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THE INTENSITY OF REFLECTED X-RAYS AND THE DISTRIBUTION OF ELECTRONS IN CRYSTALS

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Abstract

From the intensities of x-rays reflected in different orders, atomic structure-factor (or F) curves may be obtained from Darwin's formula. Duane and Compton, using different arguments, have shown that the method of Fourier analysis may be applied to a set of F values to obtain radial electron-distribution (or U) curves for the atoms of a crystal. However, Williams (Phil. Mag. **2,** 657) and Jauncey (Phys. Rev. **29,** 757) have suggested that the intensity of reflected x-rays is less than that on the classical theory because of the modified scattering of the Compton effect occurring at the expense of regular reflection. According to Williams and Jauncey, the number of electrons scattering coherently in the reflection process is a function of the angle of scattering and hence the method of Fourier analysis is invalid because this method depends on the assumption that the number of diffracting centers per atom of the crystal is independent of the angle of reflection. Havighurst (Phys. Rev. **31,** 16) takes issue with Williams and Jauncey on the following grounds: (1) A Fourier analysis of an experimental F curve gives a U curve which is reasonable (2) A Fourier analysis of the unmodified F values calculated for a model atom gives a U curve which agrees with the model and which roughly agrees with the experimental U curve (3) A Fourier analysis of the modified F values (i.e. F values modified by the Compton effect) gives a U curve which is unreasonable and does not at all agree with the experimental U curve.

The present paper is a reply to the criticisms of Havighurst. By trial a reasonable Bohr model of the chlorine ion has been found which gives modified F values at all angles in good agreement with the experimental values. Furthermore, the theoretical modified F curve has a kink at the same angle as that at which a kink occurs in the experimental F curves. This kink occurs at $\sin\theta = 0.45$ (for Mo $K\alpha$ x-rays) and is connected with the result on Jauncey's theory that at this angle the M electrons entirely cease to act as diffracting centers. Havighurst's F curves do not show this kink because he draws smooth curves. From the theoretical modified F values a U curve is plotted for a grating space of $D = 3.06$A. This U curve is similar to Havighurst's experimental U curve for the chlorine ion and has an area of 16.64 electrons in good agreement with 16.74 electrons for the experimental curve. Yet the theoretical U curve carries no particular information concerning the model from which it is derived. This is because the method of Fourier analysis is invalid.

The accuracy of experimental F values and U curves is discussed. The experimental F values for chlorine seem to be subject to an absolute error of 0.3, while the area under a U curve is easily subject to an error of 0.5 electron. Objection is raised to the practice by some authors of obtaining U curves for fictitious grating spaces. It is shown that the area under a U curve is a function of D and has no precise meaning even if crystal reflection is unaffected by modified scattering.

1. Introduction

SEVERAL papers on the distribution of electrons in the atoms of crystals as revealed by the intensities of x-rays reflected in different orders by the crystals have recently been published by R. J. Havighurst. For brevity we shall in the present paper refer to these papers as Papers I[1], II[2], III[3], IV.[4] In papers I and II, Havighurst describes how atomic structure-factor curves, or F curves, are obtained from the experimental values of the intensities in the various orders of reflection from powdered crystals. In Paper III, Havighurst applies the Fourier analysis method, as developed by Duane[5] from his quantum theory of diffraction and also subsequently by A. H. Compton[6] from the classical theory, to his experimental F curves and so obtains the distribution of the electrons in the atoms of the crystals.

Various authors have tried to find a model atom which would give F values in agreement with the experimental values and an excellent account of these efforts appears in a paper by Bragg, Darwin and James.[7] The models used, however, have until recently been based on the Bohr orbit theory of the atom. None of these models has been successful. This fact led Williams[8] and Jauncey[9] to inquire whether there might not be some effect which had been omitted from consideration when F values were calculated for a given Bohr model. It seemed to both Williams and Jauncey that such an effect might be the Compton effect. On Jauncey's theory of the unmodified line in the Compton effect,[10] coherent or unmodified scattering takes place from one set of electrons in an atom, while modified scattering takes place from a second set of electrons. Jauncey refers to the electrons of the first set as u electrons, and those of the second set as s electrons. *The effect of the application of the ideas of Williams and Jauncey to crystal reflection of x-rays is that the Fourier analysis method of finding the electron disribution in an atom is rendered invalid. This is because one of the assumptions underlying the validity is that the number of diffracting centers per atom remains constant as the angle of reflection varies; whereas the ideas of Williams and Jauncey lead to the result that the numbers of diffracting centers or u electrons, is a function of the angle of reflection.*

In Paper IV, Havighurst criticises the ideas of Williams and Jauncey and brings forward arguments to show that there is no need to apply a Compton effect correction to the electron distribution as obtained by a Fourier analysis of the experimental F curves since the electron distribu-

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[1] R. J. Havighurst, Phys. Rev. **28,** 869 (1926).

