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## Diffuse Scattering of X-Rays from Sodium Fluoride. III. Using Sensibly Monochromatic Radiation

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The Mo $K\alpha$ lines, together with a small amount of the continuous spectrum of half the wave-length, were isolated by crystal reflection and scattered from a crystal of NaF at room temperature. Ionization currents were measured by using an FP-54 pliotron and d.c. amplifier. Comparison was made with the scattering at 90° from paraffin, and $S_{class}$ was determined between $x=0.1$ and $x=1.0$. It agrees fairly well with the $S_{class}$ obtained by the author in a previous research using a band of wave-lengths. Compari-son is made between the observed $S_{class}$ and these com-puted by theory from wave-mechanics atomic structure factors, using the assumptions of zero-point-energy or no zero-point-energy. The discrepancy between experiment and theory, especially if the former assumption is correct, seems considerable enough to imply the need for some modification in the theory, probably in the incoherent scattering term.

## I. INTRODUCTION

ACCORDING to the theory of the diffuse scattering of x-rays from simple cubic crystals[1, 2, 3, 4, 5] the scattering per electron in terms of the classical Thomson value is given by

$$S = S_1 + S_2/R^3, \tag{1}$$

where

$$S_1 = (f^2 - F^2)/Z,$$

$$S_2 = 1 - f''^2/Z^2.$$

By definition

$$S_{class} = S_1 + S_2 \tag{2}$$

$S_1$ and $S_2/R^3$ represent the coherent and in-coherent scattered intensities, respectively, and $R^3 = [1 + (h/mc\lambda)$ vers $\phi]^3$ is the Breit-Dirac factor.

The diffuse scattering from KCl, NaCl and NaF has been studied using a band of wave-lengths filtered through aluminum. Harvey,[6] however, has pointed out certain objections to this use of a band of wave-lengths, and has re-peated the work on KCl using monochromatic radiation. Similar objections, but to a lesser degree, apply to the author's previous work[7] on NaF. In addition the imperfections of the avail-able artificial crystal of NaF made difficult the avoidance of diffraction effects with a band of wave-lengths. Consequently, the present re-search was undertaken to attempt to overcome these difficulties.

[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] G. G. Harvey, Phys. Rev. 43, 591 (1933).
[7] G. E. M. Jauncey and P. S. Williams, Phys. Rev. 41, 127 (1932).

## II. Experimental Method

Mo $K\alpha$ rays together with a small amount of 0.35A radiation from the continuous spectrum were reflected in the first and second orders, respectively, by a NaCl crystal from a molybdenum tube run at 20 m.a. and about 50 kv. The planes of reflection and scattering were the same. The reflected beam—the primary beam for the scattering work—passed through the scattering substance on the axis of the ionization spectrometer. Suitable screening slits were provided. The 13.7 cm brass ionization chamber contained methyl bromide at 1 atmosphere at 23°C; on it was built an evacuated metal housing containing an FP-54 pliotron and high resistance shunt of about $10^{11}$ ohm; a flexible metal conduit connected the pliotron assembly with a d.c. amplifier designed and built by DuBridge and Brown[8] in this laboratory. This was run at about 20,000 mm/volt, giving net deflections for NaF of the order of 5 cm, which corresponds to $2.5 \times 10^{-14}$ amp.

Net deflections were obtained in all cases: base readings were taken with the scattering substance removed and an equivalent absorber placed in the primary beam, which automatically corrected for scattering from the air and one unscreened slit. At the scattering angle $\phi$ deflections for the NaF, $D_{\theta\phi}$, were noted for various values of $\theta$ (angle between crystal normal and primary beam) symmetrically chosen on both sides of $\theta = \phi/2$; these were interspersed with deflections $D'_{90}$ for a paraffin slab replacing the NaF at $\theta = 45°$, $\phi = 90°$. Then the average deflection $D_\phi$
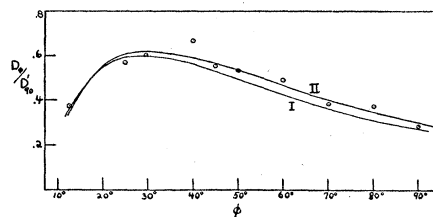


