NOVEMBER 15, 1939 PHYSICAL REVIEW VOLUME 56

The Scherrer Formula for X-Ray Particle Size Determination

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(Received July 24, 1939)

An exact derivation of the Scherrer equation is given for particles of spherical shape, values of the constant for half-value breadth and for integral breadth being obtained. Various approximation methods which have been used are compared with the exact calculation. The tangent plane approximation of v. Laue is shown to be quite satisfactory, but some doubt is cast on the use of approximation functions. It is suggested that the calculation for the ellipsoidal particle based on the tangent plane approximation will provide a satisfactory basis for future work.

1. INTRODUCTION

IN 1918, P. Scherrer[1] showed that, when parallel monochromatic radiation falls on a random oriented mass of crystals, the diffracted beam is broadened when the particle size is small. By an approximation method he obtained an expression for the half-value breadth B of the diffracted beam in the form

$$B = K\lambda/(L\cos\chi/2), \tag{1}$$

in which λ is the wave-length of the incident x-rays, L the linear dimension of particle, $\chi/2$ the Bragg angle and K a numerical constant for which he obtained the value $2(\ln 2/\pi)^{\frac{1}{2}} = 0.93$. Since then, various workers[2–6] using different approximation methods and different definitions for the breadth B have obtained different values for the constant K. As a result, those interested in using the relation (1) for the determination of particle size have rightly been in doubt as to its correct value.

The results of the preceding paper in this issue[7] include as a special case the interference function for a spherical particle. For this particle, the calculation of the distribution in angle of the diffracted beam can be carried through exactly, and a value of the Scherrer constant can be obtained. The approximation methods of other authors are also applicable in this case, and consequently it is possible to obtain an estimate of their validity by comparison with the exact calculation.

2. EXACT CALCULATION OF $J(\chi)$

Following v. Laue[3] Eq. (28) and confining our attention to the contribution from one whole-numbered point ($A_i = 2h_i\pi$) we may write, in the notation of I (Eq. (17c) etc.)

$$J(\chi) = \int\int\int \{|\Psi(U_i)|^2/(k^2|\mathbf{H}|^3 v_0)\} \times dA_1 dA_2 dA_3, \tag{2a}$$

$$k|\mathbf{H}| = \sum A_i \mathbf{b}_i, \tag{2b}$$

$$U_i = M_i(2\pi h_i - A_i), \tag{2c}$$

in which the integration (2a) is taken between the spheres $k|\mathbf{H}|$ and $(k+\Delta k)|\mathbf{H}|$. $J(\chi)$ is then a quantity proportional[8] to the intensity of the x-rays scattered through an angle χ by a random oriented mass of crystal particles of uniform size, each of which has a shape function $\Psi(U_i)$.

We shall confine ourselves here to the simple case* in which the lattice is cubic of translation $a = 1/b$ and $M_1 = M_2 = M_3 = M$. We may then write

$$|\sum A_i \mathbf{b}_i|^2 = b^2 \sum A_i^2 = \rho^2, \tag{3a}$$

$$|2\pi \sum h_i \mathbf{b}_i|^2 = 4\pi^2 b^2 \sum h_i^2 = \rho_h^2, \tag{3b}$$

$$|2\pi \sum h_i \mathbf{b}_i - \sum A_i \mathbf{b}_i|^2 = R_0^2/M^2 a^2, \tag{3c}$$

$$R_0^2 = M^2 \sum (2\pi h_i - A_i)^2 = \sum U_i^2. \tag{3d}$$

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[1] P. Scherrer, *Göttinger Nachrichten* (1918); cf. also R. Zsigmondy, *Kolloidchemie* (3rd Ed. 1920), p. 394.

[2] N. Seljakow, Zeits. f. Physik **31**, 439; **33**, 648 (1925).

[3] M. v. Laue, Zeits. f. Krist. **64**, 115 (1926).

[4] C. C. Murdock, Phys. Rev. **35**, 8 (1930).

[5] W. L. Bragg, *The Crystalline State*, Vol. 1, p. 189.

