

THEORY OF THE DIFFUSE SCATTERING OF X-RAYS BY SIMPLE CUBIC CRYSTALS

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ABSTRACT

The value of X in the previous paper by Jauncey has been determined for the case of a simple cubic crystal consisting of atoms of one kind and the formula obtained by Jauncey reduces to:

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

There are no experimental results for a crystal consisting of atoms of one kind but Jauncey and May have obtained values for the diffuse scattering of x-rays from a crystal of rocksalt. Assuming rocksalt to consist of atoms of atomic number $(11+17)/2$ or 14, we have calculated values of f' using values of F given by James and Firth. These calculated values of f' are found to be only slightly greater than the values of F at absolute zero. Also Jauncey has measured the effect of temperature on the diffuse scattering from crystals. From the above formula calculations of the ratio of the scattering at temperatures of 568° and 290°K have been made using F values given by James and Firth. The theoretical and experimental values of this ratio in one case are 1.29 and 1.33 respectively, and in another case are 1.13 and 1.18, thus showing good agreement between theory and experiment.

I. INTRODUCTION

IN THE preceding paper in this issue of the Physical Review Jauncey¹ has shown that the scattering of x-rays by a solid consisting of atoms all of the same kind is given by

$$S = 1 + (Z - 1)f'^2/Z^2 + (F^2/ZN) \sum_{r=1}^N \sum_{s=1}^N \cos k(x_r - x_s) \quad (1)$$

where the various quantities are defined in Jauncey's paper. As explained in Section 5 of that paper, the right side of Eq. (1) depends on the two simplifying assumptions: (1) the probability function for the displacement of the center of the atom from its mean position is symmetrical about the mean position, and (2) the temperature factor H is the same for all atoms. These two assumptions are probably not quite valid for an amorphous solid, but are valid for a simple cubic crystal of atoms of one kind. We shall therefore take Eq. (1) to be exactly true for this kind of crystal. The quantity x_r in Eq. (1) is the distance of the mean center, about which the r th atom is oscillating due to its thermal motion, from the reference plane defined in the previous paper.¹ In a simple cubic crystal x_r is the distance of a lattice point from the reference plane.

¹ G. E. M. Jauncey, Phys. Rev. this issue p. 1193.

II. EVALUATION OF THE DOUBLE SUMMATION

In order to avoid confusion, we shall replace x_r and x_s by w_r and w_s . It is our object to evaluate

$$\sum'_{r=1}^N \sum'_{s=1}^N \cos k(w_r - w_s).$$

Let us take a crystal parallelepiped whose sides contain $P+1$, $Q+1$, and $R+1$ atoms so that $N = (P+1)(Q+1)(R+1)$ or PQR since P , Q , and R are large numbers. Let the size of the parallelepiped be such that the absorption of x-rays in the crystal is negligible so that every atom in the crystal is bathed in x-rays of the same intensity. On the other hand, we suppose that the length of each side of the parallelepiped is many times the wave-length of x-rays. A crystal with the length of each side about 0.1 mm is what we have in mind. Let the crystal axes be parallel to the axes of rectangular cartesian coordinates with the origin at a corner of the crystal. A lattice point of the crystal will then have the coordinates

$$x = pD, \quad y = qD, \quad z = rD \quad (2)$$

where p , q , and r are integers and D is the lattice constant. Let the reference plane¹ pass through the origin of coordinates and let the direction cosines of the normal to this plane be l , m , n . The distance of a lattice point from this plane is then

$$w_{pqr} = lpD + mqD + nrD \quad (3)$$

If we imagine Z electrons massed at each lattice point of an ideal crystal, we shall have as in Eq. (6) of the previous paper¹

$$I = \left\{ Z \sum_{p=0}^P \sum_{q=0}^Q \sum_{r=0}^R \cos kw_{pqr} \right\}^2 + \left\{ Z \sum_{p=0}^P \sum_{q=0}^Q \sum_{r=0}^R \sin kw_{pqr} \right\}^2 \quad (4)$$

In the triple summations in Eq. (4) p , q , and r may be equal. Let us first sum with respect to r , so that we obtain

$$\sum_{r=0}^R \cos kw_{pqr} = \sum_{r=0}^R \cos k(A_{pq} + rnD) \quad (5)$$

where

$$A_{pq} = plD + qmD \quad (6)$$

and is a constant during this summation. Now it can be shown that²

$$\sum_{r=0}^R \cos k(A_{pq} + rnD) = \cos k \left(A_{pq} + \frac{R-1}{2} nD \right) \sin \frac{kRnD}{2} \csc \frac{knD}{2} \quad (7)$$