Fig. 1.

for NaF at $\phi$ was taken as the height at $\theta = \phi/2$ of the straight line passing through the groups of $D_{\theta\phi}$ when plotted against $\theta$, as in previous researches,[9] and the ratio $D_\phi/D'_{90}$ formed. This was done several times for each $\phi$ chosen. The average values are given in Table I, and as circles in Fig. 1.

It was found that for a value of $\phi$ such that intense regular reflection took place at $\theta = \phi/2$, $D_\phi/D'_{90}$ came out ridiculously high (compared to values at adjacent $\phi$'s) no matter how far from $\phi/2$ were taken the $\theta$'s for the $D_{\theta\phi}$. This would be expected, of course, for any very imperfect crystal. Accordingly readings were taken only at such $\phi$'s that the Bragg peak at $\theta = \phi/2$ was small or non-existent. Even this apparently did not eliminate troubles with diffraction, for the spottiness of certain points is greater than the reproducibility of results would allow.

By replacing the scatterer with a second NaCl crystal either primary wave-length could be adequately isolated. The ratios $h =$ (transmitted intensity)/(primary intensity) at normal incidence ($\theta = 0$) were measured for the NaF crystal and the paraffin slab: for the crystal $h_{0.71} = 0.220$, $h_{0.35} = 0.76$; for the paraffin $h'_{0.71} = 0.88$, $h'_{0.35} = 0.94$.

The mass per unit area of the crystal was $(\rho t) = 0.694$, that of the paraffin was $(\rho t)' = 0.282$. The formula for the latter was taken as $C_n H_{2n}$—this is sufficiently valid here since $n > 20$.

The ratio $e_{0.71}/e_{0.35} = 36$ for the primary intensities was computed from the relative energies in the corresponding 100 Debye-Scherrer rings from a slab of powdered NaF on the spectrometer table.

TABLE I.

| $\phi$ | $x_{0.71}$ | $x_{0.35}$ | $D_\phi/D'_{90}$ Expt. | 0.71A $L_1$ | $L_2$ | 0.35A $L_1$ | $L_2$ |
|---|---|---|---|---|---|---|---|
| 12.5° | .152 | .305 | .375 | .72 | .72 | .031 | .031 |
| 25 | .305 | .61 | .57 | .67 | .66 | .029 | .029 |
| 29.5 | .36 | .72 | .605 | .64 | .63 | .029 | .029 |
| 40 | .48 | .96 | .67 | .575 | .55 | .026 | .026 |
| 45 | .54 | 1.08 | .555 | .535 | .505 | .025 | .025 |
| 50 | .595 | 1.19 | .535 | .50 | .47 | .024 | .024 |
| 60 | .705 | 1.41 | .49 | .435 | .40 | .022 | .022 |
| 70 | .81 | 1.62 | .385 | .37 | .33 | .021 | .021 |
| 80 | .905 | 1.81 | .375 | .325 | .28 | .020 | .019 |
| 90 | .995 | 1.99 | .285 | .29 | .24 | .021 | .019 |

[8] L. A. DuBridge and Hart Brown, Rev. Sci. Inst. **4**, 532 (1933).