[6] F. W. Jones, Proc. Roy. Soc. **A166**, 16 (1938).

[7] A. L. Patterson, p. 972, hereafter cited as I.

[8] F. W. Jones, reference 6, p. 40, has pointed out that the "constant" implicit in (2*a*) is constant only for small variations of χ, i.e., in the neighborhood of a whole-numbered point. It also contains factors which depend on the particle size, and cannot be used directly in a discussion of the distribution of particle size.

* These conditions are not necessary for the integration of (2a). More general conditions can be set up, but so far no practical use has been made of them.

Under such conditions, we may transform the integral (2a) to polar coordinates (ρ, ϑ, φ) with the vector **G** (cf. v. Laue,[3] Eq. (28a) and Eq. (8) below) as polar vector, when it takes the form

$$J(\chi)=\int_{k|\mathbf{H}|}^{(k+\Delta k)|\mathbf{H}|}\int_0^{\pi}\int_0^{2\pi}\{|\Psi(U_i)|^2/k^2|\mathbf{H}|^3\}\times\rho^2\sin\vartheta d\rho d\vartheta d\varphi.$$

The integration with respect to ρ can be carried immediately and we obtain

$$J(\chi)=\Delta k\int_0^{\pi}\int_0^{2\pi}|\Psi(U_i)|^2\sin\vartheta d\vartheta d\varphi, \tag{4}$$

subject to the condition

$$R_0^2/M^2a^2=k^2|\mathbf{H}|^2+\rho_h^2-2k|\mathbf{H}|\rho_h\cos\vartheta. \tag{5a}$$

To integrate this expression, we must be able to write the U_i in terms of the polar coordinates. If, as in the case of a spherical particle, $\Psi(U_i)$ is a function of R_0 alone and is independent of φ (cf. I Table I), we can integrate directly with respect to φ, and make the change of variable

$$M^2a^2k|\mathbf{H}|\rho_h\sin\vartheta d\vartheta=R_0dR_0. \tag{5b}$$

We then have (omitting a factor which is constant for a given whole-numbered point)

$$J(\chi)=\int_{\Delta}^{\Sigma}|\Psi(R_0)|^2R_0dR_0, \tag{6}$$

in which

$$\delta=\sin(\chi_h/2)-\sin(\chi/2), \tag{7a}$$

$$\sigma=\sin(\chi_h/2)+\sin(\chi/2), \tag{7b}$$

$$\Delta=2Mak\delta, \tag{7c}$$

$$\sum=2Mak\sigma. \tag{7d}$$

The exact evaluation of this integral for the spherical particle will be given below.

3. Calculation of $J(\chi)$ by Approximation Methods

Instead of attempting the evaluation of the integral (2a) between the spheres $k|\mathbf{H}|$ and $(k+\Delta k)|\mathbf{H}|$, v. Laue approximates it by an integral taken over the region between the tangent planes to these spheres at the points $k|\mathbf{H}|\mathbf{G}$ and $(k+\Delta k)|\mathbf{H}|\mathbf{G}$, in which **G** is a unit vector in the direction of the vector $\sum h_i\mathbf{b}_i$ i.e.,

$$\mathbf{G}=(\sum h_i\mathbf{b}_i)/|\sum h_i\mathbf{b}_i|. \tag{8}$$

Following v. Laue,[3] Eq. (32), we may then write[9]

$$J(\chi)=\int_{\delta/\eta}^{\infty}|\Psi(R)|^2RdR, \tag{9}$$

in which the assumption of cubic symmetry and the conditions (3) are no longer required. Instead we must, however, write

$$R^2=\sum M_i^2(2\pi h_i-A_i)^2=\sum U_i^2 \tag{10a}$$

and

$$\eta=(2k)^{-1}\{\sum[(\mathbf{b}_i\mathbf{G})/M_i]^2\}^{\frac{1}{2}}. \tag{10b}$$

We note that in the special case of cubic symmetry and under the conditions (3) the quantity δ/η takes the form $\delta/\eta=\Delta=2Mak\delta$.

