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Intensity Profile of Debye–Scherrer Line from Small Crystallites

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Abstract

The exact intensity formula of the **h**-line profile from small crystallites has been obtained as the orientational average of the diffraction intensity of the **h** plane given by Ino & Minami [*Acta Cryst.* (1979), A35, 163–170]. While the formula is expressed as a triple integral including a sine Fourier integral, it can be expressed asymptotically with respect to the crystal size according to the theorem of asymptotic expansion of a Fourier integral. Hence the profile can be estimated by the sum of terms of single-integral type. The first term is of the same type as Wilson's formula but it has been shown that second and third terms improve considerably the accuracy of the asymptotic estimation especially for a very small crystal. The **h**-line profile can be successfully calculated for quite a small crystal of any shape and any crystal system by the asymptotic formula, which can be computed as easily as Wilson's formula.

1. Introduction

The diffraction from the **h** plane of a single-crystal sample is concentrated into a small region of reciprocal space **b** near the reciprocal-lattice point **h**. The intensity profile from a powdered polycrystalline sample is given by averaging the intensity distribution function $I_h(\mathbf{b})$ over all directions of vector **b**:

$$I_h(b) = \int I_h(\mathbf{b}) \, d\Omega_b/4\pi, \qquad (1)$$

where b is the magnitude of vector **b**.

The calculation of the profile was first treated by Laue (1926). He gave the intensity from a parallelepiped crystal having N_j unit cells along the $\mathbf{a}_j$ axis ($j = 1, 2, 3$) as follows:

$$I(\mathbf{b}) = |F(\mathbf{b})|^2 G(\mathbf{b}), \qquad (2)$$

with

$$G(\mathbf{b}) = \prod_{j=1}^{3} \left\{ \frac{\sin(\pi N_j b_j)}{\sin(\pi b_j)} \right\}^2, \qquad (3)$$

where $F(\mathbf{b})$ is the structure factor and **b** is expressed as $\mathbf{b} = b_1\mathbf{a}_1^* + b_2\mathbf{a}_2^* + b_3\mathbf{a}_3^*$, $\mathbf{a}_j^*$ being the reciprocal-unit-cell vectors. As an approximate function of $I_h(\mathbf{b})$ for a large crystal he adopted a Gaussian function:

$$I_h(b) \simeq |F(\mathbf{h})|^2 \prod_{j=1}^{3} N_j^2 \exp\{-\pi N_j^2 (b_j - h_j)^2\}, \qquad (4)$$

where

$$\mathbf{h} = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* \quad (h_1, h_2, h_3 \text{ integers}). \qquad (5)$$

Instead of attempting the evaluation of integral (1), he approximated it by an integral over the tangent plane to the sphere with radius b at the point $b\mathbf{h}/|\mathbf{h}|$:

$$I_h(b) \simeq \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_h(\mathbf{b}) \, db_1' \, db_2'/(4\pi b^2), \qquad (6)$$

where (b_1', b_2') are orthogonal coordinates on the tangent plane. Finally he derived the intensity profile formula as follows:

$$I_h(b) \simeq |F(\mathbf{h})|^2 N_1 N_2 N_3$$
$$\times \exp\{-\pi(b - |\mathbf{h}|)^2/\eta^2\}/(4\pi b^2 V_c \eta), \qquad (7)$$

where V_c is the volume of the unit cell and

$$\eta^2 = \sum_{j=1}^{3} \{\mathbf{a}_j^* \mathbf{h}/(N_j|\mathbf{h}|)\}^2. \qquad (8)$$

For spherical crystals with diameter D, Patterson (1939) showed $I_\mathbf{h}(\mathbf{b})$ to be proportional to

$$|S(\pi D|\mathbf{b} - \mathbf{h}|)|^2,$$

where

$$S(u) = 3(\sin u - u \cos u)/u^3 \qquad (9)$$

and derived an exact formula by integrating (1) as follows:

$$I_\mathbf{h}(b) \propto Z(x_-) - Z(x_+), \qquad (10)$$

with

$$Z(x) = x^{-4}\{(\sin x - x \cos x)^2 + x^2 \sin^2 x\}, \qquad (11)$$

where $x_- = \pi D(b - |\mathbf{h}|)$, $x_+ = \pi D(b + |\mathbf{h}|)$. Later, Warren (1978) derived exactly the same intensity formula as Patterson's by a different method.

For a crystal of general shape Wilson (1962) gave h-line profile formula by using the tangent plane approximation by Laue as follows:

$$I_\mathbf{h}^W(b) = \frac{|F(\mathbf{h})|^2}{2\pi b^2 V_c^2} \int_0^{r_h} V_\mathbf{h}(r) \cos\{2\pi(b - |\mathbf{h}|)r\} \, dr, \qquad (12)$$

where $V_\mathbf{h}(r)$ is the volume common to the crystal and its ghost shifted a distance r in the $\mathbf{h}$ direction, and r_h is the value of r for which $V_\mathbf{h}(r)$ vanishes.

