficiently calculated by the use of equation (18).

If the atomic distance vectors,  $\mathbf{m} + \mathbf{r}_{ijk}$  in equation (18), are numbered in order of increasing magnitude, the  $v$ th distance,  $r_{ij}(v)$ , will specify a particular  $k$  and  $\mathbf{m}$  such that

$$|\mathbf{m} + \mathbf{r}_{ijk}| = r_{ij}(v). \quad (21)$$

In terms of atomic distance  $r_{ij}(v)$ , equation (18) can be rewritten

$$I(b) = (V_t/V_c) \sum_{i \geq j} \sum f_i(b) f_j(b) \sum_v N_{ij}(v) j_0[2\pi b r_{ij}(v)], \quad (22)$$

where

$$N_{ij}(v) = w_{ijk} n(\mathbf{m} + \mathbf{r}_{ijk}) \bar{v}(\mathbf{m} + \mathbf{r}_{ijk}).$$

The quantity  $(V_t/V_c) N_{ij}(v)$ , therefore, means twice the number of  $ij$  atom pairs having the distance  $r_{ij}(v)$  in the crystal sample. Since for an infinite crystal  $\bar{v} = 1$ ,  $N_{ij}(v)$  tends to  $N_{ij}^\infty(v) = w_{ijk} n(\mathbf{m} + \mathbf{r}_{ijk})$ . Since  $\bar{v} \leq 1$ , for a finite crystal,  $N_{ij}(v)$  is generally less than  $N_{ij}^\infty(v)$ . The number of  $j$  atoms in the nearest neighborhood of an  $i$

Table 2. Conditions limiting possible  $(m_x, m_y, m_z)$ , represented by the conventional cell axes in Table 1, for five lattices

Type of lattice	Conditions for $(m_x, m_y, m_z)$
$P$	All integers
$C$	$m_x, m_y$ : half of the integers and $m_x + m_y = \text{integer}$ $m_z$ : integer
$I$	All integers or all half-odd integers
$F$	Half of the integers and $m_x + m_y + m_z = \text{integer}$
$R$	A third of the integers and $m_x - m_y - m_z = \text{integer}$

atom for an infinite crystal, *i.e.* the coordination number, can be derived from  $N_{ij}^\infty(1)$  as

$$N^\infty(i \rightarrow j) = N_{ij}^\infty(1)/(\varepsilon_{ij} N_i) \quad (23)$$

$$(\varepsilon_{ij} = 1 \text{ for } i=j; \quad 2 \text{ for } i \neq j).$$

On the other hand, the number corresponding to a bounded crystal, designated  $N(i \rightarrow j)$ , is similarly given by

$$N(i \rightarrow j) = N_{ij}(1)/(\varepsilon_{ij} N_i). \quad (24)$$

This number is less than the coordination number.

### Example of application

$\mathcal{Z}(\mathbf{r})$  in equation (4), characterizing the effects of size and shape on the intensity profile as given by equation (18), is a function which may be calculated as the volume shared in common by the original crystal and the crystal translated by the distance  $\mathbf{r}$ . For a spherical crystal (diameter  $D$ ), for example, we obtain

$$v(\mathbf{r}) = v_s(r) = \begin{cases} 1 - (\frac{3}{2})r + (\frac{1}{2})r^3 & \text{if } 0 \leq r \leq 1, \\ 0 & \text{otherwise.} \end{cases} \quad (25)$$

The relation  $\bar{v}(\mathbf{r}) = v_s(r)$  holds for any crystal system. For a parallelepiped crystal with edges  $D_1, D_2, D_3$  parallel, respectively, to the directions  $\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3$  ( $|\mathbf{n}_k| = 1$ ), we have

$$v(\mathbf{r}) = v_p(x_1, x_2, x_3)$$

$$= \begin{cases} (1 - |x_1|)(1 - |x_2|)(1 - |x_3|) & \text{if } |x_k| \leq 1 \\ 0 & \text{otherwise,} \end{cases} \quad (26)$$

where  $x_k = (\mathbf{r} \cdot \mathbf{n}_k)/D_k$  ( $k = 1, 2, 3$ ).

