Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size

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Existing knowledge about Scherrer constants is reviewed and a summary is given of the interpretation of the broadening arising from small crystallites. Early work involving the half-width as a measure of breadth has been completed and Scherrer constants of simple regular shapes have been determined for all low-angle reflexions $(h^2 + k^2 + l^2 \leq 100)$ for four measures of breadth. The systematic variation of Scherrer constant with *hkl* is discussed and a convenient representation in the form of contour maps is applied to simple shapes. The relation between the 'apparent' crystallite size, as determined by X-ray methods, and the 'true' size is considered for crystallites having the same shape. If they are of the same size, then the normal Scherrer constant applies, but if there is a distribution of sizes, a modified Scherrer constant must be used.

List of principal symbols

A	Projected area of crystallite
b	Additional line broadening due to size effect
D	Equation (34) and Table 6
hkl	Miller indices
H	$h + k + l$
I	Intensity
K	Scherrer constant
k	Slope of variance–range curve
L	Taper parameter
N	$h^2 + k^2 + l^2$
p	'True' crystallite size
q	Table 1
s	Distance in reciprocal space
T	Thickness of crystallite perpendicular to reflecting planes; value of t for which $U(t)$ vanishes; variance intercept (suffix)
t	Distance in a direction perpendicular to reflecting planes
$U(t)$	Volume function of crystallite of unit volume
V	Volume of crystallite
$V(t)$	Volume function of crystallite
v	k/h
W_0	Intercept of variance–range curve
$2w$	Full width at half maximum intensity (half-width)
w	l/h; half-width (suffix)
Y	Volume of unit cell
β	Integral breadth
ε	Apparent crystallite size
θ	Bragg angle
λ	Wavelength
τ	Value of t for which $V(t)$ vanishes
φ	Equation (31)
ψ	Equation (20)

The notation used is consistent throughout this review, but does not necessarily conform with that used previously in studies of crystallite-size broadening.

1. Introduction

If the crystallites making up a powder specimen are sufficiently small, the maxima of the diffraction pattern are broadened by an amount inversely proportional to the crystallite size,* and measurement of the additional broadening thus gives a means of estimating the size through the formula

$$\varepsilon = \frac{\lambda}{b \cos \theta}$$

where ε is the apparent crystallite size, λ is the wavelength of the radiation, b is the additional broadening (in radians), and θ is the Bragg angle. The 'true' size, defined as the cube root of the crystallite volume, is given by

$$p = K\varepsilon,$$

where K is a dimensionless number of the order of unity, known as the Scherrer constant, after Scherrer (1918) who first used this method of estimating crystallite sizes. The sixtieth anniversary of the publication of his paper is an appropriate time to review our existing knowledge of K. Its actual value depends on at least three things: the definition of 'breadth', the crystallite shape and the crystallite-size distribution.

(i) The definition of 'breadth'

The earliest definition of breadth, used by Scherrer, is the width of the diffraction maximum measured at a height half-way between background and peak, usu-

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* This has often been referred to as 'particle size' in the literature. The size obtained with X-ray methods is the effective length, measured in the direction of the diffraction vector, along which diffraction is coherent. Thus, 'crystallite size' is preferred, since individual particles may contain several crystallites, or domains having different orientations. The distinction is important if sizes obtained from diffraction broadening are compared with those given by other methods.

ally known as the half-width ($2w$). The second definition, introduced by von Laue (1936) (see also Jones, 1938), the integral breadth (β), is defined as the total area under the diffraction maximum divided by the peak intensity. It is thus the width of a rectangle having the same area and the same height as the actual diffraction maximum. The third measure, depending on the slope, k, of the variance of the line profile evaluated as the function of the range of integration, was introduced by Tournarie (1956a). The intercept of the variance function, W_0, yields a parameter which may also be regarded as an apparent crystallite size, ε_T. The 'true' size in this instance is $L^{1/2}\varepsilon_T$, where L, the taper parameter, depends on the angularity of the crystallites (Wilson, 1963, p. 98). In order that a direct comparison may be made between ε_T and other definitions of apparent size, $L^{1/2}$ will be replaced by K_T, the variance-intercept Scherrer constant.

The crystallite size can also be obtained from the negative initial slope of the Fourier transform of the normalized line profile (e.g. Warren, 1959). With correct interpretation of data this measure yields exactly the same apparent size as is given by the slope of the variance function of the line profile (Wilson, 1963, p. 96) and the same Scherrer constant applies.

These four measures depend on different properties of the crystallite size and shape, and hence give rise to different values of K (Tables 1, 2, 3, 4).

(ii) *The crystallite shape*

In practice, crystallites are usually irregular in shape, but on average they may often be regarded as having a regular external form. Whilst numerical results are given here only for spheres, cubes, tetrahedra and octahedra, the following discussion may readily be extended to include shapes not having cubic symmetry. Other forms of crystallite that have been considered are parallelepipeds [Table 1; see also Wilson (1962a, p. 52)], with needles and plates as special cases,

regular prisms and cylinders (Lele & Anatharaman, 1966; Louër, Weigel & Langford, 1972) and arbitrary prisms and hemispheres (Wilson, 1969). If the crystal system is non-cubic, the expressions for Scherrer constants in Table 1 still apply, but the numbers h, k, l are not the actual indices of reflexion, but are proportional to the direction cosines of the reflecting plane referred to the cubic axes of the external symmetry.

If the crystallites making up the specimen have a reasonably well defined shape, and if this shape has a reasonably well defined relation to the crystal axes, the numerical value of the Scherrer constant will depend on the indices of reflexion – unless, of course, the shape is a sphere. There are a few scattered determinations of K for the half-width (Scherrer, 1918; Murdock, 1930; Bragg, 1933, p. 189; Patterson, 1939b; Mauguin, 1943), but the relations between its values, the crystallite shape, and the indices of reflexion have not been systematically examined. This is partly because the 'apparent crystallite size' corresponding to the half-width has no obvious physical interpretation. In contrast, the apparent size corresponding to the integral breadth is simply the volume average of the thickness of the crystallites measured perpendicular to the reflecting planes, and has been evaluated systematically for the low-order reflexions from crystallites of simple regular shapes by Stokes & Wilson* (1942) [a more extensive table is given by Wilson (1962a)]. The apparent crystallite size corresponding to the slope of the variance-range curve also has a simple physical significance: it is the ratio of the total volume of the crystallites to the total area of their projection on a plane parallel to the reflecting planes.

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* There are errors on p. 314 of Stokes & Wilson (1942). The integral breadth for the 111 reflexion from a cube is 15% less than for the 100 and for an octahedron the integral breadth increases in the order 111, 100, 110.

Table 1. *Values of the integral-breadth* (K_β), *variance-slope* (K_k) *and variance-intercept* (K_T) *Scherrer constants for various shapes*

The indices h, k and l are to be interpreted as $|h|$, $|k|$ and $|l|$, and as arranged in the order $h \geq k \geq l$; $H = h+k+l$, $N = h^2+k^2+l^2$ and q is the least of $N^{1/2}p_1/h$, $N^{1/2}p_2/k$, $N^{1/2}p_3/l$.

	Scherrer constants					
	K_β		K_k		K_T	
Crystallite shape	$h \geq k+l$	$h \leq k+l$	$h \geq k+l$	$h \leq k+l$	$h \geq k+l$	$h \leq k+l$
General case	$\left[\dfrac{2}{V}\displaystyle\int_0^\tau V(t)dt\right]^{-1}$		$-\dfrac{V'(0)}{V}$		$\dfrac{V''(0)}{V}$	
Sphere	$\frac{4}{3}\left(\dfrac{\pi}{6}\right)^{1/3} = 1{\cdot}0747$		$\left(\dfrac{9\pi}{16}\right)^{1/3} = 1{\cdot}2090$		0	
Cube	$6h^3/N^{1/2}[6h^2-2(k+l)h+kl]$		$H/N^{1/2}$		$H^2/N-1$	
Tetrahedron	$2h/3^{1/3}N^{1/2}$	$H/3^{1/3}N^{1/2}$	$3h/3^{1/3}N^{1/2}$	$3H/2 \times 3^{1/3}N^{1/2}$	$2 \times 3^{1/3}h^2/N$	$3^{1/3}H^2/2N$
Octahedron	$\dfrac{2H^3}{6^{1/3}N^{1/2}[H^2+(k+l)H+2kl]}$	$\dfrac{2H^3}{6^{1/3}N^{1/2}(2H^2-N)}$	$3h/6^{1/3}N^{1/2}$	$3H/2 \times 6^{1/3}N^{1/2}$	$6^{1/3}(2h^2/N-1)$	$6^{1/3}(H^2/2N-1)$
Rectangular parallelepiped of edges p_1, p_2, p_3	$\frac{1}{2}\left[q-\dfrac{K_k}{p}\dfrac{q^2}{2}+\dfrac{K_T}{2p^2}\dfrac{q^3}{3}-\dfrac{hkl}{N^{3/2}p^3}\dfrac{q^4}{4}\right]^{-1}$		$p(h/p_1+k/p_2+l/p_3)/N^{1/2}$		$2p^2(hk/p_1p_2+kl/p_2p_3+lh/p_1p_3)/N$	

Numerical values are given by Tournarie (1956*b*) and, to a further place of decimals, Wilson (1962*b*).

(iii) The crystallite-size distribution

Even if the crystallites are more or less uniform in shape, they may not be uniform in size. A distribution of crystallite sizes will affect the various measures of breadth in different ways, and thus alter the various Scherrer constants. The details of the alteration will depend on the definition adopted for 'true' size. The usual definition when all the crystallites are assumed to have the same size and shape is the cube root of the volume of one crystallite. When there is a distribution of crystallite sizes the definition of 'true' size could be generalized in two reasonable ways, either to the mean value of the cube roots of the individual crystallite volumes, or to the cube root of the mean value of the volumes of the individual crystallites.