As mentioned above, the intensity profile has not been exactly calculated for the crystal of general shape except for a sphere. The tangent plane approximation may be good as long as $I_\mathbf{h}(b)$ is concentrated at $\mathbf{b} = \mathbf{h}$, but for small crystallites, as the average is the case, the integral (1) cannot be approximated by the integral (6). In this paper the h-line profile for crystallites of general shape will be derived by an asymptotic expansion with respect to the crystal size. Then the validity of the asymptotic estimation will be examined.

2. Exact calculation of h-line profile

According to the theory by Ino & Minami (1979), the diffraction intensity from a small crystal with a particular size and shape is properly expressed as a sum over the reciprocal-lattice vectors $\mathbf{h}$:

$$I(\mathbf{b}) = \sum_\mathbf{h} I_\mathbf{h}(\mathbf{b}), \qquad (13)$$

$$I_\mathbf{h}(\mathbf{b}) = (1/V_c^2)|F(\mathbf{b}, \mathbf{h})|^2$$
$$\times \int \mathcal{V}(\mathbf{r}) \exp[2\pi i(\mathbf{b} - \mathbf{h})\mathbf{r}] \, d\mathbf{r}, \qquad (14)$$

with

$$F(\mathbf{b}, \mathbf{h}) = \sum_\alpha f_\alpha(\mathbf{b}) \exp(2\pi i \mathbf{h} \mathbf{r}_\alpha), \qquad (15)$$

where $\mathbf{r}_\alpha$ and f_α are the position vector and the atomic scattering factor of the αth atom in the unit cell, respectively, and $\mathcal{V}(\mathbf{r})$ is the self-convolution of the shape function of the $s(\mathbf{r})$, i.e.

$$V(\mathbf{r}) = \int s(\mathbf{r}')s(\mathbf{r}' + \mathbf{r}) \, d\mathbf{r}', \qquad (16)$$

$$s(\mathbf{r}) = \begin{cases} 1 & \text{inside the crystal boundary} \\ 0 & \text{outside the crystal boundary.} \end{cases} \qquad (17)$$

If a polycrystalline sample can be considered to consist of the crystals oriented at random, the h-line intensity profile $I_\mathbf{h}(b)$ can be obtained by the integration of (1). As far as the atomic scattering factors can be regarded as spherically symmetric, $I_\mathbf{h}(b)$ can be expressed as

$$I_\mathbf{h}(b) = (1/V_c)^2|F(b, \mathbf{h})|^2$$
$$\times \int \mathcal{V}(\mathbf{r}) \exp(-2\pi i \mathbf{h} \mathbf{r}) \sin(2\pi b r)/(2\pi b r) \, d\mathbf{r}. \qquad (18)$$

In the case of a spherical crystal with diameter D,

$$\mathcal{V}(\mathbf{r}) = V_t \left\{ 1 - \frac{3r}{2D} + \frac{1}{2}\left(\frac{r}{D}\right)^3 \right\}, \qquad (19)$$

where V_t is the volume of the crystallite, and the intensity profile is given by an analytical formula

$$I_\mathbf{h}(b) = \left(\frac{V_t}{V_c}\right)|F(b, \mathbf{h})|^2 \frac{3D}{16\pi|\mathbf{h}|bV_c} \{G(x_-) - G(x_+)\}, \qquad (20)$$

where

$$G(x) = x^{-2}\left\{ 1 - \frac{\sin(2x)}{x} + \frac{\sin^2 x}{x^2} \right\} \qquad (21)$$

which is equivalent to (11).

3. Asymptotic estimation of h-line profile

Besides the crystal defined by $s(\mathbf{r})$, let us consider a standard object with unit volume and with the shape similar to the crystal, and assume that the former crystal is p times as large as the object. Hereafter p will be referred to as the 'crystal size'. Let the function of the shape and its self-convolution for the object be σ and v, and we obtain relations between σ and s, and between v and $\mathcal{V}$ as follows:

$$s(\mathbf{r}) = \sigma(\mathbf{r}/p) \qquad (22)$$

and

$$\mathcal{V}(\mathbf{r}) = p^3 v(\mathbf{r}/p). \qquad (23)$$

Substituting the v for $\mathcal{V}$ in (18) and introducing a new variable $\mathbf{x} = \mathbf{r}/p$, we obtain

$$I_\mathbf{h}(b) = |F(b, \mathbf{h})|^2 (V_t/V_c)(p^3/V_c)$$
$$\times \int v(\mathbf{x}) \exp(-2\pi i p|\mathbf{h}|x) \frac{\sin(2\pi pbx)}{2\pi pbx} \, d\mathbf{x}. \qquad (24)$$

