The Diffraction of X-Rays by Small Crystalline Particles

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The problem of the diffraction of x-rays by small crystalline particles is discussed by the methods of Fourier analysis, and the calculation of the intensity of the x-ray scattering from a single particle is reduced to the evaluation of a simple Fourier transform. This approach leads immediately to the interference functions for the parallellepipedon and the octahedron as obtained by other authors. In addition, it makes possible the detailed discussion of the interference functions for the tetrahedron, the rhombic dodecahedron, the ellipsoid, and the elliptic cylinder. The method is shown to be applicable to any polyhedron. A simple method is also given for calculating the interference function and its integral breadth for specific directions of departure from the whole-numbered points. This is applied to obtain a partial discussion of the scattering from the tetrahexahedron and the trisoctahedron.

1. INTRODUCTION

THE phenomenon of line broadening in x-ray and electron diffraction offers a very valuable method for the determination of the size of crystalline particles whose linear dimensions are less than 1000A. The ultracentrifuge, the ultramicroscope, and osmotic pressure measurements have also been applied to particle size measurements in this range. These methods, however, possess two disadvantages in common. First, they do not distinguish clearly between single particles and aggregates of particles; and second, they give only indirect information as to the shape of the particles. The diffraction method measures the size of the individual grains regardless of their relation to one another, and in addition gives a direct indication of the shape of the particles.

In 1918 Scherrer published a simple formula connecting the breadth of the lines with the size of the particles of the substance producing the pattern. The first detailed treatment of the theory of a method for obtaining the size and shape of particles was given by v. Laue.[1] His paper has provided the basis for almost all subsequent work[2] in this field. However, recent work[3–5] has indicated that some of the simplifying assumptions made by v. Laue[1] are inadequate for an exact discussion of the phenomena observed. A more extensive treatment of the problem seems therefore desirable. Following v. Laue the problem can be treated in three stages: (i) The calculation of the scattering from an isolated crystalline particle which possesses a definite orientation with respect to an incident beam of parallel radiation. (ii) The calculation of the scattering of parallel radiation from a mass of particles oriented at random but of the same size and shape (Scherrer problem). The effect of a distribution of size can also be discussed at this stage. (iii) The detailed analysis of a given experimental arrangement, taking into account the configuration of the camera and the sample, the size of the slits or aperture, the divergence of the radiation, the absorption of the sample, etc.

This paper will present a treatment of the first stage outlined above, and a detailed discussion of the dependence of the diffraction pattern of a single particle on its size and shape will be given. In a second paper, these results will be applied to the analysis of the Scherrer problem. The general approach is similar to that of v. Laue[1, 4] but the details of the method are quite different. The particle is represented by a distribution of scattering power which is periodic within its boundaries and zero outside.[6] The methods of Fourier analysis can then be applied to the discussion of the diffraction problem.

[1] M. v. Laue, Zeits. f. Krist. **64**, 115 (1926).
[2] For bibliography see G. H. Cameron and A. L. Patterson, Symposium on Radiography and X-ray Diffraction Methods, Philadelphia 1937, Am. Soc. Testing Materials, pp. 324–338.
[3] C. C. Murdock, Phys. Rev. **35**, 8 (1930).
[4] M. v. Laue, Ann. d. Physik **26**, 55 (1936).
[5] A. L. Patterson, Phys. Rev. **49**, 884 (1936).
[6] Cf. A. L. Patterson, Zeits. f. Physik **44**, 596 (1927).

2. Diffraction from a Small Crystalline Particle of Arbitrary Shape

Let us consider a distribution of matter in space whose scattering power can be represented by a density function $\rho(x_i)$ electrons per unit volume. The coordinates (x_i) are the three components of the vector $\mathbf{r}$ from the origin to the point (x_i) expressed in terms of three non-coplanar vectors $\mathbf{a}_i$ by the relation

$$\mathbf{r}=\sum_1^3 x_i\mathbf{a}_i. \tag{1}$$

If a parallel beam of monochromatic radiation of wave-length λ and intensity I_0, falls on the distribution $\rho(x_i)$ in the direction of the unit vector $\mathbf{s}_0$, and we observe the scattered intensity I in the direction of the unit vector $\mathbf{s}$, it can be shown that

