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Diffuse Scattering of X-Rays from Sylvine—More Exact Measurements

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Harvey's S values for sylvine at 295°K agree qualitatively with the theoretical S values calculated from James and Brindley's quantum-mechanical f and E_{jj} values. Quantitatively, the difference between experiment and theory is too great for comfort. Accordingly, we have made a more exact and careful determination of the experimental S values and have found a remarkable agreement between experiment and theory. This shows the excellence of the present theory of diffuse scattering and the accuracy of the f and E_{jj} values which James and Brindley have calculated by approximate methods. Our results are not in accord with the idea that the probability distribution is the same for all electrons. Also experiment has shown that turning the crystal plate in its own plane has no effect on the diffuse scattering in a given direction. This indicates that the atoms of sylvine possess spherical symmetry as far as the scattering of x-rays is concerned. Spherical symmetry is assumed in the theory.

1. INTRODUCTION

ACCORDING to the most recent development of the theory, the diffuse scattering of x-rays by crystals consisting of two kinds of atoms (such as KCl) is given by

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

where

$$S_1=(f_1^2+f_2^2-F_1^2-F_2^2)/(Z_1+Z_2) \tag{2}$$

and

$$S_2=1-\frac{\sum(E_{jj}^2)_1+\sum(E_{jj}^2)_2-\sum|E_{jk}|_1^2-\sum|E_{jk}|_2^2}{Z_1+Z_2}. \tag{3}$$

The various symbols are defined in the paper by Harvey, Williams and Jauncey,[1] the numerical subscripts referring to the two kinds of atoms. It has become the custom to use another symbol, S_{class}, which is defined by

$$S_{\text{class}}=S_1+S_2. \tag{4}$$

On the basis of wave mechanics, James and Brindley[2] have calculated values of E_{jj} (their f_0) and of f for the K^+ and Cl^- ions in sylvine. Values of F are obtained by multiplying the values of f by the Debye-Waller[3] temperature factors, using 230°K for the characteristic temperature of KCl and assuming the existence of zero point energy. The theoretical values of S and S_{class} can therefore be calculated.

Harvey has obtained experimental S_{class} values for sylvine at room temperature, first for an average wave-length of a band of x-rays[4] and second for monochromatic x-rays.[5] In both cases he obtained a maximum value of S_{class} of 2.95 at about $(\sin \phi/2)/\lambda=0.365$. Although the wave-

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[1] G. G. Harvey, P. S. Williams and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934).

[2] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

[3] P. Debye, Ann. d. Physik **43**, 49 (1914); I. Waller, Zeits. f. Physik **17**, 248 (1923).

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

[5] G. G. Harvey, Phys. Rev. **43**, 591 (1933).

mechanical S_{class} curve has the same general shape as the experimental S_{class} curve, there is a distinct difference between the absolute values of the ordinates of the two curves as shown by the fact that the maximum theoretical S_{class} value is 2.46 at $(\sin \phi/2)/\lambda = 0.59$. The difference between the experimental and theoretical values of $x(=(\sin \phi/2)/\lambda)$ for the maximum S_{class} values might be explained as due to error in drawing the experimental curves since the points are somewhat scattered, but a difference of about 0.5 in the two maximum values of S_{class} is too great for comfort. We have therefore made a careful investigation of the diffuse scattering from sylvine in order to find out whether the above discrepancy between theory and experiment can be reduced or removed.

A second object of this research was to find out whether the diffuse scattering in a given direction depends on the orientation of the crystal with respect to the plane of scattering.

