

is

$$f_h(h) = \exp(-h) \exp(-\alpha^2) \times \sum_{m=0}^{\infty} \varepsilon_m (-1)^m I_m(\alpha^2 h) I_{2m}(2\alpha h^{1/2}). \quad (4.19)$$

These series converge rapidly because  $\alpha$  has such a small magnitude.

The results of some numerical computations are shown in Fig. 2. The solid curve corresponds to the

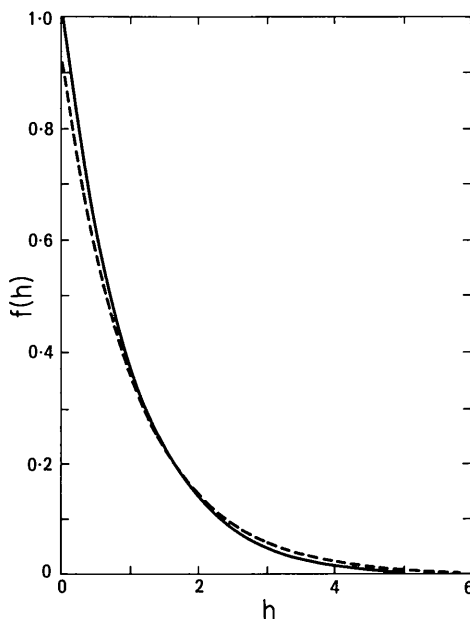


Fig. 2. Probability density function of the normalized scattered intensity, equation (4.19), for  $\alpha = 0$  (solid curve),  $\alpha = 0.3$  (broken curve).

negative exponential PDF

$$f_h(h) = \exp(-h) \quad (4.20)$$

which would arise when  $\alpha = 0$ . Even for the unrealistically large value of  $\alpha = 0.3$  (dotted curve), the PDF is only a minor perturbation of the negative exponential.

This suggests that we seek a simpler version of  $f_h(h)$  consistent with the fact that  $\alpha$  is small. To this end we employ the usual power-series expansion of the modified Bessel functions. We can easily show that

$$f_h(h) \approx (1 + \alpha^2)^{-1} \exp(-h)(1 + \alpha^2 h) \quad (4.21)$$

is an excellent approximation to (4.19) when  $\alpha$  is very small. In fact, if  $\alpha = 0.2$ , then (4.21) differs from (4.19) by less than 0.1%. This result is not surprising; after all, when  $\beta$  is small, then  $\langle U \rangle \approx 0$  in relation to  $\langle U^2 \rangle$ . The probability density function of the sum of the squares of two Gaussian distributed random variables, where first moments vanish and second moments are equal, is known to have a negative exponential probability density function.

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## Diffraction Profile from Small Crystallites with Anisotropic Temperature Factor

BY K. MIURA AND T. INO

*Department of Physics, Osaka City University, Osaka, Japan*

AND N. MINAMI

*Department of Physics, Kinki University, Osaka, Japan*

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### Abstract

The diffraction intensity from small crystallites with lattice vibrations is expressed by a sum over direct-lattice points as previously described, using atomic scattering factors modified by the anisotropic vibration tensor  $\beta$  specified by the lattice vibration, the

thermal diffuse scattering not being taken into account. Since the temperature factor for the atomic pair of the  $\alpha$ th and  $\beta$ th atoms is  $\beta_\alpha + \beta_\beta$ , the factor is proved to have the same rotation symmetry as the Laue symmetry corresponding to the atomic distance vector of the pair,  $\mathbf{r}_{\alpha\beta} = \mathbf{r}_\alpha - \mathbf{r}_\beta$ . Consequently the intensity profile for the crystallites with lattice

vibrations can be systematically and effectively calculated similarly to the crystallites without vibrations by virtue of the Laue symmetry, while an orientational average over the scattering vector  $\mathbf{b}$  of  $\exp[-\tilde{\mathbf{b}}(\beta_\alpha + \beta_\beta)\mathbf{b} + 2\pi i\mathbf{b} \cdot \mathbf{r}_{\alpha\beta}]$  is required instead of  $\exp(2\pi i\mathbf{b} \cdot \mathbf{r}_{\alpha\beta})$ . The double integral for the average can be expanded asymptotically with respect to  $\mathbf{r}_{\alpha\beta}$  to the third term by Fourier integral theory. It is concluded that (1) the first term corresponds to the formula derived by James [*Phys. Z.* (1932). 33, 737-754] and gives the correct value only if the vibration tensor is isotropic; (2) the second and third terms are required to correct for the anisotropy of the tensor.

