Second Series *August 15, 1931* *Vol. 38, No. 4*

THE

PHYSICAL REVIEW

DIFFUSE SCATTERING OF X-RAYS FROM SYLVINE

BY G. G. HARVEY
WASHINGTON UNIVERSITY, ST. LOUIS, MO.

(Received June 25, 1931)

ABSTRACT

By means of the formulas recently obtained by Compton for monatomic gases and by Jauncey and Harvey for simple cubic crystals f' values can be calculated from the observed intensities of the diffuse scattering. The formula for crystals is only valid for the case where the crystal consists of atoms of one kind. Up to the present time the only crystal for which S values were known was rocksalt, but this is a crystal consisting of two kinds of atoms. Sylvine, however, is a crystal consisting of one kind of atom, since the ions K^+ and Cl^- may be considered as argon-like atoms. In the present research S values have been obtained for sylvine at room temperature. If these S values are plotted against $(\sin \phi/2)/\lambda$, an S curve is obtained similar to that obtained by Jauncey and May for rocksalt as described by Jauncey and Harvey. Comparing the S curve for sylvine with Wollan's S curve for argon the two are tangent at $(\sin \phi/2)/\lambda = 1.05$ and beyond this appear to merge. From the formula of Jauncey and Harvey f' values for sylvine have been calculated using F values obtained by James and Brindley. Plotting the f' values for sylvine and those obtained by Wollan for argon against $(\sin \phi/2)/\lambda$, both sets of points fall on the same curve, the agreement being remarkable. Comparison is also made of these f' values with the theoretical f values obtained for a Schroedinger atom by James and Brindley. The agreement is good out to $(\sin \phi/2)/\lambda = 1.0$ but from there on the theoretical f curve falls off too rapidly. It might be expected that the theoretical f curve would fall off too slowly since f' is less than f. In this region the agreement between theory and experiment could be improved.

I. INTRODUCTION

SOME twenty-five years ago J. J. Thomson[1] investigated the theory of the scattering of x-rays by isolated electrons and obtained his famous formula for the spatial distribution of the intensity of x-rays scattered by a number of electrons acting independently of one another. In 1911 Barkla and Ayers[2] tested Thomson's formula experimentally and found that in the case of light atoms if each atom contains a number of electrons equal to half the atomic weight the Thomson formula agrees with the experimental findings for moderately soft x-rays and for angles greater than about 40°. For angles less than 40° Barkla and Ayers found that the experimental intensity of the scattered

---

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

[2] C. G. Barkla and T. Ayers, Phil. Mag. **21**, 275 (1911).

rays was in excess of the Thomson value. This phenomenon has since become known as "excess scattering." From our present viewpoint we now know that this excess scattering is due to constructive interference of rays scattered by different electrons. This idea of constructive interference was used by Laue[3] in his investigation of the scattering of x-rays from centers arranged in a geometric lattice. His investigation showed that in certain special directions the intensity of the scattered x-rays should be very great. This prediction was verified almost immediately by Friedrich and Knipping[4] who obtained what are now known as Laue spots by passing a beam of x-rays through a crystal of zinc blende. In 1914 Debye,[5] taking into account the thermal agitation of the atoms in a crystal lattice, predicted that there should be a decrease in the intensity of the specially scattered x-rays. Bragg[6] working on rocksalt found that Debye's prediction is qualitatively in agreement with the facts. As the temperature increases, the exactness with which the atoms at any instant of time fit into the lattice diminishes. An amorphous solid may be defined as one in which the atoms are not arranged in any kind of geometrical lattice and another way of describing Debye's theory of the temperature effect for crystals is to say that the decrease of intensity with increase of temperature is caused by the crystal in effect becoming more amorphous. According to Debye's theory[5] of the temperature effect there should be an increase in the diffuse scattering, which occurs in all directions, with increase in temperature due to the crystal becoming more amorphous.

