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DIFFUSE SCATTERING OF X-RAYS FROM SYLVINE AT LOW TEMPERATURE

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Abstract

By use of a modification of the photographic method described by Claus the authors have compared the intensities of x-rays of wave-length 0.43A diffusely scattered from sylvine at angles in the range 25° to 90° at a temperature of 90°K with the intensities at these same angles at a temperature of 300°K. Jauncey and Harvey have shown that the intensity of the diffusely scattered rays should be given by $S=S'-F^2/Z$, where S' is independent of the temperature and F is the atomic structure factor containing the effect of thermal agitation. With James and Brindley's F values at 90°K and 300°K theoretical values of S for 90°K have been calculated. The experimental S values at 90°K are lower than the theoretical S values. This result is in accord with that found by Claus for rocksalt. Plotting $\log (S'-S_1)/(S'-S_2)$, where the subscripts refer to the two temperatures, against $(\sin^2\phi/2)/\lambda^2$ a straight line is obtained whose slope agrees with that required by the Waller and not the Debye formula for the temperature effect. It is impossible by means of this experiment to show whether or not there is zero point energy. In order to do this an assumption concerning the electron distribution in the atom must be made.

I. Introduction

Compton[1] has shown theoretically that the intensity of x-rays diffusely scattered by a monatomic gas is given by

$$S = 1 + (Z - 1)f'^2/Z^2 \qquad (1)$$

where S is the scattering per electron in terms of the Thomson[2] value in the same direction, Z the atomic number of the gas and f' an average atomic structure factor for the atom at rest. The difference between f, the true atomic structure factor, and f' has been discussed by Jauncey[3] and Herzog.[4] Jauncey and Harvey[5,6] have subsequently shown theoretically that the in-

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[1] A. H. Compton, Phys. Rev. **35**, 925 (1930).
[2] J. J. Thomson, Conduction of Electricity through Gases, 2nd Edition, p. 325.
[3] G. E. M. Jauncey, Phys. Rev. **38**, 1 (1931).
[4] G. Herzog, Zeits. f. Physik **69**, 207 (1931).
[5] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).
[6] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931).

tensity of the diffuse scattering from simple cubic crystals consisting of atoms of one kind is given by

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

where F is the atomic structure factor, including the effect of thermal agitation, as obtained from crystal reflection. Independently Woo[7] has obtained the formula

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

where $\alpha = h/mc\lambda$ and ϕ is the angle of scattering. Woo's formula reduces to ours for small values of α. In Eq. (2) f' and Z are independent of the temperature while F for sylvine is a function of the temperature as found by James and Brindley.[8] Hence S should be a function of the temperature. With rocksalt Claus[9] has shown that at low temperatures the values of S are below their corresponding values at room temperature. However, the values of S found by Claus at low temperature did not agree with the values calculated from the room temperature values of S and James and Firth's values[10] of F at room and liquid air temperatures. It was thought that this disagreement might be due to the fact that Eq. (2) is valid only for simple cubic crystals consisting of atoms of one kind whereas rocksalt consists of atoms of two kinds. It was suggested that the diffuse scattering from sylvine, which may be considered as consisting of atoms of one kind, should be measured at low temperatures. Accordingly this research was undertaken to determine the intensity of diffuse scattering of x-rays from sylvine at low temperatures.

II. Method of Experiment

A photographic method similar to that described by Claus[9] was used. However, instead of scattering the x-rays from the front face of a thick crystal, as done by Claus, we have caused a beam of x-rays to penetrate through a thin sliver of crystal and have measured the photographic effect of the diffusely scattered x-rays which penetrate through the crystal. The arrangement is shown in Fig. 1. The crystal was enclosed in a thick copper cylinder, the lower portion of which dipped into a Dewar flask which could be filled with liquid air at will. This flask was itself enclosed in an outer case which sits on the table of a Bragg ionization spectrometer and which is of double-walled brass packed with asbestos between the walls as is shown in Fig. 2 of Claus' paper.[9] The rays entered the cavity in the copper cylinder through a thin mica window and the scattered rays emerged through a similar window. The scattered rays passed through wide windows both in the copper cylinder and outer brass case, so that with one exposure the diffuse scattering over a large range of angles could be obtained. This procedure was suggested to the authors by Dr. Claus. The outer window was covered with thin mica. Around the boundary of the window was placed a heating coil in order to prevent

[7] Y. H. Woo, Phys. Rev. **38,** 6 (1931).
[8] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121,** 155 (1928).
[9] W. D. Claus, Phys. Rev. **38,** 604 (1931).
[10] R. W. James and Elsie M. Firth, Proc. Roy. Soc. **A117,** 62 (1928).

moisture from being deposited on the window. There was no tendency for moisture to collect upon the mica windows of the copper cylinder because these windows were continually bathed in a draft of dry air rising from the reservoir of liquid air. In order to produce fiducial marks upon the developed film lead strips were placed vertically across the window in the outer casing at known angles.