## 1. Introduction

The diffraction intensity from a small crystal without lattice vibrations is given by Ino & Minami (1979) by the use of the 'random shift treatment' as follows:

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

where  $\mathbf{b}$  is the scattering vector,  $\mathbf{m}$  is the position vector of the Bravais-lattice point, and  $f_{\alpha}$  and  $\mathbf{r}_{\alpha}$  are the atomic scattering factor and the position vector of the  $\alpha$ th atom in the unit cell of the crystal respectively. In the above equation  $V_c$  is the unit-cell volume and  $V(\mathbf{r})$  denotes the self-convolution of the shape function  $s(\mathbf{r})$  for the crystal, that is

$$V(\mathbf{r}) = \int s(\mathbf{r}')s(\mathbf{r}' + \mathbf{r}) d\mathbf{r}', \quad (2)$$

$$s(\mathbf{r}) = \begin{cases} 1 & \text{inside the crystal boundary} \\ 0 & \text{outside the crystal boundary.} \end{cases} \quad (3)$$

A real crystal has an anisotropic thermal vibration specified by a vibration tensor  $\beta$ , which is usually determined by the least-squares method in crystal structure analysis. In this paper the diffraction profile from small crystallites with anisotropic thermal vibration will be discussed and it will be shown that the profile can be expressed by an asymptotic expansion with respect to  $|\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|$  and the formula of the intensity profile can be systematically and efficiently computed using the Laue-symmetry of the crystal.

## 2. Formula of intensity profile from crystallites with lattice vibrations

### (i) Atomic scattering factor modified by lattice vibrations

The effect of anisotropic thermal vibrations on the atomic scattering factor has been studied (Cochran, 1954) and it has been shown that the dynamic scattering factor  $\tilde{f}(\mathbf{b})$  is given by

$$\tilde{f}(\mathbf{b}) = f(\mathbf{b}) \exp(-\tilde{\mathbf{b}}\beta\mathbf{b}), \quad (4)$$

where  $f(\mathbf{b})$  is the atomic scattering factor of the atom

at rest and  $\beta/2\pi^2$  is the covariance matrix of the thermal displacement. In ordinary crystal structure analysis, the thermal diffuse scattering being neglected, the following structure factor is used (Jeffery, 1971):

$$F(\mathbf{h}) = \sum_{\alpha}^{uc} f_{\alpha}(\mathbf{h}) \exp(-\tilde{\mathbf{h}}\beta_{\alpha}\mathbf{h}) \exp(2\pi i\mathbf{h} \cdot \mathbf{r}_{\alpha}), \quad (5)$$

where  $\beta_{\alpha}$  is called the vibration tensor of the  $\alpha$ th atom and  $\sum_{\alpha}^{uc}$  means the sum over atoms in the unit cell.

### (ii) Formula for the intensity profile

The diffraction intensity from a small crystal with lattice vibrations can be expressed by replacing  $f(\mathbf{b})$  with  $\tilde{f}(\mathbf{b})$  in (1) except for  $\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta} = 0$ , as follows:

$$I(\mathbf{b}) = \frac{V_t}{V_c} \sum_{\alpha} f_{\alpha}^2(\mathbf{b}) + \frac{1}{V_c} \sum_{\substack{\mathbf{m} \\ (\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta} \neq 0)}} \sum_{\alpha} \sum_{\beta} f_{\alpha}(\mathbf{b}) f_{\beta}(\mathbf{b}) \times \exp[-\tilde{\mathbf{b}}(\beta_{\alpha} + \beta_{\beta})\mathbf{b}] V(\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta}) \times \exp[2\pi i\mathbf{b} \cdot (\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta})], \quad (6)$$

where  $V_t$  is the total volume of the crystal. If a polycrystalline sample consists of small crystals having shape function  $s(\mathbf{r})$  and oriented at random, the intensity from the sample is given as an average of (6) over the directions of the scattering vector  $\mathbf{b}$ . As the atomic scattering factors can be regarded as being spherically symmetric, the intensity from the polycrystal is given by

$$I(b) = \frac{V_t}{V_c} \sum_{\alpha} f_{\alpha}^2(b) + \frac{1}{V_c} \sum_{\substack{\mathbf{m} \\ (\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta} \neq 0)}} \sum_{\alpha} \sum_{\beta} f_{\alpha}(b) f_{\beta}(b) \times V(\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta}) \langle \exp[-\tilde{\mathbf{b}}(\beta_{\alpha} + \beta_{\beta})\mathbf{b}] \times \exp[2\pi i\mathbf{b} \cdot (\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta})] \rangle_{\Omega_b}, \quad (7)$$

where  $\langle \rangle_{\Omega_b}$  means an average over the orientations of  $\mathbf{b}$ . If all the atoms in the lattice are at rest, that is  $\beta_{\alpha} = 0$  ( $\alpha = 1, \dots$ ), then  $\langle \dots \rangle_{\Omega_b} = j_0(2\pi b|\mathbf{m} + \mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|)$  and (7) gives the same results obtained in the previous paper (Ino & Minami, 1979). In a similar way to the case without lattice vibrations, the summation procedure over  $\mathbf{m}$ ,  $\alpha$ ,  $\beta$  will be simplified by virtue of the crystal symmetry.