Effects of the shape and the size on the diffraction profile may be estimated by $v(\mathbf{x})$ and p in (24), respectively. With such polar coordinates (x, θ, φ) that the polar axis is directed parallel to $\mathbf{h}$, (24) is rewritten as

$$I_{\mathbf{h}}(b) = |F(b, \mathbf{h})|^2 \left(\frac{V_t}{V_c}\right) \frac{p^2}{2\pi b |\mathbf{h}| V_c} \int_0^\infty dx \int_0^{2\pi} d\varphi$$

$$\times \int_0^\pi d\theta \, v_{\mathbf{h}}(x\theta\varphi) \exp\left(-2\pi i p |\mathbf{h}| x \cos\theta\right)$$

$$\times x \sin(2\pi pbx) \sin\theta, \quad (25)$$

where $v_{\mathbf{h}}(x\theta\varphi)$ corresponds to the version of $v(\mathbf{x})$ in (24). Using the relationship $v_{\mathbf{h}}(x, \pi - \theta, \pi + \varphi) = v_{\mathbf{h}}(x\theta\varphi)$ and introducing a variable $\xi = x(b - |\mathbf{h}| \cos\theta)$, we can transform (25) to the integral over $(x\xi\varphi)$.

$$I_{\mathbf{h}}(b) = |F(b, \mathbf{h})|^2 \left(\frac{V_t}{V_c}\right)$$

$$\times \frac{p^2}{2\pi b |\mathbf{h}| V_c} \iint G_{\mathbf{h}}(x, \varphi; p) \, dx \, d\varphi, \quad (26)$$

with

$$G_{\mathbf{h}}(x, \varphi; p) = \int_{\xi_-}^{\xi_+} w_{\mathbf{h}}[x, \theta(\xi, x), \varphi] \sin(2\pi p\xi) \, d\xi, \quad (27)$$

where

$$w_{\mathbf{h}}(x\theta\varphi) = \tfrac{1}{2}\{v_{\mathbf{h}}(x\theta\varphi) + v_{\mathbf{h}}(x, \theta, \pi + \varphi)\} \quad (28)$$

and

$$\xi_\pm = x(b \pm |\mathbf{h}|). \quad (29)$$

By use of Heaviside's unit function $H(\xi)$, (27) can be further transformed as

$$G_{\mathbf{h}}(x, \varphi; p) = \int_{-\infty}^\infty g_{\mathbf{h}}(x, \varphi; \xi) \sin(2\pi p\xi) \, d\xi, \quad (30)$$

with

$$g_{\mathbf{h}}(x, \varphi; \xi) = H(\xi - \xi_-) H(\xi_+ - \xi) w_{\mathbf{h}}[x, \theta(x, \xi), \varphi]. \quad (31)$$

$g_{\mathbf{h}}(x, \varphi; \xi)$ has singularities at $\xi = \xi_-$ and $\xi = \xi_+$ corresponding to $\theta = 0$ and $\theta = \pi$ and near each singularity it can be expressed as follows:

near $\xi = \xi_-$,

$$g_{\mathbf{h}} = w_{\mathbf{h}}(x0\varphi) H(\xi - \xi_-)$$

$$+ \left(\frac{2}{x|\mathbf{h}|}\right)^{1/2} \frac{\partial w_{\mathbf{h}}(x0\varphi)}{\partial\theta} |\xi - \xi_-|^{1/2} H(\xi - \xi_-)$$

$$+ \frac{1}{x|\mathbf{h}|} \frac{\partial^2 w_{\mathbf{h}}(x0\varphi)}{\partial\theta^2} |\xi - \xi_-| H(\xi - \xi_-)$$

$$+ o(|\xi - \xi_-|); \quad (32)$$

near $\xi = \xi_+$,

$$g_{\mathbf{h}} = w_{\mathbf{h}}(x\pi\varphi) H(\xi_+ - \xi)$$

$$- \left(\frac{2}{x|\mathbf{h}|}\right)^{1/2} \frac{\partial w_{\mathbf{h}}(x\pi\varphi)}{\partial\theta} |\xi_+ - \xi|^{1/2} H(\xi_+ - \xi)$$

$$+ \frac{1}{x|\mathbf{h}|} \frac{\partial^2 w_{\mathbf{h}}(x\pi\varphi)}{\partial\theta^2} |\xi_+ - \xi| H(\xi_+ - \xi)$$

$$+ o(|\xi_+ - \xi|). \quad (33)$$

According to the theorem on Fourier integrals in § 4.3 of the book by Lighthill (1958), Fourier sine transforms of type (27) or (30) can be asymptotically expanded with respect to the size parameter p:

