

INTERPRETATION OF ATOMIC STRUCTURE FACTOR CURVES IN CRYSTAL REFLECTION OF X-RAYS

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ABSTRACT

In a previous paper (Phys. Rev., May, 1928) the authors showed that, for certain values of D the grating space of a crystal of rocksalt, the area under a radial electron distribution (or U) curve for chlorine rose above 19 electrons. This result was obtained both from Havighurst's experimental F curve and from F values calculated for a model chlorine ion, these calculated values being modified to take into account the Compton effect. This result seemed perplexing, inasmuch as both the real ion and the model ion have but 18 electrons. The present paper is a further discussion of this point. It is proved that for any symmetrical atom F values, calculated according to the classical theory and unmodified for the Compton effect but multiplied by the Debye temperature factor, give U curves the areas under which never exceed the number of electrons assumed in the model. It is also shown that an unsymmetrical atom gives F values which behave in the same way. But, since both experimental and modified theoretical F values (that is, modified to take account of the Compton effect) give U curves the areas under which do exceed the true number of electrons for certain values of D , there is an indication that the Compton effect is involved in the experimental values. The truth of this indication would invalidate the use of the Fourier analysis method as now applied. The present paper also develops the Fourier integral as a quick method of calculating a U curve from a model atom on the classical theory. It is shown that a U curve calculated from Compton's formula

$$U = (8\pi r/D) \sum_1^{\infty} (nF_n/D) \sin(2\pi r n/D)$$

for a Fourier series is a very close approximation to the true U curve given by the Fourier integral

$$U(r) = 8\pi r \int_0^{\infty} x F(\lambda x/2) \sin 2\pi r x \, dx$$

where F is the same function of $(\lambda x/2)$ as F in the series formula is a function of $\sin \theta$. An analysis by the Fourier integral of a model supposed to have all the electrons concentrated at the center together with the Debye temperature factor shows that $U(r)$ represents the distribution of electrons about a lattice point and not about the center of the atom.

I. INTRODUCTION

IN A recent issue of the Physical Review,¹ the authors have discussed the criticisms of Havighurst² on the method of Williams³ and Jauncey⁴ for correcting for the Compton effect in calculations of the theoretical atomic structure factor (or F) values to be expected for a given atom model. In our previous paper, we have raised objection to the practice by some authors of using values of the grating space of a crystal which were inordinately large

¹ Jauncey and Claus, Phys. Rev. **31**, 717 (1928).

² R. J. Havighurst, Phys. Rev. **31**, 16 (1928).

³ E. J. Williams, Phil. Mag. **2**, 657 (1926).

⁴ G. E. M. Jauncey, Phys. Rev. **29**, 757 (1927).

and entirely fictitious as there is no possibility of obtaining an experimental F value for the first order with one of these large grating spaces. However, assuming that the use of these large values of the grating space is allowable, we were led to construct Table IV of our previous paper. In this table are shown values of the area under a radial electron distribution (or U) curve for chlorine from $r=0$ to $r=D/2$, for various values of D , where D is the grating space. Table IV shows for both the experimental F curves (reasonable extrapolations being used for the F values at both the small and large angles) and the theoretical F values calculated for our model and modified for the Compton effect that the number of electrons under a U curve is over 19 even though there are only 18 electrons in our theoretical model and though we also extrapolated to $F=18$ at $\sin \theta=0.00$ in the experimental F curve. Referring to Table IV, we see that there are more electrons under the experimental curve for $D=4.44\text{\AA}$ than for $D=7.10\text{\AA}$. It is difficult to conceive how there could be less electrons between $r=0$ and $r=D/2$ for $D=7.10\text{\AA}$ than for $D=4.44\text{\AA}$. Since writing our previous paper, it has occurred to us that this peculiar variation of the area under a U curve may give some insight into the need for a Compton effect correction. Before examining into whether this peculiar variation of the area proves the need for a Compton effect correction, we shall consider the case for the variation of the area with D for classical scattering of x-rays from a model atom possessing spherical symmetry. We shall show that F values calculated classically and without a Compton effect correction for a model atom give areas under U curves which approach the number of electrons assumed in the model as D approaches infinity but that for other values of D the area is always less (although it may only be slightly less) than the number of electrons assumed in the atom. Further, we shall examine the effect of different extrapolations for the chlorine experimental F values, all extrapolations, however, ending at $F=18$ for $\sin \theta=0.00$, and we shall show that it is impossible to choose a reasonable extrapolation for which U curves for various values of D always have an area equal to or less than 18 electrons. At present we believe that the experimental F values for chlorine, for instance, are not sufficiently accurate to prove definitely that a value of D can always be found to give more than 18 electrons, but the F values found by Havighurst certainly do show this effect.

