

THE INTENSITY OF X-RAY REFLECTION, AND THE DISTRIBUTION OF THE ELECTRONS IN ATOMS.

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IN the study of the spectra of X-rays as analyzed by crystal gratings, the remarkably low intensity of the higher orders of reflection has from the first attracted a considerable amount of attention. Preliminary measurements by Mr. W. L. Bragg¹ showed that, when corrected for temperature effects, the intensities of the different orders of reflection of a given X-ray spectrum line are approximately proportional to the inverse square of the order. A more detailed experimental investigation by Professor W. H. Bragg² showed that if X-rays of a definite wave-length are reflected at a glancing angle θ by a crystal in which the successive layers of atoms are similar and are similarly spaced, the energy in the reflected beam can be expressed with considerable accuracy by the formula

$$(1) \quad E_r = \frac{C(1 + \cos^2 2\theta)}{\sin^2 \theta} e^{-B \sin^2 \theta}.$$

In this expression C is a constant depending upon the energy in the incident beam, the wave-length of the X-rays, and the nature of the crystal. The factor $e^{-B \sin^2 \theta}$ accounts for the effect of the thermal motion of the atoms. The constant B can be determined experimentally² or may be calculated from certain thermal properties of the crystal.^{3, 4} The polarization factor $(1 + \cos^2 2\theta)$ was originally deduced by J. J. Thomson⁵ for any case of the scattering of X-rays by electrons, and was first introduced into the formula for X-ray reflection by Darwin.⁴ Professor Bragg was not able to verify this polarization factor, since in his experiments θ was always small. Using rays of longer wave-length, however, the writer has been able to measure⁶ the reflection at sufficiently large glancing angles to obtain an appreciable effect due to this factor, and thus

¹ W. L. Bragg, Proc. Roy. Soc., A, 89, 468 (1914).

² W. H. Bragg, Phil. Mag., 27, 881 (1914), also W. H. Bragg and W. L. Bragg, X-rays and Crystal Structure, p. 195.

³ P. Debye, Ann. d. Phys., 43, 49 (1914).

⁴ C. G. Darwin, Phil. Mag., 27, 325 (1914).

⁵ J. J. Thomson, Conduction of Electricity through Gases, p. 326.

⁶ A. H. Compton, Phys. Rev., 7, 658 (1916).

to verify its existence. Since the sine of the glancing angle is proportional to the order of reflection, this formula includes the result found by W. L. Bragg, but is more general, as it expresses the intensity of the reflection from all possible planes in the crystal.

The theory of the intensity of X-ray reflection has been examined in considerable detail by Mr. C. G. Darwin,^{4, 7} who finds that if all the electrons which are effective in scattering the X-rays are close to the centers of the atoms, the energy in the beam reflected at an angle θ should be proportional to

$$\frac{1 + \cos^2 2\theta e^{-B \sin^2 \theta}}{\sin \theta \cos \theta}.$$

This expression differs from Bragg's experimental formula by the factor $\tan \theta$, which must be explained, as Darwin pointed out, by the fact that the electrons are not all concentrated near the centers of the atoms, but that at least some of the electrons are at distances from the atomic centers which are of the same order of magnitude as the distance between the atoms. Since the relative intensity of the different orders of X-ray reflection is thus a function of the distribution of the electrons in the atoms of the crystal, it should be possible, knowing the relative intensity of the different orders, to obtain some definite idea of the manner in which these electrons are arranged.

The possibility of finding an arrangement of the electrons which will account in a satisfactory manner for the observed intensity of X-ray reflection at different angles was suggested first by Professor Bragg⁸ and independently soon after by the writer.⁹ Both of us were able to show the nature of the effect on the intensity of reflection due to certain different distributions of the electrons in the atoms of a crystal grating, but we both neglected to consider certain important factors that must seriously modify the conclusions at which we arrived. We based our arguments on the assumption that the reflected energy would be the same for all orders if all the scattering occurred at the centers of the atoms. This is indeed true for the intensity in the middle of the reflected line, if the crystal acts as a perfect grating, but since the effective width of the spectrum line can be shown to be proportional to $1/\sin \theta \cos \theta$, the reflected energy is reduced in the same ratio. Thus instead of a factor $1/\sin^2 \theta$ there is really, as pointed out above, a factor of only $1/\tan \theta$ to be accounted for by the assumed structure of the atom. In the present paper a more complete theory will be obtained of the dependence

⁷ C. G. Darwin, *Phil. Mag.*, 27, 675 (1914).

⁸ W. H. Bragg, Bakerian Lecture, March 18, 1915; *Phil. Trans.*, A, 215, 253 (July 13, 1915).

⁹ A. H. Compton, *Nature*, May 27, 1915.

of the intensity of reflection upon the angle and upon the distribution of the electrons in the atoms of the reflecting crystal. The result obtained will be in exact accord with that found in a different manner by Darwin, but will be so expressed that it will be found possible to determine with some definiteness the distribution of the electrons in certain atoms by comparison with the observed intensities of X-ray reflection.

THE INTENSITY OF X-RAY REFLECTION.

Let us therefore obtain a general expression for the energy of a beam of X-rays of wave-length λ which is reflected at a glancing angle θ from a crystal all of whose atoms are similar. For sake of simplicity we may consider the primary beam to be polarized in such a manner that the electric vector is perpendicular to the plane of reflection. This will eliminate the polarization factor $(1 + \cos^2 2\theta)/2$. The temperature factor, $e^{-B \sin^2 \theta}$ may also be neglected if we consider the atoms to be in their positions of rest. These factors can be introduced later into the expression for the intensity of reflection without modifying the rest of the calculation.

