Scattering of X-Rays from Solids

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The total scattering of the $K\alpha$ radiation of molybdenum from powdered crystals of KCl, NaF, and MgO has been observed with an ionization chamber whose window subtended several degrees of angle at the scatterers. The scattering from NaF and MgO was found to be approximately the same as that from neon. The scattering from KCl was found to be approximately the same as that from argon. The intensities of the diffracted portion of the scattered rays from the crystals have been calculated and found to be distributed along the F^2/Z curves, thus agreeing with Jauncey's relation between gas and crystal scattering, $S_g = S_c + F^2/Z$. The sums of the diffracted intensities plus diffuse intensities have been found to follow the gas scattering curves, in agreement with Compton's formula for the scattering from a monatomic gas, $S_g = (f^2/Z) + (1 - f^2/Z^2)/R^3$. The method of measurement may be used to determine values of the structure factor for the atom at rest.

I. Introduction

A. H. COMPTON[1] has shown that the intensity of x-rays scattered from a monatomic gas or vapor is given by

$$S_g = f^2/Z + (1 - f^2/Z^2)/R^3 \tag{1}$$

where S_g is the scattered intensity relative to the value given by the Thomson theory of scattering.[2] f is an average atomic structure factor for the atom at rest, Z is the number of electrons in the atom, and $1/R^3$ is the Breit-Dirac factor. R has the value $1 + (h/mc\lambda)\text{vers }\phi$, where ϕ is the angle of scattering. G. E. M. Jauncey[3] has developed a theory of the scattering of x-rays from solids in which Eq. (1) is included as a factor in the scattered intensity. In the special case of scattering from a simple cubic crystal consisting of atoms of one kind Jauncey's theory gives[4]

$$S_c = \frac{f^2 - F^2}{Z} + \frac{1 - f^2/z^2}{R^3} = S_g - \frac{F^2}{Z} \tag{2}$$

where F is the atomic structure factor at the temperature of the crystal. Eq. (2) connects the diffuse scattering from a crystal with the scattering from a monatomic gas of the same kind of atoms as those in the crystal. The term F^2/Z represents a correction for the effect of interference between atoms in the crystal.

The energy per second emitted in a diffraction line by one of the particles in an aggregation of powdered crystals is given by[5]

[1] A. H. Compton, Phys. Rev. **35**, 925 (1930).

[2] J. J. Thomson, *Conduction of Electricity through Gases*, 2d Ed., p. 326.

[3] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

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

[5] A. H. Compton, *X-Rays and Electrons*, p. 130.

$$P = \frac{In^2\lambda^3 pF'^2 e^4(1 + \cos^2 2\theta)dV}{8(\sin \theta)m^2 c^4}, \tag{3}$$

where θ is the glancing angle of incidence on a crystal plane, p is the number of planes, F' is the structure factor for the crystal, n is the number of atoms per cm³, I is the intensity of the primary beam, and dV is the volume of the particle. If the diffracted rays are measured at a distance r with an ionization chamber whose window has a length L which is short compared to $r \sin \theta$, then the energy per second entering the ionization chamber is

$$P_s = PL/2\pi r \sin 2\theta.$$

Thomson's classical theory[2] gives the intensity scattered from the $nZdV$ electrons in one of the powdered crystal particles to be

$$I_s = \frac{InZe^4(1 + \cos^2 \phi)dV}{2m^2 c^4 r^2}, \tag{4}$$

and therefore the energy entering the ionization chamber is equal to AI_s, where A is the area of the chamber window. To get the energy per second in a diffraction line in the units corresponding to S_g and S_c of Eqs. (1) and (2) we take the ratio of P_s to AI_s. We then have

$$\frac{P_s}{AI_s} = \frac{n\lambda^3 pLrF'^2}{8\pi ZA \sin \theta \sin 2\theta}.$$

