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Corrections to the Table in Chapter 4.4, *Diffraction symbols of the space groups*, given in the 1969 edition of Volume I of *International Tables for X-ray Crystallography*. By TAKESHI YAO and HIROSHI JINNO, *Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606 Japan*

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Abstract

Corrections are given to Table 4.4.3 of *International Tables for X-ray Crystallography* [Vol. I (1969), Birmingham: Kynoch Press].

Certain errors have been found in *International Tables for X-ray Crystallography* (1969) and the corrections are given below.

(1) Table 4.4.3 *ORTHORHOMBIC. Laue Class mmm* on p. 349

In the seventeenth row from the top of the table (diffraction symbol *mmmPbcn*), in the column of the point group *mmm*:

Replace the space group *Pncn* by *Pbcn*.

(2) Table 4.4.3 *TETRAGONAL. Laue Class 4/mmm* on p. 350

In the nineteenth row from the top of the table (diffraction symbol *4/mmmPnc-*), in the column of the point group *4/mmm*:

Replace the space group *P4/ncm* by *P4₂/ncm*.

Reference

International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.

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International Tables for X-ray Crystallography*, Vol. IV. Error in table of equivalent reflections in the presence of dispersion effects. By GRAHEME J. B. WILLIAMS, *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA*

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Abstract

Table 2.3.2, *Reciprocal Lattice Points Equivalent under the Operations of a Given Noncentrosymmetric Point Group*, on

p. 151 of *International Tables for X-ray Crystallography* [Vol. IV (1974), Birmingham: Kynoch Press] contains an error for the point group 422. The entry $h\bar{k}l$ should be replaced by $h\bar{k}\bar{l}$.

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All relevant information is given in the *Abstract*.

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The line profile for a random assemblage of identical parallelepiped crystals. A correction. By G. ALLEGRA and G. RONCA, *Istituto di Chimica del Politecnico, Piazza L. da Vinci 32, 20133 Milano, Italy*

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Abstract

Allegra & Ronca [*Acta Cryst.* (1978), A34, 1006–1013] proposed an incorrect analytical expression for the line profile of identical parallelepiped crystals. The correct general expression is now given; in the special case of cubic crystals with a cubic unit cell it reduces to the expression proposed long ago by A. J. C. Wilson [*X-ray Optics* (1949), equation

26, p. 43. Methuen]. The implications of the new result upon the line profile of a polycrystalline sample obeying a Gaussian distribution of crystal sizes are discussed.

In a recent paper (Allegra & Ronca, 1978, hereinafter paper I), we proposed a general analytical expression for the line

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profile of a random assemblage of identical parallelepiped crystals of any shape (equation 9). Denoting as ΔS the difference between the general reciprocal vector length S ($=2 \sin \theta/\lambda$) and that corresponding to the Bragg point (hkl), the result was derived from the following integral (equations 4 and 4' of paper I)

$$\begin{aligned} \mathcal{I}_{hkl}(\Delta S) &\equiv \Phi(u, v, w, X) \\ &= K \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\sin^2[u(X - Y - Z)]}{(X - Y - Z)^2} \frac{\sin^2(vY)}{Y^2} \\ &\quad \times \frac{\sin^2(wZ)}{Z^2} dY dZ, \end{aligned} \quad (1)$$

where $\mathcal{I}_{hkl}(\Delta S) = \langle I_{hkl}(\Delta S) \rangle / |F^2(hkl)|$, the average being effected on the intensity scattered by a single crystal, X is proportional to ΔS and u, v, w and K are related to crystal size, unit cell dimensions and Bragg indices. Evaluation of the above integral was performed after: (i) triple partial differentiation over the variables (u, v, w) leading to a convolution integral of three functions of (X, Y, Z) of the type $\sin(px)/x$; (ii) evaluation of the resulting integral as the Fourier transform of the product of three corresponding 'step' functions; (iii) successive integration over u, v and w to get

$$\mathcal{I}_{hkl}(\Delta S) = \frac{N}{V} S_o \bar{w} \frac{\sin^2 \psi}{\psi^2}, \quad (2)$$