Let X-rays thus polarized strike the crystal C (Fig. 1) in the elementary solid angle $d\sigma$ included between $\theta + \epsilon_1, \epsilon_3$ and $\theta + \epsilon_1 + d\epsilon_1, \epsilon_3 + d\epsilon_3$, and consider the ray reflected at the angle $\theta + \epsilon_2, \epsilon_4$. Here θ is the angle

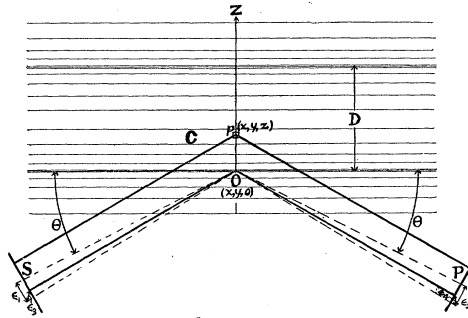


Fig. 1.

of maximum reflection, defined by the relation $n\lambda = 2D \sin \theta$, ϵ_1 and ϵ_2 are small angles measured in the plane of reflection and ϵ_3 and ϵ_4 are similar small angles taken perpendicular to this plane. We shall consider the effect of the reflected ray at the surface of a sphere of very large radius R . If $I_i \cdot d\sigma = I_i \cdot d\epsilon_1 d\epsilon_3$ is the intensity at the surface of the crystal due to this bundle of incident rays, the corresponding amplitude dA_i of the electric vector may be defined by the relation $I_i \cdot d\sigma = c(dA_i)^2$. The amplitude at the distance R of the ray scattered by a single electron may then be taken^{4, 5} as $(e^2/mC^2R)dA_i$; where e is the charge and m the

mass of the electron, and C is the velocity of light. If the electrons are held very rigidly in position, this expression might have to be slightly modified, but it seems probable that such effects are inappreciable for waves of the frequency of X-rays. The scattering due to the positive nucleus of the atom may be neglected on account of its comparatively great mass.

If we write $\phi = e^2/mC^2$, the amplitude of the reflected ray at the point P ($R, \epsilon_2, \epsilon_4$) due to a single electron near the surface of the crystal is therefore $(\phi/R) \cdot dA_i$. If $f(z)$ is the volume density of distribution of the electrons at a distance z from the middle plane of a layer of atoms in the crystal, the electric displacement at P at the time t due to a volume element of an atomic layer near the surface of the crystal is therefore

$$f(z) dx dy dz \cdot \frac{\phi}{R} dA_i \cdot \cos 2\pi \left(\frac{t}{T} - \frac{\delta + r}{\lambda} \right),$$

where T is the period of vibration, $2\pi\delta/\lambda$ is the phase angle at P due to a crystal element at (x, y, O) at the time $t = 0$, and r is the distance $2z \{ \sin \theta + (\epsilon_1 + \epsilon_2) \cos \theta \}$. Neglecting the small term $(\epsilon_1 + \epsilon_2) \cos \theta$, and writing,

$$\beta = 2\pi \left(\frac{t}{T} - \frac{\delta}{\lambda} \right),$$

we find for the displacement at P due to an element of area of a layer of atoms near the surface of the crystal,

$$\frac{\phi}{R} dA_i \cdot dx dy \cdot \int_a^b f(z) \cos \left(\beta - \frac{4\pi z \sin \theta}{\lambda} \right) dz,$$

where $b - a$ is the thickness of the atomic layer, and represents the diameter of the atoms. If N is the number of electrons per unit volume of the crystal, and D is the distance between two successive atomic layers, the number of electrons in unit area of such a layer is ND . The function $f(z)$ may therefore be written $ND F(z)$, where $F(z)$ is the probability that a given electron shall be at a distance z from the mid-plane of the atomic layer to which it belongs. Since the function $F(z)$ can nowhere be greater than at the plane of symmetry, *i. e.*, at $z = 0$, the displacement becomes a maximum when $\beta = 0$. The integral factor of the above expression then becomes,

$$\psi = \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta}{\lambda} \right) dz,$$

and the amplitude at P due to an element of area of the atomic layer considered may be written

$$\frac{\phi}{R} dA_i \cdot ND \cdot \psi \cdot dx dy.$$

If we consider an element of the crystal so small that the reflection from all of its atomic layers may be considered to be in the same phase, yet containing a large number dn of such layers, the amplitude of the reflected beam at P due to this element is evidently

$$\frac{\phi}{R} dA_i N D \psi dx dy \cdot dn.$$

Or since $dn = dz/D$, the amplitude due to a volume element of the crystal is

$$\frac{\phi}{R} dA_i N \psi dx dy dz = dA_0 \cdot dx dy dz,$$

where dA_0 is the amplitude of the reflected ray at P per unit volume of the crystal near its surface due to an incident beam of solid angle $d\sigma$.* When the rays are reflected from a depth z below the surface of the crystal, they travel a distance $2z/\sin \theta$ through the crystal before they emerge, so that the intensity is reduced by a factor $e^{2\mu z/\sin \theta}$, where μ is the absorption coefficient. The amplitude is thus reduced by a factor $e^{\mu z/\sin \theta}$, so the amplitude of the beam reflected from any part of the crystal is, per unit volume of the crystal,

$$(2) \quad dA_r = dA_0 e^{-\frac{\mu z}{\sin \theta}} = dA_i N \frac{\phi}{R} \psi e^{-\frac{\mu z}{\sin \theta}}.$$

Perfect Crystal and Long Trains of Waves.—We shall first determine the energy in the reflected beam on the assumptions (1) that the crystal has no faults, but acts as a perfect grating, and (2) that the X-rays come in trains of waves which are long compared with the depth to which they penetrate the crystal. These are the assumptions on which Darwin's theory of X-ray reflection is based, although he considers also the general nature of the modification to be expected if the crystal is imperfect. On these assumptions reinforcement will occur from all parts of the crystal struck by the rays if all the ϵ 's are zero, but when the ϵ 's differ from zero the reflections from different parts of the crystal will in general be in different phases. The difference in the path of the ray reflected from an element of the crystal at $p(x, y,$

