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REVIEWS
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X-RAY SCATTERING AND ATOMIC STRUCTURE

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A. Reflection of X-rays from Crystals

Introduction

It WAS in 1912 that Laue[1] put forth the idea that x-rays should be diffracted by a crystal in a manner similar to the diffraction of light by a ruled grating and shortly afterwards this prediction was verified by the experiments of Friedrich and Knipping.[2] During the twenty years which have elapsed since this discovery its great significance has been attested to in almost every field of x-ray research. For one thing it has given us a powerful tool for the study of atomic, molecular, and crystalline structure.

The more convenient and useful statement of the diffraction problem we owe to W. L. Bragg[3] in the form of the well-known law which bears his name

$$n\lambda = 2D \sin \theta. \tag{1}$$

This relation gives the angle θ at which a beam of x-rays of wave-length λ will be diffracted from the face of a crystal of grating space D. In the early researches in x-ray diffraction neither the wave-length of the radiation nor the grating space of the crystal was known. As W. H. and W. L. Bragg[4] stated in an early paper, "The difficulty of assigning a definite wave-length to the rays arises when we attempt to determine the value of D—". However, by considering the intensity as well as the angles at which a beam of x-rays was reflected from various faces in the crystal the Braggs[5] were able to determine completely the structure of some of the simpler crystals, and thus with the aid of the above relation the wave-length of the radiation could be calculated.

This beginning opened up two important fields of investigation. The crystal gratings for which the spacing had been determined could now be used for wave-length measurements of other x-ray lines. Also an accurate knowledge of the wave-length of various radiations makes the analysis of the structure of more complicated crystals possible. It soon became apparent, however, that a more complete knowledge of the intensity of these reflected lines was of fundamental importance in determining crystal and atomic structure in this way.

W. L. Bragg[6] deduced from preliminary intensity measurements that if correction was made for the effects of temperature the intensities of the different orders of reflection of a given spectrum line are approximately proportional to the inverse square of the order. By a more careful experimental study W. H. Bragg[7] showed that if x-rays of a definite wave-length are reflected at a glancing angle θ by a crystal in which the successive layers of atoms are similar and equally spaced the energy in the reflected beam can be expressed with considerable accuracy by the empirical relation

$$E = C \frac{(1 + \cos^2 2\theta)}{\sin^2 \theta} e^{-B \sin^2 \theta / \lambda^2} \tag{2}$$

where C is a constant which depends on the intensity and wave-length of the incident beam and the nature of the crystal used, $\exp(-B \sin^2\theta/\lambda^2)$ is a factor deduced by Debye[8] to account for the change in reflecting power with temperature of the crystal, and $(1+\cos^2 2\theta)$ is the polarization factor deduced by J. J. Thomson.[9]

The rapid decrease of intensity with increasing θ suggested the fact that the medium which is effective in scattering x-rays must extend over a considerable fraction of the distance between atomic layers. Assuming the scattering power to be concentrated in the atomic layers Darwin[10] deduced a relation for the diffracted energy which differed by a factor tan θ, from the above empirical relation. Attributing this factor, tan θ, to the fact that the electrons are distributed at varying distances from the center of the atom W. H. Bragg[11] and A. H. Compton[12] concluded that if proper account were made of this term some idea of the distribution of diffracting power in the atoms could be reached. In consideration of this diffuseness of the atom the theory of diffraction of x-rays has been derived by Darwin and Compton. Compton showed that if reasonable assumptions were made regarding the distribution of the electrons in the atom the theoretical formula gave intensities which were in agreement with experiment. Guesses as to the electron distribution which would give a theoretical intensity curve in best agreement with experiment then afforded a rough determination of the electron distribution within the atoms of the crystal.

The determination of electron distribution has more recently been put on a direct basis by the use of Fourier's series and integrals, and is considered after a more complete discussion of the intensity measurements has been made.

Theory of reflection from small crystals

Darwin[13] and Compton[14] have worked out an expression for the intensity of x-rays reflected from a small crystal on the basis of classical theory. The equation is derived for a very small crystal so it can be assumed that the whole crystal is bathed in x-rays of the same intensity. Taking their results we have for the integrated intensity

$$\frac{W\omega}{I} = \frac{1}{2} n^2 \lambda^3 F^2 \frac{e^4}{m^2 c^4} \frac{(1+\cos^2 2\theta)}{\sin 2\theta} \delta V \equiv Q \delta V. \tag{3}$$

In this equation W is the total energy diffracted by a crystal of volume δV, when it is turned past the angle θ with a uniform angular velocity, ω, (expressed in radians per sec.), I is the intensity of the incident beam, n is the number of atoms per unit volume in the crystal, e, m and c have their usual significance. F is called the structure factor and is introduced to take into consideration the distribution of the scattering medium or electrons within the atom. It can be defined as the ratio of the amplitude of the wave scattered in a given direction by the electrons in the atom to that which would be scattered by a single electron under the same conditions on the basis of classical theory. Mathematically this can be stated.

$$F = Z \int_{D/2}^{D/2} p(z) \cos\left(\frac{2\pi n z}{D}\right) dz \tag{4}$$

where Z is the atomic number, D is the grating space, and $p(z)dz$ is the probability that an electron will lie at a height between z and $z+dz$ above the atomic layer.

Extinction

Although we have in Eq. (3) an expression which represents the intensity of reflection of x-rays from a small crystal an experimental check of this relation cannot be directly realized since the intensity of reflection from a crystal which is so small that it satisfies the above conditions is not sufficient to measure. The question then arises, how close an approximation to this condition will be realized with a crystal for which the intensity is measurable. It is found that the intensity of reflection by a large crystal may disagree considerably from that by a small crystal. This is true even if correction is made for the ordinary absorption of the x-rays on passing into the crystal. It is found that when a large crystal is oriented near the angle at which it reflects a given wave-length, the upper layers of atoms shield the lower layers from the incident beam. This fact was first shown experimentally by W. H. Bragg[7] by measuring the absorption of rays passing through a crystal which was oriented at the reflecting angle.

This property of the layers of atoms shielding other atoms from the intensity of the primary beam is spoken of as extinction.

When the upper layers of atoms shield the lower layers of the same homogeneous fragment of the crystal the extinction is referred to as "primary". In this case phase relations still exist between the various parts of the reflected beam.

Even when the primary extinction is negligible the homogeneous blocks in the upper part of the crystal can shield deeper blocks from the x-rays thus also decreasing the reflected intensity. This is referred to as secondary extinction.

Perfect and imperfect crystals

In dealing with the intensity of reflection of x-rays from crystals it is necessary, because of the varying amounts of extinction present, to know something about the perfection of the crystals used. One generally pictures a crystal as an array of atoms whose atomic centers lie on parallel planes of definite spacing. Actually the large crystals with which one deals do not attain such perfection. They are probably made up of a large number of small approximately perfect crystals whose face-planes are not exactly parallel.

The theory of reflection from perfect crystals has been investigated by Darwin[13] and Ewald,[15] and it is found that the intensity of reflection varies directly as the structure factor. However, since perfect crystals do not exist except probably in submicroscopic size, and it has not been found practical to correct for the lack of perfection, this theory has not been used in determining atomic structure and will not be considered here.

Measurements of intensity of reflection from crystals shows that as the crystal becomes less perfect the intensity becomes more nearly proportional to F^2. The limit should be reached when the perfect components of the crystal are so small that both primary and secondary extinction are negligible. Real crystals can be found with considerable variation in degree of perfection, but no crystals can be strictly classed as either perfect or ideally imperfect. However, it is possible to correct for the extinction or lack of imperfection in some crystals and this has been done in several cases.

It has been found that if certain crystals are pulverized until the individual components can be just seen in a high power microscope the resultant crystalline mass is a very close approximation to an ideally imperfect crystal. Eq. (3) then gives a correct interpretation of its reflecting power when the intensities from the small component crystals are properly added.

Intensity of reflection from large crystals

Correction for absorption. Assuming we have a large crystal which is ideally imperfect, Eq. (3) can be directly applied when correction for absorption is made, and becomes

$$\frac{W\omega}{P}=\frac{Q}{2\mu} \tag{5}$$

where P now represents the power in the primary beam, μ is the linear absorption coefficient and Q is given in Eq. (3).

Correction for extinction. Since one never obtains large crystals which are ideally imperfect some account must be taken of the extinction. Fortunately a large number of the less perfect crystals are practically free from primary extinction and Darwin has shown that allowance may be made for secondary extinction by replacing the ordinary absorption coefficient in Eq. (5) by $\mu+gQ$, where g is a constant of a given crystal specimen. Hence Eq. (5) can be more correctly written

$$\frac{W\omega}{P}=\frac{Q}{2(\mu+gQ)}\cdot \tag{6}$$

In the early intensity measurements of Bragg, James and Bosanquet[16] the extinction was determined by measuring the ordinary absorption coefficient and also the apparent absorption coefficient which is obtained when the crystal is in a position to reflect. The difference between the latter and the former of these quantities is equal to gQ. If the value of Q is also determined one obtains the constant g which can be used as a factor for all reflections for the crystal specimen under investigation. Another method of determining g has been used by James and Miss Firth.[17] Since g is a constant which does not depend on wave-length, measurements of $W\omega/P$ were made for two wavelengths on the same crystal. We then have

$$\frac{(W\omega/P)_1}{(W\omega/P)_2}=\frac{Q_1}{Q_2}\cdot\frac{\mu_2+gQ_2}{\mu_1+gQ_1} \tag{7}$$

where the suffixes refer to the two different wave-lengths. In this relation Q_1/Q_2 can be obtained from known constants since F for a given spectrum is the same for all wave-lengths, and the values of μ and $W\omega/P$ can be measured, hence g can be calculated.

Measurement of integrated intensity

A general arrangement of apparatus for intensity measurements is shown in Fig. 1. A beam of x-rays made homogeneous by reflection from a crystal A is allowed to fall on a crystal B as shown. The power received in the ionization chamber when B is placed in a position to reflect cannot be taken as proportional to the intensity since it varies according to the perfection of the crystal.

The quantity $W\omega/P$, usually referred to as the integrated intensity, has been found to be an absolute quantity for a given crystal at a given wave-length and order of reflection if extinction is not present. To measure the quantity $W\omega$ from a single crystal it may be rotated through the reflecting angle at a uniform angular velocity, ω. The ionization chamber is properly oriented, the slit is opened sufficiently to receive all the energy which the crystal reflects, and the total deflection of the electrometer is taken as a measure of W. In this way if the primary beam is kept constant relative values $W\omega$ can be measured for the various orders of reflection. However it is the value of $W\omega/P$ (i.e., the fractional part of the primary beam which is reflected at a given angle θ) which is a constant for the crystal and which enables one to determine the values of F from Eq. (6). To measure this ratio accurately is a difficult experimental problem since such a small fraction of the total incident energy is reflected. Direct measurements of $W\omega/P$ for NaCl have been made by Compton,[18] Bearden[19] and Wassastjerna,[20] with molybdenum radiation and by James, Bragg and Bosanquet[16] with rhodium radiation. Because of the experimental difficulty of making direct measurements of $W\omega/P$, this latter value has been used in many investigations on other crystals as a standard of comparison for putting relative measurements of $W\omega$ in terms of the absolute quantity $W\omega/P$. In so far as so many measurements of structure factor are dependent on the accuracy of a single absolute determination of intensity it becomes important to have a reliable value which can be used as a standard. James and Miss Firth have recently made a redetermination of $W\omega/P$ for NaCl and molybdenum radiation, using the same crystal of NaCl which had been previously used by Bragg, James and Bosanquet.

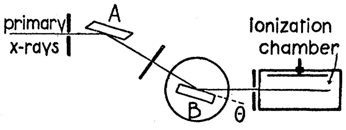

Fig. 1. Apparatus for reflecting x-rays from crystals.

It would seem that these recent absolute intensity determinations of James and Miss Firth are at present the most reliable. It would thus be desirable for them to be used as a standard of comparison until further experimentation gives us a more reliable standard. Some of their values of structure factors for the NaCl molecule for a few orders of reflection are given in Table I. The (400) reflection should preferably be considered the standard and the other reflections related to this as shown. The intensity of this reflection is sufficient for good measurements, and although the extinction is not negligible, it is small enough that the correction can be made with satisfactory accuracy.

In making a comparison of $W\omega$ for a given crystal with the standard, the crystal is placed on the spectrometer table, and the value of $W\omega$ is measured in the usual way for some convenient reflection. This crystal is then removed and replaced by the standard, from which $W\omega$ is measured for the (400) reflection. The power of the x-rays falling on the crystals is supposed to remain constant. From Eq. (6) the absolute value of F for the given plane of the crystal in question can be determined from a knowledge of the constants of the crystals, the ratio of the integrated intensity for the two crystals, and the standard value of F given in the table.

TABLE I. *Structure factors for NaCl.*

Spectrum	$F(\mathrm{Cl})+F(\mathrm{Na})$
200	20.65
220	15.62
222	13.18
400	11.60
600	6.89

Intensity of reflection from powdered crystals

Havighurst[21] has made a careful experimental study of the relation of crystal size to extinction. He finds that secondary extinction becomes negligible if the crystal is ground to a powder in which the crystal fragments are all smaller than 10^{-3} cm. Although perfect crystal particles of this size would still show a considerable amount of primary extinction the measurements seem to indicate that these small fragments are broken and distorted in the grinding process so that the primary extinction is very considerably reduced in even the most perfect crystals. He concludes that extinction can be completely eliminated for many of the less perfect crystals by reducing to a powder in which the particles are smaller than the above mentioned value, and hence the theory for an ideally imperfect crystal can be directly applied.

Because of the lack of intensity of x-rays reflected from powdered crystals, few investigators have made accurate measurements by this method. If sufficient intensity were available the most desirable experimental arrangement should be to have the beam of x-rays incident on the powder mass made homogeneous by reflection from a first crystal. Bearden[19] made measurements in this way and obtained values of the structure factor which agreed reasonably well with measurements on single crystals when the latter were corrected for extinction. The very small intensities which are obtained in this way make accurate measurements very difficult.

Havighurst[22] has made intensity measurements from powdered crystals by using molybdenum radiation which was made approximately homogeneous (Mo $K=0.71$A) by filtering through ZrO_2. In this case the exciting voltage must be sufficiently low (about 35 kv) to exclude a large part of the general radiation. In order to increase the intensity he has applied the Bragg[4] focussing condition as generalized for the case of powdered crystals. A divergent beam of x-rays is allowed to fall on the face of a thick plate of powdered crystals and if the geometry of the arrangement is related as shown in Fig. 2a the reflected x-rays will be focussed at the slit of the ionization chamber and the width of the beam at this point will be about the same as the width of the focal spot.

This method has been used in several cases with good results. However, the presence of general radiation causes some difficulty in determining the base line, and it would seem that the use of the Ross[23] balanced filter would make a decided improvement in this method.

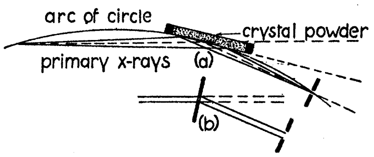

Fig. 2. Arrangement for powdered crystals, a. For reflection with focussing. b. For transmission.

Although it has been assumed above that the ionization chamber has been used to record the intensities, the photographic method has been shown to be reasonably satisfactory if care is taken in interpreting the photographic densities.

In applying Eq. (3) to the case of powdered crystals, correction must be made for absorption of the rays, the geometry of the experimental set-up must be considered, and the intensity from the crystal fragments must be properly added.

If relative values of the structure factor are measured, they can later be put in terms of the absolute values by comparison with the rock salt standard. In this case quantities which are not dependent on angle need not be considered and the following simple expressions can be used.