Table 2. *Scherrer constants for cubic crystallites*

hkl	K_w	K_β	K_k	K_T	K_w/K_β	K_k/K_β
100	0.8859	1.0000	1.0000	0.0000	0.8859	1.0000
110	0.8340	1.0607	1.4142	1.0000	0.7863	1.3333
111	0.8551	1.1547	1.7321	1.4142	0.7406	1.5000
210	0.8777	1.0733	1.3416	0.8944	0.8178	1.2500
211	0.8882	1.1527	1.6330	1.2910	0.7706	1.4167
221	0.8614	1.1429	1.6667	1.3333	0.7537	1.4583
310	0.8943	1.0673	1.2649	0.7746	0.8379	1.1852
311	0.9082	1.1359	1.5076	1.1282	0.7995	1.3272
320	0.8574	1.0698	1.3868	0.9608	0.8015	1.2963
321	0.8795	1.1394	1.6036	1.2536	0.7719	1.4074
410	0.8986	1.0583	1.2127	0.6860	0.8491	1.1458
322	0.8689	1.1556	1.6977	1.3720	0.7519	1.4691
411	0.9137	1.1174	1.4142	1.0000	0.8177	1.2656
331	0.8592	1.1262	1.6059	1.2566	0.7629	1.4259
421	0.8964	1.1324	1.5275	1.1547	0.7917	1.3490
332	0.8596	1.1513	1.7056	1.3817	0.7466	1.4715
430	0.8482	1.0667	1.4000	0.9798	0.7952	1.3125
431	0.8697	1.1240	1.5689	1.2089	0.7738	1.3958
510	0.8994	1.0506	1.1767	0.6202	0.8561	1.1200
511	0.9142	1.1018	1.3472	0.9027	0.8297	1.2227
520	0.8886	1.0713	1.2999	0.8305	0.8295	1.2133
432	0.8705	1.1501	1.6713	1.3391	0.7569	1.4531
521	0.9053	1.1224	1.4606	1.0646	0.8066	1.3013
522	0.9010	1.1452	1.5667	1.2060	0.7867	1.3680
441	0.8559	1.1141	1.5667	1.2060	0.7682	1.4063
530	0.8655	1.0719	1.3720	0.9393	0.8075	1.2800
433	0.8622	1.1554	1.7150	1.3933	0.7462	1.4844
531	0.8836	1.1219	1.5213	1.1464	0.7878	1.3560
610	0.8991	1.0444	1.1508	0.5695	0.8608	1.1019
611	0.9131	1.0893	1.2976	0.8272	0.8382	1.1914
532	0.8850	1.1478	1.6222	1.2773	0.7710	1.4133
621	0.9093	1.1121	1.4056	0.9877	0.8177	1.2639
540	0.8435	1.0648	1.4056	0.9877	0.7921	1.3200
443	0.8581	1.1533	1.7179	1.3969	0.7440	1.4896
541	0.8628	1.1128	1.5430	1.1751	0.7753	1.3867
533	0.8758	1.1553	1.6775	1.3468	0.7581	1.4520
542	0.8684	1.1409	1.6398	1.2996	0.7612	1.4373
631	0.8938	1.1175	1.4744	1.0835	0.7999	1.3194
632	0.8960	1.1429	1.5714	1.2122	0.7840	1.3750
710	0.8984	1.0394	1.1314	0.5292	0.8643	1.0884
543	0.8651	1.1529	1.6971	1.3711	0.7504	1.4720
711	0.9115	1.0793	1.2603	0.7670	0.8445	1.1676
551	0.8530	1.1055	1.5403	1.1716	0.7716	1.3933
720	0.8972	1.0627	1.2362	0.7268	0.8442	1.1633
641	0.8743	1.1126	1.5110	1.1327	0.7858	1.3580
721	0.9109	1.1026	1.3608	0.9230	0.8262	1.2342
552	0.8607	1.1340	1.6330	1.2910	0.7590	1.4400
722	0.9119	1.1264	1.4570	1.0596	0.8096	1.2935
544	0.8593	1.1551	1.7219	1.4018	0.7439	1.4907
730	0.8858	1.0723	1.3131	0.8510	0.8260	1.2245
731	0.9002	1.1117	1.4321	1.0251	0.8097	1.2881
553	0.8606	1.1487	1.6925	1.3654	0.7492	1.4733
650	0.8408	1.0637	1.4084	0.9918	0.7904	1.3241
643	0.8762	1.1523	1.6645	1.3306	0.7604	1.4444
732	0.9032	1.1364	1.5240	1.1500	0.7948	1.3411
651	0.8579	1.1046	1.5240	1.1500	0.7766	1.3796
810	0.8976	1.0354	1.1163	0.4961	0.8669	1.0781
740	0.8690	1.0725	1.3644	0.9282	0.8103	1.2721
652	0.8654	1.1320	1.6125	1.2649	0.7645	1.4244
811	0.9098	1.0712	1.2309	0.7177	0.8493	1.1491
741	0.8840	1.1111	1.4771	1.0871	0.7956	1.3294
554	0.8572	1.1540	1.7233	1.4035	0.7428	1.4933
733	0.8975	1.1481	1.5882	1.2339	0.7817	1.3834
821	0.9113	1.0942	1.3242	0.8681	0.8328	1.2103
742	0.8892	1.1365	1.5650	1.2039	0.7824	1.3771
653	0.8657	1.1474	1.6733	1.3416	0.7545	1.4583
830	0.8909	1.0701	1.2875	0.8109	0.8326	1.2031
661	0.8507	1.0992	1.5215	1.1468	0.7739	1.3843
831	0.9040	1.1056	1.3950	0.9726	0.8177	1.2617
750	0.8520	1.0680	1.3950	0.9726	0.7977	1.3061
743	0.8866	1.1502	1.6275	1.2840	0.7708	1.4150
751	0.8673	1.1053	1.5011	1.1195	0.7847	1.3581
832	0.9078	1.1293	1.4815	1.0931	0.8039	1.3118
654	0.8620	1.1539	1.7094	1.3864	0.7470	1.4815
752	0.8743	1.1312	1.5852	1.2300	0.7729	1.4014
841	0.8912	1.1082	1.4444	1.0423	0.8042	1.3034
744	0.8792	1.1549	1.6667	1.3333	0.7613	1.4431
910	0.8969	1.0321	1.1043	0.4685	0.8690	1.0700
833	0.9039	1.1422	1.5460	1.1791	0.7913	1.3535
911	0.9082	1.0645	1.2074	0.6766	0.8532	1.1342
753	0.8745	1.1467	1.6465	1.3080	0.7627	1.4359
920	0.8992	1.0543	1.1931	0.6508	0.8529	1.1317
760	0.8391	1.0630	1.4100	0.9941	0.7894	1.3265
921	0.9109	1.0868	1.2940	0.8212	0.8382	1.1907
761	0.8543	1.0986	1.5097	1.1310	0.7776	1.3741
655	0.8579	1.1550	1.7253	1.4060	0.7428	1.4938
922	0.9143	1.1092	1.3780	0.9481	0.8243	1.2423
850	0.8624	1.0712	1.4780	0.9481	0.8051	1.2865
843	0.8947	1.1466	1.5900	1.2362	0.7803	1.3867
762	0.8626	1.1245	1.5900	1.2362	0.7671	1.4140
851	0.8762	1.1052	1.4757	1.0853	0.7928	1.3353
754	0.8704	1.1539	1.6865	1.3581	0.7544	1.4616
931	0.9063	1.0996	1.3628	0.9258	0.8242	1.2394
852	0.8828	1.1296	1.5554	1.1914	0.7815	1.3770
932	0.9166	1.1222	1.4440	1.0417	0.8114	1.2867
763	0.8650	1.1412	1.6503	1.3128	0.7580	1.4461
940	0.8841	1.0727	1.3200	0.8615	0.8241	1.2305
665	0.8566	1.1543	1.7261	1.4069	0.7421	1.4954
941	0.8964	1.1046	1.4142	1.0000	0.8115	1.2803
853	0.8832	1.1451	1.6162	1.2697	0.7713	1.4115
771	0.8488	1.0944	1.5076	1.1282	0.7756	1.3776
755	0.8648	1.1555	1.7086	1.3853	0.7484	1.4786