2. Experimental Method

Because we desired greater accuracy in our readings we used a band of wave-lengths from the continuous spectrum of x-rays from a tungsten target tube operated at 51.5 kv peak rather than monochromatic rays as in the experiments of Harvey[5] and Williams.[6] The experimental method has been described in previous papers.[7, 8, 9] Referring to the paper by Jauncey and May,[9] let us introduce

$$v = \frac{[e^{-\mu t/\cos\theta} - e^{-\mu t/\cos(\phi-\theta)}]\cos(\phi-\theta)\cos\tfrac{1}{2}\phi}{\mu t[\cos\theta - \cos(\phi-\theta)]e^{-\mu t/\cos\frac{1}{2}\phi}}, \tag{5}$$

where ϕ is the angle of scattering, θ is the angle between the normal to the crystal slab and the primary beam, and μ and t are respectively the absorption coefficient and thickness of the crystal. Then, if D is the electrometer deflection corresponding to a setting θ and ϕ is kept constant, the graph of D/v against θ is a horizontal straight line excepting where Laue spots occur as shown in Fig. 1. As pointed out by Jauncey and Williams[7] it is essential to separate the Laue spots from the diffuse scattering. Previously we have plotted D against θ and this gives rise to an approximate straight line with a small slope. Fig. 1 shows how well the experimental points fall on a horizontal line. For the case where a principal axis of the crystal is perpendicular to the plane of scattering, the values of θ at which Laue spots occur are given by

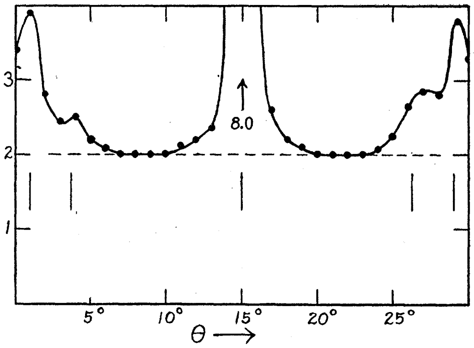

FIG. 1. Graph of D/v against θ for $\phi=30°$. The horizontal portion of the curve is important in diffuse scattering. Each experimental point of this portion is the average of numerous readings. The Laue spots occur at $\pm(\phi/2-\theta)=0°$, 11.3° and 14°.

$$\theta = \phi/2 \pm \tan^{-1} h/k, \tag{6}$$

where h and k are integers and either but not both may be zero. Eq. (6) holds so long as the wave-length

$$\lambda = (2d\sin\theta)/(h^2+k^2)^{\frac{1}{2}} \tag{7}$$

is contained in the continuous spectrum. The positions of the Laue spots according to Eqs. (6) and (7) are indicated by the vertical lines in Fig. 1.

Because $v=1$ when $\theta=\phi/2$, the average value of D/v for points not at or near Laue spots is the value assumed for D_ϕ in the right side of Eq. (17) of the paper by Jauncey and Pennell.[8] The same ionization chamber and thickness of paraffin were used as are described in this paper and so the numerical value 0.314 included in the formula for S_{exp} is the same as that used by Jauncey and Pennell. For clarity it might be well to point out that 0.314 stands for

$$\frac{Z'\rho' t'}{W'} \times \frac{1}{\cos 45°} \times \frac{K_{90°}T'_{90°}}{K_0(1+\alpha)^3}. \tag{8}$$

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[6] P. S. Williams, Phys. Rev. **46**, 83 (1934).

[7] G. E. M. Jauncey and P. S. Williams, Phys. Rev. **44**, 794 (1933).

[8] G. E. M. Jauncey and Ford Pennell, Phys. Rev. **43**, 505 (1933).

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

The value of ρt for the crystal is 0.325 g/cm^2.

