

THE PHYSICAL REVIEW

A Journal of Experimental and Theoretical Physics

VOL. 43, No. 7

APRIL 1, 1933

SECOND SERIES

Scattering of X-Rays from Powdered Crystals

G. E. M. JAUNCEY* AND FORD PENNELL, *Department of Physics, Washington University*

(Received February 9, 1933)

When monochromatic x-rays are scattered by a powdered crystal, the scattered rays consist partly of those rays which are scattered in special directions and which give rise to the Debye-Scherrer circles in a photograph and partly of those rays which are diffusely scattered and which give rise to the background between the circles. If the scattered rays from a powdered crystal enter a wide window of an ionization chamber, the intensity of the rays per unit solid angle is an average for several Debye-Scherrer circles and the diffuse background between the circles. Coven has experimentally examined this "average scattering" for the case of monochromatic x-rays, but his results are inconclusive. In our experiments we have used not only a wide window (the extreme angular width of the rays entering the window was 6°) but also a wide band of wave-lengths obtained by passing the x-rays from a tungsten target x-ray tube operated at 54.9 kv through 3.25 mm of aluminum or its equivalent. The spectral distribution of the intensity of these rays was obtained by reflection from rocksalt. The scattered intensities at average angles varying from 5° to 90° from powdered crystal brickettes of KCl, CaS, NaF and MgO were compared with the scattered intensity at 90° from paraffin. From

Jauncey and Harvey's theory of the diffuse scattering from crystals together with the theory of the intensity of the Debye-Scherrer circles, a formula has been obtained for the ionization current produced by the rays entering a narrow window and consisting of a wide band of wave-lengths of known intensity distribution. This formula was then integrated graphically so as to obtain theoretical values for the case of a wide window. The calculation of the theoretical values involves f and f' values. James and Brindley's f values as obtained from wave mechanics were used. Values of f' were calculated from data given in James and Brindley's paper and are tabulated for F^- , Na^+ , Cl^- , K^+ , neon and argon. Excellent agreement between the theoretical and experimental values of the scattered intensity is shown over the whole range of average angles of scattering for each of the crystals. It is shown that, in experiments on the diffuse scattering of x-rays by crystals, an average wave-length as determined by absorption in aluminum may to a fairly close approximation be treated as if it were a single wave-length and so the S curves obtained for KCl by Harvey and for NaF by Jauncey and Williams are reasonably accurate.

I. INTRODUCTION

ACCORDING to the theory as it has been developed by Jauncey, Harvey and Woo^{1, 2, 3, 4, 5} the intensity of the x-rays diffusely

* The senior author was aided in part by a grant from the Rockefeller Foundation to Washington University for research in science.

¹ G. E. M. Jauncey, *Phys. Rev.* **37**, 1193 (1931).

² G. E. M. Jauncey and G. G. Harvey, *Phys. Rev.* **37**, 1203 (1931).

³ G. E. M. Jauncey, *Phys. Rev.* **42**, 453 (1932).

⁴ Y. H. Woo, *Phys. Rev.* **38**, 6 (1931).

⁵ Y. H. Woo, *Phys. Rev.* **41**, 21 (1932).

scattered from a crystal consisting of atoms of one kind is given by

$$S = S_1 + S_2 / (1 + \alpha \text{vers } \phi)^3, \quad (1)$$

where

$$S_1 = (f^2 - F^2) / Z \quad (2)$$

and

$$S_2 = 1 - f'^2 / Z^2. \quad (3)$$

Furthermore, the intensity of the x-rays scattered from a monatomic gas is given by Eqs. (1) and (3) together with

$$S_1 = f^2 / Z. \quad (4)$$

For the definitions of the various quantities in Eqs. (1) to (4) the reader is referred to Jauncey's paper.³ Jauncey and Harvey⁶ have further shown that the intensity of the x-rays scattered by an inert gas is related to the intensities of the x-rays diffusely scattered and regularly reflected from the corresponding crystal by the formula

$$S_{\text{gas}} = (S + F^2/Z)_{\text{crystal}}. \quad (5)$$

The experimental S and F values for the right side of Eq. (5) have been obtained in different experiments and in different laboratories. It would be an advantage to devise an experiment in which at one and the same time the values of the sum of S and F^2/Z could be obtained. In a private discussion with A. H. Compton it developed that this might be accomplished by scattering the x-rays from a powdered crystal and by using a wide window in front of the ionization chamber so as to collect arcs of several Debye-Scherrer circles together with the diffuse scattering in between the circles. Following Compton's suggestion Coven⁷ has scattered monochromatic x-rays of wave-length 0.71Å from powdered crystals of KCl, NaF and MgO. Using Coven's notation we shall represent the sum of the intensities of the diffuse scattering and of the Debye-Scherrer diffraction circles by S_t and shall call this the total scattering. Coven found that the relation

$$S_t = S_{\text{gas}} \quad (6)$$

holds very well for KCl and argon but does not hold nearly so well for NaF or MgO and neon, the S_{gas} values for argon and neon being those obtained by Wollan.⁸

Since the conclusions to be drawn from Coven's experimental findings are uncertain and since the theory given in his paper is somewhat inadequate, we have again attacked the problem of the total scattering from powdered crystals from both the experimental and theoretical sides. Furthermore, the essential point of Compton's suggestion is that x-rays for a band of values of $(\sin \frac{1}{2}\phi)/\lambda$ enter the window of the ionization chamber for a given setting of the spectrometer.

This may be accomplished by using (1) a wide chamber window with a single wave-length, (2) a narrow window with a wide band of wave-lengths, or (3) a wide window together with a wide band of wave-lengths. Coven used the first method, while in the research to be described we have used the third method. We have measured the total scattering from powdered crystals of CaS, KCl, MgO and NaF.