Table 3. *Scherrer constants for tetrahedral crystallites*

hkl	K_w	K_β	K_k	K_T	K_w/K_β	K_k/K_β
100	1.0270	1.3867	2.0801	1.6984	0.7406	1.5000
110	0.7262	0.9806	1.4708	1.2009	0.7406	1.5000
111	0.8894	1.2009	1.8014	1.4708	0.7406	1.5000
210	0.9185	1.2403	1.8605	1.5191	0.7406	1.5000
211	0.8365	1.1323	1.6984	1.3867	0.7406	1.5000
221	0.8556	1.1556	1.7334	1.4153	0.7406	1.5000
310	0.9743	1.3156	1.9733	1.6112	0.7406	1.5000
311	0.9289	1.2543	1.8815	1.5362	0.7406	1.5000
320	0.8545	1.1538	1.7307	1.4131	0.7406	1.5000
321	0.8234	1.1119	1.6678	1.3617	0.7406	1.5000
410	0.9963	1.3453	2.0180	1.6477	0.7406	1.5000
322	0.8718	1.1772	1.7657	1.4417	0.7406	1.5000
411	0.9682	1.3074	1.9611	1.6012	0.7406	1.5000
331	0.8246	1.1135	1.6702	1.3637	0.7406	1.5000
421	0.8964	1.2104	1.8156	1.4825	0.7406	1.5000
332	0.8755	1.1826	1.7739	1.4484	0.7406	1.5000
430	0.8216	1.1094	1.6641	1.3587	0.7406	1.5000
431	0.8056	1.0878	1.6318	1.3323	0.7406	1.5000
510	1.0070	1.3598	2.0397	1.6654	0.7406	1.5000
511	0.9882	1.3344	2.0016	1.6343	0.7406	1.5000
520	0.9535	1.2875	1.9313	1.5769	0.7406	1.5000
432	0.8582	1.1588	1.7382	1.4192	0.7406	1.5000
521	0.9375	1.2659	1.8988	1.5504	0.7406	1.5000
522	0.8939	1.2070	1.8105	1.4783	0.7406	1.5000
441	0.8045	1.0863	1.6294	1.3304	0.7406	1.5000
530	0.8806	1.1891	1.7837	1.4563	0.7406	1.5000
433	0.8806	1.1891	1.7837	1.4563	0.7406	1.5000
531	0.8679	1.1720	1.7580	1.4354	0.7406	1.5000
610	1.0150	1.3679	2.0518	1.6753	0.7406	1.5000
611	0.9996	1.3497	2.0244	1.6531	0.7406	1.5000
532	0.8330	1.1248	1.6872	1.3776	0.7406	1.5000
621	0.9623	1.2994	1.9491	1.5915	0.7406	1.5000
540	0.8019	1.0828	1.6243	1.3262	0.7406	1.5000
443	0.8821	1.1911	1.7867	1.4588	0.7406	1.5000
541	0.7923	1.0699	1.6048	1.3103	0.7406	1.5000
533	0.8614	1.1631	1.7447	1.4245	0.7406	1.5000
542	0.8420	1.1370	1.7054	1.3925	0.7406	1.5000
631	0.9085	1.2268	1.8401	1.5025	0.7406	1.5000
632	0.8803	1.1886	1.7837	1.4558	0.7406	1.5000
710	1.0166	1.3728	2.0592	1.6813	0.7406	1.5000
543	0.8714	1.1767	1.7650	1.4411	0.7406	1.5000
711	1.0066	1.3593	2.0389	1.6647	0.7406	1.5000
551	0.7909	1.0680	1.6020	1.3080	0.7406	1.5000
720	0.9875	1.3334	2.0001	1.6330	0.7406	1.5000
641	0.8464	1.1429	1.7143	1.3997	0.7406	1.5000
721	0.9783	1.3210	1.9814	1.6178	0.7406	1.5000
552	0.8385	1.1323	1.6984	1.3867	0.7406	1.5000
722	0.9522	1.2857	1.9286	1.5747	0.7406	1.5000
544	0.8842	1.1939	1.7908	1.4622	0.7406	1.5000
730	0.9439	1.2746	1.9119	1.5611	0.7406	1.5000
731	0.9359	1.2638	1.8956	1.5478	0.7406	1.5000
553	0.8690	1.1735	1.7602	1.4372	0.7406	1.5000
650	0.7889	1.0653	1.5980	1.3047	0.7406	1.5000
643	0.8542	1.1541	1.7602	1.4411	0.7406	1.5000
732	0.9110	1.2328	1.8492	1.5099	0.7406	1.5000
651	0.7826	1.0567	1.5850	1.2942	0.7406	1.5000
810	1.0190	1.3760	2.0640	1.6853	0.7406	1.5000
740	0.8917	1.2040	1.8060	1.4746	0.7406	1.5000
652	0.8280	1.1180	1.6770	1.3693	0.7406	1.5000
811	1.0113	1.3655	2.0483	1.6725	0.7406	1.5000
741	0.8849	1.1949	1.7923	1.4634	0.7406	1.5000
554	0.8849	1.1949	1.7923	1.4634	0.7406	1.5000
733	0.8782	1.1859	1.7789	1.4524	0.7406	1.5000
821	0.9891	1.3355	2.0033	1.6357	0.7406	1.5000
742	0.8654	1.1682	1.7529	1.4312	0.7406	1.5000
653	0.8592	1.1602	1.7403	1.4210	0.7406	1.5000
830	0.9616	1.2984	1.9476	1.5902	0.7406	1.5000
661	0.7815	1.0550	1.5825	1.2921	0.7406	1.5000
831	0.9551	1.2896	1.9344	1.5795	0.7406	1.5000
750	0.8357	1.1284	1.6926	1.3820	0.7406	1.5000
743	0.8357	1.1284	1.6926	1.3820	0.7406	1.5000
751	0.8301	1.1209	1.6813	1.3728	0.7406	1.5000
832	0.9363	1.2643	1.8964	1.5484	0.7406	1.5000
654	0.8778	1.1852	1.7779	1.4516	0.7406	1.5000
752	0.8140	1.0991	1.6487	1.3461	0.7406	1.5000
841	0.9129	1.2326	1.8490	1.5097	0.7406	1.5000
744	0.8558	1.1556	1.7334	1.4153	0.7406	1.5000
910	1.0207	1.3782	2.0674	1.6880	0.7406	1.5000
833	0.9073	1.2251	1.8377	1.5004	0.7406	1.5000
911	1.0145	1.3699	2.0549	1.6778	0.7406	1.5000
753	0.8454	1.1416	1.7124	1.3982	0.7406	1.5000
920	1.0025	1.3537	2.0306	1.6579	0.7406	1.5000
760	0.7797	1.0529	1.5793	1.2895	0.7406	1.5000
921	0.9967	1.3458	2.0187	1.6483	0.7406	1.5000
761	0.7752	1.0467	1.5701	1.2820	0.7406	1.5000
655	0.8859	1.1963	1.7944	1.4651	0.7406	1.5000
922	0.9797	1.3229	1.9839	1.6203	0.7406	1.5000
850	0.8709	1.1759	1.7639	1.4402	0.7406	1.5000
843	0.8709	1.1759	1.7639	1.4402	0.7406	1.5000
762	0.8164	1.1024	1.6537	1.3502	0.7406	1.5000
851	0.8660	1.1694	1.7541	1.4322	0.7406	1.5000
754	0.8660	1.1694	1.7541	1.4322	0.7406	1.5000
931	0.9689	1.3083	1.9625	1.6023	0.7406	1.5000
852	0.8519	1.1504	1.7256	1.4089	0.7406	1.5000
932	0.9533	1.2873	1.9309	1.5766	0.7406	1.5000
763	0.8474	1.1442	1.7164	1.4014	0.7406	1.5000
940	0.9385	1.2672	1.9008	1.5520	0.7406	1.5000
665	0.8863	1.1968	1.7952	1.4658	0.7406	1.5000
941	0.9337	1.2607	1.8911	1.5441	0.7406	1.5000
853	0.8299	1.1206	1.6810	1.3725	0.7406	1.5000
771	0.7741	1.0453	1.5679	1.2802	0.7406	1.5000
755	0.8773	1.1847	1.7770	1.4509	0.7406	1.5000

The effect of the distribution of sizes on the Scherrer constant appropriate for use with the slope of the variance-range curve has been discussed by Wilson (1971) in terms of the first of these generalizations. The two definitions of 'true' size are, of course, easily related to one another for a given distribution (§ 6 below).

The objects of the present paper are: (i) to survey existing knowledge about Scherrer constants; (ii) to treat systematically the half-width Scherrer constant, about which little was previously known (§ 3); (iii) to tabulate Scherrer constants appropriate for use with all four commonly used measures of breadth (Tables 2, 3, 4) for all low-order reflexions $(h^2 + k^2 + l^2 \le 100)$ from crystallites of simple regular shapes; and (iv) to discuss the effect of a distribution of crystallite sizes on the integral-breadth Scherrer constant and on the half-width Scherrer constant (§ 6). It does not attempt to review the separation of crystallite-size broadening from other sources of line breadth (see, for example, Klug & Alexander, 1974, § 9.2), nor to review the theoretical basis of the calculations; these are simply picked up at convenient points in earlier publications. The fundamental papers are those of Patterson (1939a, b), which should be consulted for the basic validation of the 'tangent-plane approximation'. An elementary account is given by Wilson (1962a, pp. 37–53).

2. Volume averages and projected-area averages

Stokes & Wilson (1942) found the most natural presentation of the apparent crystallite size corresponding to the integral breadth to be the volume average

$$\varepsilon_\beta = \frac{1}{V} \int \int \int T \, dx \, dy \, dz, \qquad (1)$$

where V is the volume of the crystallite, T is the thickness of the crystal measured through the point x, y, z in the direction perpendicular to the reflecting planes, and the integration is over the entire volume of the crystallite. However, the presentation most convenient for calculation was in terms of an integration over the volume $V(t)$ common to the crystallite and its 'ghost' shifted a distance t in the direction perpendicular to the reflecting planes:

$$\varepsilon_\beta = \frac{1}{V} \int V(t) \, dt \; ;$$

the integration is over the whole range of t, positive and negative, for which $V(t)$ exists. The most natural presentation of the apparent crystallite size corresponding to the slope of the variance-range curve is an area average over the projected area of the crystallite (Tournarie, 1956a, b; Wilson, 1962a):

$$\varepsilon_k = \frac{1}{A} \int \int T \, dy \, dz, \qquad (3)$$

where A is the projected area, though it can be expressed as a volume integral

$$\varepsilon_k = \left[\frac{1}{V} \int \int \int T^{-1} \, dx \, dy \, dz \right]^{-1}, \qquad (4)$$

or in terms of the initial slope of $V(t)$:

$$\varepsilon_k = -V/V'(0), \qquad (5)$$

which is the expression from which the tabulated values of the corresponding Scherrer constant have