A second point which we wish to discuss is the closeness of the agreement between a curve as found for a model atom, assuming the classical theory, when a series of discrete F values are inserted in Compton's⁵ formula

$$U = (8\pi r/D) \sum_1^{\infty} n(F_n/D) \sin(2\pi nr/D) \quad (1)$$

and a U curve found by means of a Fourier integral when D in Eq. (1) is made to approach infinity. The U curve found by means of the Fourier integral is the correct U curve while that obtained from the Fourier series in Eq. (1) is an approximation.

⁵ A. H. Compton, X-Rays and Electrons, p. 164.

A third point to which we wish to call attention is that Paragraph 43 of Compton's "X-Rays and Electrons" is headed "Radial Distribution in Atoms." The subject matter of this paragraph leads one to infer that a U curve obtained from Eq. (1) gives the radial distribution of the electrons relative to the center of an atom in the crystal. However, we believe that the radial distribution is relative to a lattice point of the crystal and not to the center of an atom of the crystal.

II. CLASSICAL SCATTERING FROM A MODEL ATOM

Case I. As the simplest kind of atom, let us take a model consisting of Z electrons concentrated at the center. The f values (Havighurst's notation) for such a model are constant and equal to Z , while the F values are given by $Z\exp(-b \sin^2\theta)$. In our previous paper, as in Havighurst's paper, $b=2.39$ for $\lambda=0.71\text{\AA}$ reflected from rocksalt. Now $\sin\theta=n\lambda/2D$ so that $F_n=Z\exp(-n^2b\lambda^2/4D^2)$. For brevity we shall represent the Debye factor by $\exp(-n^2a^2)$ where $a^2=b\lambda^2/4D^2$. The area under a U curve from $r=0$ to $r=D/2$ according to Compton⁵ is

$$A = -2 \sum_1^{\infty} (-1)^n F_n \quad (2)$$

Putting the values of F_n for our model in Eq. (2), we have

$$A = -2Z \sum_{n=1}^{\infty} (-1)^n \exp(-n^2a^2) \quad (3)$$

We shall now determine how A varies with a and, therefore, with D . The series

$$S_1 = \exp(-a^2) - \exp(-2^2a^2) + \exp(-3^2a^2) - \dots \quad (4)$$

may be written

$$S_1 = \sum_{n=1}^{\infty} [\exp\{-a^2(2n-1)^2\} - \exp\{-a^2(2n)^2\}] \quad (4a)$$

By Cauchy's theorem $S_1 < I_1$ for $a > 0$ where

$$I_1 = \int_0^{\infty} [\exp\{-a^2(2x-1)^2\} - \exp\{-a^2(2x^2)\}] dx \quad (5)$$

By putting $y=(2x-1)$ in the first term of the integrand and $z=2x$ in the second term, we have

$$I_1 = (1/2) \int_{-1}^{\infty} \exp(-a^2y^2) dy - (1/2) \int_0^{\infty} \exp(-a^2z^2) dz \quad (6)$$

and since we are dealing with definite integrals

$$I_1 = (1/2) \int_0^1 \exp(-a^2x^2) dx \quad (7)$$

By the mean value theorem

$$I_1 = (1/2) \exp(-a^2\xi^2) \quad (8)$$

where $0 < \xi < 1$. For $a > 0$, $\exp(-a^2\xi^2) < 1$ and $I_1 < \frac{1}{2}$ and hence also $S_1 < \frac{1}{2}$.* From this it follows that A in Eq. (3) can never be greater than Z no matter what value of D is taken.