$$I=I_0C(\chi)\,|\,\varphi(A_i)\,|^2, \tag{2}$$

in which C is independent of $\rho(x_i)$ and is a known function of the angle between $\mathbf{s}$ and $\mathbf{s}_0$, of the state of polarization of the incident beam, and of certain universal constants. The function $\varphi(A_i)$ which may be called the interference function, is given by the Fourier transform[7]

$$\varphi(A_i)=v_0\int_{-\infty}^{\infty}\int\int\rho(x_i)e^{-i\Sigma A_ix_i}dx_1dx_2dx_3, \tag{3}$$

in which $v_0=(\mathbf{a}_1[\mathbf{a}_2\mathbf{a}_3])$ and the quantities A_i are coordinates in the reciprocal space, defined by the relations

$$k\mathbf{H}=\Sigma A_i\mathbf{b}_i, \quad (4a) \qquad k=2\pi/\lambda, \quad (4b)$$

$$\mathbf{H}=\mathbf{s}-\mathbf{s}_0, \quad (4c) \qquad |\mathbf{H}|=2\sin\chi/2. \quad (4d)$$

In (4a) the vectors $\mathbf{b}_i$ are the reciprocal lattice vectors associated with the vectors $\mathbf{a}_i$ by the relation

$$(\mathbf{a}_i\mathbf{b}_j)=\delta_{ij}, \tag{5}$$

in which δ_{ij} is the Kronecker delta.

We shall assume that the particle under discussion is a small perfect crystal. Within a definite boundary its electron density can be represented by the Fourier series

$$c(x_i)=\sum_{h_i=-\infty}^{\infty}\sum\sum F(h_i)e^{2\pi i\Sigma h_ix_i}, \tag{6}$$

in which $F(h_i)$ is the structure factor for the reflection of Miller indices (h_i). Outside the boundary, the density is zero. We can now define $\rho(x_i)$ for our particle by the relation

$$\rho(x_i)=c(x_i)s(x_i), \tag{7}$$

in which $c(x_i)$ is defined by (6) throughout space and

$$s(x_i)\begin{cases}=1 & \text{inside the particle boundary}\\ =0 & \text{outside the particle boundary.}\end{cases} \tag{8}$$

The integral (3) takes the form

$$\varphi(A_i)=v_0\int_{-\infty}^{\infty}\int\int c(x_i)s(x_i)e^{-i\Sigma A_ix_i}dx_1dx_2dx_3 \tag{9}$$

and is thus the Fourier transform of the product of two functions. It may consequently[8] be written

$$\varphi(A_i)=v_0\int_{-\infty}^{\infty}\int\int C(t_i)S^*(t_i-A_i)dt_1dt_2dt_3, \tag{10}$$

in which $C(t_i)$ and $S(t_i)$ are the Fourier transforms of $c(x_i)$ and $s(x_i)$, respectively, and S^* is the conjugate complex of S.

The Fourier transform of $c(x_i)$ is given by the integral

$$C(t_i)=(2\pi)^{-\frac{3}{2}}\int_{-\infty}^{\infty}\int\int\sum\sum\sum F(h_i)\times e^{i\Sigma(2\pi h_i-t_i)x_i}dx_1dx_2dx_3. \tag{11}$$

This integral may be evaluated by the use of an appropriate limiting process and can be shown to be a delta-function for the lattice of points $t_i=2\pi h_i$; the integral over the peak at $2\pi h_i$ having the value $(2\pi)^{\frac{3}{2}}F(h_i)$. With this information we can evaluate the integral (10) by inspection and write

$$\varphi(A_i)=(2\pi)^{\frac{3}{2}}v_0\sum_{h_i=-\infty}^{\infty}\sum\sum F(h_i)S^*(2\pi h_i-A_i). \tag{12}$$

[7] The double use of i as a subscript $i=1, 2, 3$ and $i=\sqrt{(-1)}$ should not lead to confusion.

[8] See for example: G. A. Campbell and R. M. Foster, *Fourier Integrals for Practical Applications* (Bell System Monograph B584, 1931), p. 39, pair 202; or Titchmarsh, *Theory of Fourier Integrals* (Oxford 1937), p. 50, §2.1.