### (iii) Simplification of summation over $(\mathbf{m}, \alpha, \beta)$

Suppose the crystal possesses the symmetry of a space group  $\mathbf{G}$  and a Laue group  $\mathbf{R}$ . Then the set of positions occupied by atoms such as  $\mathbf{m} + \mathbf{r}_{\alpha}$  can be classified into subsets  $P_1, P_2, \dots, P_n$  and the  $P_i$  set is expressed as

$$P_i = \{\mathbf{m} + \mathbf{r}_i^{(t)} | \mathbf{m} \in \Omega, t = 1, \dots, N_i\}, \quad (8)$$

with

$$\mathbf{r}_i^{(t)} = \mathcal{R}_i^{(t)}\mathbf{r}_i + \mathbf{t}_i \quad (t = 1, \dots, N_i) \quad (9)$$

where  $\mathbf{m} \in \Omega$  means that  $\mathbf{m}$  belongs to the whole direct space  $\Omega$ ,  $\mathbf{r}_i$  is a representative positional vector of the set  $P_i$  and  $\mathcal{R}_i^{(t)}$  and  $\mathbf{t}_i$  are the rotational and translational operators of the  $t$ th element in  $\mathbf{G}$  respectively. Let  $\beta_i$  be the vibration tensor for the representative atom at  $\mathbf{r} = \mathbf{r}_i$ , then  $\beta_i^{(t)}$ , the vibration tensor for the atom located at  $\mathbf{r} = \mathbf{r}_i^{(t)}$  is given by

$$\beta_i^{(t)} = \mathcal{R}_i^{(t)} \beta_i \tilde{\mathcal{R}}_i^{(t)}. \quad (10)$$

All distance vectors joining the points in the set  $P_j$  to those in the set  $P_i$  can be classified into vector sets  $D_{ij1}, D_{ij2}, \dots$  such that all the elements in each vector set are equivalent with respect to the symmetry of the Laue group  $\mathbf{R}$  and

$$D_{ijk} = \{\mathbf{m} + \mathbf{r}_{ijk}^{(s)} \mid \mathbf{m} \in \Omega, s = 1, \dots, n_{ijk}\}, \quad (11)$$

where  $\mathbf{r}_{ijk}^{(s)}$  and  $n_{ijk}$  are the equivalent distance vectors and their number in a unit cell, respectively. The  $D_{ijk}$  set can be generated by the operator of  $\mathbf{R}$  from a particular atomic distance vector  $\mathbf{m} + \mathbf{r}_{ijk}^{(s)}$  which is located inside a sectorial subspace  $\Omega_0$  shown in Table 1 of a previous paper (Minami & Ino, 1979):

$$D_{ijk} = \{R_p(\mathbf{m} + \mathbf{r}_{ijk}^{(s)}) \mid R_p \in \mathbf{R}, p = 1, 2, \dots, L\}, \quad (12)$$

with  $\mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0$ . Let  $\mathbf{r}_i^{(u)}$  and  $\mathbf{r}_j^{(v)}$  denote position vectors of the pair of atoms corresponding to the distance vector  $\mathbf{m} + \mathbf{r}_{ijk}^{(s)}$ :

$$\mathbf{r}_{ijk}^{(s)} = \mathbf{r}_i^{(u)} - \mathbf{r}_j^{(v)}, \quad \mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0. \quad (13)$$

Hence the superscripts ( $u$ ) and ( $v$ ) are to be determined by subscript  $ijk$  and  $\mathbf{m}$  under the condition:  $\mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0$ . Thus the summation over  $\mathbf{m}$ ,  $\alpha$  and  $\beta$  in (7) can be rearranged to one over the  $D_{ijk}$  vector sets and then  $\mathbf{m} + \mathbf{r}_\alpha - \mathbf{r}_\beta$  and  $\beta_\alpha + \beta_\beta$  are transformed into  $R_p(\mathbf{m} + \mathbf{r}_{ijk}^{(s)})$  and  $R_p[\beta_i^{(u)} + \beta_j^{(v)}] \tilde{R}_p$  respectively, where  $\beta_i^{(u)}$  and  $\beta_j^{(v)}$  are tensors for atoms corresponding to  $\mathbf{r}_i^{(u)}$  and  $\mathbf{r}_j^{(v)}$ . Thus  $(\dots)_{\Omega_b}$  is transformed into

$$\begin{aligned} & \langle \exp[-\tilde{\mathbf{b}} R_p(\beta_i^{(u)} + \beta_j^{(v)}) \tilde{R}_p \mathbf{b} + 2\pi i \tilde{\mathbf{b}} \cdot R_p(\mathbf{m} + \mathbf{r}_{ijk}^{(s)})] \rangle_{\Omega_b} \\ & = \langle \exp[-\tilde{\mathbf{b}}(\beta_i^{(u)} + \beta_j^{(v)}) \mathbf{b} + 2\pi i \tilde{\mathbf{b}} \cdot (\mathbf{m} + \mathbf{r}_{ijk}^{(s)})] \rangle_{\Omega_b} \end{aligned} \quad (14)$$

because  $|\det(R_p)| = 1$ . Finally, the summation over  $(\mathbf{m}, \alpha, \beta)$  can be simplified to

