THE OPTICAL PRINCIPLES OF THE LOW ANGLE SCATTERING OF X-RAYS.

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(Communicated by Prof. K. Banerjee, D.Sc., F.N.I.)

(*Received November 29, 1951; read January 1, 1952.*)

Introduction.

From the optical principles of X-ray diffraction, the intensity of the diffracted beam in any direction represented by a point (ξ, η, ζ) in the reciprocal space is given by the equation (1913)

$$I_0\,(\xi, \eta, \zeta) = \frac{\sin^2(\pi N_1 \xi)}{\sin^2(\pi\xi)} \cdot \frac{\sin^2(\pi N_2 \eta)}{\sin^2(\pi\eta)} \cdot \frac{\sin^2(\pi N_3 \zeta)}{\sin^2(\pi\zeta)}$$

where, ξ, η, ζ are the components of the radius vector of the point from the origin parallel to the three reciprocal axes. This is not zero just outside the reciprocal lattice points, but has appreciable values throughout a continuous three dimensional envelope surrounding each reciprocal lattice points. The pattern and the volume of this envelope depends on the external shape and the size of the crystal particle, the thermal motion of the molecules and the lattice defects being neglected. The smaller the size of the particle the greater is the volume of the envelope. Later on Laue (1936) calculated a relation between intensity and the crystal form factor which represents the amplitude scattered under given conditions by a continuous volume distribution of scattering matter having the same boundaries as the crystal and does not depend upon the type of the lattice upon which the crystal is built. Following is the relation :—

$$I_0\,(\xi, \eta, \zeta) = \left(\frac{\pi\xi}{\sin \pi\xi} \cdot \frac{\pi\eta}{\sin \pi\eta} \cdot \frac{\pi\zeta}{\sin \pi\zeta}\right) \left|E(\rho)\right|^2$$

where, $E(\rho)$ is the crystal form factor, ρ being the vector distance of any point ξ, η, ζ from its nearest reciprocal lattice point in the reciprocal space. By an extension of his calculation he showed that the intensity distributions have projections perpendicular to the binding faces of the crystal. The larger the area of the face the stronger and sharper are the projections. These were termed as 'Intensity Spikes' by Laue. The same calculation was further extended over the lines of all the edges surrounding the face of the crystal and it was further seen that the intensity distribution has subsidiary spikes in the directions perpendicular to surrounding edges. One entire intensity distribution pattern consists of a number of primary and subsidiary intensity spikes.

This knowledge about intensity patterns from Laue's calculation would very conveniently help to determine the shape and size of the submicroscopic particles of crystals but owing to the following difficulties it was not possible :—

(1) To take X-ray diffraction photograph of a single submicroscopic particle is not practically possible.

(2) On the other hand, the resultant intensity distribution pattern of a large number of submicroscopic particles consists of many concentric

spheres, traced out by the revolution of the reciprocal lattice points, with its surrounding system of intensity pattern, about the origin of the reciprocal lattice, as the centre of the sphere. The portion of any such spheres intersected by the sphere of reflection defines the cone of diffraction maxima and consequently, there appear only a broadening of the Debye-Scherrer lines in the photographic plate. Therefore, the only thing that is left is to observe the change in intensity along the angular breadth of the lines. Thus a relationship has been deduced by Laue (1926) and Scherrer (1920) between the breadth of the Debye-Scherrer lines as defined by them and particle size for particles of parallelopiped shapes and cubic systems.

It has been shown by Guinier (1939) that the shape and size of particles can be determined from low angle scattering also as this may be regarded as a broadening around the diffracted ray of index 000. In fact, the method of low angle scattering is more convenient than Laue's method as the former depends only on the shape and size of the particles and independent of their internal structure.

