THE FORM OF THE X-RAY DIFFRACTION BANDS
FOR REGULAR CRYSTALS OF COLLOIDAL SIZE*

By Carleton C. Murdock
Cornell University

Abstract

The form of the diffraction bands of a very fine uniform crystalline powder has been computed for the $(1, 0, 0)$, the $(1, 1, 0)$ and the $(1, 1, 1)$ planes for cubical and octahedral crystals of the regular system. The shape of the bands is approximately that of the Gauss error curve. Both the shape and the half intensity breadth vary from band to band and the variations are characteristic of the shape of the crystals. There is definite correlation between the form of the band and the direction of the corresponding Bragg planes with respect to the external features of the crystal. The mean breadth of the bands is nearly the same for cubical and octahedral crystals having the same volume. The values of the constant of Scherrer's equation are in general smaller than those computed by other investigators for the cubical case.

Secondary maxima.—A case is found in which secondary maxima of the intensity function would be sufficiently intense to be directly observable. It is pointed out that such an effect might lead to a false interpretation of the crystal structure of a very fine crystalline powder.

WHEN monochromatic x-rays are diffracted by a fine crystalline powder the diffraction bands are found to have a measurable width which is a function of the fineness of the powder. The effect is closely analogous to the low resolving power of a diffraction grating having a small number of lines. In this case we can regard the crystals as three dimensional gratings, the shape and size of which influence the form of the observed diffraction band. Scherrer[1] investigated the case of crystals of the regular (cubic) crystallographic system which are cubical in shape and gave for the half intensity breadth, B, of a diffraction band produced by the powder method,

$$B = \frac{K\lambda}{D \cos (\theta_0/2)} \tag{1}$$

in which λ is the wave-length of the incident x-rays, D, the length of one edge of the cube, and θ_0, the angle between the diffracted and the incident ray. K is a constant whose value Scherrer found to be $2 [\log 2/\pi]^{1/2}$. Two other investigators treating more general cases have obtained results which reduce to Eq. (1) for the case of cubical crystals. They obtained slightly different values of the coefficient K. Seljakow[2] investigated the case of crystals of any

[1] P. Scherrer, Nachr. Gesell. Wiss. Göttingen (1918), p. 190.
[2] N. Seljakow, Zeits. f. Physik 31, 439 (1925).

crystallographic system whose shape is a parallelopiped geometrically similar to the unit cell and whose edges are parallel to the crystallographic axes. v. Laue[3] treated the case of parallelopipeds which have edges parallel to the crystallographic axes but which are not necessarily similar to the unit cell. His development brought out two interesting facts; viz. that the breadth of the diffraction bands depends upon the shape as well as upon the size of the parallelopiped; and in the general case, that the breadth is a function of the Miller indices of the band.

Considerable use has been made of Scherrer's equation in estimating the size of crystalline powders. Particular interest attaches to the investigation of colloidal preparations of such elements as gold, silver and nickel. These elements crystallize in face-centered cubic lattices and are normally of the octahedral form. In the investigations cited above no attempt has been made to determine the shape of the diffraction band. The shape of the band should depend upon the Miller indices of the band, the shape of the crystals, and, if the crystals are not of uniform size, upon the distribution of size. It seemed desirable to investigate the theoretical breadth and shape of several diffraction bands for crystals of octahedral as well as cubical shape..

The general procedure for computations of this sort is given by v. Laue[3] and in the following discussion his notation is generally followed. Assume a parallel beam of monochromatic x-rays incident upon a crystal in a direction which we shall specify by the unit vector s_0. Consider the rays diffracted by the crystal in the direction of the unit vector s. The intensity of the diffracted beam may be expressed[4] as a periodic function of the quantities A_i defined by $A_i = k \ a_i \cdot H$; $i = 1, 2, 3$ in which $k = 2\pi/\lambda$ and $H = s - s_0$. a_1, a_2 and a_3 represent the three primitive vectors of the space lattice. In the case of fine powders the extinction effect is negligible[5] and each unit cell of the crystal may be regarded as diffracting in the direction of s rays which are identical except for phase. In the expression for the total intensity of the diffracted beam, A_1, A_2, and A_3 represent the phase differences between rays diffracted by cells adjacent respectively along the three crystallographic axes of the crystal. The principal maxima of the function occur when the phase differences, A_i, are integral multiples of 2π, i.e. when $A_i = 2\pi h_i$; $i = 1, 2, 3$ in which the quantities h_i are integers. It will be noted that h_1, h_2, and h_3 are respectively n times the Miller indices of the Bragg planes of the crystal where n is the order number.

In the cubic system, the magnitudes of the three vectors a_i are equal and we can write $|a_i| = a$. This makes it possible to regard A_1, A_2, and A_3 as the projections on the three crystallographic axes of a vector, $A = kaH$. Consider a rectangular cartesian system in which A_1, A_2, and A_3 are the coordinates with axes parallel to the crystallographic axes of the crystal. We will designate the space thus defined as A-space. Each point, A_i, of this space deter-

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

[4] M. v. Laue, Enc. Math. Wiss. **5,** 459.

[5] R. J. Havighurst, Phys. Rev. [2] **28,** 882 (1926).

mines a value of the intensity function. The points $2\pi h_i$ in A-space form a lattice which is geometrically similar to Ewald's reciprocal lattice.[6] Each such point corresponds to a principal maximum of the diffraction pattern.