[2] R. J. Havighurst, Phys. Rev. **28,** 882 (1926).

[3] R. J. Havighurst, Phys. Rev. **29,** 1 (1927).

[4] R. J. Havighurst, Phys. Rev. **31,** 16 (1928).

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

[6] A. H. Compton, X-Rays and Electrons, Chap. 5.

[7] Bragg, Darwin and James, Phil. Mag. **1,** 897 (1926).

[8] E. J. Williams, Phil. Mag. **2,** 657 (1926).

[9] G. E. M. Jauncey, Phys. Rev. **29,** 757 (1927).

[10] G. E. M. Jauncey, Phys. Rev., **25,** 314 (1925); **25,** 723 (1925); Jauncey and Compton, Nature, October 15, 1927.

tion so obtained is a reasonable one. The present paper is a reply to the criticisms of Havighurst.

Before considering Havighurst's paper in detail, the authors wish to remark that they are aware of the papers by Waller[11] and Wentzel[12] on the application of wave-mechanics to the scattering of x-rays by bound electrons. According to Waller and Wentzel coherent scattering takes place according to the classical theory and the number of diffracting centers in an atom of a crystal remains constant as the angle of reflection varies. Hence, the Fourier analysis is valid. In its present stage, however we are not prepared to accept fully Schroedinger's wave-mechanics. For the present the authors prefer to keep the Bohr model and to see how far one can go with this model. We now proceed to the detailed consideration of Havighurst's paper IV.

2. SUMMARY OF HAVIGHURST'S CRITICISM

On careful consideration of Havighurst's Paper IV, it seems to us that his most weighty objection to the ideas of Williams[8] and Jauncey[9] is that the experimental F values lead, on the application of a Fourier analysis, to electron distribution curves which are reasonable, whereas a model atom gives F values which when modified by the Compton effect in the way proposed by Williams and Jauncey lead to electron distribution curves which are not reasonable. For brevity, the radial distribution is represented by U and a radial distribution curve is called a U curve. The relation between U and the F values is given by Compton as

$$U=(8\pi r/D)\sum_{1}^{\infty}(nF_n/D)\sin(2\pi nr/D) \tag{1}$$

where r is the distance from the center of the atom. If U is plotted against r, the area under the U curve is equal to the effective number of diffracting electrons associated with an atom. For instance, in Fig. 2, Paper IV, the curve a represents the radial distribution of the electrons in a model argon atom. The area under this curve is 18 electrons for a grating space of $D=2.814$A. Further there are two humps in the curve corresponding to the ten (K+L) electrons at $r=0.22$A and eight M electrons at $r=1.0$A. The K and L electron orbits overlap each other because of the thermal vibrations of the atoms. These vibrations are estimated by James and Firth[14] to have an amplitude of about 0.2A. Havighurst then calculates F values, modified to take account of the Compton effect, for his model, and from these modified F values he obtains a U curve represented as c in Fig. 2, Paper IV, for $D=2.814$A. The area under curve c is 14.1 electrons. This means that the radius of the atom is greater than $D/2$ or 1.407A. On taking a grating space of $D=5.628$A, he obtains curve b of Fig. 2, Paper IV, which

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[11] I. Waller, Nature **120**, 155 (1927); Phil. Mag. **4**, 1228 (1927).

[12] G. Wentzel, Zeits. f. Physik, **43**, 779 (1927).