$$G_{\mathbf{h}} = \frac{1}{2\pi p}\{w_{\mathbf{h}}(x0\varphi) \cos 2\pi p\xi_- - w_{\mathbf{h}}(x\pi\varphi) \cos 2\pi p\xi_+\}$$

$$+ \frac{1}{(2\pi p)^{3/2}} \left(\frac{\pi}{2x|\mathbf{h}|}\right)^{1/2}$$

$$\times \left\{\frac{\partial w_{\mathbf{h}}(x0\varphi)}{\partial\theta} \sin\left(2\pi p\xi_- + \frac{3}{4}\pi\right)\right.$$

$$\left. - \frac{\partial w_{\mathbf{h}}(x\pi\varphi)}{\partial\theta} \sin\left(2\pi p\xi_+ - \frac{3}{4}\pi\right)\right\}$$

$$- \frac{1}{(2\pi p)^2} \frac{1}{x|\mathbf{h}|} \left\{\frac{\partial^2 w_{\mathbf{h}}(x0\varphi)}{\partial\theta^2} \sin 2\pi p\xi_-\right.$$

$$\left. + \frac{\partial^2 w_{\mathbf{h}}(x\pi\varphi)}{\partial\theta^2} \sin 2\pi p\xi_+\right\} + o(1/p^2), \quad (34)$$

by use of the following formulas.

$$\int H(\xi - \xi_-) \sin 2\pi p\xi \, d\xi = \cos(2\pi p\xi_-)/(2\pi p),$$

$$\int H(\xi_+ - \xi) \sin 2\pi p\xi \, d\xi = -\cos(2\pi p\xi_+)/(2\pi p)$$

$$\int |\xi - \xi_-|^{1/2} H(\xi - \xi_-) \sin 2\pi p\xi \, d\xi$$

$$= \frac{\pi^{1/2}}{2} \frac{1}{(2\pi p)^{3/2}} \sin(2\pi p\xi_- + \tfrac{3}{4}\pi),$$

$$\int |\xi_+ - \xi|^{1/2} H(\xi_+ - \xi) \sin 2\pi p\xi \, d\xi$$

$$= \frac{\pi^{1/2}}{2} \frac{1}{(2\pi p)^{3/2}} \sin(2\pi p\xi_+ - \tfrac{3}{4}\pi),$$

$$\int |\xi - \xi_-| H(\xi - \xi_-) \sin 2\pi p\xi \, d\xi$$

$$= -\sin(2\pi p\xi_-)/(2\pi p)^2,$$

$$\int |\xi_+ - \xi| H(\xi_+ - \xi) \sin 2\pi p\xi \, d\xi$$

$$= -\sin(2\pi p\xi_+)/(2\pi p)^2.$$

Since $w_h(x\pi\varphi) = w_h(x0\varphi) = v_h(x00)$,

$$\int_0^{2\pi} \frac{\partial w_h(x\pi\varphi)}{\partial\theta}\,d\varphi = -\int_0^{2\pi} \frac{\partial w_h(x0\varphi)}{\partial\theta}\,d\varphi$$

$$= -\int_0^{2\pi} \frac{\partial v_h(x0\varphi)}{\partial\theta}\,d\varphi$$

and

$$\int_0^{2\pi} \frac{\partial^2 w_h(x\pi\varphi)}{\partial\theta^2}\,d\varphi = \int_0^{2\pi} \frac{\partial^2 w_h(x0\varphi)}{\partial\theta^2}\,d\varphi$$

$$= \int_0^{2\pi} \frac{\partial^2 v_h(x0\varphi)}{\partial\theta^2}\,d\varphi.$$

Finally, (26) turns out to be

$$I_h(b) = |F(b, \mathbf{h})|^2 \left(\frac{V_t}{V_c}\right)\frac{p}{2\pi b|\mathbf{h}|V_c}$$

$$\times \left\{ J_1 + \frac{1}{(p|\mathbf{h}|)^{1/2}}J_2 + \frac{1}{p|\mathbf{h}|}J_3 + o\left(\frac{1}{p}\right) \right\} \quad (35)$$

with

$$J_1 = \int_0^{x_h} v_h(x00)\{\cos 2\pi px(b - |\mathbf{h}|)$$

$$- \cos 2\pi px(b + |\mathbf{h}|)\}\,dx \quad (35')$$

$$J_2 = \frac{1}{2}\int_0^{x_h} \frac{1}{x^{1/2}} v_{h\theta}(x)\{\sin[2\pi px(b - |\mathbf{h}|) + \tfrac{3}{4}\pi]$$

$$+ \sin[2\pi px(b + |\mathbf{h}|) - \tfrac{3}{4}\pi]\}\,dx \quad (35'')$$

and

$$J_3 = -\frac{1}{2\pi}\int_0^{x_h} \frac{1}{x} v_{h\theta\theta}(x)\{\sin 2\pi p(b - |\mathbf{h}|)x$$

$$+ \sin 2\pi p(b + |\mathbf{h}|)x\}\,dx \quad (35''')$$

where x_h is the value of x for which $v_h(x00)$ vanishes and

$$v_{h\theta}(x) = \int_0^{2\pi} \frac{\partial v_h(x0\varphi)}{\partial\theta}\frac{d\varphi}{2\pi}, \quad (36)$$

$$v_{h\theta\theta}(x) = \int_0^{2\pi} \frac{\partial^2 v_h(x0\varphi)}{\partial\theta^2}\frac{d\varphi}{2\pi}. \quad (37)$$