Thus the interference function $\varphi(A_i)$ is built up of a number of similar functions having their respective origins at the whole-numbered points of the reciprocal lattice. It then remains to evaluate the transform*

$$S(t_i)=(2\pi)^{-3}\int_{-\infty}^{\infty}\int\int e^{-i\Sigma t_i x_i}dx_1dx_2dx_3 \quad (13)$$

for particles of various shapes, the integral being taken throughout the interior of the particle. This function $S(t_i)$ determines completely the effect of the size and shape of the particle on the diffraction pattern and is not directly dependent on the crystal lattice. For convenience we shall define a function $\Psi(t_i)$ by the relation

$$\Psi(t_i)=(2\pi)^3 v_0 S^*(t_i)/V, \quad (14a) \qquad \Psi(0)=1, \quad (14b)$$

in which V is the volume of the particle. We shall call this function the shape function.

We note that in the present section, the only restriction on the vectors $\mathbf{a}_i$ is that they be three noncoplanar translations of the crystal lattice. We have not assumed that they are a primitive triplet, and they are not necessarily orthogonal. The results obtained are therefore quite general, and can be applied to particles of any shape and any crystal system. The only limitation is introduced by the practical problem of evaluating the integral (13) within the boundary surface of the particle.

3. Calculation of Shape Functions

The general problem of cataloging the surfaces inside of which the integral (13) can be evaluated is beyond the scope of this paper. Our main interest is in its evaluation for the various crystallographic polyhedra. Any polyhedron with plane faces can be built up from a number of irregular tetrahedra each having one vertex at an arbitrarily chosen origin within the boundary surface. Since the integral (13) is obviously additive for noninterpenetrating solids the shape function for a polyhedron will be the sum of the shape functions for its constituent tetrahedra. The shape function for a general tetrahedron with one vertex at the origin is evaluated below. It is therefore possible to evaluate such a function for any polyhedron. We also note that the ellipsoid and the skew elliptic cylinder can be transformed to the sphere and the right circular cylinder by appropriate linear transformations. The integral (13) for these latter shapes can be readily evaluated in polar and cylindrical coordinates, respectively.

Let us now consider the tetrahedron with vertices at the four noncoplanar points $x_i=0$ and $x_i=M_{ij}(i,j=1,2,3)$. We transform to a new coordinate system ξ_i in which the vertices are the origin and the three points (100), (010), (001). We then have*

$$x_i=M_{ki}\xi_k,$$

the Jacobian of the transformation being the determinant $J=|M_{ij}|$. If now we write

$$\tau_i=M_{ij}t_j,$$

the shape function for the general tetrahedron can readily be obtained in the form

$$\Psi(t_i)=(6i)\{(\tau_1\tau_2\tau_3)^{-1}+\sum_1^3[e^{i\tau_i}\tau_i(\tau_k-\tau_i)(\tau_i-\tau_j)]^{-1}, \quad (15a)$$

$$V=(1/6)Jv_0. \quad (16b)$$

We note that this function is complex, in common with the shape functions of all particles which do not possess a center of symmetry.

The particles for which shape functions have been calculated in the present paper all possess the following simple properties. They make intercepts $x_i=M_i$ on the axes. Thus when transformed to the coordinate system

$$\xi_i=x_i/M_i, \quad (16a) \qquad T_i=M_it_i, \quad (16b)$$

they make unit intercepts on the axes. In this system, the polyhedra become the symmetrical polyhedra of the cubic system, the ellipsoid becomes the unit sphere and the skew elliptic cylinder becomes the section of the unit right circular cylinder bounded by the planes $\xi_3=\pm 1$.

The shape functions which have been calculated are given in Table I. The interference functions can then be derived from them by

* This integral is obviously similar to that obtained by v. Laue, reference 4, Eq. (7) by a different method. We shall here evaluate it directly instead of by a transformation to a surface integral.

* With summation over indices occurring in pairs.

TABLE I. *Shape functions:* $U_i = M_i(2\pi h_i - A_i)$.