Let us first consider a monatomic crystal consisting of atoms located at Bravais-lattice points, such as monatomic simple, face-centered and body-centered crystals. Since  $\mathbf{r}_{111} = (000)$ ,  $n_{111} = 1$ ,  $w_{111} = 1$ ,  $\Omega_{111} = \Omega_0$ , the intensity profile is given by a quite simple formula:

$$I(b) = (V_t/V_c) f^2(b) \sum_{\mathbf{m} \in \Omega_0} n(\mathbf{m}) \bar{v}(\mathbf{m}) j_0(2\pi b |\mathbf{m}|), \quad (27)$$

where  $\Omega_0$  and the condition of  $\mathbf{m}$  are given in Tables 1 and 2. For a monatomic f.c.c. crystal with the shape of a cube as treated by Germer & White, since  $V_t/V_c = N$ ,  $\bar{v}(\mathbf{m}) = v_s[a(m_x^2 + m_y^2 + m_z^2)^{1/2}/D]$  and  $n(m_x, m_y, m_z)$  is  $n_c(m_x, m_y, m_z)$  given on the  $m3m$  row of p. 32 of *IT* (1952), equation (27) is identical to the formula of Germer & White. Although they derived  $\varepsilon_n$  as an approximate function through integrals under a particular geometrical consideration,  $\varepsilon_n$  is nothing but  $v_s$ , which has been derived straightforwardly by 'the random-shift treatment' (Ino & Minami, 1979).

For a parallelepiped crystal, since  $V_t/V_c = N_x N_y N_z$ ,  $\bar{v}(\mathbf{m}) = v_p(m_x/N_x, m_y/N_y, m_z/N_z)$ , and  $n(\mathbf{m}) = 1$  for  $\mathbf{m} = 0$ , and  $n(\mathbf{m}) = 2$  for  $\mathbf{m} \neq 0$ , equation (27) gives exactly the same formula as that derived by James. He obtained it by the orientational average of the Laue function  $G(\mathbf{b})$ . Since the diffraction intensity  $I_a(\mathbf{b})$  for the  $\rho_a$  expression is equal to  $f^2(\mathbf{b})G(\mathbf{b})$  in this case (Ino & Minami, 1979),  $I(b)$  must be equal to  $f^2(b) \langle G(\mathbf{b}) \rangle$ . The agreement between his formula and that of the present authors is natural in view of these facts.

For the monatomic b.c.c. crystal, equation (27) gives a much simpler formula than that obtained by Morozumi & Ritter. It is expressed as the sum of terms having  $\bar{v}(\mathbf{m}) = v_p(m_x/M, m_y/M, m_z/M)$  over a set  $\{m_x, m_y, m_z\}$  specified by  $Im3m$  as shown in Tables 1 and 2. For a very small crystal, this formula gives profiles considerably different from Morozumi & Ritter's calculation. The reason for this discrepancy is probably that the total number of atoms considered in their formula is  $M^3 + (M + 1)^3$ , and not  $2M^3$  which is derived from  $V_t/V_c$  in equation (27).

As an example of crystals whose basic unit cell contains more than one atom, let us consider a high-cristobalite crystal. Atoms of high cristobalite, Si and O, are placed in the special positions of  $Fd3m$ ; that is, Si: (000), ( $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ); O: ( $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ ), ( $\frac{1}{8}\frac{3}{8}\frac{3}{8}$ ), ( $\frac{3}{8}\frac{1}{8}\frac{3}{8}$ ), ( $\frac{3}{8}\frac{3}{8}\frac{1}{8}$ ) (Wyckoff, 1963). Since the space group of the vector set for this crystal is  $Fm3m$ , the specifications for equation (18) can be obtained as shown in Table 3 where Si and O are numbered as 1 and 2. Then the intensity profile is expressed as

$$I(b) = \frac{V_t}{V_c} \left[ f_1^2(b) \sum_{k=1}^2 \mathcal{J}_{11k}(b) + f_2(b) f_1(b) \mathcal{J}_{211}(b) + f_2^2(b) \sum_{k=1}^2 \mathcal{J}_{22k}(b) \right]. \quad (28)$$