* It will be noted that this expression seems to make the amplitude of the reflected beam proportional to the number of electrons and hence approximately proportional to the atomic weight of the atoms of the crystal. Though this result is confirmed by some early experiments by Mr. W. L. Bragg,¹ later experiments give different results. In the case of calcite Professor Bragg finds⁸ that the *intensity* of the beam reflected by an atom is more nearly proportional to the atomic weight than is the *amplitude*. He writes me that some of his results point one way and some the other. It seems very difficult to obtain a consistent reflection formula on the assumption that it is the intensity which is proportional to the number of electrons. The difficulty is probably to be explained by the nature of the function ψ , for if many of the electrons are at an appreciable distance from the center, the amplitude of the ray scattered by an atom will be considerably less than the sum of the amplitudes due to each electron.

z) and that reflected from an element at O (Fig. 2) is

$$x(\epsilon_2 - \epsilon_1) \sin \theta + y(\epsilon_4 + \epsilon_3) + z\{2 \sin \theta + (\epsilon_1 + \epsilon_2) \cos \theta\},$$

where second order terms in the ϵ 's are neglected. The reflected rays

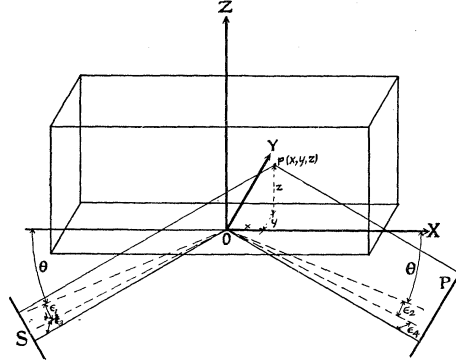


Fig. 2.

from all parts of the crystal are in the same phase when the difference in their paths is $2z \sin \theta$, so the difference in phase between the two reflected beams is

$$\delta = \frac{2\pi}{\lambda} \{x(\epsilon_2 - \epsilon_1) \sin \theta + y(\epsilon_3 + \epsilon_4) + z(\epsilon_1 + \epsilon_2) \cos \theta\}.$$

If the phase angle at P of the ray reflected from the point $(0, 0, 0)$ is $2\pi\gamma/\lambda$, the displacement due to an element of volume of the crystal at p is, by equation (2),

$$dA_0 e^{-\frac{\mu z}{\sin \theta}} \cdot \cos \frac{2\pi}{\lambda} \{\gamma - x(\epsilon_2 - \epsilon_1) \sin \theta - y(\epsilon_3 + \epsilon_4) - z(\epsilon_1 + \epsilon_2) \cos \theta\} dx dy dz.$$

The displacement at P due to the reflection from the whole crystal is therefore

$$dA_0 \int_0^\infty dz \int_{-(k/2)}^{k/2} dy \int_{z \cot \theta - l/\sin \theta}^{z \cot \theta + l/\sin \theta} dx \cdot e^{-\frac{\mu z}{\sin \theta}} \cos \frac{2\pi}{\lambda} \{\gamma - x(\epsilon_2 - \epsilon_1) \sin \theta - y(\epsilon_3 + \epsilon_4) - z(\epsilon_1 + \epsilon_2) \cos \theta\},$$

where l is the width and k the length of the slit through which the primary beam passes just before it strikes the crystal. This becomes when integrated,

$$\frac{4dA_0 BC}{gh} \cdot \frac{m \cos \frac{2\pi\gamma}{\lambda} - b \sin \frac{2\pi\gamma}{\lambda}}{m^2 + b^2},$$

where

$$B = \sin \left\{ \frac{\pi l}{\lambda} (\epsilon_2 - \epsilon_1) \right\}, \quad C = \sin \left\{ \frac{\pi k}{\lambda} (\epsilon_3 + \epsilon_4) \right\},$$

$$g = \frac{2\pi}{\lambda} (\epsilon_2 - \epsilon_1) \sin \theta, \quad h = \frac{2\pi}{\lambda} (\epsilon_3 + \epsilon_4),$$

$$m = \frac{\mu}{\sin \theta}, \quad b = \frac{4\pi}{\lambda} \epsilon_2 \cos \theta.$$

If this expression is differentiated with respect to γ and equated to zero, it is found that the maximum displacement occurs when

$$\frac{2\pi\gamma}{\lambda} = \tan^{-1} \left(\frac{b}{m} \right),$$

i. e.,

$$\sin \frac{2\pi\gamma}{\lambda} = \frac{b}{\sqrt{m^2 + b^2}}, \quad \cos \frac{2\pi\gamma}{\lambda} = \frac{m}{\sqrt{m^2 + b^2}}.$$

Substituting these values in the above equation, we find for the amplitude of the reflected beam,

$$(3) \quad dA_e = \frac{4dA_0BC}{gh\sqrt{m^2 + b^2}}.$$

The corresponding intensity of reflection is therefore,

$$dJ_e = c(dA_e)^2 = \frac{16c(dA_0)^2B^2C^2}{g^2h^2(m^2 + b^2)},$$

where c has the value assigned above. This may be expanded into the form

$$J_e d\epsilon_1 d\epsilon_3 = \frac{c^2 k^2}{\sin^2 \theta} \cdot \frac{\sin^2 \{n(\epsilon_2 - \epsilon_1)\}}{\{n(\epsilon_2 - \epsilon_1)\}^2} \cdot \frac{\sin^2 \{p(\epsilon_3 + \epsilon_4)\}}{\{p(\epsilon_3 + \epsilon_4)\}^2} \cdot \frac{A_0^2 d\epsilon_1 d\epsilon_3}{m^2 + g\epsilon_2^2},$$

where $n = \pi l/\lambda$, $p = \pi k/\lambda$, and $q = (4\pi/\lambda)\cos \theta$, and dJ_e and dA_0 are written as $J_e d\epsilon_1 d\epsilon_3$ and $A_0 \sqrt{d\epsilon_1 d\epsilon_3}$ respectively. dJ_e has its greatest value when all the ϵ 's are zero, and is then

$$dJ_{(\max)} = \frac{c(dA_0)^2 l^2 k^2}{\mu^2}.$$

The maximum intensity of the reflected beam is thus independent of θ except for the function dA_0 , a result which is in accord with that found by Webster¹⁰ on similar assumptions.