II. EXPERIMENTAL METHOD

A specimen of the substance to be examined was finely powdered and pressed into a brickette in the hollow of a brass ring. The ring containing the brickette was then mounted on the axis of an x-ray spectrometer. In the case of both CaS and MgO, waterproof cellophane was sealed over the two faces of the brass ring to prevent CO₂ and moisture from coming in contact with the sample and decomposing it. The general radiation from a tungsten tube was used to illuminate the brickette. The scattered rays were then measured by means of an ionization chamber and electrometer.

An oil immersed x-ray outfit employing the balanced circuit as described by Bennett⁹ was used to give a constant source of radiation. For reasons of convenience, the x-ray tube was mounted directly in front of the oil tank in a lead box. The maximum excitation potential as determined experimentally by the Duane-Hunt¹⁰ relation was 54,900 volts and the current through the tube was 8.1 milliamperes. The ionization chamber was 35.2 cm long and was filled with methyl bromide at 74 cm pressure at a temperature of 22°C. The diameter of the chamber was such that the x-rays travelled the whole length of the chamber without hitting the sides. The window was made of thin glass.

The readings at an angle ϕ were made as follows: The paraffin was set at an angle of 45° to the main beam between the x-ray tube and the powdered crystal brickette which was mounted on the spectrometer axis in the Crowther¹¹ position. The scattered intensity was measured at an angle ϕ . The brickette and the paraffin were

⁶ G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1071 (1931).

⁷ A. W. Coven, Phys. Rev. **41**, 422 (1932).

⁸ E. O. Wollan, Phys. Rev. **37**, 862 (1931).

⁹ R. D. Bennett, N. S. Singrich and W. C. Pierce, Rev. Sci. Inst. **2**, 226 (1931).

¹⁰ W. Duane and F. L. Hunt, Phys. Rev. **6**, 166 (1915).

¹¹ J. A. Crowther, Proc. Roy. Soc. **A86**, 478 (1912).

then interchanged. The ionization chamber was moved to 90° and the scattered intensity from the paraffin measured. The reason for this procedure is that the intensity of the primary beam penetrating the substance in the scattering position is the same irrespective of whether the paraffin or the crystal brickette is in that position.

In a preliminary experiment, the crystal brickette was removed and the paraffin slab set so as to scatter x-rays into the ionization chamber at an angle of 30° . Sheets of aluminum were placed between the paraffin and the x-ray tube and the logarithm of the intensity of the x-rays entering the chamber was plotted against the thickness of the aluminum. For thicknesses of aluminum greater than 3.25 mm the graph as shown in Fig. 1 becomes a straight line. In the

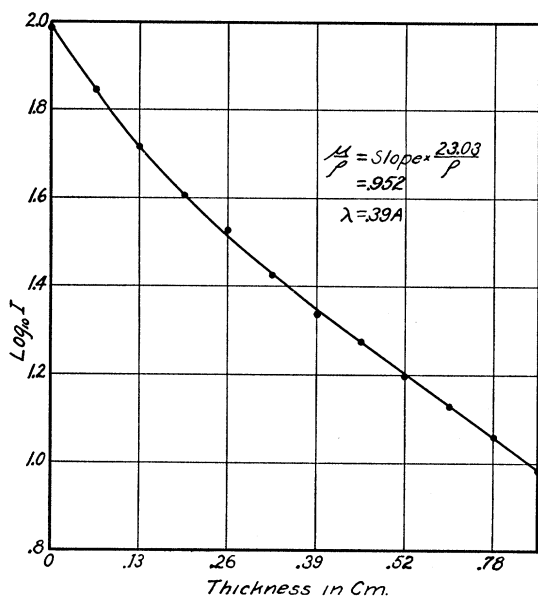


FIG. 1. Absorption in aluminum.

actual scattering experiments, a thickness of aluminum was placed in the main beam such that the absorption in the aluminum plus that in the crystal brickette and that in the paraffin slab was equal to the absorption in 3.25 mm of aluminum. The mass absorption coefficient in aluminum for the straight portion of the graph in Fig. 1 is 0.952 per g/cm². Using Compton's tables,¹²

¹² A. H. Compton, *X-Rays and Electrons*, p. 184.

this corresponds to a wave-length of 0.39A. However, we have not used this average wave-length in the way described by Harvey¹³ and by Jauncey and Williams¹⁴ but have instead obtained the distribution of the energy in the spectrum of the x-rays which have passed through 3.25 mm of aluminum.

The energy distribution with respect to wave-length was obtained in a separate experiment. We reflected the x-rays from a (1, 0, 0) face of a single crystal of rocksalt into the same ionization chamber as was used in the scattering experiment. The integrated intensity¹⁵ of x-rays of wave-length λ as reflected by a mosaic crystal is given by

$$\frac{W\omega}{I} = n^2 \frac{A\lambda^3 F^2}{4\mu} \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta}, \quad (7)$$

where θ is the glancing angle for the reflected rays. Eq. (7) holds for monochromatic rays when the crystal is rotated at an angular speed ω . W is the total energy reflected into the ionization chamber while the crystal is being turned through a reflection position for the wave-length λ . The purpose of the rotation of the crystal is to bring all the minute crystals of the mosaic crystal into the reflection position. However, when the continuous spectrum is being analyzed the difference in the orientations of the minute crystals of the mosaic causes wave-lengths of a range λ to $\lambda + d\lambda$ to be reflected and consequently each minute crystal is able to find some wave-length to reflect when the face of the large crystal is set at a glancing angle θ with the primary beam. Hence, at least approximately,

$$W = \text{const.} \times (I\lambda^3 F^2 / \mu)(1 + \cos^2 2\theta) / \sin 2\theta, \quad (7a)$$

where W is the intensity of the x-rays in the wave-length range λ to $\lambda + d\lambda$ reflected into the ionization chamber, μ is the absorption coefficient of rays of wave-length λ in the crystal and F is the atomic structure factor for the crystal. F is a function of $(\sin \theta) / \lambda$. We have used the F values for rocksalt as given by James and Firth.¹⁶ The

¹³ G. G. Harvey, *Phys. Rev.* **38**, 593 (1931).

