From the PHILOSOPHICAL MAGAZINE, vol. xliv. *September* 1922.

The Distribution of Electrons around the Nucleus in the Sodium and Chlorine Atoms.

By W. LAWRENCE BRAGG, *M.A., F.R.S., Langworthy Professor of Physics, The University of Manchester*: R. W. JAMES, *M.A., Senior Lecturer in Physics, The University of Manchester*; *and* C. H. BOSANQUET, *M.A., Balliol College, Oxford.*

1. IN two recent papers* in the Philosophical Magazine the authors have published the results of measurements made on the intensity of reflexion of X-rays by rock-salt. The mathematical formula for the intensity of reflexion, as calculated by Darwin †, involves as one of its factors the amount of radiant energy scattered in various directions by a single atom when X-rays of given amplitude fall upon it. The other factors in the formula can be evaluated. By measuring the intensity of reflexion experimentally we can therefore obtain an absolute measurement of the amplitude of the wave, scattered by a single atom, in terms of the amplitude of the incident radiation.

This measurement is of considerable interest, because it may throw some light on the distribution of the electrons around the nucleus of the atom. We regard the wave scattered by the atom, as a whole, as the resultant of a number of waves, each scattered independently by the electrons in the atom. A formula first evaluated by J. J. Thomson is used in order to calculate the amplitude of the wave scattered by a single electron. If an incident beam of plane polarized X-rays consists of waves of amplitude A, then the amplitude A′ at a distance R from the electron in a plane containing the direction of the incident radiation, and at right angles to the electric displacement, is given by

$$\frac{A'}{A} = \frac{1}{R}\frac{e^2}{mc^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here e and m are the charge and mass of the electron in electromagnetic units, and c is the velocity of light.

What we measure experimentally is the resultant amplitude of the wave-train scattered in various directions by a number Z of electrons in the atom. If all the electrons were

* Phil. Mag. vol. xli. March 1921 ; vol. xlii. July 1921.

† C. G. Darwin, Phil. Mag. vol. xxvii. pp. 315-675 (Feb. and April 1914).

difficulties of estimating intensities in this way, of the few points which they obtained on the curve for the $\frac{F+Li}{F-Li}$ ratio, of the difficulties in interpreting intensities which we have discussed in our papers, and of the large extrapolation which they had to make in order to get the limiting value of $\frac{F+Li}{F-Li}$, we feel that their results cannot be regarded as proving that the transference of the valency electron has taken place. The fact of the transference is supported by much indirect evidence, and their conclusion is probably correct.

Debye and Scherrer also compared the intensities reflected by various planes of the diamond, and concluded that the electrons in the carbon atoms were contained within a sphere of diameter 0·43 Å, assuming a uniform distribution throughout this sphere.

In all the above cases, the results were obtained by comparing the relative intensities of reflexion by various faces. The results which we have obtained, and which will be used to calculate the distribution of electrons in sodium and chlorine, are, on the other hand, absolute determinations. The intensity of reflexion was compared in each case with the strength of the primary beam of X-rays, so that the absolute efficiency of the atom as a scattering agent could be deduced.

In a paper on "The Reflection Coefficient of Monochromatic X Rays from Rock Salt and Calcite"*, Compton made comparisons of the incident and reflected beam, for the first order reflexion from cleavage faces of these crystals. He obtained results for rock-salt which were rather less than those which we afterwards obtained for a ground face, but he noted that the effect was increased by grinding the face. In our notation the results were

Compton	$\frac{E\omega}{I} = \cdot00044 \pm \cdot00002$	NaCl (100).
B. J. and B.	$\frac{E\omega}{I} = \cdot00055$	

As Compton surmised, and as we have found experimentally, this figure for the efficiency of reflexion has to be modified considerably to allow for the extinction factor. The difference

* A. H. Compton, Phys. Rev. vol. x. p. 95, July 1917.

between his results and ours is accounted for by the extinction or increased absorption of the rays at the reflecting angle. Compton pointed out that the reflexion factor was of the order to be expected from Darwin's formula, but did not use the value he obtained to solve the electron-distribution problem.

3. For the sake of convenience of reference, the formula which forms the basis of all the calculations is quoted below. Let the intensity I_0 of a beam of homogeneous X-rays, at a given point, be defined as the total energy of radiation falling per second on an area of one square centimetre at right angles to the direction of the beam. If a crystal element of volume dV, supposed to be so small that absorption of the rays by the crystal is inappreciable, be placed so that it is bathed by the X-rays, and if it is turned with angular velocity ω through the angle at which some plane in it reflects the X-rays about an axis parallel to that plane, the theoretical expression for the total quantity of energy of radiation E reflected states that

$$\frac{E\omega}{I_0} = \frac{N^2\lambda^3}{\sin 2\theta} F^2 \cdot \frac{e^4}{m^2c^4} \frac{1+\cos^2 2\theta}{2} e^{-B\sin^2\theta} dV \quad . \quad (2)$$
$$= Q\,dV.$$

In this expression

N = Number of diffracting units per unit volume *.
λ = Wave-length of X-rays.
θ = Glancing angle at which reflexion takes place.
e = Electronic charge.
m = Electronic mass.
c = Velocity of light.

