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MEASUREMENTS AND INTERPRETATION OF THE INTENSITY OF X-RAYS REFLECTED FROM SODIUM CHLORIDE AND ALUMINUM

By J. A. Bearden

Abstract

Measurements of the intensity of x-rays reflected from sodium chloride have been made by three methods: (1) *Reflection from a single crystal,* (2) *Reflection from a plate of powdered crystals,* (3) *Reflection from a powdered plate using the transmission method.* The results from single and powdered crystal measurements are not in agreement, showing that there is possibly an uncorrected extinction effect in the single crystal measurements. The results from both powdered crystal methods are in very close agreement.

Using the Fourier series formula for the electron distribution derived by Compton, *electron distribution curves* for sodium and chlorine have been obtained. The difference in the electron distribution curves for powdered and single crystals indicates that the absolute intensity measurements must be made accurate to within 1 percent before confidence can be placed in the results. It is also shown that the portion of the experimental curves extrapolated to large angles of reflection is very important.

Similar measurements and curves have been obtained for aluminum. The distribution curve and also the F curve are more satisfactory than those obtained for sodium and chlorine, showing that the experimental values for aluminum are probably more accurate than the rock salt measurements.

VARIOUS writers[1–10] have obtained theoretical expressions for the intensity of x-ray reflection, and although by independent methods, most of the formulas are in agreement with each other. The following formulas which have been derived by Compton[10] for the three most important cases of crystals, are directly applicable to experimental results:

(1) Reflection from single crystals:

$$\left.\frac{W\omega}{P}=\frac{1}{4\mu}n^2\lambda^3F^2\frac{e^4}{m^2c^4}\,\frac{1+\cos^2 2\theta}{\sin 2\theta}\right\}=\frac{Q}{2\mu}\,. \tag{1}$$

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[1] P. Debye, Ann. d. Physik, **43,** 49 (1914).

[2] C. G. Darwin, Phil. Mag. **27,** 315 and 675 (1914).

[3] C. G. Darwin, Phil. Mag. **43,** 800 (1922).

[4] W. H. Bragg, Phil. Trans. **215,** 253 (1915).

[5] A. H. Compton, Phys. Rev. **9,** 29 (1917).

[6] W. L. Bragg, James and Bosanquet, Phil. Mag. **41,** 309 (1921).

[7] H. A. Wilson, Phys. Rev. **18,** 396 (1921).

[8] P. P. Ewald, Phys. Zeits. **22,** 29 (1925).

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

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

W represents the total amount of energy reflected by the crystal as it is turned past the angle θ with a uniform angular velocity ω, P the power in the primary x-ray beam, μ the effective absorption coefficient of the crystal, n the number of atoms per unit volume of the crystal, λ the wavelength of the x-rays used, e the charge on the electron, m the mass of the electron, c the velocity of light, $(1+\cos^2 2\theta)$ the polarization factor, and F is termed the structure factor and is defined by the equation

$$F=Z\int_{-a}^{a} p\,(z)\cos\left(\frac{4\pi z}{\lambda}\sin\theta\right)dz \tag{2}$$

where a is the maximum possible distance of an electron from its atomic layer, Z is the number of electrons in the atom and $p(z)$ represents the probability that an electron will be at a distance between z and $z+dz$ from the mid-plane of the layer of atoms to which it belongs.

(2) Reflection from a plate of powdered crystals:

$$\frac{P_s}{P}=Q\frac{p}{16\pi}\,\frac{l}{\mu r}\cdot\frac{\rho'}{\rho}\,\frac{1}{\sin\theta} \tag{3}$$

(3) Reflection from a powdered plate using the transmission method:

$$\frac{P_s}{P}=Q\frac{p}{4\pi}\,\frac{l}{r}\,\frac{h\rho'}{\rho}\,\frac{1}{\sin 2\theta} \tag{4}$$

In these equations, P_s represents the power in the beam reflected by the powdered crystals at an angle θ, P the power in the incident x-ray beam, Q is defined by Eq. (1), p is the number of surfaces in a crystal of the type considered, l is the length of the slit in the ionization chamber, h is the thickness of the crystal mass, r is the distance of the ionization chamber slit from the crystal mass, ρ' is the density of the crystal mass, ρ is the density of the individual crystals, and μ is the effective absorption coefficient of the crystal mass. Thus F is the only quantity occurring in Eqs. (1), (3) and (4) which cannot be directly measured. Its value may be calculated, however, when the other factors in these equations have been determined.

