

## Scattering of X-Rays from Powdered Crystals at Low Temperatures

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Jauncey has suggested that the true atom form factor of a crystal may decrease at low temperatures. With the method of Jauncey and Pennell, x-rays have been scattered from powdered crystals of KCl and NaF at various mean angles  $\phi$  over a fairly wide range of  $(\sin \frac{1}{2}\phi)/\lambda$  at each mean angle  $\phi$  with the powdered crystal first at 295°K and then at 103°K. Changes of the order of 1 or 2 percent in the

intensity of the scattered rays were observed. Various possible explanations for this change are discussed. It is concluded that from 295 to 103°K the true atom form factors of NaF do not change, while those of KCl either do not change or decrease by very small amounts which are less than, but of the same magnitude as, those indicated in a recent paper by Harvey.

### 1. INTRODUCTION

IN a recent paper entitled *Remarks on the Scattering of X-Rays by Gases and Crystals*, Jauncey<sup>1</sup> has discussed the possibility that the true atom form factor  $f$  may be a function of the temperature. More recently Jauncey and Pennell<sup>2</sup> have shown that, if x-rays are scattered over a fairly wide range of  $(\sin \frac{1}{2}\phi)/\lambda$  by a powdered crystal into an ionization chamber set at a mean angle  $\phi$ , the intensity of the scattered x-rays entering the window of the ionization chamber is given by

$$S(\text{powder}) = G - H + L, \quad (1)$$

where

$$G = \int \left\{ \frac{f^2}{Z} + \frac{(1 - f'^2/Z^2)K_\phi T_\phi}{K_0(1 + \alpha \text{vers } \phi)^3} \right\} Id\lambda / \int Id\lambda, \quad (2)$$

$$H = \int (F^2/Z) Id\lambda / \int Id\lambda \quad (3)$$

and

$$L = \left\{ \frac{1}{4\pi} \sum_r \frac{F_r^2}{Z} \cdot \frac{\rho_r \lambda_r I(\lambda_r)}{r^3} \right\} / \int Id\lambda. \quad (4)$$

We shall refer to this paper by Jauncey and Pennell as the previous paper. In this previous paper it has been shown that so long as the

scattering angle  $\phi$  is not too small,  $L - H$  is small and consequently  $S(\text{powder})$  is approximately equal to  $G$ . The symbol  $G$  refers to the scattering from the fictitious gas obtained by changing the crystal into a gas without disturbing the electron structures of the atoms of the crystal. At room temperature it has been established by Jauncey and Harvey<sup>3, 4</sup> that  $G$  very nearly equals the  $S(\text{gas})$  for the corresponding real gas in the case of sylvine and argon. However, according to Jauncey,<sup>1</sup> it seems that  $G$  for the crystal may depart from  $S(\text{gas})$  at low temperatures. If this is the case  $S(\text{powder})$  may be a function of the temperature. In the present research this point has been tested as regards powdered KCl and powdered NaF.

### 2. EXPERIMENTAL METHOD

The same experimental method and x-rays with the same spectral distribution of intensity were used as were described in the previous paper. X-rays were scattered from the powdered crystal first at room temperature and then at liquid air temperature into the ionization chamber set at a mean angle  $\phi$ . The crystal in both cases was set so that the normal to the crystal bisected the angle of scattering  $\phi$  and in both cases was mounted in the cooling chamber which is described by Williams.<sup>5</sup> The widths of the defining slits and of the ionization chamber

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<sup>1</sup> G. E. M. Jauncey, *Phys. Rev.* **42**, 453 (1932).

<sup>2</sup> G. E. M. Jauncey and Ford Pennell, *Phys. Rev.* **43**, 505 (1933).

<sup>3</sup> G. E. M. Jauncey and G. G. Harvey, *Phys. Rev.* **38**, 1071 (1931).

<sup>4</sup> G. G. Harvey, *Phys. Rev.* **43**, 591 (1933).

<sup>5</sup> P. S. Williams, *Rev. Sci. Inst.* **4**, 334 (1933).

window were such that the variation in the angle of scattering for a given chamber setting was 5°. The "liquid air temperature" of the crystal was found, by means of a nickel-copper thermocouple, to be about 103°K.

### 3. EXPERIMENTAL RESULTS

The ratio of the ionization current produced by the rays scattered into the ionization chamber set at an angle  $\phi$  when the powdered crystal was at liquid air temperature to the current when the crystal was at room temperature was obtained for each of several values of  $\phi$ . The ratios, together with their probable errors as calculated from the experimental readings, are shown in Table I. It is seen that with certain exceptions

TABLE I. Ratio of the scattering from powdered crystals at 103°K to that from crystals at 295°K.

$\phi$	KCl	NaF
12°	0.965±0.006	1.015±0.008
15°	0.985±0.006	0.990±0.006
18°	0.995±0.008	0.960±0.006
21°	0.990±0.010	1.013±0.010
24°	0.972±0.010	
27°	0.998±0.012	
30°	0.996±0.012	
33°	0.983±0.012	
36°	0.974±0.014	

the ratios differ from unity by no more or very little more than the probable error.

### 4. DISCUSSION

Insofar as the ratios shown in Table I differ from unity by more than the probable error, there is some indication of the difference being real. Any true difference might be due to a change in  $G$ , in  $L-H$ , or to changes in both  $G$  and  $L-H$  with the temperature.

