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ELECTRON DISTRIBUTION IN THE ATOMS OF CRYSTALS.  
SODIUM CHLORIDE AND LITHIUM, SODIUM AND  
CALCIUM FLUORIDES

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ABSTRACT

**Determination of electron density by means of a Fourier analysis.** The application of the correspondence principle by Epstein and Ehrenfest to Duane's quantum theory of diffraction leads to the conclusion that the electron density,  $\rho(xyz)$ , at any point in the unit cell of a crystal may be represented by a Fourier's series the general term of which is

$$A_{n_1 n_2 n_3} \sin(2\pi n_1 x/a_1 - \delta_{n_1}) \sin(2\pi n_2 y/a_2 - \delta_{n_2}) \sin(2\pi n_3 z/a_3 - \delta_{n_3})$$

$A_{n_1 n_2 n_3}$  is proportional to the structure factor for x-ray reflection from the  $(n_1 n_2 n_3)$  plane, where  $n_1$ ,  $n_2$ , and  $n_3$  are the Miller indices multiplied by the order of reflection. Considerations of symmetry fix the values of the phase constants, and the assumption that the coefficients are all positive at the center of the heaviest atom in the unit cell fixes the algebraic signs. For crystals of the rock-salt or fluorite types the series becomes a simple cosine series in which the values of the structure factors previously determined by the author may be used as coefficients. If the atoms are assumed to possess spherical symmetry, the number of electrons in a spherical shell of radius  $r$  and thickness  $dr$  is  $U dr = 4\pi r^2 \rho dr$  and the total number of electrons in the atom is equal to the integral of  $U dr$ . A. H. Compton has obtained the same expression for the electron density in a crystal, as well as a series expression for  $U dr$ , on the basis of classical theory.

**Results of the Fourier analysis.** Application of this method of analysis to the calculated  $F$  curve from a model sodium ion shows that the series converge rapidly when the  $F$  values are uncorrected for the effect of thermal agitation, and that reliable results may be obtained after extrapolation of the experimental  $F$  curves for light atoms to zero values of  $F$ . Curves are given which show the variation of electron density along the cube edges of the unit cells of NaCl, LiF, and NaF, and along the cube diagonal of CaF<sub>2</sub>.  $U$  curves for the different atoms, showing the variation of  $U$  with  $r$ , give the following information: (1) the points of the crystal lattice are occupied by ions (no *a priori* assumptions have been made concerning the amount of electricity associated with a lattice point); (2) the sum of the radii of any two ions in a crystal is approximately equal to the distance of closest approach as determined by ordinary crystal analysis; (3) the electron distributions in the Na<sup>+</sup> of NaF and NaCl are markedly different, while the distributions in F<sup>-</sup> from all three fluorides are practically identical; (4) there is evidence of the existence of electrons in shells which are in rough agreement with Stoner's scheme of electron distribution.

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## INTRODUCTION

THE most direct means in our possession of determining the electron distribution in atoms lies in the use of experimental measurements on the scattering powers of these atoms for x-rays. From the  $F$  curves for crystals, which represent the variation of the scattering power with angle of scattering, individual  $F$  curves for the component atoms may be obtained, and the problem consists of finding the electron arrangements which will account for the experimental values of  $F$ . The experimental data used in this paper have been obtained by a powdered crystal method<sup>1</sup> which is free from error due to primary and secondary extinction.

Before considering the method of Fourier analysis which the author has used, we may mention the method of trial, used by A. H. Compton<sup>2</sup> and by Bragg, James and Bosanquet,<sup>3</sup> in which the  $F$  values for various assumed distributions are calculated and the distribution giving results which are in best agreement with the experimental data is taken as correct. This method as applied by Bragg, James and Bosanquet to the atoms of rock salt gives distributions which are in rough agreement with those obtained by the Fourier analysis. However, a direct method has obvious advantages over a method of trial.

## DETERMINATION OF ELECTRON DISTRIBUTION BY FOURIER ANALYSIS

The first suggestion of the use of a Fourier's series to express the distribution of diffracting power in a crystal seems to have been made by W. H. Bragg,<sup>4</sup> but the method was not put into practice until quite recently,<sup>5,6</sup> after the application of the correspondence principle by Epstein and Ehrenfest<sup>7</sup> to Duane's<sup>8</sup> quantum theory of diffraction. Epstein and Ehrenfest showed that any diffraction grating may be considered to be made up of a large number of superposed "sinusoidal gratings," and that the intensity of the diffracted beam in any order is proportional to the square of the coefficient of the corresponding term in the Fourier's series representing the density of diffracting power.

<sup>1</sup> Havighurst, *Phys. Rev.* **28**, 869 (1926).

<sup>2</sup> A. H. Compton, *Phys. Rev.* **9**, 49 (1917).

<sup>3</sup> W. L. Bragg, James and Bosanquet, *Phil. Mag.* **44**, 433 (1922).

<sup>4</sup> W. H. Bragg, *Phil. Trans. Roy. Soc.* **A215**, 253 (1915).

<sup>5</sup> Duane, *Proc. Nat. Acad. Sci.* **11**, 489 (1925).

<sup>6</sup> Havighurst, *Proc. Nat. Acad. Sci.* **11**, 502, 507 (1925). The electron density curves given in these preliminary papers give only relative values of the density and in addition are subject to errors arising from two sources—first, the constant term of the series was neglected, and second, the experimental  $F$  curves were not extrapolated to zero.

<sup>7</sup> Epstein and Ehrenfest, *Proc. Nat. Acad. Sci.* **10**, 133 (1924).