The factor $e^{-B\sin^2\theta}$ (the Debye factor) represents the effect of the thermal agitation of the atoms in reducing the intensity of reflexion.

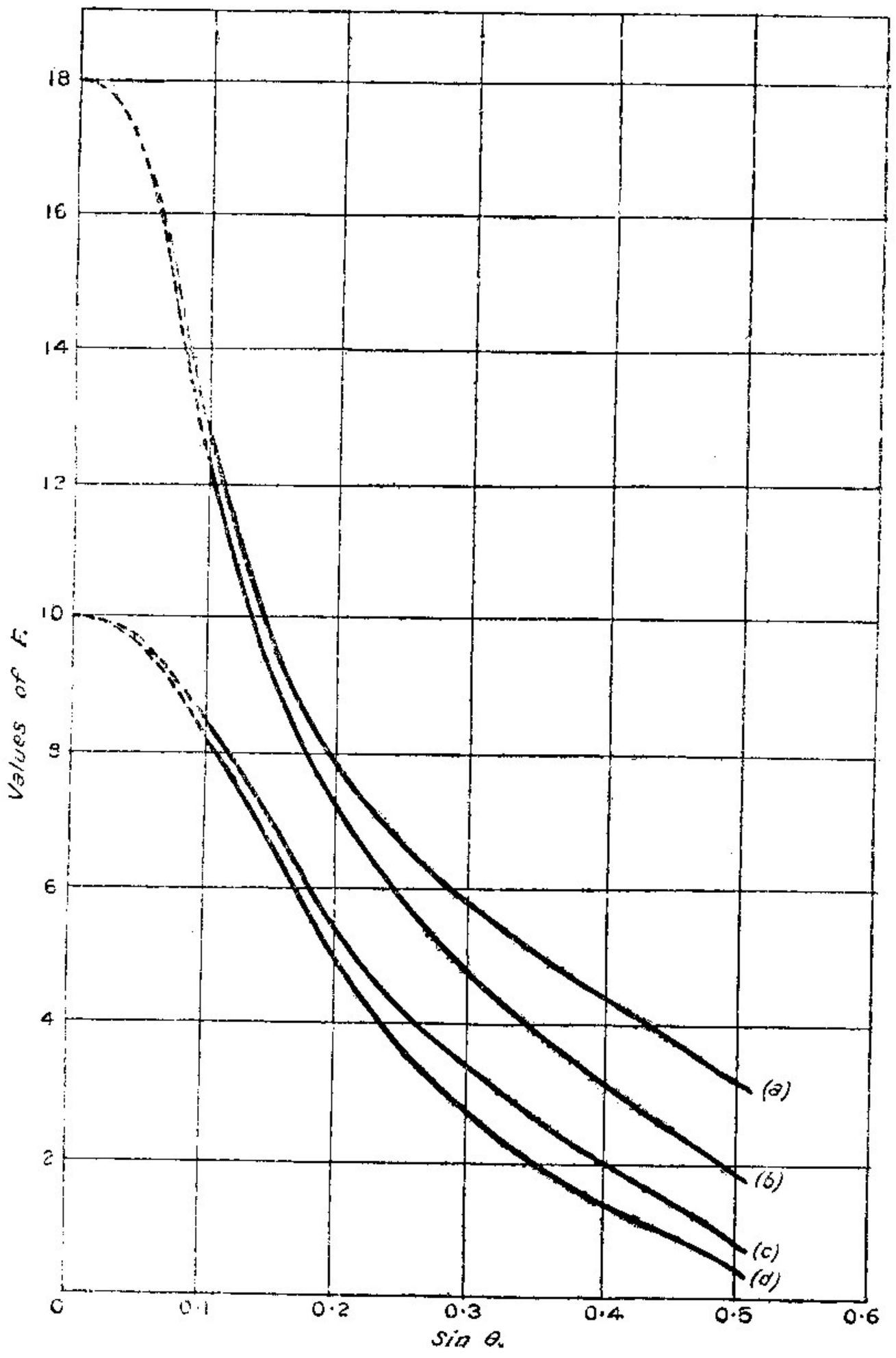
The factor F depends on the number and arrangement of the electrons in the diffracting unit. At $\theta=0$ it would have a maximum value equal to the total number of electrons in the unit, and it falls off owing to interference as θ increases.

The experimental observations have as their object the determination of Q in absolute units. In practice we cannot use a single perfect crystal so small that absorption is

* No account is taken here of the "structure factor." The diffracting units are supposed to be spherically symmetrical as regards their diffraction effects.

inappreciable. We use a large crystal consisting of numbers of such homogeneous units and deduce, from its reflecting power, the reflecting power Q per unit volume of the units of which it is composed. The assumptions made in doing this are by no means free from objections, and will be discussed later in this paper. Taking this to be justifiable, however, our experimental results yield the value of Q for rock-salt over a wide range of angles, and from them the values of F_{Cl} and F_{Na} follow directly. These values are shown in fig. 1.