Jauncey and Pennell determined the intensity distribution in the spectrum by means of their Eq. (7a). This, however, assumes that the Lorentz factor[10] is proportional to $\lambda^3/\sin 2\theta$. This is the factor for monochromatic rays when the method of integrated reflection is used. However, the "white" Lorentz factor is proportional to $\lambda^2/\sin^2\theta$ and would seem to apply to our determination of the spectral distribution. In addition to the Lorentz factor there is some uncertainty concerning the proper value of μ to be used since μ should be increased by the extinction coefficient. This coefficient probably becomes a greater proportion of the ordinary absorption coefficient at shorter wave-lengths. We therefore determined three curves—the first curve was the graph of the actual electrometer reading against λ, while the second and third curves were the graphs of the readings corrected for the "monochromatic" and "white" Lorentz factors, respectively, both the second and third curves being also corrected for the ordinary absorption coefficient. By experiment we determined that 0.75 g/cm^2 of aluminum was necessary to reduce the primary rays to half value when the rays had already passed through the paraffin ($\rho' t' = 0.493$ g/cm^2), the sylvine crystal and 0.170 g/cm^2 of aluminum which was permanently placed in the primary beam during the scattering experiments. From each of the above three curves a modified curve for the spectral distribution of the rays getting through the added 0.75 g/cm^2 of aluminum was calculated, using the values of μ for various wave-lengths in aluminum as given by Compton's tables.[11] Now comparing the area under each modified curve with that under the corresponding original curve we find that the fractions to which the primary rays are reduced are: First curve, 0.463; second curve, 0.433; third curve, 0.332. Obviously the first curve agrees best with the experimental value 0.5 and this is the curve, Fig. 2, we have used for the spectral distribution curve.

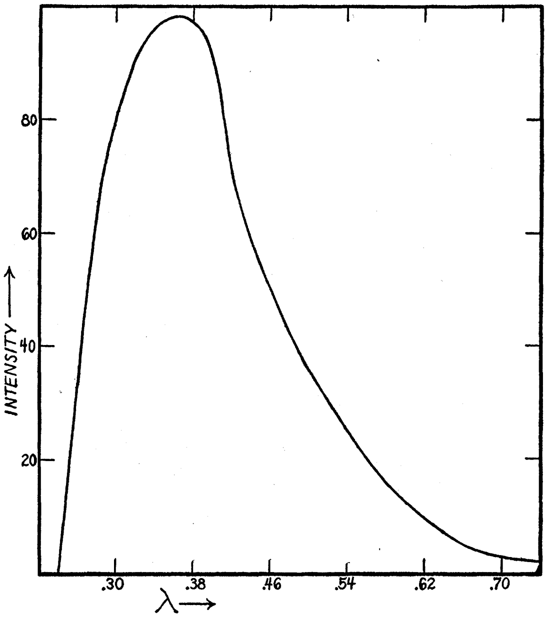

FIG. 2. Distribution-in-wave-length of the intensity in the continuous spectrum. Half-value absorption in aluminum of this spectrum corresponds to an average wave-length of about 0.38A.

At first we compared the scattering from KCl with that from paraffin and used Jauncey and Pennell's formula for calculating S_{exp}. However, in this formula it is assumed that the scattering from paraffin at 90° is entirely incoherent so that the Breit-Dirac[12] formula holds. However, from Fig. 2 it is seen that there is some intensity of $\lambda = 0.7$A present and at this wave-length some coherent radiation occurs at $\phi = 90°$. Since this part of the spectral distribution curve is somewhat uncertain,[13] we measured the absolute value of the spatial scattering coefficient per unit solid angle at $\phi = 90°$ from paraffin. This necessitates the comparison of two intensities whose ratio is in the order of 1 to 10,000. First, we made the comparison by a photographic method. A photographic film was cut into 24 rectangular pieces and these pieces were arranged in two piles of 12 pieces each. One pile was exposed to the primary x-rays for several seconds and the other to the scattered rays for several hours. Each piece was run through the microphotometer[14] and the photographic density

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[10] See F. C. Blake, Rev. Mod. Phys. **5**, 169 (1933).

[11] A. H. Compton, *X-Rays and Electrons*, p. 184.

[12] G. Breit, Phys. Rev. **27**, 362 (1926); P. A. M. Dirac, Proc. Roy. Soc. **A111**, 405 (1926).