If the powdered crystal mass, molded into a thin plate, is oriented on the center of the spectrometer table so that the perpendicular to the face always makes an angle, θ, with the primary beam which is half that made by the ionization chamber as shown in Fig. 2b, the values of the structure factor are related to the intensity by the expression

$$F^2 = A \frac{P_s}{p} \frac{\sin^2 2\theta}{(1+\cos^2 2\theta)} e^{\mu' h \sec\theta} \tag{8}$$

where P_s is the power in the reflected beam, p is the number of surfaces for the crystal plane considered, μ' is the absorption coefficient of the crystal mass whose thickness is h and A is the constant which will be evaluated by comparison with a rock salt standard. In making the above relative measurements the intensity of the primary x-rays must remain constant. For maximum intensity the effective thickness of the crystal mass should be equal to $1/\mu'$.

If the crystal powder is pressed into a briquet whose thickness is sufficient to absorb practically all the incident x-rays and this sample is oriented in the same manner as for reflection from a single crystal as shown in Fig. 1 or as shown in Fig. 2a the structure factors are related by the expression

$$F^2 = A\frac{P_s}{p}\frac{(1+\cos^2 2\theta)}{\sin^2\theta\cos\theta} \tag{9}$$

where the notation is the same as above.

Having made relative measurements of F in this way the absolute values can be obtained by comparison with a similar briquet of powdered NaCl. Since there is no extinction in the powdered crystals the stronger (220) reflection has been generally used as a standard rather than the (400) reflection usually used with single crystal measurements.

If the intensity P_s is measured for some plane in the crystal X and then with the intensity of the primary x-rays remaining constant a similar measurement is made for the (220) reflection from the briquet of the NaCl standard, the absolute structure factor for a plane of the crystal in question is obtained from the ratio of Eq. (8) or (9) for the two cases.

When the transmission method, Eq. (8), is used, the absolute value of the structure factor for the plane x is given by

$$F_x{}^2 = \frac{P_{sx}}{P_{s\mathrm{NaCl}(220)}}\frac{(h\sec\theta e^{-\mu' h\sec\theta})_{\mathrm{NaCl}(220)}}{(h\sec\theta e^{-\mu' h\sec\theta})_x}\left[\frac{pN^2F^2(1+\cos^2 2\theta)}{\sin^2\theta\cos\theta}\right]_{\mathrm{NaCl}(220)} \left[\frac{\sin^2\theta\cos\theta}{pN^2(1+\cos^2 2\theta}\right]_x. \tag{10}$$

And similarly for the reflection method, Eq. (9), we have,

$$F_x{}^2 = \frac{P_{sx}}{P_{s\ \mathrm{NaCl}(220)}}\left(\frac{pN^2F^2(1+\cos^2 2\theta)}{\mu'\sin^2\theta\cos\theta}\right)_{\mathrm{NaCl}(220)}\left(\frac{\sin^2\theta\cos\theta}{(1+\cos^2 2\theta)}\frac{\mu'}{p\ N^2}\right)_x \tag{11}$$

where N is the number of atoms per cc of the crystal and the other terms are as given above. Having obtained one absolute value of F in this way all other measured values are also standardized.

Molecular and atomic structure factors

We have seen that measurements of the integrated intensity from either powdered or single crystals make it possible to obtain the absolute magnitude of the structure factor, F, for the various angles at which x-rays are reflected. The sign of F cannot be obtained, since it is proportional to the square root of the measured intensity. Although $\sin\theta$ for a given reflection varies with the wave-length, F is a function of $\sin \theta/\lambda$, and hence is not dependent on the wave-length for a given order of reflection.*

From the definition of F we see that it is the factor in the intensity equation which represents the summing up of the amplitudes of the waves scattered by electrons having certain probable locations above the midplane of the atomic layers. The structure amplitude will depend on the number and distribution of the electrons within the space lattice of the crystal and on the phase relation of the scattered rays, which will vary with the angle of scattering.

Let us consider the structure factor for a molecule of NaCl in a rock-salt crystal in which atoms of different scattering power are present. For even orders of reflection the waves scattered by the two types of atoms will be in phase and the structure factors will be the sum of the individual atomic structure factors, i.e., $F=F_{\text{Cl}}+F_{\text{Na}}$. As the angle of scattering becomes smaller the waves scattered by all the electrons will be more nearly in phase, until at zero scattering angle the structure factor measured in electron units will be equal to Z, the number of electrons in the molecule. Fig. 3 shows values of the structure factors for the case of Na+Cl and the dotted portion of the curve represents the extrapolation to $\sin \theta/\lambda=0$, near which it can be shown that the curve is parabolic.** For odd orders of reflection the waves scattered

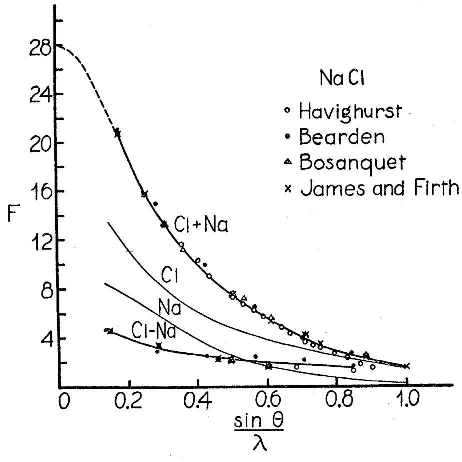

Fig. 3. Structure factors for NaCl

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* R. W. G. Wyckoff, Phys. Rev. **35**, 215 (1930) has shown that the value of F for a given order is not constant for wave-lengths near the critical absorption limit for the atoms in the crystal. The agreement between the absolute structure factor measurements on rock salt for molybdenum and rhodium radiation shows constancy of the F-values when one is sufficiently removed from a critical wave-length.

** At small angles the phase differences between the rays scattered by the various electrons are small quantities of the first order; but the structure amplitudes, which are proportional to the cosines of the phase differences, are affected only in the second order of these small quantities. Hence the structure factor curve at small angles will be parabolic in form, and will be parallel to the abscissa at $\sin \theta/\lambda=0$.

by the two kinds of atoms will be 90° out of phase, and the resultant amplitude will correspond to the difference of the atomic structure factors, i.e., $F=F_{\mathrm{Cl}}-F_{\mathrm{Na}}$, which is shown by the lower curve in Fig. 3.

For a simple crystal of this type it can be seen that the structure factor for the individual atoms can be determined by taking half the sum and half the difference of the above structure factors for the summation and difference spectra, and these are also shown in the figure.

In the curve corresponding to $F=F_{\mathrm{Cl}}-F_{\mathrm{Na}}$ no extrapolation to $\sin\theta/\lambda=0$ has been made. The point at $\sin\theta/\lambda=0$ depends on the difference of the number of electrons associated with each atom. This brings up the question of whether the atoms exist in the crystal as ions or neutral atoms. It is generally conceded from consideration of the binding forces that in crystals of the NaCl type the space lattice points are occupied by ions. For the purpose of testing this point the author[24] made measurements of the structure factor for MgO which should be an ideal crystal for such a test. This point has also been considered by Brindley[25] using data obtained by Wyckoff and Miss Armstrong.[26] From considerations of the binding forces one would expect the atoms in the crystal to be doubly ionized (Mg^{++} and O^{--}). Fig. 4 shows structure factor measurements for MgO determined independently by various investigators. If the atoms are present in the crystal as Mg^{++} and O^{--} each ion will have ten electrons associated with it and the lower curve corresponding to the difference between the scattering power of the two ions should extend to 0 at $\sin\theta/\lambda=0$. It is difficult to draw any conclusions from such an extrapolation, and this point is considered again in connection with the electron distribution calculated from these data.

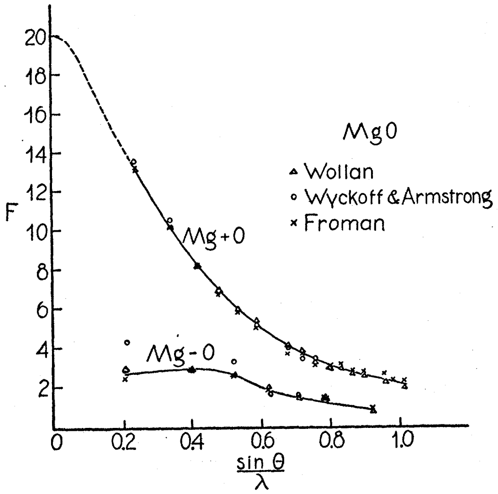

Fig. 4. Structure factors for MgO

The agreement between the observations of various investigations for crystals of NaCl and MgO can be seen from the curves of Fig. 3 and Fig. 4. The first extensive measurements on NaCl were made by Bragg, James and

Bosanquet from single crystals with rhodium radiation. These are not shown on the curve since they seem to be too large at large angles. However, the more recent measurements of Bosanquet[27] using the same crystal and apparatus are in good agreement with the other data, so that it seems that one is justified in not considering the earlier values. Havighurst's data for NaCl were obtained from powdered crystals with molybdenum radiation. In this case only relative values were measured and the absolute value of the reflection from the (220) plane as measured by Bragg, James and Bosanquet was used as a standard. The solid points represent the data obtained by Bearden who also used molybdenum radiation. Bearden made absolute intensity measurements on a single crystal, corrected for extinction, and also used the transmission and reflection methods with powdered crystals. The points in Fig. 3 represent an average of his measurements by the three methods. The most recent absolute structure factor measurements for NaCl made by James and Miss Firth are also shown. These were made with single crystals for molybdenum radiation. The agreement between the data of various observers for NaCl which represent four separate absolute determinations should give confidence in the use of NaCl as a standard of comparisons for other investigations.

In the case of MgO the work of Wyckoff and Miss Armstrong and that of the author was done with powdered crystals by the same method as used by Havighurst. Froman[28] also used powdered crystals, but the intensities were recorded photographically. His results are more erratic at large angles but his low value for the (111) reflection (first point on lower curve) is probably the most reliable. The very large value obtained by Wyckoff and Miss Armstrong and the slightly higher value of the author were probably affected by the presence of some white radiation which was not present in Froman's work since he separated the $K\alpha$ lines with a first crystal. All the data for MgO were standardized by comparison with rock salt.

Effect of temperature on x-ray reflection from crystals

The first theoretical investigation of the effect of temperature on the intensity of x-rays reflected from crystals was made by Debye.[29] In his early papers it was assumed that the atoms were bound by quasi-elastic forces to fixed positions about which they oscillated. Since this assumption is not justified, Debye[8] reconsidered the problem according to the ideas underlying the theories of specific heat developed by himself and by Born and Karman, in which the thermal motions are considered as a series of elastic waves in the crystal. In this way he showed that if f represents the structure factor for an atom at rest, its value at any temperature is given by $F=fe^{-M/2}$, for a single cubic crystal consisting of atoms of one kind.* In this exponential

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* The use of f to represent the structure factor of the atom at rest and F to represent the same quantity at any temperature T is a common notation, and will be adhered to in this paper. Debye gives e^{-M} as the temperature factor for the intensity of reflection. Since he considered the case of mosaic crystals, the intensity varies as the square of the structure factor, and hence his statement and the above are identical.

$$M = \frac{6h^2}{mk\Theta} \frac{\phi(x)}{x} \frac{\sin^2 \theta}{\lambda^2} \tag{12}$$

where m is the mass of the atom, h is Planck's constant, k is the gas constant, Θ is the characteristic temperature of the crystal which occurs in the theory of specific heats, $x=\Theta/T$, where T is the absolute temperature and $\phi(x)$ is a function of x which Debye has evaluated and given in a table in his original paper.** $\phi(x)$ varies from 1 to 0 as x varies from 0 to ∞. As an example, Θ for rock salt is 281°K, and if we consider the crystal at this temperature, $x=1$, for which $\phi(x)=0.778$. The above value of M assumes the existence of no zero-point energy. If Planck's value of the zero point energy of 1/2 quantum per degree of freedom is assumed, the value of $\phi(x)/x$ must be replaced by $(\phi(x)/x+1/4)$.

W. H. Bragg[7] made a preliminary experimental check of Debye's theory and found that the intensities of reflection from rock salt decreased with increasing temperature in a manner which was in qualitative agreement with the theory. More recent measurements by E. H. Collins[30] on powdered aluminum crystals seemed however to indicate that the decrease in intensity with increasing temperature was more rapid than Debye's theory predicted.

In 1925 I. Waller[31] resumed a study of the theoretical side of the problem by the same method of attack as that used by Debye. He arrived at a result identical with that of Debye except for a factor 2 in the exponent of the temperature factor. He obtained e^{-M} (where M has the same value as given above) as the factor by which f must be multiplied to obtain the structure factor at any temperature. This would correspond to a more rapid decrease of intensity with temperature than predicted by Debye, in agreement with the experimental findings of Collins.

R. W. James[32] and his collaborators have recently made a number of experimental studies of the effect of temperature on the reflection of x-rays by various crystals, and their work seems to indicate that the Waller modification of Debye's theory is in close agreement with experiment in a range of temperatures between that of liquid air and about 400°K. Above 400°K they find that the decrease in intensity with increasing temperature is considerably more rapid that even the modified theory indicates.

James and Miss Firth[17] made intensity measurements on crystals of rock salt at temperatures ranging between that of liquid air and 900°K. The structure factors for sodium which they obtained at room temperature, the temperature of liquid air and 900°K are shown in Fig. 5. These curves indicated how rapidly the structure factors decrease with increasing temperature.

For the sake of comparing the experimental results with the theory it was assumed that rock salt is a simple cubic crystal in which the atoms have the average mass of Na and Cl. The results obtained for temperatures up to 400°K were in good agreement with the Waller modification of the Debye theory for the case of summation spectra for which $F=(f_{\mathrm{Cl}}+f_{\mathrm{Na}})e^{-M}$, where

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** This table is reproduced together with a table of characteristic temperatures of a number of common crystals in a recent paper by James and Brindley, Phil. Mag. 12, 81 (1931).

M is the exponent corresponding to the average atom. For the difference spectra, for which they assumed $F=(f_{\mathrm{Cl}}-f_{\mathrm{Na}})e^{-M}$, the experimental results indicate a smaller value of M. This difference is likely due to the simplifying assumptions which were made. Due to the difference in the two atoms one might expect each atom to have a different value of the temperature factor, and the structure factor should be written in the form $F=(f_{\mathrm{Cl}}e^{-M_{\mathrm{Cl}}}-f_{\mathrm{Na}}e^{-M_{\mathrm{Na}}})$ in which the temperature factors are different for the two atoms. Waller has extended the theory to cover the case of crystals of unlike atoms, but let us consider first a case to which the simpler theory should be applicable.

The reflecting power of sylvine as a function of temperature has been investigated by James and Brindley.[33] In this case the atoms are so nearly alike that the difference spectra are absent, and one would expect that the crystal should be a good approximation to the simple case for which the Debye-Waller theory was originally worked out.*

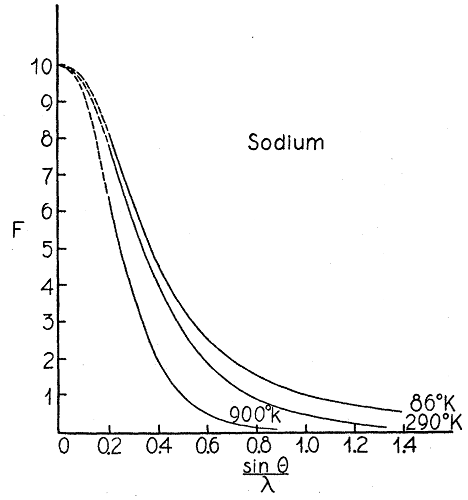

Fig. 5. Structure factors for Na at various temperatures. R. W. James and Miss Firth, reference 17.