First, let us consider the possibility of a change in  $L-H$ . Since, according to Eqs. (3) and (4), both  $L$  and  $H$  are functions of the  $F$  values and since the  $F$  values depend upon the temperature,  $L$  and  $H$  also depend upon the temperature. Also the  $F_r$  values used in calculating  $L$  are subject to small changes due to the thermal contraction of the crystal on cooling from 295 to 103°K. Using data<sup>6</sup> on the thermal expansion of KCl we find

that the grating space of KCl changes from about 3.14Å at 295°K to about 3.12Å at 103°K. Using James and Brindley's<sup>7</sup> experimental  $F$  values for KCl at liquid air temperature, we obtained curves similar to II and III in Fig. 4 of the previous paper. Also by using these  $F$  values a curve for  $H$  similar to I in Fig. 4 of the previous paper was obtained. Taking differences between the ordinates of the curves similar to III and I, we obtained values of  $L-H$  at liquid air temperature. The values of  $L-H$  at 103°K and at 295°K are shown in Table II. By referring to

TABLE II. Values of  $L-H$  for KCl.

$\phi$	103°K	295°K	Ratio
12°	0.65	0.62	1.004
15°	0.06	0.02	1.007
18°	-0.13	0.00	0.974

the previous paper it is seen that  $S_{\text{exp}}$  at  $\phi = 12^\circ$  for KCl at 295°K is 7.13. In going from 295 to 103°K the value of  $L-H$  changes from 0.62 to 0.65 so that the value of  $S_{\text{exp}}$  at 103°K should be  $7.13 + (0.65 - 0.62) = 7.16$ . The ratio of  $S_{\text{exp}}$  at 103°K to that at 295°K should therefore be 1.004. The ratios for other angles are shown in the fourth column of Table II. It is seen that because of the variation of  $L-H$  with the temperature the ratios differ somewhat from unity. It must be remarked here that the values of  $L$  and  $H$  are calculated from  $F$  values read off curves drawn through the experimental  $F$  values obtained by James and Brindley. These  $F$  values naturally are subject to experimental error. We do not believe, therefore, that the changes in the values of  $L-H$  shown in Table II should be regarded as exact. Consequently, the ratios shown in Table II should also not be regarded as exact but only as indicating the order of magnitude of the changes in the ratios to be expected due to a change of  $L-H$  with the temperature.

In the case of NaF, experimental  $F$  values at liquid air temperature were not available and so we calculated the  $F$  values both at room and at liquid air temperatures from the wave mechanics  $f$  values given in Table III of the previous paper, combined with the Debye-Waller temperature

<sup>6</sup> Int. Crit. Tab. 3, 43.

<sup>7</sup> R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

factor. In order to determine this factor, it is first necessary to find the characteristic temperature of NaF. Comparing the values of the molecular heat<sup>8</sup> of NaF at  $-150$ ,  $-100$  and  $-50^\circ\text{C}$  with the Debye specific heat function,<sup>9</sup> we find an average characteristic temperature of  $427^\circ\text{K}$ . Values of  $L-H$  at  $103^\circ\text{K}$  and at  $295^\circ\text{K}$  can now be found and ratios for NaF calculated. The ratios range from 0.989 to 1.005.

We are of the opinion that, with perhaps the exception of the ratio at  $\phi = 18^\circ$ , the experimental ratios for NaF do not differ from unity by more than the probable error plus the difference in the respective ratios produced by the change of  $L-H$  with temperature. We believe that there is no necessity to suppose a change of  $G$  with temperature. Hence, there is no definite evidence that the true atom form factors, or  $f$  values, of NaF change in going from 295 to  $103^\circ\text{K}$ .

In the case of KCl, since all the experimental ratios are less than unity, we believe that a slight change in  $G$  with temperature may be indicated. Harvey<sup>10</sup> has recently measured the diffuse scattering of x-rays of wave-length  $0.71\text{\AA}$  from KCl at room and liquid air temperatures and finds that a small decrease in the  $f$  values at liquid air temperature may be indicated. A change in  $G$  as defined by Eq. (2) is principally dependent upon a change in  $f$  and not upon a change in  $f''$ . We have therefore used Harvey's  $f$  values at room and liquid air temperatures to enable us to calculate the change in  $G$ . If now we suppose that the change in  $S_{\text{exp}}$  with temperature is due to a change in  $G$  and not in  $L-H$ , we obtain the ratios given in Table III. It is seen

that our experimental ratios in the range from  $15$  to  $24^\circ$  as shown in Table I are closer to unity than is indicated by the ratios calculated from Harvey's suggested  $f$  values for liquid air temperature.

TABLE III. *Theoretical ratios due to the change of  $G$  with temperature—KCl.*

$\phi$	Ratio
$10^\circ$	0.975
$15^\circ$	0.964
$20^\circ$	0.972
$25^\circ$	1.000

## 5. CONCLUSION

We have observed small changes in the values of  $S(\text{powder})$  for KCl and NaF in going from 295 to  $103^\circ\text{K}$ . The observed changes can be explained as due to the small changes in  $L-H$  (see Eqs. (3) and (4)) plus the experimental error. Depending upon the angle  $\phi$ , the change in  $L-H$  is sometimes an increase and sometimes a decrease. In the case of NaF, since the change in  $S(\text{powder})$  is an increase at some angles and a decrease at other angles, there is no definite indication of changes in the values of  $G$  (see Eq. (2)) and therefore no indication of changes in the true atom form factors of NaF. In the case of KCl, since the change in  $S(\text{powder})$  is a decrease at all angles, there is an indication of a decrease in the values of  $G$  and therefore an indication of a slight decrease in the true atom form factors of KCl in going from 295 to  $103^\circ\text{K}$ . The decreases in the true atom form factors of KCl, if they exist at all, are less than, but of the same order of magnitude as, the decreases suggested recently by Harvey.<sup>10</sup>

<sup>8</sup> Int. Crit. Tab. 5, 100.

<sup>9</sup> See J. K. Roberts, *Heat and Thermodynamics*, p. 404.

<sup>10</sup> G. G. Harvey, *Phys. Rev.* 43, 707 (1933).