

## Diffuse Scattering of X-Rays from Sylvine. III. Scattering at the Temperature of Liquid Air

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This paper is an extension of previous work on the diffuse scattering of homogeneous x-rays from sylvine. Measurements have now been carried out at the temperature of liquid air. It is found that taking into account uncertainties in the measurements of both the diffuse

scattering and regular reflection the formula  $S = (f^2 - F^2)/Z + (1 - f^2/Z^2)/(1 + \alpha \text{vers } \phi)^3$  probably accounts for the intensity of the scattering within the limits of experimental error for the range of temperature used.

### I. INTRODUCTION

IN a recent paper<sup>1</sup> the absolute intensity of x-rays diffusely scattered from sylvine was measured with homogeneous Mo  $K\alpha$  radiation obtained by the use of balanced filters.<sup>2</sup> It was found that the  $f$  values calculated from these measurements were in good agreement with Wollan's results<sup>3</sup> for argon except at small angles and also with the theoretical values of James and Brindley.<sup>4</sup> It was further found that the use of homogeneous radiation improved the agreement with theory at large angles as compared with the results of previous work with inhomogeneous radiation.<sup>5</sup> Previous results at the temperature of liquid air<sup>6</sup> while in qualitative agreement with theory showed a greater decrease in the scattering than was to be expected. In this work also inhomogeneous radiation was used and the intensities were measured photographically, a combination which makes it practically impossible to correct for the increased absorption of the incoherent scattering and is in general not satisfactory. The measurements here reported have been carried out with homogeneous Mo  $K\alpha$  radiation and an ionization chamber.

### II. APPARATUS AND PROCEDURE

The apparatus used in this experiment was the same as that used in the measurements at room temperature<sup>1</sup> except it was of course necessary to arrange for cooling the crystal. The cooling chamber used is shown in Fig. 1a. It consisted of an outside brass cylinder *A* the diameter of which was 3.25 inches. Celluloid windows 0.005 inch thick were provided for the x-rays. The bottom of this cylinder was threaded on the inside to receive a cap *B* which rested

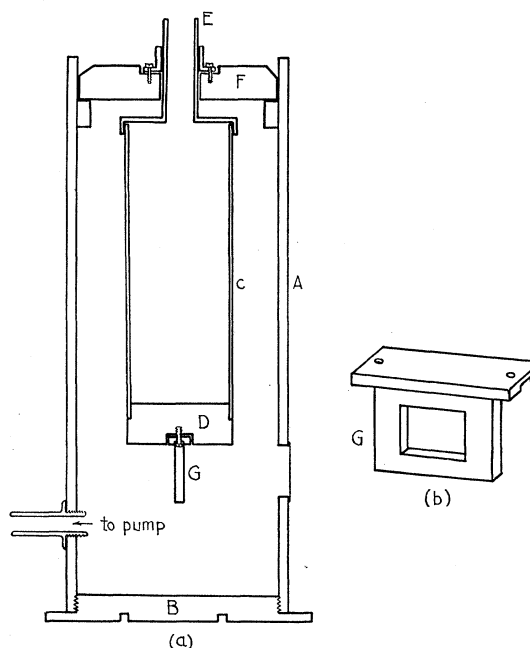


FIG. 1. Cooling chamber and crystal mounting.

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<sup>1</sup> G. G. Harvey, *Phys. Rev.* **43**, 591 (1933).

<sup>2</sup> P. A. Ross, *Phys. Rev.* **28**, 425 (1926).

<sup>3</sup> E. O. Wollan, *Phys. Rev.* **37**, 862 (1931).

<sup>4</sup> R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

<sup>5</sup> G. G. Harvey, *Phys. Rev.* **38**, 593 (1931).