Since H is the difference of two unit vectors, s and s_0, its numerical value is $2\sin(\theta/2)$ in which θ is the angle between the two vectors, s and s_0, i.e. the angle of diffraction. It follows that A, the numerical value of A, may be expressed by

$$A = ka\,|\,H\,| = (4\pi a/\lambda)\sin(\theta/2). \tag{2}$$

The direction of A is that of H and depends only upon the directions of the incident and diffracted rays. The vector A is therefore independent of the size, shape and orientation of the crystal. If the incident beam falls upon a crystalline powder, the same vector A pertains to the ray diffracted by each crystal in the direction determined by the angle θ. To each crystal of the powder there corresponds an A-space with axes parallel to the crystallographic axes of the crystal. The total intensity of the beam diffracted through the angle θ by the powder is the sum of the values of the intensities determined in the A-spaces of the several crystals by the vector, A.

The intensity function is determined by the size and shape of the crystal, the crystal lattice and the structure factor. Consider a large number, N, of crystals of uniform size, shape, space lattice and structure. Then the same intensity function, J, will pertain to the A-spaces of all the crystals and the total intensity will be found by integrating J between such limits as to include all possible orientations of the crystallographic axes. For the purpose of carrying out this integration, it is convenient to specify the orientation in terms of the direction of A_0, the radius vector of the point $2\pi h_i$ in A-space corresponding to the diffraction maximum, h_i, with which we are concerned. Let ϕ be the polar angle between the directions of A and A_0; ξ, the azimuth angle about the direction of A as a pole; and ψ, that about the direction of A_0 as a pole. The total intensity, I, will then be represented by

$$I = N\frac{\displaystyle\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} J(A_i)\sin\phi\,d\phi d\xi d\psi}{\displaystyle\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \sin\phi\,d\phi d\xi d\psi}$$

$$= \frac{N}{4\pi}\int_0^\pi \int_0^{2\pi} J(A_i)\sin\phi\,d\phi d\psi \tag{3}$$

since $J(A_i)$ is invariant with respect to ξ. This double integral is the same as that representing the integral over the surface of the sphere in A-space whose center is the origin and whose radius is A. It will be convenient to consider I as this surface integral.

The intensity function[4] for the case of a crystal whose shape is a cube with edges parallel to the crystallographic axes is well known. Expressed in terms

[6] P. P. Ewald, Zeits. f. Krist. **56**, 129 (1921).

of the intensity diffracted by one unit cell per unit solid angle in the specified direction, it is given by

$$J = \frac{\sin^2 \frac{1}{2}MA_1}{\sin^2 \frac{1}{2}A_1} \cdot \frac{\sin^2 \frac{1}{2}MA_2}{\sin^2 \frac{1}{2}A_2} \cdot \frac{\sin^2 \frac{1}{2}MA_3}{\sin^2 \frac{1}{2}A_3} \tag{4}$$

in which M is the number of unit cells along one edge of the cube. The principal maxima of J occur when $A_i = 2\pi h_i$ and the value of J at these maxima is $J_0 = M^6$. Because of its structure the intensity of the rays diffracted by a unit cell will vary with the direction thus causing the various principal maxima to have different intensities. In a study of the variation of intensity within a diffraction band, we compare the surface integrals over spheres in A-space which comprise a very thin spherical shell and we may neglect the variation of the structure factor with respect to A within this shell. This is accomplished by measuring the intensity function in terms of its maximum value at $A_i = 2\pi h_i$ for the band, h_i, under investigation and gives

$$J' = J/J_0. \tag{5}$$

Let us investigate the intensity function for an octahedron consisting of a simple cubic lattice with axes x, y, z along the diagonals of the octahedron and a single diffracting particle at each point of the lattice. Let M be the number of diffracting particles along a diagonal. We will take M to be an odd integer. We will specify the points of the lattice by the coordinate whole numbers n_1, n_2, n_3 measured parallel to the x, y, z axes respectively in terms of the length of the unit cell i.e. $x = n_1 a$, $y = n_2 a$, $z = n_3 a$. The points having a particular value of n_3 form a square parallel to the x, y plane whose diagonals extend from $-(m - |n_3|)$ to $(m - |n_3|)$ in which $m = 1/2\,(M-1)$. In this square the points having a particular value of n_2 form a row which extends from $n_1 = -n_1''$ to $n_1 = n_1''$ in which $n_1'' = m - |n_2| - |n_3|$. The resultant of the rays diffracted in the direction of s by the $(2n_1''+1)$ points comprising the n_2, n_3 row will be in phase with that diffracted in this direction by the central point, 0, n_2, n_3, of the row. The contribution of any point, n_1, n_2, n_3 to this resultant is $\cos(n_1 A_1)$ multiplied by the amplitude. Measured in terms of the ray diffracted in the direction of s by any point, the resultant is $\sum_{-n_1''}^{n_1''} \cos(n_1 A_1)$. As we now proceed to combine the resultant rays from the various rows of the n_3 square, we are combining rays having unequal amplitudes whose values are symmetrically distributed about the central row, $0, n_3$. Each component ray has the phase of the central point of its row. The resultant will therefore have the same phase as that of the ray diffracted by the central point 0, 0, n_3 of the n_3 square and will be

$$\sum_{-n_2'}^{n_2'} \left\{ \cos(n_2 A_2)\sum_{-n_1''}^{n_1''} \cos(n_1 A_1) \right\}$$

in which $n_2' = m - |n_3|$. Similarly we may combine the rays from all such squares and obtain P, the resultant amplitude of the ray diffracted by the octahedron in the direction of s.

$$P = \sum_{-m}^{m} \left\{ \cos{(n_3 A_3)} \sum_{-n_2'}^{n_2'} \left[\cos{(n_2 A_2)} \sum_{-n_1''}^{n_1''} \cos{(n_1 A_1)} \right] \right\}. \tag{6}$$

Principal maxima of P occur when $A_1 = 2\pi h_1$, $A_2 = 2\pi h_2$, $A_3 = 2\pi h_3$ where h_1, h_2, h_3 are integers. The value of these maxima is $P_0 = (4m^3 + 6m^2 + 8m + 3)/3$ and the intensity function measured in terms of the intensity at a maximum is $J' = P^2/P_0^2$. $\hfill (7)$

