INFLUENCE OF CRYSTALLITE SHAPE ON PARTICLE SIZE BROADENING OF DEBYE-SCHERRER REFLECTIONS

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ABSTRACT

Formulae for the Scherrer constant K_β, the variance Scherrer constant K_w and the taper parameter L_w for crystals having the external shapes of a triangular prism, a square prism, a hexagonal prism and a cylinder have been obtained in terms of the reflection indices and proportionality factors, *viz.*, the ratio of the height of the crystal to the square root of its basal area and the ratio of the two lattice constants of the unit cell. The numerical values of K_β, K_w and L_w have also been computed for direct application in particular cases.

1. INTRODUCTION

THE pure diffraction broadening of Debye-Scherrer reflections from any material depends among other things on the shape and size of the crystallites diffracting X-rays. Although the integral breadth has until recently been most widely used in X-ray studies as the measure of broadening, variance is now increasingly being used in mathematical treatments of X-ray intensity distributions. The latter has a decisive advantage over all other measures of breadth in that it can be corrected for instrumental broadening by simple subtraction, instead of by the Stokes (1948) method of 'unfolding'. Stokes and Wilson (1942) and Wilson (1962) respectively have shown that the integral breadth β and the variance W in reciprocal space due to particle size broadening are given by

$$\beta = \frac{K_\beta}{p} \tag{1}$$

and

$$W = \frac{(\nu_1 + \nu_2) K_w}{2\pi^2 p} - \frac{L_w}{4\pi^2 p^2} \tag{2}$$

where p is the cube root of the volume of the crystallite, $-\nu_1$ to ν_2 is the range for variance determination, K_β is the Scherrer constant, K_w is the variance Scherrer constant and L_w is the taper parameter. K_β, K_w and L_w are defined as follows:

$$K_\beta = \frac{p}{\epsilon} = \frac{V^{4/3}}{\int_{-\tau}^{\tau} V(t)\, dt} \tag{3}$$

$$K_w = -\frac{1}{V^{2/3}}\left(\frac{dV(t)}{dt}\right)_{t=0} \tag{4}$$

$$L_w = \frac{1}{V^{1/3}}\left(\frac{d^2 V(t)}{dt^2}\right)_{t=0} \tag{5}$$

where ϵ is the apparent particle size, V is the volume of the crystallite and V (t) is the volume common to the crystallite and its ghost shifted a distance t in the [hkl] direction. The integration in equation (3) is over all values of t for which there is a common volume.

The Scherrer constant K_β has been evaluated by Stokes and Wilson (1942) for cubic crystals having the external form of a rectangular parallelipiped, a tetrahedron, an octahedron and a sphere and by Mitra (1963) for triclinic crystals having the same external shape. Wilson (1962) has evaluated the variance Scherrer constant K_w and the taper parameter L_w for the same shapes as earlier considered by Stokes and Wilson (1942).

The aim of the present paper is to extend the work in this field by considering crystals having the external forms of a triangular prism, a square prism, a hexagonal prism and a cylinder. Such shapes may occur in case of crystallites of colloidal metals, metals prepared by chemical means or even deformed metals. These shapes possess respectively a 3-, 4-, 6- and ∞- fold axis of symmetry. Expressions for K_β, K_w and L_w have been obtained in terms of two parameters ρ and σ, where

$$\rho = \frac{p_2}{p_1} \quad \text{and} \quad \sigma = \frac{c}{a}, \tag{6}$$

p_1 and p_2 being respectively the square root of the basal area and the height of the crystal and c and a being the lattice constants. Numerical values of K_β, K_w and L_w have also been computed for certain values of ρ and σ with the aid of a digital computer (IBM 1620). For convenience, we have used hexagonal axes and the corresponding Miller-Bravais indices in case of the triangular and hexagonal prisms while tetragonal axes have been used for the square prism and the cylinder. The results are valid for crystals belonging to a different Bravais lattice from the one for which calculations have been made if a prior transformation of the indices of reflections is made in the usual manner.

II. Reflections from a Triangular Prism

Consider a prism having an equilateral triangle as its base and bounded by planes with the Miller-Bravais indices $10\bar{1}0$, $\bar{1}100$, $01\bar{1}0$, 0001 and $000\bar{1}$. The mathematical expression for the volume common to the crystal and its ghost takes two different forms depending on the relations between the indices HKIL of reflection. Let H, K and L be positive and arranged so that $H \geqslant K$. The symmetry is such that all permutations and changes of sign are equivalent to this arrangement. The common volume is given by

$$V(t) = V(1 - At)^2 (1 - Bt) \tag{7}$$

where

$$A = \frac{(H + 2K)d}{3^{\frac{1}{2}} a p_1}, \quad B = \frac{Ld}{c p_2} = \frac{Ld}{\rho\sigma a p_1} \tag{8}$$

and d is the interplanar distance. Inserting the value of $V(t)$ from equation (7) in equation (3), we obtain for the apparent particle size

$$\epsilon = \int_{-\tau}^{\tau} (1 - At)^2 (1 - Bt)\, dt \tag{9}$$

where τ is the smaller of $1/A$ and $1/B$. We will consider both cases in turn.