That the methods of physical optics are applicable to X-ray scattering at small angles was first pointed out by Raman and Ramanathan (1923) in the case of liquids since for small angle scattering the phase differences between rays scattered from neighbouring atoms or molecules are negligible and the internal discrete structure may be overlooked. The same arguments will naturally be applicable to the solid state and so for small angle scattering the fine structure of the scatterer is immaterial, only the sizes and shapes of the crystallites are to be taken into considerations. Guinier (1939) also arrived at the same conclusion after a very detailed and complex analysis. The study of low angle scattering has therefore a very wide scope of application in the field of determination of the size and shape of particles as it does not matter whether they are crystalline, amorphous or colloidal. In view of the importance of low angle scattering and since the optical principles are applicable to this problem we propose in this paper to investigate it as a problem of Fraunhofer diffraction. As the mathematics is considerably simplified in that way, it is expected that the scope of applicability of the method of low angle scattering may be extended to more and more complicated cases. In the present discussions we shall restrict ourselves to the cases of (1) sphere, (2) plates.

Physical Principles.

A pencil of X-rays has been considered as a parallel pencil of optical rays and the particles of any shape as continuously uniform aggregations of indefinitely small scattering units among the rays scattered from which there is no appreciable phase difference. The scattering medium as a whole is also considered to be transparent to the rays.

The maximum phase difference between the rays scattered by two neighbouring atoms is given by

$$\frac{2\pi}{\lambda} d \sin \epsilon \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where, d is the distance between the two neighbouring atoms and ϵ the angle of scattering. Since d and λ are of the same order of magnitude this phase difference becomes negligible when ϵ is small.

Now, if the entire medium be imagined to be an aggregation of indefinitely small volumes within which the phase change from the scatterers will be accordingly small, there is fair justification in considering the medium as optically continuous within those small volumes for all problems of coherent scattering. Thus we are justified in considering our problem as one of a three dimensional Fraunhofer diffraction.

Three Dimensional Fraunhofer Scattering Phenomena.

(General Treatment.)

Proceeding in the usual way of investigating the Fraunhofer class of diffraction (*vide* Drude: *Theory of Optics*, pp. 185 and 214) we may put

$$I = A^2(C^2+S^2) \quad \ldots \quad (2)$$

where,

$$C = \int \cos(\lambda x+\mu y+\nu z)\, d\tau,$$

$$S = \int \sin(\lambda x+\mu y+\nu z)\, d\tau,$$

and

$$\lambda=\frac{2\pi}{\lambda_w}\left(\alpha_1+\alpha_0\right), \quad \mu=\frac{2\pi}{\lambda_w}\left(\beta_1+\beta_0\right), \quad \nu=\frac{2\pi}{\lambda_w}\left(\gamma_1+\gamma_0\right)$$

λ_w being the wavelength of radiation,
$\alpha_1, \beta_1, \gamma_1$, being the direction cosines of the incident ray,
and $\alpha_0, \beta_0, \gamma_0$, being the direction cosines of the scattered ray, and A is given by

$$I_0 = A^2\tau^2 \quad \ldots \quad (3)$$

where, I_0 is the incident intensity and τ the volume of the scatterer. Therefore, the expression of intensity for three dimensional Fraunhofer scattering becomes—

$$\frac{I}{I_0} = \frac{1}{\tau^2}\left(C^2+S^2\right) \quad \ldots \quad (4)$$

Case of Spherical Particles.

(Non-Absorbing.)

Preliminary Assumptions.

For the sake of simplicity following assumptions have been made :—

(1) The incident ray is parallel and opposite to the direction of z-axis.
(2) The origin has been taken at the centre of the sphere and spherical polar system of co-ordinates has been introduced.