From the value of F as calculated from the above formulas it is possible to gain some knowledge of the distribution of the electrons in the atoms composing the crystal. The method of Fourier series is doubtless the best method that has been developed for obtaining a knowledge of the electronic distribution. The method was first suggested by W. H. Bragg[4] but in a manner which did not give satisfactory results. Duane[9] has applied Epstein and Ehrenfest's[11] quantum treatment of the problem

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[11] Epstein and Ehrenfest, Proc. Nat. Acad. Sci. **10,** 133 (1924).

of Fraunhofer diffraction to the determination of the electronic distribution and has obtained results which are in a very usable form. His equation for the electron distribution is in the form of a 3 dimensional Fourier series. It has been applied by Havighurst[12] to the electron distribution of several crystals with interesting results. Compton[10] working on the basis of classical electrodynamics has arrived at the same expression as that found by Duane[9] for the electron density at any point in the crystal. Assuming the atoms in the crystal to have spherical symmetry, Compton[10] has derived the following single Fourier series equation for the radial electron distribution in the atom.

$$U=\frac{8\pi r}{D^2}\sum_1^\infty nF_n \sin\frac{2\pi nr}{D} \tag{5}$$

In this equation U represents the number of electrons per Angstrom measured from the center of the atom, r the distance from the center of the atom in Angstroms, D the arbitrary grating space in Angstroms, F_n the value of the structure factor for the nth order of reflection and n the order of reflection.

The total number of electrons in the atom may be found by integrating Eq. (5). If D is taken large enough so that there will be no overlapping of the atoms, we may integrate the equation between the limits $r=0$ and $r=D/2$. Integrating we find

$$Z=-2\sum(-1)^nF_n \tag{6}$$

where Z represents the total number of electrons in the atom, n and F_n have the same meaning as in Eq. (5). Since Z is known this equation becomes very useful in making extrapolations in the experimental F_n curves to small angle of reflection.

The object of the present work was: (1) To compare the values of F as determined from the three methods indicated in Eqs. (1), (3) and (4) as a possible check on the validity of the equations. (2) To compare the electron distribution curves using these values of F in Eq. (5). (3) To determine the distribution of electrons in aluminum by the same method.

APPARATUS

In making absolute measurements of intensity the ionization method was employed. These measurements necessitate using x-rays of a single wave-length. The best method of securing really monochromatic x-rays is to use a beam which has been reflected from a crystal. In the work of

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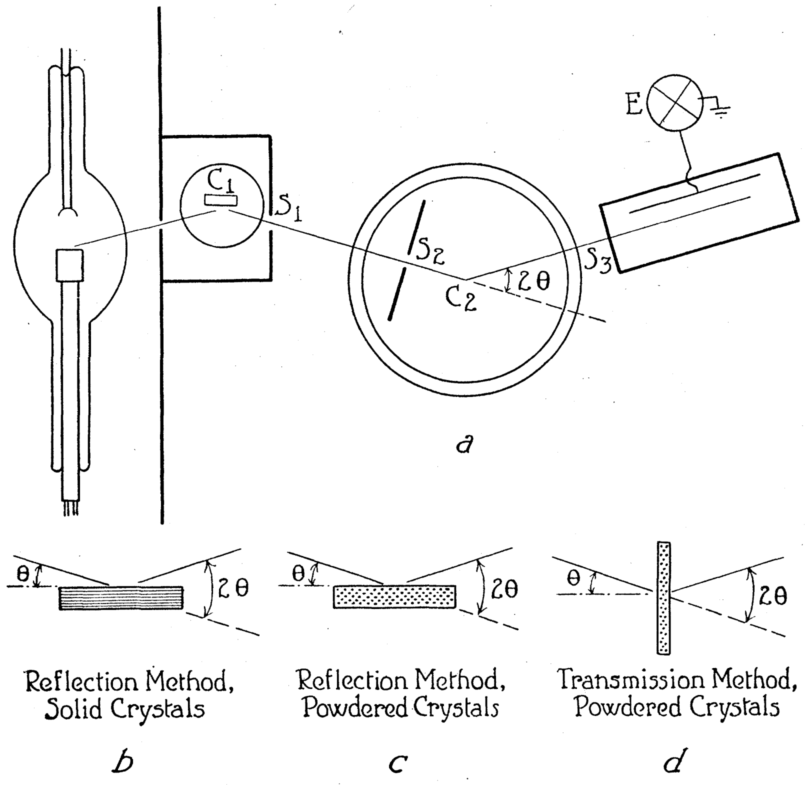
[12] R. J. Havighurst, Proc. Nat. Acad. Sci. **11**, 502 and 507 (1925).