<sup>8</sup> Duane, *Proc. Nat. Acad. Sci.* **9**, 159 (1923).

By the reverse process, we may deduce the density of diffracting power in a grating by substituting the square roots of the measured intensities of diffraction as coefficients in the Fourier's series. In a book recently published,<sup>9</sup> A. H. Compton has given a thorough discussion of the application of Fourier analysis to the problem of electron distribution on the basis of the classical theory. He derives the equations given below and applies the analysis to the data of Bragg, James and Bosanquet on rock salt with results which will be compared with those of the author.

*Linear electron density.* Consider a one-dimensional grating which contains  $Z$  electrons within a grating space  $a$ . The general term in the Fourier's series representing the linear density is<sup>7</sup>  $A_n \sin(2\pi nx/a - \delta_n)$ , where  $n$  is the order of diffraction and  $\delta_n$  is a phase constant. The linear density of diffracting power,  $P_x$ , at a point  $x$  in the grating is represented by the series

$$P_x = \sum_n A_n \sin(2\pi nx/a - \delta_n) \quad (1)$$

where  $A_n = F_n/a$  and  $F_n$  is the structure factor for the diffraction of the  $n$ th order.  $F_0 = Z$ , and the summation is taken over all values of  $n$ , positive and negative.

*Volume electron density.* The three-dimensional analogue of the general term in the Fourier's series given above is

$$A_{n_1 n_2 n_3} \sin(2\pi n_1 x/a_1 - \delta_{n_1}) \sin(2\pi n_2 y/a_2 - \delta_{n_2}) \sin(2\pi n_3 z/a_3 - \delta_{n_3}). \quad (2)$$

for the series representing the volume density,  $\rho(xyz)$ , of diffracting power at a point in the unit cell of a crystal.  $a_1$ ,  $a_2$ , and  $a_3$  are the lengths of sides of the unit cell. Unless we fix the values of the  $\delta$ 's, we find that the series based on (2) does not give a unique distribution of diffracting power; that is, an indefinitely large number of distributions will produce beams of rays of precisely the same intensities in the same directions. In order to obtain a unique distribution of diffracting power it is necessary to make two assumptions.

The first assumption is that the distribution of diffracting power conforms to the symmetry of the crystal. This symmetry fixes the values of the  $\delta$ 's. For example, if the crystal has three mutually perpendicular planes of symmetry and if we take the intersections of these planes as the axes of coordinates, the terms in the series can contain cosines only, for they must have the same values when we reverse the algebraic sign of

<sup>9</sup> A. H. Compton, "X-Rays and Electrons," Chap 5. Van Nostrand and Co., 1926. For the privilege of using the manuscript of this work, the author desires to express his thanks to Professor Compton.

either  $x$ ,  $y$  or  $z$ . In this case, therefore, the  $\delta$ 's must be odd multiples of  $\pi/2$ . The symmetry conditions often determine, also, the values of certain coefficients  $A$  as being equal to one another. If the crystal possesses such complete symmetry as that of NaCl, all the  $A$ 's having the same values of  $n_1$ ,  $n_2$ , and  $n_3$ , but interchanged in any manner, must be equal to each other.

The second assumption has to do with the algebraic signs of the coefficients  $A$ , which, being square roots of measured quantities, are undetermined as to sign by the diffraction data. In general, the intersections of planes or axes of symmetry in a crystal must be points of maximum or minimum density, and if there is an atom at such a point, it is natural to suppose that  $\rho(xyz)$  is a maximum there. There may be other points in the unit cell at which  $\rho(xyz)$  has maximum values; it is probable that the greatest maximum value of the density corresponds to the center of the heaviest atom, and that the terms in the Fourier's series are all positive at that point. We assume, therefore, that if we take the origin of coordinates at the center of the heaviest atom, all the coefficients in the Fourier's series have positive values. For the crystals of high symmetry and simple structure which are considered in this paper, the effect of these assumptions upon the form of the Fourier's series is easily worked out. The author has published elsewhere<sup>10</sup> a treatment of a more complicated crystal structure by this method.

A further assumption must be made before we can properly speak of electron distributions obtained from diffraction data. The density of diffracting power must be assumed to be proportional to the electron density. This means that all the electrons of an atom are equivalent in scattering power for x-rays, a statement to which objection may possibly be raised; for it is not certain that the inner and outer electrons of a heavy atom are equally effective as scatterers.

We may now write down the Fourier's series expressing the electron density  $\rho(xyz)$  at a point  $(xyz)$  in the unit cell of a cubic crystal of the rock-salt or fluorite type, with the origin of coordinates at the center of the heaviest atom:

$$\rho(xyz) = \sum_{n_1} \sum_{n_2} \sum_{n_3} A_{n_1 n_2 n_3} \cos 2\pi n_1 x/a \cos 2\pi n_2 y/a \cos 2\pi n_3 z/a \quad (3)$$

where  $n_1 n_2 n_3$  are the Miller indices of the different crystal planes multiplied by the order of reflection;  $A_{n_1 n_2 n_3} = 4F_{n_1 n_2 n_3}/a^3$  and  $F_{000} = Z$  = the number of electrons per molecule, there being four molecules in the unit cell. It should be noted that the experimental values of  $F$  used in this

<sup>10</sup> Havighurst, J. Am. Chem. Soc. **48**, 2113 (1926).

paper contain the Debye temperature factor, so that in Eq. (3), which gives the time average of the electron density in the unit cell, the amplitude of thermal agitation is superposed upon the actual distances of the electrons from their atomic centers.

