Diffuse Scattering of X-Rays from Sodium Fluoride

By G. E. M. JAUNCEY* AND P. S. WILLIAMS
Washington University, St. Louis

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S(class) values have been obtained for the monatomic gases argon and neon by Wollan, and for the simple cubic crystals sylvine and rocksalt by Harvey, and Jauncey and May. *F* values for the average $\frac{1}{2}(K^+ + Cl^-)$ and $\frac{1}{2}(Na^+ + Cl^-)$ atoms have been obtained by James and Brindley, and James and Firth. By means of the formulas for gases and crystals developed by Compton, and by Jauncey and Harvey, the above have yielded comparisons between *S*(class) and f' values for argon and the average sylvine atoms, and for the average $\frac{1}{2}(A+Ne)$ atoms and the average rocksalt atoms. The agreement on the whole has been excellent. The object of the present research was to make similar comparisons of the above results for neon with those for $\frac{1}{2}(Na^+ + F^-)$, by using Havighurst's *F* values for this average atom. The methods of experiment and calculation were similar to those of Jauncey and May, as modified by Harvey, except that Woo's form of the crystal formula was used to take account of the incoherent scattering. Unlike the case of argon and sylvine, we found that the f' values for the crystal of NaF are definitely lower than those for the gas neon. This implies that for weak nuclear fields the electron distribution in an atom of a crystal is perceptibly more diffuse than that in an atom of the corresponding gas. We also calculated *B* values and found that the second hump in the *B* curve which is barely indicated by Wollan's values for neon is definitely present. A Fourier analysis will therefore give a *U* curve which shows a hump for the *K* electrons of NaF.

I. INTRODUCTION

CONSIDER the case of a beam of unpolarized x-rays of intensity I_0 per unit area of the beam falling upon a speck of matter containing n molecules, where n is so small that the loss due to absorption of the x-rays in the speck may be neglected and yet so large that the intensity of the x-rays scattered by the speck per unit solid angle in a direction ϕ with the primary beam is proportional to n and to I_0, the primary intensity. We may then say that the intensity of these scattered rays is $I_{M\phi}nI_0$, where $I_{M\phi}$ is a proportionality constant for a given value of ϕ. It is possible to measure $I_{M\phi}nI_0$ experimentally, whence upon dividing by nI_0 the value of $I_{M\phi}$ may be found. We shall call $I_{M\phi}$ the scattered intensity per unit solid angle per molecule per unit primary intensity in the direction ϕ.

On the simple Thomson[1] theory of x-ray scattering, the scattered intensity from a molecule containing Z electrons is given by

$$I_{M\phi} = (Ze^4/m^2c^4)\cdot(1+\cos^2\phi)/2 \qquad (1)$$

since each of the electrons in a molecule scatters independently. However, it is found that the experimental values of $I_{M\phi}$ are not in general given by the

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[1] J. J. Thomson, The Conduction of Electricity through Gases, 2nd Ed., p. 325.

right side of (1). Barkla and Ayers[2] found that at small angles the experimental values of $I_{M\phi}$ are greater than the right side of (1) and it has now become customary to multiply the right side of (1) by a factor S, so that

$$I_{M\phi} = (SZe^4/m^2c^4)(1 + \cos^2 \phi)/2 \tag{2}$$

We shall call S the scattering factor per electron or simply the scattering factor. The value of S depends upon the electron distribution in each molecule of the speck and upon the arrangement of the molecules in the speck. The value of S may be found experimentally in all cases, but can only be calculated theoretically in particular cases. In 1930 Compton,[3] using the principles of the classical theory, showed that for the case of scattering from a monatomic gas

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

where Z is the number of electrons in an atom of the gas and f' is related to the true atomic structure factor f in a manner discussed by Jauncey[4] and Herzog.[5] In 1931 Jauncey[6] showed that for the case of scattering from a solid consisting of atoms of one kind

$$S = 1 + (Z - 1)f'^2/Z^2 + (F^2/nZ)X \tag{4}$$

where F is the atomic structure factor including the effect of thermal agitation and X is a certain double summation. Jauncey and Harvey[7] have shown that for the case of a simple cubic crystal $X = -n$, where n is the number of atoms in a speck of the crystal. Hence, for a simple cubic crystal consisting of atoms of one kind Eq. (4) becomes