In the case of scattering by amorphous substances no such special directions of great intensity as the Laue directions for crystals have been found. We have already mentioned that for an amorphous substance there is excess scattering at small angles, as found by Barkla and Ayers. In 1915 Debye[7] investigated the effect of constructive interference when the electrons of an atom of the scattering substance are arranged at equal intervals on the circumference of a circle, the atoms themselves being oriented in any direction. He found that there were directions of maximum and minimum intensity. This theory of Debye does not take into account the constructive and destructive interference between x-rays scattered by different atoms and so is only applicable to the scattering from a monatomic gas where the atoms are so far apart that interference phenomena may be neglected.

In 1917 Compton[8] investigated the effect of the arrangement of the electrons within the atom on the intensity of x-rays specially scattered (regularly reflected) from crystals. He found that the larger the volume through which the electrons of an atom may be considered as being distributed the less the intensity of the reflected rays. In other words the "larger" the atom the more amorphous in effect does the crystal become. Hence, using the ideas of Debye,

---

[3] M. Laue, Sitzungsber. d. Kgl. Bayer. Akad. d. Wiss., 303 (1912).

[4] W. Friedrich, P. Knipping and M. Laue, Ann. d. Physik **41,** 971 (1913).

[5] P. Debye, Ann. d. Physik **43,** 49 (1914).

[6] W. H. Bragg, Phil. Mag. **27,** 881 (1914).

[7] P. Debye, Ann. d. Physik **46,** 809 (1915).

[8] A. H. Compton, Phys. Rev. **9,** 29 (1917).

on this account also the diffuse scattering from crystals should be increased. In 1914 Darwin[9] developed a formula for the intensity of x-rays regularly reflected from simple cubic and parallelopipedal crystals. This formula contained a quantity which is designated by F and is now called the atomic structure factor. The atomic structure factor may be defined as the scattering power of an atom in a certain direction relative to the scattering power of an isolated electron in the same direction. In 1921 Bragg, James, and Bosanquet[10] measured the intensity of x-rays reflected from rocksalt and using Darwin's formula calculated F values. Theoretical F values can be calculated by the methods discussed in Compton's paper.[8]

In 1922 Jauncey[11] investigated experimentally the diffuse scattering from rocksalt and calcite and found that the spatial distribution of the scattered intensity was very similar to that when glass was used as the scatterer. According to Debye[5] the spatial distribution from the crystal should have been very different from that in the case of the amorphous glass. Jauncey[12] also tried the effect of temperature and found a qualitative but not a quantitative agreement with Debye's theory. This discrepancy between theory and experiment is due to the fact that Debye considered point atoms whereas the atoms must be considered as having size. In 1924 Jauncey and May[13] repeated Jauncey's experiment on rocksalt more accurately and obtained absolute values for the diffuse scattering. They found the scattering curve to be similar to that required by the Thomson theory for angles greater than about 60° but below 60° excess scattering occurs as found by Barkla and Ayers for amorphous substances and at very small angles the diffuse scattering drops to zero.

In 1928 Barrett[14] measured the spatial distribution of the intensity of x-rays scattered by gases. For the monatomic gas helium he found that the curve approximates the Thomson curve at large angles but shows excess scattering at small angles. In 1930 Compton[15] applied the principles of constructive and destructive interference to the problem of the scattering of x-rays from the electrons in the atoms of monatomic gases and obtained the formula

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

where S is the scattered intensity in a direction ϕ with the primary beam per electron relative to the scattered intensity from a single isolated electron in the same direction ϕ, Z is the number of electrons in an atom of the gas and f' is a quantity which is related to, but less than, the true atomic structure factor f without thermal vibration and which has been discussed recently by

---

[9] C. G. Darwin, Phil. Mag. **27**, 315 (1914).
[10] Bragg, James and Bosanquet, Phil. Mag. **41**, 309 (1921).
[11] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922).
[12] G. E. M. Jauncey, Phys. Rev. **20**, 421 (1922).
[13] G. E. M. Jauncey and H. L. May, Phys. Rev. **23**, 128 (1924).
[14] C. S. Barrett, Phys. Rev. **32**, 22 (1928).
[15] A. H. Compton, Phys. Rev. **35**, 925 (1930).