It is not, however, this maximum intensity which is measured in the experiments. It is customary^{2, 6} rather to have the opening into the ionization chamber which measures the reflected X-ray beam large enough to receive the rays reflected at all angles ϵ_2 and ϵ_4 . If the X-rays come from a point source, the angle ϵ_3 has all values between $-k/2r$ and

¹⁰ D. L. Webster, PHYS. REV., 5, 241 (1915).

+ $k/2r$, where r is the distance from the anticathode to the slit, and ϵ_1 has a range of values $\delta\epsilon_1 = l/r$. The energy per unit time in the reflected beam which is due to the rays incident at angles between ϵ_1 and $\epsilon_1 + d\epsilon_1$ is therefore,

$$E_{\epsilon_1} d\epsilon_1 = \int_{-\infty}^{\infty} R d\epsilon_4 \int_{-k/2r}^{+k/2r} d\epsilon_3 \int_{-\infty}^{\infty} R d\epsilon_2 \cdot J_{\epsilon} d\epsilon_1.$$

If the crystal is rotated with a constant angular velocity $\omega = d\epsilon_1/dt$, it is exposed to rays incident at the angle ϵ_1 for a time $\delta\epsilon_1/\omega = \delta t$, and the total reflected energy due to the rays incident at the angle ϵ_1 is $E_{\epsilon_1} d\epsilon_1 \cdot \delta t$. If in the time Δt the crystal moves through all angles ϵ_1 at which any appreciable radiation of wave-length λ is reflected, the whole reflected energy is thus,

$$E_r = \delta t \int_{-\infty}^{\infty} E_{\epsilon_1} d\epsilon_1 = R^2 \delta t \int_{-\infty}^{\infty} d\epsilon_4 \int_{-k/2r}^{+k/2r} d\epsilon_3 \int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\infty} d\epsilon_1 \cdot J_{\epsilon}.$$

Substituting the value of J_{ϵ} given above, and integrating, this becomes,

$$E_r = \frac{cA_0^2 R^2 l^2 k^3}{r \sin^2 \theta} \cdot \frac{\pi^3}{mn\hbar q} \delta t,$$

or

$$(4) \quad E_r = \frac{c l^2 k^2 \lambda^3 \cdot N^2 A_i^2 \phi^2 \psi^2}{2r^2 \omega \mu \sin(2\theta)}.$$

The amplitude dA_i of the beam incident in the solid angle $d\sigma$ has been defined by the relation $c(dA_i)^2 = cA_i^2 d\sigma = I_i d\sigma$, where I_i is the intensity. The energy of the radiation in the solid angle $d\sigma = d\epsilon_1 d\epsilon_3$ which passes through the slit in unit time is therefore $klI_i d\sigma = cklA_i^2 d\epsilon_1 d\epsilon_3$, and as above, putting $\delta\epsilon_1 = l/r$, $\delta\epsilon_3 = k/r$, the total energy which passes through the slit in the time Δt is

$$E_i = klI_i \cdot \delta\epsilon_1 \delta\epsilon_3 \Delta t = \frac{k^2 l^2}{r^2} \cdot cA_i^2 \Delta t.$$

Writing $\Delta\theta = \omega\Delta t$ we find for the ratio of the reflected to the incident energy,

$$(5) \quad R = \frac{E_r}{E_i} = \frac{N^2 \lambda^3 \phi^2 \psi^2}{2\mu \sin 2\theta} \cdot \frac{1}{\Delta\theta},$$

where $\Delta\theta$ is the angle through which the crystal is turned while making the observations. This result is in accord with that obtained by Darwin, but is worked out for somewhat different experimental conditions.

Imperfect Crystal.—It remains to determine the effect of changing our assumptions. Let us consider the case in which the crystal is not perfect, but is made up of a large number of small crystals, each of which acts as a separate unit. We shall have to determine the energy in the beam reflected by each little crystal, and sum up for all the component crystals.

Each component crystal will for convenience be considered to have the form of a rectangular parallelepiped of dimensions δx , δy , δz . If one of these little crystals is so small that the rays are not appreciably absorbed in passing through it, the phase of the beam reflected from the whole little crystal is the same as that of the ray reflected from its center. In a crystal whose center is at x_1 , y_1 , z_1 the amplitude contributed by a crystal element at that point is, by equation (2), $e^{-\mu z_1/\sin \theta} dA_0 dx dy dz$. If δ is the phase difference between this ray and the one reflected from the point x , y , z , the amplitude contributed by a crystal element at x , y , z is therefore $e^{-\mu z_1/\sin \theta} dA_0 \cos \delta \cdot dx dy dz$. Substituting the value of δ similar to that used above, we find for the amplitude at P of the beam reflected by the whole little crystal,

$$\begin{aligned} dA_e' &= dA_0 e^{-\frac{\mu z_1}{\sin \theta}} \int_{z_1-(\delta z/2)}^{z_1+(\delta z/2)} dz \int_{y_1-(\delta y/2)}^{y_1+(\delta y/2)} dy \int_{x_1-(\delta x/2)}^{x_1+(\delta x/2)} dx \cdot \cos \frac{2\pi}{\lambda} \\ &\quad \times \{ (x-x_1)(\epsilon_2-\epsilon_1) \sin \theta + (y-y_1)(\epsilon_3+\epsilon_4) + (z-z_1)(\epsilon_1+\epsilon_2) \cos \theta \} \\ &= dA_0 e^{-\frac{\mu z_1}{\sin \theta}} \cdot \frac{\sin \left\{ \frac{\pi \delta x}{\lambda} (\epsilon_2 - \epsilon_1) \sin \theta \right\}}{\frac{\pi \delta x}{\lambda} (\epsilon_2 - \epsilon_1) \sin \theta} \cdot \frac{\sin \left\{ \frac{\pi \delta y}{\lambda} (\epsilon_3 + \epsilon_4) \right\}}{\frac{\pi \delta y}{\lambda} (\epsilon_3 + \epsilon_4)} \\ &\quad \times \frac{\sin \left\{ \frac{\pi \delta z}{\lambda} (\epsilon_1 + \epsilon_2) \cos \theta \right\}}{\frac{\pi \delta z}{\lambda} (\epsilon_1 + \epsilon_2) \cos \theta} \cdot \delta x \delta y \delta z. \end{aligned}$$