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

## III. INTERPRETATION OF RESULTS

The observed $D_\phi/D'_{90}$ at $\phi$ is related to $S$ values by Eq. (10), reference 10, where here

$$B = h_{0.71}(e_{0.71}/e_{0.35})[K_0S_1 + K_\phi T_\phi S_2/R_\phi{}^3]_{0.71}$$
$$+ h_{0.35}[K_0S_1 + K_\phi T_\phi S_2/R_\phi{}^3]_{0.35} \quad (3)$$

and $B'$ is exactly similar in form and refers to paraffin at 90°. However, $1 + \cos^2 \phi$ is replaced by $1 + (\cos 14° \ 30')^2 \cos^2 \phi$ to account for the departure from non-polarization of the Mo $K\alpha$ induced by the reflection at the NaCl; this is sufficiently correct for the small 0.35A component. The $h$'s in (3) are computed for $\theta = \phi/2$ from the measured values at $\theta = 0$; these also (with $(\mu/\rho) \propto Z^3$) yield the $T$'s. The $K$'s are calculated from Compton's[11] tables of absorption coefficients. Everything in square brackets in Eq. (3) is taken at the indicated wave-length: for instance, the first $S_1$ is at $x = (\sin \phi/2)/(0.71)$, the second at $x = (\sin \phi/2)/(0.35)$, etc. For 0.71A, $S_1' = 0.13$, $S_2' = 0.94$; for 0.35A, $S_1' = 0$, $S_2' = 1$.[11a]

The equation cited, with Eq. (3), reduces finally to

$$D_\phi/D'_{90} = (L_1S_1 + L_2S_2)_{0.71} + (L_1S_1 + L_2S_2)_{0.35}, \quad (4)$$

where the $L$'s are the numbers given with the corresponding $x$'s in Table I, for the experimental $\phi$'s. Eq. (4) is strictly true only for infinitely small slits, but close enough in this case for the actual $\phi$ tolerance of ±2°.

By a trial and error process of postulating various $S_{class}$ vs. $x$ curves until the $D_\phi/D'_{90}$ vs. $\phi$ curve computed by Eq. (4) fits sufficiently the experimental points, $S_{class}$ can be determined between $x = 0.1$ and $x = 1.0$. $S_{class}$ values corresponding to $x > 1$ enter only the relatively small 0.35A component of Eq. (4) and cannot be accurately fixed by this experiment; conversely, any reasonable assumption (say 1) for $S_{class}$ in $1 < x < 2$ will serve for computations of $D_\phi/D'_{90}$ for $0 < \phi < 90°$.

Since $(L_1 - L_2)_{0.71}$ becomes increasingly noticeable above $\phi = 50°$, $S_2/S_1$ as well as $S_{class}$ will affect Eq. (4). The shape of the $S_2$ curve was taken as determined by $(1 - f''^2/Z^2)$, with theoretical $f''$ values as tabulated by Jauncey and Pennell.[10] The absolute value was fitted to Wollan's[12] experimental result $S_2/R \ {}^3S_1 = 3.15$ for NaF at $x = 1.22$, $\lambda = 0.71A$, giving $k$ in $S_2 = k(1 - f''^2/Z^2)$, $S_1 = S_{class} - S_2$.

## IV. DISCUSSION OF RESULTS

As a first approximation the $S_{class}$ curve obtained in the previous research[7] (Column I, Table II) was divided into components as just described and put into Eq. (4), yielding curve I of Fig. 1. Curve II is given by the $S_{class}$ curve finally selected as the net result of this experiment (Column II, Table II, and curve II, Fig. 2).

The observed $S_{class}$ may be compared with values computed by Eq. (2) from wave mechanics

TABLE II.

| | | $S_{class}$ | | |
| | Ref. 7 | Present | Wave mech.* | Wave mech.** |
| $x$ | I | II | III | IV |
|---|---|---|---|---|
| .1 | .12 | .11 | .32 | .24 |
| .2 | .67 | .66 | .81 | .59 |
| .3 | .85 | .87 | 1.09 | .92 |
| .4 | .93 | .96 | 1.19 | 1.03 |
| .5 | .97 | 1.02 | 1.19 | 1.05 |
| .6 | .99 | 1.06 | 1.16 | 1.05 |
| .7 | .99 | 1.08 | 1.12 | 1.04 |
| .8 | 1.00 | 1.10 | 1.10 | 1.03 |
| .9 | 1.00 | 1.11 | 1.09 | 1.03 |
| 1.0 | 1.00 | 1.11 | 1.08 | 1.03 |

\* With zero-point energy.
\*\* Without zero-point energy.