$$S = 1 + (Z - 1)f'^2/Z^2 - F^2/Z. \tag{5}$$

Eqs. (3), (4) and (5) are derived from the principles of the classical theory and do not take account of the Compton effect. Wentzel[8] has applied the principles of wave mechanics to the theory of the Compton effect, and Woo[9] by extending Wentzel's arguments has arrived at a formula for S of the form

$$S = S_1 + S_2/(1 + \alpha \operatorname{vers} \phi)^3 \tag{6}$$

where $\alpha = h/mc\lambda$. For both the case of a monatomic gas and the case of a simple cubic crystal consisting of atoms of one kind, Woo gives

$$S_2 = 1 - f'^2/Z^2 \tag{7}$$

For a monatomic gas, Woo gives

$$S_1 = f'^2/Z \tag{8}$$

and, for a crystal,

$$S_1 = (f'^2 - F^2)/Z. \tag{9}$$

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[2] C. G. Barkla and T. Ayers, Phil. Mag. **21,** 275 (1911).
[3] A. H. Compton, Phys. Rev. **35,** 925 (1930).
[4] G. E. M. Jauncey, Phys. Rev. **38,** 1 (1931).
[5] G. Herzog, Zeits. f. Physik **69,** 207 (1931).
[6] G. E. M. Jauncey, Phys. Rev. **37,** 1193 (1931).
[7] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37,** 1203 (1931).
[8] G. Wentzel, Zeits. f. Physik **43,** 1 and 779 (1927).
[9] Y. H. Woo, Phys. Rev. **38,** 6 (1931).

We shall call S_1 and S_2 the coherent and incoherent scattering factors, respectively. It should be noted that from Eq. (6)

$$S = S_1 + S_2 \tag{10}$$

when $\alpha = 0$. In this case, using Eqs. (7) and (8), it is seen that the right side of Eq. (10) reduces to the right side of Eq. (3); also, using Eqs. (7) and (9), the right side of Eq. (10) reduces to the right side of Eq. (5). Since Eqs. (3) and (5) were derived by means of the classical theory, we may say that the sum of the coherent and incoherent scattering factors equals the classical scattering factor.

Jauncey and Harvey[10] have noted that, if the f' values for a monatomic gas are the same as those for a crystal consisting of the same kind of atoms as the gas, f' may be eliminated from Eqs. (3) and (5), giving

$$S_{\text{gas}} = (S + F^2/Z)_{\text{cryst}}. \tag{11}$$

This relation is also valid if Woo's Eqs. (6), (7), (8) and (9) represent the true state of affairs. Since the atoms of sylvine are argon-like, the relation expressed by Eq. (11) should hold for argon and sylvine. Using the experimental S values for argon and sylvine obtained by Wollan[11] and Harvey[12] respectively, and the F values for sylvine obtained by James and Brindley,[13] Jauncey and Harvey[10] have shown that the relation expressed by Eq. (11) holds very closely for argon and sylvine.

The purpose of the present research was to test the accuracy of the relation expressed by Eq. (11) for neon and sodium fluoride. Since S values for neon and F values for sodium fluoride have already been obtained by Wollan[11] and Havighurst[14] respectively, it remained for us to determine the S values for sodium fluoride.

II. Experimental Method

The experimental method was essentially that used by Jauncey and May[15] and modified by Harvey.[12] Unpolarized x-rays from a tungsten target tube were used. The rays were made effectively homogeneous by placing 1.65 mm of aluminum in the primary beam of x-rays. This beam was scattered by a slab of sodium fluoride crystal into an ionization chamber. With the ionization chamber placed at an angle ϕ with the primary beam, the crystal was set at various positions, so that θ, the angle between the normal to the crystal slab and the primary rays, passed through the value $\phi/2$. At $\theta = \phi/2$, which is the Crowther[16] position, a Laue spot was reflected into the chamber. Readings on both sides of the Laue spot were made and an interpolated reading at the position of the Laue spot was calculated as described in the papers of Jauncey and May[15] and Harvey.[12] The ionization chamber was filled with

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

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

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

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

[14] R. J. Havighurst, Phys. Rev. **29**, 1 (1927).

[15] G. E. M. Jauncey and H. L. May, Phys. Rev. **23**, 128 (1924).