It is not possible to obtain directly the value of M from x-ray measurements of intensity at various temperatures. However, the ratio of the intensities for a given spectrum for two different temperatures is dependent on the difference, ΔM, of the respective values of M, and hence this quantity can be directly compared with the theory. If small changes in θ due to the thermal expansion of the crystal are neglected, the following expression is obtained directly from Eq. (12) and the relation of the temperature factor to the integrated intensity.

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* The effect of temperature on the reflection from aluminum has been studied by James, Brindley, and Wood, Proc. Roy. Soc. **A125**, 401 (1929). Although one would expect aluminum to be a better example of a simple crystal, KCl is of more interest in connection with subsequent discussions.

$$\frac{\lambda^2}{\sin^2\theta}\log\frac{(W\omega/P)_2}{(W\omega/P)_1} = \frac{\lambda^2}{\sin^2\theta}2\Delta M \equiv \frac{12h^2}{mk\Theta}\left\{\frac{\phi(x_1)}{x_1}-\frac{\phi(x_2)}{x_2}\right\}. \qquad (13)$$

In this equation the suffixes refer to two different temperatures and the $2\Delta M$ indicates that the Waller modification of the Debye theory is used. James and Brindley have evaluated the left side of Eq. (13) for various spectra and for various temperatures referred to room temperature. In Fig. 6 the points represent the experimental values of this quantity for temperatures between that of liquid air and about 900°K. The dotted curve gives the theoretical values of this quantity obtained from the right hand side of Eq. (13) in which they used the following values; the mean mass, m, of K and Cl $= 6.149\times10^{-23}$ gm, $\Theta = 230°$ and $\phi(x)/x$ was taken from Debye's table in which for example $\phi(x)/x = 1.033$ and 0.194 at 290°K and 86°K respectively.

The agreement between Waller's theory and experiment can be seen to be very good up to about 400°K, above which the decrease of intensity with temperature is even greater than this modified theory predicts. The Debye theory would be represented by a line whose slope would be half that of the dotted line shown. Waller[34] has pointed out that the lack of agreement between theory and experiment at high temperatures is to be expected, since in deriving the theory powers of the atomic displacements higher than the second in the expression for the energy have been neglected and this would not be justified at high temperature.

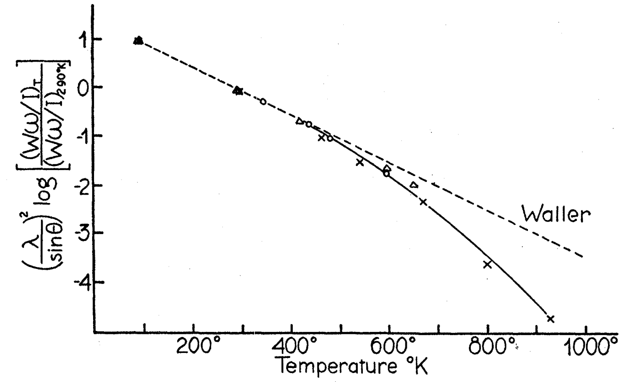

Fig. 6. Relation between experiment and theory of temperature effect in crystalline reflection. R. W. James and G. W. Brindley, reference 17.

Let us consider the application of a more exact theory to the case NaCl. Waller has derived a relation for the more general class to which this crystal belongs and working with James[35] has made a more complete study of the data of James and Miss Firth.

For the case of a crystal of the NaCl type Waller has shown that the temperature factor can be expressed in terms of the elastic constants rather than the characteristic temperature. The following expression is obtained

$$M_k = 8\pi^2\overline{u_{kx}^2}\frac{\sin^2\theta}{\lambda^2}, \qquad (14)$$

where $\overline{u_{kx}^2}$ is the mean of the squares of the displacements in any arbitrary direction x of atoms of the type k from their mean positions. For values of the temperature sufficiently high (approximately $T>\Theta/2\pi$) he has shown that the following expansion for $\overline{u_{kx}^2}$ can be made

$$\overline{u_{kx}^2} = \alpha_k + \beta_k T + \frac{\gamma_k}{T} + \frac{\delta_k}{T^3} + \cdots . \tag{15}$$

In this expression

$$\gamma_k = \frac{1}{12 k m_k}\left(\frac{h}{2\pi}\right)^2 \tag{16}$$

where m_k is the mass of the k atom, h is Planck's constant k is Bolzmann's gas constant. Hence γ_k does not depend on the atomic forces and can be directly evaluated. δ_k does depend on the atomic forces, but since its contribution to the value of M is small it can be obtained with sufficient accuracy from an approximate relation,

$$\delta_k = -\frac{113}{36}\,\frac{\Theta^2}{8\pi^2 W}, \tag{17}$$

where Θ is the characteristic temperature and W is the atomic weight. α_k is equal to zero if Planck's value of the zero point energy is asumed. The value of β_k depends on the atomic forces and cannot be directly calculated. If the values of δ_k and γ_k are calculated and zero point energy is assumed it is possible to obtain β_k from the experimental values of the intensity at various temperatures and thus the temperature factors for the individual atoms can be determined.

If the quantity $f_k e^{-M_k}$ is determined for one of the two atoms in the crystal at two temperatures, one obtains from Eqs. (14) and (15) an expression for $(M_{k_1} - M_{k_2})$,

$$\frac{\lambda^2}{8\pi^2 \sin^2\theta}(M_{k_1} - M_{k_2}) = \beta_k(T_1 - T_2) + \gamma_k\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \delta_k\left(\frac{1}{T_1^3} - \frac{1}{T_2^3}\right). \tag{18}$$

If the value of $(M_{k_1} - M_{k_2})$ is obtained from the intensity measurements at two temperatures and γ_k and δ_k are calculated from Eqs. (16) and (17), the value of β_k can be determined. Knowing the values of β_k, γ_k and δ_k the value of M_k can be calculated and thus the structure factors can be obtained for each atom at various temperatures.

Although it was not found possible to calculate β_k directly from the elastic constants, Waller and James were able to calculate a weighted mean value of β for the two atoms in the crystal, and the result was found to be in good agreement with the value determined from the experimental data.

Another interesting result is obtained directly from Eq. (15) when the values of β, γ and δ have been determined. If $\overline{u_{kx}^2}$ is the mean of the square of the total displacement of an atom, we have for a crystal of the NaCl type,

$$\overline{u_k^2} = 3\overline{u_{kx}^2}, \tag{19}$$

and hence one can obtain directly the values of $(\overline{u_k^2})^{1/2}$, the square root of the mean square amplitude of thermal vibration for the Na and Cl atoms at any temperature at which the expansion is valid. Waller and James obtain $(u_{\text{Cl}}^2)^{1/2}=0.217\text{A}$ and $(u_{\text{Na}}^2)^{1/2}=0.242\text{A}$ at 290°K, values which are approximately the same as those calculated by James and Miss Firth by another method.

Although ΔM, the quantity which can be obtained directly from the experimental data, is independent of the presence or absence of zero point energy, it is possible to get some information which bears on this point from experiments of this type. Insofar as the values of ΔM obtained from theory and experiment are in agreement between the temperatures of liquid air and about 400°K, one would expect that the calculated values of M should also be in accord with experiment in this range.

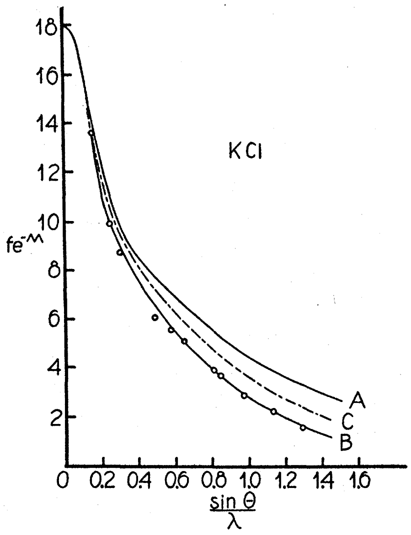

Fig. 7. Structure factors for KCl. A is theoretical curve for atom at rest, C is theoretical curve at temperature of liquid air when no zero point energy is assumed, B is same curve when zero point energy is assumed, and the circles represent the experimental data. R. W. James and G. W. Brindley. (Reference 33).

James and Brindley have calculated the structure factors for the theoretical KCl atom at rest obtained by Hartree's method of self-consistent fields and have applied the temperature factor, e^{-M}, which they obtained for KCl to these theoretical structure factors to obtain the values at the temperature of liquid air. Fig. 7 shows their results. Curve A represents the values of f calculated from the Hartree atom at rest. The dotted curve C represents the theoretical F curve after reduction to the temperature of liquid air has been made on the assumption that no zero point energy exists. The solid curve B represents the theoretical data reduced in the same way but on the assumption of the existence of zero point energy of $\frac{1}{2}$ quantum per degree of freedom. The circles represent the observed values of the structure factor at the temperature of liquid air, and the good agreement between the experimental data and the theoretical curve for which zero point energy has been assumed furnishes strong evidence for this assumption.

Another interesting application of the temperature factor in crystalline reflection has been made by B. Arakotzu and P. Scherrer[36] for the case of lithium. The crystal was maintained in a hydrogen atmosphere and relative intensity measurements were made at room temperature. The temperature factor was calculated from the constants of the crystal, Debye's value of $\phi(x)$, and the structure factors for the atom at rest determined with and without zero point energy. Fig. 8 shows the experimental points fitted arbitrarily at one point to the theoretical curve calculated by Brindley[37] according to Hartree's method of self-consistent fields. The theoretical f curves for both the lithium ion and the neutral atom are shown, and it can be seen that although no conclusion regarding the state of ionization of the lithium atom can be made, the experiment gives additional evidence for the existence of zero point energy.

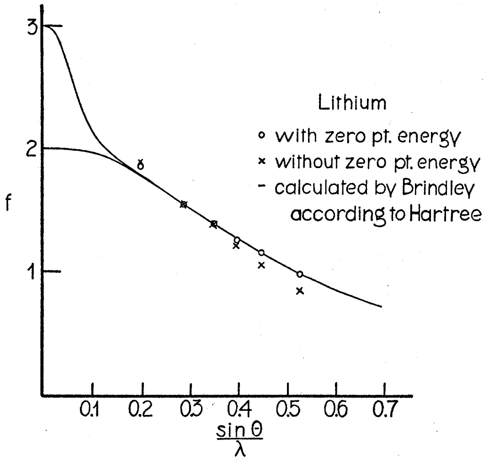

Fig. 8. Experimental and theoretical structure factor curves for the lithium atom at rest. B. Arakotzu and P. Scherrer. (Reference 36).

The effect of a magnetic field on x-ray reflection from crystals

In 1915 K. T. Compton and E. A. Trousdale[38] attempted to find an effect on the intensity and position of the spots on a Laue photograph when a crystal of magnetite was subjected to a strong magnetic field. The lack of any measurable effect led them to conclude that the ultimate magnetic particle is not a group of atoms, as the current theories indicated.

A. H. Compton and Oswald Rognley[39] later performed a similar but much more precise experiment in which the change in the intensity of a line reflected from a crystal was examined by a null ionization method when a strong magnetic field was applied to the crystal. Negative results were again obtained, and they concluded that not even the atom as a whole could be the ultimate magnetic particle and that the experiment was in better accord with the electron as the elementary magnet.

J. C. Stearns[40] has repeated the experiment with additional refinements, using crystals of iron and magnetitite. His negative results have increased the evidence in favor of the elementary magnet being associated with the electron, practically eliminating the possibility of any electron orbits as being responsible for the ferromagnetic properties of the crystal.

The effect of electric fields on x-ray reflection from crystals

If polar crystals are subjected to strong electric fields, one would expect that the ions would be displaced from their mean positions and thus have their reflecting power for x-rays altered in a manner similar to that due to the thermal displacement of the ions.

Investigations of the change in reflecting power caused by subjecting crystals of NaCl and KCl to strong electric fields have been made by J. Hengstenberg[41] and R. D. Bennett.[42] A null ionization method similar to that used for studies with magnetic fields was used. It was found possible to subject some crystals to fields as high as 700 kv before breakdown took place, but even with such strong fields and working at high orders of reflection, where the effect should be the greatest, only very small changes in the reflecting power were detected.

A calculation made by Bennett[43] on the basis of the observed change of intensity due to the applied field indicates that the atoms in the crystal are not displaced as much as would be expected if they were completely ionized. This conclusion seems to be in accord with the fact that the structure factor data for MgO fail to show evidence for an ionic lattice.

Determination of electron distribution by Fourier series

Electron density at a point. The use of Fourier series for determining electron distribution in crystals from measurements of the structure factor was first suggested by W. H. Bragg.[11] Duane[44] was however, the first to put this method of determining electron density from x-ray measurements in a satisfactory form. On the basis of the quantum theory of diffraction as applied by Epstein and Ehrenfest[45] to the problem of x-ray diffraction, he showed that the electron density, $\rho(xyz)$, at any point, (xyz), in the crystal can be represented by a series of the form

$$\rho(xyz) = \frac{1}{V} \sum \sum_{-\infty}^{\infty} \sum F_{(HKL)} \sin\left(\frac{2\pi Hx}{a} - \delta_H\right) \sin\left(\frac{2\pi Ky}{b} - \delta_K\right) \sin\left(\frac{2\pi Lz}{c} - \delta_L\right) \tag{20}$$

where V is the volume of the unit cell whose edges are a, b and c, F_{HKL} is the structure factor corresponding to the reflection of x-rays from a plane whose indices are (HKL), and δ_H, δ_K, δ_L are phase constants.

In order to determine the electron density at various points in the crystal by means of the above series it is necessary to determine the volume of the unit cell, the values of the structure factor, $F_{(HKL)}$, for all reflecting planes, (HKL), in the crystal, together with the correct signs which they must have as coefficients in the series, and the values of the phase constants. The volume of the unit cell and the absolute magnitude of the structure factor are the only quantities which are directly obtainable from x-ray measurements. The phase constants and the signs of the coefficients, $F_{(HKL)}$, must be determined from other considerations. Duane has, however, shown that it is also possible in many cases to determine the phase constants and the signs of the coefficients, and hence, in these cases evaluation of the above series is made possible. For the case in which a crystal has three mutually perpendicular planes of symmetry, and the intersection of these planes is taken as origin of coordinates, the terms in the series can contain cosines only, for they must have the same values when the algebraic sign of either x, y or z is reversed. In this case the δs must be odd multiples of $\pi/2$, and what the multiple is, is immaterial since the coefficients do not have their signs determined from x-ray data.

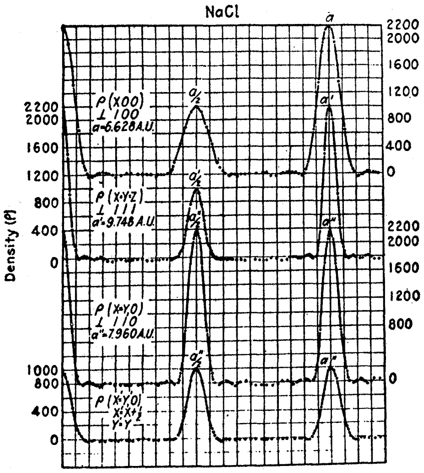

Fig. 9. Electron density in various directions in a NaCl crystal. R. J. Havighurst. (Reference. 46).

To determine the signs of the coefficients, $F_{(HKL)}$, is frequently a very difficult problem and in many cases may involve a considerable advance knowledge regarding the structure of the crystal. However, if the crystal has an atom at the origin which is considerably heavier than any other atom one may be justified in assuming all the terms positive at this point, and hence all coefficients in such a series will be positive. Compton has calculated the effect of introducing a negative coefficient or an arbitrary phase angle for the case of NaCl and finds that impossible negative values of the electron density are obtained.