FIG. 2.

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

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

[11a] Using James and Brindley's $f_0$ values [reference 12] in (1) we have (at 90°, 0.71A) for a C atom, $S_1 = 0.17$, $S_2 = 0.92$ and for H atoms $S_1 = 0$, $S_2 = 1$. Neglecting interatomic interference and weighting these by 6 and 2, respectively, (from $C_nH_{2n}$) the average $S_1'$ and $S_2'$ given are arrived at. At 90°, 0.35A a similar analysis holds.
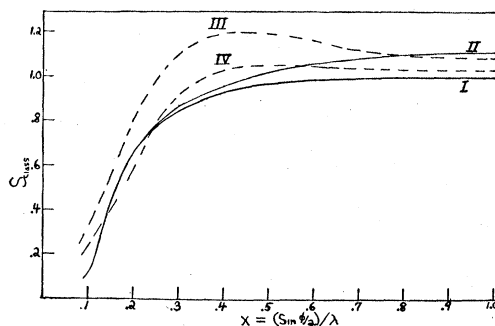
[12] E. O. Wollan, Phys. Rev. 43, 955 (1933).

atomic structure pictures. James and Brindley[13] give the electronic amplitude factors for $Na^+$ and $F^-$ in terms of $x$ and from these Jauncey and Pennell[10] have tabulated $f$ and $f''$ values for both, and their averages. $S_1 = (f^2 - F^2)/Z$ may be written $(f^2/Z)(1 - e^{-2M})$, where $M$ is the Debye-Waller temperature factor; it involves the characteristic temperature $442°K^{13a}$ of NaF and the assumptions of zero-point-energy or no zero-point-energy for the atomic nuclei. These two assumptions yield, respectively, for $S_{class}$ curves III and IV of Fig. 2 (Columns III and IV, Table II).

The curves of Fig. 2 may be compared either by absolute value or by shape. The author does not consider the former comparison very fruitful, for the absolute value of each of the observed $S_{class}$ curves depends directly on about six separate measurements and also on the opinion held as to the scattering from paraffin at 90°. In view of this the agreement within 10 percent of all the $S_{class}$ curves at $x = 1.0$ is adequate.

The difference in shape between the $S_{class}$ curves I and II of this and the preceding research is in the direction to be expected from the opening remarks on diffraction effects and is very probably real. On theoretical grounds the existence of zero-point-energy is probable. The discrepancy in shape, however, between curves II and III is considerable, the former showing no trace of a maximum at $x = 0.45$. Here also the absolute difference between the curves is large, if we accept their agreement at $x = 1.0$. The disagreement in shape between II and IV, while not so large, is still noticeable.

The conclusion seems reasonable, then, that Eqs. (1) and (2) are not adequate, at any rate if zero-point-energy exists. The fair agreement obtained by Harvey[6] for KCl between measured and calculated $f'$ values indicates that the modifications should come in $S_2$, since this is relatively much larger for NaF than for KCl. Further, Waller's[14] wave-mechanical development for $S_2$ includes an additional negative term; its calculation for the present paper was not convenient. It is unlikely that the amplitude factors used for III and IV are sufficiently in error to account for the observed discrepancy, although they may be slightly too high, since field interaction between atoms in the crystal lattice would contribute to greater atomic diffuseness. This tendency should be more pronounced for NaF than for KCl.

In conclusion the author wishes to express his appreciation to Professor G. E. M. Jauncey, under whom the work was done, for his advice and interest throughout.

[13] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).
[13a] Found by J. J. Shonka, Phys. Rev. **43**, 947 (1933). See also G. E. M. Jauncey and P. S. Williams, Phys. Rev. **44**, 794 (1933).

[14] I. Waller, Phil. Mag. **4**, 1228 (1927).