¹⁴ G. E. M. Jauncey and P. S. Williams, *Phys. Rev.* **41**, 127 (1932).

¹⁵ See reference 12, p. 128.

¹⁶ R. W. James and E. M. Firth, *Proc. Roy. Soc.* **A117**, 62 (1928).

values of μ used were those for the ordinary absorption coefficient in rocksalt. We made no attempt to correct for extinction. After obtaining values of W , Eq. (7a) was solved for I , the intensity of the x-rays in the range λ to $\lambda+d\lambda$ existing in the primary beam. Values of I were then plotted against λ . Next, it was necessary to correct for second and third order reflection of

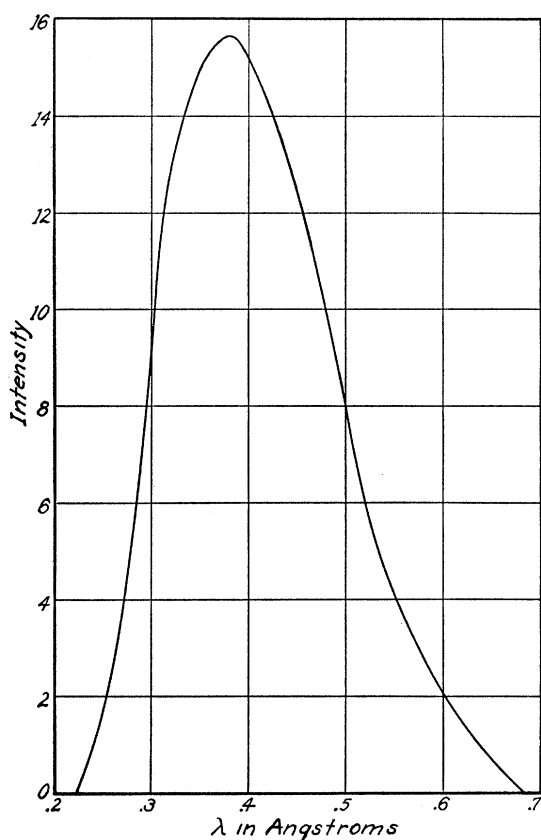


FIG. 2. Distribution of the intensity in the continuous spectrum. For ease in calculation the curve is drawn to meet the wave-length axis at $\lambda=0.68\text{\AA}$.

x-rays. The shortest wave-length present was 0.225\AA , so that second order reflection began at an apparent wave-length of 0.450\AA . For reflection from a given set of planes in a given crystal—for instance, the (1, 0, 0) planes— F is a function of the order of reflection. Hence, knowing the value of I as calculated from the first order reflection of, say, $\lambda=0.30\text{\AA}$, the values of W for the second order reflection of $\lambda=0.30\text{\AA}$

can be obtained from Eq. (7a). This value is subtracted from the experimental value of W found for a value of θ corresponding to first order reflection of $\lambda=0.60\text{\AA}$. The remaining value of W is for a value of θ corresponding to first order reflection of $\lambda=0.60\text{\AA}$. Also at $\lambda=3\times 0.225=0.675\text{\AA}$ third order reflection begins and a further correction must be made. The final corrected curve for the spectral distribution is shown in Fig. 2. It should be noted that this curve is for the spectral distribution of the x-rays as absorbed in the ionization chamber. The mass of the methyl bromide in the chamber is not sufficient to absorb completely x-rays of all the wave-lengths in the spectrum. However, the same ionization chamber was used as in the scattering experiments. The scattered rays of various wave-lengths are absorbed to the same extent in the methyl bromide as the reflected rays of the same wave-lengths in the spectral distribution experiment. We shall see later that the spectral distribution as measured by absorption in the chamber is all we need to know.

As previously mentioned, Harvey¹³ and Jauncey and Williams¹⁴ in their experiments measured the absorption coefficient of the x-rays in aluminum and from this coefficient determined the average wave-length and then used this average wave-length as if it were the wave-length of monochromatic x-rays. From the spectral distribution curve of Fig. 2, the average wave-length was found to be 0.41\AA , while the absorption coefficient obtained from the straight portion of the curve of Fig. 1 leads to an average wave-length of 0.39\AA . We submit that the agreement of these two average wave-lengths is reasonably good. We shall return later to the question of the use of an average wave-length as if it were a monochromatic wave-length.

III. FORMULAS FOR CALCULATION

Referring to the paper by Jauncey and Williams,¹⁴ we see that the energy of ionization produced per second is not equal to the rate of flow of x-ray energy into the ionization chamber unless all of the x-rays are absorbed in the gas of the chamber. When the absorption is incomplete, the situation is expressed by Eq. (20) of the above

paper. Then, eliminating s_1 and s_2 by means of Eqs. (21) and (22) of that paper, we obtain

$$C_\phi = \frac{ACt}{R^2 \cos \frac{1}{2}\phi} \cdot \frac{NZ\rho}{W} \cdot \frac{e^4}{m^2c^4} \cdot \frac{1 + \cos^2 \phi}{2} \cdot \left\{ S_1 + \frac{S_2 K_\phi T_\phi}{K_0(1 + \alpha \text{vers } \phi)^3} \right\}, \quad (8)$$

where C_ϕ and C are the ionization currents produced respectively by the scattered and the transmitted rays, S_1 and S_2 are respectively the coherent and incoherent scattering factors, K_0 and K_ϕ are respectively the fractions of the coherent and incoherent rays absorbed in the chamber, T_ϕ is a quantity introduced by Jauncey and DeFoe¹⁷ into the Crowther¹¹ formula for scattering by a slab in order to take account of the extra absorption of the incoherent scattered rays in the slab itself, A is the area of the ionization chamber window, and R the distance of the window from the scattering slab.