*Radial distribution of electrons.* From the determinations of electron density we may get information concerning the radial distribution of electrons in the separate atoms. The number of electrons in a spherical shell of radius  $r$ , thickness  $dr$ , and density  $\rho$  is

$$U dr = 4\pi r^2 \rho dr \quad (4)$$

The area under the curve of  $U$  plotted against  $r$  gives directly the number of electrons in the atom. It seems proper to assume spherical symmetry of the electron density, as is done by this procedure, but the question will be raised again later.

Compton<sup>9</sup> has derived an expression for the radial distribution which does not require the evaluation of a three-dimensional series. The number of electrons in a spherical shell is represented by a series:

$$U dr = 4\pi r / D \sum_1^{\infty} (2nF_n / D) \sin(2\pi nr / D) dr \quad (5)$$

where  $D$  is the spacing of the set of atomic planes which are perpendicular to  $r$  and  $F_n$  is the *atomic* structure factor for the order  $n$  (or for reflection by planes of spacing  $D/n$ ). Upon the assumption of spherical symmetry, any convenient spacing  $D$  in the region covered by the atomic  $F$  curve may be used as the first order spacing; but the series becomes negative when  $r/D$  is greater than 0.5, consequently the radius of the atom must be less than  $D/2$  if the values of  $U$  in the neighborhood of  $D/2$  are to be considered as dependable. The author's  $U$  curves determined for the same atom by the two different methods of Eqs. (4) and (5) are in satisfactory agreement.

It is important that we now have a method (the integration of  $U dr$ ) of determining the number of electrons grouped about a point in a crystal lattice without having made any assumption concerning the existence of ions. Indeed, we have not even assumed the existence of atoms or molecules in the exact sense that is ordinarily understood by the use of these terms—we have simply supposed that there are certain maxima of diffracting power in the unit cell of a crystal. Now that we are in possession of a method of counting the number of electrons associated with these maxima, we find ourselves able to decide what these lumps of diffracting power are—ions, neutral atoms, or molecules.

## APPLICATION OF FOURIER ANALYSIS TO A MODEL ATOM

Before an adequate idea of the limits of accuracy of the Fourier analysis can be obtained, it is necessary to know something about the convergence of the series used. The coefficients of the series come from experimental  $F$  curves which must be extrapolated to zero values of  $F$ . The questions to be answered are: (1) does the actual  $F$  curve of an atom fall to zero and remain there or does it maintain appreciable positive and negative values out to very small interplanar spacings? and (2) do the series of Eqs. (3) and (5) converge for these values?

The best method of deciding these questions appears to be that of calculating the  $F$  curve for a model atom and subjecting it to the Fourier analysis. This procedure has been carried through for a model sodium ion under assumptions designed to make a satisfactory Fourier analysis more difficult than in the cases of the light atoms to be studied experimentally. The sodium ion is built up of ten electrons on three concentric spherical shells, as follows:

2 electrons on a shell of radius 0.1A

6 electrons on a shell of radius 0.3A

2 electrons on a shell of radius 0.9A

The  $F$  values for this ion may be readily calculated from the expression<sup>11</sup>

$$f = \sum (\sin \xi) / \xi$$

where

$$\xi = (4\pi r \sin \theta) / \lambda = 2\pi r n / d$$

TABLE I

$F$  values for sodium model ion.  $F = f e^{-.0063 n^2}$

$n$	$f$	$F$	$n$	$f$	$F$	$n$	$f$
0	10.	10.	18	.51	.066	38	-.34
1	9.53	9.48	20	1.17	.093	40	-.08
2	8.42	8.22	22	1.24	.059	44	-.02
4	5.90	5.33	24	0.98	.025	48	-.44
6	4.45	3.55	26	.69	.010	52	-.47
8	3.01	2.01	28	.01	.000	56	-.07
10	1.14	0.61	30	-.53		60	.40
12	0.20	.08	32	-.73	-.0011	70	.02
14	.14	.04	34	-.83		80	.29
16	.14	.028	36	-.82	-.00022	100	-.01

and the summation is taken over each of the electrons. As a convenient first order spacing we shall choose 5.628A. The  $f$  values are given in Table I, along with  $F$  values which have been obtained by applying a temperature factor to  $f$  as follows:

<sup>11</sup> Hartree, Phil. Mag. 50, 289 (1925).

$$F = fe^{-(b\sin^2\theta)/(2\lambda^2)} = fe^{-.2n^2/d^2} = fe^{-.0063n^2}$$

This evaluation of the Debye factor is based upon W. H. Bragg's figure for rock-salt,  $b/(2\lambda^2) = 2.06$ , which will at least give the order of magnitude of the temperature effect. In Fig. 1 are shown the  $f$  and  $F$  values plotted against  $\sin \theta$  for  $\lambda = 0.1126\text{\AA}$ . This wave-length was chosen because it makes  $\sin \theta = 0.01$  for  $d/n = 5.628$  and allows the  $F$  values for 100 orders of reflection to be plotted. The author's measurements with  $\lambda = 0.710\text{\AA}$  would stop at a point equivalent to  $\sin \theta = 0.12$  in the figure.