² See, e.g. Hobson—Plane Trigonometry, 4th Edition, p. 90.

and that

$$\sum_{r=0}^R \sin k(A_{pq} + rnD) = \sin k\left(A_{pq} + \frac{R-1}{2}nD\right) \sin \frac{kRnD}{2} \operatorname{csc} \frac{knD}{2} \quad (8)$$

Summation with respect to q and then p thus yields

$$\begin{aligned} & \sum_{p=0}^P \sum_{q=0}^Q \sum_{r=0}^R \cos kw_{pqr} \\ &= \cos kD\left(\frac{P-1}{2}l + \frac{Q-1}{2}m + \frac{R-1}{2}n\right) \sin \frac{kPlD}{2} \sin \frac{kQmD}{2} \\ & \quad \sin \frac{kRnD}{2} \operatorname{csc} \frac{kLD}{2} \operatorname{csc} \frac{kmD}{2} \operatorname{csc} \frac{knD}{2} \quad (9) \end{aligned}$$

and

$$\begin{aligned} & \sum_{p=0}^P \sum_{q=0}^Q \sum_{r=0}^R \sin kw_{pqr} \\ &= \sin kD\left(\frac{P-1}{2}l + \frac{Q-1}{2}m + \frac{R-1}{2}n\right) \sin \frac{kPlD}{2} \sin \frac{kQmD}{2} \\ & \quad \sin \frac{kRnD}{2} \operatorname{csc} \frac{kLD}{2} \operatorname{csc} \frac{kmD}{2} \operatorname{csc} \frac{knD}{2} \quad (10) \end{aligned}$$

so that Eq. (4) becomes

$$I = Z^2 \cdot \sin^2 \frac{kPlD}{2} \sin^2 \frac{kQmD}{2} \sin^2 \frac{kRnD}{2} \operatorname{csc}^2 \frac{kLD}{2} \operatorname{csc}^2 \frac{kmD}{2} \operatorname{csc}^2 \frac{knD}{2} \quad (11)$$

The angle of scattering enters the problem through the relation¹

$$k = (4\pi \sin \phi/2)/\lambda. \quad (12)$$

If we have chosen values of ϕ , the scattering angle, and l, m, n the direction cosines of the normal to the reference plane, in such a way that

$$kLD \neq 2\pi a, \text{ or } kmD \neq 2\pi b, \text{ or } knD \neq 2\pi c \quad (13)$$

where a, b, c are any integers, the value of the trigonometric function on the right side of Eq. (11) is of the order unity. Now, dividing the right side of Eq. (11) by the total number of electrons, $PQRZ$, we find the scattered intensity per electron to be

$$S = \frac{ZO(1)}{PQR} \quad (14)$$

where $O(1)$ is a quantity whose magnitude is of the order unity. For a crystal of KCl, $Z=20$ and, if we are dealing with a crystal in the form of a cube the length of whose edge is 0.1 mm, the value of PQR is about 10^{17} , so that the

right side of Eq. (14) is of the order 10^{-16} which may be taken as zero. Therefore there is no diffuse scattering from an ideal simple cubic crystal whose atom centers are held exactly at lattice points with the electrons massed at the center of each atom.

If Eq. (1) is applied to this ideal crystal, the same result must be obtained as in the previous paragraph. In this case $f' = F = Z$, so that we have

$$O = 1 + (Z - 1) + (Z/N) \sum_{r=1}^N \sum_{s=1}^N \cos k(w_r - w_s) \quad (15)$$

Solving Eq. (15) for the double summation we obtain

$$\sum_{r=1}^N \sum_{s=1}^N \cos k(w_r - w_s) = -N. \quad (16)$$

Substituting this in (1), we obtain

$$S = 1 + (Z - 1)f'^2/Z^2 - F^2/Z \quad (17)$$

for the scattering per electron from a crystal of simple cubic form whose atoms are all of the same kind and each of which contains Z electrons. In Eq. (17), it will be seen by reference to the preceding paper¹ that F is the atomic structure factor which includes the effect due to thermal agitation, while f' is related to the true atomic structure factor f , which does not include the effect of thermal agitation, according to

$$f'^2 = f^2 + \left[f^2 - Z \sum_{r=1}^z E_r^2 \right] / (Z - 1) \quad (18)$$

where E_r is the average amplitude associated with the r th electron in the atom. If the average amplitude associated with one electron is the same as that associated with any other electron $f' = f$ and f' is then the true atomic structure factor.