W. L. Bragg[5] was led to make a further simplification of the discussion by considering only the intensity of the x-rays reflected while the vector **H** is in the same direction as the vector **G**. With this assumption we have simply

$$J(\chi)=|\Psi(\delta/\eta)|^2. \tag{11}$$

Although this approach is confessedly approximate, it has the advantage of being applicable to all possible forms of the function $\Psi(U_i)$.

Since the interference function $|\Psi(U_i)|^2$ is not in general a function of R alone, v. Laue[3] (Eqs. (26) and (27)) made use of approximation functions for the interference function in (9). These functions were of the type

$$f_1(A_i)=C_1\exp(-\omega_1^2R^2), \tag{12a}$$

$$f_2(A_i)=C_2(\omega_2^2R^2+1)^{-2}. \tag{12b}$$

In discussion with the author some years ago v. Laue has also suggested a third approximation function:

$$f_3(A_i)=\begin{cases}C_3(1-\omega_3^2R^2); & R^2<\omega_3^{-2}\\ 0; & R_2^2>\omega_3^{-2}.\end{cases} \tag{12c}$$

In each the constant ω is chosen so that the

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[9] B. E. Warren, Zeits. f. Krist. **99**, 448 (1938) has given a simplified discussion of some of v. Laue's analysis.

integral breadth W defined by

$$W=[f(0)]^{-1}\int\int\int_{-\infty}^{\infty} f(A_i)dA_1dA_2dA_3 \quad (13)$$

(cf. I, Eq. (18)) has the same value for the approximation function and for the interference function to be approximated.

Jones[6] (Section V (2)) has also made use of the approximation functions (12a) and (12b), but he chooses values for ω such that the approximation function and the interference function give the same value for the integral breadth (in the scale of δ) for the function $J(\chi)$ for the axial planes.

4. Exact and Approximate Calculations for Spherical Particles

From the interference function for ellipsoidal particles (I, Table I, formula 5) under the special conditions (3) we obtain the interference function for a spherical particle of radius Ma. It has the form

$$|\Psi(R_0)|^2=(9/R_0^6)(\sin R_0-R_0\cos R_0)^2. \quad (14)$$

For this function the integrals (6) and (9) can be evaluated exactly, and we can therefore obtain an insight into the nature of the tangent plane approximation. We can also estimate the accuracy of the Bragg computation. Furthermore, we can set up approximation functions of the three types (12), using both the v. Laue and the Jones criteria for evaluating ω; and apply both the exact and the tangent plane calculations to them. It is thus possible to use the exact calculation as a test of the validity of the various approximation methods and to estimate their value in cases for which the exact calculation cannot be carried through.

We substitute (14) in (6) and after integration by parts we obtain exact form*

$$J(\chi)=\Delta^{-4}[(\sin\Delta-\Delta\cos\Delta)^2+\Delta^2\sin^2\Delta] \\ -\textstyle\sum^{-4}[(\sin\sum-\sum\cos\sum)^2+\sum^2\sin^2\sum]. \quad (15)$$

The integral (9) which follows from the tangent plane approximation then obviously takes the form

$$J(\chi)=(\eta/\delta)^4\{[\sin(\delta/\eta) \\ -(\delta/\eta)\cos(\delta/\eta)]^2+(\delta/\eta)^2\sin^2(\delta/\eta)\}, \quad (16)$$

while the Bragg approximation leads to

$$J(\chi)=9(\eta/\delta)^6[\sin(\delta/\eta)-(\delta/\eta)\cos(\delta/\eta)]. \quad (17)$$

We are now in a position to compare the two approximation methods with the exact calculation for a spherical particle of a cubic crystal ($\delta/\eta=\Delta$). We note first that for all practical purposes, the expressions (15) and (16) become identical. The function $y^{-4}[(\sin y-y\cos y)^2+y^2\sin^2 y]$ has as its slope $-(4/y^5)(\sin y-y\cos y)^2$, and is therefore a monotonic decreasing function of y whose slope is small for large values of y. Since $\sum$ will usually be large compared with Δ, the second term of (15) will merely result in a very small reduction in the background intensity due to the first term. In general its effect can be neglected, although in special cases (e.g., for χ small) it may have to be taken into account. It seems therefore possible to give strong support to v. Laue's use of the tangent plane approximation. There is nothing in the analysis to lead one to suppose that the case of the spherical particle is in any way peculiar as far as this assumption is concerned, and it is to be expected that the approximation will be just as good for particles of other shapes.