Then, in spherical polar system the following relationship holds—

$$\text{(i)} \begin{cases} \alpha_1 = \beta_1 = 0, \quad \gamma_1 = \cos\pi \\ \alpha_0 = \sin\epsilon\cos\eta, \quad \beta_0 = \sin\epsilon\sin\eta, \text{ and } \gamma_0 = \cos\epsilon \end{cases}$$

where, $\alpha_1, \beta_1, \gamma_1$ = direction cosine of the incident ray.
$\alpha_0, \beta_0, \gamma_0$ = direction cosine of the scattered ray.
ϵ = the angle which the scattered ray makes with the z-axis, i.e. the angle of scattering.
η = the angle which the projection of the scattered ray on the xy-plane makes with the x-axis.

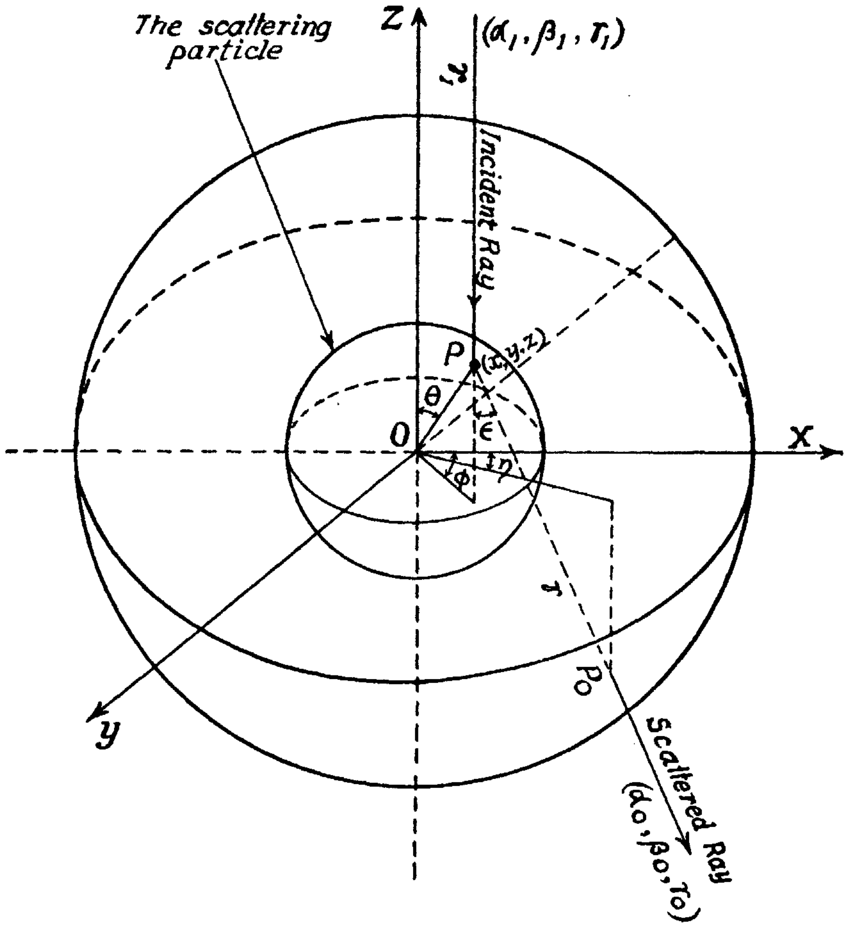

Fig. 1. Case of Spherical particle.

(ii)
$$\lambda = \frac{2\pi}{\lambda_w} \sin\epsilon \cos\eta = p \cos\eta$$

$$\mu = \frac{2\pi}{\lambda_w} \sin\epsilon \sin\eta = p \sin\eta$$

$$\text{where } p = \frac{2\pi}{\lambda_w} \sin\epsilon = \frac{2\pi}{\lambda_w}\epsilon$$

$$\nu = \frac{2\pi}{\lambda_w} (\cos\pi + \cos\epsilon)$$

$$= \frac{2\pi}{\lambda_w}(-1+1)$$

$$= 0^*.$$

* In the case of graphite irradiated by copper K_α radiation $\epsilon = 6'$, $\cos 6' = 0{\cdot}99999$. Therefore $\nu = -0{\cdot}00001 \simeq 0$.