<sup>6</sup> G. E. M. Jauncey and G. G. Harvey, *Phys. Rev.* **38**, 1925 (1931).

centrally on the crystal table of the spectrometer. The crystal table was provided with two pins which fitted into corresponding holes in *B* thus enabling the cooling chamber to be removed and replaced in the same position. Concentric with *A* was a thin brass cylinder *C* to the bottom of which was soldered a thick copper disk in which there was milled a slot to receive the crystal holder. The top of the cylinder *C* was reduced in size as shown so that the portion of metal exposed to the outside air should be as small as possible. It passed through a Bakelite cap *F* which was bolted to a brass ring. The space between *A* and *C* was evacuated by means of a Hyvac pump to a pressure of about 0.001 mm of mercury. As the tube passing through *F* is practically at liquid air temperature it is not possible to use a wax seal. To obtain a tight joint a brass collar was soldered to the tube *E* and bolted by means of six screws to the Bakelite cap. A rubber gasket well smeared with stopcock grease was found to give a reasonably tight joint even after the grease had frozen. An enlarged view of the crystal mounting *G* is shown in Fig. 1b. The crystal fitted closely in a recess in the copper mounting and was fastened with a small amount of sealing wax, the crystal being in direct contact with the metal, however. The mounting was bolted in the slot in the copper disk *D* by means of two screws. This arrangement was used so as to make it possible to change crystals without unsealing any joints except that of the cap *B*. When in use at low temperature the cylinder *C* was always kept more than half filled with liquid air although previous test had shown that the crystal temperature was practically that of liquid air so long

as any remained in the flask. The chamber worked rather better than was expected requiring about 300 g of liquid air per hour and remaining entirely free from moisture deposits.

The experimental procedure was to measure the ionization current for various values of  $\theta$ , the angle between the normal to the crystal face and the primary beam of x-rays, at room temperature and immediately after at the temperature of liquid air for a given scattering angle  $\phi$ . The ratio of these two currents for  $\theta = \phi/2$  could then be obtained.

### III. RESULTS

It has been shown<sup>7, 8</sup> that the intensity of the diffuse scattering from a simple cubic crystal consisting of atoms of one kind should on the classical theory be given by

$$S_{\text{class.}} = 1 + (Z-1)f^2/Z^2 - F^2/Z \quad (1)$$

with the usual notation. Woo<sup>9</sup> has independently shown that on taking account of the change of wave-length due to the Compton effect the scattering is given not by Eq. (1) but by

$$S = (f^2 - F^2)/Z + (1 - f^2/Z^2)/(1 + \alpha \text{vers } \phi)^3 \quad (2)$$

where the first term refers to the coherent and the second to the incoherent part of the scattering. What is actually measured, however, is the ionization current produced by the scattered radiation, or rather the ratio of the ionization currents at the two different temperatures of the crystal. By referring to the paper of Jauncey and Williams<sup>10</sup> it may easily be shown that this ratio is given by

$$\frac{i_1}{i_2} = \frac{f_1^2 - F_1^2 + (1 - f_1^2/Z^2)TZ(K_\phi/K_0)/(1 + \alpha \text{vers } \phi)^3}{f_2^2 - F_2^2 + (1 - f_2^2/Z^2)TZ(K_\phi/K_0)/(1 + \alpha \text{vers } \phi)^3} \equiv \tau, \quad (3)$$

where  $K_\phi/K_0$  is the ratio of the absorption in the ionization chamber for a wave-length  $\lambda + 0.024 \text{vers } \phi$  to that for a wave-length  $\lambda$  and the factor  $T$  is due to the fact that the modified radiation is more strongly absorbed in the

crystal itself. If it is assumed that  $F$  is the only quantity in Eq. (3) that is affected by temperature (i.e.,  $f_1 = f_2 = f$ ) then by using values of  $f$  obtained at room temperature<sup>1</sup> together with James and Brindley's values<sup>11</sup> of  $F_1$  and  $F_2$  at

<sup>7</sup> G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

<sup>8</sup> G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931).

<sup>9</sup> Y. H. Woo, Phys. Rev. **38**, 6 (1931).