[13] The minimum wave-length as given by the Duane-Hunt relation is 0.24A so that second order reflection from the rocksalt occurs at θ greater than that corresponding to first-order reflection of $\lambda = 0.48$A and so a correction in the curve had to be made.

[14] See W. D. Claus, Phys. Rev. **38**, 604 (1931).

determined.[15] The purpose of the pile of films was to determine the absorption coefficients of the primary and scattered rays in the films according to the method of Brindley and Spiers.[16] Also the area of the spot produced by the primary rays was determined. The result can be expressed by saying that the numerical factor 0.314 in Jauncey and Pennell's Eq. (17) should be replaced by 0.352. Second, we made the comparison by means of an ionization chamber and electrometer. We cut off a flash of primary rays of duration 1/60 sec. by means of a pendulum[17] as described by Jauncey and May.[9] The numerical factor is now found to be 0.358. In a third method we compared the intensity of the rays diffusely scattered from the crystal at $\phi=40°$ with that of the primary rays and found the factor to be 0.355. We therefore replaced the factor 0.314 in Jauncey and Pennell's Eq. (17) by the average value 0.355.

3. COMPARISON WITH WAVE-MECHANICAL VALUES

Values of the theoretical quantity defined by the left side of Jauncey and Pennell's Eq. (17) can be calculated from James and Brindley's[2] wave-mechanical values of f and E_{jj} together with the values of $\Sigma|E_{jk}|^2$ given by Waller and Hartree[18] and Harvey, Williams and Jauncey.[1] The values of S_{exp} and S_{th} are given in Table I. The results are also shown by the solid curve of Fig. 3. It is seen how well the experimental values agree with the theoretical. The maximum S_{exp} of 2.31 corresponds very well with the maximum S_{th} of 2.36 at $\phi=25°$. Assuming an average wave-length of 0.38A (obtained from half-value absorption) this corresponds to $x=0.57$. The reason for the slight difference between the values given here and in the introduction to this paper is that S_{class} was used there and monochromatic rays were assumed instead of the band of wave-lengths actually used.

TABLE I. *Diffuse scattering from sylvine.*

ϕ	S_{exp}	S_{th}	ϕ	S_{exp}	S_{th}
10°	1.50	1.65	37°	1.99	2.06
15°	1.95	2.05	40°	1.90	1.95
20°	2.23	2.28	45°	1.70	1.79
25°	2.31	2.36	50°	1.56	1.62
30°	2.27	2.28	60°	1.32	1.37
33°	2.14	2.21	75°	1.14	1.12
35°	2.01	2.13	90°	1.01	0.97

The excellence of the agreement shown in Table I indicates the correctness of the present theory of diffuse scattering and also the high accuracy of James and Brindley's[2] f and E_{jj} values which were calculated by approximate methods. The broken curve of Fig. 3 is based upon the assumption that the probability distribution is the same for all electrons so that $\Sigma E_{jj}^2=f^2/Z$, i.e., $f''=f$ in the notation used by Jauncey.[19] Our results show that this assumption is incorrect. The omission of the negative term $-\Sigma|E_{jk}|^2/Z$ from S_2 makes a maximum increase of 0.08 in S_{th} at $\phi=29°$. The inclusion of the negative term thus gives slightly better agreement with S_{exp} at this value of ϕ.

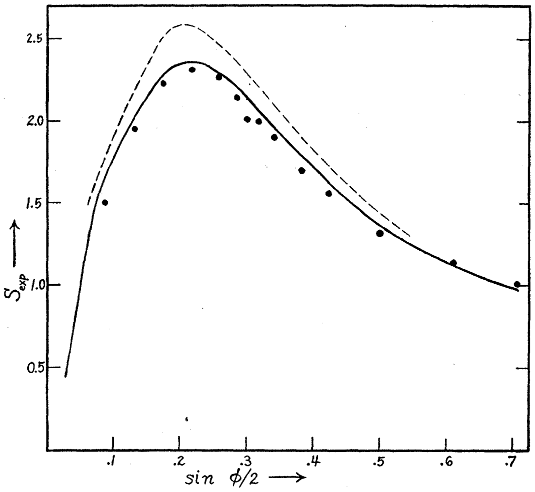

FIG. 3. Diffuse scattering of x-rays from sylvine. Black circles, experimental points; solid curve, electrons having different probability distributions; broken curve, electrons having equal probability distributions.