But the atomic structure factor F in Eq. (2) has a value $F'/2$ for a simple cubic crystal consisting of atoms of one kind. Substituting $2F$ for F' in the above expression, we then have for the energy in a powdered crystal line where the crystals are of the simple cubic type and contain similar atoms

$$\frac{P_s}{AI_s} = \frac{n\lambda^3 pLr}{2\pi A \sin \theta \sin 2\theta} \cdot \frac{F^2}{Z}. \tag{5}$$

If the ionization chamber window is of such width as to subtend several degrees of angle at the scatterer, there will be several diffraction lines entering the chamber at large angles of scattering where the lines are close together, and probably more than one line at each of the smaller scattering angles if the scattering crystals have a grating constant that is not too small. The total diffracted energy entering the chamber is then equal to the sum of the energies in the lines and may be expressed as

$$S_{d'} = \sum \left(\frac{n\lambda^3 pLr}{2\pi A \sin \theta \sin 2\theta} \cdot \frac{F^2}{Z} \right). \tag{6}$$

The total scattered intensity entering the ionization chamber is the sum of the diffuse and the diffracted intensities. Using previously measured values of F, Eq. (6) may be used to calculate the diffracted portion of the scattering and this portion may then be added to measured values of the diffuse scattering to get values of the total scattered intensitites. Values of $S_{d'}$ are in terms

of energy so the corresponding quantity representing the diffuse scattering will be represented by the area under the curve of diffuse intensity between the limits of the $(\sin \phi/2)/\lambda$ ordinate corresponding to the angle subtended by the ionization chamber window. Hence we may divide each value of S_d' by a value dx, which is the length of the ordinate corresponding to the range of scattering angle subtended by the ionization chamber window and add the quotient to the intensity of diffuse scattering at the value of the ordinate corresponding to the position of the middle of the window. The total scattered intensity is thus represented by

$$S_t = S_c + S_d'/dx = S_c + S_d, \tag{7}$$

where S_d is equivalent to S_d'/dx. If the total scattering from a powdered crystal aggregation is measured with an ionization chamber whose window subtends several degrees of angle at the scatterer, a distribution of intensity equivalent to that given by Eq. (1) is observed.
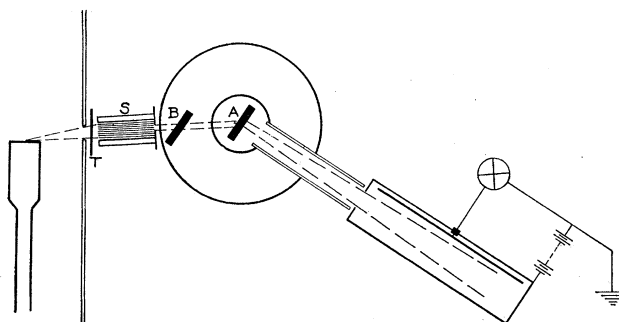

Fig. 1. Arrangement of apparatus.

The author has observed the scattered intensities from powdered crystals of KCl, NaF, and MgO, using an ionization chamber whose window subtended approximately 5 degrees of angle at the scattering plates. The observed intensities from KCl are in close agreement with the values obtained by Wollan[6] for argon and the intensities from NaF and MgO agree with Wollan's values for neon.[6] Wollan's values are in agreement with values calculated from Eq. (1), using structure factors calculated from the Hartree charge distribution.

II. APPARATUS AND PROCEDURE

Fig. 1 shows the arrangement of the apparatus. A molybdenum target x-ray tube was immersed in oil in a lead box placed close to the axis of an ionization spectrometer. The scatterers were mounted directly over the axis on the spectrometer table. The x-ray tube was operated at a potential of approximately 40 k.v. and a current of 35 m.a. A Compton electrometer indicated the ionization currents. A Soller slit, S, collimated the primary beam. The use of this slit limited the divergence of the primary rays to less than a

[6] E. O. Wollan, Phys. Rev. **37**, 862 (1931).

half-degree of angle. The scattered rays passed through a bronze tube 2.7 cm in diameter, 14 cm long, with 1.5 mm walls. This tube prevented stray radiation from entering the ionization chamber with the scattered rays. The window of the chamber was 1.67 cm high and 1.64 cm wide. The distance from the window to the axis of the spectrometer was 18.05 cm. The chamber contained methyl bromide vapor at atmospheric pressure.