<sup>10</sup> G. E. M. Jauncey and P. S. Williams, Phys. Rev. **41**, 127 (1932).

<sup>11</sup> R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

the temperature of liquid air (86°K) and room temperature (290°K), respectively, we may calculate values of  $\tau$ , the temperature effect to be expected. The values so calculated are denoted by  $\tau_c$  in Table I. The experimental values of

TABLE I.

$\phi$	$(\sin \phi/2)/\lambda$	$\tau_c$	$\tau_{\text{exp}}$	$f_1$	$f_2$	$F_1$	$F_1$ (J.&B.)
10°	0.123	0.54	0.41	15.05	15.15	14.90	14.80
20°	0.245	0.68	0.61	11.39	11.61	10.78	10.55
30°	0.365	0.68	0.62	8.83	9.03	7.85	7.65
40°	0.482	0.72	0.67	7.58	7.61	6.10	6.00
50°	0.596	0.71	0.70	6.65	6.65	5.10	5.10
60°	0.708	0.72	0.70	5.91	5.95	4.40	4.35
70°	0.804	0.74	0.73	5.50	5.6	3.85	3.70
80°	0.905	0.80	0.79	4.66	4.7	2.94	2.93
90°	0.995	0.85	0.86	4.35	4.3	2.26	2.35
100°	1.080	0.89	0.84	3.57	3.6	2.14	1.90
110°	1.154	0.92	0.90	3.22	3.25	1.59	1.55

$i_1/i_2$  are denoted by  $\tau_{\text{exp}}$ . It is seen that except at large angles of scattering the experimental ratios are in every case slightly smaller than the calculated values. At large angles the experimental ratio is subject to a larger experimental error since it is the ratio of two small quantities that is involved. In the previous work on this problem<sup>6</sup> the temperature effect for the whole range of scattering angles considered was measured at the same time on the same film so that any extraneous error would be expected to affect all angles in the same sense. In the present case, however, the various points are completely independent which together with the fact that they fall approximately on a smooth curve would seem to indicate that there actually is a slight difference in the values of  $\tau_c$  and  $\tau_{\text{exp}}$  outside of the limits of experimental error. A possible explanation would be to assume that  $f$  is also a function of temperature.  $F$  is determined by the electron distribution with respect to a lattice point whereas  $f$  depends on the distribution relative to the center of the atom. Since the distance between atoms in a crystal is of the same order as the diameter of the atom it might be thought that at room temperature the available space in which the atom can vibrate is limited whereas at low temperatures the amplitude of the thermal vibrations is smaller (by about 40 percent)<sup>11</sup> and so the atom has "more room in which to be diffuse." This would mean that  $f$  might actually decrease with de-

creasing temperature while, of course,  $F$  increases. The effect should only be noticeable at small angles of scattering since it would only be the outer shell of electrons that would be appreciably affected. Such a possibility was suggested some time ago by Professor A. Goetz in a conversation with Professor Jauncey and the writer in connection with previous work on the temperature effect.<sup>6</sup> Assuming the entire difference between  $\tau_c$  and  $\tau_{\text{exp}}$  at small angles to be due to a change in  $f$  we may calculate the change necessary to account for the discrepancy. In Table I the numbers in the fifth column ( $f_1$ ) are the  $f$  values at liquid air temperature so calculated while those in column six ( $f_2$ ) are the  $f$  values at room temperature. It is seen that a very small difference will account for the observed effect.

Another possibility is that the  $F_1$  values at liquid air temperature may be slightly in error at small angles. The correction for extinction becomes important at low temperatures and small angles and is to some extent doubtful. Assuming, then, that  $f$  is independent of temperature and taking  $F_2$  at room temperature and  $\tau_{\text{exp}}$  as known we may calculate  $F$  values at the temperature of liquid air. The next to last column in Table I shows the values so calculated while the last column gives James and Brindley's results.<sup>11</sup> Here again it is seen that a very small difference will account for the observed effect.