III. COMPARISON WITH EXPERIMENT

Unfortunately, results on the diffuse scattering by a crystal consisting of atoms all of the same kind are not available. However, in 1924 Jauncey and May³ measured the absolute intensity of x-rays diffusely scattered by a crystal of rocksalt. They obtained the curve shown in Fig. 1. The curve XYZ represents the Thomson value of the scattering. Referring to their paper, it is seen that they used x-rays containing two wave-lengths, 0.71Å and 0.40Å. The peaks A and B are due to the wave-lengths 0.40Å and 0.71Å respectively. The point C was obtained when sufficient aluminum was inserted in the primary beam to remove the longer wave-length constituent of the x-rays. We have therefore drawn the broken curve $DAFG$ of Fig. 1, and this is then due to the scattering of x-rays of wave-length 0.40Å. It seems preferable to use the curve for this wave-length, since it is known from the diagram at which

³ G. E. M. Jauncey and H. L. May, Phys. Rev. **23**, 128 (1924).

value of ϕ the scattering approaches zero. Using this curve and dividing each ordinate by the Thomson value of the scattering at the same angle we obtain the S curve shown in Fig. 2 in which the abscissa is $(\sin \phi/2)/\lambda$. This S curve is for x-rays scattered by rocksalt at 290°K.

In 1928 James and Firth⁴ obtained F values from the regular reflection of x-rays by rocksalt at various temperatures. Their F values are for Na+Cl. In order to compare the present theory with experimental values, we shall

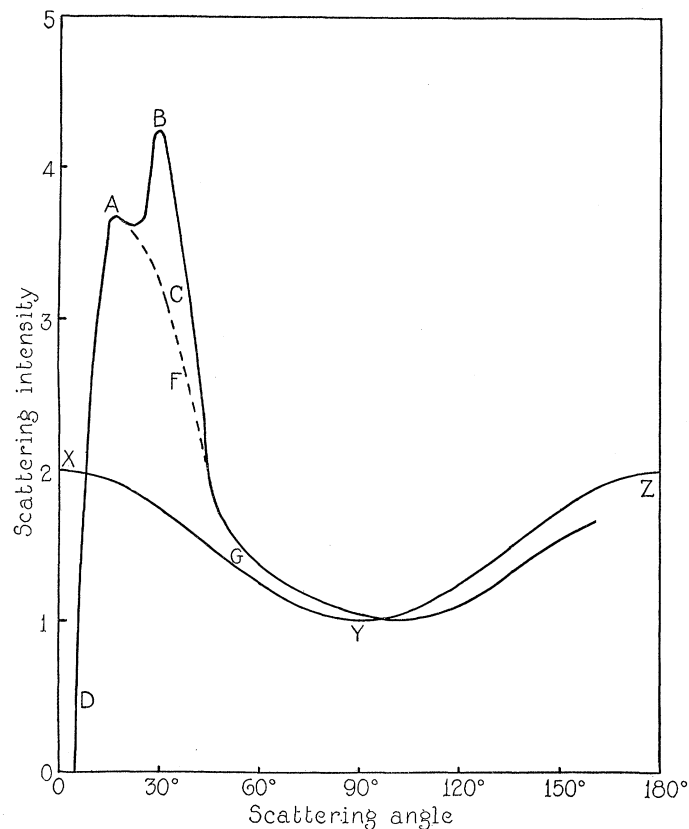


Fig. 1.

assume rocksalt to be made up of atoms of the same kind whose atomic number is $(11+17)/2 = 14$. We therefore take as F values to be substituted in Eq. (17) one half the values given for Na+Cl in the paper by James and Firth. These average F values are shown in the second column of Table I. Values of S found from Fig. 2 are shown in the third column of this table. From Eq. (17), values of f' can thus be determined and these are shown in the fourth column. James and Firth give F values extrapolated to absolute zero and the averages of these for Na and Cl are shown in the fifth column. The values in

⁴ R. W. James and E. M. Firth, Proc. Roy. Soc. **A117**, 62 (1928).

the fourth and fifth columns should be nearly but not quite equal. The true atomic structure factor f is somewhat greater than the value of F at absolute zero, if there is zero point energy.