Eq. (8) is for a given wave-length. However, in

our experiments we used the band of wave-lengths shown in Fig. 2. The intensity in the range $d\lambda$ at λ is $I(\lambda)d\lambda$ where $I(\lambda)$ is proportional to the ordinate of the graph and hence we replace C in the right side of Eq. (8) by $I(\lambda)d\lambda$. Also we shall write the left side in the form $C_\phi d\lambda$ because $C_\phi d\lambda$ is the ionization current produced by the scattered rays which are due to the primary rays in the range $d\lambda$ at λ . To obtain the ionization current D_ϕ when the whole spectrum of wave-lengths is scattered, we integrate over all wave-lengths present in the primary beam. Several of the quantities on the right side of Eq. (8) are not functions of λ and so we obtain

$$D_\phi = \frac{A}{R^2} \cdot \frac{NZ\rho t}{W} \cdot \frac{1 + \cos^2 \phi}{2 \cos \frac{1}{2}\phi} \cdot \frac{e^4}{m^2c^4} \cdot \int \left\{ S_1 + \frac{S_2 K_\phi T_\phi}{K_0(1 + \alpha \text{vers } \phi)^3} \right\} I d\lambda. \quad (9)$$

For the wave-lengths used the x-rays scattered by paraffin at 90° were almost entirely incoherent, as pointed out by Harvey¹³ and Coven.⁷ Consequently for scattering from paraffin at 90° we obtain an equation similar to Eq. (9), but with $S_1=0$ and $S_2=1$. We shall prime (') those quantities in this equation which specifically refer to paraffin. Then, dividing Eq. (9) for the crystal by the similar equation for paraffin, we obtain

$$\frac{D_\phi}{D'_{90^\circ}} = \frac{Z\rho t W'}{Z'\rho't'W} \cdot \frac{(1 + \cos^2 \phi) \cos 45^\circ}{\cos \frac{1}{2}\phi} \cdot \frac{B}{B'}, \quad (10)$$

where B is an integral for the crystal and B' is the corresponding integral for the paraffin.

We shall now consider B' , where

$$B' = \int \frac{K'_{90^\circ} T'_{90^\circ}}{K_0(1 + \alpha)^3} I d\lambda. \quad (11)$$

According to Jauncey and Williams,¹⁴

¹⁷ G. E. M. Jauncey and O. K. DeFoe, Phil. Mag. 1, 711 (1926).

$$T = (1 - e^{-g})/g, \quad (12)$$

where

$$g = (\mu_2 - \mu_1)t / \cos \frac{1}{2}\phi \quad (13)$$

and μ_2 and μ_1 are the linear absorption coefficients of the incoherent and coherent scattered rays, respectively, in the scattering slab. The value of $\rho't'$ for the paraffin slab was 0.439 g/cm^2 . From Compton's absorption tables¹² we have calculated the absorption coefficient of paraffin for various wave-lengths. Putting values in Eqs. (12) and (13) we find that T'_{90° varies from 0.990 to 1.000 over the range of wave-lengths 0.7A to 0.2A and so may be regarded as practically a constant whose value is 0.995. If μ_1 is the absorption coefficient of wave-length λ and μ_2 that of wave-length $\lambda + \delta\lambda$ in methyl bromide, the fractions absorbed are

$$K_0 = 1 - e^{-\mu_1 t} \quad (14)$$

and

$$K_{90^\circ} = 1 - e^{-\mu_2 t}, \quad (15)$$

where t is the length of the gas in the ionization chamber. The change of wave-length $\delta\lambda$ is

0.0242A, the Compton change at 90°. Consider the quantity

$$y = K_{90^\circ}/K_0(1+\alpha)^3. \quad (16)$$

The graph of y plotted against λ is shown in Fig. 3 and it is seen that y has the practically constant value of 0.884 over the range $\lambda=0.25A$ to $\lambda=0.65A$, which is the range of the wave-lengths of appreciable intensity in the spectrum, as shown in Fig. 2. Hence the factor of I in the integrand of the right side of Eq. (11) is constant with respect to the wave-length and so may be

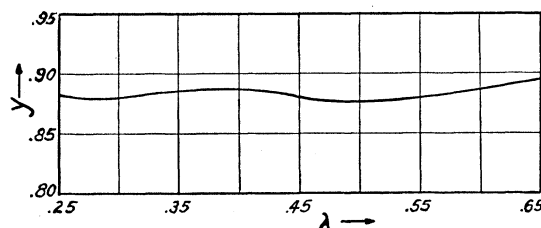


FIG. 3. Graph of $K_\phi/K_0(1+\alpha)^3$ against wave-length.

taken outside of the integral sign and we have $B' = 0.880 \int I d\lambda$. Solving Eq. (10) for $B/\int I d\lambda$, we obtain

$$\int \left\{ S_1 + \frac{S_2 K_\phi T_\phi}{K_0(1+\alpha \text{ vers } \phi)^3} \right\} I d\lambda / \int I d\lambda = 0.314 \times \frac{D_\phi}{D'_{90^\circ}} \cdot \frac{\cos \frac{1}{2}\phi}{1 + \cos^2 \phi} \cdot \frac{W}{Z \rho t} \quad (17)$$

after putting in numerical values. For convenience we shall denote the value of the right side of Eq. (17) when experimental values are inserted by S_{exp} . It is interesting to note that this same numerical formula for S_{exp} is obtained if either of the average wave-lengths mentioned in the last paragraph of §2 had been used.

IV. EXPERIMENTAL RESULTS

Values of the experimental ratio D_ϕ/D'_{90° for the respective powdered crystals were obtained and substituted in the right side of Eq. (17) and the corresponding values of S_{exp} calculated. These values of S_{exp} are shown in Tables I and II. The values of the mass per unit area of the

TABLE I. Total scattering from powdered crystals of KCl and CaS. Values of D_ϕ/D'_{90° and S_{exp} .