Equation (35) is an asymptotic expression with respect to the crystal size p and it turns out that integrals J_1, J_2 and J_3 contribute toward the intensity

profile $I_h(b)$ with their weights proportional to $1, 1/(p|\mathbf{h}|)^{1/2}$ and $1/(p|\mathbf{h}|)$, respectively. Hence, for a large crystallite whose p is large, one may approximate $I_h(b)$ only by the first term of (35), but for a small crystallite whose p is small, the second term and third term should be taken into account.

4. h-line profile for parallelepiped crystal

Let us consider the parallelepiped crystals mentioned in § 1. The function $\mathscr{V}(\mathbf{r})$ in (23) is given as

$$\mathscr{V}(\mathbf{r}) = V_c \prod_{j=1}^3 (N_j - |r_j|), \quad (38)$$

where

$$\mathbf{r} = \sum_{j=1}^3 r_j\mathbf{a}_j.$$

As derived in Appendix A† $v_h(x00)$, $v_{h\theta}(x)$ and $v_{h\theta\theta}(x)$ are given as follows:

$$v_h(x00) = \prod_{j=1}^3 (1 - t_j|\beta_j|x) \quad (39)$$

with

$$t_j = p/N_j, \text{ and } \beta_j = \mathbf{h}\mathbf{a}_j^*/|\mathbf{h}|,$$

$$v_{h\theta}(x) = -xv_h(x00)\sum_{j=1}^3 q_j \quad (40)$$

with

$$q_j = \begin{cases} (2/\pi)t_j|\mathbf{a}_j^*| & \text{if } \mathbf{h}\perp\mathbf{a}_j^* \\ 0 & \text{otherwise,} \end{cases} \quad (41)$$

and

$$v_{h\theta\theta}(x) = x\sum_{(jkl)} t_j|\beta_j|(1 - t_k|\beta_k|x)(1 - t_l|\beta_l|x) + x^2 Y, \quad (42)$$

where $\sum_{(jkl)}$ means a sum over $(jkl) = (123)$, (231), (312), and Y are given as follows:

$$Y = \begin{cases} \dfrac{2}{\pi}(1 - t_1|\beta_1|x)t_2t_3\left\{ A_{23}\sin^{-1}\dfrac{A_{23}}{(A_{22}A_{33})^{1/2}} + |B| \right\}, \\ \qquad\qquad \text{for } \beta_1 \neq 0, \beta_2 = \beta_3 = 0, \\ t_1t_2\,\text{sgn}\,(\beta_1\beta_2)A_{12}, \\ \qquad\qquad \text{for } \beta_1 \neq 0, \beta_2 \neq 0, \beta_3 = 0, \quad (43) \\ \displaystyle\sum_{(jkl)} t_jt_k(1 - t_l|\beta_l|x)\,\text{sgn}\,(\beta_j\beta_k)A_{jk}, \\ \qquad\qquad \text{for } \beta_1 \neq 0, \beta_2 \neq 0, \beta_3 \neq 0, \end{cases}$$

with

$$A_{jk} = \mathbf{a}_j^* \mathbf{a}_k^* - \beta_j \beta_k \qquad (44)$$

and

$$B = h_1 / (|\mathbf{h}| V_c). \qquad (45)$$

We can derive the **h**-line profile of small parallelepiped crystallites by substituting (39), (40), (42) into (35'), (35''), (35''') and integrating them over x from 0 to $x_\mathbf{h}$, which is the smallest value in $(t_1 |\beta_1|)^{-1}$, $(t_2 |\beta_2|)^{-1}$ and $(t_3 |\beta_3|)^{-1}$.