[14] James and Firth, Proc. Roy. Soc. **117A**, 62, (1927).

has an area of 18.2 electrons. The area of the curve is correct (the true number of electrons being 18), but the grating space is such that an atom of radius about 2.814A is obtained. Furthermore, neither curve b nor curve c has a second hump at $r=1.0$A corresponding to the M electrons. Since his experimental F values for chlorine as obtained from a crystal of rocksalt lead to a U curve, Fig. 6, Paper III having an area of 17.85 electrons (nearly 18) for $D=3.25$A and humps at $r=0.26$, 0.75 and 1.23A corresponding to the $(K+L)$, M_{III} and M_I electrons and so corresponds fairly closely to the U curve obtained from the unmodified F values of his model argon (or Cl^-) atom, and since the U curve obtained from the experimental F values does not agree anywhere nearly so closely with the U curve obtained from the modified F values of the model, Havighurst then concludes that there is no room for the Compton effect correction to the F values.

3. Remarks in Rebuttal

A sufficient reply to Havighurst is to invent a model which gives modified F values which agree with the experimental F values and which contains a reasonable distribution of electrons and for which the K, L and M critical absorption wave-lengths used in calculating the modified F values according to Jauncey's formula are also reasonable.

Before proceeding to this model, we shall examine into what is meant by "experimental" F values for chlorine. These values are not calculated directly from Eq. (1), Paper I. The real experimental F values which are obtained for a crystal of rocksalt are for (Cl+Na) and (Cl−Na). However, as a (Cl+Na) reflection cannot occur at the same angle as a (Cl−Na) reflection and as an F value for chlorine at a given angle is determined by taking one half of the sum of the F values for (Cl+Na) and for (Cl−Na) at the same angle, it is impossible to obtain a real experimental F value for chlorine. On account of this, it is the practice of Havighurst and others to draw smooth curves through the real experimental F values for (Cl+Na) and (Cl−Na) respectively. Then from these two curves, the F curve for chlorine is calculated and so-called "experimental" values for chlorine are found from this curve. As a result these "experimental" F values for chlorine are obtained sometimes from two interpolated F values for (Cl+Na) and (Cl−Na), sometimes from one interpolated and one experimental value, sometimes from two extrapolated values. Havighurst on page 872 of Paper I states that in his experiments the relative intensities of the reflected beams from a crystal of rocksalt can be measured with an error of less than five percent except in the case of weak reflections. Now F-values as calculated from Eq. (1), Paper I vary as the square root of the ratio of the reflected to the primary intensity, so that the F values are subject to an error of 2.5 percent. At the first order reflection of Mo $K\alpha$ x-rays ($\lambda=0.71$A) from the (100) planes of rocksalt, when $\sin\theta=0.126$, the experimental F value for (Cl+Na) is 20.80 as shown in Table IIA, Paper I. Hence the F values for (Cl+Na) at $\sin\theta=0.126$ is subject to an absolute error of 0.5. For the first order reflection from the (111) planes when $\sin\theta=0.109$, the experimental F

value for (Cl − Na) is 4.55 and hence is subject to an absolute error of 0.1. Hence the so-called "experimental" F value for Cl at sin $\theta = 0.109$ is subject to an absolute error of $(0.5+0.1)/2 = 0.3$. We have verified this by drawing different smooth curves, through the experimental F values for (Cl+Na) and (Cl−Na) and we find we can obtain a variation of 0.2 to 0.3 from the mean value. The percentage error of the F values for chlorine increases as sin θ increases and we are of the opinion that the absolute error falls to about 0.2 as the large angle reflections are approached. Havighurst's statement that his "experimental" U curve for chlorine, obtained from his "experimental" F values for chlorine and shown in Fig. 6 Paper III, has an area of 17.85 (nearly 18) electrons depends amongst other things on his value of F for sin $\theta = 0.109$. In Table III, Paper III, the value of F is 13.60. This may easily be 13.40 in which case the area under the curve is not 17.85 but 17.45 electrons, since the area under a U curve from $r = 0$ to $r = D/2$ is obtained from Compton's formula[6]

$$A = -2\sum_{1}^{\infty}(-1)^n F_n \qquad (2)$$

Accurate F values at all parts of the F curve are required in order to obtain the true value of A. Using the present experimental F values the writers do not believe that it is possible to obtain U curves the area under which is subject to an error of less than 0.5 electron. As a result the question as to whether the chlorine in crystal of rocksalt exists as a neutral atom or a negative ion cannot at present be decided by means of a Fourier analysis of "experimental" F values. The writers are supported in this belief by Bearden,[15] who states that absolute intensity measurements must be made precise to less than one percent in order to obtain reliable electron distribution curves for the atoms of a crystal. This means that the F values must be known to within 0.5 percent.