KCl						CaS					
ϕ	$\sin \frac{\phi}{2}$	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}	ϕ	$\sin \frac{\phi}{2}$	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}
5.0°	0.044	2.64	3.97			18°	0.156	3.27	5.10	3.22	4.36
6.0°	.052	5.02	7.59			20°	.174			2.87	3.92
7.0°	.061	6.51	9.85			22°	.191			2.78	3.83
7.5°	.065			6.00	7.95	24°	.208	2.29	3.67	2.41	3.36
8.0°	.070	6.72	10.19	6.36	8.39	30°	.259	1.80	2.99	1.99	2.87
8.5°	.074	6.89	10.46	6.60	8.70	36°	.309	1.44	2.50	1.59	2.39
9.0°	.078	6.67	10.15	6.80	8.96	42°	.358	1.13	2.05	1.32	2.07
9.5°	.083	6.56	9.96	6.60	8.70	48°	.407	0.948	1.80		
10.0°	.087	6.05	9.20	6.49	8.57	54°	.454	0.773	1.54	0.876	1.52
10.5°	.092	5.71	8.71			60°	.500	0.656	1.37		
11.0°	.096	5.75	8.77	5.95	7.88	66°	.545	0.632	1.31	0.707	1.33
12.0°	.105	5.15	7.85	5.37	7.13	72°	.588	0.505	1.12		
14.0°	.122			4.45	5.94	78°	.629	0.510	1.14	0.599	1.16
15.0°	.131	3.94	6.09			84°	.669	0.500	1.12		
16.0°	.139			3.68	4.95	90°	.707	0.470	1.00	0.597	1.10

TABLE II. Total scattering from powdered crystals of NaF and MgO. Values of D_ϕ/D'_{90° and S_{exp} .

NaF						MgO					
ϕ	$\sin \frac{\phi}{2}$	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}	ϕ	$\sin \frac{\phi}{2}$	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}	$\frac{D_\phi}{D'_{90^\circ}}$	S_{exp}
9°	0.078	9.21	4.55			30°	0.259	2.63	1.42	1.06	1.63
10°	.087	10.17	5.04	2.71	3.81	36°	.309	2.19	1.25	0.837	1.34
11°	.096	10.25	5.08	2.96	4.17	42°	.358	1.98	1.17	.738	1.23
12°	.104	9.84	4.90	3.14	4.44	54°	.454	1.54	1.11	.608	1.12
15°	.130	6.97	3.50	2.58	3.67	66°	.545	1.49	1.05	.529	1.06
18°	.156	5.34	2.71	1.90	2.75	78°	.629	1.37	1.00	.497	1.02
24°	.208	3.54	1.85	1.32	1.95	90°	.707	1.40	0.97	.486	0.96

various powdered crystal brickettes were as follows: NaF, 0.678; MgO, 0.229; KCl, 0.218; CaS, 0.242 g/cm². The width of the window of the ionization chamber subtended an angle of 4° at the axis of the spectrometer. The widths of the defining slits in the primary beam were such that the total variation in ϕ for a given setting of the ionization chamber was about 6° so long as the average angle was less than 30°. In addition to the defining slits, screening slits were added so as to prevent rays scattered by the defining slits from entering the ionization chamber. These screening slits are very important at small angles.

V. COMPARISON WITH THEORY

The left side of Eq. (17) contains S_1 and S_2 and these quantities³ are dependent upon f and f'' as

well as upon F . The atom form factors f and f'' can be calculated from wave mechanics. Tables of f values so calculated have been published by James and Brindley.¹⁸ Furthermore, James and Brindley give tables of f_0 values. The symbol f_0 refers to the same quantity as does the symbol E used by Jauncey^{1, 3} and Woo,⁵ and hence values of f'' have been calculated from James and Brindley's tables by means of the formula³

$$f''^2 = Z \sum_r E_r^2. \quad (18)$$

Because calculated values of f'' may be of use to others working in this field, these values are given in Table III. The values for neon and for argon in Table III are the averages of the corresponding values for F⁻ and Na⁺ and for Cl⁻ and K⁺, respectively. We have used Froman's

TABLE III. Atom form factors. Values of f and f'' .

$\frac{\sin \frac{1}{2}\phi}{\lambda}$	F ⁻		Na ⁺		Neon		Cl ⁻		K ⁺		Argon	
	f	f''	f	f''	f	f''	f	f''	f	f''	f	f''
0.00	10.00	10.00	10.00	10.00	10.00	10.00	18.00	18.00	18.00	18.00	18.00	18.00
.1	8.73	8.76	9.55	9.58	9.14	9.17	15.20	15.50	16.40	16.50	15.80	16.00
.2	6.69	6.89	8.18	8.23	7.44	7.56	11.50	13.10	13.36	14.05	12.43	13.57
.3	4.77	5.38	6.62	6.82	5.70	6.10	9.34	12.00	10.78	12.53	10.06	12.26
.4	3.52	4.63	5.26	5.71	4.39	5.17	7.98	10.92	8.80	11.50	8.39	11.21
.5	2.74	4.29	4.08	4.88	3.41	4.59	7.16	9.97	7.74	10.67	7.45	10.32
.6	2.23	4.10	3.22	4.43	2.73	4.27	6.47	9.01	7.04	9.82	6.75	9.42
.7	1.82	3.92	2.62	4.15	2.22	4.04	5.86	8.13	6.44	8.95	6.15	8.54
.8	1.60	3.76	2.22	4.00	1.91	3.88	5.12	7.36	5.91	8.18	5.51	7.77
.9	1.53	3.59	1.94	3.84	1.73	3.72	4.41	6.75	5.32	7.56	4.86	7.16
1.0	1.53	3.42	1.73	3.68	1.63	3.55	3.77	6.25	4.72	6.88	4.25	6.56
1.5					0.96	2.14					2.23	3.86
2.0					0.59	1.32					1.32	2.35
3.0					0.28	0.62					0.60	1.14

method¹⁹ for extrapolating the f values beyond $(\sin \frac{1}{2}\phi)/\lambda = 1.0$. For the extrapolation of the f'' values we have applied Froman's method to James and Brindley's E (or f_0) values for each type of electron and have then used Eq. (18).