Balanced filters of ZrO_2 and SrO were placed at T in the primary beam. These separated the $K\alpha$ lines from the general radiation as shown in Fig. 2, where the difference in the transmission by the ZrO_2 and the SrO is re-
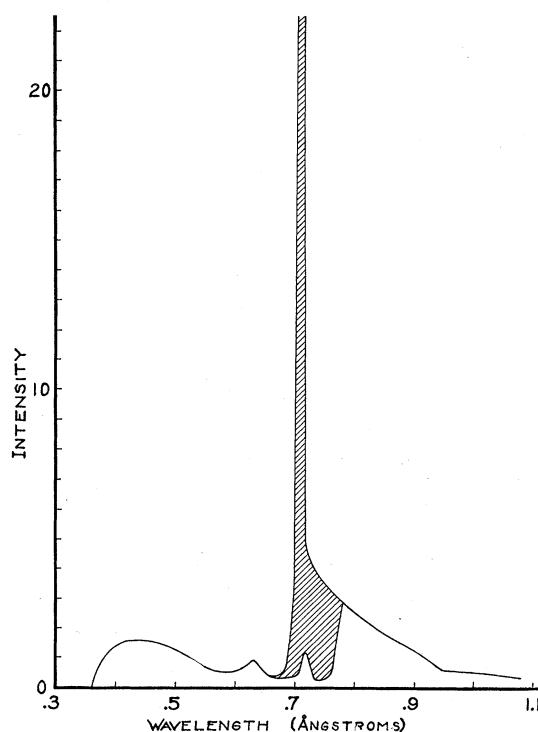

Fig. 2. Transmission through balanced filters.

presented by the shaded portion. This is the portion that was used as the primary radiation in all of the measurements of scattered intensities.

The scattering from the crystalline powders and from paraffin was observed throughout an angular range of from 20° to 100°. The scattering from each of the powdered crystal plates was compared with the scattering from a similar plate of paraffin. Since the scattering from paraffin can be calculated to a close approximation, the values of the scattered intensities for each of the other materials could be put on an absolute scale. For the $K\alpha$ radiation of molybdenum Woo[7] has found that the ratio of the incoherent to coherent radiation scattered from paraffin at 90° is 4.69. If it is assumed that for

[7] Y. H. Woo, Phys. Rev. **27**, 119 (1926).

paraffin at 90° the effect of constructive interference is negligible, the total scattering can be obtained from classical theory, if the incoherent portion is corrected by the Breit-Dirac factor. Thus, at 90°, the scattering from paraffin is given by

$$S_t = 0.825(R^{-3}) + 0.175 = 0.93.$$

From this value and the experimental measurements of relative intensities at various angles, S_t for paraffin was found to be equal to unity in the range from 30° to 70°. The comparisons of the powdered crystal intensities with the paraffin intensity were all made at 60°.

The pure, finely ground, powdered crystals were pressed into brass rings which fitted into holders that could be conveniently mounted on the spectrometer table. The paraffin was melted into a similar ring so that it could be quickly substituted for any one of the powdered crystal plates.