Of the series in Eqs. (3) and (5), the sine series of (5) will converge the more slowly because the coefficient  $F$  is multiplied by  $n$ . Let us consider the question of its convergence. It is evident that the series

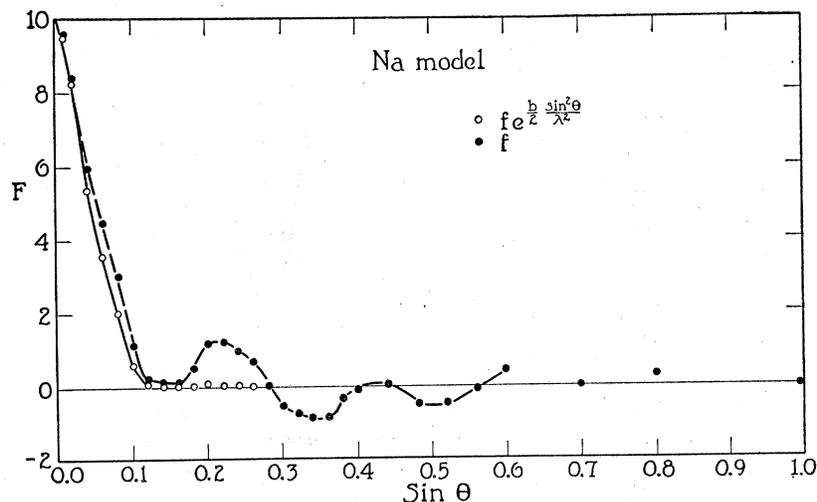


Fig. 1.  $F$  curves for a model sodium ion.

when evaluated with the  $f$ 's of Table I is probably not convergent, for in some instances  $f_n > f_0/n$ . The application of the temperature factor to  $f$  introduces a negative exponential  $n^2$ , consequently the  $F$  values of the table undoubtedly satisfy the conditions for convergence. Looking at the question from another point of view, we see that the series of Eq. (5), if used with the  $f$  values of Table I, would have to give a radial distribution showing infinite values of  $U$  at the  $r$  values of the three shells, and zero values of  $U$  at all other points. The effect of thermal agitation, however, is to spread out the shells into what is a more or less continuous distribution of electrons and the series representing  $U$  for this case should converge rather rapidly.

The series of Eq. (5) has been evaluated with the  $f$  and  $F$  values of Table I and  $D=2.814\text{\AA}$ .  $U$  is plotted against  $r$  in Fig. 2. In the heavy-line curve in the upper part of the figure, which was obtained by using the first twenty  $f$  terms, down to  $n=40$  in the table, the three shells are beginning to emerge as predominant peaks. The broken-line curves, representing the series when cut off at the end of five and eleven terms,

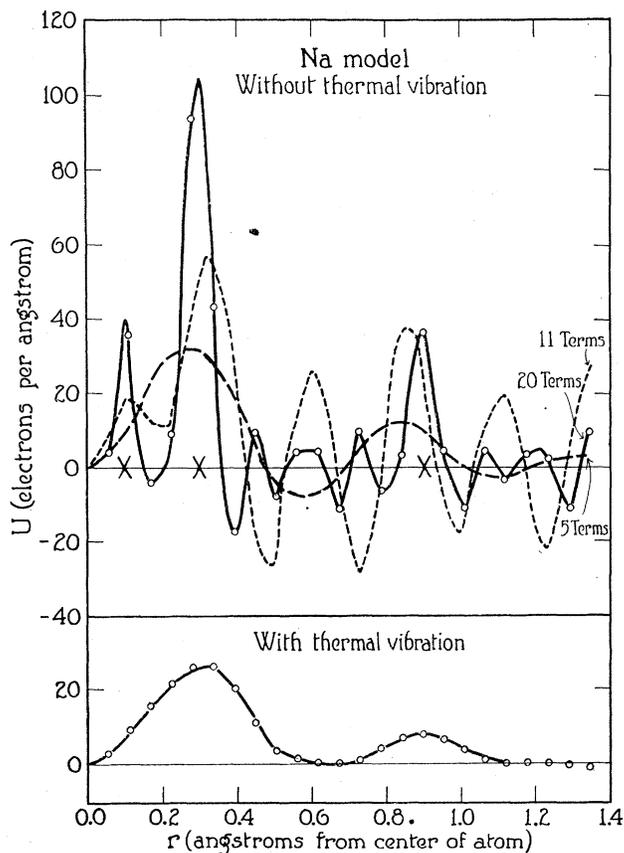


Fig. 2. Radial electron distribution in model sodium ion.

help to indicate the unsatisfactory nature of the analysis when used upon an atom which has its electrons arranged on a few stationary shells. When evaluated for 12 terms, down to  $n=24$ , with the  $F$  values of Table I, the series gives the lower curve of the figure. Its area is 9.6 electrons. The effect of thermal agitation has smoothed over the shells distinctly. When the series is cut off at the end of the sixth term, which would be the limit of the author's measurements, the curve coincides so



in the experimental  $F$  curves as a means of securing a rapidly convergent series and therefore of obtaining a more trustworthy Fourier analysis is clearly demonstrated. In an effort to determine the error due to the extrapolations which have been made for the purpose of this analysis, the author plans to continue the investigation of  $F$  curves out to smaller interplanar spacings by the use of radiation of shorter wave-length, and of apparatus which permits the measurement of reflections out to  $\theta = 90^\circ$ .