As before, the whole energy reflected by this crystal as it is turned through an angle $\Delta\theta$ at an angular velocity ω is given by

$$E_r' = R^2 \delta t \int_{-\infty}^{\infty} d\epsilon_4 \int_{-(k/2r)}^{+(k/2r)} d\epsilon_3 \int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\infty} d\epsilon_1 \cdot c(A_e')^2.$$

Substituting the above value of $A_e' = dA_e'/d\epsilon_1 d\epsilon_3$ and integrating, we obtain

$$E_r' = \frac{cA_0^2 R^2 k l \lambda^3 e^{-\frac{2\mu z_1}{\sin \theta}}}{2r^2 \omega \sin \theta \cos \theta} \delta x \delta y \delta z.$$

The energy reflected from the whole crystal is of course the sum of the energies reflected from all the component crystals, *i. e.*, $E_r = \Sigma E_r'$, or replacing the summation sign by an integral,

$$\begin{aligned} (4a) \quad E_r &= \int_0^{\infty} dz \int_{-(k/2)}^{+(k/2)} dy \int_{z \cot \theta - (l/2) \sin \theta}^{z \cot \theta + (l/2) \sin \theta} dx \cdot \frac{cA_0^2 R^2 k l \lambda^3 e^{-\frac{2\mu z}{\sin \theta}}}{2r^2 \omega \sin \theta \cos \theta} \\ &= \frac{c^2 k^2 \lambda^3 N^2 A_i^2 \phi^2 \psi^2}{2r^2 \omega \mu \sin 2\theta}, \end{aligned}$$

which is the same as was found in the case of a perfect crystal. Although this result has been obtained from the consideration of one particular type of imperfect crystal, it is evident that the same formula will hold in whatever manner the crystal is divided into its components.

Short Trains of Waves.—It has been pointed out by Webster¹⁰ that if X-rays do not come in long trains like light waves, but come rather in trains which are short compared with the depth to which they penetrate the crystal, the intensity of the reflected beam at the angle of maximum reflection is proportional to $1/\sin^2 \theta$. He has since noted, however,¹¹ that the breadth of the reflected line increases with θ so that the total reflected energy does not obey the same law. The following analysis will show that the total energy reflected in this case is the same as with long trains of waves. If we consider the primary beam to be made up of trains M waves in length, the total number of reinforcing layers is M/n , where n is the order of the reflection. The thickness of the crystal which is effective in reinforcement at any instant is therefore

$$\delta z = \frac{M}{n} D,$$

where D is the distance between two adjacent layers of atoms. If the point x_1, y_1, z_1 is the center of the part of the crystal which has reflected the ray reaching P ($R, \epsilon_2, \epsilon_4$) at any particular instant, the amplitude of of the reflected wave at P at that instant is

$$\begin{aligned} dA_0' e^{-\frac{\mu z_1}{\sin \theta}} \int_{z_1 \mp (MD/2n)}^{z_1 + (MD/2n)} dz \int_{-(k/2)}^{k/2} dy \int_{z \cot \theta - (l/2) \sin \theta}^{z \cot \theta + (l/2) \sin \theta} dx \\ \times \cos \frac{2\pi}{\lambda} \left\{ \begin{array}{l} (x - x_1)(\epsilon_2 - \epsilon_1) \sin \theta \\ + (y - y_1)(\epsilon_4 + \epsilon_3) \\ + (z - z_1)(\epsilon_1 + \epsilon_2) \cos \theta \end{array} \right\} \\ = dA_0' e^{-\frac{\mu z_1}{\sin \theta}} \cdot \frac{k l M D}{n \sin \theta} \cdot \frac{\sin u}{u} \cdot \frac{\sin v}{v} \cdot \frac{\sin w}{w}, \end{aligned}$$

where

$$u = \frac{\pi l}{\lambda} (\epsilon_2 - \epsilon_1), \quad v = \frac{\pi k}{\lambda} (\epsilon_3 + \epsilon_4), \quad w = \frac{2\pi M D}{n \lambda} \epsilon_2 \cos \theta,$$

and the corresponding intensity is

$$c(dA_0')^2 e^{-\frac{2\mu z_1}{\sin \theta}} \frac{k^2 l^2 M^2 D^2}{n^2 \sin^2 \theta} \cdot \frac{\sin^2 u}{u^2} \cdot \frac{\sin^2 v}{v^2} \cdot \frac{\sin^2 w}{w^2}.$$

Since by hypothesis the primary train of waves is short compared with the depth to which it penetrates the crystal, the length of the reflected train will depend, not on that of the incident one, but only upon the depth

of penetration. In order to find the mean intensity of the reflected beam at this angle, we must therefore integrate this intensity over the whole length of the reflected train, and divide by the average distance between successive trains of waves. If this distance is ρ , the mean intensity of the reflected beam at this angle is thus,

$$\begin{aligned} \frac{c}{\rho} (dA_0')^2 \frac{k^2 l^2 M^2 D^2}{n^2 \sin^2 \theta} \cdot \frac{\sin^2 u}{u^2} \cdot \frac{\sin^2 v}{v^2} \cdot \frac{\sin^2 w}{w^2} \int_0^\infty e^{-\frac{2\mu z}{\sin \theta}} \cdot 2 \sin \theta \, dz \\ = \frac{c(dA_0')^2 l^2 k^2 M^2 D^2}{\rho n^2 \mu} \cdot \frac{\sin^2 u}{u^2} \cdot \frac{\sin^2 v}{v^2} \cdot \frac{\sin^2 w}{w^2}. \end{aligned}$$