1. $\tau = 3^{\frac{1}{2}} a p_1/(H + 2K)\, d$. Performing the integration in equation (9) and substituting in equation (3), we obtain

$$K_\beta = 2 \cdot 3^{\frac{1}{2}} \rho^{4/3} \sigma (H + 2K)^2 d a^{-1} (4\rho\sigma H + 8\rho\sigma K - 3^{\frac{1}{2}} L)^{-1} \tag{10 a}$$

2. $\tau = \rho\sigma a p_1/Ld$. Proceeding as above, we have

$$K_\beta \doteq 2 \cdot 3^{5/2} \rho^{-\frac{2}{3}} \sigma^{-1} L^3 d a^{-1} (\rho^2\sigma^2 H^2 + 4\rho^2\sigma^2 K^2 + 2 \cdot 3^{5/2} L^2 - 8 \cdot 3^{\frac{1}{2}} \rho\sigma KL - 4 \cdot 3^{\frac{1}{2}} \rho\sigma LH + 4\rho^2\sigma^2 KH)^{-1} \tag{10 b}$$

Substituting in equations (4) and (5) the values of $[dV(t)/dt]_{t=0}$ and $[d^2 V(t)/dt^2]_{t=0}$ obtained from equation (7), we get

$$K_w = 3^{-\frac{1}{2}} \rho^{-\frac{1}{3}} \sigma^{-1} d a^{-1} (2\rho\sigma H + 4\rho\sigma K + 3^{\frac{1}{2}} L) \tag{11}$$

$$L_w' = 2 \cdot 3^{-3/2} \rho^{-\frac{1}{3}} \sigma^{-1} (H + 2K)^2 d^2 a^{-2} (\rho\sigma H + 2\rho\sigma K + 2 \cdot 3^{\frac{1}{2}} L). \tag{12}$$

Values of K_β, K_w and L_w for small values of H, K, L calculated from the above equations are given in Table I.

TABLE I *a*

The Scherrer constant for crystals having the form of a triangular prism

Sl. No.	HK.L	ρ = 2·0			ρ = 1·0			ρ = 0·5		
		σ=2·0	σ=1·0	σ=0·5	σ=2·0	σ=1·0	σ=0·5	σ=2·0	σ=1·0	σ=0·5
1	00·1	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
2	10·0	0·72	0·72	0·72	0·57	0·57	0·57	0·45	0·45	0·45
3	10·1	0·77	0·76	0·74	0·73	0·89	1·00	0·85	1·21	1·48
4	10·2	0·76	0·74	0·70	0·89	1·00	1·03	1·21	1·48	1·58
5	10·3	0·75	0·72	0·68	0·97	1·03	1·03	1·39	1·56	1·60
6	10·4	0·74	0·70	0·67	1·00	1·03	1·03	1·48	1·58	1·60
7	10·5	0·73	0·69	0·66	1·02	1·03	1·02	1·53	1·59	1·60
8	10·6	0·72	0·68	0·66	1·03	1·03	1·02	1·56	1·60	1·60
9	11·0	1·24	1·24	1·24	0·99	0·99	0·99	0·78	0·78	0·78
10	11·2	1·23	1·09	0·89	1·09	1·12	1·12	1·12	1·41	1·59
11	11·4	1·09	0·89	0·77	1·12	1·12	1·08	1·41	1·59	1·63
12	20·1	0·76	0·77	0·76	0·65	0·73	0·89	0·62	0·85	1·21
13	20·3	0·77	0·75	0·72	0·82	0·97	1·03	1·06	1·39	1·56
14	20·5	0·75	0·73	0·69	0·93	1·02	1·03	1·31	1·53	1·59

III. REFLECTIONS FROM A SQUARE PRISM

Consider a crystal whose external shape is that of a square prism bounded by planes whose Miller indices are 100, 010, 001, $\bar{1}00$, $0\bar{1}0$, $00\bar{1}$. Let the indices *hkl* of reflection be positive. The common volume is then given by

$$V(t) = V(1 - Ct)(1 - Dt)(1 - Et) \tag{13}$$

where

$$C = \frac{hd}{ap_1}, \quad D = \frac{kd}{ap_1}, \quad E = \frac{ld}{cp_2} = \frac{ld}{\rho\sigma a p_1}. \tag{14}$$

Also let the indices be arranged in the order $h \geqslant k$. This is merely a matter of naming the axes. Proceeding in the same way as between equations (7) and (10) in Section II, we obtain (τ is the smaller of $1/c$ and $1/E$)

1. $\tau = ap_1/hd$

$$K_\beta = 6\rho^{4/3}\sigma h^3 da^{-1}(6\rho\sigma h^2 + kl - 2lh - 2\rho\sigma hk)^{-1} \tag{15 a}$$