$$\begin{aligned} I(b) &= \frac{V_t}{V_c} \sum_i f_i^2(b) + \sum_{i \neq j} \sum_k f_i(b) f_j(b) \sum_k J_{ijk}(b), \\ J_{ijk}(b) &= \frac{1}{V_c} w_{ijk} \sum_{\substack{\mathbf{m} \\ (\mathbf{m} + \mathbf{r}_{ijk}^{(s)} \in \Omega_0)}} \sum_{s=1}^{n_{ijk}} n(\mathbf{m} + \mathbf{r}_{ijk}^{(s)}) \tilde{V}(\mathbf{m} + \mathbf{r}_{ijk}^{(s)}) \\ & \quad \times \langle \exp[\tilde{\mathbf{b}}(\beta_i^{(u)} + \beta_j^{(v)}) \mathbf{b}] \\ & \quad \times \exp[2\pi i \tilde{\mathbf{b}} \cdot (\mathbf{m} + \mathbf{r}_{ijk}^{(s)})] \rangle_{\Omega_b}, \end{aligned} \quad (15)$$

with

$$\tilde{V}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} = 0 \\ (1/L) \sum_{p=1}^L V(R_p \mathbf{r}) & \text{otherwise,} \end{cases} \quad (16)$$

where  $w_{ijk}$  is the multiplicity weight for the set  $D_{ijk}$ ,  $n(\mathbf{m} + \mathbf{r}_{ijk})$  is the multiplicity of the  $\mathbf{m} + \mathbf{r}_{ijk}$  vector and  $L$  is the order of the group  $\mathbf{R}$ .

### 3. The asymptotic estimation of $\langle \exp(-\tilde{\mathbf{b}}\beta\mathbf{b}) \exp(2\pi i \tilde{\mathbf{b}} \cdot \mathbf{R}) \rangle_{\Omega_b}$

Let  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  be the unit-cell vectors of the crystal,  $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$  their reciprocal vectors and let us introduce a Cartesian reference system having axes  $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$  with  $\mathbf{e}_3 = \mathbf{R}/R$ . Then the orientational average of  $\langle \exp(-\tilde{\mathbf{b}}\beta\mathbf{b}) \exp(2\pi i \tilde{\mathbf{b}} \cdot \mathbf{R}) \rangle_{\Omega_b}$  is expressed with polar coordinates of  $\mathbf{b}$ ,  $(b, \theta, \varphi)$  [ $\theta = \angle(\mathbf{b}, \mathbf{R})$ ], as

$$\begin{aligned} & \langle \exp(-\tilde{\mathbf{b}}\beta\mathbf{b}) \exp(2\pi i \tilde{\mathbf{b}} \cdot \mathbf{R}) \rangle_{\Omega_b} \\ & = (1/4\pi) \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \\ & \quad \times \exp[-b^2 \beta(\theta, \varphi)] \exp(2\pi i b R \cos \theta) \\ & = Q(b, \beta^*, R) \end{aligned} \quad (17)$$

with

$$\begin{aligned} \beta(\theta, \varphi) &= \beta_{11}^* \sin^2 \theta \cos^2 \varphi + \beta_{22}^* \sin^2 \theta \sin^2 \varphi \\ & \quad + \beta_{33}^* \cos^2 \theta + 2\beta_{12}^* \sin^2 \theta \sin \varphi \cos \varphi \\ & \quad + 2\beta_{23}^* \sin \theta \cos \theta \sin \varphi \\ & \quad + 2\beta_{31}^* \sin \theta \cos \theta \cos \varphi, \end{aligned} \quad (18)$$

where  $\beta^*$  is the tensor relative to the Cartesian coordinates, as given by

$$\beta = C\beta\tilde{C} = DG\beta G\tilde{D}, \quad (19)$$

with  $C_{ij} = (\mathbf{e}_i \cdot \mathbf{a}_j)$ ,  $D_{ij} = (\mathbf{e}_i \cdot \mathbf{a}_j^*)$  and  $G_{ij} = (\mathbf{a}_i \cdot \mathbf{a}_j)$ . Letting  $\xi$  be  $\cos \theta$  and using Heaviside's unit function  $H(\xi)$ , one can rewrite (17) as

$$\begin{aligned} Q(b, \beta^*, R) &= (1/4\pi) \int_0^{2\pi} d\varphi \\ & \quad \times \int_{-\infty}^{\infty} d\xi F(\xi, \varphi) \exp(2\pi i b R \xi) \end{aligned} \quad (20)$$

with

$$F(\xi, \varphi) = H(1 - \xi) H(1 + \xi) G[\theta(\xi), \varphi] \quad (21)$$

where

$$G[\theta(\xi), \varphi] = \exp[-b^2 \beta(\theta, \varphi)]. \quad (22)$$

$F(\xi, \varphi)$  is singular at  $\xi = 1$  and  $\xi = -1$  corresponding to  $\theta = 0$  and  $\theta = \pi$  respectively and near each singular point it can be expressed as follows:

