Diffuse Scattering of X-Rays from Sodium Fluoride. II. Scattering at the Temperature of Liquid Air

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The ratio of the intensity of x-rays diffusely scattered by a single crystal of NaF at 86°K to that of x-rays scattered by the crystal at 295°K has been determined at each of several angles ranging from 10° to 42°. The x-rays consisted of a continuous band of wave-lengths, of which the spectral distribution of intensity was known. From Shonka's value of 442°K for the characteristic temperature of NaF together with his f values for zero point energy, we have calculated the theoretical ratios for different angles. The experimental and theoretical ratios agree very well. The importance of being sure of the absence of Laue spots in this type of experiment is discussed. The experiment was performed by fixing the scattering angle ϕ and varying the crystal angle θ as in the original method of Jauncey and May. If θ is kept constant and ϕ varied there is no sure criterion for the absence of Laue spots. A formula for the ratio at zero scattering angle is given and at small angles the experimental ratio should approach this value. Curves showing the contrast in behavior of the Laue, diffuse and "total" (*see* Jauncey and Pennell) scattering from NaF and KCl with change of temperature from 295°K to 86°K are given.

I. INTRODUCTION

ACCORDING to the theory of Jauncey, Harvey and Woo[1, 2, 3, 4, 5] the intensity of the x-rays diffusely scattered from a crystal consisting of atoms of one kind is given by

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

where $S_1=(f^2-F^2)/Z$ and $S_2=1-f''^2/Z^2$. There is some uncertainty as to the equality of f and f''. If, say, the K electrons are distinguishable from the L electrons in one and the same atom, then $f''>f$, but, if all the electrons form an electron gas about the nucleus and no electron can be distinguished as a K or an L electron, then $f''=f$. Recently, the senior author and Dr. G. G. Harvey had the opportunity of discussing with Dr. Ivar Waller of the University of Upsala the equality of f and f''. It appears that the f_0's used by James and Brindley[6] merely represent convenient steps in the calculation of the f values and are not to be considered as representing anything physical about particular electrons. According to this view, $f=f''$. Partly for convenience and partly for the reason just cited we shall in this paper assume $f=f''$.

II. EXPERIMENTAL METHOD

Jauncey, Claus and Harvey[7, 8, 9] have at various times measured the change of the intensity of the x-rays diffusely scattered from crystals of NaCl and KCl produced by a change in temperature and have found a qualitative but not quantitative agreement with theory. In these experiments, x-rays of an average wave-length as determined by absorption in aluminum were used. More recently, however, Harvey[10] has used monochromatic x-rays of wave-length 0.71A with sylvine at a temperature of 86°K (liquid air) and has found reasonably good quantitative agreement with theory. Jauncey and Pennell[11] have recently shown how a band

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

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

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

[4] Y. H. Woo, Phys. Rev. **38**, 6 (1931).

[5] Y. H. Woo, Phys. Rev. **41**, 21 (1932).

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

[7] G. E. M. Jauncey, Phys. Rev. **20**, 421 (1922).

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

[9] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1925 (1931).

[10] G. G. Harvey, Phys. Rev. **43**, 707 (1933).

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

of wave-lengths from the continuous radiation may be used in scattering experiments provided that the distribution of the intensity among the wave-lengths in the band is known. In this present research we have therefore used the band of wave-lengths whose intensity distribution is shown in Fig. 1.

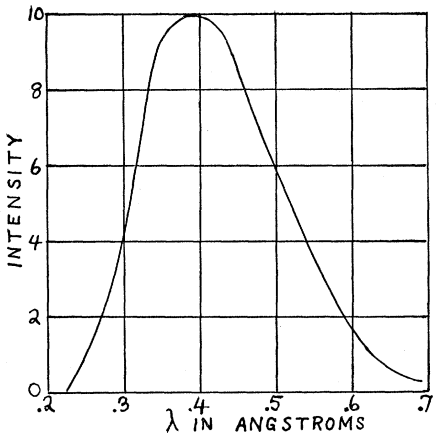

FIG. 1. Distribution of intensity in the continuous spectrum of x-rays.

However, in the present research we have found that the lack of good quantitative agreement with theory as cited above[7, 8, 9] is due not so much to the assumption of an average wave-length when a band of wave-lengths was used as to a fault in the experimental method. It is very necessary in experiments on the diffuse scattering of x-rays from crystals to be sure that Laue spots are not included in the radiation entering the window of the ionization chamber. The criterion for the absence of Laue spots is that the electrometer readings fall on a straight line when plotted against the crystal angle, which is measured between the normal to the crystal plate and the primary beam. An example of this is shown in Fig. 4 of a paper by Jauncey and May.[12] Applying this criterion much more carefully than heretofore we have found that the effect of the central Laue spot spreads out more than is to be expected from the geometry of the slit system. Hence at each angle of scattering we have taken a set of readings with the crystal angle increased by steps of 1 degree. This was first done at room temperature and then again at liquid air temperature. We thus obtained two curves similar to Jauncey and May's Fig. 4 for a given angle of scattering. The ratio of the ordinates of the two interpolated points gives the ratio of the scattering coefficients at the two temperatures.