Fig. 1.



(*a*) F_{Cl} corrected for Debye factor. (*c*) F_{Na} corrected for Debye factor.
(*b*) F_{Cl} uncorrected „ „ (*d*) F_{Na} uncorrected „ „

4. We must now consider more closely the significance of the factor F. The most simple case is that of a crystal containing atoms of one kind only. Parallel to any face of the

crystal we can suppose the atoms all to lie in a series of planes, successive planes being separated by a distance d. We get the nth order spectrum formed at a glancing angle by the reflexion from such a set of planes if

$$2d \sin \theta = n\lambda.$$

This spectrum represents the radiation diffracted by the atoms in a direction making an angle 2θ with the incident beam, and it is formed because in this particular direction the radiation scattered by *any* pair of atoms lying in successive planes differs in phase by $2n\pi$. Thus the amplitude of the beam scattered in this direction is the *sum* of the amplitudes scattered by all the neighbouring atoms taking part in the reflexion.

Let us consider the contribution to the reflected beam of a group of atoms lying in a reflecting plane. To obtain the amplitudes of the reflected wave, we sum up the amplitudes contributed by the electrons in all the atoms, taking due account of the fact that the electrons do not in general lie exactly in the reflecting plane and so contribute waves which are not in phase with the resultant reflected wave. By symmetry, the phase of the resultant wave will be the same as that reflected by electrons lying exactly in the geometrical plane passing through the mean positions of all these atomic centres. The phase of the wave scattered in a direction θ by an electron at a distance x from the plane differs from that of the resultant wave by an amount

$$\frac{4\pi}{\lambda} x \sin \theta.$$

We will suppose that there is in every atom an electron which is at a distance a from the centre, and that all directions of the radius joining the electron to the atomic centre are equally likely to occur in the crystal. In finding the effect of these electrons for all atoms (M in number) of the group, we may take it as equivalent to that of M electrons distributed equally over a sphere of radius a. It can easily be shown that, if x is the distance of an electron from the plane, all values of x between $+a$ and $-a$ are equally likely for both cases. Such a shell scatters a wave which is less than that scattered by M electrons in the plane in the ratio $\frac{\sin \phi}{\phi}$, where

$$\phi = \frac{4\pi}{\lambda} a \sin \theta.$$

The average contribution of the electron in each atom to the F factor is therefore $\frac{\sin\phi}{\phi}$, and not unity as it would be if the electron were at the centre of the atom.

If there are n electrons at a distance a from the centre of the atom, their contribution to the F factor would be

$$n.\frac{\sin\phi}{\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Any arrangement of n electrons at a distance a from the centre of the atom, provided that all orientations of the arrangement were equally probable, would make the same contribution to the F factor. For example, eight electrons arranged in a ring about the nucleus would give the same value for F as eight electrons arranged at the corners of a cube, or eight electrons rotating in orbits lying on a sphere of radius a. This illustrates the limitations of our analysis, which cannot distinguish between these cases. We can only expect to get information from our experimental results as to the average distance of the electrons from the atomic centre, and this for the average atom.

Suppose now that any atom contains a electrons at a distance r_1 from the nucleus, b at a distance r_2, c at a distance r_3 . . . n at a distance r_n, then the value of F for the average atom would be given by

$$\mathrm{F}=a\frac{\sin\phi_1}{\phi_1}+b\frac{\sin\phi_2}{\phi_2}+c\frac{\sin\phi_3}{\phi_3}+\ldots+n\frac{\sin\phi_n}{\phi_n} \quad . \quad . \quad (4)$$

Thus, given the distribution of the electrons on a series of shells or rings, we can calculate the value of F for any value of θ. The problem we have to solve here, however, is the converse of this. We have measured the value of F for a series of values of θ, and wish to determine from the results the distribution of the electrons. We have seen above that there is no unique solution of this problem, but we can get some idea of the type of distribution which will fit the experimental curves.

In order to do this, we suppose the electrons to lie on a series of shells, of definite radii r_1, r_2, ... and determine the number of electrons a, b, c on the various shells which will give values of F corresponding to those observed experimentally. Suppose, for example, we take six shells uniformly spaced over a distance somewhat greater than

the atomic radius is expected to be. For any given value of θ we have

$$F = a\frac{\sin\phi_1}{\phi_1} + b\frac{\sin\phi_2}{\phi_2} + c\frac{\sin\phi_3}{\phi_3} + d\frac{\sin\phi_4}{\phi_4} + e\frac{\sin\phi_5}{\phi_5} + f\frac{\sin\phi_6}{\phi_6} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We chose from the experimental curve six values of θ evenly spaced over the range of values at our disposal, and for each of these values read from the curve the value of F. Since definite radii have been assumed for the shells, the values of $\frac{\sin\phi_1}{\phi_1}$, etc., can be calculated for each value of θ.