Jauncey.[16] The distinction between f' and f has also been pointed out by Herzog[17] in a recent paper.

Recently Jauncey[18] has applied the idea of interference to the problem of the scattering of x-rays by a solid consisting of atoms of one kind and has obtained the formula

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

where F is the atomic structure factor including the effect of thermal vibration, N is the number of atoms scattering, X is a certain double summation and the other quantities have the same significance as in Eq. (1). The double summation X has been evaluated by Jauncey and Harvey[19] for the case of diffuse scattering by a simple cubic crystal consisting of atoms of one kind and Eq. (2) then becomes

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

Jauncey and Harvey[19] and Jauncey[16] have pointed out that there is a relation between the scattering of x-rays by gases and by crystals. In these papers, [19,16] however, they were forced to make use of the results of Jauncey and May [13] for rocksalt, whereas Eq. (3) is only valid for a crystal consisting of atoms of one kind. It is very desirable therefore that the spatial distribution of the intensity of x-rays diffusely scattered by such a crystal should be investigated. Sylvine, which consists of the ions K^+ and Cl^-, may be considered as such a crystal and the diffuse scattering from sylvine should be related to the scattering from argon. While our papers[18,19] were in print a paper by Wollan[20] on the scattering from gases, including argon, appeared. The need for an investigation of the diffuse scattering by sylvine is therefore obvious and hence this paper.

II. Apparatus and Procedure

Fig. 1 shows a diagram of the apparatus used. A tungsten target tube placed at an angle of 45° to the plane of scattering so as to produce effectively unpolarized rays was operated at about 65 kv and 10 m.a. A constant source of a.c. with full wave rectification, described elsewhere,[21] was applied to the tube. The continuous radiation of a tungsten tube was used for several reasons. First, with a substance having as high an absorption coefficient as sylvine it is necessary to use moderately hard rays in order to obtain a measureable intensity of the scattered radiation. Second, the radiation from a molybdenum tube even when filtered through zirconium oxide consists of two wave-lengths as appear in the paper of Jauncey and May[13] and the occurrence

---

[16] G. E. M. Jauncey, Phys. Rev. July 1, 1931.

[17] G. Herzog, Zeits. f. Physik **69**, 207 (1931).

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

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

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

[21] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 698 (1931).

of these two wave-lengths makes interpretation of the results difficult. If it is desired to use line radiation it is necessary to use the balanced filter method described by Ross.[22] Moreover, a balanced filter necessitates the use of differential readings which, when the intensity is weak, may introduce considerable error in the final results. The x-ray beam passed through the three slits S_1, S_2, and S_3 to the crystal C. The slits consisted of small circular holes, S_1 and S_2 defining the beam while S_3 was slightly larger than the beam and served to eliminate any radiation scattered from the slit S_2. C was a crystal of sylvine about 1 cm square and a surface density of 0.214 gm/cm^2 mounted with its faces vertical on the axis of a Bragg ionization spectrometer. The scattered radiation was collected in the ionization chamber B which was filled with air saturated with ethyl bromide vapor. The chamber was fitted with a U-tube containing liquid ethyl bromide surrounded by a water bath kept at a constant temperature of 22°C to insure a constant density of the vapor. At this temperature the vapor pressure of ethyl bromide is[23] 415 mm of mercury. This was very necessary as for the wave-length used the length of the ionization chamber, which was 43 cm, was not sufficient to absorb the radiation completely. The angular width of the primary beam through the slits S_1 and

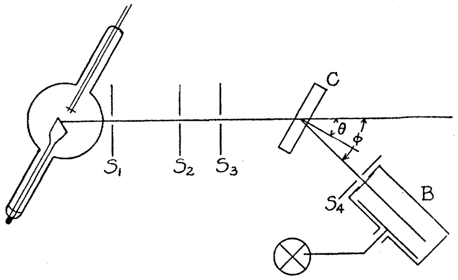

Fig. 1. Diagram of apparatus.