An investigation of the variation of P with respect to M shows that if P is expressed in terms of new variables, $u_i = 1/2 \, M(A_i - 2\pi h_i)$, it is approximately independent of M in the neighborhood of the point $2\pi_{h_i}$. If we now write the expression for J_∞', the limit of J' as M approaches the summations of Eq. (6) become definite integrals which may be evaluated. The result of the integration is

$$J_\infty' = 6 \left\{ \frac{(u_1^2 - u_2^2)u_3 \sin{u_3} + (u_2^2 - u_3^2)u_1 \sin{u_1} + (u_3^2 - u_1^2)u_2 \sin{u_2}}{(u_1^2 - u_2^2)(u_2^2 - u_3^2)(u_3^2 - u_1^2)} \right\}. \tag{8}$$

An investigation of Eq. (8) shows that the distribution of the values of J_∞' about the origin of u_i is nearly spherical i.e. J_∞' is approximately a single valued function of $u = (u_1^2 + u_2^2 + u_3^2)^{1/2}$. For any given value of u, maxima or minima occur if (a) $u_j = u_k = 0$, (b) $u_i = u_j$, $u_k = 0$, or (c) $u_i = u_j = u_k$. On the sphere in A-space whose radius is u and whose center is $2\pi h_i$ these maxima and minima occur at intersections with diameters parallel respectively to (a) the axes of the space lattice, (b) the diagonals of squares bounding the unit cells, and (c) the diagonals of the unit cells. The values of J_∞' for these three conditions are given by

$$
\begin{array}{lll}
\text{(a)} & J_\infty' = \dfrac{6}{u_i^3}(u_i - \sin{u_i}), & u = u_i \\[4mm]
\text{(b)} & J_\infty' = \dfrac{3}{u_i^3}(\sin{u_i} - u_i \cos{u_i}), & u = \sqrt{2}u_i \\[4mm]
\text{(c)} & J_\infty' = \dfrac{3}{4u_i^3}[(1 + u_i^2)\sin{u_i} - u_i \cos{u_i}], & u = \sqrt{3}u_i
\end{array} \tag{9}
$$

and are shown as functions of u in curves Ia, Ib, and Ic of Fig. 1. For values of $u > 5.7$, minima at which $J_\infty' = 0$ occur at other points on the sphere. It follows that when $u < 5.7$ all values of J_∞' must lie in the narrow strip enclosed between the curves and when $u > 5.7$, in that enclosed between the curves and the line $J_\infty' = 0$.

The nature of the approximation involved in using Eq. (8) instead of Eq. (7) is shown by curves Ia, Ib and Ic of Fig. 2. Here the corrections which must be applied to J_∞' in order to obtain the value of J' for the case, $M = 11$ are plotted against u. The correction curves for larger values of M are of the same general form with maxima and minima approximately at the same values of u, but they have smaller values for the ordinates. The correction for any

value of u is approximately inversely proportional to M^2. For values of M which ordinarily occur these corrections are small.

The secondary maxima of the function J' defined by Eqs. (6) and (7), lie on the diagonals of the cubes of the lattice formed in A-space by the principal maxima points, $2\pi h_i$. At the centers of these cubes where three such diagonals intersect there occur secondary maxima at which the intensity is approximately three times that at the neighboring secondary maxima. The large ordinate at $u = 29.9$ in curve Ic of Fig. 2 is due to such a large secondary maximum. In the derivation of Eq. (6), M was assumed to be odd. If M were even, no secondary maxima would occur at these points in A-space.
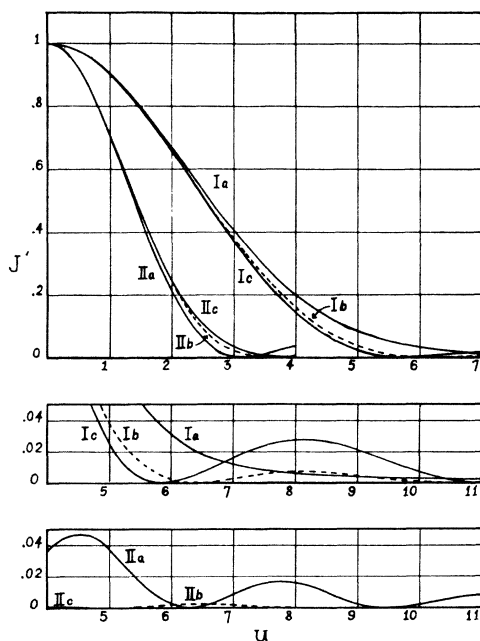

Fig. 1. The intensity function, J_∞', plotted against u; (I), for octahedral crystals; (II), for cubical crystals. u is measured parallel to the radius vector A_0 of (a) the (1, 0, 0) maximum, (b) the (1, 1, 0) maximum, (c) the (1, 1, 1) maximum.