For a given value of ϕ , S_1 and S_2 are functions of λ alone. Since in the case of the diffuse scattering from a single crystal S_1 and S_2 are given by Eqs. (2) and (3), respectively, it is seen that S_1 and S_2 may be calculated from wave mechanics. In our experiments we have not used single large crystals but have scattered x-rays from brickettes of powdered crystals and so it is

necessary to find formulas for S_1 and S_2 for our experimental case. The formula for S_2 remains as given in Eq. (3), but the formula for S_1 is changed. We now proceed to the derivation of the formula for S_1 for the case of a powdered crystal.

Referring to Eq. (5.23) on p. 131 of A. H. Compton's *X-Rays and Electrons*, we see that for a powdered crystal brickette placed in the Crowther position

$$\frac{P_s}{P} = \frac{N^2 \rho^2 \lambda^3 F^2}{W^2} \cdot \frac{e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 \phi}{2 \sin^2 \phi} \cdot \frac{p \lambda \rho'}{4 \pi R \rho}, \quad (19)$$

where P_s is the intensity of the Debye-Sherrer

¹⁸ R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

¹⁹ D. K. Froman, *Phys. Rev.* **36**, 1339 (1930).

circle diffracted into an ionization chamber window whose height is l , P is the intensity of the primary beam penetrating the brickette, ρ is the density of a little crystal in the brickette and ρ' the overall density of the brickette. Now the intensity I_ϕ of the coherent part of diffusely scattered x-rays entering the chamber window is given by

$$\frac{I_\phi}{P} = \frac{A}{R^2} \cdot \frac{NZ}{W} \cdot \frac{e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 \phi}{2} \cdot \frac{\rho' t S_1}{\cos \frac{1}{2} \phi}, \quad (20)$$

where S_1 is given by Eq. (2). If both a Debye-Scherrer circle and the coherent part of the diffuse scattering on either side of the circle enter the ionization chamber window, Eqs. (19) and (20) combine to give

$$\frac{I_\phi + P_s}{P} = \frac{A}{R^2} \cdot \frac{NZ}{W} \cdot \frac{e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 \phi}{2} \cdot \frac{\rho' t}{\cos \theta} \times \left\{ S_1 + \frac{N \rho \lambda^3}{W} \cdot \frac{F^2}{Z} \cdot \frac{\rho l R}{16 \pi A \sin^2 \theta \cos \theta} \right\}, \quad (21)$$

where $\theta = \frac{1}{2} \phi$. Hence, if we represent the coherent scattering factor for a powdered crystal by S_1' , we have

$$S_1' = S_1 + \frac{N \rho \lambda^3}{W} \cdot \frac{F^2}{Z} \cdot \frac{\rho l R}{16 \pi A \sin^2 \theta_r \cos \theta_r}. \quad (22)$$

Because the second member of Eq. (22) depends upon the particular Debye-Scherrer circle which enters the chamber, various quantities are subscripted with r . For the r^{th} circle we have

$$\lambda_r = 2d_r \sin \theta_r, \quad (23)$$

where, for a simple cubic crystal,

$$d_r = d_1 / (r)^{\frac{1}{3}}. \quad (24)$$

The counter r is given by

$$r = \alpha^2 + \beta^2 + \gamma^2, \quad (25)$$

where α , β and γ are integers or zero but not more than two of them may be zero. The counter r according to Eq. (25) may be any integer excepting 7, 15, 23, 28, 31 and so on. But for a simple cubic crystal the principle grating space is given by

$$d_1 = (W/N\rho)^{\frac{1}{3}}. \quad (26)$$

Now the area A of the ionization chamber

window may be replaced by lw where w is the width of the window. Furthermore, the width w may be replaced by $R\delta\phi$, where R is the distance of the window from the axis of the spectrometer and $\delta\phi$ is the angle subtended by the width of the window. Hence, after eliminating λ_r from Eq. (22) by means of Eqs. (23), (24) and (26), we obtain

$$S_1' = S_1 + \frac{F_r^2}{Z} \cdot \frac{\rho_r}{(r)^{\frac{1}{3}}} \cdot \frac{\tan \theta_r}{2\pi\delta\phi}. \quad (27)$$

This quantity S_1' replaces S_1 in the integrand in the numerator of the left side of Eq. (17). However, since, for a given angle ϕ , F_r only has values for particular values of λ , the integral as applied to the second term on the right of Eq. (27) becomes a summation. In this summation the $I(\lambda)d\lambda$ which appears under the integral is replaced by $I(\lambda_r)\delta\lambda_r$. The quantity $\delta\lambda_r$ is due to the angular width $\delta\phi$ of the window. Differentiating Eq. (23) and then dividing the equation so obtained by Eq. (23), we obtain after rearrangement

$$\delta\lambda_r = \frac{1}{2} \lambda_r \cot \theta_r \delta\phi. \quad (28)$$

The left side of Eq. (17) in virtue of Eqs. (2), (3) and (28) becomes

$$S_{\text{th}} = G - H + L, \quad (29)$$

where

$$G = \int \left\{ \frac{f^2}{Z} + \frac{(1-f''/Z^2)K_\phi T_\phi}{K_0(1+\alpha \text{vers } \phi)^3} \right\} Id\lambda / \int Id\lambda \quad (30)$$

and

$$H = \int (F^2/Z) Id\lambda / \int Id\lambda \quad (31)$$

and

$$L = \left\{ \frac{1}{4\pi} \sum_r \frac{F_r^2}{Z} \cdot \frac{\rho_r \lambda_r I(\lambda_r)}{(r)^{\frac{1}{3}}} \right\} / \int Id\lambda. \quad (32)$$