Potassium chloride

The scattering from a thin plate of the KCl powder 2.5 cm in diameter and having a mass per unit area of 0.141 g/cm² was compared with the scattering from the paraffin which was also 2.5 cm in diameter and had a mass per unit area of 0.275 g/cm². The arrangement of the two was as shown in Fig. 1, where one scatterer is in the primary beam at A and the other in the primary beam at B, each plate being set so that the normal to its surface made an angle of 30° with the primary beam. The ionization chamber was set at the scattering angle of 60°. The intensity with the KCl at A and the paraffin at B was first observed. Then the intensity with the paraffin at A and the KCl at B was observed. The ratio of the first intensity to the second multiplied into the ratio of the masses per unit area and the ratio of the values of Z/W for the samples then gave the value of S_t for KCl at 60°. Z is atomic number and W is atomic weight. The paraffin was assumed to be equivalent to a molecule of $C_{24}H_{50}$, for which Z/W has a value of 0.5. No correction for absorption of the x-rays in the samples was necessary since by this method of comparison the portion of the primary rays transmitted by the scatterer at A does not change when the scatterers are interchanged in their positions at A and B. The intensity of the scattered rays entering the ionization chamber from each substance was of the same order of magnitude by this method, even though the absorption in the KCl was much greater than that in the paraffin.

Relative values of the scattering from KCl were observed by reflections from a plate of the powdered crystals 4.5 cm in diameter and thick enough to absorb completely the $K\alpha$-rays of molybdenum. The scatterer was always set so that the face of the crystal plate was at an angle equal to half the scattering angle. Thus the absorption of the primary and scattered rays was approximately the same in the thickness of the plate penetrated, and proportional to the reciprocal of the absorption coefficient. For the relative values, therefore, no absorption correction was necessary. The relative values of S_t were given by the relative intensities multiplied into the ratios of the values of the polarization factor, $1 + \cos^2\phi$.

Sodium fluoride

The intensities from paraffin and the NaF plate, which had a mass per unit area of 0.470 g/cm^2, were of the same order of magnitude and the comparison between them at 60° was made without resorting to the method used for KCl of placing both samples in the primary beam. When a scatterer is at A and none at B (Fig. 1), S_t is proportional to $(W/mZ)(I_\phi/i_\phi)(1+\cos^2 \phi)^{-1}$, where Z is atomic number, W is atomic weight, m is mass per unit area, I_ϕ is the scattered intensity, and i_ϕ is the portion of the primary rays penetrating the scatterer. i_ϕ is equal to $Ie^{-m\mu/\rho\cos(\phi/2)}$ where I is the incident ray intensity and μ/ρ is the mass absorption coefficient of the incident rays in the scatterer. The absorption of the Mo $K\alpha$ rays in the paraffin and in the NaF plate was measured with the Compton double crystal x-ray spectrometer.[8] μ/ρ for paraffin was found to have a value of 0.52 and for NaF 2.63. Relative intensities for NaF at various scattering angles were measured from the same scatterer that was compared with paraffin.

Magnesium oxide

The MgO plate that was compared with paraffin at 60° had a mass per unit area of 0.331 $g/cm.^2$ The intensity comparison was made exactly as it was for NaF and paraffin. μ/ρ for MgO was calculated to be 3.18 from the values of the atomic absorption coefficients for Mg and O given on page 182 of Compton's *X-Rays and Electrons*. The relative intensities were measured from reflections from a thick plate of the powdered MgO crystals as was done for KCl.

III. EXPERIMENTAL RESULTS

Froman[9] and Harvey[10] have respectively measured the intensities of the lines from powdered KCl and the diffuse scattering from a single crystal of KCl. Froman's values of F for KCl have been used to calculate values of S_d for values of ϕ between 15° and 90°, each value extending over a range of 5° and differing from adjacent values by 5°. Thus for each value of ϕ the energy in all the diffraction lines included in the 5° range made up the value of S_d. The sum of the S_d values would represent the sum of the energy in the diffraction lines between the minimum and maximum values of ϕ, 15° and 90°. At each value of ϕ the value of S_d was added to the value of S_c as shown in Fig. 3. S_g is the theoretical curve for argon as calculated by Hartree by his method of self-consistent fields. The data for the curve were taken from a paper by Herzog.[11] His values for the incoherent radiation have been reduced by the Breit-Dirac factor before being added to the values of the coherent radiation to get the values of S_g from which the curve was drawn. The F^2/Z curve was drawn from Froman's data. The circles are values of S_d and the crosses are the values of S_c+S_d. The author's experimental values of S_t, as given in column 3 of Table I, are plotted as dots.