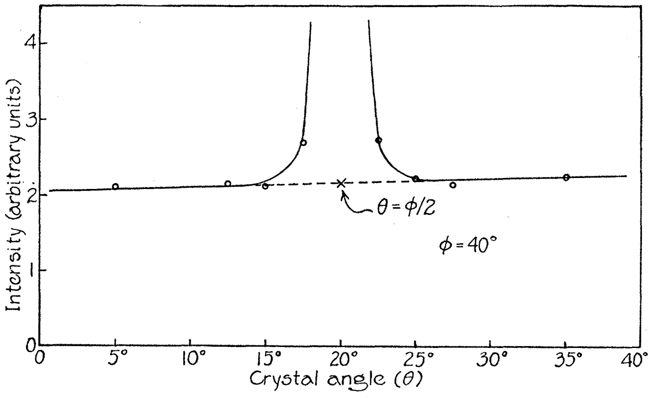

Fig. 2.

---

[22] P. A. Ross, Phys. Rev. **28**, 425 (1926).

[23] Int. Crit. Tables, III, p. 217.

S_2 was about one degree. The angular width of the scattered beam was determined by the slit S_4 and was never more than three degrees. The height of the slit S_4 was such that no part of the scattered beam could strike the sides of the ionization chamber. As this slit was about 2 cm high, it would have been necessary at small angles to apply a correction to the apparent scattering angle due to the finite height of the slit, if straight slits had been used. This correction can be avoided if the slit S_4 is made in the arc of an ellipse and this was done (actually a circular arc was used since the difference is not detectable for such a small arc) a series of slits being made with arcs appropriate to the various angles of scattering. The ionization current was measured by means of a Compton electrometer, having a sensitivity of about 8000 mm/volt, by the rate of charge method.

The procedure followed in measuring the scattered intensity was essentially that of Jauncey and May.[13] With the chamber set at a fixed angle ϕ the ionization current was measured for various values of θ, the angle between the normal to the crystal face and the primary x-rays, both above and below the value $\phi/2$. At $\theta=\phi/2$, of course, special scattering (regular reflection) occurs for any value of ϕ if continuous radiation is used. A typical curve obtained is shown in Fig. 2 for $\phi=40°$. It will be seen that for values of θ not too near $\phi/2$ the points lie on a straight line. Hence we may interpolate and find the value of the intensity that would be obtained at $\theta=\phi/2$ if regular reflection did not take place. This value of the intensity is needed in order to apply the Crowther formula[24]

$$I_\phi = I_\phi' t s_\phi \sec\theta \qquad (4)$$

where I_ϕ is the intensity scattered in the direction ϕ per unit solid angle. I_ϕ' is the intensity of the primary beam after passing through a scattering block of thickness t set at $\theta=\phi/2$. s_ϕ is the spatial scattering coefficient in the direction ϕ and $\theta=\phi/2$. No filtering material was placed in the primary beam since the crystal itself acted as a filter. The effective wave-length was obtained

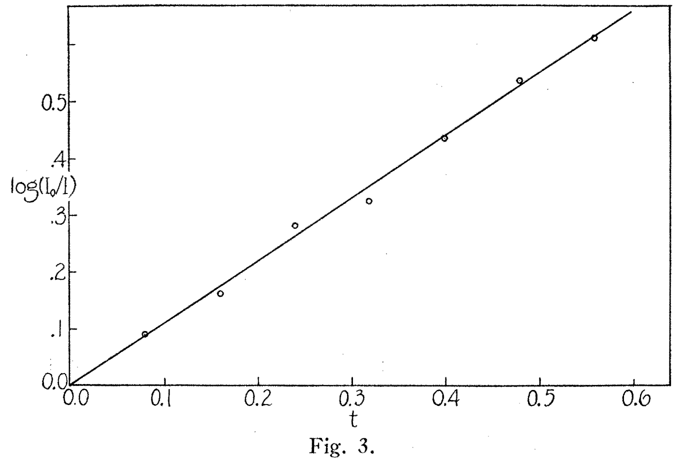

Fig. 3.