[16] J. A. Crowther, Proc. Roy. Soc. **A86**, 478 (1912).

air saturated with ethyl bromide at a temperature of 22°C, at which temperature the vapor pressure of the bromide[17] is 415 mm of mercury. The length of the ionization chamber was 43 cm. The effective wave-length of the x-rays passing through the aluminum filter and the crystal in the Crowther position was found by observing the absorption in further sheets of aluminum. The effective wave-length was 0.39A when the x-ray tube was operated at about 65 k.v. peak and 10 m.a.

Instead of comparing the intensity of the x-rays scattered at an angle ϕ from the crystal with those of the rays scattered from the crystal at some standard angle such as 60° as in Harvey's experiment, we compared the intensity of the rays scattered from the crystal in a direction ϕ with that of the rays scattered from a slab of carbon at a constant angle of 40°. Not only were the intensity of the scattered rays compared but also the intensities of the transmitted rays. Then, later, the intensity of the rays scattered from the carbon slab were compared with that of the rays scattered from a slab of paraffin at 90°, and also the intensities of the transmitted rays were compared. We were therefore able to calculate the ratio of the intensity of the x-rays scattered by the crystal at an angle ϕ to that of the rays scattered by paraffin at 90°, and also the ratio of the intensity of the primary beam transmitted through the crystal when in the Crowther position corresponding to a scattering angle ϕ to that of the primary beam transmitted through the paraffin when in the Crowther position corresponding to a scattering angle of 90°. We shall call these two ratios the scattering ratio and the transmitted ratio, respectively.

It must be noted that the ratios actually observed are ratios of ionization currents and not ratios of intensities. This difference comes in because the length of the ionization chamber is not sufficient for the complete absorption of the x-rays entering the chamber. The values of the ratios are shown in Table I.

TABLE I. *Experimental ratios. Sodium fluoride to paraffin.*

$(\sin \frac{1}{2}\phi)/\lambda$	Scattering	Transmission
0.109	0.26	1.333
.218	2.47	1.333
.327	3.02	1.331
.434	3.16	1.327
.540	3.20	1.317
.647	3.14	1.310
.855	2.77	1.282
1.057	2.46	1.243
1.250	2.19	1.196
1.447	1.91	1.140
1.631	1.73	1.072
1.812	1.59	1.000

The surface density of the crystal was 1.443 gm/cm^2 while that of the paraffin was 0.701 gm/cm^2.

III. INTERPRETATION OF THE RESULTS

Crowther's formula[16] for the intensity of the x-rays scattered in a direction ϕ from a slab of material whose thickness is t is

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[17] International Critical Tables, III, p. 217.

$$I_\phi = (AIt/R^2 \cos \tfrac{1}{2}\phi) \cdot s \tag{12}$$

where I is the intensity per unit area of the rays transmitted through the slab when held in the Crowther position, A is the area of the ionization chamber window, R is the distance of the window from the slab, and s is the linear spatial scattering coefficient per unit solid angle in a direction ϕ. At the time Eq. (2) was derived by Crowther, the Compton effect was unknown. Jauncey and Defoe[17] have considered the effect of the division of the scattered rays into coherent and incoherent rays and have shown that the simple Crowther formula must be replaced by

$$I_\phi = (AIt/R^2 \cos \tfrac{1}{2}\phi)(s_1 + s_2 T) \tag{13}$$

where s_1 and s_2 are respectively the coherent and incoherent linear spatial scattering coefficients per unit solid angle in a direction ϕ, and where T is a complicated expression involving the absorption coefficients of the coherent and incoherent scattered x-rays in the slab, in the air between the slab and in the aluminum window of the chamber. T is a function of the scattering angle ϕ. We shall write

$$I_\phi = I_{\phi 1} + I_{\phi 2} \tag{14}$$

where $I_{\phi 1}$ and $I_{\phi 2}$ are the intensities of the coherent and incoherent rays respectively. From Eq. (13),

$$I_{\phi 1} = (AIt/R^2 \cos \tfrac{1}{2}\phi) \cdot s_1 \tag{15}$$

and

$$I_{\phi 2} = \frac{AIt}{R^2 \cos \frac{1}{2}\phi} s_2 T. \tag{16}$$

Let the fractions of $I_{\phi 1}$ and $I_{\phi 2}$ which are absorbed in the ethyl bromide of the ionization chamber be K_0 and K_ϕ respectively. Then, if $C_{\phi 1}$ and $C_{\phi 2}$ are the respective ionization currents produced, we have