[8] A. H. Compton, Rev. Sci. Inst. **2**, 365 (1931).

[9] D. K. Froman, Phys. Rev. **36**, 1330 (1930).

[10] G. G. Harvey, Phys. Rev. **38**, 593 (1931).

[11] G. Herzog, Zeits. f. Physik **70**, 583 (1931).

Jauncey and Williams[12] have recently measured the diffuse scattering from a single crystal of NaF. Their values were kindly sent to the author by Professor G. E. M. Jauncey and have been used together with the F values
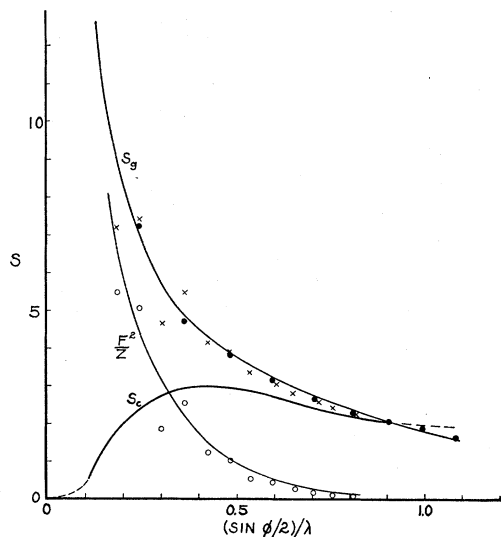

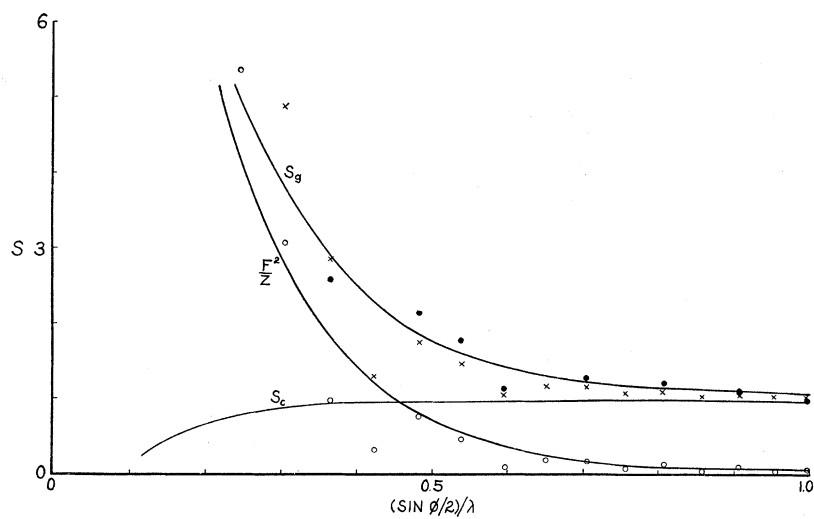Fig. 3. Scattering from KCl. Dots S_t experimental, circles S_d, crosses $S_c + S_d$, S_g from argon.

Fig. 4. Scattering from NaF. Dots S_t experimental, circles S_d, crosses $S_c + S_d$, S_g from neon.

of Havighurst[13] to calculate values of $S_c + S_d$ as shown by the crosses in Fig. 4. The F^2/Z curve is also from the data of Havighurst. The S_g curve for neon is again from Herzog's values.[11] The author's experimental values of S_t for

[12] G. E. M. Jauncey and P. S. Williams, Phys. Rev. **41**, 127 (1932).
[13] R. J. Havighurst, Phys. Rev. **29**, 1 (1927).

NaF are shown by the dots. These values appear in column 4 of Table I. Values of S_d are shown by the circles.