Substituting the coordinates of these points, $(2\pi h_i - \pi)$, for A_i in Eq. (6) we obtain $P = (-1)^m (3/M) \ (M^2+1) \ /(M^2+5)$ which gives a value of J approximately $9/M^2$ times that at the neighboring principal maxima. Colloidal crystals have been examined by x-rays[7] for which the equivalent value of M was as small as 9. Crystals of this size, having octahedral shape and a simple cubic lattice would form an x-ray powder spectrogram in which these large secondary maxima should be directly observable as faint diffraction bands. The principal maxima points, $2\pi h_i$, form in A-space a simple cubic lattice, geometrically similar to the reciprocal lattice[8] of the crystal. If we include the large secondary maxima points, $(2\pi h_i - \pi)$, the reciprocal lattice becomes body-centered. Since the reciprocal lattice of a face-centered crystal is a body-

centered lattice, the observed diffraction pattern would be similar to that of a face-centered crystal. The relative strengths of the bands would be very much like that observed in the diffraction pattern of sodium fluoride.
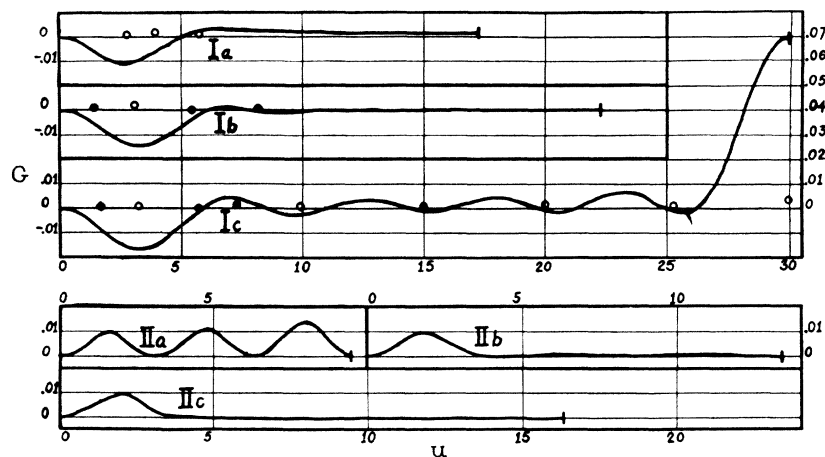

Fig. 2. The correction function, $G(M, u_i) = J' - J_\infty'$ plotted against u; for a simple cubic lattice; (I) octahedral crystals, $M=11$; (II) cubical crystals, $M=6$. The small circles show corresponding values for a face-centered lattice. u is measured parallel to the radius vector A_0 of (a) the (1, 0, 0) maximum, (b) the (1, 1, 0) maximum, (c) the (1, 1, 1) maximum.

The intensity function in the case of a cubical crystal may be treated in the same way as in the case of an octahedral cystal. If we express J' of Eq. (5) in terms of u_i and take the limit as M approaches ∞ we obtain

$$J_\infty' = \frac{\sin^2 u_1}{u_1^2} \cdot \frac{\sin^2 u_2}{u_2^2} \cdot \frac{\sin^2 u_3}{u_3^2}. \tag{10}$$

The conditions for maxima and minima of this function are similar to those for Eq. (8). Curves IIa, IIb, and IIc of Fig. 1 show the corresponding maxima and minima as functions of u. In this case additional minima at which $J_\infty' = 0$ occur for values of $u > 3.3$. Curves IIa, IIb, and IIc of Fig. 2 show the corrections to be added to J_∞' to obtain the value of J' for the case, $M = 6$. Here also the correction for a particular value of u is inversely proportional to M^2.

Since crystals having face-centered lattices are of particular interest, the intensity functions have been developed also for diffracting particles at the points of a face-centered lattice. In the octahedral case, the result is

$$J' = \left[\frac{P+Q}{P_0+Q_0}\right]^2 \tag{11}$$

in which

$$Q = \sum_{-m+1}^{m-1} \left\{ \cos (n_3 A_3)\, 4 \sum_0^{n_2'-1} \left[\cos (n_2 A_2 + \tfrac{1}{2}A_2) \sum_0^{n_1''} \cos (n_1 A_1 + \tfrac{1}{2}A_1) \right] \right\}$$

[7] R. Zsigmondy, "Kolloidchemie," Leipzig 1920, p. 406.
[8] cf. A. L. Patterson, Zeits. f. Physik 44, 596 (1927).

+two other terms formed from the first by a rotation of subscripts and $Q_0 =$ $4m^3+6m^2+2m$. The limit of J' as M approaches ∞ is identical with J_∞' as given by Eq. (8). The corrections to be added to J_∞' to obtain J' are so small that the curves have not been drawn. The points indicated by the small circles in Fig. 2 indicate some of the values for $M = 11$.

In the case of crystals of cubical shape with a face-centered lattice

$$J' = \left(\frac{R+S}{R_0+S_0}\right)^2 \tag{12}$$

in which $R = J^{1/2}$ as given by Eq. (4), $R_0 = M^3$,

$$S = \frac{\sin \frac{1}{2}MA_1}{\sin \frac{1}{2}A_1} \cdot \frac{\sin \frac{1}{2}(M-1)A_2}{\sin \frac{1}{2}A_2} \cdot \frac{\sin \frac{1}{2}(M-1)A_3}{\sin \frac{1}{2}A_3}$$

+ two other terms formed from the first by rotation of subscripts and $S_0 =$ $3M(M-1)^2$. The limit of J' as M approaches ∞ is identical with J_∞' as given by Eq. (10). The corrections to be added to J_∞' to obtain J' are larger than in
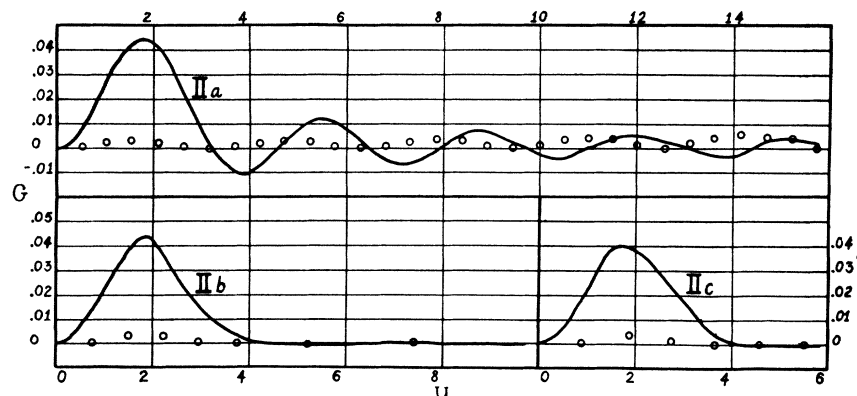