TABLE I *b*

The variance Scherrer constant for crystals having the form of a triangular prism

Sl. No.	HK.L	$\rho=2\cdot0$			$\rho=1\cdot0$			$\rho=0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	00·1	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
2	10·0	0·96	0·96	0·96	0·76	0·76	0·76	0·60	0·60	0·60
3	10·1	1·13	1·14	1·02	1·09	1·23	1·25	1·18	1·50	1·68
4	10·2	1·14	1·02	0·87	1·23	1·25	1·17	1·50	1·68	1·69
5	10·3	1·08	0·93	0·80	1·26	1·21	1·13	1·63	1·70	1·67
6	10·4	1·02	0·87	0·76	1·25	1·17	1·10	1·68	1·69	1·66
7	10·5	0·97	0·83	0·74	1·23	1·15	1·08	1·69	1·68	1·65
8	10·6	0·93	0·80	0·72	1·21	1·13	1·07	1·70	1·67	1·64
9	11·0	1·66	1·66	1·66	1·32	1·32	1·32	1·04	1·04	1·04
10	11·2	1·76	1·62	1·30	1·62	1·64	1·48	1·64	1·86	1·89
11	11·4	1·62	1·30	1·01	1·64	1·48	1·29	1·86	1·89	1·79
12	20·1	1·07	1·13	1·14	0·95	1·09	1·23	0·93	1·18	1·50
13	20·3	1·15	1·08	0·93	1·18	1·26	1·21	1·37	1·63	1·70
14	20·5	1·11	0·97	0·83	1·25	1·23	1·15	1·58	1·69	1·68

TABLE I *c*

The taper parameter for crystals having the form of a triangular prism

Sl. No.	HK.L	$\rho=2\cdot0$			$\rho=1\cdot0$			$\rho=0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	00·1	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
2	10·0	0·46	0·46	0·46	0·29	0·29	0·29	0·18	0·18	0·18
3	10·1	0·83	0·86	0·64	0·80	0·92	0·73	0·85	1·05	0·87
4	10·2	0·86	0·64	0·36	0·92	0·73	0·43	1·05	0·87	0·52
5	10·3	0·75	0·46	0·24	0·84	0·55	0·29	0·99	0·67	0·36
6	10·4	0·64	0·36	0·18	0·73	0·43	0·22	0·87	0·52	0·27
7	10·5	0·54	0·29	0·14	0·63	0·35	0·18	0·76	0·43	0·22
8	10·6	0·46	0·24	0·12	0·55	0·29	0·15	0·67	0·36	0·18
9	11·0	1·37	1·37	1·37	0·87	0·87	0·87	0·55	0·55	0·55
10	11·2	1·94	1·73	1·11	1·75	1·75	1·23	1·76	1·93	1·44
11	11·4	1·73	1·11	0·57	1·75	1·23	0·67	1·93	1·44	0·81
12	20·1	0·69	0·83	0·86	0·59	0·80	0·92	0·57	0·85	1·05
13	20·3	0·87	0·75	0·46	0·90	0·84	0·55	1·00	0·99	0·67
14	20·5	0·81	0·54	0·29	0·89	0·63	0·35	1·04	0·76	0·43

2. $\tau = \rho\sigma a p_1 / l d$

$$K_\beta = 6\rho^{-\frac{2}{3}}\,\sigma^{-1}\, l^3\, d a^{-1}\, (6l^2 - 2\rho\sigma k l - 2\rho\sigma l h + \rho^2\sigma^2 h k)^{-1}. \qquad (15\,b)$$

Equation (22) of Stokes and Wilson (1942) is a special case of equation (15 *a*) and can be arrived at by putting $\rho = \sigma = 1$ in it.

Again, proceeding in the same way as in Section II, we have for the variance Scherrer constant and the taper parameter

$$K_w = \rho^{-\frac{2}{3}}\,\sigma^{-1}\, d a^{-1}\, (\rho\sigma h + \rho\sigma k + l) \qquad (16)$$

$$L_w = 2\rho^{-\frac{1}{3}}\,\sigma^{-1}\, d^2 a^{-2}\, (kl + lh + \rho\sigma h k). \qquad (17)$$

Wilson's (1962) expressions for the variance Scherrer constant and taper parameter for a crystal of cubic shape form a special case of equations (16) and (17) and can be obtained by putting $\rho = \sigma = 1$ in them.

Values of K_β, K_w and L_w from equations (15) to (17) are given in Table II.