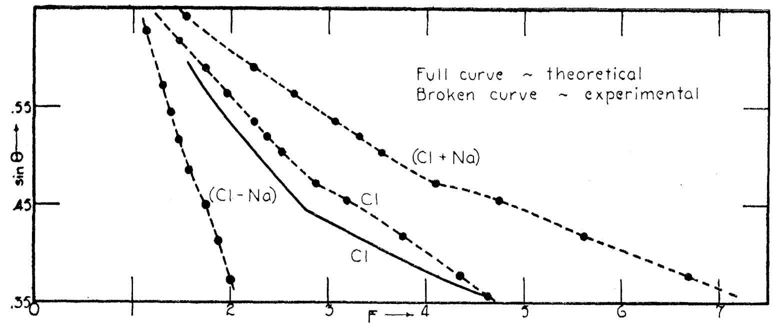

Fig. 1. Atomic Structure Factor for the Atoms in Rocksalt.

The drawing of a smooth "experimental" F curve for chlorine masks any real kinks in the curve which might occur if the true F curve could be found. This is a very important point for on Jauncey's theory small kinks

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[15] J. A. Bearden, Phys. Rev. 29, 20 (1927).

should occur in an F curve. In the experimental F curve for (Cl+Na) the experimental F values do not fall on a smooth curve. This is very evident in the F curve for (Cl+Na) at sin $\theta = 0.47$ as shown in Fig. 1. Since the F values of (Cl−Na) apparently fall on a smooth curve, the writers have obtained a set of "experimental" F values for chlorine by adding the interpolated F values for (Cl−Na) to the experimental F values for (Cl+Na) and halving the result. The experimental F values of (Cl+Na) are taken from Table IIA, Paper I. This set of values is shown in the second column of Table I.

TABLE I. *F values for chlorine*

sin θ	"Experiment"	Theory	sin θ	"Experiment"	Theory
(.109)	(13.40)	13.22	.418	3.74	3.25
.126	12.32	12.37	.455	3.23	2.66
.178	9.22	9.82	.472	2.86	2.50
.218	7.84	8.16	.504	2.52	2.21
.252	6.94	7.10	.520	2.38	2.12
.309	5.58	5.65	.535	2.24	2.00
.357	4.63	4.61	.564	1.97	1.75
.378	4.35	4.10	.590	1.74	1.58
.399	3.98	3.66	.617	1.47	1.37

The F value for sin $\theta = 0.109$ was obtained from the experimental F value for (Cl−Na) and a slightly extrapolated F value for (Cl+Na). This extrapolation is necessary since the smallest experimental value of sin θ for (Cl+Na) is 0.126. We have used a grating space of $D = 3.06$A which is intermediate between $D = 2.814$A for the (100) planes and 3.25A for the (111) planes of rocksalt. This was done in order to obtain an F value for the first order as near a real experimental value as possible. For $D = 3.06$A, the first order reflection of Mo Kα x-rays occurs at sin $\theta = 0.116$. A curve is drawn through the "experimental" F values of Table I so as to show any kinks which appear. F values are read off from this curve at multiple values of sin $\theta = 0.116$ and a U curve obtained. The U curve so obtained is shown as the broken curve in Fig. 2, and is similar to Havighurst's curve in Fig. 6, Paper III. Like Havighurst's curve, it has three definite humps at $r =$ 0.27, 0.76, and 1.21A. However, our curve differs from Havighurst's curve in that while his has an area of 17.85 electrons, ours has an area of 16.74 electrons, the two values differing by 1.11 electrons. Some of this difference is due to the fact that Havighurst used a grating space of 3.25A while we have used a grating space of 3.06A. Using a grating space of 3.25A we have obtained an area of 17.2 electrons. The remainder of the difference is due to the different ways in which an F curve may be drawn through the experimental values, and to the different ways of extrapolating at small angles. We have used Havighurst's own extrapolated values at large angles to obtain our F values in this region, but we disagree with Havighurst that the particular kind of extrapolation of the F values to zero at large angles does not make an appreciable difference in the area under the U curve, although the general shape of the U curve seems to be unaffected. We shall return to this point later. Obviously from Eq. (2) if the area is measured out to $D/2$ the area depends on the high order F values. We also disagree with Havighurst that his experimental U curve resembles so very closely the U curve for the model argon atom. The U curve for the model argon atom has only two humps while the experimental U curve for chlorine has three humps. We now proceed to our model.