$$C_{\phi 1} = K_0 I_{\phi 1} \tag{17}$$

$$C_{\phi 2} = K_\phi I_{\phi 2}. \tag{18}$$

Also, if C is the ionization current produced by the transmitted rays,

$$C = K_0 I. \tag{19}$$

Hence, replacing the I's in Eq. (14) by the C's and taking account of Eqs. (15) and (16), we obtain, after rearranging and putting $C_\phi = C_{\phi 1} + C_{\phi 2}$,

$$C_\phi = \frac{ACt}{R^2 \cos \frac{1}{2}\phi} \left\{ s_1 + \frac{K_\phi T}{K_0} s_2 \right\} \tag{20}$$

C_ϕ is the actual measured ionization current. The relation between s_1 and S_1 is

$$s_1 = S_1 (NZ\rho/W) \cdot (e^4/m^2c^4) \cdot (1 + \cos^2 \phi)/2 \tag{21}$$

while that between s_2 and S_2 is

$$s_2 = S_2 \frac{(NZ\rho/W) \cdot (e^4/m^2c^4)}{(1 + \alpha \operatorname{vers} \phi)^3} \cdot \frac{(1 + \cos^2 \phi)}{2} \tag{22}$$

where ρ is the density of the slab, N is Avogadro's number, Z is the number of electrons in a molecule, and W is the molecular weight of the slab. If the scattering is from a slab of crystal, we use the values of S_1 and S_2 as given by Woo's Eqs. (7) and (9).

According to Harvey,[12] when x-rays of wave-length 0.39A are scattered at 90° from paraffin, the scattered rays are almost entirely incoherent, so that for this case, we may take $S_1=0$ and $S_2=1$. Hence, for scattering from paraffin at 90° we obtain an equation similar to Eq. (20), but with $s_1=0$ and s_2 given by Eq. (22) when $S_2=1$. In this equation for the scattering of paraffin, let us represent the ionization currents by P's. Dividing Eq. (20) by this equation for paraffin, we obtain after rearranging and taking account of Eqs. (7) and (9) for a crystal

$$K_0(f'^2-F^2)/Z_C+K_\phi T_C\cdot\frac{1-f'^2/Z_C^2}{(1+\alpha\,\mathrm{vers}\,\phi)^3}=\frac{K_{90^\circ}T_P}{1+\cos^2\phi}\cdot\frac{\cos\frac{1}{2}\phi}{\cos 45^\circ}\cdot\frac{\rho_P t_P}{\rho_C t_C}\cdot(W/Z)_C\cdot(Z/W)_P\cdot C_\phi/P_{90}\cdot P/C\cdot 1/(1+\alpha)^3. \tag{23}$$

Quantities with the subscript C refer to the crystal of sodium fluoride, while those with the subscript P refer to the paraffin. In the present case the changes of absorption due to change of wave-length in the air between the scattering slab and the ionization chamber and in the aluminum chamber window are negligible, so that T reduces to

$$T=(1-e^{-g})/g \tag{24}$$

where

$$g=(\mu_2-\mu_1)t/\cos\tfrac{1}{2}\phi. \tag{25}$$

The quantities μ_2 and μ_1 are the linear absorption coefficients of the incoherent and coherent scattered rays in the scattering slab.

All quantities in Eq. (23) except f' are either known, can be calculated, or can be measured. Eq. (23) therefore enables us to find f'. These values of f' are shown in Table II. Values of F^2/Z as given by Havighurst[14] are also shown in this table. Knowing f' we can find S_1 and S_2 by means of Eqs. (9) and (7) and hence also S(class), where

$$S(\text{class})=S_1+S_2. \tag{26}$$

The values of S_1, S_2 and S(class) are also shown in Table II.