For example, let us calculate the **h**-line profile $(h_1 \geq h_2 \geq h_3 \geq 0)$ for a cubic crystal (lattice constant a) with the shape of a cube whose edges are parallel to the axes of the crystal. Since $\mathbf{a}_j^* = \mathbf{a}_j / a^2$, $t_j = a$, $\beta_j = h_j / (ha)$, $x_\mathbf{h} = h / h_1$, where

$$h = (h_1^2 + h_2^2 + h_3^2)^{1/2}, \qquad (46)$$

then

$$v_\mathbf{h}(x00) = \prod_{j=1}^{3} (1 - h_j x / h), \qquad (47)$$

$$v_{\mathbf{h}\theta}(x) = \begin{cases} -\dfrac{4}{\pi} x(1-x), & \text{for } h_1 > 0,\ h_2 = h_3 = 0, \\[2mm] -\dfrac{2}{\pi} x(1 - h_1 x / h)(1 - h_2 x / h), \\[2mm] & \text{for } h_1 \geq h_2 > 0,\ h_3 = 0, \\[2mm] 0, & \text{for } h_1 \geq h_2 \geq h_3 > 0 \end{cases} \qquad (48)$$

and

$$v_{\mathbf{h}\theta\theta}(x) = \begin{cases} x\left\{ 1 - \dfrac{2x(1-x)}{\pi} \right\}, & \text{for } h_1 > 0,\ h_2 = h_3 = 0, \\[2mm] (h_1 + h_2) x / h - 3 h_1 h_2 x^2 / h^2, \\[2mm] & \text{for } h_1 \geq h_2 > 0,\ h_3 = 0, \\[2mm] (h_1 + h_2 + h_3) x / h \\[1mm] \quad - 3(h_1 h_2 + h_2 h_3 + h_3 h_1) x^2 / h^2 \\[1mm] \quad + 6 h_1 h_2 h_3 x^3 / h^3, & \text{for } h_1 \geq h_2 \geq h_3 > 0; \end{cases} \qquad (49)$$

J_1 and J_3 can be integrated analytically, while J_2 can be easily computed by a numerical integration. The intensities of $\mathbf{h} = (100)$, (110) and (111) for a cubic crystal with cubic shape containing 100 unit cells were computed by the asymptotic formulas. In order to examine the validity of the asymptotic forms, the exact intensities expressed by a double integral in Appendix B^* were computed by using the IBM4300 computer of the Computer Center of Kinki Univer-

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* See deposition footnote.

sity. Fig. 1 shows the plots of

$$b|\mathbf{h}| I_\mathbf{h}(b) / |F(b, \mathbf{h})|^2 (V_i / V_c)$$

versus ba for the asymptotic estimation and the exact calculation, and their differences multiplied by five.
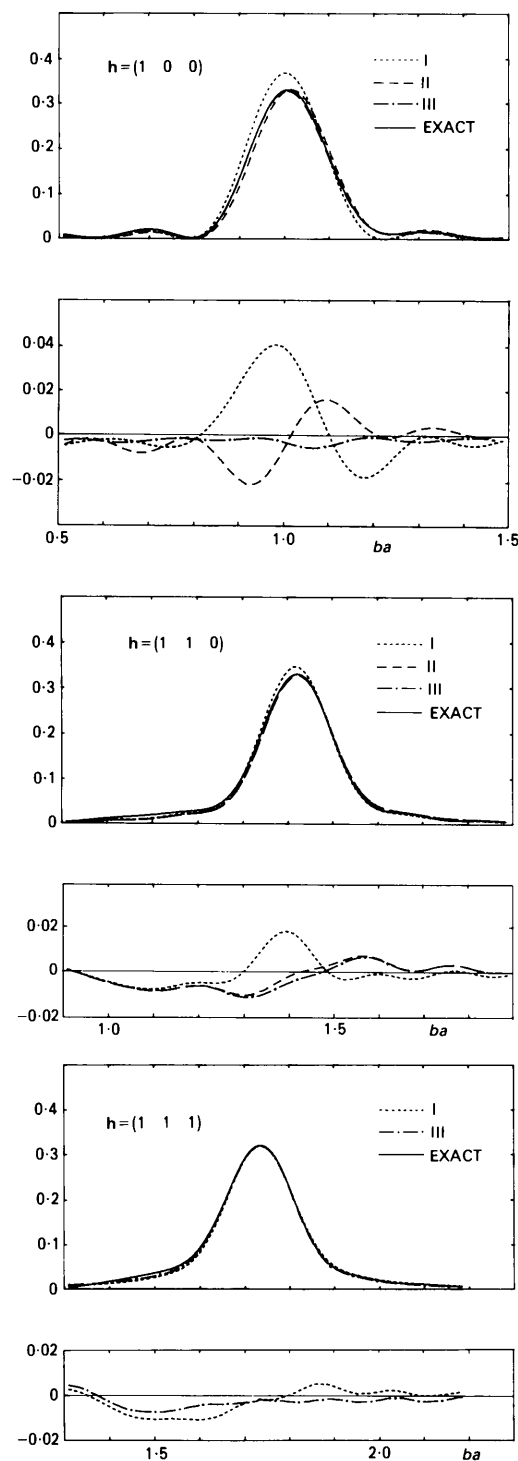

Fig. 1. Plots of $b|\mathbf{h}| I_\mathbf{h}(b) / |F(b, \mathbf{h})|^2 (V_i / V_c)$ *versus ba* for a cubic crystal with cubic shape containing 100 cells.