Since  $w_{111} = 2$ ,  $\Omega_{111} = \{xyz | x \geq y \geq z \geq 0\}$ , and  $w_{112} = 1$ ,  $\Omega_{112} = \{xyz | x \geq y \geq z \geq 0 \text{ or } x \leq y \leq z \leq 0\}$ ,  $\mathcal{J}_{111}$  and  $\mathcal{J}_{112}$  for Si-Si can be expressed as

$$\mathcal{J}_{111}(b) = 2 \sum_{m_x \geq m_y \geq m_z \geq 0} n_c(m_x, m_y, m_z) \bar{v}(m_x, m_y, m_z) \times j_0[2\pi b a(m_x^2 + m_y^2 + m_z^2)^{1/2}], \quad (29)$$

$$\mathcal{J}_{112}(b) = \sum_{\substack{m_x \geq m_y \geq m_z \geq -1 \\ \text{or} \\ m_x \leq m_y \leq m_z \leq -1}} n_c(m_x + \frac{1}{4}, m_y + \frac{1}{4}, m_z + \frac{1}{4}) \times \bar{v}(m_x + \frac{1}{4}, m_y + \frac{1}{4}, m_z + \frac{1}{4}) j_0\{2\pi b a[(m_x + \frac{1}{4})^2 + (m_y + \frac{1}{4})^2 + (m_z + \frac{1}{4})^2]^{1/2}\}. \quad (30)$$

Similarly,  $\mathcal{I}_{211}$  for Si—O, and  $\mathcal{I}_{221}$  and  $\mathcal{I}_{222}$  for O—O can be obtained from Table 3. The intensities for the cubic crystal with edges parallel to the crystal axes were calculated from equation (28) with  $\bar{v}(x,y,z) = v_p(x/D,y/D,z/D)$  derived from equation (26). Fig. 1 shows the plots of the function  $I(b)/[V_i/V_c] \sum_{i=1}^2 N_i f_i^2(b)$  versus  $2\pi ba$  for high-cristobalite crystals of cubic shape containing 1, 8, 27, 64 and 125 unit cells. The positions of the first few powder reflections are shown at the bottom for comparison.

For a diamond crystal, since C atoms are put in the positions identical in symmetry with Si atoms in high-cristobalite, the intensity can be given by  $(V_i/V_c) f^2(b) \sum_{k=1}^2 \mathcal{I}_{11k}(b)$  in equation (28). After  $(m_x, m_y, m_z)$  in  $\mathcal{I}_{111}$ , equation (29), has been replaced by  $(p/4, q/4, s/4)$  ( $p, q, s$ : positive integers;  $p \geq q \geq s \geq 0$ ) and  $(m_x + \frac{1}{4}, m_y$

+  $\frac{1}{4}, m_z + \frac{1}{4}$ ) in  $\mathcal{I}_{112}$ , equation (30), has been replaced by  $(p/4, q/4, s/4)$  or  $(-p/4, -q/4, -s/4)$ , the intensity is expressed simply in terms of  $(pqs)$  as

$$I(b) = 2 \left( \frac{V_i}{V_c} \right) f^2(b) \sum_{p=0}^p \sum_{q=0}^q \sum_{s=0}^s n'(p,q,s) \bar{v} \left( \frac{p}{4}, \frac{q}{4}, \frac{s}{4} \right) \times j_0[\pi ba(p^2 + q^2 + s^2)^{1/2}/2]. \quad (31)$$

where

$$n'(p,q,s) = \begin{cases} n_c(p,q,s): & p,q,s \text{ for all even and} \\ & p+q+s = 4 \times \text{integer,} \\ n_c(p,q,s)/2: & p,q,s \text{ for all odd,} \\ 0: & \text{otherwise.} \end{cases} \quad (32)$$