Hence, for each value of θ, we have an equation involving numerical coefficients and the quantities a, b, c, d, e, f, so that if six such equations are formed we may calculate these quantities.

If Z is the total number of electrons in the atom we have

$$Z = a + b + c + d + e + f, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and this will be taken as one of our equations (corresponding to $\theta = 0$). In calculating the results for sodium and chlorine we have assumed the atom to be ionized, and have taken $Z_{Cl} = 18$ and $Z_{Na} = 10$.

It will be evident that this method of solution is somewhat arbitrary, and that the results we get will depend on the particular radii assumed for the shells. By assuming various radii for the shells, however, and solving the simultaneous equations for the number of electrons on each, we find that the solutions agree in the number of electrons assigned to various regions of the atom.

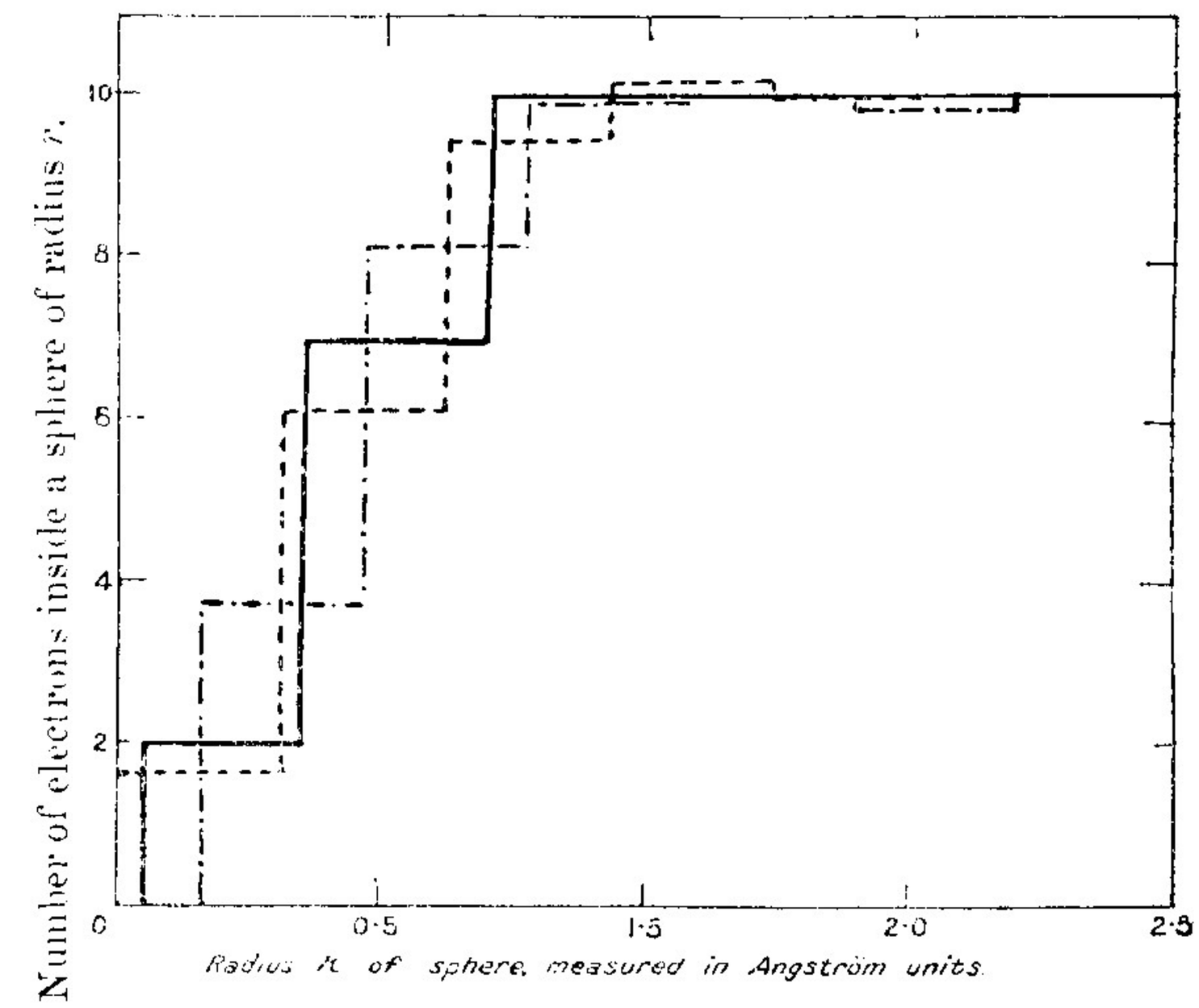
As a test of the method of analysis, a model atom was taken which was supposed to have electrons arranged as follows :—

2	on a shell		0·05 Å	radius.
5	,,	,,	0·35	,,
3	,,	,,	0·70	,,

The F curve for this model was calculated. Then the simultaneous equations for the electron distribution were solved, just as if this curve had been one found experimentally. This was done for two arbitrarily chosen sets of radii, taken out to well beyond the shell at 0·70 Å.