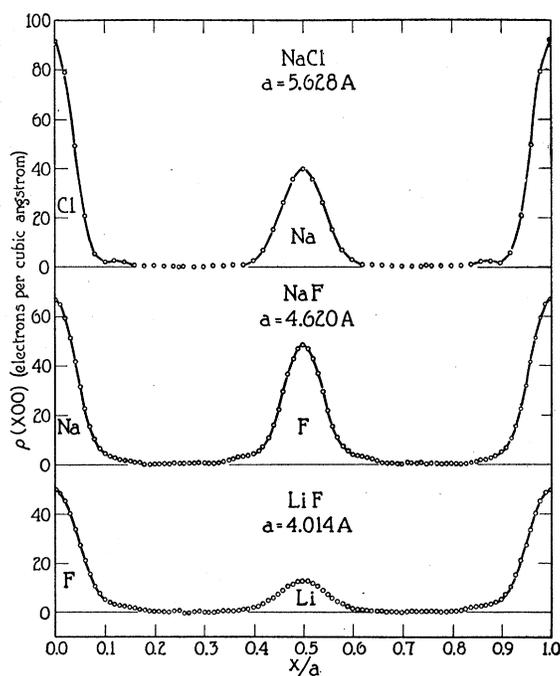


Fig. 3. Electron density in crystals.

#### ELECTRON DISTRIBUTION IN CRYSTALS

We may now calculate electron distributions from Eq. (3), and on the basis of the author's  $F$  curves extrapolated to zero, with considerable confidence in the results. The  $F$  values to be used as coefficients, given in Table II, are, as a rule, identical with the measured values given in the previous paper, although in a few cases where measured points fell noticeably off a smooth curve, interpolated values are substituted. Interpolated values are given for the reflections which were not measured, while below the dotted lines the points were all taken from extrapolated curves.

The electron density,  $\rho(x00)$ , along the cube edge of the unit cell of the crystals here considered is

$$\rho(x00) = 4/a^3 \sum_{n_1} \sum_{n_2} \sum_{n_3} F_{n_1 n_2 n_3} \cos 2\pi n_1 x/a \quad (6)$$

The curves of  $\rho(x00)$  plotted against  $x/a$  are given in Fig. 3. Going out from the center of an atom, they all show the same rapid decrease of electron density at the start, followed usually by a rather sharp change of slope which produces a hump on the  $U$  curve. One feature of these curves cannot be observed clearly, because the scale of the figure is too small; for each curve there is only one very narrow region between the

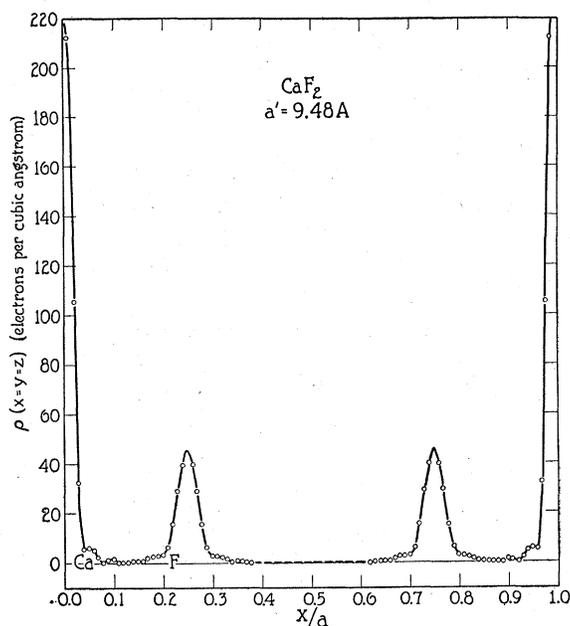


Fig. 4. Electron density in  $\text{CaF}_2$ .

atoms where the density becomes practically zero. In other words, the atoms extend physically well out into the unit cell, almost touching each other, although the electron density over a large part of the region is very small. There is a sharp drop to zero density at the limit of the atom, which is much more evident in the  $U$  curves, where  $\rho$  is magnified by multiplication by  $r^2$ . The electron distributions in other directions through the unit cell have been calculated from Eq. (3), giving curves similar to those of the figure.

The  $\rho(x00)$  curve from  $\text{CaF}_2$  has no peak at its middle, for there is merely a series of Ca atoms along the cube edges of the unit cell. In order

to get evidence of the existence of fluorine peaks, it is necessary to work out the curve for  $\rho(x=y=z)$ , the density along the cube diagonal. Not only is the three dimensional series, required in this case, a much more laborious one to evaluate than the one-dimensional series of Eq. (5), but also the  $F$  curve for Ca falls rather slowly toward zero, so that the extrapolation would have to be made out to very high values of the  $n$ 's, still further increasing the labor of evaluating the series. Consequently an indirect method of determining  $\rho(x=y=z)$  was adopted. The  $F$  curve for Ca was extrapolated and the values for the higher orders of the (111) planes determined.  $U dr$  values were determined from Eq. (5) on the basis of the  $F(111)$  data, and, from the curve of  $U$  against  $r$ ,  $\rho(x=y=z)$  was calculated for the desired values of  $r$  by Eq. (4). By a similar procedure with the  $U$  curve of fluorine from  $\text{CaF}_2$ , the  $\rho(x=y=z)$  values for fluorine were obtained. The two sets of data have been united in the curve of Fig. 4. There is, of course, no data to cover the middle of the curve, which is a region of zero density. Incidentally, the fact that the  $F$  curves for heavy atoms fall rather slowly to zero indicates that they are not very suitable for this Fourier analysis.

