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THE SCATTERING OF X-RAYS BY GASES AND CRYSTALS

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ABSTRACT

Recently A. H. Compton and Jauncey and Harvey have obtained theoretical formulas for the scattering of x-rays by gases and crystals respectively. By means of these formulas f' values can be calculated. From measurements on the diffuse scattering by rocksalt, Jauncey and Harvey have calculated f' values for the average atom, or $(Na^+ + Cl^-)/2$, in rocksalt. Wollan has also recently obtained f' values for neon and argon. The f' values for the average of neon and argon, or $(Ne + A)/2$ are compared with those for $(Na^+ + Cl^-)/2$ and an excellent agreement is found. Also these two sets of experimental f' values are shown to be in excellent agreement with the quantum mechanics model of Waller and James. It is shown that the difference between f' and f, the true atomic structure factor, is not negligible and that the error in assuming f to be given by f' may be as large as 20 or 30 percent at large values of $(\sin \phi/2)/\lambda$. Also it is pointed out that only f, but not f', values may be used in the Fourier analysis method of unravelling crystal structure.

I. SCATTERING BY NEON, ARGON AND ROCKSALT

IN 1930 A. H. Compton[1] developed the theory of the scattering of x-rays by monatomic gases and obtained the formula

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

where S is the scattered intensity in a direction ϕ with the primary beam per electron relative to the scattered intensity from a single isolated electron in the same direction ϕ, Z is the number of electrons in an atom of the gas scatterer, and f' is a quantity to be defined later. More recently Jauncey and Harvey [2,3] have developed the theory of the diffuse scattering of x-rays by simple cubic crystals consisting of atoms of one kind and have obtained the formula

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

where F is the atomic structure factor of the atoms in the crystal. The quantity f' in Eqs. (1) and (2) is related to f, the true atomic structure factor, according to[2]

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[1] A. H. Compton, Phys. Rev. **35**, 925 (1930).

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

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

$$f'^2 = f^2 - \left(Z \sum_{r=1}^{Z} E_r^2 - f^2\right)/(Z-1) \qquad (3)$$

where E_r is the average amplitude of the waves scattered by the rth electron in the atom and where the true atomic structure factor f is given by

$$f = \sum_{r=1}^{Z} E_r \qquad (4)$$

the difference between F and f is that F contains the effect of the thermal motions of the atoms, while f does not. In virtue of Eq. (4), the quantity

$$Z \sum_{r=1}^{Z} E_r^2 - f^2 = Z^2 \left\{ \left(\sum_{r=1}^{Z} E_r^2 \right)/Z - \left(\sum_{r=1} E_r/Z \right)^2 \right\}. \qquad (5)$$

The quantity in the braces is essentially positive because the mean of the squares of a set of numbers is greater than the square of the mean of the same set of numbers. Hence in Eq. (3) $f' < f$, unless all the E's are equal. Since it is not likely that the E for a K electron is the same as the E for an L or M electron, it seems that $f' < f$.

Eq. (2) strictly only applies to crystals consisting of atoms of one kind. However, since no diffuse scattering measurements have been made on crystals like sylvine which may be considered as consisting of atoms of one kind, Harvey and the writer[3] were forced to make use of the results obtained by Jauncey and May[4] for rocksalt at room temperature. We treated rocksalt as a crystal consisting of atoms of one kind, the atomic number being $(11+17)/2$ or 14. Also, using the average of the F values for Na^+ and Cl^- obtained by James and Firth[5] at room temperature, we applied Eq. (2) and calculated f' values for an atom which is the average of Na^+ and Cl^-. Just a month before the publication of our papers[2,3] a paper by Wollan[6] on the scattering of x-rays by gases appeared. In particular, Wollan has determined the experimental values of S for neon and argon and from these S values he has by the use of Eq. (1) calculated the f' values for these gases. It is interesting to compare the average of the f' values found for neon and argon by Wollan with the average of the f' values for Na^+ and Cl^- which we have calculated[3] from Jauncey and May's and James and Firth's results. The comparison is shown in Fig. 1, where f' is plotted against $(\sin \phi/2)/\lambda$. The f' values for $(Ne+A)/2$ and for $(Na^+ + Cl^-)/2$ are shown as black circles and crosses, respectively. The two sets of points fall very closely on the same curve for values of $(\sin \phi/2)/\lambda$ less than 0.65 and the agreement is remarkable. For values of $(\sin \phi/2)/\lambda$ larger than 0.65 the f' values seem to separate. However, it is in this region that the Compton effect[7] becomes operative, and this effect was not properly taken account of in the experiments of Jauncey and May, which were done in 1923. Also in this region the experimental error in F be-

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

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

[6] E. O. Wollan, Phys. Rev. **37,** 862 (1931).