Bragg and his collaborators[13] this method was used only for the first order reflection, whereas in this experiment the method has been used for all orders of reflection. In this way the error introduced in choosing a base line for measuring relative intensities is greatly reduced. The disposition of the apparatus was similar to that first employed by Compton.[14] Fig. 1 shows the arrangement of the apparatus used throughout the present experiment. X-rays from a molybdenum-target water-cooled x-ray tube were incident upon the crystal C_1 which was set to reflect the $K\alpha$ lines of molybdenum. These lines were further collimated by slits S_1 and S_2, so that the width of the beam passing across the spectrometer table C_2 was less than 0.8 mm. The x-ray spectrometer was designed by Compton for this particular type of work. The ionization chamber was about 12 cm in diameter so that it was almost impossible for β-rays produced by the x-rays to be absorbed by the walls or electrode of the



Reflection Method, Solid Crystals

Reflection Method, Powdered Crystals

Transmission Method, Powdered Crystals

Fig. 1. Apparatus and method of mounting crystals.

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[13] W. L. Bragg, James and Bosanquet, Phil. Mag. **41,** 309 (1921) and **42,** 1 (1921).

[14] A. H. Compton, Phys. Rev. **10,** 95 (1917).

ionization chamber. This is an important point in all measurements of absolute intensities as it was found that by using ionization chambers less than 5 cm in diameter, errors of more than 50 percent could easily be made unless the slits were extremely small and the ionization chamber accurately set parallel to the x-ray beam being measured. The ionization chamber was filled with methyl bromide and the ionization current measured by a Compton electrometer the sensitivity of which was about 5 meters per volt. The slit S_3 was in all cases wide enough to include the entire beam reflected by the crystal C_2.

In order to secure enough intensity to make accurate measurements on the higher orders of reflection it was necessary to operate the x-ray tube at 45 to 50 milliamperes using a potential of 70 kilovolts. For the first order reflections it was possible to reduce the current to 30 milliamperes and the voltage to 35 kilovolts thereby eliminating any second order x-rays that might be reflected by the crystal C_1. In order that the relative intensities and also the absolute measurements could be made with accuracy it was necessary to have a source of x-rays that would be constant over a long period of time. Several of the ordinary methods of obtaining constant current through the tube at constant voltage were tried but it was found that an arrangement suggested by W. D. Coolidge gave the best results. As a constant source of x-rays is essential to many x-ray problems a diagram of the connections is shown in Fig. 2. Using this arrangement it was possible to keep the source of x-rays constant to within 1 percent over a period of several hours. The rectifiers in this circuit were two 85 kv. 8.5 kw. kenotrons.

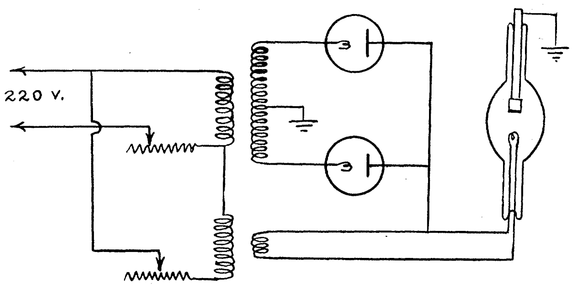

Fig. 2. Diagram of electrical connections.