Fig. 3. The correction function, $G(M, u_i) = J' - J_\infty'$ plotted against u for a face-centered lattice and cubic crystals, $M = 10$. The small circles show corresponding values for a simple cubic lattice. u is measured parallel to the radius vector A_0 of (a) the (1, 0, 0) maximum, (b) the (1, 1, 0) maximum, (c) the (1, 1, 1) maximum.

the other cases studied. The curves are shown in Fig. 3 for $M = 10$. As in the other cases the positions of the maxima of these curves vary but slightly with M. In this case the ordinates are approximately inversely proportional to M. For the purpose of comparison, corrections for the case of the cubical shape with a simple cubic lattice for $M = 10$ are shown in Fig. 3 by small circles.

The narrow limits, between which all values of the intensity function must lie as shown in Fig. 1, make it possible to select an integrable function of u which closely approximates J. An approximate solution of our problem may be obtained by substituting this function for J in Eq. (3) and performing the integration. An investigation[9] of the case of octahedral crystals by this

[9] C. C. Murdock, Phys. Rev. [2] 31, 304 (1928).

method gave the value of the constant K of Eq. (1) as 1.6 when D was measured through the center of the octahedron from corner to corner. The investigation showed that the value of K was different for the various diffraction bands. The method of procedure, however, is not suitable for the study of this variation or for the determination of the form of a diffraction band.

Let us represent the function, J_∞', by the expression, $e^{-u^2/p^2} + F(u_i)$ in which the value of p is so selected that the first term approximates J_∞' for the case under consideration. We may now express J of Eq. (3) as

$$J = J_0 J' = J_0 \{ J_\infty' + G(M, u_i) \} = J_0 \{ e^{-u^2/p^2} + F(u_i) + G(M, u_i) \} \qquad (13)$$

in which $G(M, u_i)$ represents the correction to be added to J_∞' in order to obtain J'. The ordinates of Figs. 2 and 3 are values of G for the particular cases shown. We will use u^2 in place of ϕ as the variable of integration.

$$u^2 = u_1^2 + u_2^2 + u_3^2$$
$$= \tfrac{1}{4} M^2 [A^2 + 4\pi^2 h^2 - 4\pi(h_1 A_1 + h_2 A_2 + h_3 A_3)]$$
$$= \tfrac{1}{4} M^2 [A^2 + 4\pi^2 h^2 - 4\pi h A \cos \phi]$$

in which $h^2 = h_1^2 + h_2^2 + h_3^2$. Therefore $d(u^2) = \pi h A M^2 \sin \phi \, d\phi$.

In terms of u^2 the limits of integration of Eq. (3) become v^2 and w^2 where $v = \tfrac{1}{2} M(A - 2\pi h)$ and $w = \tfrac{1}{2} M(A + 2\pi h)$. These limits are such that the integration may be considered as a surface integration over the surface of a sphere in A-space whose diameter is $2A$. In changing variables from A_i to u_i we shifted the origin to the point, $2\pi h_i$, associated with the diffraction band, h_i, with which we are concerned. We also changed the scale of the space by the factor $1/2 M$. In terms of the new scale, the diameter of the sphere of integration is $AM = w + v$. The diameter of the sphere which passes through the point $2\pi h_i$ is $2\pi h M = w - v$. The point $2\pi h_i$ is not the only point on the surface of this sphere at which a principal maximum of J occurs. For example on the sphere of integration for the (1, 1, 1) diffraction band there are eight points, $2\pi h_i$, corresponding to the following values of h_i; 1, 1, 1; -1, 1, 1; 1, -1, 1; 1, 1, -1; 1, -1, -1; -1, 1, -1; -1, -1, 1; and -1, -1, -1. Let N' represent the number of such points. Since J is a periodic function of A_i, the integration indicated in Eq. (3) includes the values of J in the neighborhood of all these points and the contribution to the integral in the neighborhood of each point is identical. J_∞' is not a periodic function. It can approximate $J_0 J$ only in the neighborhood of the point, $2\pi h_i$. In its integration the limits should be fixed so as to include $1/N'$ times the area of the sphere and the integral should be multiplied by N'. It will not be found necessary to specify exactly the upper limit of this integration. Its order of magnitude may be ascertained by taking the upper limit of u^2 as r^2, where r represents the radius of a circle whose area is $1/N'$ times the area of the sphere. Thus $\pi r^2 = 4\pi^3 h^2 M^2 / N'$ and $r^2 = 4\pi^2 M^2 h^2 / N'$. The value of h^2/N' is $1/6$ for the (1, 0, 0) and the (1, 1, 0) diffraction bands, but has a larger value for each of the other bands. The upper limit of integration is therefore of the order of magnitude of $2/3 \, \pi^2 M^2$ or larger.

Making these substitutions in Eq. (3) we obtain

$$I = \frac{NN'J_0}{4\pi^2 hA M^2} \left[\int_{v^2}^{r^2} e^{-u^2/p^2} d(u^2) + \int_{v^2}^{r^2} f(u,v) d(u^2) + \int_{v^2}^{r^2} g(M,u,v) d(u^2) \right]$$

$$= \frac{NN'J_0}{4\pi^2 hA M^2} [U + V + W], \tag{14}$$

in which $f(u,v) = 1/2\pi \int_0^{2\pi} F(u_i) \, d\psi$, the average value of F with respect to ψ, $g(M, u, v) = 1/2\pi \int_0^{2\pi} G(M, u_i) \, d\psi$ and U, V, and W represent respectively the three integrals of the equation.