[7] A. H. Compton, Phys. Rev. **21,** 483 (1923).

comes large and also the f' values for the gases become very sensitive to small changes in S. It therefore seems reasonable to suppose that the discrepancy between the (Ne+A)/2 and the $(\mathrm{Na}^+ + \mathrm{Cl}^-)/2$ f' values at large values of $(\sin \phi/2)/\lambda (\sin \phi/2)/\lambda$ is due to experimental error and to neglect of the Compton effect in the f' values for $(\mathrm{Na}^+ + \mathrm{Cl}^-)/2$.

In Fig. 1 the broken curve is the F curve for $(\mathrm{Na}^+ + \mathrm{Cl}^-)/2$ for a temperature of 290°K. The F values shown by this curve were used by Jauncey and Harvey in calculating f' from S for $(\mathrm{Na}^+ + \mathrm{Cl}^-)/2$. Waller and James,[7a] using the new quantum mechanics, have devised model Na^+ and Cl^- ions and the f values for the model atom of $(\mathrm{Na}^+ + \mathrm{Cl}^-)/2$ are given by the full curve in Fig. 1. It will be seen that the black circles showing Wollan's f' values for (Ne+A)/2 lie very closely to the Waller-James curve, even out to values of $(\sin \phi/2)/\lambda$ as large as 1.0. At first sight this seems to show excellent agreement between the Waller and James' model atom and Wollan's experimental results. However, Wollan's values are f' values, whereas Waller and James' values are f values. At the beginning of this paper it was pointed out that $f' < f$ and the question arises as to whether the difference $f - f'$ is or is not negligible.

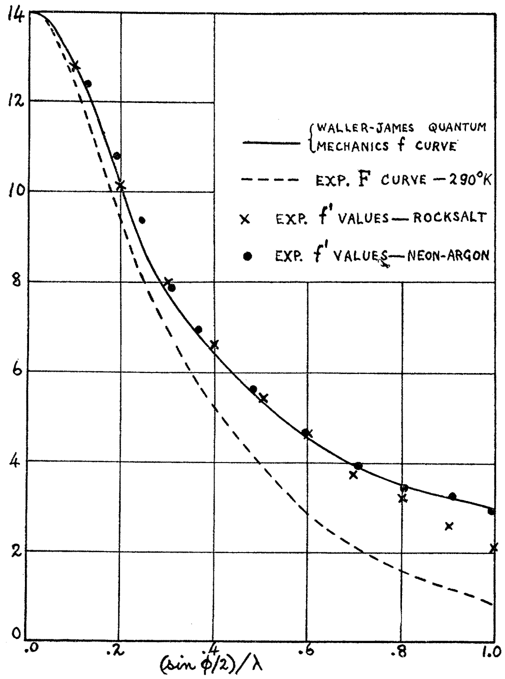

Fig. 1. Comparison of f' values for neon-argon with those for rocksalt.

II. Evaluation of $f - f'$

In order to answer the question just raised, we shall consider model ions of Na^+ and Cl^-. Pauling[8] has shown how model atoms based on the new quan-

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[7a] I. Waller and R. W. James, Proc. Roy. Soc. A117, 214 (1927).

[8] L. Pauling, Proc. Roy. Soc. **A114,** 181 (1927).

tum mechanics may be devised. As the calculations are tedious and as it is only desired to obtain the order of magnitude of $f-f'$, we shall assume that the Na^+ ion consists of 2 K electrons and 8 L electrons and the Cl^- ion of 2 K, 8 L, and 8 M electrons, and that no correction need be made for interpenetrating orbits. Let the probability of a given K electron being between the spheres of radii r and $r+dr$ measured from the nucleus of the atom be $u_K dr$, where

$$u_K = (1/2a_K{}^3)r^2 \exp\,(-\,r/a_K). \tag{6}$$

In Eq. (6), a_K is a parameter. Similarly there are probability functions u_L and u_M for the L and M electrons respectively given by

$$u_L = (1/a_L{}^5 4!)r^4 \exp\,(-\,r/a_L) \tag{7}$$

and

$$u_M = (1/a_M{}^7 6!)r^6 \exp\,(-\,r/a_M) \tag{8}$$

If r_m is the radius at which a probability function $u(r)$ becomes a maximum, then, for the respective u's,

$$a_K = r_m/2;\ a_L = r_m/4 \text{ and } a_M = r_m/6. \tag{9}$$

From Pauling's curves,[8] we have taken r_m to be 0.05A and 0.33A, respectively, for the K and L electrons of Na^+ and 0.04A, 0.18A and 1.02A, respectively, for the K, L and M electrons of Cl^-.