---

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

by measurement of the absorption coefficient by inserting sheets of aluminum in the *scattered* beam. This was done for several scattering angles. That the radiation penetrating the crystal was effectively homogeneous is shown by Fig. 3 in which $\log_{10}(I_0/I)$ is plotted against t, the thickness of the absorbing sheet and a straight line is obtained. Fig. 3 was obtained for a scattering angle of 40° and gave a mass absorption coefficient in aluminum of 0.96 gm^{-1}. From Compton's table of absorption coefficients,[25] this corresponds to a wave-length of 0.385A. The various wave-lengths thus obtained are shown in Table I. The average of all the values of the wave-length shown in Table I is 0.39A and since there is no apparent trend to the values with increasing angle, the value of 0.39A has been taken as a close estimate of the effective wave-length and was used in all calculations. Further evidence for the homogeneity of the radiation was furnished by the fact that for most values of ϕ the Laue spot at $\theta=\phi/2$ was not very intense. It was intense, however, at values of ϕ in the vicinity of which the Bragg law was satisfied for the above value of the wave-length. Further, there was no appreciable intensity of incoherent radiation, since the measured wave-length at 90° was no greater than that found at smaller angles.

TABLE I. *Effective wave-lengths.*

Scattering angle	Mass absorption coefficient in aluminum	Wave-length *A*
20°	0.964	0.390
30°	1.005	0.400
40°	0.955	0.385
50°	0.850	0.370
60°	0.975	0.392
90°	1.005	0.400

III. EXPERIMENTAL RESULTS

Experimental values of the scattering coefficient s_ϕ were obtained in the following manner. A curve such as the one shown in Fig. 2 was taken at the desired angle ϕ using the appropriate slit at s_4 (Fig. 1). Then using the same slit a similar curve was run at a large angle, such as 60°, where the shape of the slit has practically no effect on the value of the scattering angle. From Eq. (4) we may now obtain the values of s_ϕ relative to the value at 60° by means of the relation

$$s_\phi/s_{60}=\frac{\cos\phi/2}{\cos 30^\circ}\times\frac{(I_\phi/I_\phi')}{(I_{60}/I'_{60})}\,. \tag{5}$$

The reason 60° was chosen for comparison rather than 90° was due to the fact that the intensity at 90° is very weak which makes it more difficult to obtain accurate readings. Hence 60° was used and was later carefully compared with the scattering at 90° by the same method. This procedure, however, gives only relative values of s_ϕ whereas absolute values are necessary

---

[25] A. H. Compton, "X-Rays and Electrons," p. 184.

in order to obtain true values of S. Now Jauncey and the author[21] have shown that in the vicinity of 90° the shape of the scattering curve from paraffin is accurately given by the Dirac formula.[26] If we further assume that the Dirac formula also gives the absolute value correctly in this region then we may obtain absolute values of s_ϕ for sylvine by comparison with the value for paraffin at 90°. This is the same method as that used by Wollan[20] who took hydrogen at 90° as a standard. Hence values of (I_ϕ/I_ϕ') were measured at 90° for a scattering block of paraffin and also for the crystal of sylvine. When paraffin was used the sylvine crystal was placed in the primary beam so that the radiation would be the same in the two cases, the paraffin having practically no effect on the hardness of the rays. The absolute value of the spatial mass scattering coefficient at 90° for sylvine, s_2/ρ_2, is then given by