The time during which the x-rays were allowed to pass through the ionization chamber was controlled by an electromagnet which operated a lead slit in the path of the x-ray beam C_1C_2. The electromagnet was operated by a Victor x-ray timing switch. By this method it was found that any period of time up to 30 seconds could be reproduced to within 0.01 of a second. The method of taking readings was to allow the x-rays to pass through the ionization chamber for a definite length of time producing a certain deflection of the electrometer which could be read very accurately.

Experiments on Rock Salt

Single crystal. Probably the most complete and accurate previous work that has been done on the intensity of x-ray reflection is that of Bragg, James and Bosanquet[13] using the single crystal method. It was thought advisable to repeat their experiments for two reasons. (1) Their results are considered to be reasonably accurate and therefore would serve as a possible check on the writer's apparatus, suitable for determining the possibility of systematic errors which might not have been detected otherwise. (2) The measurements could be extended to the higher orders of reflection using the monochromatic x-rays instead of the direct radiation from the tube as was used by Bragg and his collaborators,[13] thence obtaining a higher degree of precision than was probably attained in their experiments.

The apparatus used was exactly as that shown in Fig. 1, Part *a*, with the single crystal mounted as shown in Part *b* of the same figure. The ionization chamber with the slit S_3 0.5 cm wide was set at an angle 2θ so as to receive the entire line reflected by the crystal as the crystal was rotated through its angle of reflection for the particular order being measured. The power of the reflected beam was measured at intervals of 5 minutes of arc in the usual manner of obtaining ionization spectra. The time required to map out such a reflection was only a few minutes and in every case in which the results have been retained the intensity of the source was the same after the curve was taken as before. The crystal was then removed from the spectrometer table and the power in the incident beam C_1C_2 was measured. The ratio of the area under the reflection curve to the power in the direct beam gave the absolute reflecting power of the crystal. Instead of making absolute measurements on all the orders of reflection as above, it was found better to make the absolute measurements only on the first few orders of reflection and then to compare the higher orders of reflection with the first. Measurements were made in this manner on all of the more important planes of rock salt.

The other experimental value that is needed in Eq. (1) in order to determine F is the effective absorption coefficient μ. In the experiments of Bragg, James and Bosanquet[13] corrections were made for secondary extinction. Since the difference in wave-length of the rhodium x-rays used by Bragg and his collaborators[13] and the molybdenum Kα rays used by the writer is small, the extinction coefficient has been assumed to be proportional to the absorption coefficient in the two experiments. That is, in order to obtain the effective absorption for the present experiment, we have taken the normal absorption coefficient for the molybdenum Kα line and added to this the relative percent correction for secondary extinction as determined in the experiment of Bragg, James and Bosanquet.[13] Using this value of the absorption coefficient with the measured absolute reflecting power we can calculate the numerical value of the structure factor F. In order to compare the experimental results of this experiment with those of Bragg, James and Bosanquet[13] it is necessary to compare the values of F as they are independent of the experimental conditions and depend only on the order of reflection. The values of F calculated from the writer's experiment are shown plotted against the sine of the reflecting angle θ in Fig. 3, curves D and G. The points thus plotted fall on the curve drawn within two or three percent representing the values of $F_{\mathrm{Cl}}+F_{\mathrm{Na}}$ and $F_{\mathrm{Cl}}-F_{\mathrm{Na}}$. Using the experimental values given by Bragg, James and Bosanquet[13] and calculating in a similar manner the values of F one obtains values most of which are slightly higher than those shown by the broken line D. If one takes the values of F from their F curves it is found that they do not agree accurately with the values which I calculate from their experimental results. The difference is in many cases as much as 5 percent and in general the values taken from the curves are lower than the values calculated from the experimental data. The difference is probably due to some correction that has been applied in one case and not in the other. The values obtained by the writer seem to be in better agreement with the values calculated from their experimental results than with their F curves.