In our model we suppose the chlorine to exist as an ion with the various electrons distributed as in Table II. The critical absorption wave-lengths for the various electrons are also shown.

TABLE II. *Model Cl^- ion*

Kind of electrons	Number	Radius of Orbit	Critical absorption Wave-length λ_s	$(2h/mc\lambda_s)^{1/2}=(2\alpha_s)^{1/2}$
K	2	0.033A	4.38A	0.106
L	8	0.29	69.0	0.0265
M	8	0.925	310.0	0.0125

For simplicity in calculation we have assumed circular orbits, and have omitted the fine structure of the L and M levels. On Jauncey's theory[9] the proportion of, say, the K electrons which are in the u state is

$$y_K=0.5-\frac{\alpha\sin\theta}{2(2\alpha_K)^{1/2}}+\frac{(2\alpha_K)^{1/2}}{8\alpha\sin\theta} \tag{3}$$

where $\alpha=h/mc\lambda$, $\alpha_K=h/mc\lambda_K$, λ is the wave-length of the primary x-rays and λ_K is the K critical absorption wave-length. The numerical values of y for the K, L and M electrons are obtained from the following equations:

$$\left.\begin{aligned} y_K&=0.5-0.160\sin\theta+0.390\ /\sin\theta\\ y_L&=0.5-0.635\sin\theta+0.0965/\sin\theta\\ y_M&=0.5-1.350\sin\theta+0.0454/\sin\theta \end{aligned}\right\} \tag{4}$$

We can now calculate what Havighurst calls the f values from Eq (10) of Jauncey's paper.[9] The F values (Havighurst's notation) are calculated from these by multiplying the f values by the Debye temperature factor $\exp.(-2.39\sin^2\theta)$ which is the factor used by Havighurst. The theoretical F values so found are shown in the third column of Table I. It will be noticed that the greatest differences between the experimental and theoretical F values are 0.57 at $\sin\theta=0.455$ and 0.60 at $\sin\theta=0.178$. We have put the error in the experimental F values at 0.3. With the exception of the two regions mentioned the differences are of the order of the experimental error. However, we have used a simple model in which there is no fine structure of the L and M levels and in which the orbits assumed are circular and we are confident that if we split up the L and M levels into sublevels and consider elliptical as well as circular orbits we can find a model which will everywhere give theoretical F values differing from the experimental values by no more than the experimental error. The theoretical and experimental F curves for chlorine are shown as full and broken curves respectively in Fig. 1 for the range $\sin\theta = 0.35$ to $\sin\theta = 0.65$.

It will be noticed that both the experimental and theoretical curves show a kink at about $\sin\theta = 0.45$. At present the writers do not believe that the experimental accuracy is such as to prove the existence of a kink in the experimental curve, yet it is interesting that a kink occurs in both curves at the same place. Havighurst's curves do not show the kink because he draws smooth curves. The kink in the theoretical curve comes at a value of $\sin\theta$ which makes y_M of Eqs. (4) zero. This means that at this angle the M electrons entirely cease to act as diffracting centers, all of them being in the s state. This critical value of $\sin\theta$ is determined by the value of λ_M assumed in our model which is 310A. From curves by Compton and Mohler[16] the critical absorption wave-length for the M_{I} level is 270A while that for the M_{III} level is 1000A. Our value of λ_M is therefore of the proper order of magnitude. It is very likely that the M levels of chlorine vary with the chemical compound. In Paper I, Havighurst has found that different experimental F curves are found for sodium according to whether NaF or or NaCl is used. According to Havighurst, this difference indicates a tightening of the electron atmosphere of sodium in NaF. On our ideas this tightening means amongst other things a decrease in the critical absorption wave-lengths. Hence some variation in the critical absorption wave-lengths in our model from those given by Compton and Mohler is to be permitted. We therefore feel that the values we have used in Table II are reasonable. Also, the radii of the circular orbits are reasonable. We therefore believe that by the method of trial we have found a model of the chlorine ion which is a reasonable one and which gives F values in reasonable agreement with the experimental F values.