near  $\xi = 1$ ,

$$\begin{aligned} F(\xi, \varphi) &= H(1 - \xi) \sum_{n=0}^4 g_n(0, \varphi) |1 - \xi|^{n/2} \\ & \quad + o(|1 - \xi|^2), \end{aligned} \quad (23)$$

near  $\xi = -1$ ,

$$\begin{aligned} F(\xi, \varphi) &= H(1 + \xi) \sum_{n=0}^4 (-1)^n g_n(\pi, \varphi) |1 + \xi|^{n/2} \\ & \quad + o(|1 + \xi|^2), \end{aligned} \quad (24)$$

where

$$\begin{aligned} g_0(\theta, \varphi) &= G(\theta, \varphi), \\ g_1(\theta, \varphi) &= 2^{1/2} \partial G(\theta, \varphi) / \partial \theta, \\ g_2(\theta, \varphi) &= \partial^2 G(\theta, \varphi) / \partial \theta^2, \\ g_3(\theta, \varphi) &= \frac{1}{6(2)^{1/2}} \left[ 4 \frac{\partial^3 G(\theta, \varphi)}{\partial \theta^3} + \frac{\partial G(\theta, \varphi)}{\partial \theta} \right], \\ g_4(\theta, \varphi) &= \frac{1}{6} \left[ \frac{\partial^4 G(\theta, \varphi)}{\partial \theta^4} + \frac{\partial^2 G(\theta, \varphi)}{\partial \theta^2} \right]. \end{aligned} \quad (25)$$

According to theorem 19 on Fourier integrals by Lighthill (1958), (20) can be expressed as:

$$\begin{aligned} Q(b, \beta^*, R) &= \frac{1}{2} \left( \int H(1-\xi) \sum_{n=0}^4 \langle g_n(0, \varphi) \rangle_\varphi \right. \\ &\quad \times |1-\xi|^{n/2} \cos(2\pi b R \xi) d\xi \\ &\quad + \int H(1+\xi) \sum_{n=0}^4 (-1)^n \langle g_n(\pi, \varphi) \rangle_\varphi \\ &\quad \times |1+\xi|^{n/2} \cos(2\pi b R \xi) d\xi \left. \right) \\ &\quad + o(1/R^3), \end{aligned} \quad (26)$$

where  $\langle \rangle_\varphi$  means the average over the range  $(0, 2\pi)$  of  $\varphi$ .

Since

$$\begin{aligned} \partial^n G(0, \varphi) / \partial \theta^n &= \partial^n G(\pi, \varphi) / \partial \theta^n, \\ g_n(\pi, \varphi) &= (-1)^n g_n(0, \varphi) \end{aligned}$$

and

$$\begin{aligned} &\int_{-\infty}^{\infty} H(1-\xi) |1-\xi|^{n/2} \cos(2\pi b R \xi) d\xi \\ &= \int_{-\infty}^{\infty} H(1+\xi) |1+\xi|^{n/2} \cos(2\pi b R \xi) d\xi, \\ Q(b, \beta^*, R) &= \sum_{m=0}^2 \langle g_{2m}(0, \varphi) \rangle_\varphi \int_{-\infty}^{\infty} H(1-\xi) \\ &\quad \times |1-\xi|^m \cos(2\pi b R \xi) d\xi + o(1/R^3). \end{aligned}$$

Finally one can obtain an asymptotic formula with respect to  $R$ :

$$\begin{aligned} Q(b, \beta^*, R) &= \exp(-\beta_{33}^* b^2) (J_1 + J_2 + J_3) \\ &\quad + o(1/R^3), \end{aligned} \quad (27)$$

with

$$J_1 = \frac{\sin(2\pi b R)}{2\pi b R}, \quad (28)$$

$$J_2 = \frac{\cos(2\pi b R)}{(2\pi b R)^2} (A_1 b^2 - 2A_2 b^4), \quad (29)$$

$$\begin{aligned} J_3 &= -\frac{\sin(2\pi b R)}{(2\pi b R)^3} [A_1 b^2 + (\frac{1}{2} A_3^2 + 2\beta_{12}^{*2} + A_1^2 - 10A_2) b^4 \\ &\quad - 2(2A_1 A_2 + A_3 A_4 + 4\beta_{12}^* \beta_{23}^* \beta_{13}^*) b^6 + 2A_2^2 b^8], \end{aligned} \quad (30)$$

and

$$\begin{aligned} A_1 &= \beta_{11}^* + \beta_{22}^* - 2\beta_{33}^*, & A_2 &= \beta_{13}^{*2} + \beta_{23}^{*2}, \\ A_3 &= \beta_{11}^* - \beta_{22}^*, & A_4 &= \beta_{13}^{*2} - \beta_{23}^{*2} \end{aligned} \quad (31)$$

by use of the following formulas derived from Table I in Lighthill's (1958) book:

$$\begin{aligned} \int_{-\infty}^{\infty} H(1-\xi) \cos(2\pi b R \xi) d\xi &= \frac{\sin(2\pi b R)}{2\pi b R}, \\ \int_{-\infty}^{\infty} H(1-\xi) |1-\xi| \cos(2\pi b R \xi) d\xi &= -\frac{\cos(2\pi b R)}{(2\pi b R)^2}, \\ \int_{-\infty}^{\infty} H(1-\xi) |1-\xi|^2 \cos(2\pi b R \xi) d\xi &= -\frac{2 \sin(2\pi b R)}{(2\pi b R)^3}. \end{aligned} \quad (32)$$