TABLE II *a*

The Scherrer constant for crystals having the form of a square prism

Sl. No.	*hkl*	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	100	1·26	1·26	1·26	1·00	1·00	1·00	0·79	0·79	0·79
2	001	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
3	110	1·34	1·34	1·34	1·06	1·06	1·06	0·84	0·84	0·84
4	101	1·23	1·07	0·85	1·07	1·06	1·07	1·06	1·35	1·55
5	111	1·34	1·25	1·03	1·14	1·15	1·15	1·06	1·29	1·54
6	210	1·35	1·35	1·35	1·07	1·07	1·07	0·85	0·85	0·85
7	201	1·28	1·23	1·07	1·06	1·07	1·06	0·92	1·06	1·35
8	102	1·07	0·85	0·73	1·06	1·07	1·06	1·35	1·55	1·61
9	211	1·37	1·33	1·19	1·13	1·15	1·14	0·98	1·11	1·37
10	112	1·25	1·03	0·83	1·15	1·15	1·12	1·29	1·54	1·63
11	221	1·36	1·34	1·25	1·11	1·14	1·15	0·95	1·06	1·29
12	212	1·33	1·19	0·94	1·15	1·14	1·13	1·11	1·37	1·57
13	310	1·34	1·34	1·34	1·07	1·07	1·07	0·85	0·85	0·85
14	301	1·28	1·27	1·18	1·04	1·07	1·07	0·88	0·97	1·17
15	103	0·93	0·77	0·70	1·07	1·07	1·04	1·49	1·59	1·61
16	311	1·36	1·35	1·27	1·11	1·14	1·14	0·93	1·02	1·22
17	113	1·13	0·91	0·77	1·16	1·14	1·09	1·45	1·61	1·63

TABLE II *b*

The variance Scherrer constant for crystals having the form of a square prism

Sl. No.	*hkl*	$\rho=2\cdot0$			$\rho=1\cdot0$			$\rho=0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	100	1·26	1·26	1·26	1·00	1·00	1·00	0·79	0·79	0·79
2	001	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
3	110	1·78	1·78	1·78	1·41	1·41	1·41	1·12	1·12	1·12
4	101	1·41	1·34	1·13	1·34	1·41	1·34	1·42	1·68	1·77
5	111	1·89	1·82	1·54	1·67	1·73	1·63	1·59	1·83	1·94
6	210	1·69	1·69	1·69	1·34	1·34	1·34	1·06	1·06	1·06
7	201	1·38	1·41	1·34	1·21	1·34	1·41	1·16	1·42	1·68
8	102	1·34	1·13	0·92	1·41	1·34	1·21	1·68	1·77	1·73
9	211	1·79	1·80	1·68	1·53	1·63	1·67	1·39	1·62	1·85
10	112	1·82	1·54	1·19	1·73	1·63	1·41	1·83	1·94	1·87
11	221	1·86	1·89	1·82	1·57	1·67	1·73	1·38	1·59	1·83
12	212	1·80	1·68	1·37	1·63	1·67	1·53	1·62	1·85	1·91
13	310	1·59	1·59	1·59	1·26	1·26	1·26	1·00	1·00	1·00
14	301	1·35	1·39	1·40	1·15	1·26	1·39	1·04	1·25	1·54
15	103	1·22	1·00	0·83	1·39	1·26	1·15	1·76	1·76	1·70
16	311	1·67	1·71	1·68	1·41	1·51	1·60	1·24	1·44	1·70
17	113	1·68	1·33	1·02	1·70	1·51	1·30	1·93	1·91	1·80

TABLE II *c*

The taper parameter for crystals having the form of a square prism

Sl. No.	*hkl*	$\rho=2\cdot0$			$\rho=1\cdot0$			$\rho=0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	100	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
2	001	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
3	110	1·59	1·59	1·59	1·00	1·00	1·00	0·63	0·63	0·63
4	101	0·63	0·79	0·63	0·80	1·00	0·80	1·01	1·26	1·01
5	111	2·12	2·12	1·59	1·78	2·00	1·67	1·68	2·10	1·89
6	210	1·27	1·27	1·27	0·80	0·80	0·80	0·50	0·50	0·50
7	201	0·37	0·63	0·79	0·47	0·80	1·00	0·59	1·01	1·26
8	102	0·79	0·63	0·37	1·00	0·80	0·47	1·26	1·01	0·59
9	211	1·66	1·85	1·76	1·33	1·67	1·78	1·20	1·68	1·96
10	112	2·12	1·59	0·88	2·00	1·67	1·00	2·10	1·89	1·19
11	221	1·92	2·12	2·12	1·45	1·78	2·00	1·22	1·68	2·10
12	212	1·85	1·76	1·21	1·67	1·78	1·33	1·68	1·96	1·56
13	310	0·95	0·95	0·95	0·60	0·60	0·60	0·38	0·38	0·38
14	301	0·26	0·48	0·73	0·32	0·60	0·92	0·41	0·76	1·16
15	103	0·73	0·48	0·26	0·92	0·60	0·32	1·16	0·76	0·41
16	311	1·24	1·44	1·59	0·98	1·27	1·57	0·86	1·26	1·71
17	113	1·87	1·15	0·58	1·88	1·27	0·68	2·08	1·49	0·83