TABLE II. *f' and S values for sodium fluoride.*

$(\sin\frac{1}{2}\phi)/\lambda$	F^2/Z	f'	S_1	S_2	S(class)	B
0.109	8.65	9.27	—	0.141	0.141	2.53
.218	4.95	7.20	0.240	.482	.722	3.94
.327	2.37	5.00	0.130	.750	.880	4.10
.434	.99	3.23	0.053	.895	.948	3.52
.540	.45	2.21	0.038	.951	.989	3.05
.647	.20	1.51	0.028	.977	.995	2.45
.855	.05	.74	0.005	.994	.999	1.59
1.057	.00	.17	0.003	1.000	1.003	.45
1.250	.00	.55	0.030	.997	1.027	1.72
1.447	.00	.48	0.023	.998	1.021	1.74
1.631	.00	.46	0.021	.998	1.019	1.87
1.812	.00	.00	0.000	1.000	1.000	.00

Compton has introduced a quantity B which is given by

$$BZ = 8\pi f'(\sin \phi/2)/\lambda. \tag{27}$$

The values of B are shown in the seventh column of Table II. This quantity is used in Compton's Fourier analysis method of obtaining the electron distribution within an atom.

IV. COMPARISON WITH THE SCATTERING FROM NEON

Wollan's S(class) values for neon, our S(class) values for sodium fluoride and Havighurst's F^2/Z values for sodium fluoride are shown by curves I, II and III respectively, of Fig. 1. Curve IV shows the values of S(class)$+F^2/Z$ for sodium fluoride. It is seen that, unlike the case of sylvine and argon, the (S(class)$+F^2/Z$) curve for sodium fluoride falls definitely below the S(class) curve for neon. Wollan's f' values for neon and our f' values for sodium fluoride are shown by curves I and II respectively, in Fig. 2. Comparing these curves, we note that the f' values for sodium fluoride are definitely below those for neon, so that the electron distribution for the average atom in a crystal of NaF is more diffuse than that for an atom of the gas neon. It is reasonable to expect that, when the atoms of a gas are concentrated into a crystal, there should be a distortion of the electron distribution of the atoms. This distortion explains the difference between the f' values for NaF and those for neon and it also explains the difference between the curves I and IV of Fig. 1. We might expect the distortion to be greater in the case of NaF than in the case of KCl, since the nuclear field of an atom in NaF is much weaker than that of an atom in KCl. This explains why there is such good

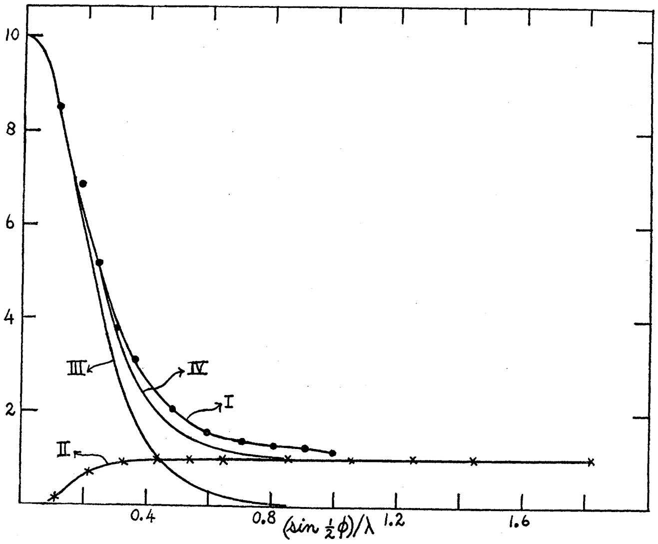

Fig. 1. Comparison of scattering from neon and NaF. Curve I—S(class) for neon (Wollan); Curve II—S(class) for NaF; Curve III—F^2/Z for NaF (Havighurst); Curve IV—S(class) $+F^2/Z$ for NaF.

agreement between argon and sylvine but not such good agreement between neon and sodium fluoride.