Reflection from a plate of powdered rock salt crystals. In this method a plate of powdered crystals as shown in Part *c* of Fig. 1 replaced the single crystal used in the last method. The crystal plate was prepared by pressing the finely powdered crystals into a plate about 4 mm thick, then in order to eliminate the orientation produced at the surface by the compressing block, about 1 mm of the surface was shaved off. This surface was placed at an angle θ with the primary beam and the ionization chamber at an angle 2 θ. The width of the slit S_3 in the ionization chamber was so adjusted as to include the entire beam reflected by the crystal mass. It was only necessary to make one measurement on a reflection, then remove the crystal plate and measure the power in the direct beam. As in the last case, it was found better to measure this ratio directly only for the first few orders of reflection and then compare the other orders of reflection with the first.

The values obtained by this method are, within experimental error, in exact accord with the results obtained by the transmission method and so will not be given separately.

Reflection from a powdered plate using the transmission method. In the transmission method, shown in Part *d* of Fig. 1, a plate of the powdered crystals is placed on the center of the spectrometer table and the x-rays allowed to pass through the crystal plate instead of being reflected as was done in the last case. The thickness of the crystal plate was made equal to the reciprocal of the absorption coefficient, which is the correct thickness to give the maximum intensity in the reflected lines. The normal to the surface of the plate was set at an angle θ with the primary beam and the ionization chamber at an angle $2\ \theta$. As in the last method the ionization chamber slit S_3 was adjusted so as to include the entire line reflected by crystal mass. Instead of removing the plate to measure the power in the direct beam as was done in the other two methods, the crystal plate was left on the spectrometer table with the normal to the surface making zero angle with the incident beam. The power in the beam transmitted through the plate was then measured with the ionization chamber set at zero angle. The advantage of measuring the power in the incident beam in this manner is that the absorption coefficient does not enter into the theoretical formula for the intensity of reflection. Theoretically primary extinction would also be negligible if the crystals were as small as 10^{-6} cm, but experimentally[15] it is found in the case of rock salt that primary extinction is of little importance even for crystals as large as 10^{-3} cm. This means that a crystal of rock salt is by no means a perfect crystal. Since the extinction is thus negligible the results obtained with the powdered crystals should be more precise than the results from single crystal measurements.

The absolute intensity measurements obtained by the transmission method were substituted in Eq. (4) from which the values of the structure factor F were calculated for the various planes and orders of reflection. These values are plotted against the sine of the reflecting angle θ in Fig. 3, curves C and G. The curve G represents both powdered and single crystal $F_{\mathrm{Cl}}-F_{\mathrm{Na}}$ as the values were so nearly the same that they could not be distinguished. It will be noticed that the curves representing

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[15] R. J. Havighurst, Proc. Nat. Acad. Sci. **12,** 375 (1926).

$F_{\text{Cl}}+F_{\text{Na}}$ for the single and powdered crystals do not agree except for the (100) plane and in the higher orders of reflection. It is believed that this difference is too great to be an experimental error. The difference is more likely due to the fact that sufficient correction has not been made for secondary extinction in the single crystal measurements. It was for the first order of the (100) plane that Bragg, James and Bosanquet[13] made their most careful correction of secondary extinction, and for this point the two methods agree fairly well. Also it has been shown that extinction is inappreciable for the higher orders of reflection and here again we find the two methods in agreement. It seems justifiable to conclude that for the single crystals sufficient correction has not been made for secondary extinction in the orders of reflection which do not agree with the values obtained by the powdered method.