In this research the cooling chamber was similar to that described by Williams,[13] with a modification to allow for varying the crystal angle during a run. A charcoal trap in liquid air provided the necessary vacuum in the cooling chamber.

III. Experimental Results

The experimental ratios are shown in the fourth column of Table I.

TABLE I. *Diffuse scattering of x-rays from NaF ratios: 86°K/295°K.*

	$\sin \frac{1}{2}\phi$	Theory	Experiment
0°	0.000	0.662	
10°	.087	.710	0.773
15°	.130	.756	.749
20°	.174	.813	.790
26°	.225	.858	.840
32°	.275	.898	.877
37°	.317	.921	.900
40°	.342	.934	.918
42°	.359	.939	.930
45°	.383	.947	

It should be mentioned here that there was considerable lapse of time between the readings at room temperature and those at liquid air temperature. In order to correct for any variation in the sensitivity of the electrometer each set of readings was compared with a set of readings obtained by scattering from a carbon slab held in the primary beam transmitted through the crystal and maintained throughout the experiment at room temperature.

IV. Comparison with Theory

S_1 of Eq. (1) is a function of F, the atom form factor with respect to a lattice point of the crystal. But F is a function of the temperature

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

[13] P. S. Williams, Rev. Sci. Inst. **4**, 334 (1933).

according to the Debye-Waller[14, 15] formula

$$F=fe^{-Bx^2}, \tag{2}$$

where f is the atom form factor with respect to the center of the atom (the "true" atom form factor), $x\equiv(\sin\frac{1}{2}\phi)/\lambda$,

$$B=(6h^2/\mu k\Theta)\{\phi(z)/z+0.25\}, \tag{3}$$

μ is the mass of an atom of the crystal, h and k are Planck's and Boltzmann's constants, Θ is the characteristic temperature, $z=\Theta/T$, and $\phi(z)$ is a function evaluated by Debye. In the formula for B, Eq. (3), zero point energy is assumed.

Very fortunately for us a paper by Shonka[16] on the Laue or directed scattering of x-rays from NaF has appeared. The intensity of the Laue scattering corrected for extinction is proportional to F^2. From the intensities of the Laue scattering at room and liquid air temperatures, Shonka has obtained a characteristic temperature of 442°K. From Havighurst's F values for NaF at room temperature,[17] Shonka has then calculated the f values for this crystal on the assumption of zero point energy.

In our experiment the greatest angle of scattering was 42°. At values of ϕ no greater than 42° and for the wave-lengths used, the Breit-Dirac factor $1/(1+\alpha \text{ vers } \phi)^3$ is very nearly unity and for simplicity we have taken it as unity. Also in Eq. (17) of Jauncey and Pennell's paper[11] we may put $K_\phi=K_0$ and $T_\phi=1$. The theoretical ratio of the intensity of the diffuse scattering at 86°K to that at 295°K is therefore given by

$$R=\frac{\int\{Z^2-f^2+Zf^2(1-e^{-2B_1x^2})\}Id\lambda}{\int\{Z^2-f^2+Zf^2(1-e^{-2B_2x^2})\}Id\lambda}, \tag{4}$$

where $B_1=0.381$, $B_2=0.871$ (the values of B at 86°K and at 295°K, respectively), Z is the atomic number and I is the intensity distribution represented by Fig. 1. From Shonka's f values for zero point energy together with the spectral distribution shown in Fig. 1 we have evaluated each integral in Eq. (4) by quadrature and have then determined the theoretical ratios which are shown in the third column of Table I. The agreement between the theoretical values in the third column and the experimental values in the fourth column is good. With the exception of the experimental ratio at 10° our experimental ratios are all less but only slightly less than the theoretical ratios. Harvey[10] has also found for KCl that the experimental ratios are less than the theoretical ratios. We doubt, however, that the differences in the case of NaF represent any real discrepancy between the experimental and theoretical ratios.

V. Ratio at Zero Scattering Angle

By reference to Table I it is seen that a theoretical ratio is given for $\phi=0°$. At this angle the formula for R, Eq. (4), becomes indeterminate. However by differentiating the integrands of both numerator and denominator it can be shown that for each wave-length present the ratio approaches the value

$$R_{\phi=0°}=(-d^2f/dx^2+2B_1Z^2)/(-d^2f/dx^2+2B_2Z^2). \tag{5}$$

Wollan[18] has shown that at small values of $x\equiv(\sin\frac{1}{2}\phi)/\lambda$ the curve of f *versus* x assumes the parabolic shape

$$x^2=a(Z-f). \tag{6}$$

If this is fitted to an experimental f curve at a small value of x, then a may be obtained. In this case (5) reduces to

$$R_{\phi=0°}=(1+aB_1Z^2)/(1+aB_2Z^2). \tag{7}$$

Fitting (6) to Shonka's zero point energy f curve for NaF at $x=0.1$, we obtain $a=0.0175$, whence $R_{\phi=0°}=0.662$.