Table 4. *Scherrer constants for octahedral crystallites*

hkl	K_w	K_β	K_k	K_T	K_w/K_β	K_k/K_β
100	0.8151	1.1006	1.6510	1.3480	0.7406	1.5000
110	0.8613	1.0377	1.1674	0.0000	0.8300	1.1250
111	0.9354	1.1438	1.4298	0.9532	0.8178	1.2500
210	0.8709	1.1075	1.4767	1.0442	0.7863	1.3333
211	0.9057	1.1061	1.3480	0.7783	0.8188	1.2187
221	0.9153	1.1185	1.3758	0.8406	0.8183	1.2300
310	0.8556	1.1138	1.5662	1.2057	0.7682	1.4062
311	0.8863	1.1211	1.4934	1.0753	0.7905	1.3320
320	0.8752	1.0902	1.3737	0.8360	0.8028	1.2400
321	0.8977	1.0955	1.3237	0.7205	0.8194	1.2083
410	0.8442	1.1123	1.6017	1.2662	0.7590	1.4400
322	0.9247	1.1304	1.4015	0.8954	0.8180	1.2398
411	0.8685	1.1207	1.5565	1.1888	0.7750	1.3889
331	0.8983	1.0963	1.3256	0.7253	0.8194	1.2092
421	0.8895	1.1133	1.4411	0.9756	0.7990	1.2945
332	0.9271	1.1334	1.4079	0.9088	0.8179	1.2422
430	0.8740	1.0786	1.3208	0.7133	0.8103	1.2245
431	0.8889	1.0835	1.2951	0.6476	0.8204	1.1953
510	0.8367	1.1101	1.6189	1.2951	0.7537	1.4583
511	0.8557	1.1178	1.5886	1.2442	0.7656	1.4213
520	0.8631	1.1128	1.5329	1.1471	0.7756	1.3776
432	0.9167	1.1203	1.3796	0.8489	0.8183	1.2315
521	0.8784	1.1183	1.5071	1.1006	0.7855	1.3477
522	0.8966	1.1174	1.4370	0.9675	0.8024	1.2860
441	0.8884	1.0827	1.2933	0.6426	0.8205	1.1944
530	0.8747	1.0982	1.4157	0.9247	0.7965	1.2891
433	0.9300	1.1371	1.4157	0.9247	0.8179	1.2450
531	0.8872	1.1026	1.3953	0.8825	0.8046	1.2654
610	0.8317	1.1083	1.6285	1.3111	0.7504	1.4694
611	0.8467	1.1148	1.6069	1.2751	0.7595	1.4414
532	0.9027	1.1021	1.3391	0.7575	0.8190	1.2150
621	0.8683	1.1188	1.5470	1.1721	0.7761	1.3827
540	0.8724	1.0710	1.2892	0.6316	0.8146	1.2037
443	0.9309	1.1382	1.4181	0.9296	0.8179	1.2459
541	0.8829	1.0749	1.2737	0.5883	0.8214	1.1850
533	0.9185	1.1226	1.3847	0.8600	0.8182	1.2335
542	0.9076	1.1085	1.3536	0.7911	0.8187	1.2211
631	0.8814	1.1115	1.4605	1.0134	0.7930	1.3140
632	0.8967	1.1132	1.4151	0.9235	0.8056	1.2712
710	0.8282	1.1069	1.6344	1.3208	0.7482	1.4766
543	0.9244	1.1301	1.4009	0.8942	0.8180	1.2396
711	0.8403	1.1124	1.6183	1.2941	0.7554	1.4547
551	0.8823	1.0740	1.2715	0.5818	0.8215	1.1839
720	0.8494	1.1133	1.5874	1.2421	0.7629	1.4259
641	0.8842	1.0936	1.3607	0.8071	0.8085	1.2442
721	0.8599	1.1177	1.5727	1.2168	0.7693	1.4070
552	0.9057	1.1061	1.3480	0.7783	0.8188	1.2187
722	0.8768	1.1216	1.5307	1.1433	0.7817	1.3648
544	0.9322	1.1398	1.4214	0.9363	0.8178	1.2470
730	0.8657	1.1117	1.5175	1.1195	0.7787	1.3650
731	0.8747	1.1153	1.5046	1.0960	0.7842	1.3490
553	0.9230	1.1284	1.3971	0.8862	0.8180	1.2382
650	0.8710	1.0657	1.2683	0.5724	0.8173	1.1901
643	0.9147	1.1177	1.3740	0.8367	0.8183	1.2293
732	0.8892	1.1183	1.4677	1.0272	0.7952	1.3125
651	0.8787	1.0688	1.2580	0.5414	0.8222	1.1771
810	0.8256	1.1058	1.6382	1.3271	0.7466	1.4815
740	0.8740	1.1012	1.4334	0.9605	0.7936	1.3017
652	0.9001	1.0986	1.3310	0.7383	0.8192	1.2115
811	0.8356	1.1105	1.6258	1.3065	0.7524	1.4640
741	0.8817	1.1043	1.4225	0.9386	0.7984	1.2882
554	0.9326	1.1404	1.4225	0.9386	0.8178	1.2474
733	0.8999	1.1148	1.4119	0.9169	0.8073	1.2665
821	0.8531	1.1162	1.5900	1.2465	0.7642	1.4245
742	0.8945	1.1069	1.3913	0.8739	0.8081	1.2569
653	0.9173	1.1211	1.3813	0.8526	0.8182	1.2321
830	0.8605	1.1134	1.5458	1.1701	0.7728	1.3884
661	0.8782	1.0680	1.2560	0.5350	0.8223	1.1760
831	0.8682	1.1166	1.5354	1.1515	0.7775	1.3750
750	0.8748	1.0838	1.3434	0.7677	0.8071	1.2396
743	0.9041	1.1040	1.3434	0.7677	0.8189	1.2168
751	0.8815	1.0865	1.3345	0.7465	0.8113	1.2283
832	0.8817	1.1202	1.5052	1.0971	0.7871	1.3437
654	0.9283	1.1349	1.4111	0.9153	0.8179	1.2433
752	0.8930	1.0891	1.3085	0.6826	0.8199	1.2015
841	0.8776	1.1102	1.4675	1.0268	0.7904	1.3218
744	0.9153	1.1185	1.3758	0.8406	0.8183	1.2300
910	0.8238	1.1050	1.6409	1.3315	0.7455	1.4850
833	0.8931	1.1192	1.4585	1.0096	0.7980	1.3032
911	0.8321	1.1090	1.6310	1.3151	0.7503	1.4707
753	0.9095	1.1110	1.3591	0.8036	0.8186	1.2233
920	0.8401	1.1112	1.6116	1.2830	0.7560	1.4504
760	0.8699	1.0619	1.2535	0.5272	0.8192	1.1805
921	0.8476	1.1146	1.6023	1.2672	0.7604	1.4375
761	0.8758	1.0643	1.2462	0.5035	0.8229	1.1709
655	0.9333	1.1412	1.4242	0.9420	0.8178	1.2480
922	0.8615	1.1193	1.5750	1.2208	0.7697	1.4071
850	0.8751	1.0954	1.4000	0.8923	0.7989	1.2781
843	0.8997	1.1123	1.4000	0.8923	0.8089	1.2587
762	0.8942	1.0907	1.3125	0.6927	0.8198	1.2033
851	0.8809	1.0978	1.3922	0.8759	0.8025	1.2682
754	0.9212	1.1261	1.3922	0.8759	0.8181	1.2363
931	0.8623	1.1167	1.5576	1.1907	0.7722	1.3949
852	0.8916	1.1006	1.3696	0.8270	0.8102	1.2444
932	0.8747	1.1205	1.5326	1.1465	0.7806	1.3677
763	0.9105	1.1124	1.3623	0.8107	0.8185	1.2246
940	0.8670	1.1110	1.5087	1.1035	0.7804	1.3580
665	0.9335	1.1415	1.4249	0.9433	0.8178	1.2483
941	0.8729	1.1134	1.5010	1.0894	0.7840	1.3480
853	0.9011	1.1000	1.3342	0.7458	0.8192	1.2129
771	0.8754	1.0636	1.2445	0.4978	0.8230	1.1700
755	0.9280	1.1346	1.4104	0.9139	0.8179	1.2431

been obtained. A projected-area average for the integral-breadth apparent crystallite size, corresponding to (3) for the variance-slope size, is easily obtained from (1) by choosing the coordinate system so that one of the axes, say x, is perpendicular to the reflecting planes. The thickness T is then independent of x, and integration over x gives another T, so that

$$\varepsilon_\beta = \frac{1}{V} \int \int T^2 \mathrm{d}y \mathrm{d}z. \tag{6}$$

Obviously $V = A\langle T \rangle_A$, where the angle brackets indicate averaging over the projected area. With a similar notation to indicate averaging over the crystallite volume, we can write

$$\varepsilon_\beta = \langle T \rangle_V = \langle T^2 \rangle_A / \langle T \rangle_A, \tag{7}$$

$$\varepsilon_k = \langle T^{-1} \rangle_V^{-1} = \langle T \rangle_A. \tag{8}$$

The area-average expression for ε_β was derived in the early days of the subject by Waller (1939) and somewhat later by Bouman & de Wolff (1942).