Case II. We shall now consider a model made up of Z electrons all on a sphere of radius s , the temperature factor being supposed to be constant and equal to unity. Compton⁶ gives the atomic structure factor in this case as $F = Z \sin(4\pi s \sin \theta/\lambda)/(4\pi s \sin \theta/\lambda)$, or since $\sin \theta = n\lambda/2D$, $F_n = Z(\sin n\phi)/n\phi$ where $\phi = 2\pi s/D$. The area A then becomes

$$A = (2Z/\phi) \{ \sin \phi - (1/2) \sin 2\phi + (1/3) \sin 3\phi - (1/4) \sin 4\phi + \dots \} \quad (9)$$

The series

$$S_2 = (1/\phi) \{ \sin \phi - (1/2) \sin 2\phi + (1/3) \sin 3\phi - (1/4) \sin 4\phi + \dots \} \quad (10)$$

has the property that $S_2 = 1/2$ for $-\pi < \phi < \pi$. This can be seen at once by expressing the function $y = \phi/2$ as a Fourier series in sines of multiples of ϕ between $\phi = -\pi$ and $\phi = \pi$. For all reasonable values of s in our model $s < D/2$ and hence $\phi < \pi$, so that $A = Z$ in Eq. (9) for all values of D . In an actual numerical calculation the series S_2 converges slowly and so a large number of terms has to be taken, and to permit this, the wave-length of the x-rays has to be small so that the limiting value of n as given by the Bragg equation may be large. Hence, we again find that A can never be greater than Z no matter what value of D is taken so long as λ is small.

Case III. As a third model, we shall consider the case of Z electrons on a sphere of radius s , the center of the sphere thermally vibrating so that there is a Debye temperature factor $\exp(-b \sin^2\theta)$. We now have $F_n = Z \exp(-n^2a^2) \cdot (\sin n\phi)/n\phi$ and hence

$$A = -(2Z/\phi) \sum_{n=1}^{n=\infty} (-1)^n (1/n) \sin n\phi \exp(-n^2a^2) \quad (11)$$

and we are led to the consideration of the series

$$S_3 = \sum_{n=1}^{n=\infty} \left[\frac{\exp\{-a^2(2n-1)^2\} \sin(2n-1)\phi}{(2n-1)\phi} - \frac{\exp\{-a^2(2n)^2\} \sin 2n\phi}{2n\phi} \right] \quad (11a)$$

Again by Cauchy's theorem $S_3 < I_3$ for $a > 0$ where

$$\begin{aligned} I_3 &= \int_0^\infty \left[\frac{\exp\{-a^2(2x-1)^2\} \sin(2x-1)\phi}{(2x-1)\phi} - \frac{\exp\{-a^2(2x)^2\} \sin 2x\phi}{2x\phi} \right] dx \\ &= (1/2) \int_0^1 \frac{\exp(-a^2x^2) \sin x\phi dx}{x\phi} \end{aligned} \quad (12)$$

* We are indebted to Professor W. H. Roever of the Mathematics Department of Washington University for this proof.

⁶ A. H. Compton, Phys. Rev. **9**, 29 (1917).

By the mean value theorem

$$I_3 = (1/2) \exp(-a^2\xi^2) \cdot (\sin \xi\phi)/\xi\phi \quad (12a)$$

where $0 < \xi < 1$. Hence as in Case I, $I_3 < 1/2$ and also $S_3 < 1/2$. Again A cannot be greater than Z no matter what value of D is taken.

Case IV. In the ion of chlorine we have K , L , and M electrons. If each of these groups is moving in circular orbits which are oriented at random, the F values for each group when inserted in Eq. (2) will give values of A which are not greater than the number of electrons assumed in each respective group. If the F values for all the groups are added together, then A will not be greater than the total number of electrons in all the groups assumed in the model. Further, even if some of the electrons are revolving in ellipses or in more complicated orbits, then so long as the axes of these orbits are oriented in random directions, such orbits can be considered as supplying dN electrons between the spheres of radii r and $r+dr$ and the F values for these dN electrons when inserted in Eq. (2) will not give more than dN electrons. Hence, we see that any atom model which on the average possesses spherical symmetry must give values of A which can never be greater than the number of electrons assumed in the model, whatever value of D we may choose.