where: $N = N_1 N_2 N_3$ and N_1, N_2 and N_3 are the respective numbers of unit cells along \mathbf{a}, \mathbf{b} and \mathbf{c} (unit cell axes), which are parallel in their turn to the crystal edges; V is the unit cell volume; $S_o = S(hkl)$; \bar{w} is the lowest among the three quantities $\bar{u}, \bar{v}, \bar{w}$ (respectively proportional to u, v, w , equation 1) defined as:

$$\bar{u} = \frac{N_1}{a^* |q_1|}; \quad \bar{v} = \frac{N_2}{b^* |q_2|}; \quad \bar{w} = \frac{N_3}{c^* |q_3|}; \quad (3)$$

$$q_1 = ha^* + kb^* \cos \gamma^* + lc^* \cos \beta^*,$$

$$q_2 = ha^* \cos \gamma^* + kb^* + lc^* \cos \alpha^*,$$

$$q_3 = ha^* \cos \beta^* + kb^* \cos \alpha^* + lc^*,$$

$$\psi = \pi \bar{w} S_o \Delta S.$$

Soon after the appearance of paper I, Professor A. J. C. Wilson pointed out to one of us that (2) showed discrepancies with some of his results. This prompted our re-examination of the problem, which led us to discover the following error in our mathematical sequence.

The triple integration referred to in point (iii) (before equation 2, see above) was performed between zero and the general value for each of the three variables (u, v, w) to ensure that the result vanishes for any of them being zero. Actually, the procedure is incorrect, although it seems to be suggested by inspection of (1), because u and v cannot vanish independently of w in (2); in fact, this equation is only valid under the constraints $u \geq w, v \geq w$ (≥ 0). It may be proved that the correct solution is given by (2) plus three

functions: one depends on (\bar{u}, \bar{w}, ψ), another on (\bar{v}, \bar{w}, ψ) and the third on (\bar{w}, ψ) only. It is best obtained by applying directly to (1) the same deconvolution technique adopted in paper I for its triple partial derivative with respect to u, v and w . In fact, as a function of X , (1) is the convolution of three functions of the type $\sin^2(px)/x^2$ (p being u, v or w), and its Fourier transform is the product of the corresponding Fourier transforms. Apart from a constant factor, each of these is a function of the type $\xi(t) = (2p - |t|)(t = \text{transformed variable})$ in the interval $-2p \leq t \leq 2p$ and zero otherwise; in fact it is easy to verify that

$$\begin{aligned} \sin^2(px)/x^2 &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \xi(t) e^{-itx} dx \\ &= \frac{1}{2} \int_0^{2p} (2p - t) \cos(tx) dx. \end{aligned} \quad (4)$$

Consequently, the Fourier transform of $\Phi(X)$ (see equation 1) is given by

$$\begin{aligned} \varphi(t) &= \int_{-\infty}^{+\infty} \Phi(X) e^{itX} dX \\ &= K \frac{\pi^3}{8} (2u - |t|)(2v - |t|)(2w - |t|), \end{aligned} \quad (5)$$

for $-2w \leq t \leq 2w$ and zero otherwise. Antitransformation gives

$$\begin{aligned} \Phi(u, v, w, X) &= K \frac{\pi^2}{8} \int_0^{2w} (2u - t)(2v - t) \\ &\quad \times (2w - t) \cos(tX) dt, \end{aligned} \quad (6)$$

and, remembering from paper I that $\bar{u} = u/a^* |q_1|, \bar{v} = v/a^* |q_1|, \bar{w} = w/a^* |q_1|$ and

$$K \pi^2 = S_o \frac{q_2 q_3}{|q_1^3|} \frac{b^* c^*}{V a^{*3}},$$

after suitable substitutions we get

$$\begin{aligned} \mathcal{I}_{hkl}(\Delta S) &= \frac{N}{V} S_o \bar{w} \left\{ \frac{\sin^2 \psi}{\psi^2} \right. \\ &\quad \left. + \left[\bar{w} \left(\frac{1}{\bar{u}} + \frac{1}{\bar{v}} \right) \frac{\psi(1 + \cos 2\psi) - \sin 2\psi}{2\psi^3} \right. \right. \\ &\quad \left. \left. - \frac{\bar{w}^2 2\psi^2 \cos 2\psi - 4\psi \sin 2\psi + 3(1 - \cos 2\psi)}{4\psi^4} \right] \right\}, \end{aligned} \quad (1')$$