The apparent size obtained from the intercept of the variance–range curve cannot readily be represented as a volume average or as a projected-area average. It is most conveniently expressed in terms of the initial second derivative of $V(t)$:

$$\varepsilon_T = V / V''(0). \tag{9}$$

There are no analogous simple expressions for the half-width apparent crystallite size ε_w. First approximations may be obtained by using the first few terms of a power-series expansion for the line profile. This is proportional to

$$I(s) = \frac{1}{A} \int \int \frac{\sin^2 (\pi T s)}{(\pi s)^2} \mathrm{d}y \mathrm{d}z, \tag{10}$$

where s is expressed in reciprocal-space units [Wilson (1962a, p. 39); the proportionality factor has been altered]. Using the series expansion for $\sin^2$ gives

$$\begin{aligned}
I(s) &= \frac{1}{A} \int \int [T^2 - \tfrac{1}{12}T^4(2\pi s)^2 \\
&\quad + \tfrac{1}{360}T^6(2\pi s)^4 - \tfrac{1}{20160}T^8(2\pi s)^6 + \ldots] \mathrm{d}y \mathrm{d}z \\
&= \langle T^2 \rangle_A - \tfrac{1}{12}\langle T^4 \rangle_A (2\pi s)^2 \\
&\quad + \tfrac{1}{360}\langle T^6 \rangle_A (2\pi s)^4 - \tfrac{1}{20160}\langle T^8 \rangle_A (2\pi s)^6 + \ldots.
\end{aligned} \tag{11}$$

The value of s for which $I(s)$ falls to half value thus lies between the solutions of the two equations

$$(2\pi s)^2 - 6 \frac{\langle T^2 \rangle_A}{\langle T^4 \rangle_A} = 0 \tag{12}$$

and

$$-\tfrac{1}{30} \frac{\langle T^6 \rangle_A}{\langle T^4 \rangle_A}(2\pi s)^4 + (2\pi s)^2 - 6 \frac{\langle T^2 \rangle_A}{\langle T^4 \rangle_A} = 0. \tag{13}$$

Equation (12) gives as an upper limit for the half-width apparent crystallite size

$$\varepsilon_w = \frac{1}{2s} = \frac{\pi}{6^{1/2}} \left(\frac{\langle T^4 \rangle_A}{\langle T^2 \rangle_A} \right)^{1/2}. \tag{14}$$

A lower limit, which is normally a better approximation, can be derived from (13):

$$\begin{aligned}
\varepsilon_w &= \frac{1}{2s} = \frac{\pi}{6^{1/2}} \left(\frac{\langle T^4 \rangle_A}{\langle T^2 \rangle_A} \right)^{1/2} \\
&\times \left\{ \tfrac{1}{2} \left[1 + \left(1 - \frac{4\langle T^2 \rangle_A \langle T^6 \rangle_A}{5\langle T^4 \rangle_A^2} \right)^{1/2} \right] \right\}^{1/2},
\end{aligned} \tag{15}$$

which is 10 to 20% lower, but depends, of course, on the value of $\langle T^2 \rangle_A \langle T^6 \rangle_A / \langle T^4 \rangle_A^2$ for the crystallite shape and the indices of reflexion. This factor has the value unity for reflexions from the faces of a cube, and may be taken as unity as a first approximation for any reflexion from a crystallite without pronounced anisotropy of shape. The numerical value of the multiplier in (15) is then 0·8507, so that, approximately,

$$\varepsilon_w = 0·85 \frac{\pi}{6^{1/2}} \left(\frac{\langle T^4 \rangle_A}{\langle T^2 \rangle_A} \right)^{1/2}. \tag{16}$$

The half-width, therefore, gives a crystallite size approximately proportional to the ratio of the root-mean-fourth-power to the root-mean-square value of the thickness of the crystallite. The degree of approximation obtained is illustrated in Fig. 1. The contours in the upper-left corner are derived from accurate numerical calculations, and those in the lower-right corner from (16). The qualitative features of the variation with crystallographic direction are well reproduced, but the numerical values may differ by as much as 3%. A series that may occasionally be useful can be obtained by a reversion of (11) in the usual way (Abramowitz & Stegun, 1964, p. 16), giving
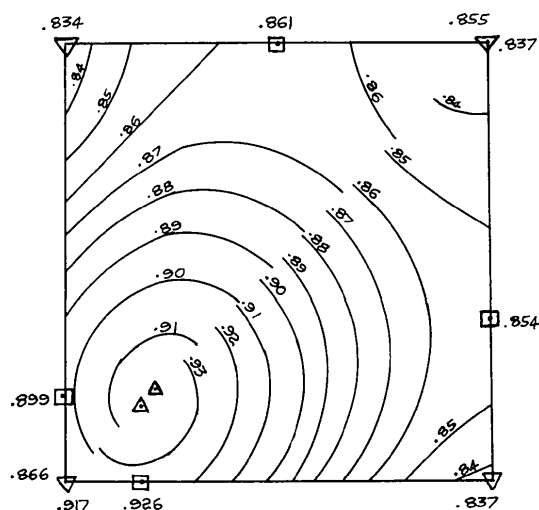

Fig. 1. Comparison of exact (upper left) Scherrer constants for the half-width of reflexions from cube-shaped crystals with those calculated from the approximate equation (16) (lower right). The contours are reflected across the diagonal joining 0,0 to 1,1.

$$(2\pi s)^2 = 6\frac{\langle T^2 \rangle_A}{\langle T^4 \rangle_A}\left[1 + \frac{\langle T^2 \rangle_A \langle T^6 \rangle_A}{5\langle T^4 \rangle_A^2}\right.$$
$$\left. + \left(\tfrac{2}{25}\langle T^6 \rangle_A^2 - \tfrac{3}{140}\langle T^4 \rangle_A \langle T^8 \rangle_A\right)\frac{\langle T^2 \rangle_A^2}{\langle T^4 \rangle_A^4} + \ldots\right]. \quad (17)$$

This agrees with (15) up to terms in $\langle T^6 \rangle_A^2$. The area averages, if wanted in any particular case, would probably be obtained most easily in terms of $V(t)$:

$$\langle T^n \rangle_A = -\frac{n(n-1)}{2V'(0)}\int t^{n-2}V(t)\mathrm{d}t. \quad (18)$$

The Scherrer constants are, for each measure of line breadth, given by

$$K_j = p/\varepsilon_j. \quad (19)$$

3. Scherrer constants for the half-width

For crystallites having any shape for which $V(t)$ can be expressed as a cubic with constant coefficients and continuous derivatives, the line profile is given by (Wilson, 1962a, p. 47, equation 25)

$$I(s) = Y^{-1}[a_1\psi^{-2} + a_2\psi^{-2}\cos 2\psi$$
$$+ a_3\psi^{-3}\sin 2\psi + a_4\psi^{-4}(1 - \cos 2\psi)], \quad (20)$$

where Y is the volume of the unit cell, $\psi = \pi s\tau$ [τ being the value of t for which $V(t) = 0$], $a_1 = -\tau^2 V'(0)/2$, $a_2 = \tau^2 V'(\tau)/2$, $a_3 = -\tau^3 V''(\tau)/4$ and $a_4 = \tau^4 V'''/8$. For small crystallites, $I(s) = I(-s)$ and has a maximum value at $s = 0$ given by

$$I(0) = 2Y^{-1}\int_0^\tau V(t)\mathrm{d}t. \quad (21)$$

Expressions for τ, $V'(0)$, etc. are listed in Table 5 for various shapes having cubic symmetry. The half-width is then given by the value of ψ for which $I(s) = \tfrac{1}{2}I(0)$, or

$$2w_s = 2\psi_w/\pi\tau. \quad (22)$$

For the purpose of calculating line-profile parameters and Scherrer constants it is convenient to take the cube root of the volume of the crystallites, or 'true size' (p), as unity. [The actual magnitude of $I(s)$ must be multiplied by p^4 for $p \neq 1$, but the Scherrer constants are not affected.] The half-width Scherrer constant, K_w, is then equal to $2w_s$.

ψ_w can be obtained in the usual way by the successive application of Newton's method:

$$\psi_w = g - [I(g) - \tfrac{1}{2}I(0)]/I'(g), \quad (23)$$

where g is an approximate value of ψ_w and

$$I'(\psi) = 2U^{-1}[a_2\psi^{-2}\sin 2\psi + a_1\psi^{-3}$$
$$+ (a_2 - a_3)\psi^{-3}\cos 2\psi + (\tfrac{3}{2}a_3 - a_4)\psi^{-4}\sin 2\psi$$
$$+ 2a_4\psi^{-5}(1 - \cos 2\psi)]. \quad (24)$$

K_w does not display a wide variation with hkl or crystallite shape and a value of 0·90 may be taken as

a first approximation (see Scherrer, 1918, for example). The initial value of g is then given by (22).

The values of K_w calculated from (23) to a precision of better than 5 parts in 10^5 for $N(= h^2 + k^2 + l^2) \leq 100$ are listed in Tables 2, 3 and 4 for cubes, tetrahedra and octahedra respectively. Included in the same tables are the following parameters: (i) the integral-breadth Scherrer constant

$$K_\beta = [YI(0)]^{-1} = \left[2\int_0^\tau U(t)\mathrm{d}t\right]^{-1}, \quad (25)$$

where $U(t)$ [$= V(t)/p^3$] is the volume function of a crystallite of unit volume and T [$= \tau/p$] is the value of T for which $U(t)$ vanishes; (ii) the variance-slope Scherrer constant

$$K_k = -U'(0); \quad (26)$$

(iii) the variance-intercept Scherrer constant

$$K_T = [U''(0)]^{1/2}$$
$$(= L^{1/2}, \text{ where } L \text{ is the taper parameter}); \quad (27)$$

(iv)

$$K_w/K_\beta = 2w/\beta = \varepsilon_\beta/\varepsilon_w; \quad (28)$$

and (v)

$$K_k/K_\beta = \pi^2 k/\beta = \varepsilon_\beta/\varepsilon_k. \quad (29)$$

For spherical crystallites (all reflections) $K_w = 0.8290$, $K_\beta = 1.0747$, $K_k = 1.2090$, $K_T = 0$, $K_w/K_\beta = 0.8300$ and $K_k/K_\beta = 1.250$. The algebraic expressions for K_β, K_k and K_T are given in Table 1 for the shapes considered above and also for rectangular parallelepipeds.

For crystallites having the same size, the ratios (iv) and (v) depend only on their shape and orientation with respect to the crystallographic axes. The important factor $2w/\beta$ provides information on the nature of the profile, being in effect a 'form factor' (Langford, 1978). If, for example, the profile is assumed to be a Voigt function [the convolution of Gaussian and Cauchy (Lorentzian) profiles], the widths of the constituent functions can be determined from this factor. The ratio $2w/\beta$ for a Voigt profile has limiting values of 0·6366 for a Cauchy function and 0·9395 for a Gaussian function. If a rapid analysis of line breadth is required, perhaps at the expense of accuracy, the constituent Gaussian and Cauchy components of the half-width or integral breadth can be used to make corrections for instrumental effects or separate different contributions to diffraction broadening.