Referring again to Table IV of our previous paper, we see that the experimental F curve for chlorine leads to an area of 19.74 electrons at $D = 4.44\text{\AA}$, while at $D = 35.5\text{\AA}$, the area is 18.08 electrons. The question arises as to whether this difference of 1.66 electrons is due to errors in reading the F values off the experimental F curve. We drew our experimental F curve on graph paper in such a way that 20 millimeter divisions along the ordinates measured an F value of unity, while 20 millimeter divisions along the abscissae measured $\sin \theta = 0.1$. We could thus read our F values to 0.05 and we estimated to one-fifth of a millimeter so that we estimated our F values to 0.01. To test our accuracy we calculated the theoretical F values for the model of our previous paper, these F values, however, being uncorrected for the Compton effect. These F values were calculated for the same angles as the angles for the experimental F values shown in Table I of the previous paper and were calculated to the second decimal place. The curve was then drawn so as to pass through an F value of 18 at $\sin \theta = 0$. Such an F curve from $\sin \theta = 0.617$ where $F = 0.52$ was then extrapolated to zero at $\sin \theta = 1.00$. The largest value of A in Eq. (2) was found to be 18.20 for $D = 3.94\text{\AA}$. The correct value of A is slightly less than 18 so our error of reading from the F curve is such as to produce an error of 0.20 electrons in the area under a U curve. But the greatest value of A in Table IV of the previous paper is 19.74 for the experimental F curve and this is too great to be explained as due to errors in reading F values from the curve. We next tried different extrapolations both at small angles and at large angles for the experimental F curve. The F value for first order reflection for $D = 4.44\text{\AA}$, or $\sin \theta_1 = 0.08$, is an extrapolated value on the experimental F curve. A reasonable extrapolation, such as is shown by the dashed line in Fig. 1, gives an area greater

than 19 electrons for this value of D . To make $A=18$ electrons for $D=4.44\text{\AA}$, it is necessary to make $F_1=14.70$. As the F value for $\sin \theta=0.109$ is 13.40, this makes an awkward kink in the F curve at $\sin \theta=0.109$ as shown by the broken and full curves in Fig. 1. Nor does this improve matters at other values of D . Also, for the extrapolation at the large angles, an F value which will bring A nearer 18 for one value of D will make A still greater than 18 for another value of D . We have thus been unable to find an extrapolation either at the small or the large angles which will give values of A never greater than 18, the F value assumed at $\sin \theta=0.00$. If the F value at $\sin \theta=0.00$ is assumed to be 17, which is the value for a neutral chlorine

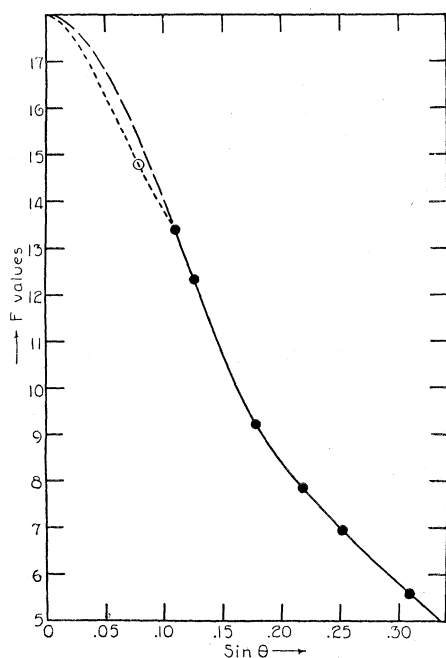


Fig. 1. Experimental F curve for chlorine, showing extrapolations. Broken and dashed curves, extrapolations; black circles, experimental F values; white circle, extrapolated point to give 18 electrons for $D=4.44\text{\AA}$.

atom, the situation is still worse; but, if F is assumed to be 20 at $\sin \theta=0.00$, then it might be possible to find an extrapolation which would give F values such that A was always less than 20 electrons. This is an unreasonable number of electrons according to our present ideas. We are convinced that Havighurst's experimental F curve shows the peculiarity that a value of D can be found such that the area under the U curve is greater than the number of electrons assumed or believed to be present in the ion or atom.