$$\frac{s_2}{\rho_2} = \frac{s_1}{\rho_1} \times \frac{(I_\phi/I_\phi')_2}{(I_\phi/I_\phi')_1} \times \frac{(\rho_1 t_1)}{(\rho_2 t_2)} \tag{6}$$

where s_1/ρ_1 is calculated from the Dirac formula, $(\rho_1 t_1)$ is the mass per unit area of the paraffin slab, $(\rho_2 t_2)$ the same quantity for the crystal, ρ_1 and ρ_2 are the densities of paraffin and sylvine respectively, $(I_\phi/I_\phi')_2$ is the ratio of scattered to transmitted intensity for sylvine and $(I_\phi/I_\phi')_1$ the same quantity for paraffin.

Practically all of the radiation scattered by paraffin is incoherent. Jauncey and the author[21] applied Wentzel's formula[27] in the form given by Compton[15] to calculate the percentage of coherent radiation present. From Pauling's[28] distribution function for helium modified to apply to the K electrons of carbon it was shown that[29]

$$I_{\text{coh}} = 4I_e/(1 + 0.022x^2)^4 \tag{7}$$

where I_e is the classical value of the scattering from a single electron and $x = (4/\lambda) \sin \phi/2$. In the present case this becomes $I_{\text{coh}} = 0.186\ I_e$ and since only the K electrons of the carbon in the paraffin scatter coherently the ratio of coherent to total scattered radiation at 90° is 2.3 percent, which may be neglected. Since the ionization chamber did not completely absorb the radiation entering it, it was necessary to correct for the change of wave-length. Let μ/ρ be the mass absorption coefficient of ethyl bromide for the wavelength 0.39A and μ'/ρ the corresponding quantity for the wave-length scattered at 90° from paraffin (0.39+0.024A) and let m be the mass of ethyl bromide per unit area of cross section of the ionization chamber. Then the observed value of $(I_\phi/I_\phi')_1$ must be multiplied by

$$\frac{1 - e^{-(\mu/\rho)m}}{1 - e^{-(\mu'/\rho)m}}$$

---

[26] P. A. M. Dirac, Proc. Roy. Soc. **A111,** 405 (1926).

[27] G. Wentzel, Zeits. f. Physik **43,** 779 (1927).

[28] L. Pauling, Proc. Roy. Soc. **A114,** 181 (1927).

[29] The exponent "4" was inadvertently omitted from the denominator in Eq. (12) of reference 9.

to give the correct value to be inserted in Eq. (6) since the longer wave-length is more completely absorbed. We thus obtain from Eq. (6) the absolute value of s_ϕ/ρ for sylvine at 90° and consequently at all angles. The final values for s_ϕ/ρ for sylvine are given in the second column of Table II. Each value of s_ϕ/ρ is divided by the corresponding Thomson value and values of S are obtained. These are shown in the third column of Table II.

TABLE II. *Scattering of x-rays from sylvine.*

$(\sin \phi/2)/\lambda$	s_ϕ/ρ	S	F	f'
0.112	0.50	0.50	15.0	15.1
0.224	2.18	2.19	10.0	11.4
0.335	2.82	2.88	7.0	9.4
0.445	2.80	2.95	5.2	8.1
0.555	2.58	2.80	3.85	7.1
0.665	2.22	2.50	2.75	6.05
0.877	1.71	2.13	1.31	4.8
1.082	1.36	1.90	0.50	4.2
1.281	1.08	1.71	0.12	3.7
1.470	0.88	1.49	0.00	3.05
1.648	0.69	1.33	0.00	2.5
1.811	0.59	1.17	0.00	1.8