This series has not been used in many cases, since the number of terms which must be evaluated make the calculations very laborious. Havighurst[46] has evaluated the series for a number of crystals, but only for such special directions as along a cube edge or diagonal, in which case the series reduces to a single summation.

Fig. 9 shows curves which Havighurst has obtained for the electron density along various lines in a rock salt crystal. This represents the first calculations of this type, and the data of Bragg, James and Bosanquet were used. Havighurst[47] has made similar calculations using his own values of the structure factor determined from powdered crystals of NaCl, NaF, LiF and CaF. He has also used this series for evaluating the parameters in crystals of the mercury halides.[48]

It is of interest to note that in deriving series of this type no assumptions have been made regarding the existence of atoms. The fact that the electron density rises to maximum values at regular intervals which are in accord with the spacings calculated from measurements of the molecular weight, density, and Avagadro's number, and also that the electron count associated with each hump is approximately equal to the atomic number, are definite results of the experimental investigations.

Electron density per unit height above the midplane of an atomic layer. Compton[49] has obtained a Fourier series which represents the number of electrons per unit height at any height, z, above the midplane of an atomic layer. Assuming the crystal to have a center of symmetry, the phase constants need not be included and the series has the form,

$$P = Zp(z) = \frac{Z}{D} + \frac{2}{D} \sum_{1}^{\infty} F_n \cos\left(\frac{2\pi n z}{D}\right), \tag{21}$$

where Z is the number of electrons in the unit for which the structure factor, F_n, is measured, D is the grating space of the crystal in the direction considered, n is the order of reflection for the planes perpendicular to which the electron density is to be determined. F_n can usually be assumed to be positive for the simple type of crystals to which this series has been applied. This one-dimensional series is much more readily evaluated than the three-dimensional series due to Duane, and in many cases gives just as valuable information regarding the position of the atoms in the crystal.

Let us apply this series to the structure factor data for MgO. If we consider the value of P along a line perpendicular to the (100) plane, the electron density will rise to a maximum at values of z equal to zero, $D/2$, D etc., but these maxima will correspond to the sum of the electron density of the Mg and O atoms since the (100) planes contain both atoms. A more interesting result is obtained by determining P along a cube diagonal. For this case D will be the grating space for the (111) planes, and F_n will be $F_{(111)}$, $F_{(222)}$ etc., corresponding to alternate values of F from the difference and summation spectra, and Z is equal to 20, the number of electrons in the molecule. Fig. 10 gives the curve obtained by solving the series when we use the F values given by the first seven orders of reflection. This series is rapidly convergent and only seven terms give a good representation of P. This curve shows humps of two sizes corresponding as one would expect to the layers of atoms consisting of all Mg and all O. There is seen to be a considerable amount of overlapping of the electron densities from the two atoms. This may or may not mean that the atoms themselves overlap, because this picture represents the projection of atoms on a line where the atoms are present in the lattice as closely packed spheres. In this respect the series representing the electron density at a point gives a better resolution of the electrons associated with each atom. The structure factors which were used in evaluating this series were measured at room temperature, and the resultant electron distribution curves correspond to a time average of the true electron density on which the thermal agitation has been superimposed.

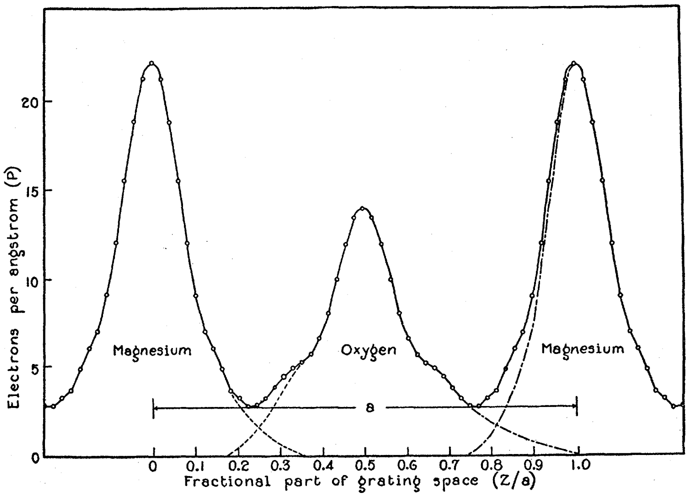

Fig. 10. Projection of the electron density in MgO on cube diagonal.

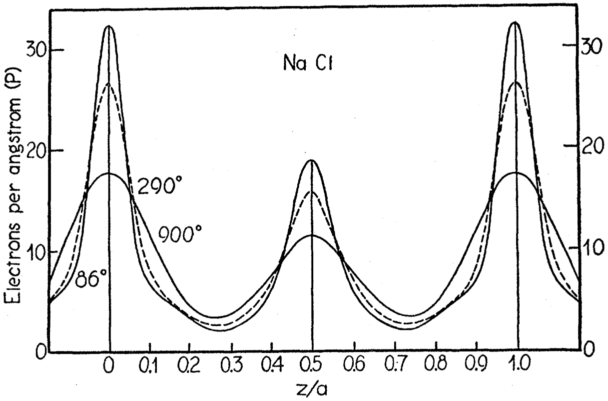

Fig. 11. Projection of the electron density in NaCl at various temperatures on cube diagonal. R. W. James and Miss Firth. (Reference 17)

Fig. 11 shows the result of the same type of analysis made by James and Miss Firth using their structure factor data for rock salt at various temperatures, and one sees how the electron density becomes less diffuse as the amplitude of thermal vibration decreases. Even at 86°K, however, the electron density between the atoms has not been reduced to zero. Due to this overlapping of the projection of electron density this type of analysis gives no definite information regarding the degree of ionization of the atoms in the crystal.

In Fig. 10 for MgO extrapolations have been made for the case of the ions and the neutral atoms. The dot and dash line shows how the electron densities could be divided to represent the ions (Mg^{++} and O^{--}) while the dotted—line is a similar extrapolation assuming the atoms to be present in the neutral state. One can readily see that either of these cases or some intermediate state is possible as far as this type of analysis is concerned.

Projection of electron density on a plane. Recently W. L. Bragg[50] has derived a Fourier series which represents the projection of the electron density on various crystal planes. If one considers a crystal which has a center of symmetry at the origin, the phase constants need not be included and the series assumes the following form when the projection of electron density, $\rho(yz)$, per unit area at a point, (yz), on the (100) face of the crystal is desired,

$$\rho(yz) = \frac{1}{A} \sum_{-\infty}^{\infty} \sum F_{(OKL)} \cos 2\pi\left(\frac{Ky}{b} + \frac{Lz}{c}\right). \qquad (22)$$

In this equation A is the area of the (100) face of the unit cell and $F_{(OKL)}$ are the values of the structure factor for all values of K and L, H being equal to zero.

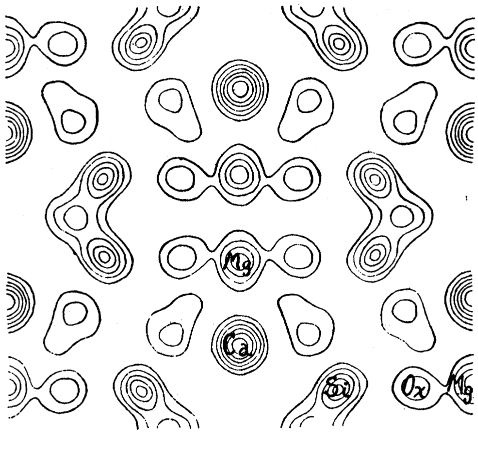

Fig. 12. Projection of electron density in diopside on the (100) face. W. L. Bragg, (Reference 50).

The projection of the electron density on the (010) and (001) faces of the crystal are of similar form and the three series must usually be evaluated in order to determine the parameters of all the atoms in the crystal under investigation.

Bragg has applied the series to the somewhat complete structure factor data obtained by himself and West[51] for the crystal diopside, $CaMg\,(SiO_3)_2$, whose structure depends on the evaluation of 14 parameters. As previously mentioned, only the absolute magnitude of the coefficients of the series are determined from x-ray measurements, and the signs of these coefficients must be determined from some previous knowledge of the crystal structure. In the case of diopside a previous determination of the crystal structure had been made by Bragg and West by the usual method of trial and error, and a satisfactory solution had been obtained. From this information the signs of the coefficients which were sufficiently large to be significant could be readily obtained. The resulting Fourier analysis gave a structure in which the location of all the atoms agreed within one half of one percent of the previous determination. An example of the projection of electron density on the (100) face of this crystal is shown in Fig. 12. The atoms can be distinguished by the number of contour lines associated with them. In a few cases two atoms of oxygen lie directly below each other and these are identified by three contour lines rather than the two which characterize the individual oxygen atoms.

In so far as the determination of the parameters by the use of Fourier series in this case involved a previous determination of the crystal structure, one might wonder what value such an analysis has. Bragg has pointed out that in many cases the use of this series in conjunction with the usual trial and error method should facilitate the determination of the structure as well as furnish a check on the results.

The complete structure of $NaClO_3$ and $KClO_3$ have been determined by Zachariasen[52] using a combination of this Fourier series and the trial and error method. These crystals do not have a center of symmetry, but as he mentions a center of symmetry in the plane on which the projection is made will suffice to eliminate the phase constants.

Radial electron distribution. The series which have been discussed above make it possible to determine the distribution of the electrons in the crystal lattice and thus to locate positions of maximum density which can be identified with the various atoms of which the crystal is composed. Having made such an analysis it is of interest not only to locate the atoms within the crystal but also to determine the probable arrangement of the electrons within the atom itself.

If the values of the electron density, $\rho(xyz)$, per unit volume have been determined for various points throughout the crystal, the radial electron distribution for the various atoms can be readily determined. Calling $U(r)$ the number of electrons per angstrom at a distance r from the center of the atom, we have

$$U(r) = 4\pi r^2 \rho(xyz). \tag{23}$$

If one plots $U(r)$ against r the resultant curve gives a good representation of the average radial distribution of the electrons within the atom. The total number of electrons in the atom is obtained by taking the area under such a curve.

This method of obtaining $U(r)$ is subject to the same objections regarding the labor involved as were mentioned in connection with the series for determining $\rho(xyz)$.

Compton[49] has derived a series by which the radial electron distribution is more readily evaluated than by the above method. He shows that the value of P from Eq. (21) is related to $U(r)$ by the expression

$$U(r) = 2r\frac{dP}{dr}, \tag{24}$$

from which $U(r)$ can be determined directly from the slope of the P curve at various values of r, or the P series can be differentiated giving the series

$$U(r) = \frac{8\pi r}{D^2}\sum_1^\infty nF_n \sin\left(\frac{2\pi nr}{D}\right), \tag{25}$$

in which F_n represents the structure factor of the atom for the nth order of reflection, and D is the grating space for the planes considered. In order to evaluate this series one must be able to determine the structure factors for the individual atoms as was shown to be possible for crystals of the NaCl type when the number of electrons associated with each atom is assumed.

This series has the disadvantage of being slowly convergent due to the coefficient nF_n. Since the higher orders of reflection decrease rapidly with increasing temperature the series will be more rapidly convergent when applied to data at high temperatures. When the series is evaluated from structure factor data obtained at room temperature, the resultant electron distribution curve gives a diffuse picture of an atom due to the thermal agitation which the atom possesses in the crystal. The picture corresponds to a time exposure of an atom in constant vibration.

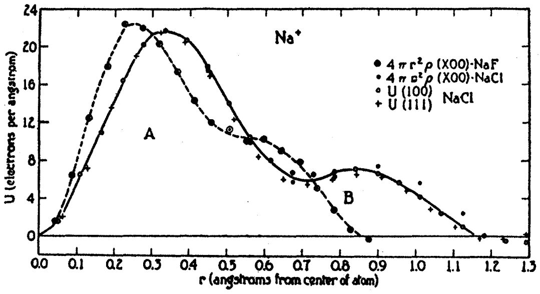

Fig. 13. Radial electron distribution for the sodium atom in NaCl and NaF. R. J Havighurst. (Reference 47).

A number of investigators have obtained electron distribution curves of this type using the one-dimensional series due to Compton.[49] Havighurst[47] has determined $U(r)$ for a number of atoms using his powder crystal data. He has used both Eqs. 23 and 25 and the results of the two determinations are in very good agreement.

Using his structure factor data for NaCl shown in Fig. 3 he has calculated $U(r)$ for the atoms of sodium and chlorine. The results are shown in Figs. 13 and 14. In Fig. 13 a curve obtained from data on NaF is also included. It will be noticed that the Na$^+$ ion from NaF appears more concentrated than the similar ion obtained from NaCl. This difference is quite likely due to the smaller amplitude of thermal agitation for the sodium atoms in NaF.

The second hump of electron density labeled *B* in the case of sodium may or may not be a true configuration of the average electron density. A similar hump was obtained by the author for Mg in Mg O, while analysis of the data of Bragg James and Bosanquet by Havighurst, and Beardens analysis of his own data show one smooth curve for the sodium atom.

In Fig. 14 for the electron distribution in chlorine the same question arises. In any case, however, the *B* and *C* humps taken together represent the *M* electrons. The *A* part of the curve corresponds to approximately ten electrons and as would be expected represents the unresolved *K* and *L* groups.

It can be seen from both electron distribution curves that the various methods of calculation give results which are in agreement within experimental error.

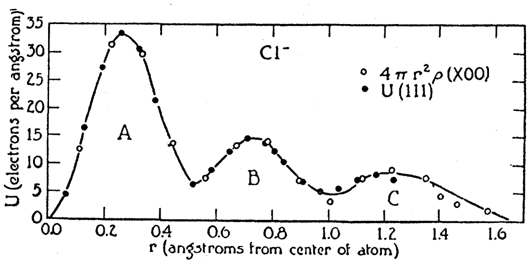

Fig. 14. Radial electron distribution for the chlorine atom in NaCl. R. J. Havighurst. (Reference 47).

A more interesting radial electron distribution curve would be obtained if the structure factor data were first corrected to correspond to the atom at rest, as can be done from the Debye-Waller temperature theory and the data obtained by the various investigators at different temperatures if one assumes the existence or absence of zero point energy. A calculation of this type has been made by Compton and the author using the crystal reflection data of James and Miss Firth for chlorine, and is shown in Fig. 29 in connection with scattering of x-rays by gases. Measurements of the intensity of x-rays scattered by gases are independent of temperature, and give directly the structure factor of the atom at rest. The electron distributions which have been calculated for these data are similar, but are more directly obtainable than is true for the case of crystal reflection. Curves of this type are shown in Figs. 24, 26 and 28. From the agreement of the crystal data and the gas data one might consider that these curves also represent an analysis of electron distribution of the corresponding atoms in crystals.

The x-ray "microscope"

A very interesting analogy between the results of x-ray analysis of electron distribution and the formation of images of minute bodies by means of an optical microscope has been made by W. H. Bragg.[53]

As is well known the resolving power of an instrument is inversely proportional to the wave-length of the radiation used to illuminate the body under investigation. Although the ordinary optical instrument is thus restricted by the lower limit of the visible spectrum, the use of the photographic plate and ultraviolet radiation has increased the resolving power obtainable by approximately a factor of two.

If a system of lenses could be developed to handle x-rays as can be done for the visible and neighboring spectra the resulting arrangement would have a resolving power of ten thousand times that now available, and molecules would be subject to direct photographic investigation. This may seem like a fantastic idea, but actually it can be realized at present in a somewhat indirect way.