Following the method developed by Claus[9] exposures of 1, 2, and 3 hours were run at room temperature; then liquid air was poured into the Dewar flask and after the sylvine crystal had come to an equilibrium temperature (90°K) as registered by a copper-iron thermocouple an exposure of 4 hours was run; during this exposure the level of the liquid air in the Dewar flask was kept constant as described by Claus.[9] Next, the liquid air was allowed to evaporate off and the crystal to come to room temperature after which a set

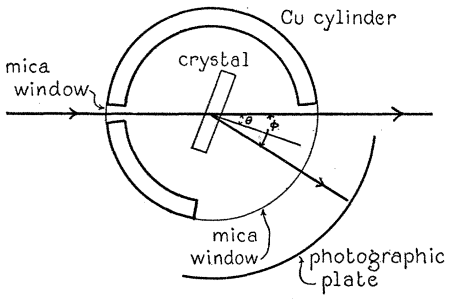

Fig. 1. Diagram of apparatus.

of 3, 2 and 1 hour exposures was run. All seven exposures were obtained on the same film. The film was then developed and run through a microphotometer and the relative intensities of the diffuse scattering at room temperature (300°K) and 90°K obtained for scattering angles between 25° and 90°.

The wave-length was obtained by measuring the absorption in aluminum of the scattered beam. This was done photographically and the wave-length could be obtained at all angles on the same film. However, the absorption coefficient was found not to vary in any definite way with the angle within the limits of measurement possible and so the mean value for several angles was used. This corresponds to a wave-length of 0.43A which we take to be the average wave-length.

TABLE I.

$x=(\sin\phi/2)/\lambda$	Intensity at 90°K / Intensity at 300°K				$S_{300°K}$	$S_{90°K}$	
	A	B	C	Ave.		Exp.	Th.
0.503	0.41	0.55	0.53	0.50	2.88	1.44	1.96
0.603	0.48	0.53	0.55	0.52	2.63	1.37	1.87
0.700	0.51	0.58	0.58	0.56	2.42	1.36	1.79
0.795	0.61	0.59	0.61	0.60	2.27	1.36	1.74
0.880	0.69	0.68	0.64	0.67	2.14	1.43	1.75
0.985	0.75	0.71	0.69	0.72	2.00	1.44	1.75
1.075	0.75	0.78	0.75	0.76	1.90	1.45	1.73
1.162	0.81	0.88	0.83	0.84	1.80	1.51	1.70

III. Experimental Results

Three separate runs were made for three settings of the crystal angle θ (see Fig. 1) and three films were obtained. The results of the photometric measurements of these films are shown in columns A, B and C of Table I, the average value being shown in the fifth column.

IV. Comparison with Theory

In the sixth column of Table I are shown the S values for sylvine at room temperature as obtained by Harvey.[11] In the seventh column are shown the S values at 90°K obtained by multiplying Harvey's experimental S values for room temperature by the respective ratios shown in column five. Wollan[12]

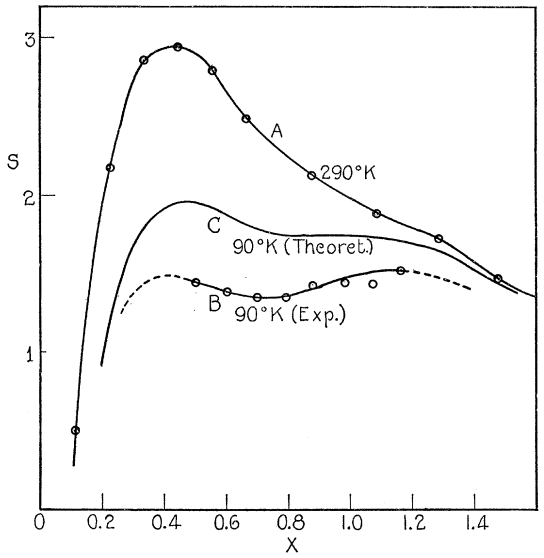

Fig. 2. Curves A and B show experimental S values for sylvine at room and liquid air temperatures. Curve C shows theoretical values at liquid air temperature.