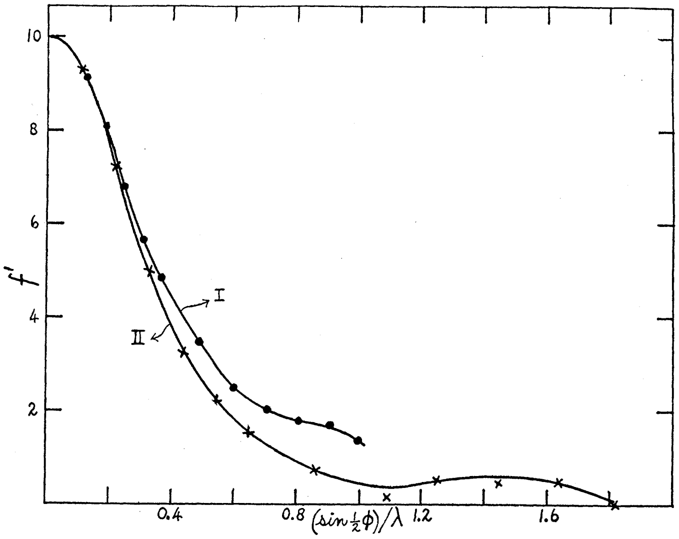

Fig. 2. Comparison of f' values. Curve I—Neon (Wollan); Curve II —NaF (Jauncey and Williams).

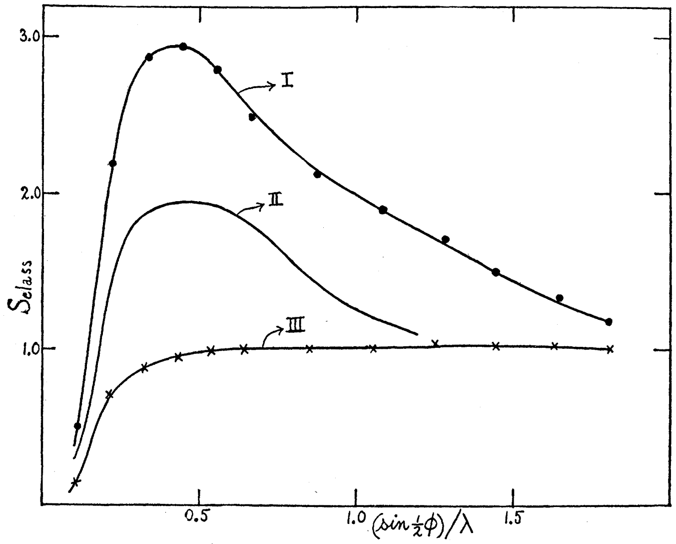

Fig. 3. Comparison of S(class) values for crystals. Curve I—sylvine (Harvey); Curve II—rock-salt (Jauncey and May); Curve III—NaF.

By referring to the seventh column of Table II, it is seen that our B values indicate two humps in the B curve in agreement with the B curve for neon which Wollan gives. It is the presence of the second hump which, according to

Wollan, causes the separation of the K electrons in the Fourier analysis of neon. We may say then that our B values support qualitatively Wollan's finding of a hump for the K electrons of neon in the U curve which he obtains by means of a Fourier analysis of his B curve for neon.

In this connection, the senior author wishes to remark that, as he[4] has already pointed out, the Compton Fourier analysis method in its present form is applicable only if $f'=f$. The senior author is not at present willing to admit that $f'=f$. Indeed, Woo has recently shown that the experimental evidence is rather in favor of $f'\neq f$. Jauncey[4] has shown that $f'<f$ if

$$\left(\sum_r E_r\right)^2 < Z \sum_r E_r^2 \tag{28}$$

which is always the case unless all the E's are equal. All the E's can be equal only if the individual electrons of an atom are indistinguishable from one another as far as the scattering of x-rays is concerned. The senior author is not at present willing to admit that the electrons in an atom are indistinguishable from one another.

V. COMPARISON WITH SYLVINE AND ROCKSALT

An interesting comparison of the S curves for sylvine,[12] rocksalt[7] and sodium fluoride is shown by curves I, II, and III respectively of Fig. 3. It is seen that as the average atomic number decreases the hump of the S curve diminishes until in the case of NaF the presence of a hump is by no means obvious.

In conclusion it should be pointed out that we found it necessary to use Woo's formula for the diffuse scattering from crystals in preference to Jauncey and Harvey's formula. For sylvine the scattered radiation is principally coherent so that the classical formula of Jauncey and Harvey is sufficiently approximate. However, in the case of sodium fluoride it is necessary to take account of the fact that a considerable portion of the scattered radiation is incoherent. Woo's separation of the scattered radiation into coherent and incoherent radiation has enabled us to allow for the difference in the absorption of the two kinds of radiation in the ionization chamber, and also for the extra absorption of the incoherent radiation in the crystal itself.

We wish to thank Professor H. M. Randall of the University of Michigan for supplying the crystal of sodium fluoride.