Fig. 5 shows the results for MgO. The author is grateful to Dr. Wollan for the values of diffuse scattering from a single crystal of MgO which he has recently measured but not yet published. These have been used to draw the S_c curve. Values of S_d as shown by the circles were calculated from Wollan's[14] values of F for powdered MgO crystals. The F^2/Z curve is also drawn from Wollan's values. Values of S_c+S_d are shown by the crosses and the author's experimental values of S_t by the dots. These are the values appearing in column 5 of Table I. The S_g curve for neon is the same as the one in Fig. 4.
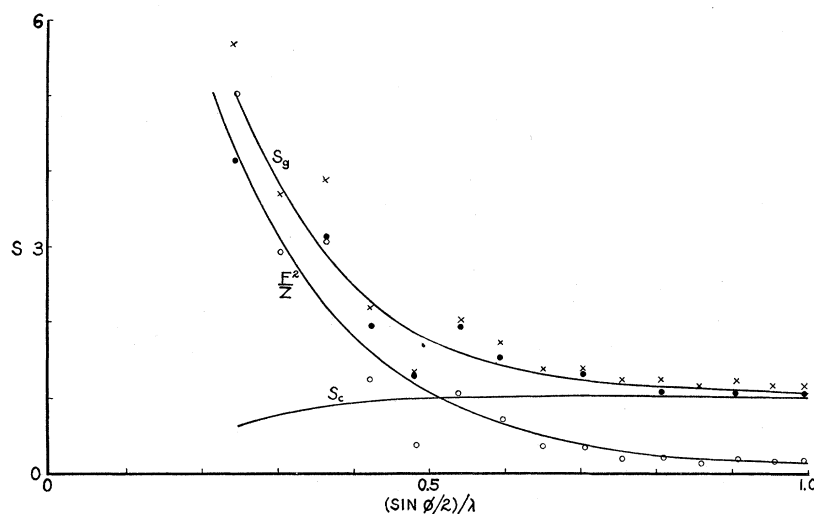

Fig. 5. Scattering from MgO. Dots S_t experimental, circles S_d, crosses S_c+S_d, S_g from neon.

The values of the total scattering, S_t, observed by the author for powdered crystals of KCl, NaF, and MgO and for paraffin are all shown in Fig. 6 together with the theoretical curves for neon and argon. The crosses indicate the values for KCl, the circles are the NaF values, the large dots are for MgO, and the small dots for paraffin.

TABLE I. *Values of S_t for paraffin and powdered crystals.*

Angle	$(\sin \phi/2)/\lambda$	KCl	NaF	MgO	Paraffin
20°	0.245	7.25		4.16	1.22
30	0.365	4.77	2.59	3.13	1.00
35	0.423			1.96	
40	0.482	3.83	2.15	1.30	1.00
45	0.539		1.78	1.95	
50	0.596	3.14	1.13	1.55	1.00
60	0.705	2.65	1.28	1.31	1.00
70	0.808	2.28	1.20	1.10	1.00
80	0.906	2.01	1.10	1.09	0.93
90	0.996	1.85	1.00	1.06	0.93
100	1.082	1.80			0.89

[14] E. O. Wollan, Phys. Rev. **35**, 1019 (1930).