and Harvey[11] have respectively shown that the experimental S values for argon and sylvine give f' values which are identical when calculated from Eqs. (1) and (2). Since the S values for a monatomic gas cannot vary with the temperature and since the f' values for sylvine are equal to those for argon, the f' values for sylvine are independent of the temperature. Jauncey and Harvey[13] have recently discussed this and have shown the experimental relation

$$S_{\text{gas}} = (S + F^2/Z)_{\text{crystal}}. \tag{4}$$

We may rewrite the equation for a crystal in the form

$$S = S' - F^2/Z \tag{5}$$

[11] G. G. Harvey, Phys. Rev. **38,** 593 (1931).
[12] E. O. Wollan, Phys. Rev. **37,** 862 (1931).
[13] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38,** 1071 (1931).

where $S'=1+(Z-1)\,f'^2/Z^2$ is the S value for the atoms of sylvine when in the gaseous form. S' is independent of the temperature and so S varies with the temperature in virtue of the variation of F with the temperature. James and Bridley[8] have obtained F values for sylvine at liquid air temperature and from these F values the theoretical S values shown in the eighth column of Table I have been obtained. It is immediately seen that the experimental S values are all lower than the theoretical S values. The disagreement between the S values shown in columns seven and eight of Table I may be due to experimental error in the average ratios shown in column five or it may be due to experimental error in James and Brindley's F values at liquid air temperature or the disagreement may be real. The authors are at present unwilling to decide among these various possibilities. However, this disagreement in the case of sylvine is in accord with the disagreement found by Claus[9] for rocksalt. The experimental S values for sylvine at room and liquid air temperatures are shown as curves A and B in Fig. 2. The theoretical values at liquid air temperature are shown as curve C in this figure.

The experimental S curve for room temperature contains a hump at $x=0.45$ and a suspicion of a hump at $x=1.25$. The theoretical curve at 90°K definitely has two humps. Our experimental curve at 90°K has humps at $x=0.40$ and $x=1.15$ so that although there is disagreement between the absolute values of the ordinates of the theoretical and experimental S curves for 90°K, yet the two curves do have the same general shape.

Eq. (5) may be written

$$S' - S = F^2/Z \tag{6}$$

and assuming Debye's formula[14] for the temperature effect we have

$$F^2 = f^2 e^{-M} \tag{7}$$

where

$$M = \frac{6h^2}{\Theta mk}\,\frac{\Phi(z)}{z}\,\frac{\sin^2\phi/2}{\lambda^2} \tag{8}$$

or

$$M = \frac{6h^2}{\Theta mk}\left\{\frac{\Phi(z)}{z}+\frac{1}{4}\right\}\frac{\sin^2\phi/2}{\lambda^2}\,. \tag{9}$$

Eq. (8) holds for the absence and Eq. (9) for the presence of zero point energy. In these equations Θ is the characteristic temperature of the crystal as occurs in the Debye theory of specific heats, $z=\Theta/T$, $\Phi(z)=1/z\int_0^z(y\,dy/e^y-1)$, ϕ is the scattering angle and the other quantities have their usual significance. We shall write

$$\frac{6h^2}{\Theta mk}\,\frac{\Phi(z)}{z}\,\frac{\sin^2\phi/2}{\lambda^2} \equiv Bx^2 \tag{10}$$

where $x=(\sin\phi/2)/\lambda$. According to Waller[15] M in Eq. (7) should be replaced by $2M$. Hence, if the value of x is kept constant and the temperature varied,

$$S' - S \propto e^{-Bx^2} \text{ or } e^{-2Bx^2} \tag{11}$$

[14] P. Debye, Ann. d. Physik **43**, 49 (1914).
[15] I. Waller, Zeits. f. Physik **17**, 398 (1923).

according as to which formula is used. The value of S and the value of B depend upon the temperature so that if S_1 and B_1 are the values of S and B respectively at temperature T_1 and S_2 and B_2 the values at T_2 we have

$$\log \frac{S' - S_1}{S' - S_2} = (B_2 - B_1)x^2 \text{ or } 2(B_2 - B_1)x^2 \tag{12}$$

so that if $\log (S'-S_1)/(S'-S_2)$ is plotted against x^2 a straight line should be obtained whose slope is either (B_2-B_1) or $2(B_2-B_1)$ according as the Debye or Waller formula is correct. For the range of temperatures used in our experiment these values are 1.15 and 2.30 respectively. It is important to note in Eq. (12) that because only the difference (B_2-B_1) is involved this method tells us nothing regarding the presence or absence of zero point energy. Plot-