K_k/K_β is simply the ratio of the volume average of the thickness to the mean thickness, measured in a direction perpendicular to the reflecting planes, and is proportional to k/β (equation 29). In general, this ratio is more sensitive than $2w/\beta$ to the shape of the crystallites and for the regular shapes considered previously has values in the range 1·0 to 1·5. Inspection of the values of K_k/K_β for different reflections may often provide information on the approximate shape of the crystallites.

The normalized line profile for tetrahedra ($K_w/K_\beta =$ 0·7406) is independent of hkl, aside from a scale factor, and it is the same as the profiles for cubes (111 reflexion) and octahedra (100 reflexion). The normalized profile for spheres ($K_w/K_\beta = 0·8300$) is identical with that for octahedra (110 reflexion). These profiles are plotted for ψ (and hence s) ≥ 0 in Figs. 2 and 3. Other equivalences are the 110 and 210 reflexions for cubes and octahedra, respectively, and also the 210 and 111 reflexions for these shapes.

Voigt functions having the same half-width (and integral breadth) and area as the profiles for spheres and tetrahedra are also plotted in Figs. 2 and 3. For spheres, the Cauchy and Gaussian components of the integral breadth of $I(\psi)/I(0)$ are $\beta_c = 3·3563$ and $\beta_g = 6·0980$ and for tetrahedra, $\beta_c = 4·3425$ and $\beta_g = 3·0866$. In both cases the Voigt function is a good approximation to the line profile near the peak and for ψ small, the region of importance when using the half-width. There is also reasonable agreement in the tails of the profile, particularly for tetrahedra. For large ψ the form of the profile is dominated by the inverse-square term in (20), the trigonometric terms becoming less significant as ψ increases. The equivalent Voigt function appears to tend to the same limiting value for large ψ.

4. Comparison between apparent sizes

Each measure of breadth yields a different apparent crystallite size for a particular 'true size', shape and reflexion, and the physical significance of the integral-breadth and variance-slope sizes has been discussed

in § 2. A graphic representation of the difference between these apparent sizes is given in Fig. 4, where the 'true size' and the value based on the half-width are also included for comparison. The diagram shows the various sizes obtained from the hkl reflexions indexed with respect to equal axes parallel to the edges of a cube; the crystal system need not necessarily be cubic. The 001, 110 and 111 planes for this configuration are perpendicular to the 110 direction and it is convenient to view the crystallite in this direction, as in Fig. 4.
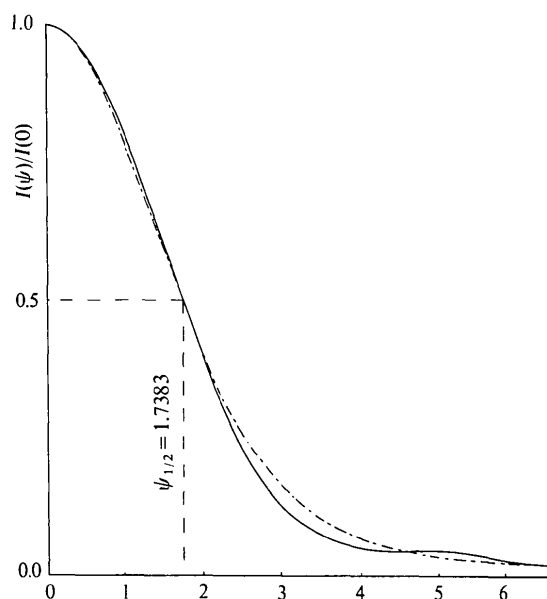
Fig. 3. Line profile for spheres (all hkl) and octahedra (110 reflexion). —— $I(\psi)/I(0) = \psi^{-2} - \psi^{-3} \sin 2\psi + \frac{1}{2}\psi^{-4}(1 - \cos 2\psi)$; —·—·— $I(\psi)/I(0) = 1·3738 \mathrm{Re}\{\omega[0·58132\psi + i0·31052]\}$ (Voigt approximation); $I(\psi) = UI(s)$, $\psi = \pi\tau s$.
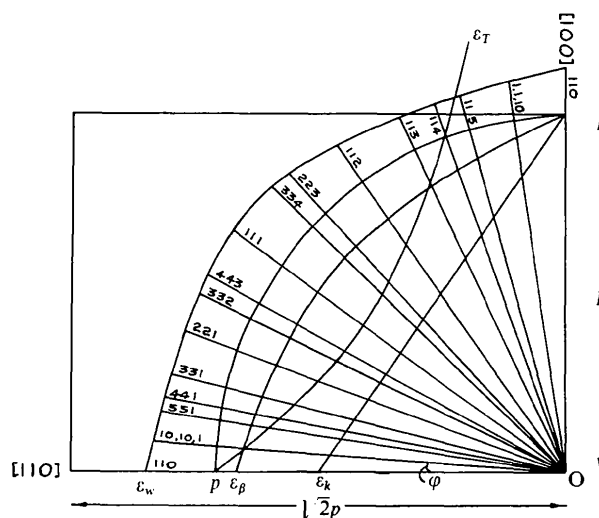
Fig. 2. Line profile for tetrahedra (all hkl), cubes (111 reflexion) and octahedra (100 reflexion). —— $I(\psi)/I(0) = 15[2\psi^{-2} - \psi^{-4}(1 - \cos 2\psi)]$; —·—·— $I(\psi)/I(0) = 2·0342 \mathrm{Re}\{\omega[0·57387\psi + i0·79323]\}$ (Voigt approximation); $I(\psi) = UI(s)$, $\psi = \pi\tau s$.

Fig. 4. Cube section parallel to 110 planes, showing apparent size (measured radially from O) for hhl reflexions.

From the loci of ε it can be seen that

$$\varepsilon_w > p \ge \varepsilon_\beta \ge \varepsilon_k \tag{30}$$

for cubes and hhl reflexions, a result that holds generally for all hkl and the shapes considered previously, except for the 100 and 110 reflexions from tetrahedra, and some high-order reflexions with plane normals close to those of 100 and 110. The locus of ε_k is linear and of the form

$$\varepsilon_k(\sin \varphi + 2^{1/2} \cos \varphi) = p, \tag{31}$$

where $\varphi(=\tan^{-1} l/2^{1/2}h)$ is the angle between the hhl and 110 directions. $\varepsilon_k = p$ for the 100 reflexion and is a minimum for the 111. ε_β is given by

$$3\varepsilon_\beta = (2 \times 2^{1/2} - \tan \varphi)(\sec \varphi)p ; \tag{32}$$

$\varepsilon_\beta = p$ for the 100 reflexion and is a minimum for the 322. There is no simple expression for the locus of ε_w, but it has a maximum value for the 111 reflexion and has minimum near 115 and 221. The locus of the fourth apparent size, ε_T, is

$$\varepsilon_T(1 + 2 \times 2^{1/2} \tan \varphi)^{1/2} = (\sec \varphi)p. \tag{33}$$

$\varepsilon_T = p$ for the 110 and 114 reflexions, is a minimum for the 111 and tends to infinity as φ approaches 90° (100 reflexion).

5. Variation of apparent size with hkl for crystallites of simple shape

At first sight the apparent crystallite size seems to be a random function of the indices of reflexion, as may be seen by inspecting tables of Scherrer constants [see, for example, Tables 2, 3, 4 or Wilson (1962a, pp. 44 and 53)]. However, it has been shown in the previous section that, for the particular case of hhl reflexions from a cube, the variation is systematic and it is of interest to consider the general case for crystallites having cubic symmetry.

The apparent crystallite size is a function only of the ratios of the indices of reflexion, as is implicit in (31) to (33), so that its variation with direction, for any particular crystal shape and 'true size', can be represented as a relief map. The expressions for the Scherrer constants reviewed earlier and given by Stokes & Wilson (1942) and Wilson (1962a, b) are based on (i) the moduli of the indices of reflexion, and (ii) an ordering of the axes so that h is not smaller than k or l. It is thus convenient to choose as variables $v = k/h$ and $w = l/h$. The apparent crystallite size (which is the 'true' particle size divided by the Scherrer constant) may then be plotted as a function of v and w over a square area defined by $0 \le v, w \le 1$. In practice it is convenient to plot relief maps of the dimensionless Scherrer constants (Fig. 5), which are proportional to the reciprocal of the apparent sizes. The relief map exhibits a pattern of ridges and valleys, with highest, lowest and saddle points, the details of which depend on the crystal shape. Since the expressions are sym-

metrical in v and w, there must be a smoothly rounded ridge or valley lying above the line $v = w$. The expressions are reflected across the lines $v = 0$ and $w = 0$, so that these also must have ridges or valleys above them, but, since the modulus of the variable is involved, they may be cusp-shaped, as are the valleys above $v + w = 1$ for tetrahedra and octahedra, and not smoothly rounded. It is possible in principle for there to be other ridges and valleys, or peaks, but none have been found for simple shapes having cubic symmetry.