SHAPE FUNCTIONS	$M_1M_2M_3W$	$N/(M_1M_2M_3)$
1. Parallelepipedon {100}		
$\Psi(U_i) = \prod_1^3 [\sin U_i/U_i]$	π^3	8
2. Octahedron {111}		
$\Psi(U_i) = 6\sum_1^3 [U_i \sin U_i (U_k^2 - U_i^2)^{-1}(U_i^2 - U_j^2)^{-1}]$	$6\pi^3$	4/3
3. Tetrahedron {111}		
$\Psi(U_i) = 3\sum_1^3 \frac{U_i(i \cos U_i \sin U_j \sin U_k - \sin U_i \cos U_j \cos U_k)}{(U_k^2 - U_i^2)(U_i^2 - U_j^2)}$	$3\pi^3$	8/3
4. Rhombic Dodecahedron {110}		
$\Psi(U_i) = \frac{16\Sigma\{U_i \sin \frac{1}{2}U_i[\cos \frac{1}{2}U_i - \cos \frac{1}{2}U_j \cos \frac{1}{2}U_k]\}}{(U_1+U_2+U_3)(-U_1+U_2+U_3)(U_1-U_2+U_3)(U_1+U_2-U_3)}$	$4\pi^3$	2
5. Ellipsoid		
$\Psi(U_i) = 3R^{-3}(\sin R - R \cos R)$; $R^2 = U_1^2 + U_2^2 + U_3^2$	$6\pi^2$	$4\pi/3$
6. Elliptic Cylinder		
$\Psi(U_i) = 2(\rho U_3)^{-1} J_1(\rho) \sin U_3$; $\rho^2 = U_1^2 + U_2^2$	$4\pi^2$	2π

means of the expression

$$\varphi(A_i) = V\sum\sum\sum F(h_i)\Psi(U_i), \qquad (17a)$$

$$U_i = M_i(2\pi h_i - A_i), \qquad (17b)$$

obtained by combining (12) and (14). We see that each whole-numbered point (h_i) in the reciprocal space is surrounded by a function

$$VF(h_i)\Psi(U_i), \qquad (17c)$$

whose form depends on the shape of the particle and whose extent depends on the scale factors M_i in (17b) and through them on the size of the particle. M. v. Laue[1] was the first to discuss the significance of functions of this type in the reciprocal space. From them we can calculate the intensity ratio I/I_0 (for given s and s_0) from (2) by making use of the relation (4).

Laue[1] has also introduced the concept of the integral breadth of an intensity function. This he defined as the ratio of the integral of $|\varphi(A_i)|^2$ over the neighborhood of a whole-numbered point to its maximum value. It is readily seen that the breadth W so defined is given by*

$$W = v_0^2(2\pi)^3 V^{-2} \int\int\int |S(t_i)|^2 dt_1 dt_2 dt_3 = (2\pi)^3 v_0 V^{-1}. \qquad (18)$$

If we write

$$V = Nv_0, \qquad (19)$$

in which N is the total number of unit cells in the particle, (18) takes the simple form

$$W = (2\pi)^3/N. \qquad (20)$$

The breadth W is thus inversely proportional to the number of unit cells N and is independent of the shape of the particle. However, in using this concept of breadth in setting up approximation functions for $|\varphi(A_i)|^2$ v. Laue was able to restore the dependence on the scale factors M_i. Values of $M_1M_2M_3W$ together with the corresponding values of $N/(M_1M_2M_3)$ are included in Table I.

It should be pointed out that the shape function obtained here for the parallelepipedon has already[9] been shown to be equivalent to the form obtained by M. v. Laue in his first paper on x-ray diffraction. The function obtained for the octahedron is identical with that given by Murdock[3] Eq. (8); while the result obtained by v. Laue and Riewe[10] can also be reduced to this form.

Obviously, it is possible by the present method to calculate shape functions for polyhedra other than those given above. The polyhedra of lower

* Since $S(t_i)$ is the Fourier transform of $s(x_i)$, the result (18) follows from the well-known identity (cf. Campbell and Foster, reference 8, p. 8, pair 202 footnote)

$$\int\int\int |s(x_i)|^2 dx_1 dx_2 dx_3 = \int\int\int |S(t_i)|^2 dt_1 dt_2 dt_3$$

and the special form of $s(x_i)$ given by (8). See also Titchmarsh, reference 8, formula (2.13), p. 50.

[9] A. L. Patterson, Zeits. f. Physik **44**, 596 (1927). This point has also been discussed more recently by K-H. Riewe, Zeits. f. Krist. **96**, 85 (1937).