The numerical value of the right side of Eq. (29) is determined by the wave-mechanics values of f and f'' and hence we shall designate this numerical value by S_{th} . If our theory is correct, S_{exp} as given by the right side of Eq. (17) should equal S_{th} . We have not used the theoretical values of F in the calculation of S_{th} because of the uncertainty of the Debye-Waller temperature factor, but have used the values of F as experi-

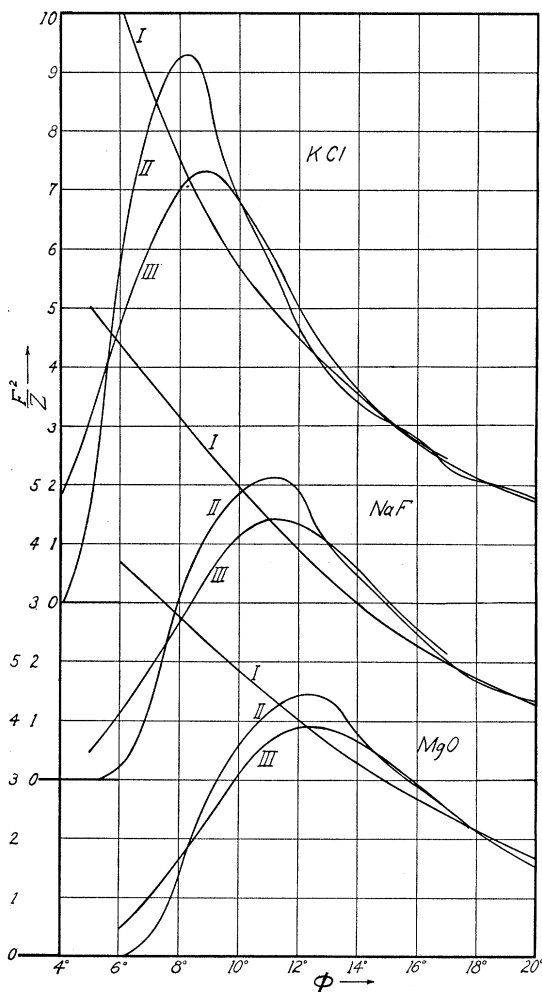


FIG. 4. Curves I, F^2/Z averaged over the wave-length band shown in Fig. 2 and an ionization chamber window width of 6° ; curves II, L (see Eq. (32)) averaged over the wave-length band; curves III, L averaged over the wave-length band and the window width.

mentally obtained for KCl by James and Brindley,²⁰ for NaF by Havighurst,²¹ and for MgO by Froman.²²

Values of H as defined by Eq. (31) have been calculated for a given crystal for various values of ϕ and have been plotted against ϕ . Each of these values of H is for a small range of angles about ϕ . However, in our experiments, the range of angles was intentionally large, being about 6° for a given setting of the ionization chamber.

²⁰ R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

²¹ R. J. Havighurst, Phys. Rev. **29**, 1 (1927).

²² D. K. Froman, Phys. Rev. **36**, 1330 (1930).

We have therefore obtained the value of H as averaged over a range of 6° for each average value of the angle. The graphs for these average values of H are designated by the Roman numeral I in Fig. 4. Likewise, L as defined by Eq. (32) was plotted against ϕ (curve II) and from this curve average values of L were obtained. The graphs for these average values of L are designated by the Roman numeral III in Fig. 4. It is seen that for a given crystal there is an angle above which $(L-H)$ is nearly zero. For angles above this particular value, therefore, $S_{th}=G$ approximately. But G , in virtue of Eq. (30), is the value of S_{th} for the corresponding inert gas. Hence the relation as expressed by Eq. (6) should approximately hold for angles greater than the particular angle for each crystal. As the angles are made smaller than the par-

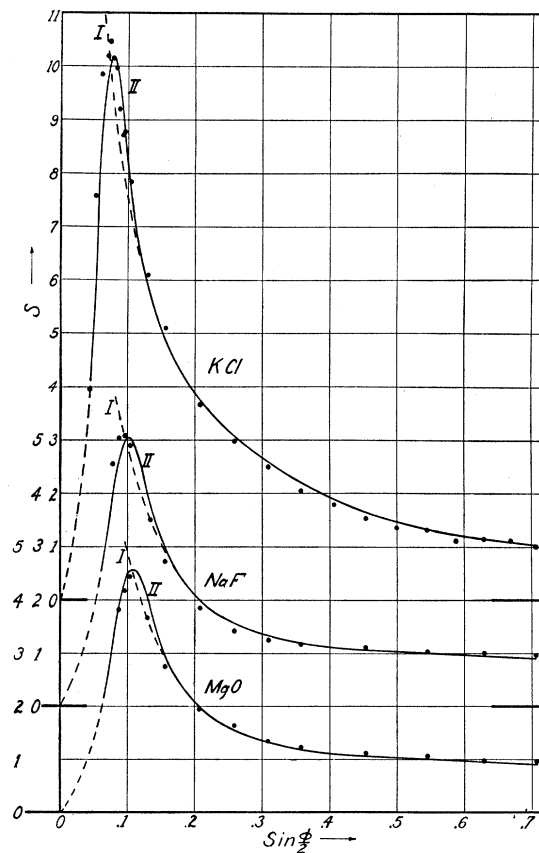


FIG. 5. Scattering of x-rays by powdered crystals. Curves I, theoretical S values for argon or neon; curves II, theoretical S values for powdered crystals (see Eq. (29)); black circles, experimental points.

ticular angle, the value of $(L-H)$ first increases, then decreases, and finally becomes a large negative number. At zero angle, $(L-H)$ very nearly equals $-Z$.