IV. REFLECTIONS FROM A HEXAGONAL PRISM

Consider a right prism having a regular hexagon as its base bounded by planes with the Miller-Bravais indices $10\bar{1}0$, $01\bar{1}0$, $\bar{1}100$, 0001, $\bar{1}010$, $0\bar{1}10$, $1\bar{1}00$, $000\bar{1}$. The mathematical expression for the volume common to the crystal and its ghost takes two different forms depending on the indices of reflection. Suppose that the indices H, K and L are positive and arranged in the order $H \geqslant K$. All permutations and changes of sign are equivalent to this arrangement due to symmetry. The common volume is either an irregular hexagonal right prism bounded by displaced $\bar{1}100$, $\bar{1}010$, $0\bar{1}10$ and $000\bar{1}$ planes and by undisplaced $1\bar{1}00$, $10\bar{1}0$, $01\bar{1}0$ and 0001 planes or a right prism having a parallelogram as its base, bounded by displaced $\bar{1}010$, $0\bar{1}10$ and $000\bar{1}$ planes and by undisplaced $10\bar{1}0$, $01\bar{1}0$, and 0001 planes depending on the indices of reflection and the relative magnitudes of t and p_1. The expressions for the common volume corresponding to the above two cases are as follows:

$$\mathrm{V}(t) = \mathrm{V}\left(1 - \tfrac{4}{3}\mathrm{F}t + \tfrac{4}{3}\mathrm{FG}t^2 - \tfrac{4}{3}\mathrm{G}^2 t^2\right)(1 - \mathrm{B}t) \quad \text{for} \quad t \leqslant \frac{1}{2\mathrm{G}} \tag{18 a}$$

$$\mathrm{V}(t) = \tfrac{4}{3}\mathrm{V}(1 - \mathrm{F}t)(1 - \mathrm{G}t)(1 - \mathrm{B}t) \quad \text{for} \quad t \geqslant \frac{1}{2\mathrm{G}} \tag{18 b}$$

where

$$\mathrm{F} = \frac{(2\mathrm{H} + \mathrm{K})\,d}{12^{1/2}\,ap_1}, \quad \mathrm{G} = \frac{(\mathrm{H} + 2\mathrm{K})\,d}{12^{1/2}\,ap_1}, \quad \mathrm{B} = \frac{\mathrm{L}d}{cp_2} = \frac{\mathrm{L}d}{\rho\sigma ap_1}. \tag{19}$$

It can be readily shown that V (t) is continuous at $t = 1/2\mathrm{G}$ by differentiation equations (18) with respect to t. A slight generalization of the procedure already used above to obtain ϵ leads to

$$\epsilon = 2\left[\int_0^{\tau_1}\left(1 - \tfrac{4}{3}\mathrm{F}t + \tfrac{4}{3}\mathrm{FG}t^2 - \tfrac{4}{3}\mathrm{G}^2 t^2\right)(1 - \mathrm{B}t)\,dt + \tfrac{4}{3}\int_{\tau_1}^{\tau_2}(1 - \mathrm{F}t)(1 - \mathrm{G}t)(1 - \mathrm{B}t)\,dt\right]. \tag{20}$$

The values of τ_1 and τ_2 depend on p_1 and p_2 as well as on the indices of reflection and are summarized in Table III. In the last two cases the second integral in equation (2) vanishes. Inserting the proper limits, performing the integrations in equations (20) and substituting the value of ϵ in equation (3), we obtain the following four expressions for K_β:

1. $\tau_1 = 12^{1/2}\, ap_1/2\,(H + 2K)\,d,\ \tau_2 = 12^{1/2}\, ap_1/(2H + K)\,d$

$$K_\beta = 72\rho^{4/3}\sigma\,(2H + K)^3\,(H + 2K)^2\,da^{-1}\{8.12^{1/2}\rho\sigma\,(2H + K) \times (H + 2K)\,(16H^2 + 40HK + 7K^2) + 12^{1/2}L\,(K^3 - 186HK^2 - 180H^2K - 40H^3)\}^{-1}. \qquad (21\ a)$$

2. $\tau_1 = 12^{1/2}\, ap_1/2\,(H + 2K)\,d,\ \tau_2 = \rho\sigma ap_1/Ld$

$$K_\beta = 78.12^{1/2}\rho^{4/3}\sigma\,(H + 2K)^2\,L^3\,da^{-1}\{4\rho^4\sigma^4\,(2H + K)\,(H + 2K)^3 - 12^{1/2}\rho^3\sigma^3\,(H+K)\,(H+2K)^2L + 24.12^{1/2}\rho^2\sigma^2\,(H+2K)^2L^2 - 2.12^{1/2}\rho\sigma\,(H + 2K)\,L^3 + 3L^4\}^{-1}. \qquad (21\ b)$$