Since $n\lambda = 2D \sin \theta$, this may be written:

$$J_\epsilon d\sigma = \frac{cM^2 \lambda^2 k^2 l^2 (dA_0')^2}{4\rho \mu \sin^2 \theta} \cdot \frac{\sin^2 u \sin^2 v \sin^2 w}{u^2 v^2 w^2}.$$

When $u = v = w = 0$, this intensity is a maximum, and the resulting expression agrees with that obtained by Webster. To obtain the whole energy of the reflected beam, however, we must have as before,

$$E_r = R^2 \delta t \int_{-\infty}^{\infty} d\epsilon_4 \int_{-(k/2r)}^{+(k/2r)} d\epsilon_3 \int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\infty} d\epsilon_1 \cdot J_\epsilon,$$

and substituting the above value of J_ϵ this becomes

$$E_r = \frac{cM\lambda^4 k^2 l^2 (A_i')^2 N^2 \phi^2 \psi^2}{2r^2 \omega \rho \mu \sin 2\theta}.$$

The mean value of the square of the amplitude of the incident beam is evidently $A_i^2 = A_i'^2 \cdot M\lambda/\rho$, so the energy of the reflected beam is as formerly,

$$(4b) \quad E_r = \frac{cl^2 k^2 \lambda^3 N^2 A_i^2 \phi^2 \psi^2}{2r^2 \omega \mu \sin 2\theta},$$

where cA_i^2 now represents the mean intensity of the incident beam instead of its intensity at a given instant.

If there is any difference in the reflecting power of a crystal according to its degree of perfection or the nature of the incident rays, it must therefore be accounted for by a difference in the value of the absorption coefficient μ , since all the other factors in equation (4) have definitely defined values. It has been found by Darwin⁷ that the value of this absorption coefficient does differ according to the degree of perfection of the crystal. This results from the fact that a sort of selective absorption occurs near the angle of maximum reflection, which is great only in the case of a crystal that is nearly perfect. Darwin concludes, however, that this effect may be accounted for by inserting a constant factor into

the reflection formula.* We may therefore consider the expression here derived for the energy of the reflected beam of X-rays to hold for any crystal and any beam of X-rays if μ is taken as the *effective* absorption coefficient.

If a beam of X-rays of wave-length λ , polarized so that its electric vector is perpendicular to the plane of incidence, is reflected at an angle θ from a crystal in which all the atomic layers are equally spaced and whose atoms have no thermal motion, the energy in the reflected beam is therefore given by equation (5) as

$$E_r = \frac{E_i N^2 \lambda^3 \phi^2 \psi^2}{\Delta\theta 2\mu \sin 2\theta},$$

where E_i is the whole energy of the radiation of wave-length λ which strikes the crystal as it is turned with uniform angular velocity through an angle $\Delta\theta$, and $\Delta\theta$ is large enough to include all the angles at which rays of wave-length λ are reflected. N is the number of electrons per unit volume of the crystal, μ is the effective absorption coefficient of the X-rays in the crystal at the angle of reflection, and may differ by a constant factor from the coefficient of absorption at other angles. ϕ is the amplitude at unit distance of the ray scattered by a single electron, and has the value e^2/mC^2 . ψ is a factor depending upon the arrangement of the electrons in the atomic layers, and has the value

$$\int_a^b F(z) \cos\left(\frac{4\pi \sin \theta}{\lambda} z\right) dz,$$

where $b - a$ is the diameter of an atom, and $F(z)$ is the probability that

* The statement that this correction for selective absorption at the angle of maximum reflection can be accounted for by the insertion of a constant factor into the reflection formula implies that this absorption is equally strong in all orders. Darwin has shown (*loc. cit.*) that this means a high degree of imperfection of the reflecting crystal. If the crystal is more perfect, the selective absorption must be large compared to the normal absorption and be proportional to $1/\sin 2\theta$. This would make the reflected energy E independent of the angle except for the factor ψ . Darwin considers the fact that the reflected energy at the larger angles is known to fall off rapidly to be sufficient proof that the reflecting crystals cannot be so perfect. It is to be noted, however, that since it is possible, as will be shown below, completely to explain the low intensity of the higher orders by assuming the proper distributions of the electrons in the atoms, the existence of this diminution cannot properly be used to prove the imperfection of the crystal. The fact that the absorption coefficient μ which is to be used in the reflection equation is found by Darwin to be of the same order of magnitude as the normal absorption coefficient indicates, however, that the selective absorption is not large, and hence that the crystal must be very imperfect. The writer has recently made a series of experiments comparing the rate of falling off of the higher orders when tungsten and rhodium rays are reflected from the same crystal. These experiments, which will be published in the near future, indicate rather definitely the existence of the term $\sin 2\theta$ in the denominator of the reflection expression, which would not occur if the crystal used were not sufficiently imperfect to make the absorption coefficient approximately constant.

a given electron will be at a distance z from the mid-plane of the atomic layer to which it belongs. This factor corresponds to the "excess scattering" factor introduced by Darwin.⁴ As pointed out above, if the primary beam of X-rays is unpolarized, the factor $\frac{1}{2}(1 + \cos^2 2\theta)$ will have to be introduced, and to account for the thermal motion of the atoms the factor $e^{-B \sin^2 \theta}$ must also be included. Introducing these factors, writing $\sin 2\theta = 2 \sin \theta \cos \theta$, and expanding the terms ϕ and ψ , the complete expression for the energy of the reflected beam becomes:

$$(6) \quad E_r = \frac{E_i}{\Delta\theta} \cdot \frac{N^2 \lambda^3}{2\mu} \cdot \frac{1 + \cos^2 2\theta}{4 \sin \theta \cos \theta} \left(\frac{e^2}{mC^2} \right)^2 \\ \times \left\{ \int_a^b F(z) \cos \frac{4\pi z \sin \theta}{\lambda} dz \right\}^2 \cdot e^{-B \sin^2 \theta}.$$

It may be remarked that this same equation holds when the crystal remains stationary if the angular aperture $\Delta\theta$ of the slit as observed from the anticathode includes all the angles at which X-rays of wavelength λ are reflected.