(iii) In the intensity equation (4) which is given by

$$\frac{I}{I_0}=\frac{1}{r^2}(C^2+S^2),\ S=0.$$

Then (4) becomes—

$$\frac{I}{I_0}=\frac{C^2}{r^2} \quad \ldots \quad (5)$$

(iv)

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$
$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

(v)

$$C=\int_0^{2\pi}\int_0^{\pi}\int_0^{R} r^2 \sin\theta \, dr \, d\theta \, d\phi \cos\left[\lambda \sin\theta \cos\phi+\mu \sin\theta \sin\phi\right]$$

$$=\int_0^{2\pi}\int_0^{\pi}\int_0^{R} r^2 \sin\theta \, dr \, d\theta \, d\phi \cos\left[rp \sin\theta \cos\phi'\right] \quad \text{where } \phi' = (\phi-\eta)$$

$$=\int_0^{R}\int_0^{\pi} r^2 \sin\theta \, dr \, d\theta \int_{-\eta}^{2\pi-\eta} \cos\left[rp \sin\theta \cos\phi'\right] d\phi'$$

THE INTEGRAL IN ϕ'.

$$=\int_{-\eta}^{2\pi-\eta} \cos\left[rp \sin\theta \cos\phi'\right] d\phi'$$

$$=\text{Real part in} \int_{-\eta}^{2\pi-\eta} e^{i[rp \sin\theta \cos\phi']} d\phi' \quad \ldots \quad (6)$$

$$=\int_{-\eta}^{2\pi-\eta} e^{i[rp \sin\theta \cos\phi']} d\phi'$$

$$=\int_{-\eta}^{2\pi-\eta}\left[1+irp \sin\theta \cos\phi'+\frac{(irp \sin\theta \cos\phi')^2}{2!}+\ldots\right.$$
$$\left.+\ldots+\frac{(irp \sin\theta \cos\phi')^{2m}}{2m!}+\ldots\right] d\phi'$$

Now,

$$\int_{-\eta}^{2\pi-\eta} \cos\phi' \, d\phi' = 0, \qquad \int_{-\eta}^{2\pi-\eta} \cos^2\phi' \, d\phi' = \frac{2\pi}{2}$$

$$\int_{-\eta}^{2\pi-\eta} \cos^3\phi' \, d\phi' = 0, \qquad \int_{-\eta}^{2\pi-\eta} \cos^4\phi' \, d\phi' = 2\pi \cdot \tfrac{3}{8}$$

$$\ldots \ldots \qquad \ldots \ldots$$

The odd powers cancel and consequently.

$$\int_{-\eta}^{2\pi-\eta} \cos^{2m}\phi' \, d\phi' = \frac{(2m-1)(2m-3)\ \ldots\ 3.1}{2m(2m-2)\ \ldots\ 4.2} 2\pi$$

Therefore, the integral in ϕ', i.e. the real part in (6)

$$= 2\pi\left[1-\frac{r^2 p^2 \sin^2\theta}{2\,!}\cdot\frac{1}{2}+\frac{r^4 p^4 \sin^4\theta}{4\,!}\cdot\frac{3}{8}+\ldots\ldots-\ldots\ldots\right.$$

$$\left.(-1)^m \frac{(2m-1)(2m-3)\ldots\ldots 3.1}{2m(2m-2)\ldots\ldots 4.2}\cdot\frac{p^{2m} r^{2m}\sin^{2m}\theta}{2m\,!}+\ldots\ldots\right]$$

THE INTEGRAL IN θ.