In the optical case all the work involved in constructing an image is performed by the lens system of the microscope. Since lenses cannot be used for x-rays, the work of constructing the image must be performed by the individual. According to Abbe's theory of image formation there is a definite relation between the intensity of the spectra obtained from a grating and the image of the grating. In the case of a crystal a similar relation holds, and with this information Bragg was able to construct a photograph of a crystal cell. Without going into the details of obtaining a photograph of this type Fig. 15 has been reproduced here to show the results obtained. This photograph represents the appearance of a cell in a crystal of diopside as viewed perpendicular to the (100) face. A comparison of the photograph with the contour map of electron density of the same face, Fig. 12, should make it possible to identify at least some of the atoms in the photograph.

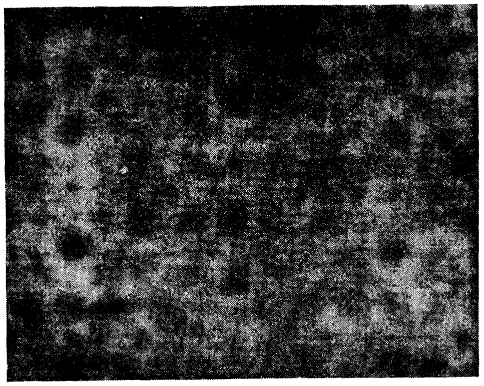

Fig. 15. Photograph of the projection of the electron density in a diopside crystal on the (100) face. W. L. Bragg. (Reference 53).

B. The Scattering of X-rays by Gases

Introduction

Although the coherent scattering of x-rays by crystals was as early as 1914 given a satisfactory theoretical treatment which made it possible to predict with considerable accuracy the distribution of the electrons within the atom, the diffuse scattering by amorphous matter has presented theoretical difficulties which have only in the last two or three years been solved in a manner which seems to be reasonably satisfactory.

On the basis of classical theory J. J. Thomson[9] showed that the independent scattering by a single electron whose diameter is small compared to the wave-length of the incident radiation can be represented by the expression

$$I_e = \frac{Ie^4(1 + \cos^2 \phi)}{2m^2R^2c^4}, \tag{26}$$

where I_e is the intensity of the scattered x-rays at a distance R from the scattering electron, I is the intensity of the primary beam, ϕ is the angle of scattering, $(1+\cos^2\phi)$ is the polarization factor and e, m and c have their usual significance.

If all the electrons in an atom could be assumed to scatter independently Thomson's theory would give ZI_e as the atomic scattering, and the angular distribution of the intensity would be given by the polarization factor, $(1+\cos^2\phi)$. The early experiments of Crowther,[54] and Barkla and Ayers[55] showed that the intensity of scattering in the forward direction was considerably greater than the Thomson theory predicted. On the basis of Crowther's experiments Webster[56] suggested that this excess scattering at small angles could be accounted for in terms of constructive interference between the rays scattered by the various electrons in the atom. A satisfactory explanation of the excess scattering has been sought by a number of investigators on the basis of the interference produced for various assumed distributions of the electrons within the atom. Debye[57] and Thomson have independently calculated the scattering to be expected from groups of electrons at fixed distances from each other. Various other atomic models have been considered by Schott,[58] Compton,[59] Glocker,[60] Kaupp[61] and others which account for the excess scattering at small angles with various degrees of approximation.

However, it is not only in the forward direction of scattering that the experiments differ from the Thomson theory. It is found that for light scattering elements the experimental intensity is less than the classical theory predicts at large angles of scattering. This is the part of the problem which was not until recently given a satisfactory explanation. To explain this decrease in intensity at large angles of scattering Compton[59] in 1921 was lead to postulate an electron whose diameter is not negligible compared to the wave length of the incident radiation. He found that if the electron was assumed to have a radius of 0.05A° the intensity calculated on the basis of an assumed distribution for the carbon atom was in good agreement with the experiments of Barkla and Ayers both regarding the excess scattering and the decrease in intensity at large angles.

The discovery of the Compton[62] effect and the development of the wave mechanics has made such a postulate unnecessary and has led to a generally satisfactory theory for the intensity of scattering from individual atoms.

Recent theories of scattering

Wentzel[63] and Waller[64] have independently, on the basis of wave mechanics, derived an expression for the intensity of scattering of x-rays by a single atom. The atom has been assumed to have spherical symmetry and to consist of a continuous Schroedinger charge distribution.

Unlike the case of crystal reflection, the scattering from individual atoms involves the Compton modified radiation. This radiation is incoherent, and hence the expression for intensity must involve both a coherent and an incoherent term. According to Wentzel* the intensity of the coherent and incoherent parts of the scattered radiation is given by the following expressions

$$I_{\text{coh}} = I_e\left\{\sum_1^Z f_n\right\}^2 \tag{27}$$

$$I_{\text{inc}} = ZI_e\left\{1 - \frac{1}{Z}\sum_1^Z (f_n)^2\right\} \tag{28}$$

where I_e is the Thomson scattering by a single electron and f_n is the structure factor corresponding to the nth electron and is given by

$$f_n = \int_0^\infty u_n(r)\frac{\sin kr}{kr}\,dr,$$

where $u_n(r)$ is the charge between r and $r+dr$ for the nth electron in the atom expressed in electron units, and $k = 4\pi/\lambda \sin\phi/2$. As far as this theory is concerned it is immaterial whether $u_n(r)$ is interpreted according to Schrödinger as a continuous charge distribution or if $u_n(r)\,dr$ represents the probability of the nth electron lying between r and $r+dr$ as interpreted by Born and Heisenberg.

The total scattering can be obtained by adding Eqs. (27) and (28), and if we change the units to correspond to the scattering per electron relative to the Thomson value, we have

$$S = \frac{I}{ZI_e} = S_{\text{coh}} + S_{\text{inc}} = \left[\frac{1}{Z}\left\{\sum_1^Z f_n\right\}^2 + \left\{1 - \frac{1}{Z}\sum_1^Z (f_n)^2\right\}\right]. \tag{29}$$

On the basis of classical theory Raman[65] and Compton[66] have independently derived an expression for the intensity of scattering of x-rays by a single atom, which in this case has been assumed to consist of discrete electrons distributed at random about the nucleus.

Compton obtains the following expression for the total scattering

$$S = \frac{I}{ZI_e} = \left[\frac{f^2}{Z} + 1 - \frac{f^2}{Z^2}\right], \tag{30}$$

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* Waller's theory for the scattering from an atom differs from that of Wentzel by a small term which arises from the inclusion of the Pauli exclusion principle.

where $f = Z\int_0^\infty u(r)\,(\sin kr/kr)dr$, and corresponds to the structure factor of the atom at rest. In this case $u(r)\,dr$, the probability of an electron lying between r and $r+dr$, is assumed to be the same for every electron in the atom.

For the purpose of identifying the coherent and incoherent parts of the classical equation, Compton has compared it with the expression for the total scattering obtained by Wentzel, Eq. (29).*

The first terms of Eqs. (29) and (30) can be seen to be identical from the definitions of f_n and f, since $Z\,u(r) = \sum_1^Z u_n(r)$. The term $(1 - f^2/Z^2)$ of Eq. (30) is identical with the incoherent part of Eq. (29) only if $f^2/Z^2 = (1/Z)\sum_1^Z (f_n)^2$ or in other words if the structure factor corresponding to every electron in the atom is the same. This is the assumption on which the classical theory has been derived, and if its validity is granted the total scattering equations obtained from either theory are identical.

Eqs. (29) and (30) cannot be directly compared with experiment, since in deriving the equation for the incoherent radiation Wentzel has assumed the limiting case of very long wave lengths for which the scattering by a free electron is identical with that calculated on the classical theory. For shorter wave-lengths Breit[67] and Dirac[68] have shown that the modified or incoherent radiation is reduced in intensity according to the relation**

$$S_{\text{inc}} = S_{\text{class}}/R^3 \tag{31}$$

where $R = (1 + \gamma \text{ vers } \phi)$ and $\gamma = h/mc\lambda$.

Compton has applied this factor to the incoherent part of the total scattering equation which gives

$$S = S_{\text{coh}} + \frac{S_{\text{inc}}}{R^3} = \left\{ \frac{f^2}{Z} + \frac{1 - f^2/Z^2}{R^3} \right\} \tag{32}$$

where S is now directly comparable with experiment.

Eq. (32) can be directly solved for the atomic structure factor giving

$$f = Z \left\{ \frac{S - \dfrac{1}{R^3}}{Z - \dfrac{1}{R^3}} \right\}^{1/2\dagger} \tag{33}$$

Having determined the value of f from the measured intensities, the electron distribution for the atom at rest can be directly calculated by the use of Fourier series or integrals.

---

* Raman has identified the coherent and incoherent parts of the scattering equation by purely classical arguments.

** A relation due to Klein and Nishina, Zeits. f. Physik **52**, 853 (1929) is presumably a closer approximation than Eq. (31) when the wave-length is so short that the velocity of the recoil electrons approaches that of light.

† Compton expresses the above equation as $f = Z\{(S-1)/(Z-1)\}^{1/2}$ in which case he has applied the correction factor R^3 to the modified radiation to obtain what he terms the classical value of S. In Eq. (33) the modified scattering has been reduced by the factor R^{-3} to make S correspond to the measured value. Either method gives the same value of F.

If Wentzel's Eq. (29), in which the structure factor for the electrons in the various energy states may be different, is used to express the total scattering, then it is not possible to solve directly for the $\sum_1^Z f_n$ from which the average charge distribution for the atom can be determined. However, if the distribution of charge is calculated according to Hartree's[69] method of self consistent fields, the values of $u_n(r)$ can be calculated for every electron in the atom and the coherent and incoherent scattering can be determined from Eqs. (27) and (28). The total scattering can then be determined from Eq. (29) if the incoherent term is corrected by the Breit-Dirac factor. A comparison of the calculated and experimentally determined total scattering then furnishes a check of the calculated charge distribution for the atom. This gives an indirect method of determining the electron distribution for an atom, a method similar to that initially used by Compton and Bragg for the case of structure factor measurements for crystals.

Measurements of intensity of x-rays scattered from monatomic gases

Measurements of the intensity of x-rays scattered by monatomic gases should very approximately satisfy the conditions on which the above theories have been derived. The atom will on the average at least be spherically symmetrical, and unless the pressure is very high the interference effects will be confined to the electrons of a single atom, the distance of separation being too great for any appreciable interatomic interference.

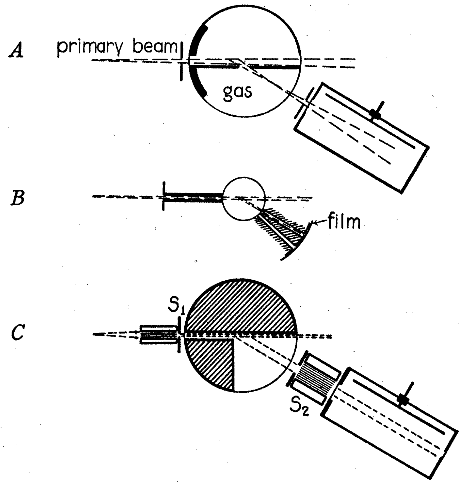

Fig. 16. Apparatus used in scattering x-rays from gases, *A*, Barrett, *B*, Hertzog, *C*, Wollan.

Few measurements of the intensity of x-rays scattered by gases gave been made due to the low intensities with which one has to deal. In 1928 Barrett[70] measured the variation of the scattered intensity with angle for helium and argon as well as for some of the diatomic gases. He used an ionization method of measuring the intensity, the arrangement of the apparatus being shown in Fig. 16a. For some of the measurements a Ross balanced filter was used to separate out the K_α radiation of molybdenum, but in most cases general radiation was used. The lack of knowledge of the exact wave-length of the radiation used introduces some uncertainty; but in as far as can be expected the measurements are in agreement with more recent data.

Similar measurements have recently been made by Herzog[71] using the photographic method of recording the scattered intensity. In his first experimental arrangement the energy scattered at various angles was superimposed on the same part of the photographic plate. From the geometry of the set-up he was able to get the intensity of the scattered radiation corresponding to any angle of scattering over the range of angles included on the plate. It would seem that this method is not well adapted to accurate results, and more recently he[72] has redesigned the apparatus as shown in Fig. 16b. A copper tube was used and the radiation made approximately homogeneous ($K_\alpha =$ 1.54A) by passing through a nickel filter. With this arrangement he has measured the scattering from argon as a function of the scattering angle between 30° and 160°.

Simultaneous with the work of Herzog, measurements of the intensity of scattering by helium, neon and argon were made by the author[73] using the ionization method of measuring the scattered intensity. The arrangement of the apparatus is shown in Fig. 16c. Soller slits were used to collimate the primary and scattered beam and also to determine the volume of gas effective in scattering. For the heavier gases, neon and argon, the radiation was made homogeneous (Mo $K_\alpha = 0.71$A) by the use of the Ross double filter method. For helium general radiation was used, but here the lack of homogeneity is less important since the difference between maximum and minimum intensities is comparatively small.

After making measurements of the intensity of scattering as a function of the scattering angle for each gas a comparison of the intensities of scattering from the various gases at 90° was made. In this case an absolute measurement of the intensity (i.e., the ratio between the scattered and primary intensity) for one substance at 90° is sufficient to put all the intensity measurements on an absolute basis. Direct absolute intensity measurements for a gas would be difficult due to the very great difference between the intensity of the primary and the scattered beam.

A fair approximation to the absolute intensity of scattering from hydrogen or helium can be obtained by correcting the scattering given by the Thomson formula, Eq. (26), by the Breit-Dirac factor. Since the radiation from hydrogen or helium at 90° should be approximately all modified, the observed intensity of scattering by a single electron should be given by

$$(I_e)_{\text{obs}} = \frac{Ie^4(1+\cos^2\phi)}{2m^2R^2c^4}(1+\gamma \operatorname{vers}\phi)^{-3}. \tag{34}$$

If we likewise express this in terms of the quantity S, which is the ratio of the observed intensity per electron to the value predicted by Thomson's theory, we have for the case of hydrogen or helium at 90°

$$S = \frac{(I_e)_{\text{obs}}}{(I_e)_{\text{class}}} = \frac{1}{(1+\gamma \text{ vers } \phi)^3} = 0.91 \text{ for } \lambda = 0.71A. \qquad (35)$$

This value can then be used as a standard when the K_α lines of molybdenum are used. For the sake of ease of comparison oxygen was used as a secondary standard, and the value of S at 90° was found to be 0.96.

Fig. 17 shows the results of the absolute intensity measurements for the first three monatomic gases together with the oxygen and hydrogen standards as determined by the author. It is not possible to make a direct comparison of these data with those of Herzog and Barrett because the wave-lengths used in each case were different. If the experimentally determined values of S were dependent on $\sin \phi/2/\lambda$ only, as is true for intensity measurements on crystals where the radiation is all coherent, such a comparison could be readily made. However, due to the presence of the modified part of the scattered intensity as previously mentioned the factor $(1+\gamma \text{ vers } \phi)^{-3}$ which is equivalent to $(1+2(h/mc)(\sin^2\phi/2)/\lambda)^{-3}$ is introduced, and the intensity is a function of $(\sin^2\phi/2)/\lambda$ rather than of $(\sin \phi/2)/\lambda$.