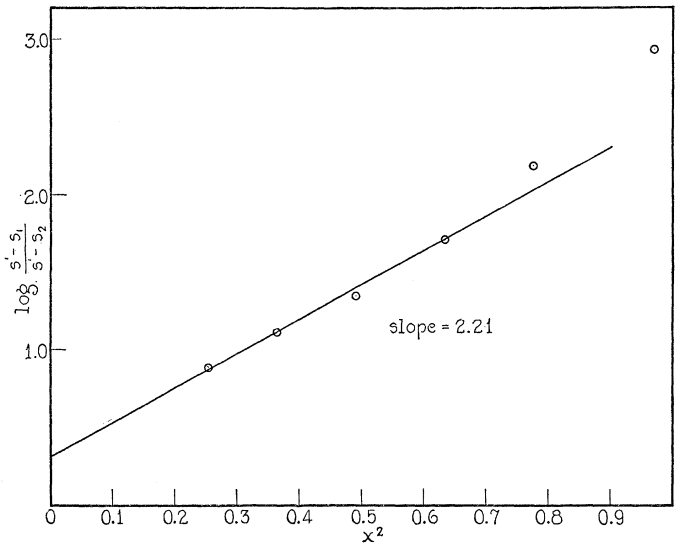

Fig. 3. Plot of experimental values.

ting our experimental values we obtain the curve as shown in Fig. 3. It is seen that between $x=0.5$ and $x=0.8$ the curve is a straight line whose slope is 2.21. For values of x beyond 0.8 no reliance can be placed on the points since the ordinate depends on the ratio of two differences each of which is subject to considerable uncertainty due to the fact that S' approaches S for large values of x. This explains why the last two points in Fig. 3 do not fall on the curve. It might be objected that this slope depends somewhat on the wave-length which we have assumed and also upon the correctness of the angle of scattering. Actually, of course, the wave-length and scattering angle are averages. We therefore supposed a possible variation of $\pm 2°$ in the scattering angle and ± 0.02A in the wave-length. We then constructed nine different curves similar to Fig. 3 and obtained nine different values of the slope. With the exception of one value all the slopes came out between 2.00 and 2.35. We therefore feel considerable confidence in our value of 2.21 which is distinctly in agreement with Waller's value of 2.30 and not with Debye's value.

Eq. (6) may be written.

$$Z(S' - S) = f^2 e^{-2Kx^2} e^{-2Bx^2} \tag{13}$$

where $K \equiv (3h^2/2\Theta mk)$ is due to zero point energy and is independent of the temperature. The slope of the curve in Fig. 3 shows that B has the Waller value but indicates nothing as regards the existence or non-existence of zero point energy. In Eq. (13) both f and e^{-Kx^2} are independent of the temperature but are functions of x. Information concerning K can be obtained only if an assumption is made concerning the values of f. Three possibilities have been considered. First, if a model of the atom of argon is assumed, values of the true atomic structure factor, or f values, can be calculated for this model. If these values are substituted in the values of the product above mentioned the value of K can be determined. Second, we may assume that f is equal to f', as is done by Compton[1] and Wollan[12]. Third, we may assume zero point energy according to the Waller theory[15] and calculate f values. All of these methods require a high degree of accuracy in the experimental values. Instead of attempting to perform these calculations we have preferred to take the values of S at 300°K and 90°K together with F values at 300°K and from these to calculate F values at 90°K from the relation

$$Z(S_{300°} - S_{90°}) = F^2_{90°} - F^2_{300°}. \tag{14}$$

The values so calculated are shown in the second column of Table II. James and Brindley's values are shown in column three for comparison.

TABLE II.

x	$F_{90°K}$		x	$F_{90°K}$	
	J and H	J and B		J and H	J and B
0.503	6.71	6.00	0.880	3.79	2.95
0.603	5.76	5.04	0.985	3.79	2.35
0.700	5.01	4.24	1.075	2.91	1.94
0.795	4.42	3.53	1.162	2.30	1.54

James and Brindley's F values for sylvine at room temperature fitted our theory most excellently because when combined with Harvey's S values[11] for sylvine at room temperature the resulting f' values agree remarkably well with Wollan's f' values for argon.[12] It seems peculiar that James and Brindley's F values for sylvine at liquid air temperature when combined with the results of this present paper do not fit the theory so well.

V. CONCLUSION

We have shown that the diffuse scattering of x-rays from sylvine decreases with decrease of temperature. For temperatures of 300°K and 90°K the decrease is a function of x such that it supports Waller's formula[15] as opposed to Debye's formula[14] for the temperature effect. However, the decrease is greater than that required by the theory of Jauncey and Harvey[6] for the diffuse scattering from crystals if the F values of James and Brindley[10] at liquid air temperature are used. It is suggested that more work is needed on the effect of temperature both on the diffuse scattering and regular reflection from crystals before more definite conclusions can be drawn.