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[15] See G. E. M. Jauncey and H. W. Richardson, J. O. S. A. **24**, 125 (1934).

[16] G. W. Brindley and F. W. Spiers, Phil. Mag. **16**, 686 (1933).

[17] The approximate distance by which the pendulum should be pulled out before being released can be calculated but the exact distance can be found experimentally by plotting the electrometer deflection against the distance. There is a point of inflection at the correct distance. Also at the correct distance the readings repeat very well but as the distance departs from the correct value the readings scatter more and more.

[18] I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 119 (1929).

[19] G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).

We wish to notice that the difference between S_{exp} and S_{th} at $\phi = 35°$ is somewhat larger than our experimental error which we place at about 0.05 in S_{exp} in this region. We made repeated trials in this region and always found S_{exp} somewhat less than S_{th}. A rather large difference also occurs at $\phi = 10°$ and 15°; but at these small angles the experimental difficulties increase and the difference is probably not greater than the experimental error. Considering all the values of ϕ, there is a tendency for all the experimental points to fall below the theoretical curve. This is probably due to error in the determination of the numerical factor mentioned at the end of the last section.

4. Effect of Crystal Orientation

In all the work done hitherto in this laboratory x-rays have for convenience been scattered from a crystal with one axis perpendicular to the scattering plane. We have now tried the effect of turning the crystal plate in its own plane upon the S_{exp} values. When the crystal is oriented so that no principal axis is perpendicular to the scattering plane, Eqs. (6) and (7) for the positions of the Laue spots become more complicated and contain a third integer l. The S_{exp} values for the axis making angles of 0°, 22.5° and 45° with the perpendicular are shown in the second, third and fourth columns of Table II. It is seen that turning the crystal in its own plane has no noticeable effect. The theory of diffuse scattering has been developed on the assumption of spherical symmetry in the atoms.[20] Our results are in accord with this assumption in the case of sylvine.

Table II. *Effect of crystal orientation*—S_{exp} values.

ϕ	0°	22.5°	45°
15°	1.95	1.99	1.93
25°	2.31	2.31	2.29
35°	2.01	2.00	2.01
50°	1.56	1.54	1.54

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

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The Verdet Constant of Heavy Water

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The Verdet constants of samples of water containing 0, 31.1, and 99.7 percents of heavy hydrogen atoms have been measured for the wave-lengths λ5893 and λ5460.7A at 20°C. The results are given in tabular form. From these data the Verdet constant of pure heavy water (H^2_2O) is found to be 3.93 percent less than that of ordinary water for both wave-lengths. Nonlinearity of the Verdet constant-concentration relation leads to the calculation of an apparent Verdet constant for H^1H^2O which is 0.85 percent less than the Verdet constant of ordinary water. Values of the relative molecular rotatory power and of the magnetic rotatory dispersions are also given.

The Verdet constants of ordinary and of heavy water have been measured for two wave-lengths of light.

The measurements were made by use of the Schmidt and Haensch Faraday effect apparatus. The optical system of the instrument consists of a triple field polarizer with the Lippich half-shade adjustment and an analyzing Nicol whose position may be read to 0.01°. The magnetic field was produced by the attached electromagnet with an iron core, drilled parallel to the magnetic field. The mean axial field strength was determined by calibration against a standard solenoid by the ballistic galvanometer deflection method. The test coil used between the magnet pole pieces in calibration was of approximately the same dimensions as the cell used to contain the liquids whose Verdet constants were determined. The current for the electromagnet was supplied from storage batteries, and was determined by