TABLE III  
*Atomic F values for use in Fourier's series*

Plane	Ca <sup>++</sup>	CaF <sub>2</sub> F <sup>-*</sup>	NaCl Na <sup>+</sup>	NaCl Cl <sup>-</sup>	NaF Na <sup>+</sup>	NaF F <sup>-</sup>	LiF Li <sup>+</sup>	LiF F <sup>-</sup>	Mean Fluorine F <sup>-**</sup>
111	15.90	7.35	8.80	13.60	8.35	7.15	1.26	5.89	7.35
222	10.75	3.20	5.46	7.84	4.90	3.49	0.88	2.72	3.32
333	7.32	1.75	3.05	5.15	2.65	1.59	0.41	1.30	1.62
444	5.30	1.05	1.60	3.40	1.30	0.94	0.14	0.65	0.86
555	3.97	0.65	0.72	2.10	0.72	0.53	0.06	0.37	0.55
666	2.80	0.27	0.10	1.15	0.28	0.28			0.27
777	2.10			0.31					
888	1.22								
999	0.30								
200	15.00		8.58				1.25		
400	9.80		4.62				0.73		
600	6.15		2.23				0.24		
800	4.55		1.00				0.11		
10 00	2.95		0.20						
12 00	2.15						0.02		
14 00	1.10								
16 00	0.10								

\* Values taken from  $F_F$  curve with  $D(111) = 2.67\text{\AA}$ .

\*\*  $D(111) = 2.67\text{\AA}$ .

## RADIAL ELECTRON DISTRIBUTION IN ATOMS

We have seen that the radial distribution may be determined by the use of Eq. (4) or Eq. (5). In most cases the writer has used both methods, and the results have always been in satisfactory agreement. Table III contains atomic  $F$  values for use in Eq. (5), for the different orders of the (100) and (111) planes, the values being taken from smooth curves and those below the dotted lines being extrapolated.

The  $U$  curves invariably show humps which seem to indicate the existence of definite electron shells. While the evidence for and against the actual existence of these humps will be considered later, it is interesting on the assumption of their reality to compare the electron arrangements which they give with Stoner's<sup>12</sup> scheme for the distribution of electrons in atoms.

Stoner's arrangement for the argon atom (chlorine or calcium ion) is as follows:

2 K electrons with $n$ 1, $j$ 1, $k$ 1
2 L                                    2,    1,    1
2 L                                    2,    1,    2
4 L                                    2,    2,    2
2 M                                    3,    1,    1
2 M                                    3,    1,    2
4 M                                    3,    2,    2

The neon atom ( $\text{Na}^+$  or  $\text{F}^-$  ion) corresponds to the above arrangement without the M electrons. The inner quantum number,  $j$ , need not be considered here.

*Sodium and chlorine.* The full-line curve in Fig. 5 represents  $U$  for Na in NaCl. The curve is almost identical with one obtained by Compton<sup>9</sup> by a similar analysis of the results of Bragg, James and Bosanquet.<sup>13</sup> The area under the curve is 10.4 electrons, indicating that we have here a positive  $\text{Na}^+$  ion. The area of the hump  $B$  is approximately 2, while that of  $A$  is 8. Upon the basis of Stoner's scheme, we should interpret these humps as follows:  $A$  contains the 2 K electrons and the 6 circular L electrons;  $B$  contains the 2 L electrons with elliptical orbits.

There was some difficulty in obtaining a  $U$  curve from Eq. (5) for chlorine, as Cl occupies much more space than Na. The  $U(111)$  curve does not extend to the limit of the atom, as it is based upon too small a spacing. Compton solved this difficulty by extrapolating the  $F$  curve for Cl toward  $\sin \theta = 0$ , upon the assumption that  $F_0 = 18$ , and using a

<sup>12</sup> Stoner, Phil. Mag. **48**, 719 (1924).

<sup>13</sup> W. L. Bragg, James and Bosanquet, Phil. Mag. **42**, 1 (1921).

larger spacing for  $D$  in the series. This requires the assumption, which we wish to avoid, of an ionized chlorine atom, consequently we must rely chiefly upon the  $U$  values obtained from  $\rho(x00)$  which are in agreement with the  $U(111)$  values as far as the latter may be used. The area under the curve of Fig. 6 is 17.85 electrons, indicating the existence of

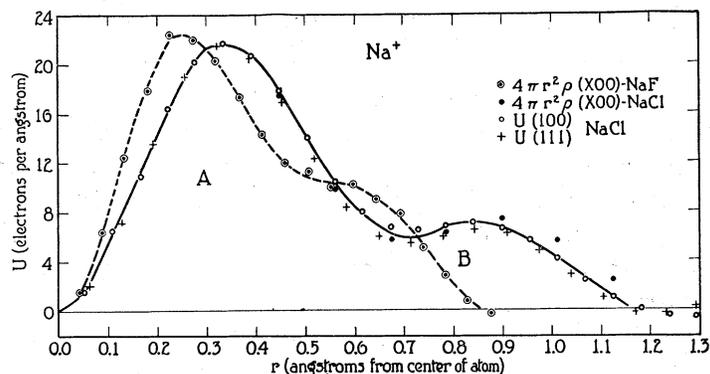


Fig. 5. Radial electron distribution in  $\text{Na}^+$ .

the  $\text{Cl}^-$  ion. The hump  $A$  contains 10 electrons, which are probably those belonging to the K and L levels, leaving us with 8 M electrons to account

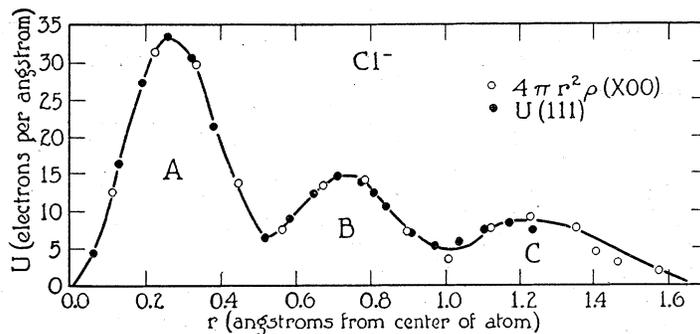


Fig. 6. Radial electron distribution in  $\text{Cl}^-$ .