The relief maps of Fig. 5 show, for cubes, tetrahedra and octahedra, the half-width, integral-breadth, variance-slope and variance-intercept Scherrer constants. In spite of the apparent complexity of the maps, the contours in many cases are governed by simple mathematical relations. The simplest contours occur if $V(t)$ is a function only of $1 + v^2 + w^2$ (N/h^2 in the notation of Table 1). The line profiles are then the same for all values of h, k and l lying on circles in the v, w plane. Inspection of Table 1 shows that this is the case only for crystals of tetrahedral shape and $h \ge k + l$; for such crystals the contours will be circles for *any* measure of line breadth, and hence, in particular, for the four measures plotted in Fig. 5. Certain measures, in particular the variance slope and the variance intercept, depend only on the first and second derivatives of $V(t)$, and will thus give circular contours if these derivatives are functions only of $1 + v^2 + w^2$, even if higher derivatives involve v and w in a different fashion. Inspection of Table 1 shows that crystals of octahedral shape fall into this class for $h \ge k + l$. Somewhat more complex contours arise if $V(t)$ is a function only of $(1 + v^2 + w^2)/(1 + v + w)^2$ or, in the notation of Table 1, N/H^2. The curve

$$1 + v^2 + w^2 = D(1 + v + w)^2 \tag{34}$$

is a conic section with one axis along the diagonal line $v = w$; it is an ellipse for $D < \frac{1}{2}$, a parabola for $D = \frac{1}{2}$, and an hyperbola for $D > \frac{1}{2}$. The centre of the ellipse is at $v = w = D/(1 - 2D)$. Inspection of Table 5 shows that crystals of octahedral and tetrahedral shapes satisfy the condition for $h \le k + l$. In this region $D < \frac{1}{2}$ and, therefore, the contours will be ellipses of determinate shape for any measure of line breadth, and hence, in particular, for the four measures plotted in Fig. 5. Cube-shaped crystals satisfy the condition only for $V'(0)$ and $V''(0)$, so that the contours for particle size based on variance slope and variance intercept are conic sections, but those based on half-width and integral breadth are not. The parabola separating the ellipses from the hyperbolae passes through the points $v, w = 0,1$ and $1,0$. For crystals of tetrahedral shape $V(t)$ is a perfect cube, and the line profiles are of the same *shape* (though of the same breadth only on the same contour) for all hkl; for crystals of octahedral shape the line profiles have the same shape only for those hkl on the same ellipse in the region $h \le k + l$. For cube-shaped crystals and octahedra in the region $h \ge k + l$ the line shape varies even along a contour of

constant breadth. The radii of the circular contours are given by $(4D-1)^{1/2}$, where D is listed in Table 6, and the semi-axes of the elliptical contours are

$(3D-1)^{1/2}/(1-2D)^{1/2}$ and $(3D-1)^{1/2}/(1-2D)$. In the parts of the figure where the contours are not circles or other conic sections (half-width and integral breadth
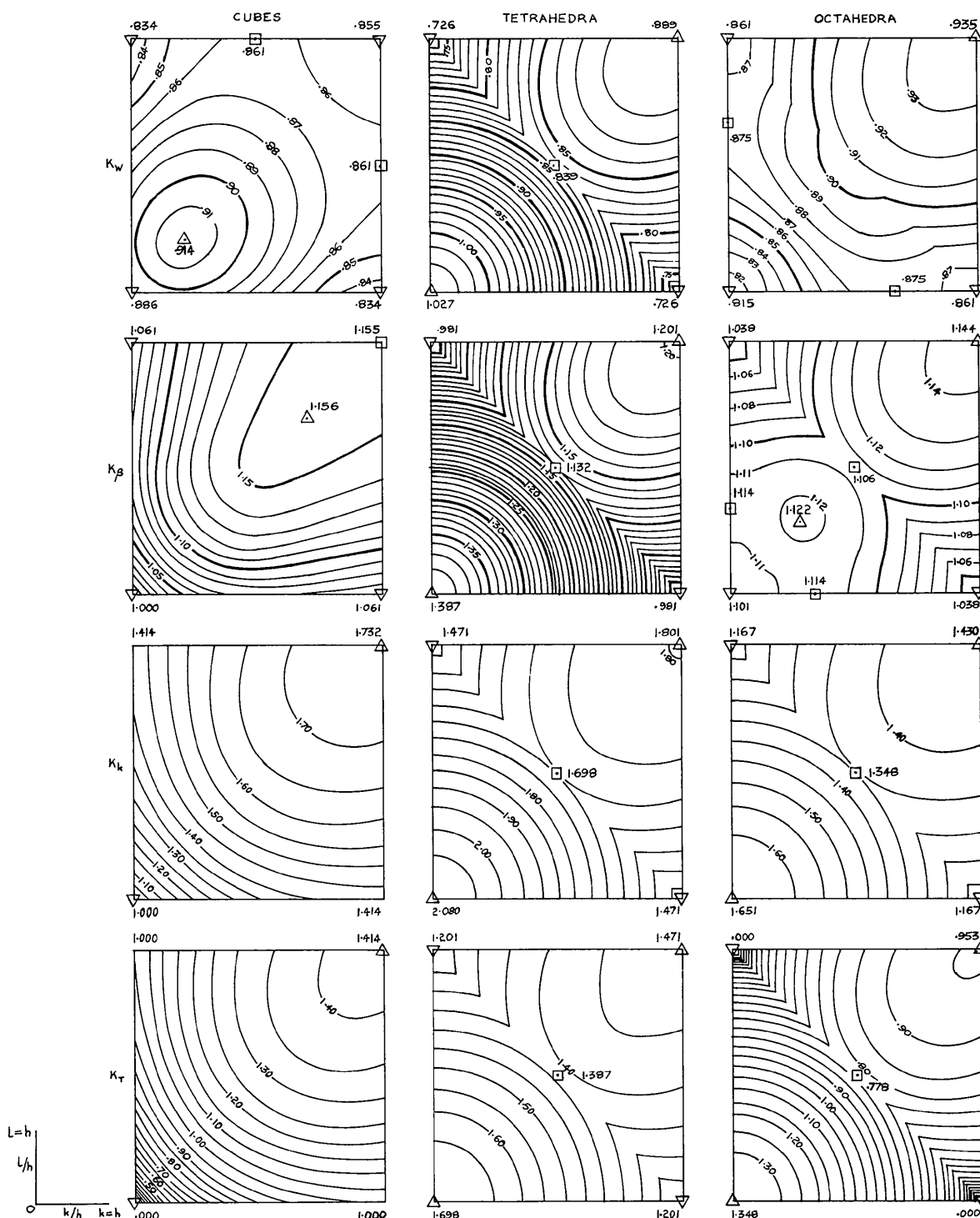

Fig. 5. Relief maps showing variation of half-width (K_w), integral-breadth (K_β), variance-slope (K_k) and variance-intercept (K_T) Scherrer constants with v $(=k/h)$ and w $(=l/h)$ for cubes, tetrahedra and octahedra. Contours at intervals of 0·01 for K_w, K_β and 0·05 for K_k, K_T. △, ▽, ▢ represent true maxima, minima and saddle points, and also limiting values.

Table 5. *Derivatives of V(t), etc. for spheres, cubes, tetrahedra and octahedra*

A = diameter of spheres or edge length of cubes, tetrahedra and octahedra, p = cube root of volume of crystallites, $H = h+k+l$ and $N = h^2+k^2+l^2$.

	Spheres	Cubes	Tetrahedra		Octahedra	
			$h \geq k+l$	$h \leq k+l$	$h \geq k+l$	$h \leq k+l$
B	$\left(\dfrac{6}{\pi}\right)^{1/3}$	1	$3^{1/3}$		$6^{1/3}$	
C	1	$N^{1/2}$	$N^{1/2}$		$N^{1/2}$	
p	$\dfrac{A}{B}$	A	$\dfrac{A}{2^{1/2}B}$		$\dfrac{2^{1/2}A}{B}$	
$\tau \times \dfrac{1}{BCp}$	1	$\dfrac{1}{h}$	$\dfrac{1}{h}$	$\dfrac{2}{H}$	$\dfrac{1}{H}$	
$V'(0) \times \dfrac{BC}{3p^2}$	$-\tfrac{1}{2}$	$-\dfrac{H}{3}$	$-h$	$-\dfrac{H}{2}$	$-h$	$-\dfrac{H}{2}$
$V'(\tau) \times \dfrac{BC}{3p^2}$	0	$-\dfrac{1}{3h}[h^2-(k+l)h+kl]$	0	0	$-\dfrac{2kl}{H}$	$-\dfrac{1}{2H}(H^2-2N)$
$V''(0) \times \dfrac{C^2}{2Bp}$	0	$\tfrac{1}{2}(H^2-N)$	h^2	$\dfrac{H^2}{4}$	$h^2-\dfrac{N}{2}$	$\dfrac{H^2}{4}-\dfrac{N}{2}$
$V''(\tau) \times \dfrac{C^2}{2Bp}$	$\dfrac{\pi}{4}$	$(k+l)h-2kl$	0	0	$\tfrac{1}{2}(H^2-hH-4kl)$	$N-\dfrac{H^2}{4}$
$V''' \times \tfrac{1}{2}C^3$	$\dfrac{\pi}{4}$	$-3hkl$	$-h^3$	$-\dfrac{H^3}{8}$	$-\dfrac{H}{2}[H^2-3(k+l)H+6kl]$	$-\dfrac{H}{2}(H^2-3N)$
$\displaystyle\int V(t)dt \times \dfrac{2}{BCp^4}$	$\tfrac{3}{2}$	$\dfrac{1}{3h^3}[6h^2-2(k+l)h+kl]$	$\dfrac{1}{h}$	$\dfrac{2}{H}$	$\dfrac{1}{H^3}[H^2+(k+l)H+2kl]$	$\dfrac{1}{H^3}(2H^2-N)$

for cube-shaped crystals and for octahedron-shaped crystals in the region $h \geq k+l$) they do not appear to have any generally recognized simple shape.