3. $\tau_1 = \tau_2 = 12^{1/2}\, ap_1/(2H + K)\,d$

$$K_\beta = 3.12^{1/2}\rho^{4/3}\sigma\,(2H + K)^2\,da^{-1}\{16\rho\sigma\,(2H + K) - 5.12^{1/2}L\}^{-1}. \qquad (21\ c)$$

4. $\tau_1 = \tau_2 = \rho\sigma ap_1/Ld$

$$K_\beta = 9.12^{1/2}\rho^{-1/3}\sigma^{-1}L^3\,da^{-1}\{2p^2\sigma^2\,(H - K)\,(H + 2K) - 4.12^{1/2}\rho\sigma\,(2H + K)\,L + 9.12^{1/2}L^2\}^{-1}. \qquad (21\ d)$$

Utilising equations (4), (5) and (18 *a*), we obtain for the variance Scherrer constant and taper parameter

TABLE III

The values of τ_1 and τ_2 for crystals having the form of a hexagonal prism

Relation between F, G, B	$1/\tau_1$	$1/\tau_2$
1. 2G > F > B –	2G	F
2. 2G > B > F –	2G	B
3. F = 2G > B –	F	F
4. B > 2G ⩾ F –	B	B

TABLE IV (A)

The Scherrer constant for crystals having the form of a hexagonal prism

Sl. No.	HK. K	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	00·1	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
2	10·0	1·32	1·32	1·32	1·05	1·05	1·05	0·83	0·83	0·83
3	10·1	1·31	1·17	0·93	1·12	1·12	1·11	1·08	1·34	1·55
4	10·2	1·17	0·93	0·78	1·12	1·11	1·09	1·34	1·55	1·62
5	10·3	1·03	0·83	0·73	1·12	1·10	1·06	1·48	1·61	1·62
6	10·4	0·93	0·78	0·70	1·11	1·09	1·05	1·55	1·62	1·62
7	10·5	0·87	0·75	0·69	1·11	1·07	1·04	1·59	1·62	1·62
8	10·6	0·83	0·73	0·68	1·10	1·06	1·04	1·61	1·62	1·61
9	11·0	1·31	1·31	1·31	1·04	1·04	1·04	0·82	0·82	0·82
10	11·2	1·27	1·11	0·87	1·11	1·10	1·09	1·10	1·37	1·56
11	11·4	1·11	0·87	0·74	1·10	1·09	1·07	1·37	1·56	1·61
12	20·1	1·34	1·31	1·17	1·10	1·12	1·12	0·95	1·08	1·34
13	20·3	1·24	1·03	0·83	1·12	1·12	1·10	1·22	1·48	1·61
14	20·5	1·09	0·87	0·75	1·11	1·11	1·07	1·42	1·59	1·62

TABLE IV (B)

The variance Scherrer constant for crystals having the form of a hexagonal prism

Sl. No.	HK.L	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	00·1	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
2	10·0	1·56	1·56	1·56	1·24	1·24	1·24	0·98	0·98	0·98
3	10·1	1·68	1·59	1·33	1·54	1·59	1·49	1·53	1·78	1·87
4	10·2	1·59	1·33	1·04	1·59	1·49	1·30	1·78	1·87	1·80
5	10·3	1·45	1·15	0·91	1·55	1·38	1·22	1·86	1·84	1·74
6	10·4	1·33	1·04	0·85	1·49	1·30	1·17	1·87	1·80	1·71
7	10·5	1·23	0·97	0·81	1·43	1·25	1·14	1·85	1·77	1·70
8	10·6	1·15	0·91	0·78	1·38	1·22	1·11	1·84	1·74	1·67
9	11·0	1·35	1·35	1·35	1·07	1·07	1·07	0·85	0·85	0·85
10	11·2	1·49	1·40	1·17	1·41	1·47	1·37	1·47	1·73	1·80
11	11·4	1·40	1·17	0·94	1·47	1·37	1·23	1·73	1·80	1·75
12	20·1	1·66	1·68	1·59	1·42	1·54	1·59	1·30	1·53	1·78
13	20·3	1·65	1·45	1·15	1·59	1·55	1·38	1·69	1·86	1·84
14	20·5	1·52	1·23	0·97	1·58	1·43	1·25	1·83	1·85	1·77

TABLE IV (C)