$$=\sum_{m=0}^{m=\infty}(-1)^m\frac{(2m-1)(2m-3)\ldots\ldots 3.1}{2m(2m-2)\ldots\ldots 4.2}\cdot\frac{2\pi}{2m\,!}p^{2m}r^{2m}\int_0^{\pi}\sin^{2m+1}\theta\,d\theta$$

$$=4\pi\sum_{m=0}^{m=\infty}(-1)^m\frac{(2m-1)(2m-3)\ldots\ldots 3.1}{2m(2m-2)\ldots\ldots 4.2}\cdot\frac{1}{(2m)\,!}$$

$$\times\frac{2m(2m-2)\ldots\ldots 4.2}{(2m+1)(2m-1)\ldots\ldots 5.3}\times p^{2m}r^{2m}$$

THE INTEGRAL IN r.

$$=4\pi\sum_{m=0}^{m=\infty}(-1)^m\frac{(2m-1)(2m-3)\ldots\ldots 3.1}{2m(2m-2)\ldots\ldots 4.2}\cdot\frac{1}{(2m)\,!}$$

$$\times\frac{2m(2m-2)\ldots\ldots 4.2}{(2m+1)(2m-1)\ldots\ldots 5.3}\cdot p^{2m}\int_0^R r^{2m+2}\,dr$$

$$=4\pi\sum_{m=0}^{m=\infty}(-1)^m\frac{p^{2m}}{(2m+1)\,!}\cdot\frac{R^{2m+3}}{(2m+3)}$$

$$=\tfrac{4}{3}\pi R^3\sum_{m=0}^{m=\infty}(-1)^m\frac{3(2m+2)}{(2m+3)\,!}p^{2m}R^{2m}$$

$$=\frac{4}{3}\pi R^3\sum_{m=0}^{m=\infty}(-1)^m\frac{3(2m+2)}{(2m+3)!}u^{2m}$$

where $pR = u$, R being the particle size. .. .. (7)

Therefore,

$$C=\tau\sum_{m=0}^{m=\infty}(-1)^m\frac{3(2m+2)}{(2m+3)\,!}u^{2m}$$

$$=\tau\left[1-\frac{u^2}{2.5}+\frac{u^4}{2.4.5.7}-\ldots\ldots\right]$$

From (5)

$$\frac{I}{I_0}=\left[1-\frac{u^2}{5}+u^4\left(\frac{1}{140}+\frac{1}{100}\right)-\ldots\ldots\right]$$

$$=\left[1-\frac{u^2}{5}+\left(\frac{u^2}{5}\right)^2\frac{1}{2\,!}\cdot\frac{6}{7}-\ldots\ldots\right] \quad .. \quad .. \quad .. \quad .. \quad (8)$$

By making particle size sufficiently small* in (8) we can write—

$$I = I_0 e^{-\frac{u^2}{5}} \text{ (approx.)} \quad \ldots \quad (9)$$

$$\log I = -\frac{4\pi^2}{5\lambda^2} R^2\epsilon^2 \log e + \log I_0 \quad \ldots \quad (10)$$

(9) and (10): Guinier's formula.