The first integral, U, of Eq. (14) has the same value for each band, h_i, and may be written

$$U = \int_{v^2}^{r^2} e^{-u^2/p^2} d(u^2) = p^2 e^{-v^2/p^2} \tag{15}$$

if r^2/p^2 is large. Since $r^2/p^2 \geq \frac{2}{3}\pi^2 M^2/p^2$ and M^2/p^2 is of the order of 10 for the smallest colloidal crystals so far studied,[7] this assumption is justified.

The second integral, V, of Eq. (14) varies from band to band. It may be evaluated graphically by the following method. Contour plots are made of the function, $F(u_i) = J_\infty' - e^{-u^2/p^2}$ for a number of values of u. These may be made on the surfaces of spheres, the radii of which are taken as equal to u. It has been found more convenient, however, to make plots which are the projections of such spherical plots upon planes tangent to the sphere and perpendicular to the direction of the vector A_0. From these plots the curves for $F(u_i)$ at various values of u and v are plotted as functions of ψ and integrated by inspection to obtain the values of $f(u,v)$. These values are then plotted as functions of u^2 for various values of v and the integrals evaluated graphically.

It is not practicable to carry out this process to the upper limit of integration. For large values of u, the value of f becomes small but remains finite and small errors in the function produce large errors in the integral due to the fact that the integration is performed with respect to the square of u. If s^2 is the upper limit of the graphical integration it leaves a part, $\int_{s^2}^{r^2} f(u,v) d(u^2)$, unevaluated. By properly choosing the value of s, the error involved in neglecting this part of the integral may be compensated in making the experimental observations. In an experiment the incident radiation will not be strictly monochromatic. Moreover there will be some generally scattered radiation. Both of these effects will give a background intensity superimposed upon that which we are computing. In practice the intensity is measured on either side of a diffraction band and from these data the background intensity is estimated for the points in the band on the assumption that there are no maxima or minima in the background intensity in that region. If the value of s is taken two or three times the largest value of v used, this assumption is also justified for $\int_{s^2}^{r^2} f(u, v) \, d(u^2)$ and the part of the intensity proportional to it will be automatically subtracted from the measured intensity as part of the background correction.

The third integral, W, of Eq. (14) may be evaluated by the method used for the evaluation of V. If, however, G can be approximated by an integrable function of u, it will be simpler to proceed as in the case of J_∞'. An examination of the correction curves of Figs. 2 and 3 shows that the (a), (b) and (c) curves of each set are practically identical for the smaller values of u and that for the larger values, two curves of each set have small ordinates. Advantage may be taken of this to approximate G by the function $Cu^2 e^{-u^2/p^2}$ which gives as a first approximation

$$W = Cp^2(p^2 + v^2)e^{-v^2/p^2}.\tag{16}$$

C is a function of M. It may be expressed for the various cases studied as shown in Table I.

<div align="center">TABLE I.</div>

	Cube	Octahedron
Simple lattice	$C = 1/(3M^2)$	$C = -1/(2M^2)$
Face-centered lattice	$C = 1/(3M)$	$C = 0$

The remainder, $G - Cu^2 e^{-u^2/p^2}$, may now be integrated by the method described for the evaluation of V.

Since W depends upon M, which, in general, can only be known as a result of the solution of our problem, we will first investigate the case in which W is negligible. If $W = 0$, Eq. (14) may be written

$$I = \frac{NN'J_0 L}{4\pi^2 hA M^2},\tag{17}$$

in which $L = U + V$. L is the surface integral over the sphere of $N'J_\infty'$. The only quantities in the second member of Eq. (17) which depend upon v, are L and A. If, therefore, we measure the intensity in terms of its maximum value, I_0, for which $v = 0$, we obtain

$$I' = I/I_0 = L'A_0/A,\tag{18}$$

in which $L' = L/L_0$ and L_0 represents the value of L when $v = 0$. The factor A_0/A may be written by Eq. (2) as $\sin(\theta_0/2) \div \sin(\theta/2)$ in which θ_0 is the value of θ corresponding to the maximum, h_i. In this form it is seen to be determined by directly observable quantities. Within a diffraction band θ differs only slightly from θ_0 and the factor may be written $1/(1 + \frac{1}{2}\cot(\theta_0/2)\Delta\theta)$ where $\Delta\theta = \theta - \theta_0$. Since this factor is unsymmetrical with respect to $\Delta\theta$ it introduces asymmetry in the diffraction band. It is due to the fact that the integrations for values of v which are numerically equal but of opposite sign, are performed over spheres of different areas. In the graphical process for the evaluation of V another source of asymmetry occurs. It is due to the curvature of the spherical surface. No case has yet been found in which this second asymmetry is large enough to be taken into consideration. Because of the small value of

s used in the evaluation of V an integration in the spherical surface is practically the same as an integration in the tangent plane perpendicular to the vector, A_0. If the integration is performed in this plane, the asymmetry due to curvature does not appear in the result.

We may now write Eq. (18) as

$$L' = [1 + \tfrac{1}{2} \cot (\theta_0/2)\Delta\theta] I'. \tag{19}$$

In this form there are collected in the second member the experimentally observable factors and the first member is a symmetrical function which may be computed for any band h_i from the integrals U and V of Eq. (14). U is the same for all bands. If V is integrated over the tangent plane it will vary from band to band due to the variation of the direction of the vector A_0. This is, however, the same for all bands having the same Miller indices. It follows that the function L' will be the same for all orders of a diffraction band and need only be computed for one order.

The function L' has been computed for the $(1, 0, 0)$, the $(1, 1, 0)$, and the $(1, 1, 1)$ diffraction bands in the cases of cubical and octahedral crystals. In the cubical case, the value of p was taken as $\sqrt{3}$, contour plots were made for eight values of u, and the graphical integration performed to the limit $s^2 = 90$. In the octahedral case the value of p was taken as 3, contour plots were made for eleven values of u, and the graphical integration performed to the limit $s^2 = 120$. Table II gives the resulting values of L' as determined. The uncertainty in the values due to the errors of the operation are of the order of ± 0.005. Since L' is a symmetrical function the values are given for the positive values of v only.