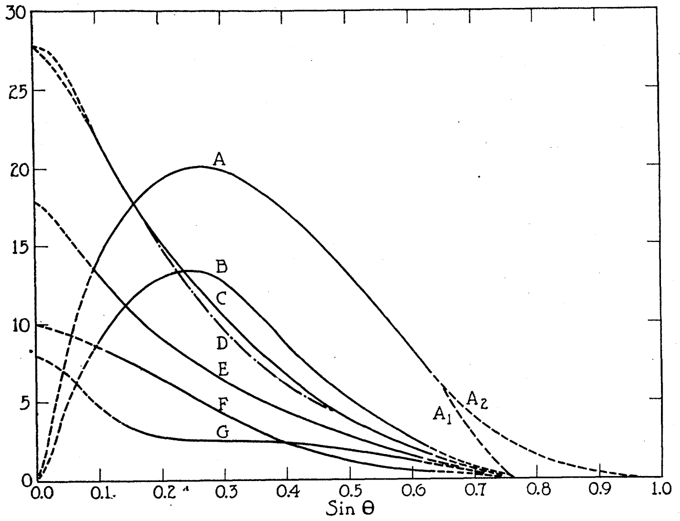

Fig. 3. Curves D and G represent the $F_{\text{Cl}}+F_{\text{Na}}$ and $F_{\text{Cl}}-F_{\text{Na}}$ values respectively for single crystals. Curves C and G represent the corresponding values for powdered crystals. E and F represent the F_{Cl} and F_{Na} values respectively, A and B are the corresponding nF_n curves.

From Fig. 3 it will be seen that experimental determinations of F have only been made up to an angle whose sine is 0.6. The reason for this is that the intensity of the reflected rays for higher orders of reflection is less than one three-millionths of the intensity in the incident beam, and measurements of such intensity are extremely difficult to make. Any extrapolation beyond the last experimental point is doubtful as will be shown in the discussion of the electron distribution curves. Probably the best extrapolation is to extend the curve smoothly to the axis, but this is only a guess as it is quite possible for the curve to cross the axis, that is, for the values of F to become negative.

The curves E and D represent the F_{Cl} and the F_{Na} values which are derived directly from the $F_{Cl}-F_{Na}$ and the $F_{Cl}+F_{Na}$ curves for powdered crystals. If the values of F are taken from these two curves and multiplied by the corresponding order of reflection we obtain the curves A and B which represent the powdered crystal nF_n values which are used in Eq. (5) to obtain the electron distribution curves. The order here refers to the arbitrary grating space D used in Eq. (5). The broken part of the curves correspond to the extrapolated portions of the curves.

ELECTRON DISTRIBUTIONS CURVES FOR SODIUM AND CHLORINE

Compton[10] has calculated the electron distributions for sodium and chlorine from Eq. (5) using the single crystal measurements of Bragg, James and Bosanquet.[13] Since the absolute values obtained by the writer are in agreement with these measurements, separate distribution curves for the single crystal measurements will not be given.

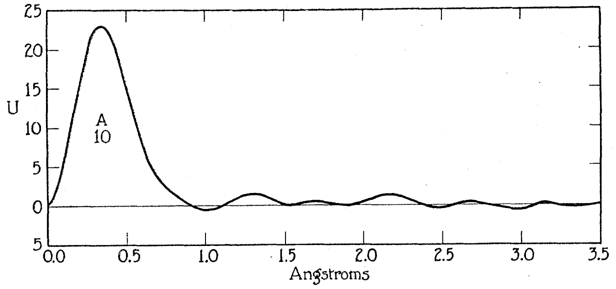

Fig. 4. Sodium electron distribution curve.

Sodium. Substituting the sodium nF_n values from curve B, Fig. 3, in the electron distribution Eq. (5) one obtains the electron density as a function of the distance from the center of the atom. Plotting the density against the distance from the center of the atom we obtain the curve in Fig. 4. The value of the arbitrary grating space D used in constructing this curve was 7.1A, a large grating space being used in order to study the distribution of the electrons in the individual atomic layers. This curve shows only one large peak which is at 0.4A and a number of small erratic oscillations which, as has been pointed out by Compton,[10] are probably due to experimental errors. Integrating the peak A we find that it represents a little less than 10 electrons. The resolving power of the present method is not great enough to separate the K and L electrons into separate peaks but gives only the average position of all the electrons in the atom.