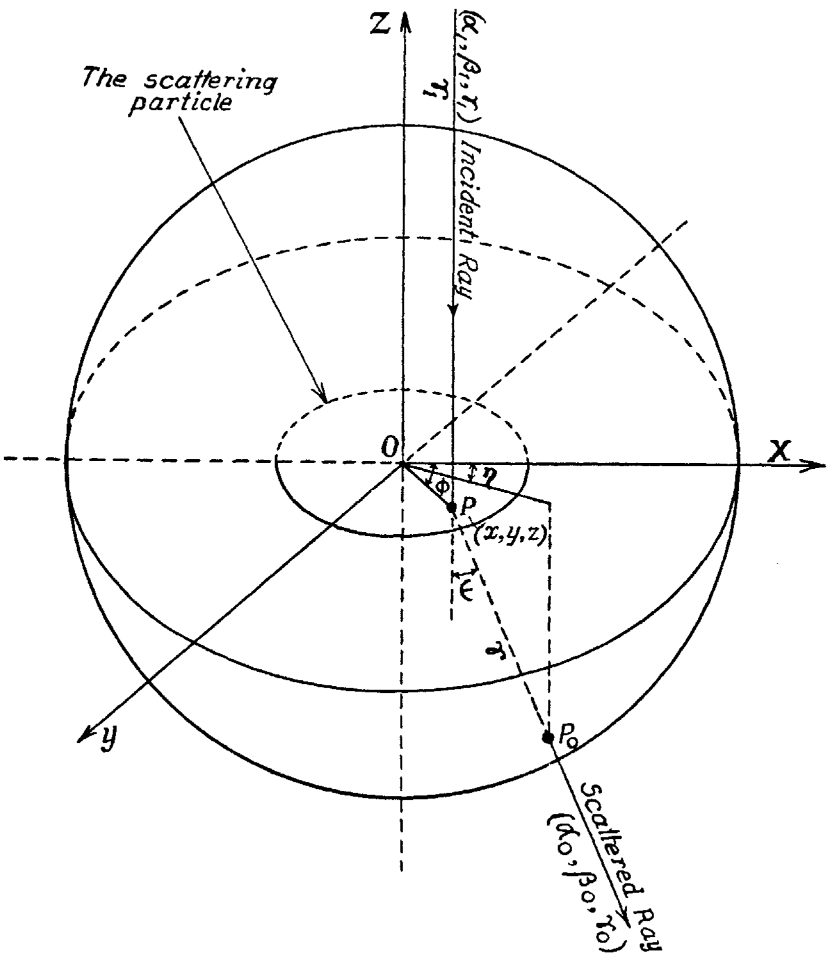

Fig. 2. Case of plate shaped particle.

* When, $R = 100$ Å, $\epsilon = 6' = 17 \times 10^{-4}$ radians $\lambda_\omega = 1{\cdot}5$ Å for copper K_α radiation, we get—

$$u = \frac{2\pi}{\lambda_w} \epsilon R = \frac{10}{15} \text{ (approx.)}$$

$$\left(\frac{u^2}{5}\right)^2 \cdot \frac{1}{2!} = \frac{1}{110} \text{ (approx.)}$$

$$\frac{1}{7} \cdot \left(\frac{u^2}{5}\right)^2 \frac{1}{2!} = \frac{1}{800} \text{ (approx.)}$$

Therefore, for particles of magnitude 100 Å, we are making an error of 0·12 per cent in coming from (8) to (9). For particles of much lower dimensions the error is much smaller.

Plate Shaped Particles.

(Non-Absorbing.)

Preliminary Assumptions:

(1) A circular plate has been taken into consideration.
(2) The origin has been taken at the centre of the circle and its plane coincides with the xy-plane.
(3) The incident ray is parallel and opposite to z-axis.

Then taking relation (i) of the case of spherical particles and previous others, following relations are obtained

$$C=\int_0^{2\pi}\int_0^R r\,d\phi\,dr\cos\left[r\{\lambda\cos\phi+\mu\sin\phi\}\right]$$

$$=\int_0^{2\pi}\int_0^R r\,d\phi\,dr\cos\left[rp\cos\phi'\right]$$

where,
$$\lambda=\frac{2\pi}{\lambda_w}\sin\epsilon\cos\eta=p\cos\eta,$$

$$\mu=\frac{2\pi}{\lambda_w}\sin\epsilon\sin\eta=p\sin\eta,$$

$$\phi'=\phi-\eta.$$

Integral in ϕ'.

$$=\int_{-\eta}^{2\pi-\eta}\cos\left[rp\cos\phi'\right]d\phi'$$

$$=\text{Real part in}\int_{-\eta}^{2\pi-\eta}e^{irp\cos\phi'}\,d\phi'.$$

$$\int_{-\eta}^{2\pi-\eta}e^{irp\cos\phi'}\,d\phi'=\int_{-\eta}^{2\pi-\eta}\left[1+irp\cos\phi'+\frac{(irp\cos\phi')^2}{2!}+\cdots\cdots+\frac{(irp\cos\phi')^{2m}}{(2m)!}+\cdots\cdots\right]d\phi'.$$

As before, all the odd powers cancel after integration and only the even powers remain which contribute to real parts.