for. The areas of  $B$  and  $C$  are more nearly 5 and 3 than 6 and 2, although the latter values might be taken to indicate the presence of six  $3_2$  electrons in orbits of moderate eccentricity, and two  $3_1$  electrons in orbits of greater eccentricity. Hartree's<sup>11</sup> calculations, however, indicate that the effective radii of the  $3_2$  and  $3_1$  electrons are practically the same. In this connection it should be stated that according to calculations by both

Hartree and Compton, an electron in an interpenetrating orbit spends much the larger part of its time in the outer portion of its orbit, so that its effective radius for the purpose of x-ray scattering and its maximum radius are very nearly the same. Compton's curve for Cl, based upon the data of Bragg, James and Bosanquet which are very nearly identical with those of the author, but also based upon an  $F$  curve extrapolated toward  $\sin \theta = 0$ , shows an extra hump, while the radius of the atom is 2.0A. This discrepancy throws some doubt upon the reality of these humps.

*Calcium.* The  $U$  curve for Ca given in Fig. 7 is strikingly similar to that for  $\text{Cl}^-$ , except that the electrons are contained within a radius less than two thirds that of the chlorine ion. Almost a positive proof of the existence of the  $\text{Ca}^{++}$  ion in the lattice is to be seen in the fact that the area under the curve is exactly 18 electrons, for the neutral atom would

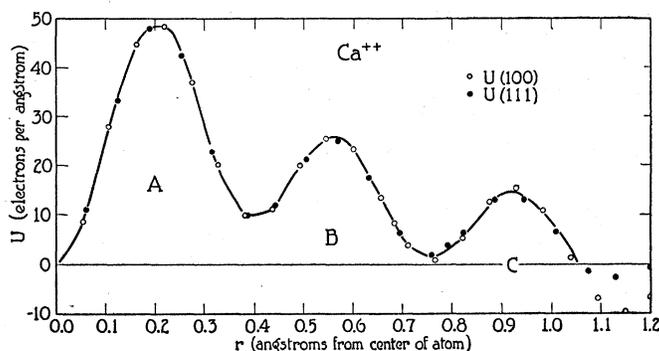


Fig. 7. Radial electron distribution in  $\text{Ca}^{++}$ .

contain 20 electrons. The area of hump  $A$  is 10 electrons, while  $B$  and  $C$  contain 6 and 2 electrons respectively.

*Sodium in sodium fluoride.* The broken-line curve of Fig. 5 is the  $U$  curve of Na from NaF. A very interesting difference exists between the sodium ion in the two compounds, an apparent compression of the whole ion having taken place in NaF. As the area under the curve is only 9.2 electrons, the analysis is not particularly satisfactory in this instance, but the addition of sufficient area to bring the electron content to 10 would not make the two distributions alike. One is brought to the conclusion that the forces acting upon the ion in the two crystals are of rather different magnitudes.

*Lithium.* The  $U$  curve for lithium, given in Fig. 8, is the least satisfactory of the group, because we meet the same absolute amount of error,

due to deficiencies of the experimental data and of the analysis, in electron densities which are very small, so that the percentage errors are large.

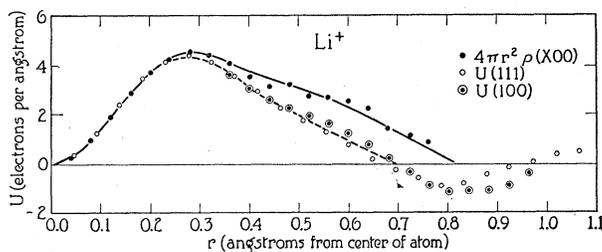


Fig. 8. Radial electron distribution in  $\text{Li}^+$ .

There is a noticeable difference between the  $U$  curves obtained in different ways, and these curves can be changed considerably by different methods of smoothing out the experimental  $F$  curve for Li. The difference between the results obtained from Eq. (5) and those from Eq. (4) is undoubtedly due to the fact that the experimental  $F$  values were used without change in the determination of  $\rho(x00)$ , while the  $F$  curve of Li, upon which is based the  $U(111)$  curve, being determined by subtraction of rather large and nearly equal  $(F+\text{Li})$  and  $(F-\text{Li})$  values, showed considerable irregularity and was smoothed out. However, the area under the full-line curve is 2.0 electrons; and there is no reason to believe that we are dealing with anything but the  $\text{Li}^+$  ion with two K electrons.

*Fluorine.* As has been pointed out, the  $F$  curves for fluorine from all three fluorides are very closely similar, hence it was not considered necessary to reproduce separate  $U$  curves for each crystal. The values used in obtaining Fig. 9 were taken from the mean  $F$  curve of fluorine,

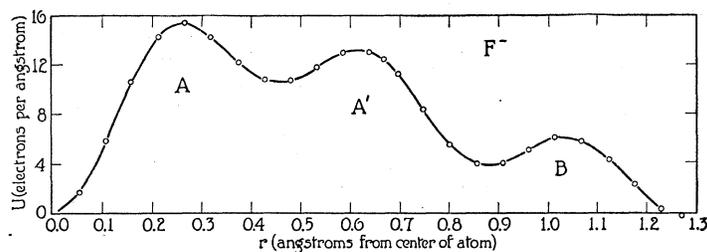


Fig. 9. Radial electron distribution in  $\text{F}^-$ .

given in the previous paper,  $D$  for the first order being 2.67Å.  $U$  curves from the individual  $F$  curves have also been worked out, and they show

only unimportant differences at large values of  $r$ . Corresponding to the  $F^-$  ion, the area under the curve is 9.95 electrons. The striking thing about this curve is the existence of the  $A'$  hump. We should, of course, assign  $B$  to the two L electrons in elliptical orbits, as in the case of  $Na^+$ , but there is nothing in the sodium curve to correspond with  $A'$ . Whether in the spreading out of the electron atmosphere which takes place during the formation of a negative ion the inner electron groups separate somewhat, or whether the  $A'$  hump is merely due to a deficiency of the analysis, is uncertain.