From (29) and (30), it is proved that the conditions for  $J_2 = 0$  are  $\beta_{11}^* + \beta_{22}^* - 2\beta_{33}^* = 0$  and  $\beta_{13}^* = \beta_{23}^* = 0$  and the conditions for  $J_2 = 0$  and  $J_3 = 0$  are  $\beta_{11}^* = \beta_{22}^* = \beta_{33}^*$  and  $\beta_{12}^* = \beta_{23}^* = \beta_{31}^* = 0$ , that is, the vibration tensor be isotropic. Since for an isotropic vibration tensor,  $\beta(\theta, \varphi)$  in (18) turns out to be  $\beta_{33}^*$ ,  $Q(b, \beta^*, R)$  is exactly equal to  $\exp(-\beta_{33}^* b^2) J_1(2\pi b R)$ . Hence the asymptotic expression in (27) is a quite reasonable formula and the correction for the anisotropy of the tensor is to be made by  $J_2$  and  $J_3$  through the factor  $A_1, A_2$  etc. Equation (20) shows that  $Q(b, \beta^*, R)$  can be characterized by the two factors  $\beta^*/R^2$  and  $bR = X$  such that

$$\begin{aligned} Q(b, \beta^*, R) &= (1/4\pi) \int_0^{2\pi} d\varphi \int_{-1}^1 d\xi \\ &\quad \times \exp \left\{ -\frac{\beta[\theta(\xi), \varphi]}{R^2} X^2 + 2\pi i X \xi \right\} \\ &= \mathbf{Q}(\beta^*/R^2, bR). \end{aligned} \quad (33)$$

Regarding  $\mathbf{Q}(\beta^*/R^2, bR)$ , the correction for the anisotropy is to be made by  $A_1/R^2, A_2/R^4$  etc. If  $A_1/R^2 \gg A_2/R^4, A_1/R^2 \gg A_3/R^2, A_1/R^2 \gg A_4/R^4, (\beta_{11}^* + \beta_{22}^* - 2\beta_{33}^*)/R^2$  turns out to be the main factor standing for the anisotropy of the tensor. Since  $J_1$  and  $J_3$  vanish at  $X = n/2$  ( $n$ : integer), the errors of  $J_1$  are evident at these points.

#### 4. Evaluation of $Q(b, \beta^*, R)$ by the use of the asymptotic formula

In order to examine the validity of the asymptotic formula (27), the numerical double integral in (20) was computed by the method for numerical integration (Clenshaw & Curtus, 1960; Hasegawa, Torii & Ninomiya, 1983) using the FACOM M-180 (II) AD computer of the Computer Center of Osaka City University.

Table 1. *Vibration tensors for examples (a), (b) and (c)*

	$\beta_{11}^*$	$\beta_{22}^*$	$\beta_{33}^*$	$\beta_{12}^*$	$\beta_{13}^*$	$\beta_{23}^*$
(a) Si-O pair $R = 1.6036 \text{ \AA}$	0.4079	0.3439	0.1406	-0.06821	-0.05555	0.06024
(b) Si-O pair $R = 3.5278 \text{ \AA}$	0.3718	0.3460	0.1744	-0.06680	-0.1181	0.03046
(c) Assumed pair $R = 1.20 \text{ \AA}$	0.60	0.60	0.10	0.0	0.0	0.0

Table 2. *The crystal data and vibration tensors of  $\alpha$ -quartz determined by Young & Post (1962)*

Space group	$P3_12$
Lattice constants	$a = 4.9128 \text{ \AA}$ $c = 5.4042 \text{ \AA}$
Positional parameters	
Si (3a)	$u = 0.4705$
O (6c)	$x = 0.4152$ $y = 0.2678$ $z = 0.1184$
Vibration tensors ( $\text{\AA}$ )	
	$\beta_{11}^*$ $\beta_{22}^*$ $\beta_{33}^*$ $\beta_{12}^*$ $\beta_{13}^*$ $\beta_{23}^*$
Si	0.0049   0.0027   0.0049   0.0   0.0   -0.0001
O	0.0143   0.0081   0.0090   0.0085   -0.0032   -0.0042

(a) Si-O pair  
 $R = 1.6036 \text{ \AA}$   
 $(\beta_{11}^* + \beta_{22}^* - \beta_{33}^*)/R^2 = 0.18$

(b) Si-O pair  
 $R = 3.5278 \text{ \AA}$   
 $(\beta_{11}^* + \beta_{22}^* - 2\beta_{33}^*)/R^2 = 0.097$

(c) An assumed pair  
 $R = 1.20 \text{ \AA}$   
 $(\beta_{11}^* + \beta_{22}^* - 2\beta_{33}^*)/R^2 = 0.69$