The comparison between the two analyses (dotted curves) and the atom model we started with (continuous curve) is shown in fig. 2. The abscissæ represent the radii of the shells in Å, the ordinates the total number of electrons inside a shell of that radius. When the limits of the atomic structure are reached, the curve becomes horizontal at the value 10, corresponding to the ten electrons. The analyses not only indicate with considerable accuracy the way in

Fig. 2.



which the electron-content grows as we pass to spheres of larger radii, but also tell definitely the outer boundary of the atomic structure. Both give a number of electrons very nearly equal to zero in the shells outside 0·70 Å.

5. The F curves for sodium and chlorine can be solved in the same manner. We have expressed our results in two ways.

First, we have supposed the electrons to be grouped on shells. The numbers of electrons on each shell, and the radii of the shells, have been so adjusted as to give the best possible fit to the experimental curves. In the case of sodium it is found that a fit can be obtained with two shells, and in the case of chlorine with three shells. The

numbers of electrons on each shell, and the radii of the shells, are as follows :—

Sodium.

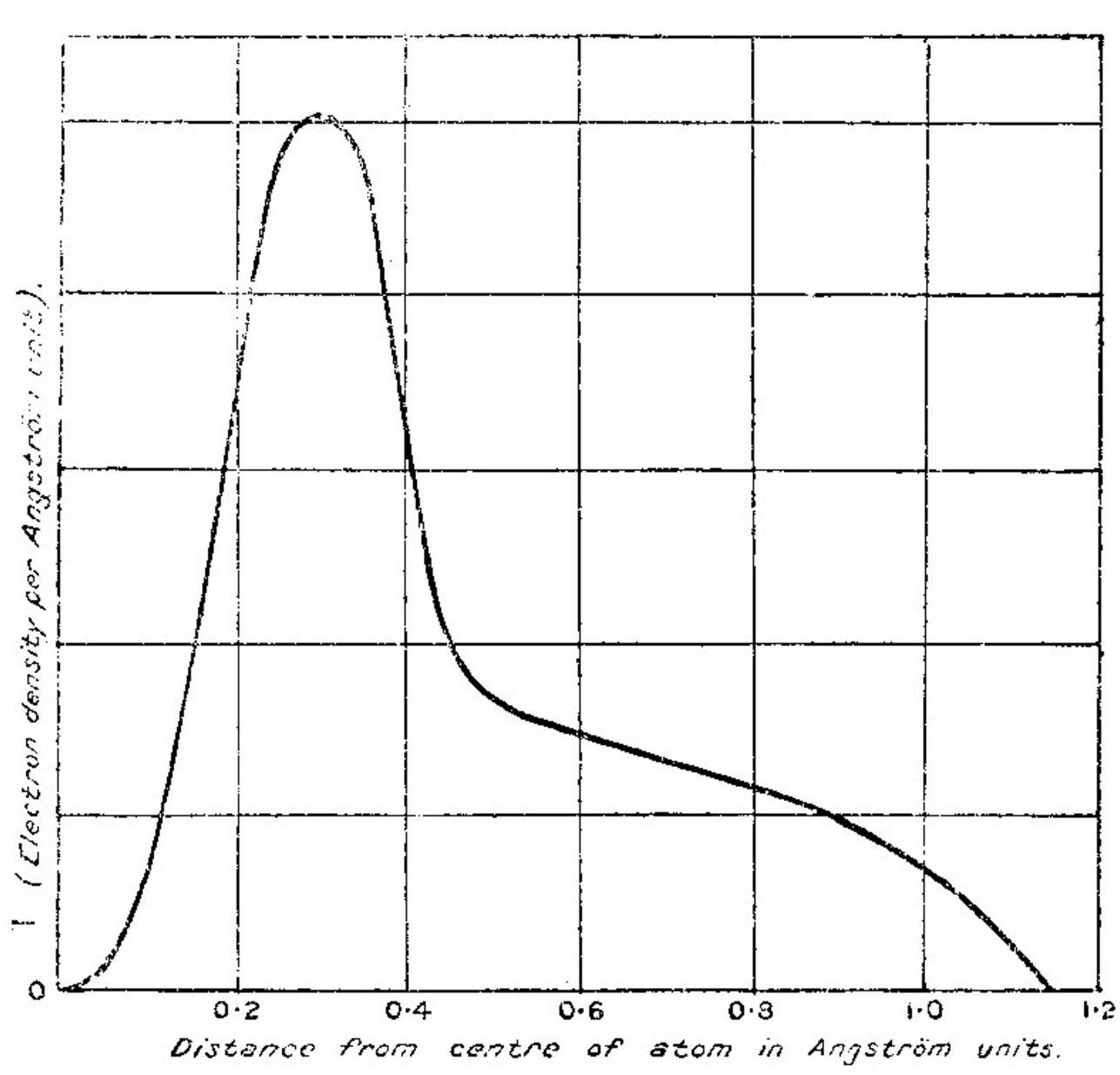
7 electrons on a shell of radius 0·29 Å.
3 „ „ „ 0·76 „

Chlorine.