Comparing the electron distribution curve for sodium obtained from the powdered crystal values with the curve obtained by Compton[10] using the single crystal measurements we find that they do not agree as closely as one might wish. The second peak at 0.9A containing 2 electrons as found by Compton[10] does not occur at all in the curve obtained by the writer from powdered crystal measurements. This indicates that a high degree of precision must be attained in the experimental determinations before confidence can be placed in the distribution curves. It must be remembered, however, that the sodium experimental values are dependent upon the difference in the atomic reflecting power of chlorine and sodium. Hence the intensity reflected is very weak and the probable experimental errors are greatly increased. About the only safe conclusions to be reached in the case of sodium are—(1) Most of the electrons are concentrated at a distance between 0.4A and 0.5A from the center of the atom. (2) The radius of the sodium atom is probably less than 1.2A.

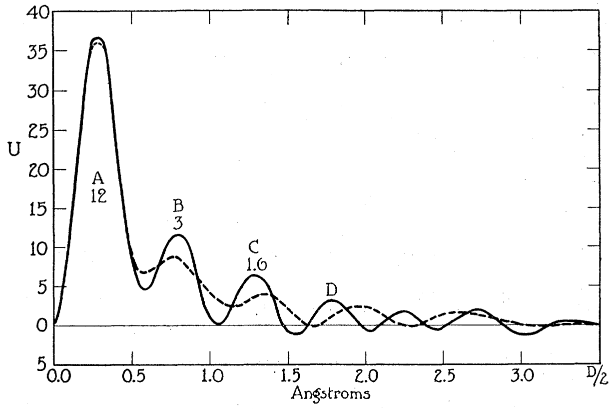

Fig. 5. Chlorine electron distribution curve.

Chlorine. For chlorine we will not only make a comparison of the distribution curves for single and powdered crystals, but also the effect of different extrapolations beyond the last experimental point of the F curves on the electron distribution curves. Substituting the nF_n values from curve A, Fig. 3, in Eq. (5) as above, one obtains the electron distribution curves shown in Fig. 5. The solid line represents the electronic distribution if one uses the extrapolation A_1 from the nF_n curve A in Fig. 3, and the dotted line the extrapolation A_2 of the same nF_n curve. These curves are very different from the sodium curve in that there are several important peaks and the density of electrons is much greater near the center of the atom. The difference in the two chlorine curves for the different extrapolations shows clearly the importance of the extrapolated part of the experimental curves in Fig. 3. The general form and position of the peaks are quite similar to the curves obtained by Compton[10] from the single crystal measurements but the sizes of the peaks are different. The peaks in these curves are much better resolved than those obtained from the single crystal measurements. If we integrate the area under the separate peaks we find that the peak *A* represents 12 electrons, *B* 3 electrons, *C* 1.6 electrons and the remaining peaks 1.4 electrons. The fact that we get fractional parts of an electron in the peaks beyond 1.*A* probably means that the experimental values are not accurate enough to give exact distributions in the exterior part of the atom. In the corresponding curves for single crystals measurements Compton[10] obtained 10 electrons in peak *A*, 4 in *B*, 2 in *C* and 2 in *D*. The difference in the magnitude of the distribution for the different peaks indicates as in sodium that a high degree of precision must be obtained before considerable confidence can be placed in the results. To the writer it seems that the absolute intensity measurements must be made precise to less than 1 percent in order to obtain reliable distribution curves in a crystal such as rock salt. This estimate, of course, refers to the actual value of the different peaks and not to the general form of the curve or to the approximate distribution of the electrons. It seems safe to conclude that the distribution of electrons in chlorine is different from that in sodium and that the radius of the chlorine atom is greater than that of the sodium atom. Any definite conclusions concerning the detailed structure of chlorine or sodium seems unwarranted.