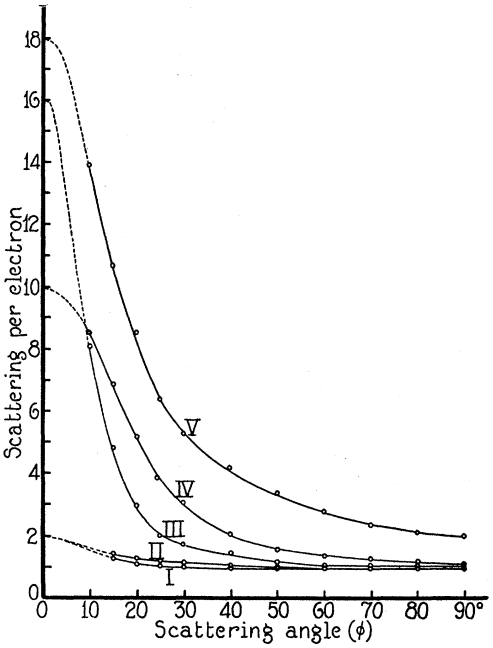

Fig. 17. Intensity of x-rays scattered by gases. I, hydrogen. II, helium. III, oxygen. IV, neon. V, argon.

If one calculates the percent of coherent and incoherent radiation, and increases the incoherent part of the data of Herzog, Barrett and the author by the Breit-Dirac relation, the results should be approximately comparable. The data of the author are in absolute units while those of Barrett and Herzog must be fitted to the curve at some value of S. Due to the different values of λ used, the data cover considerably different parts of the scattering curve. Fig. 18 shows the agreement between the various scattering data for argon and the theoretical scattering curve calculated by Waller and Hartree.[74]

The above experiments represent the scattering by relatively light gases. We have an example of the scattering by a very heavy gas in the experiment of Scherrer and Staeger[75] on the scattering from mercury vapor. The very strong absorption of copper K_α radiation in mercury vapor made it necessary to use a quite different experimental arrangement than was used for the lighter gases. The mercury vapor was forced through a jet to form a fine pencil of the vapor, from which the radiation was scattered and its intensity measured photographically. In this case only relative intensities were measured and the results are shown together with a theoretical scattering curve in Figure 22.

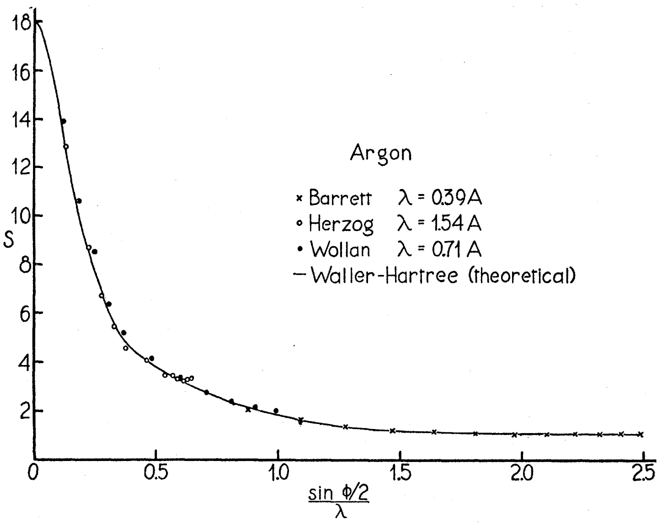

Fig. 18. Theoretical and experimental scattering curves for argon.

Comparison of theoretical and experimental scattering curves

It is of interest to compare the experimental scattering data with the total scattering calculated from the theoretical charge distribution in the atom as determined by Hartree according to his method of self consistent fields. By Hartree's method the charge distribution associated with every electron in the atom can be determined, and a different value is obtained for electrons in the various energy levels. An example of such a calculation for neon is shown in Fig. 19, in which the light lines represent the charge distribution for the various electron groups and the solid line represents the total charge distribution associated with the whole atom.

To calculate the total scattering by Wentzel's Eq. (29) from the Hartree charge distribution it is necessary to determine the values of the structure factor, f_n, associated with the various electrons in the atom. This can be done with the aid of the integral defining f_n by means of graphical integration. The total scattering can then be determined directly from Eq. (29) when the Breit-Dirac factor is applied to the incoherent part of the scattered radiation.

In deriving the classical theory the assumption has been made that the scattering by every electron in the atom is the same. It should be of interest to see what effect this assumption will have on the total scattering as calculated from the same theoretical charge distribution for the atom. The difference which this assumption introduces is present only in the incoherent part of the scattering equation. In Wentzel's theory the fact that no assumption is made regarding the identity of the charge associated with each electron in the atom leads to the term $\sum_1^Z (f_n)^2$ while the equivalent term in Compton's theory is f^2/Z or $1/Z\{\sum f_n\}^2$. This last term can also be calculated from Hartree's charge distribution for the atom and hence the corresponding total scattering can be determined from Compton's theory.

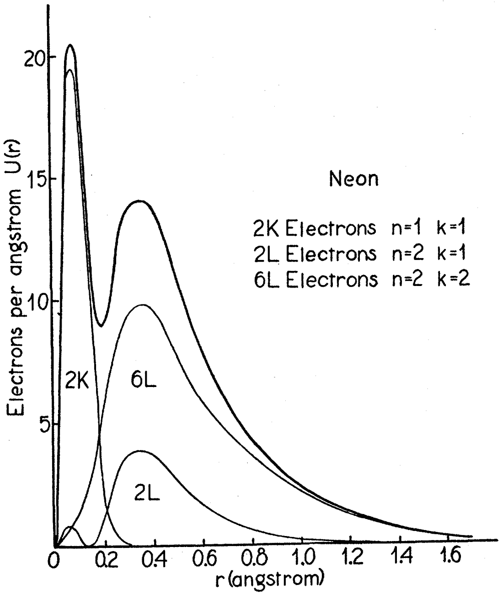

Fig. 19. Theoretical charge distribution in neon according to Hartree. G. Herzog. (Reference 76)

Herzog[76] has determined the difference in the structure factors calculated from the Hartree distribution on the basis of these two theories, and has compared the results with the experimental data. His results seem to indicate that the assumption on which the classical theory is based, namely, that the scattering by all the electrons in the atom is on the average the same, is not in good accord with the experimental data. Herzog has also calculated the total scattering on the basis of Wentzel's theory and from his calculations the total scattering from Compton's theory can be readily determined. A direct comparison of the calculated and experimental values of the total scattering can then be made.

For the case of helium the distribution of charge associated with each of the two electrons will be the same, so that Eqs. (29) and (30) give the same values for the total scattering. Fig. 20 shows the theoretical curve calculated from Eqs. (29) or (30) and corrected by the Breit-Dirac factor. The circles represent the experimental scattering data of the author and the crosses represent the data obtained by Barrett. The coherent and incoherent scattering are represented by the light lines. The low values obtained by the author at small angles may be due to the use of general radiation. The high value obtained by Barrett may be caused by the presence of some heavy gas as an impurity, as he suggests is probably the case.

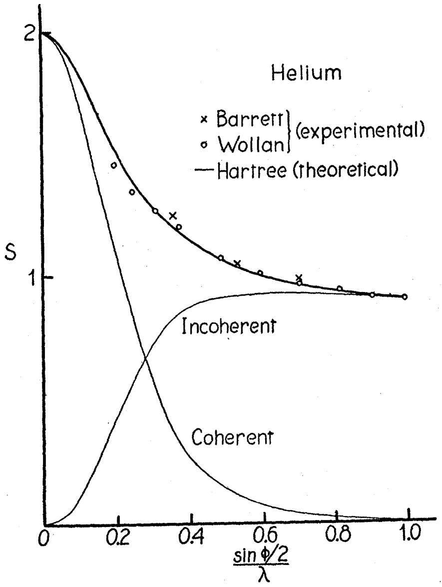

Fig. 20. Theoretical and experimental scattering curves for helium.

In the case of argon the radiation is only partially modified even at 90° and the total scattering as calculated by the two theories is very nearly the same, the difference having a maximum value of about 2 percent which is within the experimental error and cannot be represented on the graph. A comparison of the experimental data for argon with the theoretical scattering curve has already been made in Fig. 18.

For the case of neon the difference between the total scattering as calculated by the two theories is quite appreciable, being about 10 percent at 90°. A comparison between theory and experiment is shown in Fig. 21. The solid line represents the total scattering as calculated from Wentzel's theory and the dotted line shows the higher value which is obtained when the Compton equation is used. The coherent and incoherent scattering are shown by the light lines and the difference between the two theories only exists for the incoherent scattering as shown. Although the experimental data for the total scattering seem to fall between the two theoretical curves it has been pointed out by Herzog that the relative values of the scattering data are in better agreement with the total scattering curve calculated on Wentzel's theory and he suggests that the absolute value may be too high. This may easily be the case, but no very definite conclusions can be drawn on this basis. In either case the agreement between the experimental and theoretical scattering curves should give confidence in the accuracy of the Hartree method of determining the charge distribution in the atom.

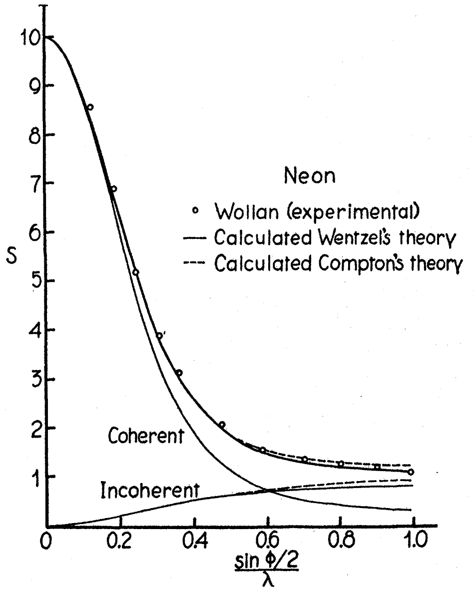

Fig. 21. Theoretical and experimental scattering curves for neon. Theoretical curves based on Hartree's charge distribution.

For the heavy elements no calculations of structure factors have been made by Hartree's method, but an approximate method due to Thomas[77] and Fermi[78] gives good results in these cases. The theory of scattering from heavy elements is also much simplified due to the fact that practically all the scattered radiation is coherent. Hence the intensity of the scattered radiation is given by

$$I = I_e f^2. \tag{36}$$

Woo[79] has made a comparison of the scattering by mercury vapor as measured by Scherrer and Staeger with the theoretical scattering calculated by the Thomas-Fermi method. Since the scattering measurements were not in absolute units the data are fitted to the theoretical curve at one angle. The comparative results are shown in Fig. 22.

Scattering by polyatomic gases

In so far as the above theories represent the scattering by individual atoms, only the monatomic gases have been considered. The theory of scattering of x-rays by polyatomic gases has been developed by Debye[80] in which, however, only the coherent radiation has been included. Woo[81] has shown how the equation must be modified in order to give the total scattering consisting of both the coherent and incoherent radiation. The incoherent term Woo takes directly from the scattering equation of Compton for single atoms.

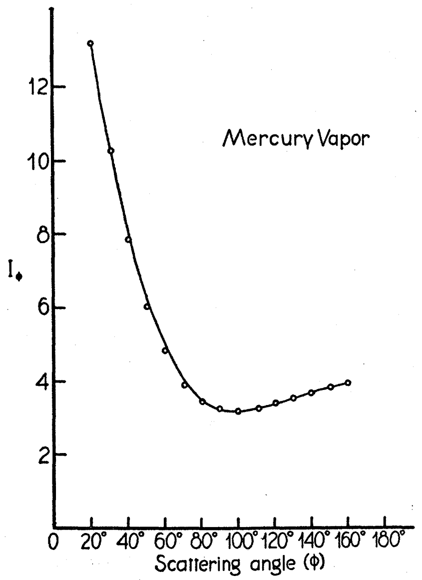

Fig. 22. Theoretical and experimental scattering curves for mercury vapor. Y. H. Woo. (Reference 79). Circles, Scherrer and Staeger: Unbroken curve calculated by Woo according to Thomas and Fermi.

The scattering by a gas molecule containing n atoms arranged at fixed distances from each other as developed originally by Debye and modified by Woo is given by the equation

$$I = I_e \left\{ \sum_1^n \sum_1^n f_i f_j \frac{\sin x_{ij}}{x_{ij}} + \sum_1^n \frac{Z_i - \dfrac{f_i^2}{Z_i}}{R^3} \right\} \tag{37}$$

where I_e is the Thomson scattering, f_i and f_j are the structure factors for the ith and jth electrons, $X_{ij} = (4\pi l_{ij} \sin \phi/2)/\lambda$ where l_{ij} is the distance between the ith and jth electrons and R^{-3} is the Breit-Dirac factor.

Debye[82], Bewilogua[83] and others have measured the intensity of scattering by various gas molecules and have used the coherent part of the above relation to determine the interatomic distances and the atomic arrangement in the molecule.

For complicated atoms it would be impossible to determine the structure factor without considerable knowledge of the molecular structure. However, for the scattering by a diatomic gas consisting of like atoms the above equation assumes the much simpler form

$$S = \frac{I}{2ZI_e} = \left\{ \left(1 + \frac{\sin x}{x}\right) \frac{f^2}{Z} + \frac{1 - \frac{f^2}{Z^2}}{R^3} \right\}. \tag{38}$$

This equation can be solved for the structure factor of the atom in terms of the scattered intensity and the distance between the atoms in the molecule. In many cases the interatomic distances can be obtained from band spectra data and hence a measure of the absolute intensity gives a method of determining the structure factor for the atoms in a diatomic gas. Absolute intensity measurements for diatomic gases have been made by the author[84] for H_2, O_2 and N_2, the first two being shown in Fig. 17. Accurate values of the structure factor for light elements cannot be obtained by this method, however, since the atoms in the molecule cannot be assumed to maintain their spherical symmetry. In the case of O_2 and N_2 it is probable that the calculated structure factors will be a reasonably good approximation to the true values.

Determination of electron distribution in atoms of monatomic gases

If one assumes as Compton does in his derivation of the scattering equation that on the average every electron in the atom scatters the same as any other electron, the atomic structure factor can be determined from measurements of the intensity of x-rays scattered by monatomic gases as shown in Eq. (33).

The structure factor is related to the distribution of the electrons in the atom by the relation

$$f = Z \int_0^\infty u(r) \frac{\sin \pi r x}{\pi r x} dr \tag{39}$$

where Z is the number of electrons in the atom. $u(r)dr$ is the probability of an electron lying between r and $r+dr$ from the center of the atom and $x = (4/\lambda) \sin \phi/2$ where ϕ is the scattering angle and λ is the wave-length of the incident x-rays.

From this expression, the quantity $Z\ u(r) \equiv U(r)$, which represents the number of electrons per angstrom at any distance r from the center of the atom, can be determined by means of a Fourier series or integral. Compton has shown the integral to have the form

$$U(r) = Zr \int_0^\infty B \sin(\pi r x) dx, \tag{40}$$

where B is related to the structure factor f or the measured intensity S by the relation

$$B = \frac{2\pi x f}{Z} = 2\pi x \left\{ \frac{S - \frac{1}{R^3}}{Z - \frac{1}{R^3}} \right\}^{1/2}. \tag{41}$$

The electron distribution in the helium atom. The first determination of electron distribution from measurements of the intensity of x-rays scattered from gases was made by Compton[66] using the data obtained by Barrett for helium. Although only three experimental points are used the results obtained should be quite reliable if a reasonable extrapolation of the B curve is made.

For small values of x the structure factor curve can be shown to be of a parabolic form $f=Z+bx^2$ and since $B=2\pi xf/Z$ the slope of the B curve at $x=0$ will be $(dB/dx)_{x=0}=2\pi$ for any scattering material. Although it is seen from Fig. 23 that Barrett's data do not determine the position of the maximum value of B, with the aid of a knowledge of the slope at $x=0$ this maximum can be determined with considerable accuracy. The author's[85] data for helium begin at $x=0.76$ and the experimentally determined maximum is very near the one used by Compton for Barrett's data.