10 electrons on a shell of radius 0·25 Å.
5 „ „ „ 0·86 „
3 „ „ „ 1·46 „

Secondly, we have solved the simultaneous equations for the distribution in shells with several sets of radii, and drawn a smooth curve through the points so obtained in such a way as to represent the density of distribution of the electrons as a continuous function of the distance from

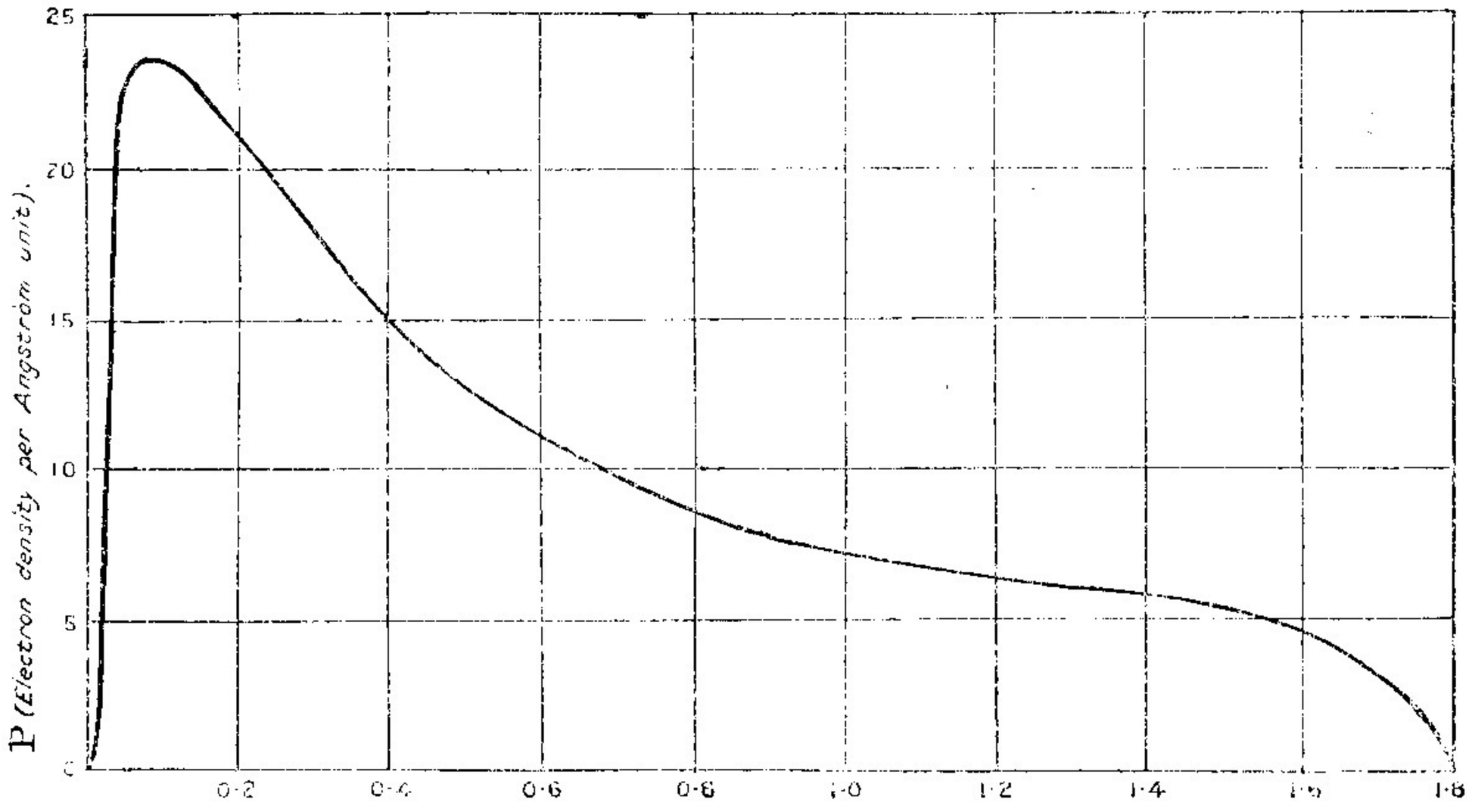
Fig. 3.



the atomic centre. The density P is so defined that Pdr is the number of electrons whose distance from the centre lies between r and $r+dr$. The curves which we obtain for sodium and for chlorine are shown in figs. 3 and 4. The

total number of electrons in the atom is represented by the area included between the curves and the axis.

Fig. 4.



Distance from centre of atom in Ångström units.

The following table shows the agreement between the F curves found experimentally and those calculated from the electron distributions:—

TABLE I.—Sodium.