A summary of the results at both room and liquid air temperature is shown in Fig. 2. The solid curves were calculated from James and Brindley's theoretical values<sup>4</sup> of  $f$  and experimental values<sup>11</sup> of  $F$  at the two temperatures.  $S_{\text{class}}$  values have been calculated rather than  $S$  values so as to give curves which should be independent of the wave-length. The experimental points at room temperature are taken from<sup>1</sup>. In order to obtain  $S_{\text{class}}$  values at liquid air temperature without making any assumption as to what quantities are affected by temperature the following method was used. It was found that the ratios of the calculated values of  $S_{\text{class}}$  at liquid air temperature to those at room temperature differ by not more than one percent from  $\tau_c$ ; i.e., the ratios of the ionization currents are equal to the ratios of the  $S_{\text{class}}$  values to within one percent. Hence the experimental

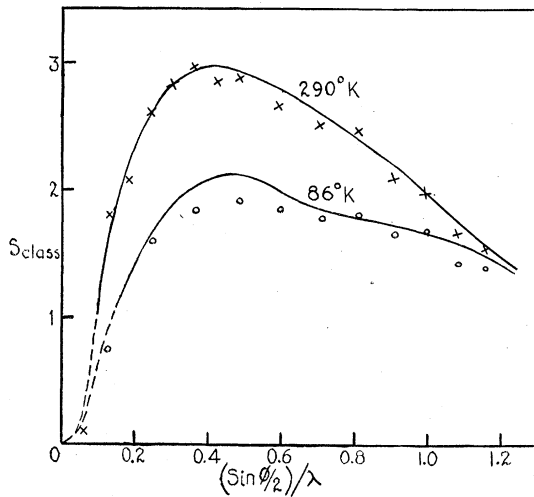


FIG. 2. Summary of the results on the scattering of x-rays from sylvine at both room and liquid air temperatures.

values of  $S_{\text{class}}$  at room temperature were multiplied by  $\tau_{\text{exp}}$  to obtain  $S_{\text{class}}$  at the temperature of liquid air. It is seen that at room temperature the experimental points fall on both sides of the calculated curve and probably agree with it within experimental error, while at liquid air temperature the experimental points are predominately on the lower side as pointed out before.

It may not be unnecessary to point out that in calculating such curves one must be very careful to use values of  $f$  and  $F$  as accurate as possible since it is essentially the difference of the squares of these two quantities that is involved. In fact at small angles  $(Z-1)f^2/Z$  is nearly equal to  $F^2$  and as it is necessary to obtain some of these values by interpolation it

is essential to use accurate values. It is even then quite possible to obtain values of  $S$  differing by one or two percent depending on the error in reading the curves. A possible check is to see that the  $S$  values lie on a smooth curve. In view of this it may be that the agreement between the calculated and observed values is nearly as close as can be expected.

### III. CONCLUSION

Measurements of the intensity of the diffuse scattering of homogeneous x-rays from sylvine give values of the atomic structure factor  $F$  at the temperature of liquid air which are slightly less than those obtained by James and Brindley from experiments on reflection. The difference, however, is only about one percent and it seems that taking into account the uncertainty of the extinction correction and the experimental error in the intensity measurements in the two cases, the difference is probably explainable without the necessity of introducing any further assumption. As pointed out at the beginning of this paper previous work on the same problem using inhomogeneous radiation gave rather unsatisfactory results. In this connection it is interesting to note that in the case of scattering from  $\text{CCl}_4$  and  $\text{SiCl}_4$  the use of monochromatic radiation has also improved the agreement between the theoretical and observed temperature effect.<sup>12, 13</sup>

In conclusion the author wishes to express his appreciation to Professor Arthur H. Compton for his continued interest and suggestions throughout the course of the work.

<sup>12</sup> R. W. James, Phys. Zeits. 33, 737 (1932).

<sup>13</sup> W. van der Grinten. Phys. Zeits. 33, 769 (1932).