Let us take two parallel planes at distances z and $z+dz$ respectively from the nucleus of an atom, and let the probability of a given electron being between the planes be $p(z)dz$. The relation between $p(z)$ and $u(r)$ is, as is obvious from Compton's paper[1]

$$p(z) = (\tfrac{1}{2}) \int_{r=z}^{r=\infty} u(r)dr/r\, \cdot \tag{10}$$

We can therefore immediately obtain the p-functions for the K and L electrons of Na^+ and for the K, L and M electrons of Cl^-. The quantity E_r of Eqs. (3), (4) and (5) is then given by

$$E_r = \int_{-\infty}^{+\infty} p_r \cos kz dz \tag{11}$$

where $k = (4\pi \sin \phi/2)/\lambda$ and the subscript r may represent either a K, L or M electron. Performing the integration of Eq. (11), we obtain

$$\begin{aligned} E_K &= 1/(1+x^2)^2;\ E_L = (1-x^2)/(1+x^2)^4; \\ E_M &= (1-x^2/3)(1-3x^2)/(1+x^2)^6 \end{aligned} \tag{12}$$

where $x = ka_K$, ka_L or ka_M, respectively. In virtue of Eq. (4), values of f, and in virtue of Eq. (3), values of f' can be found. In Fig. 2, the difference $f-f'$ is plotted against $(\sin \phi/2)/\lambda$, curves being shown for Na^+ and Cl^-. It is seen that the maximum values of $f-f'$ for Na^+ and Cl^- are 0.45 and 0.39 respectively, which are not negligible numbers. At $(\sin \phi/2)/\lambda = 0.995$, the values of $f-f'$ for Na^+ (or neon) and Cl^- (or argon) are 0.44 and 0.19 respectively. At this value of $(\sin \phi/2)/\lambda$, Wollan obtained f' values of 1.37 and 4.49 for neon and argon respectively, so that the true atomic structure factors for neon and argon might be as large as 1.81 and 4.68 if the models we have chosen are reasonably correct. The error in assuming that the true atomic structure factor is given by f' may thus be of the order of 20 to 30 percent in the case of neon and 4 percent in the case of argon. Fig. 9 of Wollan's paper shows the curve for the experimental f' values for neon falling below the curve for the f values for the theoretical Na^+ model. This is as it should be, although it appears that the differences $f-f'$ are somewhat larger than we have calculated for our model Na^+ ion in this paper. However, the curve for $f-f'$ depends on the model chosen. It is at large values of $(\sin \phi/2)\lambda$ that the difference $f-f'$ becomes important, and it is also in this region that the experimental error becomes fairly large. So altogether the values of the true atomic structure factor reported in this region must be subject to considerable error. It should be noted that the Fourier analysis methods of unravelling atomic structure as developed by Duane[9] and Compton[10] are applicable only to f and not to f' values.

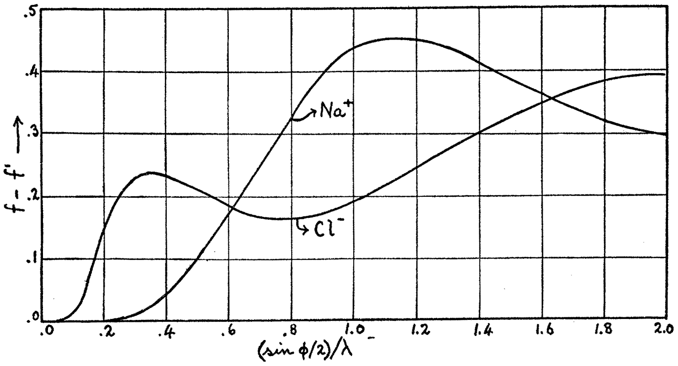

Fig. 2. Curves for $f-f'$.

The hump which occurs at $(\sin \phi/2)/\lambda = 0.34$ in the $(f-f')$ curve for Cl^- in Fig. 2 is caused by the M electrons. We might average the Na^+ and Cl^- curves of Fig. 2 and obtain a curve for $(Na^+ + Cl^-)/2$ and so obtain some idea of the corrections to be made to the f' values for $(Na^+ + Cl^-)/2$. The f values so obtained in the region of $(\sin \phi/2)/\lambda > 0.65$ fall more closely to the Waller-James curve of Fig. 1 than do the f' values, the agreement being good out to $(\sin \phi/2)/\lambda = 0.80$. When Wollan's f' values are corrected for $f-f'$, his points at large angles fall above the Waller-James curve.

Taking everything into account, it must be said that Wollan's results for neon and argon, our results for rocksalt, and the Waller-James theoretical f values agree very well with one another.

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[9] W. Duane, Proc. Nat. Acad. Sci. **11**, 489 (1925).

[10] A. H. Compton, "X-Rays and Electrons," Chapter V.