The exact value of  $Q$  computed and the differences of the  $Q$  from the calculated values  $J_1$ ,  $J_2$  and  $J_3$ : (I)  $Q - \exp(-\beta_{33}^* b^2) J_1$ , (II)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2)$  and (III)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2 + J_3)$  are plotted *versus*  $bR$  for three examples (a), (b) and (c) in Fig. 1, where (I), (II), (III) and the exact calculation of  $Q$  are plotted by broken, chain, dotted and solid lines respectively. Examples (a) and (b) correspond to two (Si-O) atomic distance pairs in an  $\alpha$ -quartz crystal and their atomic distances and tensors  $\beta^*$  are shown in Table 1. These values were calculated from the crystal data (Young & Post, 1962) which are tabulated in Table 2. Example (c) is an assumed pair whose tensor is diagonal, as shown in Table 1. As seen in Fig. 1, the errors in  $J_1$  are greatest and least for (c) and for (b) respectively and the magnitudes of  $(\beta_{11}^* + \beta_{22}^* - 2\beta_{33}^*)/R^2$  are greatest and least for (c) and (b). The dotted curves for (III) for (a) and (b) are not drawn, because the errors in (27) are too small.

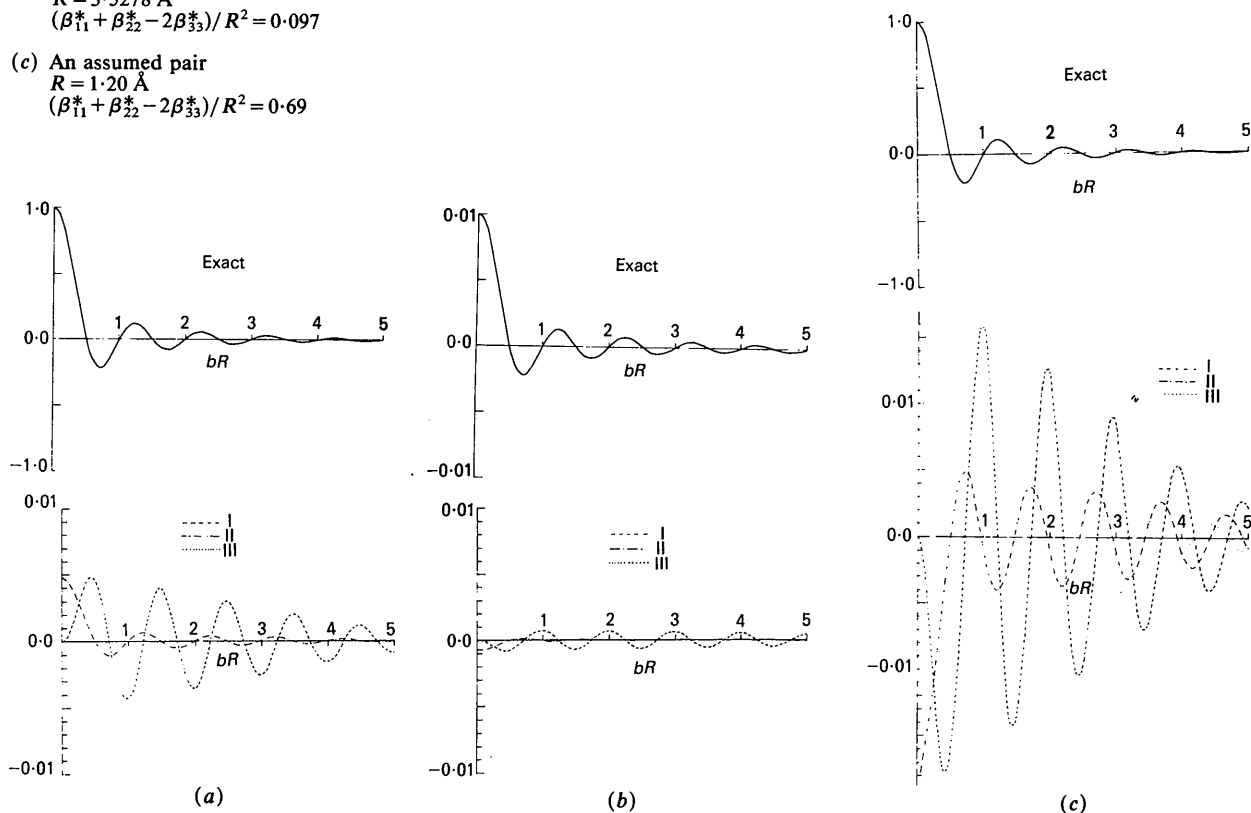


Fig. 1. The plots of (I)  $Q - \exp(-\beta_{33}^* b^2) J_1$ , (II)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2)$ , (III)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2 + J_3)$  and the exact calculation of  $Q$  vs  $bR$  for examples (a), (b) and (c).