The taper parameter for crystals having the form of a hexagonal prism

Sl. No.	HK.L	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	00·1	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
2	10·0	1·83	1·83	1·83	1·15	1·15	1·15	0·73	0·73	0·73
3	10·1	2·62	2·51	1·74	2·33	2·50	1·90	2·32	2·74	2·21
4	10·2	2·51	1·74	0·93	2·50	1·90	1·08	2·74	2·21	1·31
5	10·3	2·11	1·23	0·61	2·23	1·40	0·73	2·54	1·67	0·90
6	10·4	1·74	0·93	0·46	1·90	1·08	0·55	2·21	1·31	0·68
7	10·5	1·45	0·74	0·36	1·62	0·87	0·44	1·91	1·07	0·54
8	10·6	1·23	0·61	0·30	1·40	0·73	0·37	1·67	0·90	0·45
9	11·0	2·75	2·75	2·75	1·73	1·73	1·73	1·09	1·09	1·09
10	11·2	3·56	3·08	1·91	3·10	3·02	2·07	3·04	3·25	2·38
11	11·4	3·08	1·91	0·96	3·02	2·07	1·11	3·25	2·38	1·34
12	20·1	2·36	2·62	2·51	1·87	2·33	2·50	1·66	2·32	2·74
13	20·3	2·64	2·11	1·23	2·51	2·23	1·40	2·65	2·54	1·67
14	20·5	2·32	1·45	0·74	2·39	1·62	0·87	2·67	1·91	1·07

$$K_w = 12^{-\frac{1}{2}} \rho^{-\frac{1}{2}} \sigma^{-1} d a^{-1} (2\rho\sigma H + \rho\sigma K + 12^{\frac{1}{2}} L) \tag{22}$$

$$L_w = 4.3^{-3/2} \rho^{\frac{1}{2}} \sigma^{-1} d^2 a^{-2} [\rho\sigma (H + 2K)(H - K) + 12^{\frac{1}{2}} (2H + K) L] \tag{23}$$

K_β, K_w and L_w calculated from equations (21) to (23) are given in Table IV.

V. REFLECTIONS FROM A CYLINDER

Consider a crystal having the shape of a cylinder bounded at its two ends by planes whose Miller indices are 001 and $00\bar{1}$. Let the indices *hkl* of reflection be positive. The common volume is given by

$$V(t) = V\left(1 - \frac{2}{\pi}\sin^{-1} Nt - \frac{2}{\pi} Nt\sqrt{1 - N^2 t^2}\right)(1 - MNt). \tag{24}$$

where

$$M = \frac{2l}{\rho\sigma\pi^{\frac{1}{2}}(h^2 + k^2)^{\frac{1}{2}}}, \quad N = \frac{\pi^{\frac{1}{2}}(h^2 + k^2)^{\frac{1}{2}} d}{2ap_1}. \tag{25}$$

It is convenient to define a new variable ϕ as follows:

$$\phi = \sin^{-1} Nt. \tag{26}$$

Equation (24) now becomes

$$V(t) = V(\phi) = V\left(\frac{1-2\phi}{\pi} - \frac{\sin 2\phi}{\pi}\right)(1 - M\sin\phi) \tag{27}$$

Inserting this in equation (3), we get

$$\epsilon = \frac{2}{V}\int_0^{\Phi} V(\phi)\, d\phi \cdot \frac{dt}{d\phi} = \frac{2}{N}\int_0^{\Phi}\left(1 - \frac{2\phi}{\pi} - \frac{\sin 2\phi}{\pi}\right)$$

$$\times (1 - M\sin\phi)\cos\phi \cdot d\phi. \tag{28}$$

When M is less than or equal to unity (in magnitude), Φ takes the value $\pi/2$ but if it is greater than unity, $\Phi = \sin^{-1}(1/M)$.

1. $\Phi = \pi/2$

$$K_\beta = 6\pi^{3/2}\rho^{4/3}\sigma(h^2+k^2)\, da^{-1}\{32\rho\sigma(h^2+k^2)^{\frac{1}{2}} - 6\pi^{\frac{1}{2}} l\}^{-1}. \tag{29}$$

2. $\Phi = \sin^{-1}(1/M)$. In this case the expression for K_β becomes too cumbersome if expressed explicitly in terms of h, k, l and ρ, σ. As such, it is expressed in terms of M, N, p_1 and ρ.

TABLE V (A)

The Scherrer constant for crystals having the form of a cylinder

Sl. No.	hkl	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	100	1·32	1·32	1·32	1·04	1·04	1·04	0·83	0·83	0·83
2	001	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
3	110	1·32	1·32	1·32	1·04	1·04	1·04	0·83	0·83	0·83
4	101	1·28	1·12	0·91	1·12	1·15	0·98	1·15	1·23	1·16
5	111	1·32	1·22	0·99	1·12	1·11	1·07	1·02	1·20	1·22
6	210	1·32	1·32	1·32	1·04	1·04	1·04	0·83	0·83	0·83
7	201	1·33	1·28	1·12	1·10	1·12	1·15	0·96	1·15	1·23
8	102	1·12	0·91	0·67	1·15	0·98	0·79	1·23	1·16	0·93
9	211	1·33	1·30	1·15	1·10	1·12	1·13	0·95	1·10	1·23
10	112	1·22	0·99	0·78	1·11	1·07	0·89	1·20	1·22	1·06
11	221	1·33	1·32	1·22	1·09	1·12	1·11	0·92	1·02	1·20
12	212	1·30	1·15	0·93	1·12	1·13	1·01	1·10	1·23	1·19
13	310	1·32	1·32	1·32	1·04	1·04	1·04	0·83	0·83	0·83
14	301	1·33	1·32	1·23	1·09	1·11	1·12	0·92	1·01	1·20
15	103	0·97	0·76	0·57	1·06	0·87	0·68	1·21	1·04	0·77
16	311	1·33	1·32	1·24	1·09	1·11	1·12	0·91	1·00	1·19
17	113	1·10	0·89	0·65	1·14	0·97	0·78	1·23	1·15	0·91