For a cubic shape, the intensity profiles were computed and compared with the curves given in the paper of Tiensuu *et al.* The agreement is seemingly good. For a spherical crystal (diameter  $D$ ), equations (31) and (32) may be compared with Ergun's formula. Although  $\bar{v}(p/4, q/4, s/4) = v_p[a(p^2 + q^2 + s^2)^{1/2}/4D]$  is equal to  $\epsilon$  in Ergun's formula and the summation condition of  $(p,q,s)$  in equation (31) is the same as that in his formula,  $n'(p,q,s)$  in equation (32) does not agree with his  $n$  value for  $p,q,s$  all odd.

Let us consider the coordination number for a high-cristobalite crystal and the dependence of  $N(i \rightarrow j)$  on the size of the crystal with a cubic shape. By the use of equation (24), these numbers for  $N(\text{Si} \rightarrow \text{Si})$ ,  $N(\text{Si} \rightarrow \text{O})$ ,  $N(\text{O} \rightarrow \text{Si})$  and  $N(\text{O} \rightarrow \text{O})$  were calculated and are given in Table 4. The radial distribution functions (RDF's) for this crystal,  $4\pi r^2 D(r)$ , are illustrated in Fig. 2 where it is supposed that the constituent atom has an atomic scattering factor proportional to its atomic number and that the crystal has the Debye temperature factor  $\exp[-(2\pi b\Delta)^2/2]$  ( $\Delta = 0.2 \text{ \AA}$ ). As shown in Fig. 2, even for a very small crystallite consisting of several unit cells, one can detect the peaks corresponding to the nearest-neighbour distances  $r(\text{O}-\text{Si})$ ,  $r(\text{O}-\text{O})$ ,  $r(\text{Si}-\text{Si})$  in the RD curve. However, as can be seen from Table 4, the apparent coordination numbers  $N(i \rightarrow j)$  derived from the area under the peaks in the RDF are much less than the true one and vary with the size of the crystal. Hence on the estimation of the coordination number in a sample using the RDF obtained from the

Table 3. Specification for the vector set of a high-cristobalite crystal

Atom pairs	(ijk)	$r_{ijk}$	$n_{ijk}$	$w_{ijk}$	$R_{ijk}^{(s)}$ ( $s = 1, \dots, n_{ijk}$ )*
Si—Si	(111)	(000)	1	2	(xyz)
	(112)	( $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ )	2	1	(xyz), ( $\bar{x}\bar{y}\bar{z}$ )
O—Si	(211)	( $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ )	8	2	(xyz), ( $x\bar{y}\bar{z}$ ), ( $\bar{x}y\bar{z}$ ), ( $\bar{x}\bar{y}z$ ), ( $\bar{x}y\bar{z}$ ), ( $\bar{x}yz$ ), ( $x\bar{y}z$ ), ( $x\bar{y}\bar{z}$ )
	(221)	(000)	1	4	(xyz)
O—O	(222)	( $\frac{1}{4}\frac{1}{4}0$ )	6	2	(xyz), (zxy), (yzx), ( $\bar{x}\bar{y}\bar{z}$ ), (zxy), ( $\bar{y}zx$ )

\* The symbol for the operator  $\mathbf{R}$  is just the vector formed by the action of the operator  $\mathbf{R}$  on the vector (xyz) (Jones's faithful symbol). For example, (xyz) and ( $\bar{x}\bar{y}\bar{z}$ ) mean operators 1 and  $\bar{1}$  respectively.