THE DISTRIBUTION OF THE ELECTRONS IN ATOMS.

By comparing this equation with Bragg's experimental formula (1) it should be possible to determine the form of the function $F(z)$, and hence to find the mean distances of the electrons from the centers of their respective atoms. We shall first attempt a direct solution of the problem, and shall find that there is no possible distribution of the electrons in atoms which will give Bragg's formula as it stands; but a slightly modified form of his law will be found to lead to a definite value of $F(z)$, thus determining the probable distance of an electron from the center of its atom. On comparison with experiment it will be shown, however, that the differences in the intensities of reflection by different crystals are such that no single distribution of the electrons can explain the reflection from all crystals. Arbitrarily chosen distributions which will explain satisfactorily the observed differences between the reflections from certain crystals will then be described, and these will be of considerable interest in connection with certain hypotheses concerning the structure of the atom.

Direct Method.—According to equation (6), if X-rays of wave-length λ are reflected by a certain crystal at two different angles, θ and θ_1 , the ratio of the energy in the reflected beam in the two cases is

$$(7) \quad \frac{E}{E_1} = \frac{\frac{1 + \cos^2 2\theta}{\sin \theta \cos \theta} \left\{ \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta}{\lambda} \right) dz \right\}^2 e^{-B \sin^2 \theta}}{\frac{1 + \cos^2 2\theta_1}{\sin \theta_1 \cos \theta_1} \left\{ \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta_1}{\lambda} \right) dz \right\}^2 e^{-B \sin^2 \theta_1}}.$$

Bragg's experimental formula (1) gives this ratio as

$$(8) \quad \frac{E}{E_1} = \frac{\frac{1 + \cos^2 2\theta}{\sin^2 \theta} e^{-B \sin^2 \theta}}{\frac{1 + \cos^2 2\theta_1}{\sin^2 \theta_1} e^{-B \sin^2 \theta_1}}$$

and on comparing these two expressions, we find

$$(9) \quad \frac{\left\{ \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta}{\lambda} \right) dz \right\}^2}{\left\{ \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta_1}{\lambda} \right) dz \right\}^2} = \frac{\tan \theta_1}{\tan \theta}.$$

Extracting the square root, and substituting

$$\begin{aligned} x &= \frac{4\pi \sin \theta_1}{\lambda} z, & \phi(x) &= F \left(\frac{\lambda x}{4\pi \sin \theta_1} \right) = F(z), \\ \alpha^2 &= \frac{\tan \theta}{\tan \theta_1}, & \beta &= \frac{\sin \theta}{\sin \theta_1}, \\ r &= \frac{4\pi \sin \theta_1}{\lambda} a, & s &= \frac{4\pi \sin \theta_1}{\lambda} b, \end{aligned}$$

this equation may be reduced to the form

$$(10) \quad \int_r^s \phi(x) \{ \alpha \cos(\beta x) \pm \cos x \} dx = 0.$$

From this equation we have to evaluate the function $\phi(x)$ and the limits of integration, r and s .

This seems to be a difficult form of integral equation to attack by direct mathematical methods. It is possible by graphical methods to show that there are an infinite number of solutions of the form $\phi(x) = c \sin px$, if $r = -s$, where the constants c and p can have any value. These solutions, however, imply that the probability function ϕ becomes negative at certain points, which is meaningless, so that they do not apply to this problem. There are also an infinite number of solutions of the type

$$\phi(x) = c_1 \sin^n p_1 x + c_2 \cos^m p_2 x + c_3,$$

if p_1 and p_2 are integers, r and s are integral multiples of π , β is an integer, c_1 , c_2 , n , m , may have any value, and c_3 is large enough to prevent the expression from becoming negative. Experiment shows, however, that β is not necessarily an integer, so that these solutions also do not apply. Other possible solutions are not obvious.

The necessary form of the function $F(z)$, and hence also of the function

$\phi(x)$ can be found, however, by certain physical considerations. If we consider the primary beam of X-rays to be plane polarized, and the reflecting crystal to be at a very low temperature, the experimental law expressed in equation (8) becomes $E/E_1 = \sin^2 \theta_1 / \sin^2 \theta$. The ratio of the intensity of the reflected beam at two different angles thus depends only upon the angles at which reflection occurs, and is independent of the wave-length of the reflected beam. Thus with the layers of atoms at a distance a apart and with a beam of X-rays of wave-length λ , the ratio of the reflected energy at the two angles θ and θ_1 is the same as when the layers are at a distance ma apart using X-rays of wave-length $m\lambda$. Since, however, the ratio of these intensities is determined by the distribution of the electrons in the atomic layers, this means that this distribution shall be the same on the scale ma as it is on the scale a . That is, if the density of distribution is p times as great at $z = (1/q)a$ as at $z = (n/q)a$, it must be also p times as great at $z = (1/q)(ma)$ as at $z = (n/q)(ma)$, or

$$p = \frac{F\left(\frac{1}{q}a\right)}{F\left(\frac{n}{q}a\right)} = \frac{F\left(\frac{1}{q}ma\right)}{F\left(\frac{n}{q}ma\right)},$$

and in general

$$(11) \quad \frac{F(z)}{F(nz)} = \frac{F(mz)}{F(nmz)},$$

where the constants n and m may have any value. The only type of function which will satisfy this relation may be shown to be

$$\begin{aligned} F(z) &= b_1 z^{-p} & [z > 0] \\ &= b_1 (-z)^{-p} & [z < 0], \end{aligned}$$

where b_1 and p are arbitrary constants. Since

$$(12) \quad \phi(x) = F(z) = b_1 \left\{ \frac{\lambda x}{4\pi \sin \theta} \right\}^{-p} = bx^{-p} \quad [x > 0].$$

Equation (11) shows that the density of distribution of the electrons can vanish nowhere unless it is everywhere zero, so the limits of integration of equation (10) must be $-\infty$ and ∞ . This of course corresponds to an atom with an infinite radius.