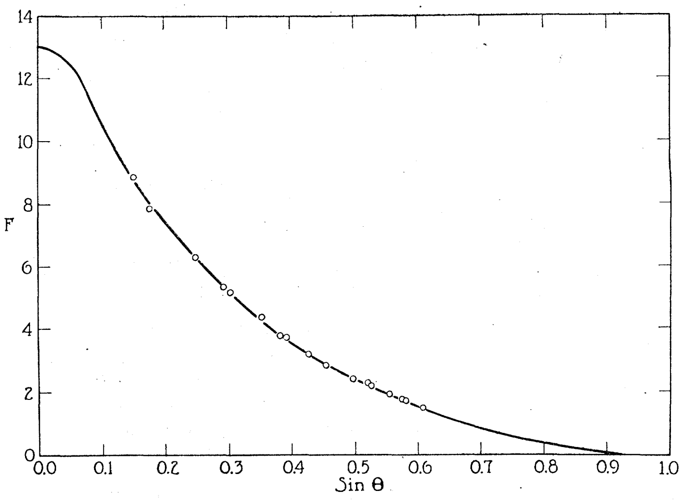

Fig. 6. *F* curve for aluminum.

INTENSITY MEASUREMENTS AND THE ELECTRON DISTRIBUTION OF ALUMINUM

Experiments were made on aluminum in exactly the same manner as described in the transmission method for rock salt. The F_n curve for aluminum is shown in Fig. 6. The extrapolation made for the higher orders of reflection was merely a smooth continuation of the experimental curve. The extrapolation for small angles of reflection was made as before using Eq. (6). For aluminum it was necessary to use two points from this extrapolated portion of the curve because there are no reflections from aluminum crystals at angles smaller than $\sin\theta = .15$. Substituting in the Fourier series Eq. (5), the electron distribution curve shown in Fig. 7 was obtained. The area under the curve out to 1.75A represents very accurately 13 electrons, and the area from 1.75A out to the center of the atomic plane $D/2$ is very nearly zero. Resolving the curve as before and measuring the areas under the peaks it is found that peak A represents 8 electrons, B 3 electrons, C 1 electron and D 1 electron. In each case the values are accurate whole numbers as near as planimeter measurements could be made. As remarked in the case of sodium and chlorine the oscillations beyond 1.75A are probably due to experimental errors. Their size is proportional to r and hence cannot account for any appreciable part of the four peaks A, B, C and D.

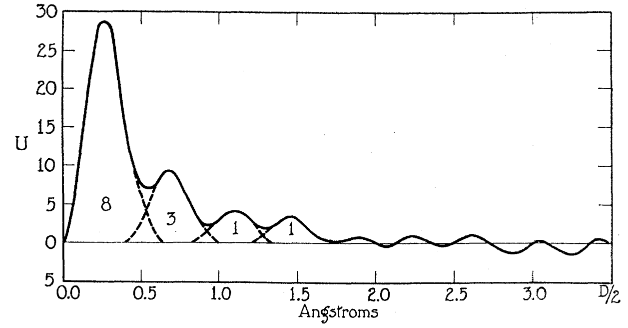

Fig. 7. Aluminum electron distribution curve.

Thus from aluminum we get results which appear to be more precise than those obtained from rock salt. The values of F_n fall on a very smooth curve indicating a higher degree of precision than was obtained in the case of rock salt. The resolution of the electron distribution curve into four components such that each contained a whole number of electrons is somewhat arbitrary, but the resolution in each case seems to be a reasonable one.

CONCLUSIONS

It is by no means certain that the theoretical equations on which this discussion is based are correct. For these expressions are based upon the classical electrodynamics, whose reliability applied to problems of the present type is open to question, in view of its failure to account for such phenomena of x-ray scattering as the Compton and allied effects. Nevertheless, as far as these experiments have been made they seem to support in every way the theoretical developments. This is borne out by the following facts: (1) The probable radius of the atom as determined by this means is in no case an impossible radius. (2) The distribution of the electrons in the atom is quite consistent with distributions determined by other methods. (3) Using the electron distribution curves obtained by Compton[10] from the single crystal measurements, Bieler has calculated the magnetic susceptibility of the chlorine and sodium ion, which is of the same order of magnitude as is found experimentally. There is thus no evidence of any failure of the classical electrodynamics as applied to calculations of the intensity of x-ray reflection.

In conclusion the writer wishes to express his appreciation to Professor A. H. Compton for suggesting the problem and for his advice and assistance in this work. He is also indebted to Mr. C. S. Barrett for his assistance in the computations.

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