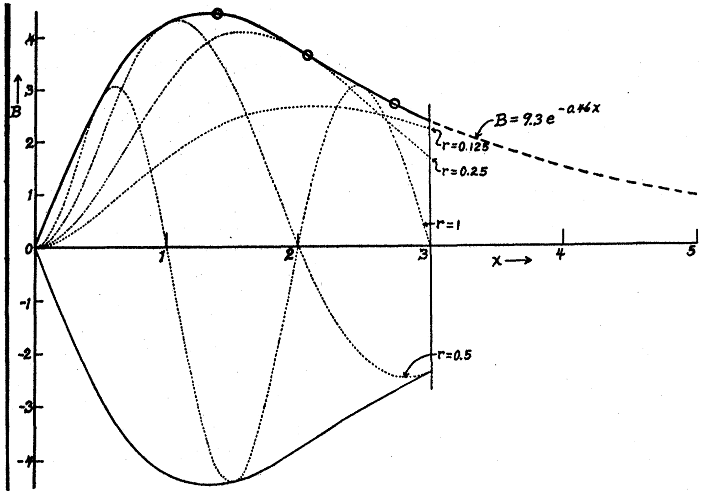

Fig. 23. B-curve for helium from Barrett's data. A. H. Compton (Reference 66).

The data for large values of x are not used since B is proportional to $\{S-(1/R)^3/Z-(1/R)^3\}^{1/2}$ and a very small error in the value of S will cause a very large error in B. It is better to assume that the B curve gradually approaches zero as x increases. If one assumes an exponential falling off of the B curve the integral expressing $U(r)$ can be expressed as the sum of two integrals one of which can be directly integrated.

$$U(r) = Zr(\Phi_1 + \Phi_2) \tag{42}$$

where

$$\Phi_1 = \int_0^{x_1} B \sin(\pi r x) dx \tag{43}$$

$$\Phi_2 = \int_{x_1}^{\infty} B \sin(\pi r x) dx. \tag{44}$$

The first of these integrals can be evaluated graphically by plotting the values of B sin $(\pi r x)$ for various values of r(as shown in the figure) and the areas between the limits $x = 0$ and $x = x_1$ determined by a planimeter.

In the second integral putting $B = be^{-ax}$ and evaluating the integral one gets

$$\Phi_2 = B_1 \frac{a \sin (\pi r x_1) + \pi r \cos (\pi r x_1)}{a^2 + \pi^2 r^2} \cdot \tag{45}$$

The constants a and b are determined from the experimental curve, b being equal to B_1 at $x = x_1$ from the condition for continuity of the curve at that point.

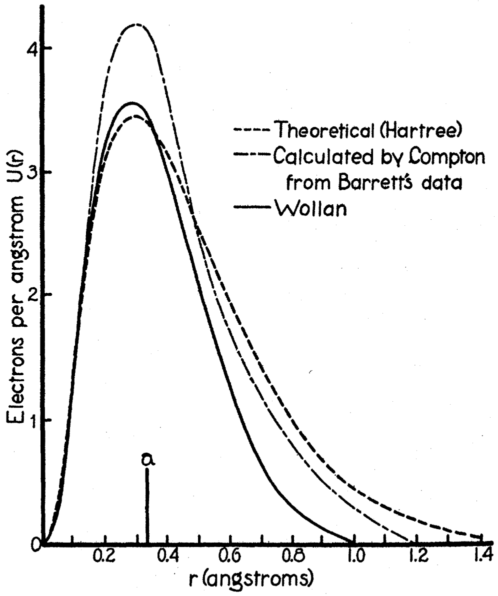

Fig. 24. Radial electron distribution curves for the helium atom. a is radius of first Bohr orbit.

The radial electron distribution curve determined in this way from the data of Barrett and the author together with the theoretical curve calculated by Hartree are shown in Fig. 24. The lack of agreement between the author's and the theoretical curve at large values of r results from the fact that the intensity at small angles is lower than that given by the theoretical scattering curve.

The electron distribution in the argon atom. The B curve calculated from the author's data for argon is shown in Fig. 25. The experimental data only give a small part of the total curve, but a maximum value has been reached and B must approach zero at large values of x. Extrapolating this curve to zero by a parabolic equation the electron distribution has been determined in a manner similar to that described for helium. The calculated distribution is plotted together with the theoretical distribution for argon calculated by Hartree in Fig. 26. Although the average electron distribution determined from experiment is in agreement with the theoretical, the *K* and *L* shells are not resolved. This could hardly be expected from the amount of experimental data at hand. Using *x*-rays of shorter wave-length and carrying the measurements to larger scattering angles it should be possible to increase the resolving power of the apparatus sufficiently to determine these finer details in the electron distribution curve.

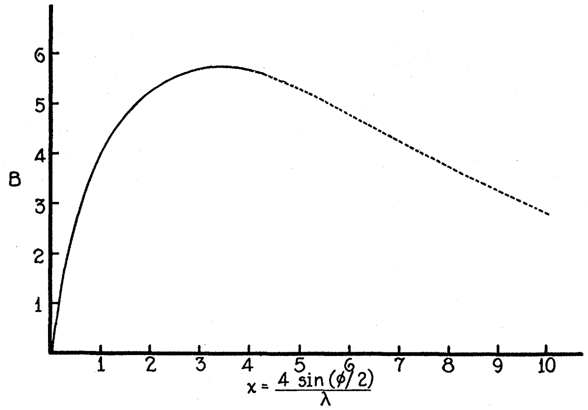

Fig. 25. *B*-curve for argon, solid line from experiment, dotted line extrapolated.

The electron distribution in the Neon atom. The calculation of the electron distribution curve for neon is of special interest because the experimental data furnish a more complete part of the *B* curve than was true for the case of argon. The experimental part of the *B* curve is shown by the solid line in Fig. 27 and the broken line is a similar curve calculated from the charge distri-

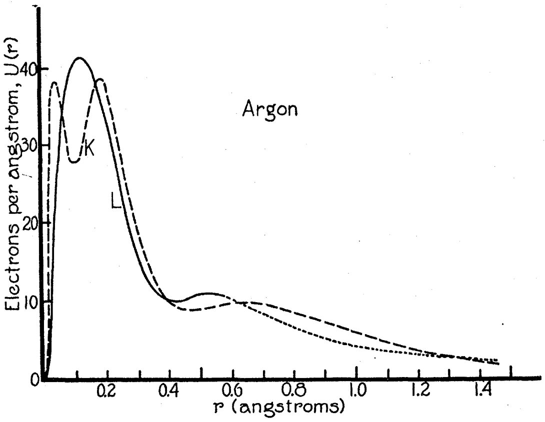

Fig. 26. Radial electron distribution curves for argon. Solid line from experiment, broken line theoretical according to Hartree.

bution determined by James, Waller and Hartree[86] for the Na+ ion.* The second maximum in this curve is due to the contribution of the *K* electrons.

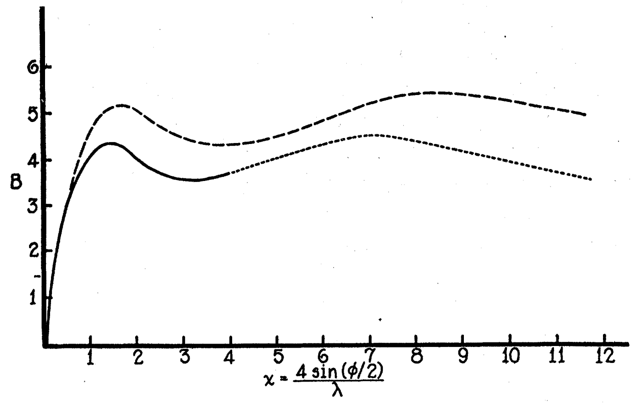

Fig. 27. Broken line is *B*-curve for the Na+ ion from Hartree atom, solid line is experimental part of *B*-curve for neon, dotted line shows how this curve was extrapolated to get electron distribution in neon.

Since the experimental *B* curve is of the form shown and must approach zero at large values of *x* a second maximum must also be present. The theoretical

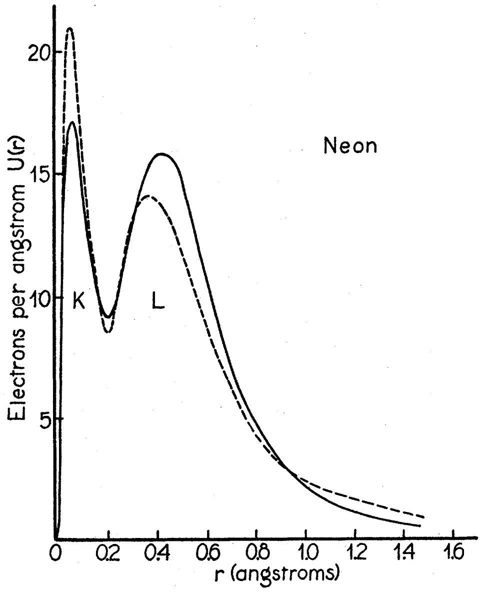

Fig. 28. Radial electron distribution curves for neon. Solid line from experiments, broken line theoretical according to Hartree.

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* Na+ was used since the neon curve was not available to the author at the time the calculation was made.

curve was used as a guide in making the extrapolation shown by the dotted line in the figure. Any extrapolation would resolve the K and the L electron groups but would not give as satisfactory a curve. The data were analysed in a manner similar to that used for helium, but it was necessary to carry the graphical intergation to $x=8$. From $x=8$ to $x=\infty$ an exponential extrapolation was used in which the value of B was given by $B=7.105\ e^{-0.058x}$.

The electron distribution curve which results from this analysis is shown in Fig. 28 together with the theoretical curve for neon calculated by Hartree. The agreement is closer than one could expect from the extent of the experimental part of the curve, but if the experimental data in this case could be carried to larger angles and shorter radiation a very reliable distribution should be obtained.

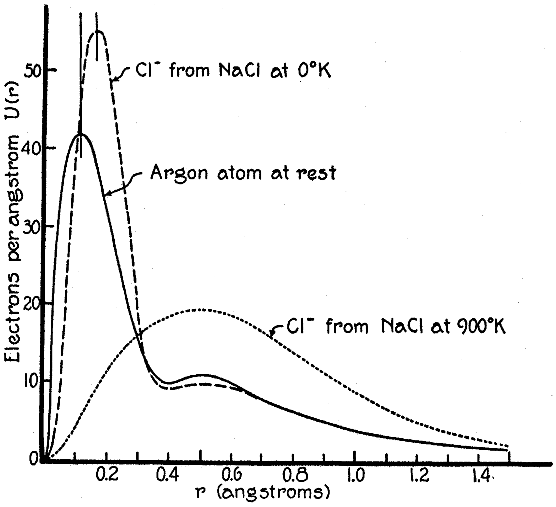

Fig. 29. Radial electron distribution curves showing the effect of thermal agitation and zero-point energy.

Zero point energy. A comparison of the radial electron distribution curve for argon, which represents the atom at rest, with a similar curve for the Cl^- ion at 0°K as determined from the data of James and Miss Firth should furnish a good check of the existence of zero point energy for the ion in the crystal. This method has the advantage over that used by James that no assumptions are made regarding atomic models. The curves for the argon atom at rest, the Cl ion at 0°K and at 900°K are shown in Fig. 29. The distance of separation of the peaks of intensity for argon and the Cl ion corresponds approximately to the average amplitude of vibration at zero degrees if zero point energy of 1/2 quantum per degree of freedom is assumed for the Cl ion in the crystal.

C. DIFFUSE SCATTERING OF X-RAYS FROM CRYSTALS

Theories of diffuse scattering

In connection with his theoretical investigation of the effect of temperature on the intensity of x-rays regularly reflected from crystals Debye was lead to predict that the regular Bragg reflection should be accompanied by a diffuse scattering in all directions, and that the intensity of this diffuse scattering should be a function of the temperature proportional to $(1-e^{-M})f^2$, where M has the value given by Eq. (12).

In 1922 Jauncey[87] scattered x-rays from rock salt and found that the intensity of the diffusely scattered radiation was greater than Debye's theory predicted, and also that the intensity varied much more slowly with the temperature than indicated by the above relation.

Recently, Jauncey and Woo have independently derived a theory for the diffuse scattering which seems to be in good accord with experiment. Jauncey[88] has developed a general theory for the scattering from solids from classical considerations, and obtains an expression for the diffuse scattering which involves a complicated summation which has not been evaluated for the general case. Jauncey and Harvey[89] have evaluated the above mentioned summation for the case of a simple cubic crystal consisting of atoms of one kind, and obtain for the scattering per electron

$$S = 1 + (Z-1)\frac{f^2}{Z^2} - \frac{F^2}{Z}, \tag{46}$$

where f is the atomic structure factor for the atom at rest* and $F=e^{-M}f$, using Waller's modification of Debye's theory.

Woo[90] has arrived at the same expression in which, however, he has included the Breit-Dirac correction factor. He considers that the expression developed by Debye gives correctly the coherent part of the diffusely scattered intensity when the Waller modification is introduced in the temperature factor, but that an incoherent term must also be included. Since the incoherent part of the expression involves no interference effects he concludes that this term can be taken directly from the expression of Compton for scattering by a single atom. Adding the incoherent and coherent terms and correcting the latter by the Breit-Dirac factor he obtains the equation

$$S = \left[\left(1 - e^{-2M}\right)\frac{f^2}{Z} + \frac{1-\dfrac{f^2}{Z^2}}{(1-\gamma\ \mathrm{vers}\ \phi)^3}\right], \tag{47}$$

which reduces to Jauncey's expression if the correction factor is omitted.

Intensity measurements of diffusely scattered x-rays

In 1924 Jauncey and May[91] made measurements of the diffuse scattering of x-rays from rock salt. The apparatus was arranged in a manner similar to that shown in Fig. 2b, except that a single crystal was used. The general rad-

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* Eq. (44) was given by Jauncey in the form $S=1+(Z-1)(f'^2/Z^2)-(F^2/Z)$ where f' is equal to the true atomic structure factor, f, only if the scattering by all the electrons in the atom is the same. In any case the f of Eq. (44) is the same as that of Compton's Eq. (30) for scattering by a gas and since it has not as yet been possible experimentally to detect any difference between f and f' the f of Eq. (44) has been defined as the true atomic structure factor.

iation from a molybdenum x-ray tube was filtered through sufficient aluminum to obtain an effectively homogenous beam of wave-length $\lambda = 0.40$A. The ionization chamber was placed at an angle ϕ and intensity measurements were made for various angles θ of the crystal in the region of $\theta = \phi/2$. In this way a Laue spot was superimposed on the background of diffuse scattering as shown in Fig. 30. The diffuse scattering at $\theta = \phi/2$ was determined by interpolation as shown by the circle in the figure. By obtaining the diffuse scattering in this way the relation between the intensity and the scattering angle is much simpler than if an arbitrary value of θ were used. If one solves directly for S, the scattering per electron, the Crowther formula takes the form

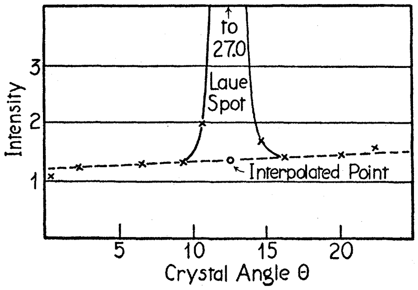

Fig. 30. Method of obtaining diffuse scattering at $\theta = \phi/2$, G. E. M. Jauncey and H. L. May. (Reference 71).

$$S = \frac{I_\phi}{I_\phi' t \sec\theta \dfrac{Npd}{W} \dfrac{e^4}{2R^2m^2c^4}(1 + \cos^2\phi)}, \tag{48}$$

where I_ϕ is the scattered intensity at a distance R from the crystal, I_ϕ is the intensity of the primary beam after traversing the crystal when it is oriented at $\theta = \phi/2$, t is the thickness of the crystal, N is Avogadro's number, p is the number of electrons per molecule, d is the density of the crystal, W is its molecular weight and e, m and c have their usual significance.