In order to see the influence of vibrational anisotropy on the intensity profile  $sI(s)$  ( $s = 2\pi b$ ) and the radial distribution function  $4\pi RD(R)$  (RDF) for small crystallites, those functions were calculated for two crystals of spherical shape with a diameter of 14 Å. Both crystals have the same crystal parameter as shown in Table 2 but they have different vibration tensors. Vibration tensors for one crystal are anisotropic as shown in Table 2, while those for the other crystal are equivalent isotropic vibration tensors, whose diagonal elements are  $\beta_{Si}^* = 0.09799 \text{ \AA}^2$  and  $\beta_O^* = 0.1991 \text{ \AA}^2$ , reduced by Hamilton's (1959) method from the real anisotropic tensors

shown in Table 2. For the sake of convenience, the atomic scattering factors of Si and O were assumed constant as 14 and 8. In Fig. 2 curves of  $sI(s)$  versus  $s(\text{\AA}^{-1})$  and RDF versus  $R(\text{\AA})$  are drawn with solid and broken lines for the former and the latter respectively, where considerable difference between them can be observed. It can be concluded that the effect of anisotropy of the vibration tensor cannot be neglected in the case of small crystallites.

### 5. Discussion

For a gas molecule with thermal vibrations James (1932) derived diffraction intensity formula  $J_{Jms}$  as follows:

$$J_{Jms} = \exp(-\beta_{33}^* b^2) \frac{\sin(2\pi bR)}{2\pi bR} + \frac{2b^2}{(2\pi bR)^2} \left( \beta_{33}^* - \frac{\beta_{11}^* + \beta_{22}^*}{2} \right) \times \left[ \frac{\sin(2\pi bR)}{2\pi bR} - \cos(2\pi bR) \right]. \quad (34)$$

His formula is quite different from (27) except for the first term. In Fig. 3 (I)  $Q - \exp(-\beta_{33}^* b^2) J_1$ , (II)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2)$ , (III)  $Q - \exp(-\beta_{33}^* b^2) \times c(J_1 + J_2 + J_3)$  and (IV)  $Q - J_{Jms}$  are plotted by broken, chain, dotted and double chain lines for example (a); the dotted line is indistinguishable from the abscissa in the figure, because the magnitude of (III) is too small. It is seen that James's formula gives a worse approximation as  $bR$  becomes larger and his second term does not correct his first term, although in the asymptotic formula (27), the second and third terms advance the first approximation, as described in § 4.

In summary, (1) the effect of anisotropy of the vibration tensor cannot be neglected in the case of small crystallites. (2) Precisely speaking, the error of the first approximation should be estimated by the magnitude of  $(\beta_{11}^* + \beta_{22}^* - 2\beta_{33}^*)/R^2$ , but not of  $\beta_{33}^*/R^2$  and accurate calculation can be obtained by formula (27).

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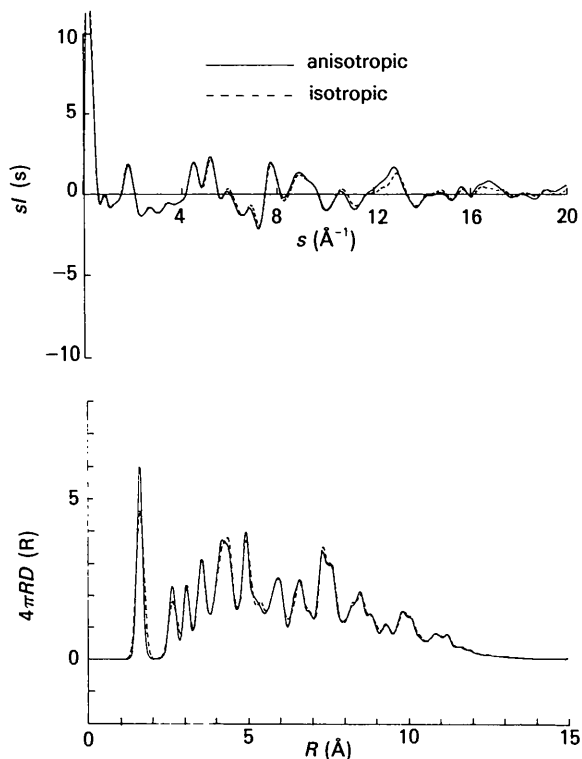


Fig. 2. Intensity profile  $sI(s)$  and the radial distribution function (RDF) for crystallites with anisotropic and isotropic vibration tensors.

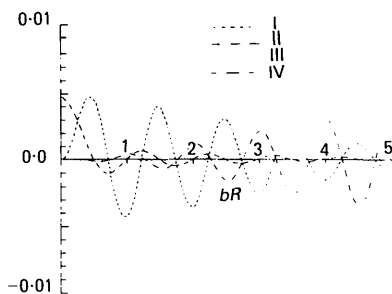


Fig. 3. The plots of (I)  $Q - \exp(-\beta_{33}^* b^2) J_1$ , (II)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2)$ , (III)  $Q - \exp(-\beta_{33}^* b^2)(J_1 + J_2 + J_3)$  and (IV)  $Q - J_{Jms}$  vs  $bR$  for example (a).