Their three kinds of asymptotic estimations, (I) including only the J_1 term, (II) including J_1 and J_2 terms and (III) including the three terms in (35), are plotted by dotted, broken and dot-dash lines, respectively, and the exact calculation by a solid line. In the case of the (100)-line profile, the estimation (I) does not give a good approximation near the peak, but the J_2 term improves the peak height and the estimation (III) gives almost the exact intensity. For the (110) profile the second term of the asymptotic expansion advances the approximation similarly to the case of the (100) line, but the third term is ineffective. For the (111) profile, since the second term vanishes and the third term is a small value, then the first term gives a good approximation.

5. Conclusion

Converting x and $v_\mathbf{h}(x\theta\varphi)$ in (35')–(35''') into r and $\mathscr{V}_\mathbf{h}(r\theta\varphi)$, respectively, according to (23), we obtain a formula which does not contain explicitly the size parameter p:

$$I_\mathbf{h}(b) = |F(b, \mathbf{h})|^2 \frac{1}{2\pi b |\mathbf{h}| V_c^2}$$

$$\times \{I_1 + I_2 + I_3 + o(V_t)\}, \qquad (50)$$

with

$$I_1 = \int_0^{r_\mathbf{h}} V_\mathbf{h}(r)[\cos\{2\pi(b-|\mathbf{h}|)r\}$$

$$- \cos\{2\pi(b+|\mathbf{h}|)r\}] \, dr, \qquad (50')$$

$$I_2 = \frac{1}{2|\mathbf{h}|^{1/2}} \int_0^{r_\mathbf{h}} \frac{V_{\mathbf{h}\theta}(r)}{r^{1/2}}[\sin\{2\pi(b-|\mathbf{h}|)r + \tfrac{3}{4}\pi\}$$

$$+ \sin\{2\pi(b+|\mathbf{h}|)r - \tfrac{3}{4}\pi\}] \, dr, \qquad (50'')$$

and

$$I_3 = \frac{1}{2\pi|\mathbf{h}|} \int_0^{r_\mathbf{h}} \frac{V_{\mathbf{h}\theta\theta}(r)}{r}[\sin\{2\pi(b-|\mathbf{h}|)r\}$$

$$+ \sin\{2\pi(b+|\mathbf{h}|)r\}] \, dr, \qquad (50''')$$

where

$$V_\mathbf{h}(r) = \mathscr{V}_\mathbf{h}(r00), \qquad (51)$$

$$V_{\mathbf{h}\theta}(r) = \int_0^{2\pi} \frac{\partial \mathscr{V}_\mathbf{h}(r0\varphi)}{\partial \theta} \, d\varphi/2\pi, \qquad (52)$$

$$V_{\mathbf{h}\theta\theta}(r) = \int_0^{2\pi} \frac{\partial^2 \mathscr{V}_\mathbf{h}(r0\varphi)}{\partial \theta^2} \, d\varphi/2\pi. \qquad (53)$$

For large crystallites $I_\mathbf{h}(b)$ can be well approximated

by the first term only of (50), but for small crystallites more terms should be taken into account as mentioned in § 3.

6. Discussion

Instead of $I(\mathbf{b})$ in (13), which is the most proper expression for a bounded small crystal, let us consider the term $I_e(\mathbf{b})$ previously discussed (Ino & Minami 1979) as follows:

$$I_e(\mathbf{b}) = \sum_\mathbf{h} I_\mathbf{h}^e(\mathbf{b})$$

with

$$I_\mathbf{h}^e(\mathbf{b}) = (1/V_c)^2/|F(\mathbf{h})|^2$$

$$\times \int \mathscr{V}(\mathbf{r}) \exp[2\pi i(\mathbf{b}-\mathbf{h})\mathbf{r}] \, d\mathbf{r}. \qquad (54)$$

Since (54) is obtained by replacing $F(\mathbf{b}, \mathbf{h})$ in (14) by $F(\mathbf{h})$, the asymptotic expansion of the $\mathbf{h}$-line profile can be readily derived by the substitution of $F(\mathbf{h})$ into $F(\mathbf{b}, \mathbf{h})$ in (50):

$$I_\mathbf{h}^e(b) = |F(\mathbf{h})|^2 \frac{1}{2\pi b |\mathbf{h}| V_c^2}\{I_1 + I_2 + I_3 + o(V_t)\}. \qquad (55)$$