Sin θ.		0·1.	0·2.	0·3.	0·4.	0·5.
F	Observed	8·32	5·40	3·37	2·02	0·76
	Shells {0·29 Å, 0·76}	8·56	5·59	3·33	2·19	0·93
	Smooth Curve ...	8·57	5·40	3·20	1·91	1·00

TABLE II.—Chlorine.

Sin θ.		0·1.	0·2.	0·3.	0·4.	0·5.
F	Observed	12·72	7·85	5·79	4·40	3·16
	Shells {0·25 Å, 0·86, 1·46}	12·53	7·73	5·90	4·61	2·69
	Smooth Curve ...	12·70	7·80	5·55	4·10	3·20

6. We have also made an approximate calculation of the F curve to be expected from an atom of the type proposed by Bohr *. In the ionized sodium atom containing

* Nature, cvii. p. 104 (1921).

10 electrons, two are supposed to describe circular one-quantum orbits about the nucleus, while, of the remaining eight, four describe two-quantum circular orbits and four two-quantum elliptical orbits. We have calculated the size of these orbits from the quantum relationship and the charges; this can only be done very approximately, owing to the impossibility of allowing for the interaction of the electrons. We take the following numbers :—

Radius of 1 quantum ring	0·05 Å.
,, 2 ,, ...	0·34 ,,
Semi-major axis of ellipses * ...	0·42 ,,

To get a rough idea of the diffracting power of such an atom, we suppose, first, that the orientation of the orbits is random so that the average atom has a spherical symmetry, and also that the periods of the electrons in their orbits are so large compared with the period of the X-rays that we need not consider the effect of their movements.

The calculation of the effect of the circular orbits offers no difficulties. To allow for the effect of the ellipses, the following method was used. The elliptical orbit was divided into four segments, through each of which the electron would travel in equal times. It was then assumed that, on the average, one of the four electrons describing ellipses would be in the middle of one of these segments. This gives four different values of the radius vector, corresponding in the average atom to four spherical shells of these radii.

We thus calculate the value of F for an atom having

2	electrons on a shell of radius	0·05	A.U.
4	,, ,, ,,	0·34	,,
1	,, ,, ,,	0·27	,,
1	,, ,, ,,	0·55	,,
1	,, ,, ,,	0·70	,,
1	,, ,, ,,	0·78	,,

* The elliptical two-quantum orbit of a single electron about the sodium nucleus would have a semi-major axis equal to the radius of the two-quantum circle. We have used the larger value 0·42 to make some allowance for the fact that part of the orbit lies outside the inner electrons, so that the effective nuclear charge is reduced.

This gives the following figure for F_{Na} :—

Sin θ.	0·1.	0·2.	0·3.	0·4.	0·5.
F calculated	8·73	5·04	3·76	2·53	1·80
F observed	8·32	5·40	3·37	2·02	0·76

The agreement, of course, is not perfect, but one must remember that no attempt has been made to adjust the size of the orbits to fit the curve. The method of calculation too is very rough, although it must give results of the right order. The point to be noticed is that the curve is quite of the right type, and there is no doubt that an average distribution of electrons of the nature given by such an atom model could be made to fit the observed value of F quite satisfactorily.

7. The points which appear to us to be most doubtful in the above analysis of our results are the following :—

(*a*) We have assumed that each electron scatters independently, and that the amount of scattered radiation is that calculated for a free electron in space according to the classical electromagnetic theory. It is known that for very short waves this cannot be so, since the absorption of γ rays by matter is much smaller than scattering would account for, if it took place according to this law. On the other hand, the evidence points towards the truth of the classical formula in the region of wave-lengths we have used (0·615 Å).

(*b*) We have used certain formulæ (given in our previous papers, to which reference has been made) in order to calculate the quantity we have called Q in equation (2) from the observed intensity of reflexion of a large crystal. Darwin * has recently discussed the validity of these formulæ. The difficulty lies entirely in the allowance which has to be made for "extinction" in the crystal. X-rays passing through at the angle for reflexion suffer an increased absorption owing to loss of energy by reflexion.

Darwin has shown that this extinction is of two kinds, which he has called primary and secondary. If the crystalline mass is composed of a number of nearly-parallel homogeneous crystals, each so small that absorption in it is inappreciable even at the reflecting angle, then secondary extinction alone takes place. At the reflecting angle the

* Phil. Mag. vol. xliii. p. 800, May 1922.

X-rays suffer an increased absorption, because a certain fraction of the particles are so set as to reflect them and divert their energy. We made allowance for this type of extinction in our work, and Darwin concludes that our method of allowance, while not rigorously accurate mathematically, was sufficiently so for practical purposes.

Primary extinction arises in another way. The homogeneous crystals may be so large that, when set at the reflecting angle, extinction in each crystal element shelters the lower layers of that element from the X-rays. Darwin has calculated that this will take place to an appreciable extent for the (100) reflexion if the homogeneous element is more than a few thousand planes in depth. A large homogeneous element such as this does not produce an effect proportional to its volume, since its lower layers are ineffective, and a crystal composed of such elements would give too weak a reflexion. Our method of allowing for extinction will not obviate this effect.