TABLE III. *Experimental and theoretical F values used in Fourier analysis*

n	$\sin\theta$	F_n Experiment	F_n Theory	n	$\sin\theta$	F_n Experiment	F_n Theory
1	0.116	(13.00)	12.81	5	0.580	1.83	1.65
2	0.232	7.46	7.68	6	0.696	(.78)	.98
3	0.348	4.78	4.76	7	0.812	(.03)	.48
4	0.464	3.03	2.57	8	0.928	(.00)	(.15)

The theoretical and experimental F values for D = 3.06A (or first order reflection at $\sin\theta = 0.116$) are shown in Table III, the extrapolated values being shown in parentheses.*

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[16] Compton and Mohler, Nat. Res. Council Bull., **48**, 109 (1924).

* It will be seen that the theoretical F value for $\sin\theta = 0.928$ is extrapolated. We have used this extrapolated value because the calculated F values do not approach zero quickly enough at large angles. Our extrapolation of the theoretical F values is of the same nature as the extrapolation used for the experimental F values at large angles.

Theoretical and experimental U curves plotted from these values are shown as the full curve and dotted curves respectively in Fig. 2. It is seen that our theoretical U curve corresponds very well with the experimental U curve. Our curve has three humps at $r=0.27$, 0.56 and 1.28A, agreeing roughly with the three humps on the experimental U curve obtained by us from Havighurst's experimental F values for (Cl+Na) and (Cl−Na), and also with Havighurst's own U curve of Fig. 6, Paper III. The area under our theoretical U curve in Fig. 2 out to $r=D/2=1.53$A is 16.64 electrons as found by Eq. (2). To show that the area under a U curve is susceptible to the F values at large angles, we have only to remember that in Table III the theoretical F values for n = 6, 7, and 8 correspond to what are the extrapolated values in the experimental set of F values. We could stop our calculated theoretical F values at F_5 and then extrapolate for the higher F values. A reasonable set of such values would be $F_6=0.94$, $F_7=0.23$ and $F_8=0.00$, which would give a U curve area of 16.92 electrons.

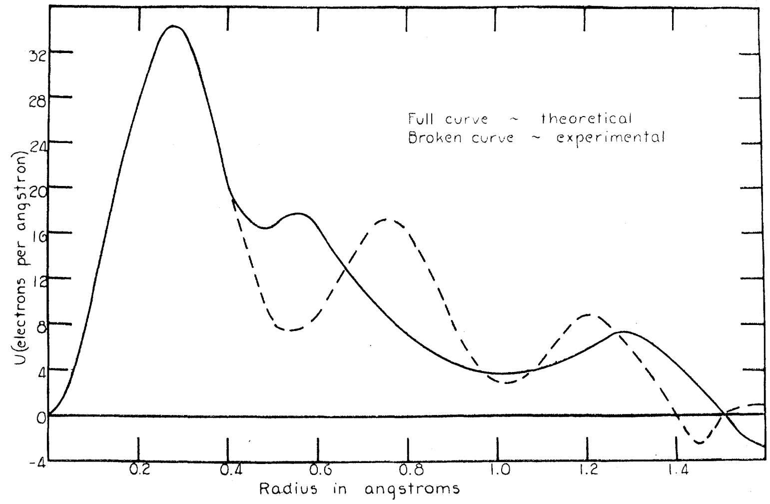

Fig. 2. Radial Distribution Curves or the Chlorine Ion.

The point to which we call attention is that we have devised a model chlorine ion which gives theoretical F values, these values being modified by the Compton effect according to Jauncey's theory,[9] in fair agreement with the experimental F values for chlorine. Also when a Fourier analysis is applied to our theoretical F values, a U curve is obtained which agrees in its general shape with the experimental U curve and gives the number of electrons within experimental error of the number given by the experimental U curve. Yet our U curve carries with it no particular information concerning the model from which we have derived the modified F values which have been used in obtaining our U curve. Had we used our model to calculate unmodified F values (that is, F values in which no account has been taken of the Compton effect) we would have obtained a U curve similar to curve *a* for the argon model in Fig. 2, Paper IV, that is, a *U* curve with a hump due to the $(K+L)$ electrons at about 0.29A and a second hump due to the *M* electrons at about 1.0A. In this latter case the *U* curve does tell us something about the model.

The reason that our theoretical *U* curve tells us very little about the model from which it is calculated is that the Fourier analysis is not valid in this case since this validity is based on the assumption that the number of diffracting centers per atom remains constant as the angle of scattering varies. On Jauncey's theory, this number does depend on the scattering angle and hence the Fourier analysis is invalid and the *U* curve has no particular meaning.