[10] M. v. Laue and K-H. Riewe, Zeits. f. Krist. **95**, 414 (1936), Eq. (12).

symmetry which involve only 0 and 1 as Miller indices are very simple to calculate; while those which involve mixed indices (i.e., $\{hk0\}$, $\{hkk\}$, or $\{hkl\}$) are somewhat more complicated, but can readily be obtained if the necessity arises.

4. The Form of the Interference Function for Specific Directions

All the information which we may hope to obtain about the shape of the diffracting particle is contained in the function $|\varphi(A_i)|^2$. In particular, the simple derivation of the Scherrer equation given by W. L. Bragg[11] indicates that the breadth of an x-ray deflection depends to a large extent on the variation of the function $|\Psi(u_i)|^2$ along a line perpendicular to the plane producing the reflection. While this aspect of the problem will be dealt with in more detail in a later paper, we can obtain considerable information as to the effect of particle shape on x-ray diffraction by considering the variation of $|\Psi(u_i)|^2$ along the directions perpendicular to the principal planes of the crystal. The departure from spherical symmetry of this function will give us a direct measure of the possibility of the determination of the shape for a given case.

The shape of the particle depends on (i) the crystallographic form of its bounding faces, (ii) the scale factors M_i, and (iii) the shape of the elementary cell. We shall confine ourselves here to (i) and reserve the discussion of (ii) and (iii). For this reason, we shall assume that $M_1=M_2=M_3$ and that the lattice is cubic. Then, if u be the departure from the whole-numbered point measured in the direction of the normal to the plane in question, we can define a function $\psi(u)$ which will give the variation of $\Psi(U_1)$ along that normal. Functions $\psi(u)$ for the shapes of Table I are exhibited in Table II. They are obtained from the functions of Table I by the following substitutions

Plane	U_1	U_2	U_3
(100)	u	0	0
(110)	v	v	0
(111)	w	w	w

in which $v=u/\sqrt{2}$ and $w=u/\sqrt{3}$. Limiting values must be taken where necessary.

The function $\psi(u)$ can also be obtained directly from (13). It is given by the relation

$$\psi^*(u)=V^{-1}\int_{-\infty}^{\infty}A(x)e^{-iux}dx, \qquad (21)$$

in which $A(x)$ is the area of section of the particle by the plane of indices (h_i) whose perpendicular distance from the origin is x. We have used this approach to check the functions of Table II, and thus indirectly those of Table I.

We can now define an integral breadth B_I

[11] W. L. Bragg, *The Crystalline State* (London, 1933), Vol. I, p. 189.

Table II. *Shape functions $\psi(u)$ for specific directions.* (*For notation see text.*)

Shape	Direction	$\psi(u)$	B_I	$B_{\frac{1}{2}}$	β_I	$\beta_{\frac{1}{2}}$
1. Cube {100}	[100]	$\sin u/u$	3.142	2.783	3.142	2.783
	[110]	$\sin^2 v/v^2$	2.962	2.834	2.962	2.834
	[111]	$\sin^3 w/w^3$	2.993	2.851	2.993	2.851
2. Octahedron {111}	[100]	$6(u-\sin u)/u^3$	5.655	5.248	3.112	2.888
	[110]	$3(\sin v-v\cos v)/v^3$	5.332	5.133	2.934	2.825
	[111]	$3[(1+w^2)\sin w-w\cos w]/(4w^3)$	5.509	5.097	3.032	2.805
3. Tetrahedron {111}	[100]	$3(\sin u-u\cos u)/u^3$	3.770	3.630	2.614	2.517
	[110]	$3(2v-\sin 2v)/(4v^3)$	3.999	3.711	2.772	2.573
	[111]	$3e^{-iw}\{[4w-\sin 4w]+i[\cos 4w+8w^2-1]\}/(32w^3)$	4.897	3.754	3.396	2.603
4. Rhombic Dodecahedron {110}	[100]	$16\sin\frac{1}{2}u(1-\cos\frac{1}{2}u)/u^3$	4.817	4.626	3.035	2.914
	[110]	$\sin\frac{1}{2}v(v\cos\frac{1}{2}v+2\sin\frac{1}{2}v)/v^2$	4.813	4.590	3.032	2.892
	[111]	$8\sin w(1-\cos\frac{1}{2}w)/w^3$	4.807	4.577	3.028	2.883
5. Sphere	[hkl]	$3(\sin u-u\cos u)/u^3$	3.770	3.630	3.039	2.925
6. Circular Cylinder	[hk0]	$2J_1(u)/u$	3.395	3.233	3.133	2.983
	[001]	$\sin u/u$	3.142	2.783	2.899	2.568
	[hk1]	$2\sin vJ_1(v)/v^2$	3.162	3.031	2.918	2.797

TABLE III. *Integral breadths for complex polyhedra* ($h>k$).