The integral breadths B_I and the half-value breadths $B_{1/2}$ (in the scale of δ) for the functions (16) and (17) are given in Table I together with the corresponding value of the Scherrer constant[10] K_I and $K_{1/2}$. It is seen that for the sphere, the Bragg approximation agrees with the exact calculation within 10 percent. This is unfortunately not close enough to enable us to place immediate trust in the results obtained by this approach for discussions of particle shape. It should be noted that values of the Scherrer

Table I. *Scherrer constants.*

	B_I/η	K_I	$B_{\frac{1}{2}}/\eta$	$K_{\frac{1}{2}}$
Exact (16)	4.189	1.333	3.477	1.107
Bragg (17)	3.770	1.200	3.630	1.155

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* The scales have been chosen for (15), (16), and (17) so that they all have a maximum value unity.

[10] L in the Scherrer equation is then the diameter of the spherical particle. For particles of the same volume, the value obtained by Scherrer would correspond to 1.15 (cf. Murdock, reference 4, p. 20) and I, Eq. (25). Note also that B is redefined.

constant can be calculated by the Bragg method for all the functions given in the previous paper (I, Table II and Eq. (23)) and that the integral breadth B and the Scherrer constant K can be obtained to this approximation for any particle for which the curve of cross-sectional areas can be set up. A detailed examination of the nature of the Bragg approximation should therefore be of great value for discussions of particle shape.

It is hoped that in the future, tangent plane calculations can be carried out for some of the exact interference functions which have been obtained (I, Tables I and II).

We can now test the approximation functions (12a–c). We note that both the exact (6) and the tangent plane (9) integrals can be evaluated for functions of this type. We shall confine ourselves here to the tangent plane integral since it has been set up under more general conditions and has been shown to lead to almost the same results as the exact integral. We may use both the v. Laue and the Jones method for evaluating the constants ω. The values obtained and the corresponding values of the Scherrer constants K_I and $K_{1/2}$ are given in Table II.

These results show that the use of approximation functions in integrations of the type involved in deriving the Scherrer formula are by no means to be trusted. We see that the Laue approximation which has been made to give identical values for the integral breadth in the reciprocal space leads to very divergent values for the constant K_I, one measure of the integral breadth in the scale of χ; while the values for $K_{1/2}$ (another measure of that breadth) show relatively good agreement with one another. This latter result can only be described as fortuitous. The Jones approach forces the equality of the constant K_I for the various functions, but leads of course to quite different values for the integral breadth in the reciprocal space, and to quite discordant values for the constant $K_{1/2}$. The reason for this lies of course in the behavior of these functions at infinity.[11] The identity of the integral breadths is no guarantee for the identity of any other property of these curves. Furthermore, two curves which have been matched by any of the criteria discussed above, cannot be expected to agree after being subjected to an infinite integration of the nature of that involved in the derivation of the Scherrer formula.

Table II. *Scherrer constants from approximation functions.*

	ω		K_I		$K_{\frac{1}{2}}$	
	v. Laue	Jones	v. Laue	Jones	v. Laue	Jones
Exact			1.333		1.107	
$f_1(A_i)$	0.455	0.423	1.241	1.333	1.166	1.252
$f_2(A_i)$	0.550	0.750	1.817	1.333	1.157	0.849
$f_3(A_i)$	0.305	0.255	1.115	1.333	1.133	1.353

In the discussion of the effect of the size and shape of the sample and of the nature of the radiation such as has been given by v. Laue[3] and Brill and Pelzer[12] it seems that the use of approximation functions is inevitable. The results of the present paper indicate that the conclusions drawn from such an analysis should be examined critically. It seems that the approximation functions must be chosen with much more care, particularly with respect to their behavior at infinity. Perhaps the more purely empirical approach suggested by Jones[6] will provide the best means for making allowance for the dimensions of the sample. It is, however, of great importance that the fundamental discussion given by v. Laue[3] be placed on a sound basis.