It seems to us that the need for the Compton effect correction can neither be proved nor disproved from a consideration of the experimental *F* curves and the *U* curves resulting therefrom. On the other hand, a reasonable Bohr model of an atom cannot be found which will give unmodified *F* values in agreement with the experimental *F* values while it is possible to find a reasonable Bohr model which will give modified *F* values which differ from the experimental values by no more than the experimental error. We believe that the experimental *F* curves show that either the *F* values for a Bohr model atom must be modified to take account of the Compton effect or that the Bohr type of model must be abandoned. If we accept the idea of Schroedinger that the square of his function ψ is a measure of the electric density in the atom then the *U* curves which are obtained from the *F* values give us a measure of the continuous distribution of electric density in the atom, provided that the coherent scattering from this diffuse distribution of electricity is not affected by the Compton effect. Until it can be shown experimentally that the coherent scattering from an atom is not affected by the modified scattering, we believe that there is something to be said from the point of view of this paper.

4. Concluding Remarks

We regard it as extremely unfortunate that our views on the role of the Compton effect in crystal reflection require that the Fourier analysis method of unravelling atomic structure is invalid. There is no way as far as we can determine to make allowance for the Compton effect in a Fourier analysis. The only method is to assume a model and then to test it. This method of trial is extremely tedious. Nevertheless we feel that at present any electron distribution curve obtained by applying a Fourier analysis to a set of *F* values has very little basis of reality. We note in the literature on the subject that many writers in applying the Fourier analysis method use fictitious grating spaces. Usually these fictitious grating spaces are of the order of two or three times the real grating space between planes in the crystal. We object to this use of large fictitious grating spaces because they cause the first *F* value to come at an angle where there is no possibility of measuring the intensity of reflected x-rays. Such an *F* value for chlorine, for instance, is obtained from extrapolated *F* values for (Cl+Na) and (Cl−

Na). We feel that, even if the Compton effect does not enter into the reflection process in the way supposed by Jauncey, the U curves obtained by the use of fictitious F values are themselves largely fictitious. We have found the area under a U curve to be very susceptible to the particular grating space used. It is assumed by some writers that when a grating space of a certain size has been found to give, say, 18 electrons in the case of Cl^-, then all greater values of D give the same number of electrons for the area under the U curve out to $r = D/2$. This, however, is not necessarily the case. Using the experimental F values of Table I and adding an F value of 18 at zero value of sin θ, we have plotted an experimental F curve. From this curve we have read off various sets of F values for various values of D. From each of these sets of F values a U curve may be plotted and the area under the U curve from $r=0$ to $r=D/2$ may be found from Eq. (2). In Table IV the values of the area for the several values of D are shown under "experiment." The values under sin θ_1 are for first order reflection of Mo Kα x-rays by the corresponding grating spaces. Similarly, sets of theoretical F values have been found and the areas under the corresponding U curves obtained. The values of the area for the several values of D in this case are shown under "theory" in Table IV.

TABLE IV. *Area under U curves*

D	sin θ_1	Area (electrons)		D	sin θ_1	Area (electrons)	
		"Experiment"	"Theory"			"Experiment"	"Theory"
∞	.00	18.00	18.00	3.94A	.09	19.00	16.68
35.50A	.01	18.08	18.02	3.55	.10	18.34	17.16
7.10	.05	18.18	19.28	3.26	.109	17.28	17.18
5.92	.06	18.36	18.88	3.23	.11	17.20	17.14
5.07	.07	18.64	18.50	2.73	.13	16.04	15.74
4.44	.08	19.74	17.96	2.36	.15	13.90	14.10

In addition to the area at $D = \infty$, there is one other value of D for which the area is 18 electrons for both the "experimental" and the "theoretical" areas. It is interesting to note that the maximum area in either case is above 19 electrons. For the "experimental" areas the maximum occurs at $D = 4.44$A. If 19.74 electrons are included between $r = 0$ and $r = D/2 = 2.22$A, one would not expect that a less number of electrons would be included between $r = 0$ and $r > 2.22$A. This seems to us to prove that the Fourier analysis method of unravelling the structure of the atom is not suited to settling fine distinctions and differences, or, in other words, its resolving power is low.*

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* The calculations in this paper were made by means of a Monroe calculating machine. Such a machine adds greatly to the facility with which a U curve may be plotted.