SHAPES	FORM	α	$N/M_1M_2M_3$	DIRECTION	B_I	β_I
Tetrahexahedron	$\{hko\}$	$h/(h+k)$	$8\alpha^2$	[100]*	$\pi(8+7\alpha)/(15\alpha)$	$\alpha^{\frac{1}{3}}B_I$
				[110]	$\sqrt{2}\pi(1-9\alpha+45\alpha^2+3\alpha^3)/(60\alpha^3)$	$\alpha^{\frac{1}{3}}B_I$
	{210}	2/3	32/9	[100]	3.979	3.037
				[110]	3.971	3.030
Trisoctahedron	$\{hhk\}$	$h/(2h+k)$	4α	[100]	$\pi(3+20\alpha-6\alpha^2)/(15\alpha)$	$(\alpha/2)^{\frac{1}{3}}B_I$
	{221}	2/5	8/5	[100]	5.257	3.074

* The shape function for the tetrahexahedron $\{hk0\}$ in the [100] direction has also been obtained in the form

$$\psi(u)=2\left[(1-3\alpha+3\alpha^2)\sin\alpha u-\alpha u(1-\alpha)(1-2\alpha)\cos\alpha u-\alpha^3\sin u\right]\left[\alpha^3u^3(1-\alpha)^2\right]^{-1}.$$

for the function $\psi(u)$ by the relation

$$B_I=\int_{-\infty}^{\infty}|\psi(u)|^2du, \tag{22}$$

which can be evaluated directly. From (21), however, we can obtain an expression for B_I which is strictly analogous to (18), i.e.,

$$B_I=2\pi V^{-2}\int_{-\infty}^{\infty}A^2(x)dx. \tag{23}$$

We can thus obtain B_I from the curve of areas without calculating $\psi(u)$. The values of B_I given in Table II have been checked by both methods. A few values of B_I for the twenty-four-fold forms of cubic holohedry obtained from (23) are given in Table III.

Another method of characterizing the breadth of a function of the type $\psi(u)$ is by means of the half-value breadth $B_{\frac{1}{2}}$ defined by the equation

$$|\psi(B_{\frac{1}{2}}/2)|^2=(1/2)|\psi(0)|^2. \tag{24}$$

Values of $B_{\frac{1}{2}}$ for the functions which have been computed are also given in Table II.

In order to be able to compare breadths for particles of different shape, it is necessary to establish some standard property which all particles must possess. Murdock has proposed a comparison on the basis of equal volumes. This is also suggested by the relation (20) and will be adopted here. We shall compute values of B_I and $B_{\frac{1}{2}}$ for particles having a volume $V=8M_1M_2M_3v_0$. Such values, which we shall denote by β_I and $\beta_{\frac{1}{2}}$, are also included in Tables II and III. They are connected with the corresponding B, for a given particle, by the relation

$$\beta=N^{\frac{1}{3}}(8M_1M_2M_3)^{-\frac{1}{3}}. \tag{25}$$

A comparison of the values of β for the various shapes suggests that it will be difficult to recognize complex forms from the measurements of breadth alone. In order to do this an accurate knowledge of the shape of the interference function is required, and this is difficult to obtain by means of x-rays from a random oriented powder sample. It may be that electron diffraction, following the suggestion of v. Laue,[4] may prove more fruitful for this purpose. Our results do, however, indicate that the approximate shape of a particle can be obtained from accurate x-ray measurements. It should certainly be possible to decide which of the simple shapes of Table II provides the closest approximation to the shape of a particle belonging to the cubic system. In investigating crystals of lower symmetry it will be necessary to calculate the interference functions for the simple forms of the system in question, and to prepare a table corresponding to Table II with which to compare the experimental results.

It is not profitable to discuss at this point the relative merits of the half-value breadth and the integral breadth as indices of particle size or shape. It should however be noted that for the functions calculated, the integral breadth is consistently higher than the half-value breadth by amounts varying from 4 to 30 percent.