III. MODIFICATION OF CLASSICAL SCATTERING BY THE COMPTON EFFECT

Since in Section II of this paper we have shown that classical scattering from a model assumed to possess spherical symmetry on the average requires

that the area under a U curve be always less than the number of electrons assumed in the model, and since on the other hand the experimental F values do not show this result, we believe that this proves that either the atoms do not on the average possess spherical symmetry or that the Compton effect has to be taken into account.

We shall first consider the effect on the area under a U curve when an unsymmetrical model is taken. As an example of an unsymmetrical atom, we may take an atom which consists of a nucleus and Z electrons, the nucleus being in a crystal plane and the Z electrons remaining at a certain distance z from the plane. If one half of the atoms are orientated with their electrons above the plane and one half below the plane, the atomic structure factor⁷ is given by $F_n = Z \cos(4\pi z \sin \theta/\lambda) = Z \cos n\phi$ where $\phi = 2\pi z/D$.

Eq. (1) is only valid for an atom possessing spherical symmetry but if the F values given by $F_n = Z \cos n\phi$ are treated as coming from a symmetrical atom, then the area under the U curve so obtained is given by Eq. (2) and we are led to the series

$$S_4 = \cos \phi - \cos 2\phi + \cos 3\phi - \cos 4\phi + \dots \quad (13)$$

This series is obtained by differentiating $S_2\phi$ and since $S_2 = 1/2$, we have $S_4 = 1/2$ for $-\pi < \phi < \pi$. When the temperature factor is included, we have $F_n = Z \exp(-n^2 a^2) \cos n\phi$ and we are led to the series

$$S_5 = \sum_{n=1}^{n=\infty} [\exp \{-a^2(2n-1)^2\} \cos (2n-1)\phi - \exp \{-a^2(2n)^2\} \cos 2n\phi] \quad (14)$$

Proceeding as in Case III we have $S_5 < I_5$ for $a > 0$ where

$$I_5 = (1/2) \int_0^1 \exp(-a^2 x^2) \cos x\phi \, dx \quad (15)$$

By the mean value theorem

$$I_5 = (1/2) \exp(-a^2 \xi^2) \cos \xi\phi \quad (15a)$$

where $0 < \xi < 1$. Hence $I_5 < 1/2$ and also $S_5 < 1/2$ and $A \gg Z$. Any unsymmetrical atom can be considered as made up of dN electrons at a distance between z and $z+dz$ from a crystal plane, dN being a function $Zp(z)dz$. These dN electrons give values which when substituted in Eq. (2) make $A \gg dN$. Summing for all distances from the crystal plane, we find that even for an unsymmetrical atom the F values calculated on the basis of the classical theory possess the property that the right hand side of Eq. (2) is never greater than the number of electrons assumed in the atom.

We shall now consider the effect of the correction due to the Compton effect on the value of the right hand side of Eq. (2). It may be a coincidence but it is nevertheless a fact that when A is calculated by means of Eq. (2) for different values of D for Havighurst's experimental and the modified

⁷ A. H. Compton, X-Rays and Electrons, p. 121.