TABLE II.

v	Cube L'			v	Octahedron L'		
	(1, 0, 0)	(1, 1, 0)	(1, 1, 1)		(1, 0, 0)	(1, 1, 0)	(1, 1, 1)
0	1.000	1.000	1.000	0	1.000	1.000	1.000
1	.728	.692	.680	1	.874	.891	.905
1.41	.500	.445	.466	2	.591	.631	.673
1.73	.333	.300	.333	2.6	.428	.456	.504
2	.221	.211	.268	3.2	.292	.305	.348
2.5	.074	.123	.170	4	.177	.145	.170
3	.027	.089	.131	5	.105	.060	.051
3.5			.094	6	.064	.046	.020
4	.054	.072	.069	7	.039	.040	.025

Experimentally we measure the width of a diffraction band in terms of differences in the angle of diffraction. By the definition of v, and by Eq. (2), we obtain

$$v = \tfrac{1}{2}M(A - 2\pi h) = (2\pi a M/\lambda)[\sin (\theta/2) - \sin (\theta_0/2)].$$

If we substitute $d/d\theta$ (sin $\theta/2$) $\Delta\theta$ for sin $(\theta/2) - \sin (\theta_0/2)$ we obtain

$$v = (\pi a M/\lambda) \cos (\theta_0/2)\Delta\theta.$$

Let v' represent the value of v for which $I' = 1/2$ and, following Scherrer, let B represent the half intensity breadth of a diffraction band, measured in radians. Then

$$v' = (\pi a M/\lambda) \cos (\theta_0/2) (B/2)$$

and

$$B = (2v'/\pi) \lambda/(Ma \cos (\theta_0/2)). \qquad (20)$$

This is identical with Eq. (1) obtained by Scherrer since $Ma = D$, the length of the crystal along a crystallographic axis. Thus we obtain for the value of K, $2v'/\pi$. For comparing crystals of different shape, it is convenient to measure the size of the crystal in terms of D', the cube root of the volume. D' may be used in place of D in Scherrer's equation, if a suitably modified constant K' is used in place of K. For the cubical shape $D' = D$ and $K' = K$. For the octahedral shape $D'^3 = 1/6 D^3$ and $K' = K/6^{1/3}$ Table III shows the values of v', K and K' as computed from the data of Table II.

TABLE III.

| Indices | Cube | | Octahedron | | |
	v'	$K = K'$	v'	K	K'
(1, 0, 0)	1.41	0.90	2.32	1.48	0.81
(1, 1, 0)	1.32	0.84	2.45	1.56	0.86
(1, 1, 1)	1.36	0.87	2.62	1.67	0.92

These values are in general smaller than the results of previous investigations. Scherrer's value of K as computed from Eq. (1) is 0.94. Seljakow[2] obtained 0.92 and v. Laue[3] 0.90 for the value of K for the cubical case. The previous investigation[9] of the octahedral case gave $K = 1.6$ or $K' = 0.88$, a value 7 percent less than Scherrer's value of K. This difference was attributed to the shape of the crystal and it was concluded that the values of the crystal volumes which have been estimated by the use of Scherrer's equation were too large by 20 percent if the true shape of the crystals was octahedral. It now appears that the smaller value of K was due not so much to the shape of the crystals as to the method of computation. An examination of Table III shows that the mean values of K' in the cubical case and in the octahedral case are practically the same. Both Seljakow[2] and v. Laue[3] used methods which may be regarded as the substitution of a function of u for the intensity function.

The results shown in Table III illustrate the dependence of the half intensity width of a diffraction band upon the indices of the band. The numerical order of the values of K in the two cases is different. In the cubical case the largest value of K is that of the (1, 0, 0) band while in the octahedral case it is that of the (1, 1, 1) band. In each case, the value of K for the diffraction band which is associated with a Bragg plane, parallel to a face of the crystal, is larger than the values which are associated with the other planes.

The shape of the crystals not only influences the relative width of the diffraction bands but also the form of the bands. This is shown in Fig. 4 in which

L' is plotted against v/v', or what is the same thing, $2\Delta\theta/B$. On this scale the half intensity width of all the diffraction bands is 2 and their shapes can be directly compared.

The upper halves of all the curves are practically the same and are sufficiently approximated by the exponential relation $L' = e^{-(v/1.2v')^2}$ which is
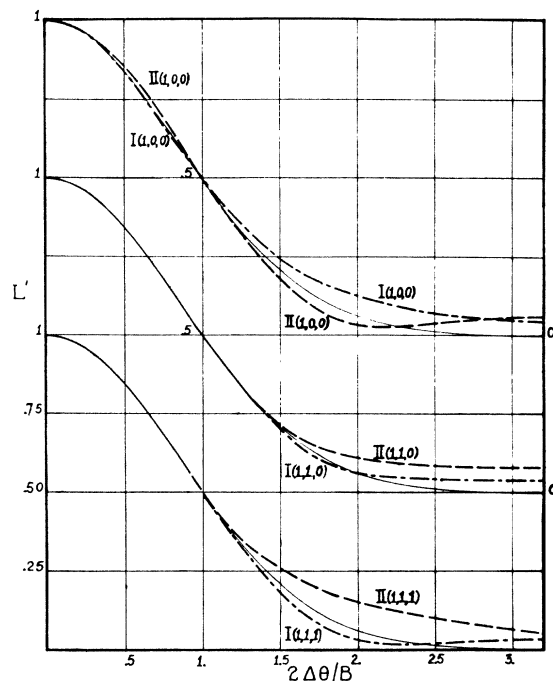