Substituting $I_\mathbf{h}^e(\mathbf{b})$ into $I_\mathbf{h}(\mathbf{b})$ of (6), one can derive the tangent plane approximation of $I_\mathbf{h}^e(b)$:

$$I_\mathbf{h}^e(b) \simeq \frac{|F(\mathbf{h})|^2}{4\pi b^2 V_c^2} \int \mathscr{V}(\mathbf{r}) \exp(-2\pi i \mathbf{h}\mathbf{r})$$

$$\times \left\{\int\int \exp(2\pi i \mathbf{b}\mathbf{r}) \, db_1' \, db_2'\right\} d\mathbf{r}. \qquad (56)$$

Since

$$\int\int \exp(2\pi i \mathbf{b}\mathbf{r}) \, db_1' \, db_2' = \exp(2\pi i b r_3')\delta(r_1')\delta(r_2'),$$

where (r_1', r_2') are coordinates on the tangent plane and r_3' is a coordinate parallel to the $\mathbf{h}$ direction, it can be proved that (56) is identical with the Wilson formula (12). Compared with (55), his formula (12) appears to be a modification of the first term in (55), such that the term $1/(2\pi b|\mathbf{h}|)$ in (55) is changed into $1/2\pi b^2$ and the term $\cos\{2\pi(b+|\mathbf{h}|)r\}$ in (50')
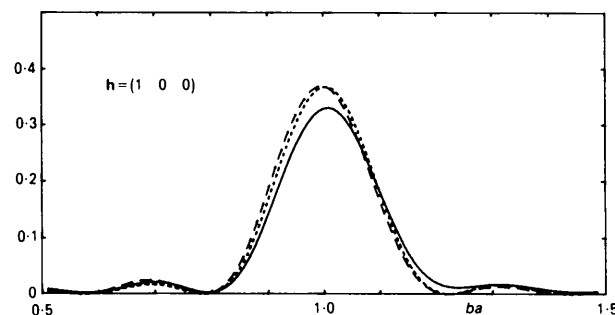

Fig. 2. Plots of $b|\mathbf{h}|I_\mathbf{h}(b)/|F(\mathbf{h})|^2(V_t/V_c)$ versus ba for the first term of (55) (dotted line), Wilson's formula (broken line) and the exact intensity (solid line) from the same crystal as used in Fig. 1.

vanishes. Fig. 2 shows a comparison of the first term of (55) with Wilson's formula. They agree well with each other, especially for $b > |\mathbf{h}|$. Consequently, Wilson's formula is almost the same as the first term of the asymptotic expression of $I_\mathbf{h}(b)$ in (55), which is not as correct as $I_\mathbf{h}(b)$ of (13), and hence Wilson's formula gives a poor approximation as the crystal size decreases.

For a spherical crystallite, since $V_\mathbf{h}(r) = V_t\{1 - 3r/2D + \frac{1}{2}(r/D)^3\}$, (19), and $V_{\mathbf{h}\theta}(r) = V_{\mathbf{h}\theta\theta}(r) = 0$, (50) agrees with the exact form (20). As shown for a cubic crystallite in Fig. 1, the asymptotic expression (50) gives an excellent agreement with the exact

intensity. It can be concluded that the intensity profile can be exactly calculated by the asymptotic expansion including three single integrals, which can be calculated as easily as the Wilson's formula.

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A Simple Interpretation of Integrated Direct Methods – Isomorphous Replacement Probability Distributions

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Abstract

Integrated direct methods – isomorphous probability distributions [Hauptman (1982). *Acta Cryst.* A38, 289–294] are interpreted in terms of the familiar parameters of the isomorphous replacement method, the diffraction ratio and the differences in the diffraction intensities of a native protein and its heavy-atom derivative. The analysis shows that the reliability of the phase estimates is a function of the degree of heavy-atom substitution in the derivative. It clearly pinpoints the most favorable conditions for retrieving phase information from the intensity data of an isomorphous pair of structures. Finally, it provides a means to determine *a priori* the overall reliability of the phase estimates and to design the calculations accordingly.

1. Introduction

Crystallographic studies of molecular structures have been traditionally divided into two groups, those of macromolecules and those of small molecules. Although the central problem of any crystal structure

determination, the so-called phase problem, is shared by both groups, the techniques developed in the pursuit of a solution to this problem have followed significantly different courses. Bearing in mind the intrinsic differences between the two groups, it has nevertheless been felt, in the last few years, that the expertise acquired in both fields, when properly integrated, could strengthen the present methods of structure determination, whether applied to small or large molecules. The theoretical basis of integrated direct methods – isomorphous replacement techniques has been introduced recently (Hauptman, 1982). The distributions, although presented in a form suitable for computation, are rather complex and impermeable to straightforward interpretation in terms of the diffraction experiment performed. In the present paper we wish to show how a form of the distributions, in terms of the experimental parameters, can be obtained easily through simple mathematical manipulations. The gains from such an exercise are twofold. Not only can we acquire a better understanding of the behavior and scope of the distributions but we can also gain valuable information on how to improve the experiment.