We cannot be sure, therefore, that we have obtained a true measure of Q for the strong reflexions. The F curve may be too low at small angles. It is just here that its form is of the highest importance in making deductions as to atomic structure. Until this important question of the size of the homogeneous elements has been settled, we must regard our results as provisional.

(*c*) The allowance for the thermal agitation of the atom (the Debye factor) is only approximate; it depends on a few measurements made by W. H. Bragg in 1914. In order to see how much error is caused by our lack of knowledge of the Debye factor, we have calculated the electron distribution without making any allowance for it. The result may appear at first rather surprising; the electron distribution so calculated is almost indistinguishable from that which we found before, when allowance for the Debye factor had been made. This is so, although the factor is very appreciable for the higher orders of spectra, reducing them at ordinary temperatures to less than half the theoretical value at absolute zero. The difference which the factor makes can best be shown by comparing the radii of the shells which give the best fit with (1) the F curve deduced directly from the experimental results, (2) the F curve to which the Debye factor has been applied.

	(1). Radius (without allowance for thermal agitation).	(2). Radius (with allowance for thermal agitation).
Sodium.—Seven electrons	0·31	0·29
Three electrons	0·79	0·76
Chlorine.—Ten electrons	0·28	0·25
Seven electr ns.....	0·81	0·86
Three electrons.. ...	1·46	1·46

A little consideration shows the reason for this. The form of the F curve at large angles is almost entirely decided by the arrangement of the electrons near the centre of the atom. A slight expansion of the grouping in this region causes a large falling off in the intensity of reflexion. This is shown in the analysis by the slight increase (0·02 to 0·03 Å) in the radius of the shell which gives the best fit to the uncorrected curve. The effect of the thermal agitation is to make the electron distribution appear more widely diffused ; however, the average displacement of the atom from the reflecting plane owing to its thermal movements is only two or three hundredths of an Ångström unit at ordinary temperatures, and so we get very little alteration in our estimate of the electron distribution. The uncertainty as to the Debye factor, therefore, does not introduce any appreciable error in our analysis of electron distribution.

8. It is interesting to see whether any evidence can be obtained as to whether a valency electron has been transferred from one atom to the other or not. This may be put in another way : can we tell from the form of the F curves in fig. 1 whether their maxima are at 10 and 18 or at 11 and 17 respectively? It appears impossible to do this ; and, when we come to consider the problem more closely, it seems that crystal analysis must be pushed to a far greater degree of refinement before it can settle the point. If all the electrons were grouped close to the atomic centres, and if the transference of an electron meant that one electron passed from the Na group to the Cl group, then a solution along the lines of that attempted by Debye and Scherrer for LiF might be possible. The electron distributions we find extend, on the other hand, right through the volume of the crystal. The distance between Na and Cl centres is 2·81 Å, and we find electron distributions 1 Å from the centre in sodium and 1·8 Å from the centre in chlorine. If the

valency electron is transferred from the *outer region* of one atom to that of the other, it will still be in the region between the two atoms for the greater part of the time, since each atom touches six neighbours, and the difference in the diffraction effects will be exceedingly small. It is for this reason that we think Debye and Scherrer's results for LiF, which were not absolute measurements such as the above, were not adequate to decide whether the transference of a valency electron has taken place.

We have assumed that the atoms are ionized in calculating our distribution curves. If, on the other hand, we had assigned 11 electrons to sodium and 17 to chlorine, we should have obtained curves of much the same shape but with an additional electron in the outermost shells of sodium and one less in those of chlorine.

9. *Summary.*—We have attempted to analyse the distribution of electrons in the atoms of sodium and chlorine by means of our experiments on the diffraction of X-rays by these atoms. The results of the analysis are shown in figs. 3 and 4.

The principal source of error in our conclusions appears to be our ignorance as to the part played by "extinction" in affecting the intensity of X-ray spectra. The distributions of the electrons are deduced from the F curves (fig. 1). The most important parts of these curves are the initial regions at small angles, for errors made in absolute values in this region alter very considerably the deductions as to electron distribution. The exact form of the curve at large angles is of much less interest. Now, it is in this initial region, corresponding to strong reflexions such as (100), (110), (222), that extinction is so uncertain a factor. Until the question of extinction is satisfactorily dealt with, the results cannot be regarded as soundly established.

If our results are even approximately correct, they prove an important point. There cannot be, either in sodium or chlorine, an outer "shell" containing a group of eight electrons, or eight electrons describing orbits lying on an outer sphere. Such an arrangement would give a diffraction curve which could not be reconciled with the experimental results. Eight electrons revolving in circular orbits of the same radius would give the same diffraction curve as eight electrons on a spherical shell, and are equally inadmissible. On the other hand, it does seem possible that a combination of circular and elliptical orbits will give F curves agreeing with the observations.