

- ⁴ *Proc. Roy. Soc., Lond.*, **A 87**, 511 (1912).
⁵ *Phys. Rev.*, **7**, 403 and 599 (1916).
⁶ *Proc. Nat. Acad. Sci.*, **3**, 181 (1917).
⁷ Other investigators who have performed similar experiments elsewhere: B. A. Wooten, *Phys. Rev.*, **13**, 71 (1919); F. C. Hoyt, *Phys. Rev.*, **18**, 333 (1921).
⁸ *Phys. Rev.*, **25**, 581 (1925).
⁹ Barkla and Sadler, *Phil. Mag.*, **16**, 550 (1908).
¹⁰ M. de Broglie, *Paris Compt. rend.*, **158**, 1493 and 1785 (1914).
¹¹ Clark and Duane, *Proc. Nat. Acad. Sci.*, **11**, 174 (1925).
¹² Webster and Ross, *Proc. Nat. Acad. Sci.*, **11**, 224 (1925).
¹³ Duane and Hunt, *Phys. Rev.*, **6**, 166 (1915); A. W. Hull, *Phys. Rev.*, **7**, 156 (1917); D. L. Webster, *Phys. Rev.*, **7**, 599 (1916); Blake and Duane, *Phys. Rev.*, **10**, 624 (1917); A. Müller, *Archives Sciences*, **46**, 63 (1918); C. T. Ulrey, *Phys. Rev.*, **11**, 401 (1918); E. Wagner, *Ann. Physik.*, **57**, 401 (1918), and *Jahrbuch Radioakt.*, **16**, 190 (1919); Duane, Palmer and Yeh, *Proc. Nat. Acad. Sci.*, **7**, 237 (1921).

THE CALCULATION OF THE X-RAY DIFFRACTING POWER AT POINTS IN A CRYSTAL

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In order to explain the diffraction of radiation on the quantum theory, the writer proposed¹ an hypothesis according to which the momenta of the radiation quanta are transferred to the diffracting material in multiples of h/a where h is Planck's action constant and a is a "grating space." The momenta of a quantum transferred in the directions of three axes may be written

$$p_1 = \frac{h}{\lambda} (\alpha - \alpha_0) = \pm \frac{n_1 h}{a_1}, \quad p_2 = \frac{h}{\lambda} (\beta - \beta_0) = \pm \frac{n_2 h}{a_2},$$

$$p_3 = \frac{h}{\lambda} (\gamma - \gamma_0) = \pm \frac{n_3 h}{a_3}, \quad (1)$$

in which λ represents the wave-length, α_0 , β_0 and γ_0 , the direction cosines of the quantum before diffraction and α , β and γ , the direction cosines after diffraction and n_1 , n_2 and n_3 are whole numbers.

By an interesting application of the conception of "sinusoidal gratings" and of the "correspondence principle" Epstein and Ehrenfest² have extended this theory and have calculated the probability of the deflection of a quantum in the direction given by Equations (1). When a very large number of quanta strike the diffracting system, this probability represents the intensity of the radiation deflected in the said direction. The theory

shows that the intensity is proportional to the square of the coefficient of the term in the triple Fourier series, representing the density, $\rho(x, y, z)$, of the diffracting material (or diffracting power), which corresponds to the transfers of momenta given by Equations (1). The general term in the Fourier series representing the density may be written

$$A_{n_1 n_2 n_3} \sin\left(\frac{2\pi n_1 x}{a_1} - \delta_{n_1}\right) \sin\left(\frac{2\pi n_2 y}{a_2} - \delta_{n_2}\right) \sin\left(\frac{2\pi n_3 z}{a_3} - \delta_{n_3}\right) \quad (2)$$

A is the constant coefficient and the δ 's are space phase angles. The correspondence between Equations (1) and the terms (2) means those equations and terms which have the same values of the n/a 's.

Epstein and Ehrenfest have shown, also, that, insofar as Fraunhofer diffraction is concerned, the proposed quantum theory and the wave theory reach identical conclusions, so that the above Fourier series analysis may be regarded as deducible from the wave theory.