Therefore, the integral in ϕ'

$$=2\pi\sum_{m=0}^{m=\infty}(-1)^m\frac{(2m-1)(2m-3)\ \cdots\cdots\ 3.1}{2m(2m-2)\ \cdots\cdots\ 4.2}\cdot\frac{1}{(2m)!}\cdot r^{2m}p^{2m}.$$

INTEGRAL IN r.

$$= 2\pi \sum_{m=0}^{m=\infty} (-1)^m \frac{(2m-1)(2m-3)\ \ldots\ 3.1}{2m(2m-2)\ \ldots\ 4.2} \cdot \frac{1}{(2m)!} p^{2m} \int_0^R r^{2m+1}\, dr$$

$$= 2\pi \sum_{m=0}^{m=\infty} (-1)^m \frac{(2m-1)(2m-3)\ \ldots\ 3.1}{2m(2m-2)\ \ldots\ 4.2} \cdot \frac{1}{(2m)!} \frac{p^{2m} R^{2m+2}}{(2m+2)}$$

$$C = 2\pi R^2 \sum_{m=0}^{m=\infty} (-1)^m \frac{1}{2^{2m+1}(m+1)!\, m!} u^{2m}$$

$$= 2\pi R^2 \left[\frac{1}{2} - \frac{u^2}{2^2 . 4} + \frac{u^4}{2^2 . 4^2 . 6} - \ \ldots \right]$$

Therefore, from (5)

$$\frac{I}{I_0} = 1 - \frac{u^2}{4} + \frac{1}{2!}\left(\frac{u^2}{4}\right)^2 \frac{5}{6} - \ \ldots$$

$$= e^{-\frac{u^2}{4}} \text{ (approx.)} \qquad \ldots \qquad (11)$$

Approximation in (11) is done by making particle size sufficiently small as explained in the case of spherical particles.

$$\log I = -\frac{\pi^2}{\lambda^2} \epsilon^2 R^2 \log e + \log I_0, \qquad \ldots \qquad (12)$$

where $u = pR = \frac{2\pi}{\lambda} \epsilon R$ as before.

RESULTS.

The theoretical equations (10) and (12) are for a single particle. But in actual practice we deal with a number of particles possibly with various gradations in size. So, what we get experimentally is their average particle size.

If n be the number of particles and $\bar{R}$ their average size, then equations (10) and (12) become,

$$\log I = -\frac{4\pi^2}{5\lambda_w^2} \epsilon^2 \bar{R}^2 \log e - \log n + \log I_0 \qquad \ldots \qquad (13)$$

$$\log I = -\frac{\pi^2}{\lambda_w^2} \epsilon^2 \bar{R}^2 \log e - \log n + \log I_0 \qquad \ldots \qquad (14)$$

respectively. The graphs of equations (13) and (14) become straight lines having slopes—

$$-\frac{4\pi^2 \bar{R}^2}{5\lambda_w} \log e \text{ and } -\frac{\pi^2}{\lambda_w^2} \bar{R}^2 \log e.$$

From the slope it is easy to calculate the particle size.

The author is grateful to Prof. K. Banerjee for his kind interest and advice in the work.

Abstract.

Laue calculated the shape of the intensity pattern corresponding to the shape of crystalline particles. But that was not practically useful for determining the shape of submicroscopic particles. Moreover, Laue and Scherrer's formula of particle size are only applicable for particles with rectangular parallelopiped shape and cubic crystals. X-ray low angle scattering phenomena is universally useful for determining the shape and size of submicroscopic particles of crystals, liquids and amorphous substances. By applying optical principles, the formula for particle size and intensity of X-ray low angle scattering has been obtained.

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