Fig. 4. The (1, 0, 0) (n), the (1, 1, 0) (n) and the (1, 1, 1) (n) diffraction bands for, (I) octahedral crystals, (II) cubical crystals. The scales are such that the maximum intensity is 1 and the half intensity breadth is 2. The unbroken line shows the corresponding Gauss error curve.

plotted in unbroken lines in the figure. The lower halves of the curves show marked variations. Three types occur:

(a) that illustrated by I(1, 1, 1) and II(1, 0, 0), falls slightly below the exponential curve to a minimum and then rises to a secondary maximum;

(b) that illustrated by I(1, 1, 0) and II(1, 1, 0) follows the exponential curve until well below the half intensity point and then becomes nearly parallel to the v/v' axis;

(c) that illustrated by I(1, 0, 0) and II(1, 1, 1) lies well above the exponential curve throughout the lower half of the curve and continues to approach the axis of v/v' to the limits of the computation.

There is a correlation between the type of curve and the Bragg plane associated with the diffraction band. Type (a) occurs when the Bragg plane is parallel to the faces of the crystal, the (1, 0, 0) for the cube and the (1, 1, 1) for the octahedron. These are the same bands which show large values of K.

Type (c) occurs when the Bragg planes are perpendicular to lines connecting opposite corners of the crystal, the (1, 1, 1) for the cube and the (1, 0, 0) for the octahedron. Type (b) occurs for the (1, 1, 0) band in both cases. In both the cube and the octahedron the (1, 1, 0) planes are perpendicular to lines connecting the centers of opposite edges of the crystal. The extension of this correlation to the case of crystals of dodecahedral shape would suggest that in this case the (1, 1, 0) diffraction band would be of type (a).

These results have been obtained by assuming that the third integral, W, of Eq. (14) was negligible. This will not be true if M is very small. By Eq. (20) and Table II we may now estimate the value of M and compute corrections to account for the finite value of W. If $W \neq 0$, we must write in place of L' of Eqs. (18) and (19), $(L+W)/(L_0+W_0)$ in which W_0 is the value of W when $v = 0$.

If W is small compared with L_0 we may write $(L+W)/(L_0+W_0) = L' + (W/L_0) - (W_0/L_0)L'$ and compute W by Eq. (16) taking $p^2 = (1.2v')^2 = L_0$. This gives for the correction to be applied to L',

$$\Delta L' = W/L_0 - (W_0/L_0)L' = Cv'^2 \left\{ (v/v')^2 e^{-v^2/p^2} - 1.2^2(L' - e^{-v^2/p^2}) \right\}. \quad (21)$$

This may be readily computed. C is given in Table I; v' in Table II; v/v' are the abscissa of Fig. 4; and e^{-v^2/p^2} are the corresponding ordinates of the unbroken line curves of Fig. 4.

At the half intensity point, Eq. (21) reduces to $\Delta L' = \frac{1}{2}Cv'^2$. If we assume the slope at the half intensity point to be that of the unbroken line curve we obtain for the correction to be applied to v',

$$\Delta v' = 0.72Cv'^3. \quad (22)$$

Thus v' may be corrected for the finite value of W by multiplying it by the factor $(1+0.72\ Cv'^2) = (1+1.8\ CK^2)$. Since K and K' are proportional to v' this same correction factor may be applied to them and also to the values of D and M as computed by Scherrer's equation.

Eqs. (8) and (10) have been derived for the face-centered, as well as for the simple lattice. They may be shown to hold for the body-centered lattice as well. It follows that J', its integral, L, and the results shown in Tables II and III and Fig. (4) hold for any of these space lattices. However, the corrections to these results computed by Eqs. (21) and (22) vary with the space lattice. The corrections have been derived on the assumption that the diffracting material is concentrated at the points of the lattice. Actually these points are merely centers of space distributions of diffracting material. Since the corrections depend upon the distribution of diffracting material within the unit cell, a more exact determination of W than that given by Eq. (16) does not seem to be warranted by the assumptions.

It has been assumed throughout the discussion that the crystalline powder is made up of crystals of uniform size. In practice this assumption is frequently not justified. Any attempt to determine the size distribution from the x-ray diffraction pattern requires a knowledge of the theoretical form of

the band for the case of uniform size. Indeed it was this requirement which instigated this investigation. The closeness with which the form of the diffraction bands agrees with the Gauss error curve as shown in Fig. 4 makes it possible to assume this form for the purpose of estimating the distribution of particle size. The (1, 1, 0) band is particularly suitable for this purpose. It is hoped that studies of the form of the (1, 0, 0) and (1, 1, 1) bands together with studies of the relative width of the bands will lead to information as to the shape of the colloidal crystals in cases where there is approximate uniformity of shape.

The shape of the x-ray diffraction bands of a very fine uniform crystalline powder has been computed for the (1, 0, 0), (1, 1, 0) and (1, 1, 1) planes of cubical and octahedral crystals of the regular system. The results are shown in Fig. 4 plotted to such scales that the maximum ordinate is 1 and the half intensity breadth, 2. The coefficient K of Eq. (1) which relates the half intensity breadth of a band to the size of the crystal has been computed for each case. The values are shown in Table III. In comparing these theoretical results with experimental data, one must take care to comply with the following conditions.

(a) The experimental data must be corrected for "background" radiation and instrumental errors.

(b) The corrected data must be multiplied by the asymmetrical factor, $[1 + \frac{1}{2} \cot(\theta_0/2) \Delta\theta]$ of Eq. (19).

(c) An approximate value of M should be computed by Eq. (20) and Table III.

(d) The corrections to the ordinates of Fig. 4 may then be computed by Eq. (21) and Table I and the approximate value of M may be corrected by the factor $(1 + 1.8 \ CK^2)$.