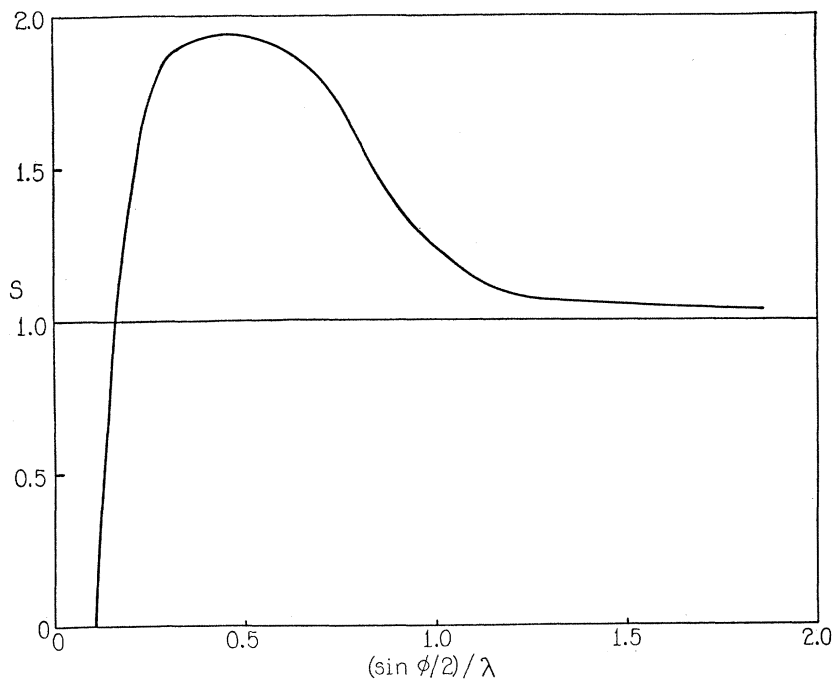


Fig. 2.

TABLE I.

$(\sin \phi/2)/\lambda$	$F_{290^\circ K}$	$S_{290^\circ K}$	f'	$F_0^\circ K$
0.1	12.3		12.8*	12.8
0.2	9.4	1.24	10.1	9.9
0.3	6.9	1.82	8.0	7.6
0.4	5.2	1.93	6.6	6.1
0.5	3.9	1.94	5.4	4.8
0.6	2.8	1.88	4.6	4.0
0.7	2.1	1.77	3.8	3.3
0.8	1.6	1.56	3.2	2.8
0.9	1.2	1.38	2.6	2.4
1.0	0.8	1.26	2.1	2.0
1.1	0.5	1.17	1.7	1.6
1.2	0.3	1.10	1.6	1.4

* By extrapolation.

As zero angle of scattering is approached, f' and F each approach Z and S approaches zero. This agrees with the experimental curves shown in Figs. 1 and 2.

In 1922, Jauncey⁵ found a temperature effect for the diffuse scattering by rocksalt. The temperatures used by Jauncey were 290°K and 568°K. From

the values given by James and Firth,⁴ F values at 568°K can be interpolated. The wave-lengths used by Jauncey were 0.28Å and 0.36Å at 15° and 30° scattering angle respectively. The ratios of the values of S found are shown in the fifth column of Table II. F values obtained from James and Firth are shown in the second and third columns. Values of f' obtained from Fig. 2 and Eq. (17) are shown in the fourth column. Now putting the values of $F_{290^\circ K}$ and $F_{568^\circ K}$ in Eq. (17) and using the appropriate f' values, we obtain theoretical values for $S_{290^\circ K}$ and $S_{568^\circ K}$. The ratios of these values are shown in the sixth column.

TABLE II.

$(\sin \phi/2)/\lambda$	$F_{290^\circ K}$	$F_{568^\circ K}$	f'	$S_{568^\circ K}/S_{290^\circ K}$	
				Exp.	Theory
0.467	4.25	3.20	5.8	1.33	1.29
0.720	1.95	0.90	3.7	1.18	1.13

It is seen that there is good agreement between the experimental and theoretical values of the ratios.

For a monatomic gas Compton⁶ has shown that

$$S = 1 + (Z - 1)f'^2/Z^2 \quad (19)$$

so that from the experimental values of S values of f' can be obtained. If x-rays are scattered by a simple cubic crystal of the same chemical element as the gas, values of f' can be obtained from the experimental values of S and F for the crystal. The values of f' for the gas should nearly agree with those for the crystal, the slight difference being due to the structure of an atom in a crystal being affected by the proximity of other atoms.

⁵ G. E. M. Jauncey, Phys. Rev. **20**, 421 (1922).

⁶ A. H. Compton, Phys. Rev. **35**, 925 (1930).