VI. Comparison of Diffuse, Laue, and Total Scattering of X-Rays

Shonka[16] has measured the ratios of the intensities of the Debye-Sherrer circles produced by the Laue scattering of x-rays from a powdered crystal of NaF. Assuming a wave-length of $\lambda=0.4$A, we have plotted Shonka's ratios against

[14] P. Debye, Verh. deutsch Phys. Ges. **15**, 678 (1913).
[15] I. Waller, Zeits. f. Physik **17**, 398 (1923).
[16] J. J. Shonka, Phys. Rev. **43**, 947 (1933).
[17] R. J. Havighurst, Phys. Rev. **28**, 869 (1926).
[18] E. O. Wollan, Rev. Mod. Phys. **4**, 205 (1932).

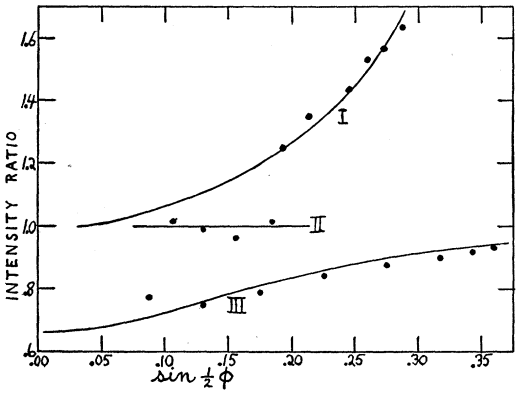

FIG. 2. Ratios of the intensities of the Laue, total and diffuse scattering at 86°K to those at 295°K for NaF. Curve I, Laue scattering (Shonka); curve II, total scattering (Jauncey and Pennell); curve III, diffuse scattering (this research). A wave-length of 0.4A is assumed for curve I in order to plot against sin ½φ.

sin ½φ and the points obtained are shown in the vicinity of curve I in Fig. 2. Jauncey and Pennell[11] have scattered a band of wave-lengths into an ionization chamber with a wide window and have measured the intensity of the "total" scattering from a powdered crystal. This total scattering consists of both the diffuse scattering between the Debye-Sherrer circles and the Laue scattering in these circles. In a more recent experiment Jauncey and Pennell[19] have shown that there is almost no change in the intensity of the total scattering when the temperature of a powdered crystal is changed from 295°K to 103°K. The ratios for the total scattering from NaF are shown as the points in the vicinity of curve II (a straight line). Lastly, in this present research we have obtained the ratios shown in the fourth column of Table I for the diffuse scattering from a single crystal of NaF. These ratios are shown as the points in the vicinity of curve III in Fig. 2. The curves are the theoretical curves for the respective cases. Fig. 2 contrasts very well the behavior of the Laue, diffuse and total scattering of x-rays from NaF with change of temperature from room to liquid air temperature.

[19] G. E. M. Jauncey and Ford Pennell, Phys. Rev. **44**, 138 (1933).

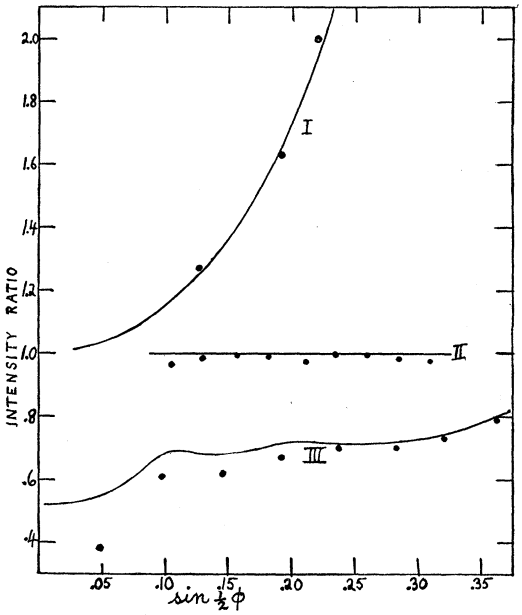

FIG. 3. Ratios of the intensities of the Laue, total and diffuse scattering at 86°K to those at 295°K for KCl. Curve I, Laue scattering (James and Brindley); curve II, total scattering (Jauncey and Pennell); curve III, diffuse scattering (Harvey). A wave-length of 0.4A is assumed for curves I and III in order to plot against sin ½φ.

From the experimental results of James and Brindley,[20] Harvey[10] and Pennell and Jauncey,[19] we have constructed Fig. 3 for KCl in the same way as Fig. 2 has been constructed for NaF. The characteristic temperature for KCl is 230°K. It will be noticed that curve III of Fig. 3 has humps. These humps are characteristic of the theoretical curve for the ratio for diffuse scattering when monochromatic x-rays are used as was the case in Harvey's experiment.[10] Similar humps occur in the theoretical ratio for NaF for monochromatic rays. However, in the present research we used a band of wave-lengths whose intensity distribution is shown in Fig. 1. The effect of such a band is to iron out the humps in the theoretical curve for the ratio plotted against sin ½φ. Hence no humps appear in curve III, Fig. 2, for NaF.

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