CONCLUSION

In the approximation methods of v. Laue[3] and Jones[6] the use of the expression (10b) is equivalent to the assumption of an ellipsoidal particle. They compare their approximation functions for such a particle with the exact interference function for a particle which is a parallepipedon in shape, and obtain various values for ω which lead to the values for the Scherrer constant given in Table II. The results of the present paper seem to indicate that it would be safest to assume that the particle is ellipsoidal at the start and to use the values for the Scherrer constant obtained for the exact function for an ellipsoidal particle. Then, in a case in which the Scherrer formula is directly applicable, or after the application of an empirical analysis such as that given by Jones,[6] the values of L obtained from a given crystallographic form would be representative of the mean dimension of the particle in the direction

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[11] Cf. M. v. Laue, Ann. d. Physik **26**, 59 (1936).

[12] R. Brill, Zeits. f. Krist. **68**, 387 (1928); R. Brill and H. Pelzer, *ibid.* **72**, 398 (1929); **74**, 147 (1930), etc.

normal to the faces of that form. If the assumption of an ellipsoidal particle is well-founded, the breadth should vary in the way suggested by (10b). If not, the departures from the ellipsoidal shape can be examined in the light of Table II of the preceding paper[7] and an indication of the actual particle shape can be obtained.

The work reported in this and the preceding paper was commenced at the Massachusetts Institute of Technology. It is a pleasure for the writer at this time to express his thanks to Professor J. C. Slater for the privilege of working in his laboratory, and to Professor B. E. Warren for many valuable discussions.

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The Far Infra-Red Absorption Spectrum and the Rotational Structure of the Heavy Water Vapor Molecule

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(Received September 7, 1939)

An investigation has been made of the spectrum of heavy water vapor (D_2O) in the region from 23μ to 135μ. The instrument used was a self-recording spectrograph of large aperture, using echelette gratings, vacuum thermopile, and a system of filters, shutters, and *reststrahlen* plates to remove higher order spectral impurity. The radiation path in the spectrograph could be evacuated. From this research the experimental positions and relative intensities of 210 pure rotation absorption frequencies were obtained. Absorption maxima were located with an accuracy of about 0.05 cm^{-1}. Lines 0.5 cm^{-1} apart were partially resolved, higher resolution and dispersion being of little advantage since the true width of these absorption lines was of this same order of magnitude. The energy levels of a zeroth-order approximation to the D_2O asymmetric rotator molecule were computed through quantum number $j=11$, and corrected for zero point vibration and centrifugal stretching in the ground state. A comparison of the positions and intensities of the experimental data with those of the transitions between these "key" levels showed a rather good agreement. These levels were therefore corrected to fit the data, and checked for consistancy by means of series regularities and combination relations. In all, 111 distinct energy levels based on the experimental data were computed. A graph of the experimental data contrasted with a similar graph of the transitions based on these corrected levels gives a clear picture of the success of the analysis.

I. INTRODUCTION

A LARGE amount of work has been done on the spectral analysis of ordinary water in its vapor state. Information concerning the molecule as a whole is largely limited to studies of the absorption frequencies occurring in the infra-red region of the electromagnetic spectrum. The vibration-rotation bands of H_2O have been examined a number of times.[1] Since the discovery[2] of the heavy hydrogen isotope, H^2 (often called deuterium, D), similar studies[3] have been made upon D_2O. In more recent years the extension of the spectrum of H_2O into the region of pure rotation frequencies has been made.[4] One of these latter studies[5] succeeded in establishing the rotational energy levels of the ground state with high accuracy. The present investigation was undertaken in the attempt to parallel this H_2O analysis with a similar study of D_2O.

The problem has been to map the far infra-red pure rotation absorption spectrum of heavy

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[5] Randall, Dennison, Ginsberg and Weber, Phys. Rev. **52**, 160 (1937) (this paper will hereafter be referred to as RDGW).