TABLE V (B)

The variance Scherrer constant for crystals having the form of a cylinder

Sl. No.	*hkl*	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	100	1·42	1·42	1·42	1·13	1·13	1·13	0·90	0·90	0·90
2	001	0·63	0·63	0·63	1·00	1·00	1·00	1·59	1·59	1·59
3	110	1·42	1·42	1·42	1·13	1·13	1·13	0·90	0·90	0·90
4	101	1·55	1·45	1·20	1·46	1·50	1·40	1·51	1·76	1·82
5	111	1·55	1·52	1·34	1·40	1·50	1·47	1·37	1·65	1·81
6	210	1·42	1·42	1·42	1·13	1·13	1·13	0·90	0·90	0·90
7	201	1·53	1·55	1·45	1·34	1·46	1·50	1·25	1·51	1·76
8	102	1·45	1·20	0·96	1·50	1·40	1·24	1·76	1·82	1·76
9	211	1·52	1·55	1·48	1·32	1·44	1·51	1·22	1·47	1·73
10	112	1·52	1·34	1·07	1·50	1·47	1·32	1·65	1·81	1·80
11	221	1·51	1·55	1·52	1·29	1·40	1·50	1·16	1·37	1·65
12	212	1·55	1·48	1·24	1·44	1·51	1·42	1·47	1·73	1·82
13	310	1·42	1·42	1·42	1·13	1·13	1·13	0·90	0·90	0·90
14	301	1·51	1·55	1·53	1·28	1·39	1·49	1·14	1·35	1·63
15	103	1·31	1·05	0·86	1·46	1·31	1·17	1·82	1·79	1·71
16	311	1·50	1·55	1·54	1·27	1·38	1·49	1·13	1·33	1·61
17	113	1·43	1·18	0·94	1·50	1·39	1·23	1·77	1·82	1·75

TABLE V (C)

The taper parameter for crystals having the form of a cylinder

Sl. No.	*hkl*	$\rho = 2\cdot0$			$\rho = 1\cdot0$			$\rho = 0\cdot5$		
		$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$	$\sigma=2\cdot0$	$\sigma=1\cdot0$	$\sigma=0\cdot5$
1	100	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
2	001	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
3	110	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
4	101	0·32	1·29	5·15	0·81	3·24	12·97	2·04	8·17	32·68
5	111	0·16	0·64	2·57	0·41	1·62	6·48	1·02	4·09	16·34
6	210	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
7	201	0·08	0·32	1·29	0·20	0·81	3·24	0·51	2·04	8·17
8	102	1·29	5·15	20·59	3·24	12·97	51·88	8·17	32·68	130·72
9	211	0·06	0·26	1·03	0·16	0·65	2·59	0·41	1·63	6·54
10	112	0·64	2·57	10·29	1·62	6·48	25·94	4·09	16·34	65·36
11	221	0·04	0·16	0·64	0·10	0·41	1·62	0·26	1·02	4·09
12	212	0·26	1·03	4·12	0·65	2·59	10·38	1·63	6·54	26·14
13	310	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
14	301	0·04	0·14	0·57	0·09	0·36	1·44	0·23	0·91	3·63
15	103	2·90	11·58	46·32	7·30	29·18	116·72	18·38	73·53	294·12
16	311	0·03	0·13	0·51	0·08	0·32	1·30	0·20	0·82	3·27
17	113	1·45	5·79	23·16	3·65	14·59	58·36	9·19	36·77	147·06

$$K_\beta = 12\pi\rho^{\frac{1}{3}} M^2 N p_1 \left\{12\pi M + 32M^2 - (24M + 6M^3)\sin^{-1}\frac{1}{M} - (10 + 23M^2)\left(1 - \frac{1}{M^2}\right)^{\frac{1}{2}}\right\}^{-1} \quad (29\ b)$$

The variance Scherrer constant and the taper parameter are given by the following:

$$K_w = \pi^{-\frac{1}{2}} \rho^{-\frac{2}{3}} \sigma^{-1} d a^{-1} \{2\rho\sigma (h^2 + k^2)^{\frac{1}{2}} + \pi^{\frac{1}{2}} l\} \quad (30)$$

$$L_w = 4\pi^{-\frac{1}{2}} \rho^{-\frac{1}{3}} \sigma^{-1} (h^2 + k^2)^{\frac{1}{2}} l d^2 a^{-2}. \quad (31)$$

Table V gives the values of K_β, K_w and L_w calculated from the above equations.

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