theoretical (corrected for the Compton effect) F curves, the value of A in both cases becomes greater than Z for certain values of D . To take a particular case, we shall consider the L electrons in the model of the chlorine ion as given in our previous paper. The atomic structure factor for these electrons is given by $F=Z y H'$ where

$$y=0.5-0.635 \sin \theta+0.0965/\sin \theta$$

and

$$H' = 1 - y \left\{ 1 - \sin (4\pi s \sin \theta/\lambda)/(4\pi s \sin \theta/\lambda) \right\} \quad (16)$$

and where $s=0.29\text{\AA}$ the radius of the L orbit. Replacing $\sin \theta$ by $n\lambda/2D$, this leads to the series

$$S_7 \equiv \sum_1^{\infty} y_n H_n' \quad (17)$$

The value of S_7 has been plotted against $\sin \theta_1$ where θ_1 is the angle at which first order reflection occurs for a grating space D and the curve is shown in Fig. 2. Unlike all the previous series, it is seen that S_7 may be greater than $1/2$ and so the F values for a model atom corrected for the Compton effect

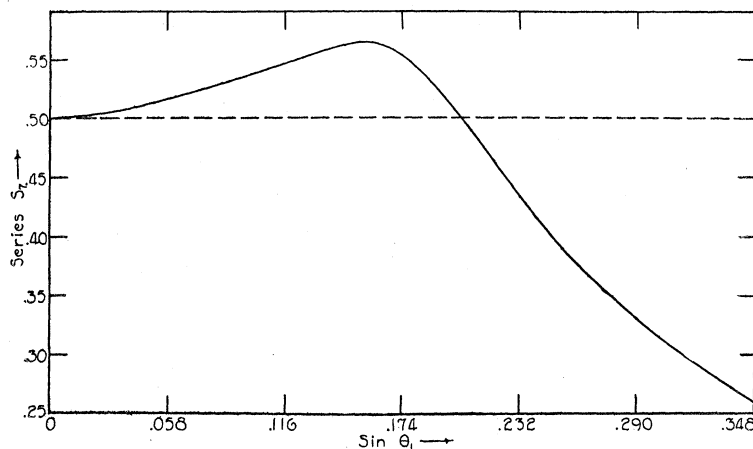


Fig. 2. Curve showing that series S_7 may exceed $1/2$.

lead to values of the right hand side of Eq. (2) which for particular values of D are greater than Z , the number of electrons assumed in the atom. If it can be definitely shown that the experimental F values possess the property that a value of D can be found such that A in Eq. (2) can be made greater than Z the number of electrons which we can reasonably expect to be present in the atom then it seems to us that something in addition to the classical theory is required. Since the Compton effect correction to a model gives F values such that A can be made greater than Z , we believe that this gives us an excellent method for testing whether the Compton effect does or does not enter into the regular reflection of x-rays by crystals. Havighurst's F

values seem to us therefore to show the need for a Compton effect correction. If the Compton effect has to be taken into account, the present method of Fourier analysis is invalid as we showed in our previous paper and Eq. (1) has no particular meaning.

IV. FOURIER INTEGRAL

If D in Eq. (1) approaches infinity, the series of Eq. (1) approaches the Fourier integral

$$U(r) = 8\pi r \int_0^\infty x F(\lambda x/2) \sin 2\pi r x \, dx \quad (18)$$

where F in the Fourier integral is the same function of $(\lambda x/2)$ as F in the series is a function of $\sin \theta$. The Fourier integral form has an advantage over the series in that when a U curve for a model atom is desired it may happen that for the model the value of the right side of Eq. (18) expressed as a function of r can be found by integration and the labor of finding the value of the series in Eq. (1) is saved.

For instance, we shall apply the Fourier integral to Case I, Section II of this paper. This gives

$F(\sin \theta) = Z \exp(-b \sin^2 \theta)$, so that $F(\lambda x/2) = Z \exp(-b\lambda^2 x^2/4) = Z \exp(-a^2 x^2)$ where $a^2 = b\lambda^2/4$ and Eq. (18) becomes⁸

$$U(r) = (4\pi^2 \pi^{1/2} Z/a^3) r^2 \exp(-\pi^2 r^2/a^2) \quad (19)$$

$U(r)$ is a maximum when $r = a/\pi$, that is, the most probable displacement of the atom due to the thermal vibrations is a/π and this may be represented by α so that