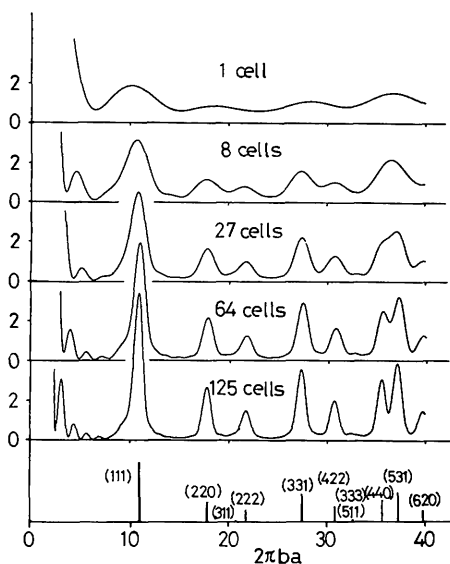


Fig. 1. The plots of the function  $I(b)/[(V_i/V_c) \sum_{i=1}^2 N_i f_i^2(b)]$  for high-cristobalite crystals with cubic shape.

Table 4.  $N(i \rightarrow j)$  of a high-cristobalite crystal with cubic shape

Number of cells	$N(\text{O} \rightarrow \text{Si})$	$N(\text{Si} \rightarrow \text{O})$	$N(\text{O} \rightarrow \text{O})$	$N(\text{Si} \rightarrow \text{Si})$
1	1.340	2.680	3.375	1.688
8	1.648	3.296	4.594	2.680
27	1.760	3.520	5.042	3.081
64	1.830	3.660	5.273	3.296
125	1.854	3.708	5.415	3.430
$\infty$	2	4	6	4

diffraction intensity, even if the sample is assumed to be composed of small crystallites so isolated that the interference among them may be neglected, the  $\bar{v}$  function should be taken into account as the correction factor.

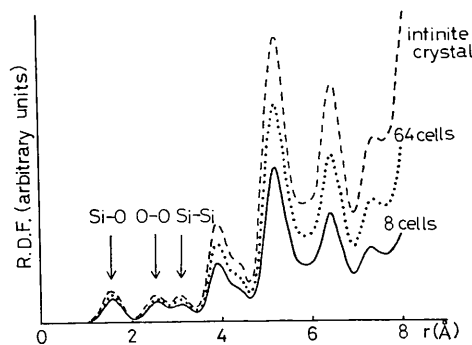


Fig. 2. The radial distribution function  $4\pi r^2 D(r)$  for high-crystallite crystals.

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## Extinction in Sodium Fluoride

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### Abstract

X-ray intensity measurements for a single crystal of sodium fluoride obtained at four wavelengths by Howard & Jones [*Acta Cryst.* (1977), **A33**, 776–783] have been re-analysed using both the Cooper–Rouse and Becker–Coppens extinction formalisms in order to study the wavelength dependence of the extinction in this crystal, since the original analysis was unable to account for the wavelength dependence of the intensities of the strong reflections. The results indicate that the crystal is intermediate between type I and type II in nature and are consistent with the wavelength dependence predicted by the theories, although the extinction is not large enough at the shorter wavelengths to provide a useful test of the validity of the theoretical wavelength dependence. The analysis also demonstrates some of the possible consequences of the use of unbalanced weighting schemes and of inappropriate models for the scattering factors.

### Introduction

In a recent study of the electron distribution in sodium fluoride, Howard & Jones (1977) carried out a series of accurate X-ray diffraction measurements on a single crystal of sodium fluoride at four different wavelengths, using Ag  $K\alpha$ , Mo  $K\alpha$ , Cu  $K\alpha$  and Co  $K\alpha$  radiations. These authors analysed their results using six sets of theoretical scattering factors and concluded that the best model for the electron distribution in sodium fluoride was given by the model 2 scattering factors of Aikala & Mansikka (1972) which take into account the overlap of the wave functions within the crystal environment as well as incorporating a contraction of the  $2p$  orbital of the  $F^-$  ion compared with that in the free ion (the AM2 model).

In analysing their results Howard & Jones included a correction for extinction using the Zachariasen (1967) model, but also considered possible amendment of the angle dependence in line with that predicted by Becker