#### DISCUSSION OF RESULTS

The results of the foregoing analysis may be grouped into two classes: those which allow an unambiguous interpretation, and those which do not. Let us consider the first class.

(1) It appears to be definitely proven that the lattice points of the crystals are occupied by ions. Commencing with no *a priori* assumption as to the amount of electricity associated with a lattice point, we have found in each case that the number of electrons was almost exactly the same as the number in the ion which might be expected to reside at that point.

(2) The Fourier analysis determines definitely the radius of the ion. The volume density curves fall quite accurately to zero over a small region between the ions, while the  $U$  curves determine sharply the radii. Comparison of the distance of closest approach of ions as determined by ordinary x-ray analysis with the sum of the radii of the ions determined in this analysis shows that the sum of the radii is in every case very slightly less than the distance of closest approach. We accordingly are led to form the usual picture of the unit cell of a crystal: one which contains a number of spherical electron systems practically in contact with each other and distributed regularly over the lattice points, each system having a dense electron atmosphere near its center which becomes extremely rarefied at its outer limit. Whether the valence electrons remain between ions all the time, rotate about pairs of ions, or pass completely over to the negative ions, is not decided; all we may be certain of is that the diffracting power of a valence electron unites with that of a negative ion.

The ionic radii of Wasastjerna,<sup>14</sup> discussed in a recent paper on interatomic distances by W. L. Bragg,<sup>15</sup> and which are based upon a theoretical consideration of atomic force-fields, correspond exceedingly closely with the radii determined in this analysis.

<sup>14</sup> Wasastjerna, Soc. Scient. Fenn. Comm. Phys. Math. **38**, 1 (1923).

<sup>15</sup> W. L. Bragg, Phil. Mag. **2**, 258 (1926).

(3) The electron distribution of an atom may be modified by the external forces which act upon it in a crystal. The  $\text{Na}^+$  ion is found to possess different electron distributions in  $\text{NaF}$  and  $\text{NaCl}$ , probably because of a combination of differences in chemical, crystal lattice and thermal forces. On the other hand, the electron distributions of  $\text{F}^-$  are practically the same in  $\text{LiF}$ ,  $\text{NaF}$  and  $\text{CaF}_2$ .

Turning now to results which are somewhat ambiguous, we are met at once with the question of the reality of the humps in the curves of radial distribution. There is reason to believe that a shell-like electron structure exists in atoms, and the results of this analysis are in rough agreement with the predictions of Stoner's scheme. The persistence of the humps in both  $\text{Ca}^{++}$  and  $\text{Cl}^-$ , although one ion has only two-thirds as large a radius as the other, is evidence of their reality. On the other hand, we have the discrepancy between Compton's  $U$  curve for  $\text{Cl}^-$  and that of the author, the two curves being obtained from practically the same data by slightly different methods of analysis. Also there is a subsidiary hump in the  $U$  curve for  $\text{F}^-$  which is not readily explained. Perhaps the best method of investigating this question of shell structure would be to study a model argon atom in the manner of the investigation carried out above for the sodium ion.

Although we have assumed spherical symmetry of the electron distributions for the purposes of a part of this analysis, such an assumption cannot be completely justified. Probably the atoms in crystals of low symmetry are not spherically symmetrical, but the nearest approach to this condition would be expected in a cubic crystal of high symmetry. It is impossible to decide from existing experimental data upon intensity of reflection that spherical symmetry does not exist, the irregularities of the  $F$  curves being in general so small that they could be ascribed to experimental error. Any lack of symmetry would be expected to show on the  $U$  curves at large values of  $r$ , and there are differences between these curves when they are evaluated for reflections in different directions through the crystal, but these differences also may be attributed to deficiencies in the analysis.

A further point which has been raised in connection with the use of experimental  $F$  curves for the determination of electron distributions has to do with the effect of the Compton scattering. Since the amount of radiation scattered with a change of wave-length increases with the angle of scattering, it might be supposed that this increase takes place at the expense of the energy scattered with unmodified wave-length. That is, the  $F$  curve might drop off at large angles for two reasons—first, because of the spatial distribution of electrons in the atoms, and second,

because an increasing fraction of the secondary radiation is being scattered with a change of wave-length and hence is not subject to interference. This idea seems not unreasonable, yet, on the other hand, there is reason for the belief that the two scattering processes take place side by side without influencing each other. It seems that the foregoing analysis, which gives electron distributions containing the proper number of electrons and of the dimensions to be expected from the results of ordinary crystal analysis, is a strong argument for the reliability of the experimental *F* curves and speaks definitely in favor of the idea that the Compton scattering is a separate and distinct process from the ordinary scattering.

In conclusion, the author wishes to express his appreciation of the aid and advice of Professor William Duane, who suggested this problem.

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