The positions of maxima, minima and saddle points are marked in Fig. 5. Those at $0,0$; $1,0$; $0,1$; $\tfrac{1}{2},\tfrac{1}{2}$; and $1,1$ are exactly located by the symmetry and boundary conditions. For the half-width the peak at $\tfrac{1}{5},\tfrac{1}{5}$, and the saddle points near $1,\tfrac{1}{2}$; $\tfrac{1}{2},1$ and $\tfrac{1}{5},0$; $0,\tfrac{1}{5}$ for cube-shaped crystals and the saddle points at $\tfrac{2}{3},0$; $0,\tfrac{2}{3}$ for octahedron-shaped crystals have only been located numerically, but the peaks and saddle points for the integral breadths can be located exactly for these shapes. The detailed calculations are given in the Appendix.* For cubes the integral-breadth Scherrer constant K_β is found to have its maximum $1\cdot1556$ at $v=w=\tfrac{2}{3}$, that is for the reflexion 322 and its higher orders. The saddle points are at $v=\tfrac{1}{2}$, $w=0$ or *vice versa*, that is for the reflexion 210 and its higher orders; the value of K_β is $1\cdot0733$. For octahedra the local maximum occurs at $v=w=(1+19^{1/2})/18=0\cdot29772$ and has the value $1\cdot12167$. It does not correspond to any reflexion with rational indices, but is only very slightly higher than the values for 311 ($1\cdot1211$) and 722 ($1\cdot1216$). The saddle points are at $v=\tfrac{1}{3}$, $w=0$ or *vice versa*, that is for the the reflexion 310 and its higher orders; the value of K_β is $1\cdot1138$.

In addition to giving a visual indication of the behaviour of K (and hence apparent crystallite size) for various shapes, the relief maps also give the values

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* The Appendix has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33086 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 6. *Values of D (§ 5)*

Measure of breadth	Cubes	Tetrahedra	Octahedra
$2w$	–	$0\cdot26370/K_w^2$	–
β	–	$(3^{1/3}K_\beta)^{-2}$	–
k	$1/K_k^2$	$9(2 \times 3^{1/3}K_k)^{-2}$	$9(2 \times 6^{1/3}K_k)^{-2}$
W_0	$1/(1+K_T^2)$	$3^{1/3}/2K_T^2$	$6^{1/3}/2(K_T^2+6^{1/3})$

of K for any reflexion with sufficient accuracy for most practical purposes. Furthermore, they have several features which are of use in certain applications. For example, all the maps in Fig. 5 display little variation in K around the point 111. Thus, in applications where information about the shape of the crystallite is less important than obtaining a reliable estimate of the size, reflexions for which $\tfrac{1}{2}h \leq k, l \leq h$ would be used. On the other hand, a rapid variation in K with hkl is desirable if a study of the shape of the crystallites is to be made and for this purpose reflexions with $0<k$, $l \leq \tfrac{1}{2}h$ are suitable in many cases. For some shapes and measures of breadth it is possible to select reflexions for which the apparent size is equal, or roughly equal, to the true size, a feature which would yield useful information in some instances.

6. Effect of a crystallite-size distribution

A complication arises if the crystals are not all of the same shape and size. In many, perhaps most, practical cases it would be unreasonable to expect uniformity of either shape or size, but sometimes it may be reasonable to assume constancy of shape but variation in size. There is an ambiguity about the definition of 'true mean crystallite size' when there is a distribution of sizes: is it the mean value of the cube roots of the

Table 7. *Effective Scherrer constants when there is a distribution of crystallite sizes, for two definitions of 'true' crystallite size*

Measure of breadth	Effective Scherrer constant	
	'True' size cube root of mean volume, $\langle p^3\rangle^{1/3}$	'True' size mean cube root of volume, $\langle p\rangle$
Half-width (first approximation)	$K_w\langle p^3\rangle^{1/3}\langle p^4\rangle^{1/2}/\langle p^6\rangle^{1/2}$	$K_w\langle p\rangle\langle p^4\rangle^{1/2}/\langle p^6\rangle^{1/2}$
Integral breadth	$K_\beta\langle p^3\rangle^{4/3}/\langle p^4\rangle$	$K_\beta\langle p\rangle\langle p^3\rangle/\langle p^4\rangle$
Variance slope	$K_k\langle p^2\rangle/\langle p^3\rangle^{2/3}$	$K_k\langle p\rangle\langle p^2\rangle/\langle p^3\rangle$
Variance intercept	$K_T\langle p\rangle^{1/2}/\langle p^3\rangle^{1/6}$	$K_T\langle p\rangle^{3/2}/\langle p^3\rangle^{1/2}$

volumes of the individual crystals, or is it the cube root of the mean volume of the individual crystals? If $P(p)\mathrm{d}p$ is the fraction of crystals whose 'true particle size' lies between p and $p+\mathrm{d}p$ (for an infinitesimal variation $\mathrm{d}p$ there is no ambiguity), the first definition gives the mean true particle size as

$$\langle p\rangle = \int pP(p)\mathrm{d}p, \tag{35}$$

whereas the second gives it as the cube root of

$$\langle p^3\rangle = \int p^3 P(p)\mathrm{d}p. \tag{36}$$

Either definition can legitimately be used, provided that it is made clear which. The early papers frequently mention the importance of considering particle-size distributions (for example, Murdock, 1930, p. 22), but do not appear to derive any general conclusions about its effects. It is fairly clear that, qualitatively, the line profile resulting from a specimen containing a distribution of particle sizes will have a sharper maximum and longer tails than a specimen containing the same number of crystals and the same total quantity of material but with the crystals all of the same size. One would thus expect the effective Scherrer constant for a specimen containing a distribution of particle sizes to be less than that for a specimen of uniform particle size (confidently for the integral breadth, probably for the half-width and variance intercept, very uncertainly for variance slope).

The effective Scherrer constants for the four measures of breadth and the two definitions of true mean particle size are collected in Table 7. Those for the variance slope and the variance intercept are taken from Wilson (1968)* (where the true mean particle size was taken as $\langle p\rangle$) and Wilson (1971)† (where the true

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* There is an error in (17) of Wilson (1968). This should read

$$\frac{p_2^2}{p_1} = \langle p\rangle + \frac{W_p}{\langle p\rangle}.$$

† Equations (5), (25) and (36) of Wilson (1971) contain errors. The third term of (5) is

$$\tfrac{1}{2}(\pi s)^{-2}\cos 2\pi sT[-K+LT-\tfrac{1}{2}MT^2+\ldots+\tfrac{1}{4}(\pi s)^{-2}(M+\ldots)+\ldots],$$

(25) is

$$V'(t)=\int_{t/T}^{x} U'(t/p)p^2 P(p)\mathrm{d}p,$$

and the second term of (36) is $-L/(4\pi^2 p^2)$.

mean particle size was taken as $\langle p^3\rangle^{1/3}$). Those for the integral breadth can be derived in the following way. From (24) of Wilson (1971), the effective volume function when there is a distribution of particle sizes is

$$V(t)=\int_{t/T}^{\infty} p^3 U(t/p)P(p)\mathrm{d}p. \tag{37}$$

The apparent particle size is then (equation 2)

$$\varepsilon_\beta = \frac{2}{V(0)}\int_0^\infty V(t)\mathrm{d}t$$

$$= \frac{2}{V(0)}\int_0^\infty \int_{t/T}^\infty p^3 U(t/p)P(p)\mathrm{d}p\mathrm{d}t, \tag{38}$$

where the integration over p is to be done first. On interchanging the order of integration this becomes

$$\varepsilon_\beta = \frac{2}{V(0)}\int_0^\infty \int_0^{pT} p^3 P(p)U(t/p)\mathrm{d}t\mathrm{d}p, \tag{39}$$

which becomes, on making the substitution $x=t/p$,

$$\varepsilon_\beta = \frac{2}{V(0)}\int_0^\infty p^4 P(p)\mathrm{d}p\int_0^T U(x)\mathrm{d}x \tag{40}$$

$$= \langle p^4\rangle/\langle p^3\rangle K_\beta. \tag{41}$$

To obtain $\langle p\rangle$ it is necessary to multiply ε_β by $\langle p\rangle\langle p^3\rangle K_\beta/\langle p^4\rangle$, and to obtain $\langle p^3\rangle^{1/3}$ it is necessary to multiply by $\langle p^3\rangle^{4/3}K_\beta/\langle p^4\rangle$, in agreement with the effective values of K_β given in Table 7. A similar manipulation of (18) shows that

$$\langle T^n_{\text{dist}}\rangle_A = \langle p^{n+2}\rangle\langle T^n\rangle_A/\langle p^2\rangle p^n. \tag{42}$$

To the extent to which (14) or (16) is valid, therefore, K_w must be multiplied by $\langle p\rangle\langle p^4\rangle^{1/2}/\langle p^6\rangle^{1/2}$ if $\langle p\rangle$ is desired, and by $\langle p^3\rangle^{1/3}\langle p^4\rangle^{1/2}/\langle p^6\rangle^{1/2}$ if $\langle p^3\rangle^{1/3}$ is desired.

The multipliers of K_β, K_k and K_T can be expressed in terms of the skewness and excess of the function giving the distribution of particle sizes. They are, in general, less than unity, in accordance with the qualitative expectation, but it seems to be possible to devise distributions that will make one or more of them greater than unity; these distributions are heavily skewed to small p, and/or have the variance of the crystallite size large in comparison with the square of the mean size.

It will be noticed that the factors multiplying the

various K's are functions of the crystallite-size distributions, but do not depend on the indices of reflexion. A distribution of sizes, therefore, does not introduce any additional complication into an attempt to deduce the crystallite shape from the variation of apparent crystallite size with the indices of reflexion. Conversely, if the crystallite shape is known or assumed, so that values can be assigned to the K's, the values of $\langle p^4 \rangle$, $\langle p^3 \rangle$, and $\langle p^2 \rangle$ can be expressed in terms of measurable quantities multiplied by $\langle p \rangle$.

7. Conclusions

The breadths of diffraction maxima for crystallites having the same shape vary systematically with the indices of reflexion. A study of this variation gives information about the shape of the crystallites and enables their 'true' size to be estimated. Simple geometrical shapes having cubic symmetry are considered in this paper and references to analyses of additional commonly considered shapes are given in § 1(ii). The theoretical considerations of §§ 2 and 3 enable the method to be extended to cover other polyhedra. In general, the shape of crystallites is irregular, but in practice the form often approximates, on average, to some regular shape which can be deduced from the breadths of several reflexions.

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