IV. Discussion

Fig. 6 shows that the measured values of the total scattering from KCl are in excellent agreement with the theoretical argon curve. Wollan's experimental values of the scattering from argon are slightly higher than the theoretical curve at values of (sin $\phi/2$)/λ below 0.7 and above 0.9. Hence the agreement between the author's values of the scattering from KCl and the scattering from argon is better for the theoretical values than for the experimental values. The experimental values of the total scattering from NaF and MgO are in good agreement with the theoretical neon curve for the higher values of (sin $\phi/2$)/λ. At the lower values of (sin $\phi/2$)/λ the points do not lie
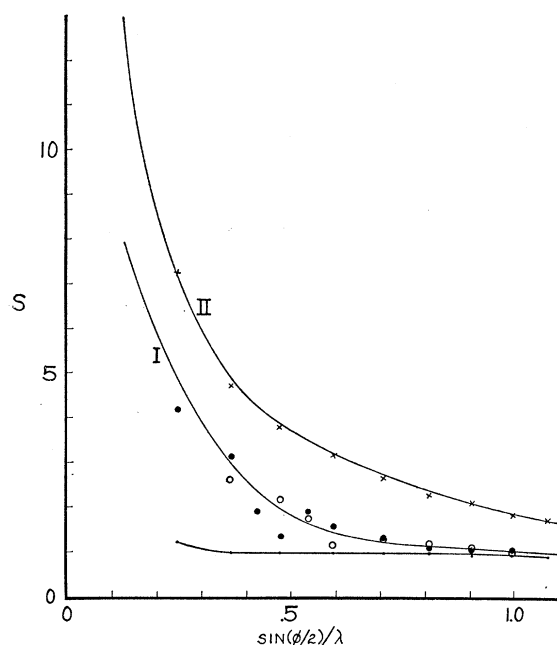

Fig. 6. Values of S_t. Crosses KCl, circles NaF, large dots MgO, small dots paraffin. Curve I neon (theoretical), curve II argon (theoretical).

on a smooth curve. This is to be expected, because crystals of NaF and MgO have a small grating constant. The diffraction lines are consequently widely separated and a good average of the diffracted energy is not obtained. However, the average distribution of the points appears to lie along the gas scattering curve. The larger grating constant of KCl insures a good average of the diffracted portion of the energy throughout the whole range of scattering angles at which observations were made. This explains the excellent agreement of the KCl values with the gas curve at all points.

Jauncey and Williams[12] have found that the values of $S_c + F^2/Z$ for NaF are lower than the values of the scattered intensities from neon. The author's calculated values of $S_c + S_d$, as shown by the crosses in Fig. 4, are also lower than the gas scattering curve. The author's experimental values of the total

scattering from NaF are on the average higher than the values of $S_c + S_d$, but slightly less than Wollan's neon values. The values of $S_c + S_d$ are probably more reliable than the experimental values of the total scattering because of the difficulty of averaging the diffracted energy in the ionization chamber. The values of $S_c + S_d$ for MgO lie slightly above the theoretical curve for neon and are in good agreement with Wollan's experimental measurements of the neon intensities. The $S_c + S_d$ values for KCl are slightly lower than the argon theoretical curve, and the author's values of the total scattering lie between the $S_c + S_d$ values and the argon curve. The difference between the values is, however, less than the probable uncertainty in the determination of the absolute value of the total scattering by comparison with paraffin. Using the F values of Froman[9] for powdered KCl, the values of $S_c + F^2/Z$ fall exactly on the theoretical argon curve. James and Brindley[15] have measured the F values for a single crystal of KCl and have found them to be slightly greater than Froman's values. Using these F values of James and Brindley, the $S_c + F^2/Z$ values for KCl agree better with Wollan's values of the argon intensities than with the theoretical curve. Jauncey and Harvey[16] have used. Wollan's and James and Brindley's values in testing the $S_c + F^2/Z$ relation.

In a former paper[17] the author has published the results of measurements of the total scattering from aluminum, copper, and lead sheets. Since a sheet of metal consists of a collection of small crystals, we may consider it to be a plate of powdered crystals of the metal. The total scattering from a metal sheet measured with a wide-window ionization chamber should thus be approximately the same as the scattering from the same metal in the vapor state, for values of $(\sin \phi/2)/\lambda$ greater than 0.5. This method of measurement yields values of the atomic structure factor for the atom at rest, since from Eq. (1) we have

$$f^2 = \frac{(S - R^{-3})}{(Z - R^{-3})} Z^2.$$

[15] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).
[16] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1071 (1931).
[17] A. W. Coven, Phys. Rev. **38**, 1424 (1931).