If we reverse the line of thought, and attempt to deduce the density, $\rho(x, y, z)$, of the diffracting power (or the density of the electron distribution) in a crystal from the measured intensities of the various reflected beams by adding together the corresponding terms in the Fourier series, we find that these intensities do not determine the phase angles, δ . In other words, an indefinitely large number of distributions of diffracting power will produce beams of rays of precisely the same intensities in the same directions. It becomes necessary, therefore, to make further fundamental assumptions.

As one of these assumptions, we may suppose that the distribution of diffracting power conforms to the symmetry of the crystal. This symmetry fixes the values of many, sometimes of all, of the δ 's as being either $\pi/2$ or zero. For example, if the crystal has three mutually perpendicular planes of symmetry and if we take the intersections of these planes as axes of coördinates, the terms in the series can contain cosines only, for they must have the same values when we reverse the algebraic sign of either x , y , or z . In this case, therefore, the δ 's must be odd multiples of $\pi/2$. What the multiples of $\pi/2$ really are is immaterial, since the coefficient, A , is the square-root of a measured quantity and its algebraic sign is not determined by the diffraction data.

As a second example, suppose that the crystal has three mutually perpendicular, two-fold axes of symmetry. In this case, if we take these axes as the axes of coördinates, each term in the Fourier series may contain the product of three cosines, but, unless the coördinate planes are also planes of symmetry, the series must contain terms with trigonometric sines. These sines, however, must occur in pairs. A term cannot contain the product of one sine and two cosines, nor can it be the product of three sines; for the term must have the same value when we change the algebraic signs

of any two of the three coördinates x , y , z . In this case, therefore, the symmetry of the crystal fixes the values of the δ 's in each term as being either all three $\pi/2$, or one of them $\pi/2$ and the other two zero.

The symmetry conditions often determine, also, the values of certain constants A , as being equal to each other. If the crystal possesses such complete symmetry as that of sodium chloride, all the A 's having the same values of n_1 , n_2 and n_3 , but interchanged in any manner, must be equal to each other.

The permissible values of the δ 's and the coefficients, A , which must equal each other can be deduced without difficulty from the symmetry conditions, where the symmetry is less complete than in the above mentioned examples.

Neither the intensities of the diffracted beams of rays nor the symmetry conditions determine the algebraic signs of the coefficients, A . It follows, therefore, that an indefinitely large number of distributions of diffracting power not only will produce diffracted beams of the same relative intensities but will also conform to any given symmetry conditions. Sometimes such considerations as the exact position of the point chosen as origin of coördinates, the fact that $\rho(x, y, z)$ should not change its sign, the amount of diffracting material near a given point as compared with the number of electrons in an atom, etc., may enable us to decide which algebraic signs should be used for the more important terms. In general, if the crystal possesses three mutually perpendicular planes of symmetry, the intersections of these planes must be a point at which the density has either a maximum or a minimum value, and, if there is an atom at this point, it is natural to assume that the value of $\rho(x, y, z)$ is a *maximum* there. There may, however, be other points in the crystal at which $\rho(x, y, z)$ has maximum values. For instance, in sodium chloride, we may suppose that the value of $\rho(x, y, z)$ at the center of a chlorine atom is greater than that at the center of a sodium atom. Further, if in a case like sodium chloride, we take the origin of coördinates at the center of a chlorine atom and, therefore, at a point where $\rho(x, y, z)$ has its *greatest* maximum value, it is natural to suppose that the terms in the Fourier series are all positive at that point. Taking this point as origin of coördinates, this means that all the coefficients, A , are positive.

If we analyze a crystal such as sodium chloride in accordance with the theory here proposed, we do not make any assumptions to the effect that the crystal contains atoms or molecules. We simply assume that the fundamental principles of the theory represent the facts and that the distribution of the diffracting power conforms to the crystal symmetry. In addition, we assume that if we take the origin of coördinates at the center of the heaviest atom, all of the coefficients in the Fourier series have positive values. It will be shown by Dr. Havighurst in subsequent notes that the

analysis based on these fundamental assumptions leads to the conclusion that the diffracting power groups itself around points corresponding to the positions of the atoms as determined by other methods of X-ray analysis.