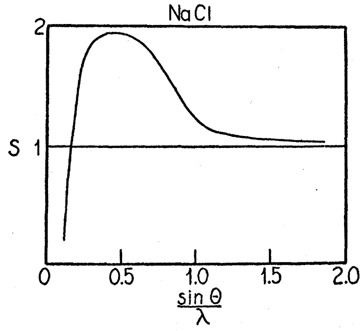

Fig. 31. S-curve for diffuse scattering from NaCl. G. E. M. Jauncey and G. G. Harvey (Reference 89).

The value of I_ϕ' was measured directly by Jauncey and May by allowing the primary beam to enter the ionization chamber for a very short time. The S curve which they obtained for rock salt is shown in Fig. 31.

Recently, Harvey[92] has made similar measurements of the intensity of x-rays diffusely scattered by sylvine. The method used was essentially the same as that used by Jauncey and May except in the method of measuring the intensity of the primary beam. Relative values of S were first measured and then the data were standardized by comparing the intensity of diffuse scattering with the scattering from a block of paraffin, a method which is essentially the same as that used by the author for gases. The values of S obtained in this way are represented by the lower curve in Fig. 34.

Calculation of the structure factor

If the crystals of rock salt and sylvine are assumed to be simple cubic having atoms of only one kind, the theory of Jauncey and Woo can be used for determining the structure factor, f, for the atom at rest. Since, however, the theory involves also the values of $F=e^{-M}f$, measurements of the diffuse scattering at room temperature alone are not sufficient to determine f unless, the exponent, M, of the temperature factor is previously known. However it is possible to determine f without any knowledge of the effects of temperature on the reflecting power of the crystal if measurements of the structure factor, F, and the diffuse scattering, S, are made at the same temperature.

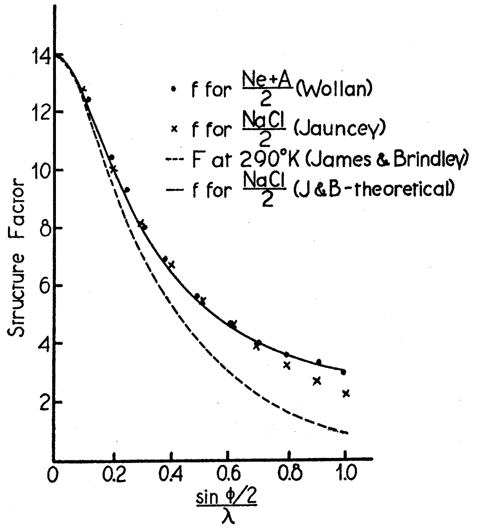

Fig. 32. Structure factor curves. G. E. M. Jauncey. (Reference 93).

Using the values of F as measured by James and Miss Firth, Jauncey[93] has calculated from the intensities of diffuse scattering from rock salt the average structure factor curve for the Na^+ and Cl^- ions, and has compared the results with the corresponding theoretical curve calculated by Waller and James from wave mechanics, and also with the average of the structure factor curves for neon and argon as determined by the author. These curves are shown together in Fig. 32. The curves from wave mechanics and the experiments on gases are in good agreement as would be expected from previous comparisons. The curve from Jauncey's measurements is in good agreement with the others except at large values of $(\sin\phi/2)/\lambda$, where it is considerably lower. Part of this difference is to be expected since no account is made by Jauncey for the effect of the Breit-Dirac factor on the incoherent part of the radiation. The fact that rock salt is not a simple cubic crystal of atoms of one kind as has been assumed in deriving Eqs. (46) or (47) may also account for part of the difference.

The objections which have been just mentioned in regard to the measurements on rock salt should be of little significance in connection with Harvey's data for sylvine. This crystal is approximately simple cubic and the atoms are sufficiently heavy to make the Breit-Dirac correction smaller than the experimental errors. Harvey has calculated the values of f by combining his diffuse scattering measurements with the regular reflection data of James and Brindley according to Eq. (46) and has compared the results with the scattering from argon. These curves are shown together with other data in Fig. 33 and the agreement is seen to be reasonably satisfactory.

The effect of temperature on the diffuse scattering of x-rays by crystals

According to Debye's original prediction that the intensity of the x-rays diffusely scattered from a crystal should be proportional to $(1-e^{-M})f^2$, one sees that a decrease in temperature produces a decrease in the intensity of the scattered radiation, an effect which is opposite to that observed for the case of regular reflection from crystals. It can also be seen that according to Debye's theory the diffuse scattering should approach zero as the amplitude of thermal vibration of the atoms approaches zero.

According to Jauncey's early measurements of the effect of temperature on the intensity of the diffuse scattering, the decrease of the intensity with decreasing temperature was not as great as the above theory indicates even if the Waller modification is introduced. In the newer theory of scattering, Eqs. (46) or (47), an additional term has been introduced which accounts for the intensity of scattering from the atoms of the crystal when they act independently of each other, a term which is independent of the temperature, and hence the smaller temperature effect which is experimentally observed is at least qualitatively account for.

According to the theory the exponent, M, of the temperature factor as determined by measurements of the diffuse scattering at various temperatures should be identical with that obtained from intensity measurements of x-rays regularly reflected from crystals, in the range of low temperatures where the theory seems to be valid. Recently, measurements of the intensity of diffuse scattering as a function of temperature have been made by Claus[94] for rock salt and by Jauncey and Harvey[95] for Sylvine. The values of the temperature factor obtained by these investigators are not in good agreement with those which James and his collaborators have obtained from measurements of the intensity of x-rays regularly reflected from crystals. It is difficult to see how such a discrepancy can be accounted for. The values of *M* which have been measured by James and his collaborators are in every case in good accord with the values calculated by the Debye-Waller theory from the constants of the crystal. When the temperature factor is used to calculate the structure factors of the atom at rest assuming zero point energy the results are in good accord with similar values obtained from the scattering of x-rays by gases and also theoretical structure factors calculated from Hartree's electron distribution curves.

Further, if one combines the data of diffuse scattering with the regular reflection data according to Eq. (47), values of the structure factor of the atom at rest are obtained which are in good accord with values of the structure factors obtained by other methods.

Due to the uncertainties which exist in these measurements it is probably better to leave the discussion of these data until a more thorough experimental study of the effect has been made.

D. Comparison of Various Methods of Obtaining Atomic Structure Factors

We have seen in part A how measurements of the intensity of x-rays regularly reflected from crystals have been satisfactorily treated from a theoretical point of view, and hence how it is possible to obtain values of the structure factor for the atoms of which the crystals are composed. When the structure factor data thus obtained are analyzed by means of Fourier series or integrals one obtains information regarding the disposition of the electrons about the nucleus of the atom. When the intensities are measured at room temperature the electron distribution curves thus obtained correspond to a diffuse picture of the atom, due to the fact that they are in constant thermal vibration about their mean positions.

The theories relating the temperature of the crystal have made it possible to obtain structure factor data for the atom at rest from measurements of the reflected intensity at various temperatures when certain quite justifiable assumptions are made. One is then able to obtain a picture of the atom at rest from measurements of this type.

The more recently developed theory for the scattering of x-rays by individual atoms discussed in part B has made it possible to obtain atomic structure factors by an entirely independent method. In this case measurements are made of the intensity of x-rays scattered by gases, and since the interference effects take place only between the various electrons of the atom, the intensity is independent of thermal vibration. Hence one obtains directly the structure factors corresponding to the atom at rest. From measurements of this type then it is possible to obtain the distribution of the electrons for an atom at rest, and one would expect the results to be in accord with similar ones obtained from measurements of the intensity of x-rays regularly reflected from crystals. The fact that these two types of experiments do give results which are in good accord gives confidence in the theories of scattering from which the calculations have been made.

A third method of obtaining the atomic structure factors results from measurements of the diffuse scattering of x-rays from crystals as discussed in part C. In this case one is also able to obtain the structure factor of the atoms at rest if the temperature factor is known, or if the diffuse scattering data are combined with measurements of regular reflection at the same temperature.

We thus have three entirely independent methods of obtaining the atomic structure factors from which calculations of the electron distribution of these atoms can be made.

Data are available for comparing the structure factors calculated by these three methods. The intensity of x-rays regularly reflected from crystals have been measured at various temperatures for sylvine from which the average

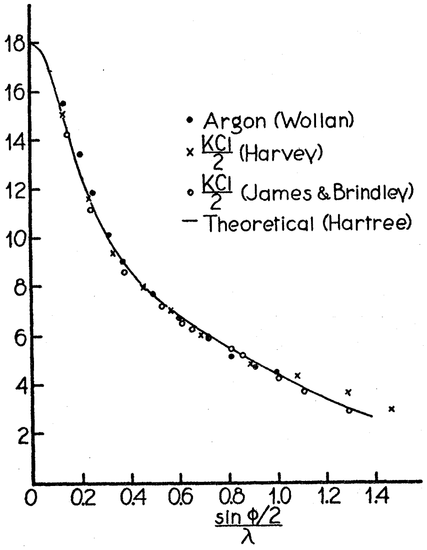

Fig. 33. Structure factor data obtained by various methods.

structure factor for the K^+ and Cl^- ions at rest can be determined. Measurements of the scattering of x-rays from argon gas give the structure factor of the argon atom at rest which should be approximately identical with the average structure factor for the K^+ and Cl^- ions. Combining the data for diffuse scattering from sylvine with the structure factors determined from regular reflection from crystals one obtains another independent determination of f.

Fig. 33 shows a comparison of the structure factors for the atom at rest obtained by these three types of experiments. The agreement is seen to be very good except for a couple of points at large values of $(\sin\phi/2)/\lambda$.

The solid line in the figure is the theoretical structure factor curve for the average K^+ and Cl^- ions as calculated by James and Brindley according to Hartree's method of self-consistent fields. This curve can also be seen to be in good accord with the experimental data. The more approximate method of calculating structure factors due to Thomas and Fermi is also in good agreement with the other values for the case of an atom as heavy as the one considered. This method does not give accurate results for lighter elements and at large angles and has not been included in the figure.

From the curves in Fig. 33 one sees that four independent methods of obtaining the structure factor of an atom give results which are in agreement within experimental error, and one feels justified in concluding that the theories of x-ray scattering have been developed to a satisfactory state and thus a reasonably accurate knowledge of the distribution of the electrons within an atom can be obtained.

An empirical relation

A very interesting relation between the three types of experiments which have been discussed has been pointed out by Jauncey[96] in connection with Eq. (46) for the diffuse scattering. An inspection of this equation and Eq. (30) for the scattering of x-rays by gases will show that one can write

$$S_g = S_c + \frac{F^2}{Z}, \tag{49}$$

where S_c is the scattering per electron as measured by the diffuse scattering from a crystal, S_g is the scattering from the same atoms in the gaseous state,

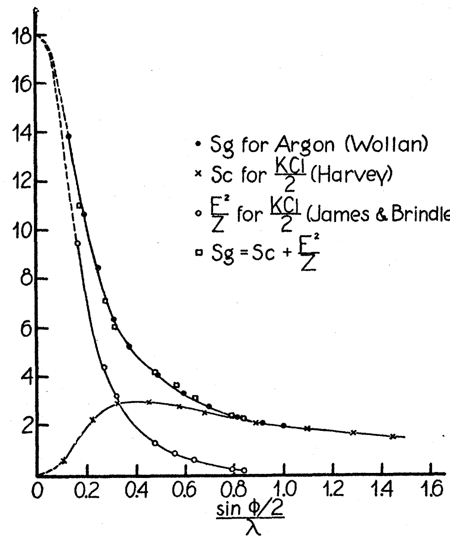

Fig. 34. Scattering curves for gases and crystals.

and F is the structural factor obtained from measurements of regular reflection from the crystal at the same temperature at which S_c has been measured. This equation then gives a relation between the results of the three type of experiments discussed above. If we assume again that argon is a good approximation to gaseous KCl, data are available to check this relation. In Fig. 34 three curves are plotted, namely: the scattering by argon, the diffuse scattering by sylvine and the quantity F^2/Z as determined from crystal reflection from sylvine at room temperature.

According to Eq. (49) the values of S_g determined by adding the two lower curves should agree with the measured scattering by argon. The squares represent the values which have been calculated in this way, and the agreement with the upper curve is seen to be very satisfactory.

CONCLUDING REMARKS

It has been the aim in this paper to give a summary of the results of some of the most important theoretical and experimental investigations of the intensity of scattered x-rays as related to the determination of the structure factors and the electron distribution of atoms.

A thorough discussion of the theory of the regular reflection of x-rays from crystals and its relation to the determination of structure factors and electron distribution curves is given by Compton in his book "X-rays and Electrons". Many of the equations in part A of the present paper are taken in the exact form in which he has given them.

A review of this part of the subject has also been made by W. L. Bragg in a Report of the Solvay Conference 1928.

The more recent theoretical and experimental investigations of the intensity of x-rays scattered by gases and the diffuse scattering from crystals have given results which are so closely related and which are in such good agreement with those obtained from measurements of the intensity of x-rays regularly reflected from crystals that it has seemed desirable to make a more complete review of the field.

Several phases of the problem of x-ray scattering which are not so directly related to the structure of the atom have not been considered. A brief review of the scattering of x-rays by liquids has already been given by Stewart in an earlier issue of this Journal. The scattering of x-rays by gases with the view of determining the arrangements of atoms in molecules has been studied by Debye and Bewilogua, and the results of these investigations is summarized to some extent in a lecture by Debye (Proc. Phys. Soc. **42,** 340 (1930)) and Bewilogua's dissertation (Phys. Zeits. **32,** 365, (1931)).

An interesting result of the experimental and theoretical work which has been discussed in this paper is the good agreement which seems to exist between the structure factor data which has been determined from x-ray measurements and the theoretical values of the structure factor as determined from the charge distribution in the atom as calculated by Hartree's method of self-consistent fields. This means that when the structure factor for an atom is desired for purposes of crystal analysis or otherwise a calculation can be made with considerable reliance on the results. This is not the easiest thing to do, however, since each calculation of this type is a very laborious process. However, James and Brindley (Phil. Mag. **12,** 89 (1931)), have recently published a review of the problem of determining structure factors in this way.

They have shown how the structure factor for most of the light atoms can be determined by interpolation from the values which have already been calculated. For the heavy elements the approximate method of calculating the structure factors due to Thomas and Fermi give results which are in good accord with the experiment.

In conclusion, the writer wishes to thank Professor A. H. Compton for the helpful criticisms and suggestions which he has given.

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C. Diffuse scattering of x-rays from crystals

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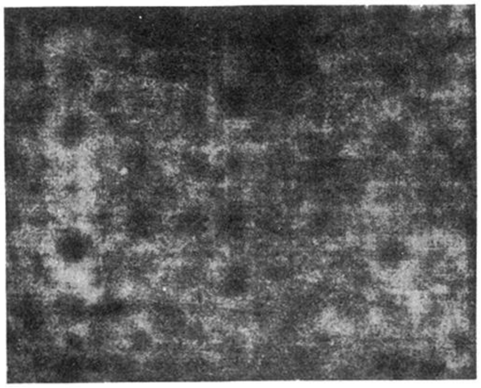

Fig. 15. Photograph of the projection of the electron density in a diopside crystal on the (100) face. W. L. Bragg. (Reference 53).