IV. DISCUSSION

The values of S for sylvine are shown by the black circles in Fig. 4. Wollan's values of S for argon[29] are shown by the crosses in this figure. It is important to note that Wollan's S curve for argon seems to be tangent to the S curve for sylvine at about $(\sin \phi/2)/\lambda = 1.05$. It is unfortunate that Wollan does not have S values beyond this point so that we might be sure that the S curves for sylvine at room temperature (295°K) and argon merge beyond this point. Barrett[14] measured the scattering from argon at values of $(\sin \phi/2)/\lambda$ greater than 1.05 but his values seem to be relative rather than absolute since Waller and Hartree[30] have pointed out that it seems to be necessary to multiply Barrett's values by a factor to bring his S values into conformity with their theoretical S values. The writer has tried adjusting Barrett's S values but they do not seem to follow Wollan's S curve in the region of $(\sin \phi/2)/\lambda = 0.995$. If the S curves for argon and sylvine do merge at $(\sin \phi/2)/\lambda = 1.05$, as seems to be the case if Wollan's values are used, then this is so quite apart from either the theory of Compton[15] or that of Jauncey and Harvey.[19] It means that in the region beyond $(\sin \phi/2)/\lambda = 1.05$ the spatial mass scattering coefficients of sylvine and argon are indistinguishable and that the interaction of the x-rays scattered by different atoms of the solid crystal disappears.

In order to calculate the quantities f' of Eq. (3) it is necessary to know the values of F, the atomic structure factor at room temperature. James and Brindley[31] give values of F for sylvine at 86°K and 290°K but the values at 290°K extend only to $(\sin \phi/2)/\lambda = 0.828$ although those at 86°K go as far as

---

[30] I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 119 (1928).

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

$(\sin \phi/2)/\lambda = 1.275$. If we assume as an experimental fact that the temperature factor is of the form $e^{-B\sin^2\phi/2}$ where B is a function of the temperature we may calculate the difference in the B's for the above two temperatures for all those values of F which are given at both temperatures. This was actually done and it was found that the difference in B's was practically constant for all values of F and, further, agreed with Waller's modification[32] of the Debye formula,[5] as found by James and Brindley[31] Hence for these values of F which are given only at the lower temperature we may use this value of the temperature factor and calculate the F values at room temperature. These F values are shown in the fourth column of Table II. The f' values for sylvine are then obtained from Eq. (3) and are shown in the fifth column of Table II.

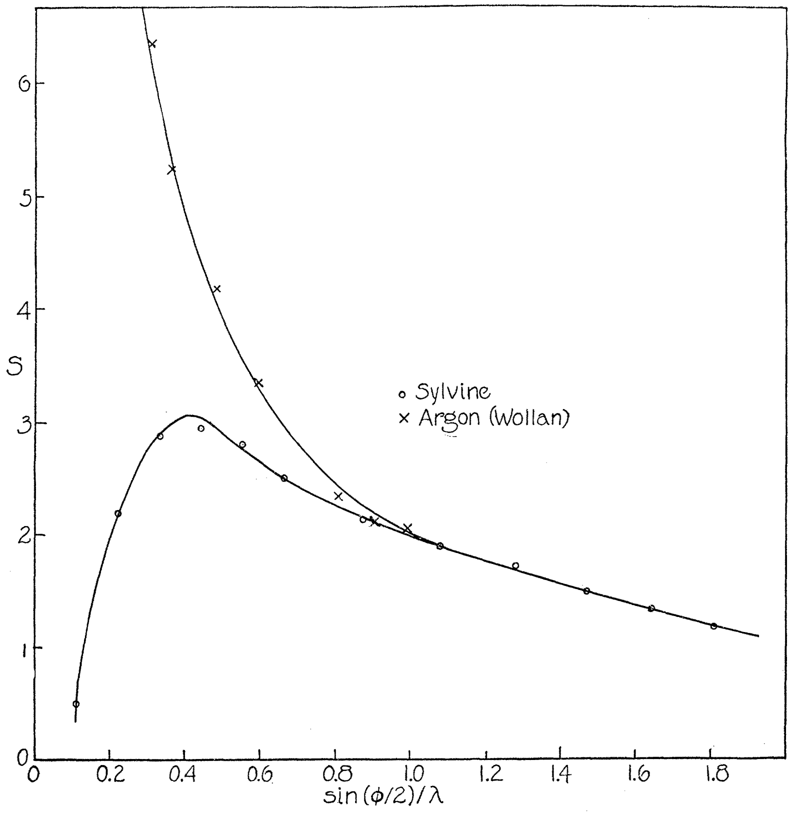

Fig. 4.