Using the values of f and f'' for neon and argon shown in Table III, we have calculated the values of G as defined by Eq. (30). As for the graphs of the average values of H and L , the values of G were averaged over an angular width of 6° . These average values of G are plotted against $\sin \frac{1}{2}\phi$ and the resulting graphs are designated by the Roman numeral I in Fig. 5. Graphs of S_{th} averaged over an angular width of 6° are now obtained and are designated by the Roman numeral II in Fig. 5. Since G very nearly equals $+Z$ at zero angle, S_{th} in virtue of Eq. (29) becomes $Z-Z$ or zero at zero angle.

Values of S_{exp} are shown as black circles in Fig. 5. It is seen how closely these circles fall upon the respective S_{th} curves. Particularly is this the case for KCl where the experimental points were taken down to angles as low as 5° . The experimental points follow the theoretical curve up to the maximum and then follow it by rapidly dropping as the angle approaches zero. An S_{th} curve for CaS is not shown because F values for this crystal were not available.

VI. CONCLUDING REMARKS

We feel that the agreement between our theory and the experimental results as shown by the curves and experimental points in Fig. 5 is excellent. Such discrepancy as appears is probably due to numerical approximations in the theory and to experimental errors.

With regard to Coven's experiment⁷ with monochromatic rays, we believe that the relation expressed by Eq. (6) is only approximately true for particular angles of scattering, but is not generally true. The argument as developed in Eqs. (19) to (27) leads to an equation similar to Eq. (27), but with a summation sign in front of the second term on the right side of this equation. For monochromatic rays and a wide window, we arrive at

$$S_i = S_{gas} - \frac{F^2}{Z} + \sum_r \frac{F_r^2}{Z} \cdot \frac{p_r \tan \theta_r}{(r)^{\frac{3}{2}} 2\pi \delta \phi}. \quad (33)$$

It is seen that the discrepancy between S_i and

S_{gas} is equal to the algebraic sum of the second and third terms on the right side of Eq. (33). Values of the second term with a positive sign have been plotted against the angle for the case of KCl and $\lambda=0.71\text{\AA}$ as shown by the curve in Fig. 6. Values of the third or summation term in Eq. (33) have been calculated for particular angles and are shown in Fig. 6 as black dots and white circles. The black dots refer to the case for a 10° window and the white dots to that for a 7° window. The curve in Fig. 6 depends also upon the

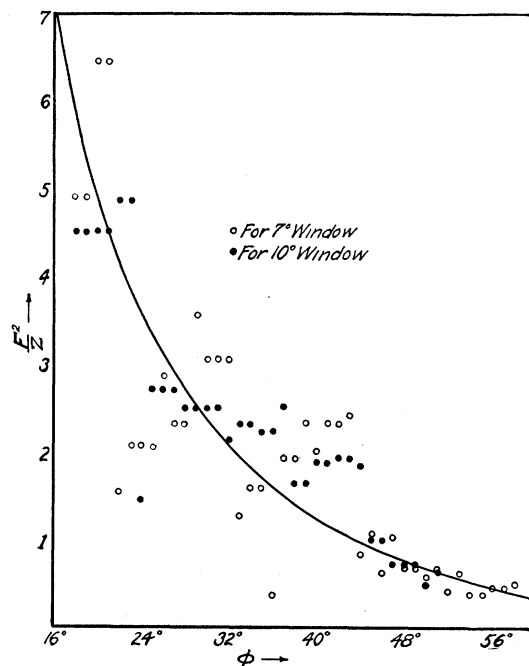


FIG. 6. Scattering of $\lambda=0.71\text{\AA}$ from a powdered crystal of KCl. Curve, values of F^2/Z averaged over a window width of 6° ; circles, values of third term on right side of Eq. (33) for different window widths.

width of the window but only slightly. The curve shown is for a 6° window. If a 7° window is used, the discrepancy between S_i and S_{gas} for a given angular setting of the ionization chamber is equal to the difference between the ordinate of a white circle and that of the curve for this setting. For a 10° window, the discrepancy is equal to the difference between the ordinate of a black circle and that of the curve. It is seen that, generally speaking S_i is not equal to S_{gas} .

In previous experiments performed in this laboratory on the diffuse scattering of x-rays from crystals an average wave-length has been

determined from an absorption curve such as shown in Fig. 1. This average wave-length has then been treated as a single wave-length and values of S plotted against $(\sin \frac{1}{2}\phi)/\lambda$. There has been some objection to this procedure. However, we have pointed out at the end of the last paragraph of §2 that the average wave-length as obtained from the spectral distribution is very nearly that obtained from absorption measurements. Also, at the end of §3 it is pointed out that the numerical formula for S_{exp} is very nearly independent of the precise wave-length assumed if the x-rays are supposed to consist of a single wave-length. Hence, in experiments such as those of Harvey¹³ and of Jauncey and Williams,¹⁴ the values of S are reasonably accurate. The trouble, however, arises in the values of $(\sin \frac{1}{2}\phi)/\lambda$ to which the respective values of S should be assigned. As a result of our present investigation it seems that, excepting in those portions of the graphs of S versus $(\sin \frac{1}{2}\phi)/\lambda$ where the slope is large, the values of $(\sin \frac{1}{2}\phi)/\lambda$ may be calculated from the angle and that value of λ which is found

from the absorption curve. It seems, then, that a beam of x-rays which has passed through a sufficient thickness of aluminum acts for scattering purposes very nearly as if it were made up of monochromatic rays. The homogeneity of x-rays which had passed through a sufficient thickness of aluminum was noted several years ago by C. G. Barkla. The S curves shown in the papers by Harvey and by Jauncey and Williams are therefore reasonably accurate, excepting at small angles. As a result of this present investigation, we now believe that the proper procedure is to obtain the distribution of energy in the spectrum of the x-rays used and to calculate from theory the scattering to be expected at each angle. These theoretical values are then compared with the experimental values. For convenience the curve of the theoretical values and the points representing the experimental values are plotted against $(\sin \frac{1}{2}\phi)$.

In conclusion, we wish to thank Dr. J. A. Van den Akker for much help and advice in regard to the assembling of the all-in-oil x-ray outfit.