where the symbols have the meaning already defined in (3). As an example, the above expression reduces to that obtained by Wilson long ago for the special case of a cubic crystal with a cubic unit cell (cf. Wilson, 1949, equation 26, p. 43). It may be interesting to observe that the integral over ΔS from $-\infty$ to $+\infty$ gives the correct value N/V for both (2) and (6) (a misleading feature for us), because it is possible to show that the 'new' terms within square brackets in (1') give a zero contribution upon integration. The peak intensity

[i.e. $\mathcal{I}_{hkl}(\Delta S = 0)$] divided by $\int_{-\infty}^{+\infty} \mathcal{I}_{hkl}(\Delta S) d\Delta S = N/V$ gives the apparent particle size as

$$\varepsilon = S_o \bar{w} \left\{ 1 - \frac{1}{3} \bar{w} \left(\frac{1}{\bar{u}} + \frac{1}{\bar{v}} \right) + \frac{1}{6} \frac{\bar{w}^2}{\bar{u}\bar{v}} \right\}, \quad (7)$$

which also reduces to (19) (p. 39) of Wilson (1949) as a special case.

Equation (2) of paper I may be written as

$$\Delta S = \Delta x^* q_1/S_o + \Delta y^* q_2/S_o + \Delta z^* q_3/S_o, \quad (8)$$

where Δx^* , Δy^* and Δz^* are the components along \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* of the vector $\Delta \mathbf{S}$, parallel to $\mathbf{S}(hkl) = \mathbf{S}_o$. This means that q_1/S_o , for example, is the cosine of the angle between \mathbf{S}_o and \mathbf{a}^* . In the special case in which \mathbf{S}_o is exactly aligned with one of the crystal edges, e.g. the edge parallel to \mathbf{c} , \mathbf{S}_o is orthogonal to both \mathbf{a}^* and \mathbf{b}^* ; consequently $q_1 = q_2 = 0$ and both \bar{u} and \bar{v} tend to infinity (cf equations 3, this paper). In this case (6) exactly reduces to (2); the effective crystal thickness (see equations 12, paper I and equations 3, this paper) is given by $S_o \bar{w} = N_3 S_o/c^* |q_3| = N_3/c^* |\cos(\widehat{\mathbf{S}_o \mathbf{c}^*})| = N_3 c =$ length of the crystal edge along \mathbf{c} , as expected. Consequently, (19) of paper I, although incorrect in general because of the error discussed above, exactly represents in this case the line profile for a Gaussian distribution of crystal

sizes. More generally, (6) is better approximated by (2), the smaller the ratios \bar{w}/\bar{v} and \bar{w}/\bar{u} are as compared with unity; this condition may be fulfilled (cf. equations 3) either when N_1 and N_2 are large compared with N_3 or when q_1 and q_2 are small compared with q_3 , or both. In terms of the Gaussian distribution of crystal sizes

$$P(N_1, N_2, N_3) = 8\alpha\beta\gamma/\pi^{3/2} \exp(-\alpha^2 N_1^2 - \beta^2 N_2^2 - \gamma^2 N_3^2) \quad (9)$$

(cf. equation 13, paper I), the average values of $(\bar{u}, \bar{v}, \bar{w})$ are given by $(1/\alpha a^* |q_1|, 1/\beta b^* |q_2|, 1/\gamma c^* |q_3|)$. Consequently, the larger $\gamma c^* |q_3|$ is than both the other corresponding quantities, the better the true intensity profile is approximated by (19), paper I.

We want to express our appreciation to Professor Wilson for his extremely important and helpful criticism.

References

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 WILSON, A. J. C. (1949) *X-ray Optics*. London: Methuen.