$$U(r) = (4Z/\alpha^3 \pi^{1/2}) r^2 \exp(-r^2/\alpha^2) \quad (20)$$

The form of the right hand side of Eq. (20) shows that the distribution of the thermal displacements of the atom is a Maxwell distribution. This is as it should be because the form of the Debye temperature factor can be obtained from the assumption of thermal displacements distributed according to the Maxwell law.⁹ Since $\alpha = a/\pi$ we have $\alpha = \lambda(b)^{1/2}/2\pi$. Since $b = 2.39$ for $\lambda = 0.71\text{\AA}$ reflected from rocksalt at room temperature, the numerical value of α is 0.175\AA in good agreement with a value of 0.20\AA estimated by James and Firth¹⁰ by another method. Since in this case the electrons of the model are concentrated at the center of the atom and since $U(r)$ is a maximum when $r = \alpha = 0.175\text{\AA}$, we see that $U(r)$ cannot mean the distribution of electrons relative to the center of the atom but must be relative to a lattice point of the crystal. $U(r)$ represents the distribution of the excursions of the atom from this lattice point.

⁸ Peirce's Integral Tables, No. 508.

⁹ See Compton, X-Rays and Electrons, p. 170.

¹⁰ James and Firth, Proc. Roy. Soc. **A117**, 62 (1928).

Applying the Fourier integral to the Case III, Section II of this paper, we obtain

$$U(r) = (Z/\alpha s \pi^{1/2}) r \{ \exp [-(r-s)^2/\alpha^2] - \exp [-(r+s)^2/\alpha^2] \} \quad (21)$$

We are now in a position to find the U curve for the model atom of our previous paper, when the F values are uncorrected for the Compton effect. This curve is shown in Fig. 3. The points shown are the values of U found from Eq. (1) when $D=3.06\text{\AA}$ or $\sin \theta_1=0.116$. It will be seen that the points fall almost exactly on the curve and this shows the accuracy of the Fourier series method because a curve plotted from Eq. (1) is almost indistinguishable from a curve plotted from the Fourier integral Eq. (18). It will be noticed that only two humps occur. The hump due to the K electrons is obliterated. This again brings out the point that a U curve gives the

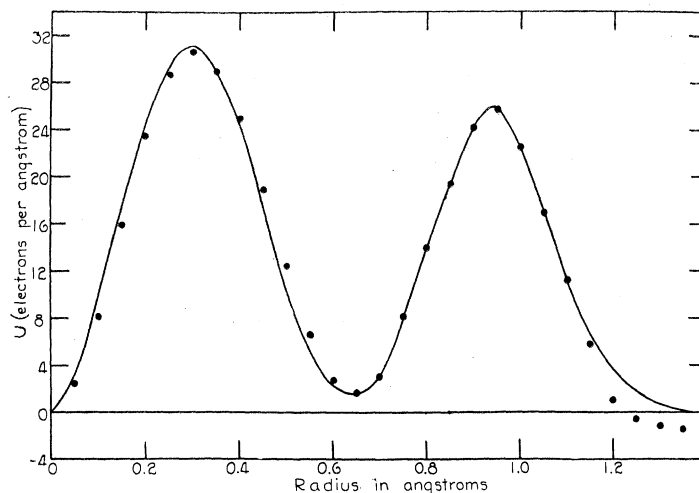


Fig. 3. Electron distribution as given by the Fourier integral and the Fourier series. Full curve, Fourier integral; black circles, Fourier series.

distribution relative to a lattice point. The most probable thermal displacement is 0.175\AA while the radius of the K orbit is 0.033 in our model. The K and L electrons are merged together giving a maximum at 0.300\AA which is somewhat greater than the radius of 0.29 assumed for the L orbit, while the M electrons give a maximum at 0.940\AA instead of at 0.925\AA the value of the radius assumed for the M orbit. It is thus seen that the thermal vibrations cause the maxima for the L and M electrons to come somewhat further out than assumed in the model, but, of course, this is to be expected since a U curve gives the distribution relative to a lattice point and not relative to the center of the atom.

WASHINGTON UNIVERSITY,
 ST. LOUIS, Mo.
 April 6, 1928.