In order to compare the f' values for sylvine with those found by Wollan[20] for argon, both sets of values are shown in Fig. 5, the black circles representing f' values for sylvine and the crosses the f' values for argon. It is seen that both sets of f' values fall on practically the same curve. The agreement is

---

[32] I. Waller, Upsala Univ. Arsskrift (1925).

remarkable. The full curve shown in Fig. 4 is the average of the theoretical *f* values for K^+ and Cl^- calculated by James and Brindley[31] on the basis of a Schroedinger charge distribution in the ions calculated by Hartree's method of the self-consistent field.[33] It is seen that the agreement between theory and experiment is good out to values of $(\sin \phi/2)/\lambda$ of about 1.0 but beyond this the theoretical curve drops off too rapidly. However the experimental points are f' values and these should be somewhat *less* than the *f* values, especially at larger angles,[16] so that the agreement between theory and experiment in the region beyond $(\sin \phi/2)/\lambda = 1.0$ could be improved.

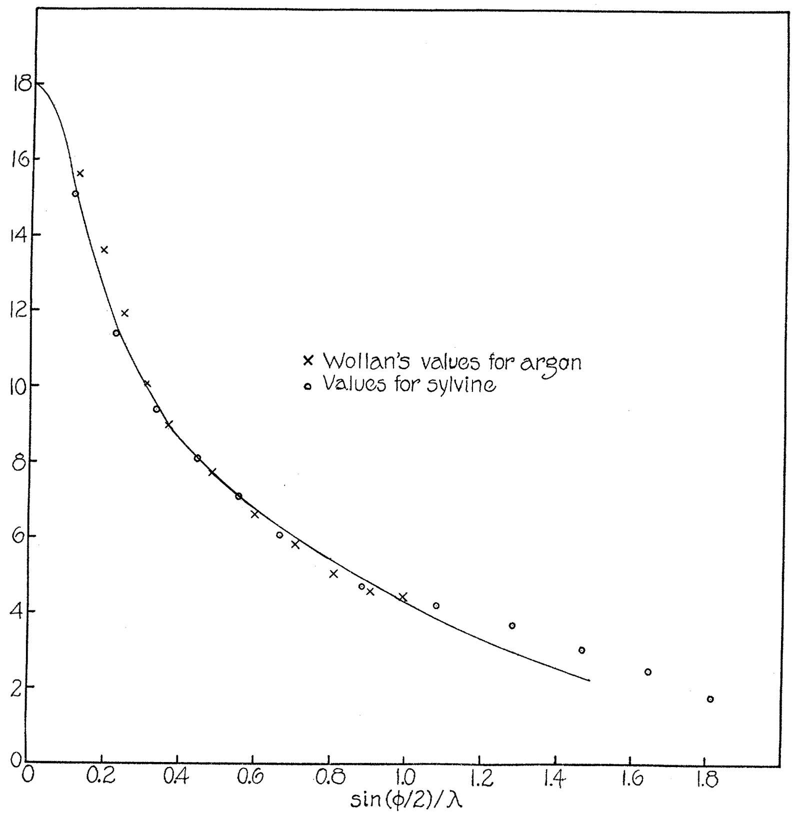

Fig. 5.

In conclusion, the writer wishes to thank Professor G. E. M. Jauncey for suggesting this problem and for much useful discussion and aid during the progress of this research. Also the writer's thanks are due to Professor H. M. Randall of the University of Michigan for supplying the crystal of sylvine.

---

[33] D. R. Hartree, Proc. Camb. Phil. Soc. **24,** 89 and 111 (1928).