In deducing the intensities of the beams of X-rays from the experimental observations, a number of corrections must be applied as follows: (a) A correction for the absorption of the radiation by the crystal. This includes not only the ordinary absorption but also the selective absorption, both primary and secondary, that occurs when the analyzing crystal lies in such a position as to reflect the incident beam of rays. (b) Corrections due to the methods employed in making the measurements. These depend upon whether large, single crystals are used or the well-known powder method. They also depend upon the exact way in which the intensity is estimated, i.e., whether by the photographic or the ionization method and in the latter case, whether or not the crystal or ionization chamber is turned at a constant velocity through a given angle. (c) Corrections due to the polarization factor. (d) Corrections due to the fact that the diffraction of X-rays by a crystal, although very approximately Fraunhofer diffraction, is not strictly speaking exactly so. The quantum theory, as developed above, applies only to Fraunhofer diffraction, that is to diffraction in which the rays in the incident beam are parallel to each other and, also, those in the observed deflected beam are parallel to each other. We know that the equations deduced from the classical wave theory do not in general represent the experimental facts observed in the scattering of radiation. This seems to be true in all cases in which there are transformations of energy to or from radiant energy. As a first approximation, however, we may perhaps use the classical wave theory to deduce the corrections to be applied for the very slight lack of parallelism in the beams of X-rays. The above corrections have been so thoroughly discussed from the point of view of the classical wave theory in the literature on the subject³ that it is not necessary to enter into details here.

Strictly speaking, the theory developed here represents the distribution throughout the space occupied by the crystal of what we may call the time average of the density of the diffracting power. The passage from this to the space distribution of the time average of electron density involves an additional assumption. If we assume that the two densities are proportional to each other, the Fourier series represents the distribution in space of the time average of the electron density. It is interesting to compare the results obtained by this Fourier series analysis, as represented in the calculations made by Dr. Havighurst, with the results obtained by Compton, Debye and Scherrer, Bragg, James and Bosanquet and Bijvoet and Karsen (l. c.).

Except in such cases as those above mentioned, in which the electron

distribution is calculated, the ordinary analysis of crystals by means of X-rays determines the positions of certain points, which are supposed to coincide with the mean positions of the centers of the atoms. Undoubtedly the points do coincide with the centers in simple structures. In the more complicated structures, however, in which the analysis fixes the values of certain parameters, the points may or may not coincide exactly with the centers. The values of the parameters are calculated from the relative intensities of the diffracted beams of rays, and in this calculation it is assumed, tacitly or otherwise, that the diffracting power has certain space distributions about the points. Undoubtedly, the values of the parameters of the points can be determined with considerable accuracy, for a slight change in them makes a great change in the relative intensities of reflections of higher orders. The relative intensities of these reflections of higher orders, however, depend upon the distribution of diffracting power about the points and a slight change in this distribution also corresponds to a very great change in the intensities. Hence the closeness with which the points determined by the analysis lie to the actual mean positions of the atoms depends to a considerable extent upon the precision with which the assumed distribution of diffracting power agrees with its real distribution. In the method of analysis described above the positions of the points corresponding to maximum densities of diffracting power can be determined with considerable accuracy.

If the crystal reflects abnormally, theoretically the Fourier integrals should be used instead of the Fourier series.

¹ *Proc. Nat. Acad. Sci.*, May, 1923, p. 159.

² *Proc. Nat. Acad. Sci.*, April, 1924, p. 133.

³ Debye, *Ann. Physik.*, **43**, 1914, p. 49; Darwin, *Phil. Mag.*, **27**, 1914, pp. 315 and 675; W. H. Bragg, *Phil. Mag.*, **27**, 1914, p. 881; *Phil. Trans.*, **A**, **215**, 1915, p. 253; A. H. Compton, *Physic. Rev.*, **9**, Jan., 1917, p. 29; Debye and Scherrer, *Phys. Zeitschr.*, **19**, 1918, p. 474; W. L. Bragg, James and Bosanquet, *Phil. Mag.*, **41**, **42**, 1921, pp. 309, 1; Darwin, *Phil. Mag.*, **43**, 1922, p. 800; Bijvoet and Karssen, *Rec. Trav. Chim.*, **42**, 1923, p. 859; James, *Phil. Mag.*, **49**, 1925, p. 585.