Substituting this value for $\phi(x)$, and remembering that the function under the integral sign is symmetrical on both sides of the plane $z = 0$,

equation (10) may be written

$$(13) \quad \int_0^{\infty} x^{-p} \{ \alpha \cos \beta x \pm \cos x \} dx = 0$$

The integral is a known one,¹² the solution being

$$\begin{aligned} & (\alpha\beta^{p-1} \pm 1) \frac{\pi}{2\Gamma(p)} \sec\left(\frac{p\pi}{2}\right) \text{ for } [0 < p < 1] \\ & \infty \text{ for } [p \geq 1] \\ & \text{indeterminate for } [p \leq 0]. \end{aligned}$$

This integral can vanish only when

$$\alpha\beta^{p-1} \pm 1 = 0$$

or

$$\frac{\cos \theta}{\cos \theta_1} = \left\{ \frac{\sin \theta}{\sin \theta_1} \right\}^{2p-1}.$$

Since θ and θ_1 can have any values, it is obvious that there is no constant value of p which will satisfy this equation. Thus there is no solution of the integral equation (10) which meets the conditions. We must conclude, therefore, that there is no possible distribution of the electrons in the atomic layers which will give Bragg's experimental law as it stands.*

If equation (1) is modified by inserting the factor $\cos \theta$ in the denominator, its value is not greatly changed, since θ is usually small. This modification changes the quantity on the right-hand side of equation (9) to $\sin \theta_1 / \sin \theta$, and the coefficient α in equations (10) and (13) becomes $(\sin \theta / \sin \theta_1)^{1/2}$, the other quantities remaining unchanged. In this case the left hand side of equation (13) vanishes only when

$$\frac{\sin^{1/2} \theta}{\sin^{1/2} \theta_1} \cdot \left\{ \frac{\sin \theta}{\sin \theta_1} \right\}^{p-1} = 1,$$

or

$$p = \frac{1}{2}$$

(14) whence

$$\begin{aligned} F(z) &= b_1 z^{-1/2} & [z > 0] \\ &= b_1 (-z)^{-1/2} & [z < 0]. \end{aligned}$$

Thus although Bragg's law in its original form is not given by any possible

¹¹ D. L. Webster, *PHYS. REV.*, 7, 696 (1916).

¹² Bierens de Haan, *Nouv. Tables d'integrales definies.*

* On somewhat different assumptions from those used here, Professor Bragg has found a distribution of the scattering material which leads to the law $E/E_1 = n_1^2/n^2$, where n is the order of reflection.⁸ The distribution he finds is, however, a function of the distance between the atomic layers, and so cannot truly represent the arrangement of the electrons in the atoms. In fact it is possible to show by reasoning similar to that used above that on his assumptions also there is no distribution of the electrons which will give his law for the intensity of reflection.

distribution of the electrons, it can be obtained in a slightly modified form if the density of distribution of the electrons is inversely proportional to the square root of the distance from the mid-plane of the atomic layer to which they belong.

The quantity $F(z)$ represents the probability that a given electron shall be at a distance z from the middle of its layer of atoms at any instant. It is evident, therefore, that the relation $\int_{-\infty}^{\infty} F(z) dz = 1$ or $\int_0^{\infty} F(z) dz = \frac{1}{2}$ must be satisfied. The constant b_1 in equation (12), representing the probability $F(z)$ at unit distance from the mid-plane is thus defined by the expression

$$b_1 \int_0^{\infty} z^{-p} dz = \frac{1}{2},$$

or

$$b_1 = 0,$$

since

$$\int_0^{\infty} z^{-p} dz = \infty$$

for all values of p . This means that there can be no appreciable density of distribution of the electrons in the atomic layer unless there are an infinite number of electrons in it. It is evident therefore that the function $F(z)$ cannot have the form $b \cdot z^{-p}$. According to the argument above, this means that the relative intensity of the beam of X-rays reflected at different angles must depend not only upon the angle of reflection, but also upon the wave-length of the incident beam of X-rays.

Empirical Method.—Since there is no possible distribution of the electrons in the atoms which will give a law of reflection of the form of Bragg's empirical expression, let us see if it is not possible to find some arbitrary distribution which will give a reflection formula fitting the experimental data better than his law. In order conveniently to compare data obtained with different crystals and with X-rays of different wave-lengths, let us remember, according to equation (7), that the part of the ratio E/E_1 which is due to the diffuseness of the atomic planes is

$$U^2 = \frac{\left\{ \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta}{\lambda} \right) dz \right\}^2}{\left\{ \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta_1}{\lambda} \right) dz \right\}^2} = \frac{\psi^2}{\psi_1^2} = \frac{E}{E_1} \cdot \frac{\frac{1 + \cos^2 2\theta_1}{\sin \theta_1 \cos \theta_1} \cdot e^{-B \sin^2 \theta_1}}{\frac{1 + \cos^2 2\theta}{\sin \theta \cos \theta} \cdot e^{-B \sin^2 \theta}}.$$

From any assumed distribution of electrons $F(z)$ the theoretical values of

$$(15) \quad U = \frac{\psi}{\psi_1}$$

may be calculated for different angles of reflection, and by comparison with the corresponding experimental values as given by the equation

$$(16) \quad U = \left\{ \frac{E}{E_1} \cdot \frac{\frac{1 + \cos^2 2\theta_1}{\sin \theta_1 \cos \theta_1} \cdot e^{-B \sin^2 \theta_1}}{\frac{1 + \cos^2 2\theta}{\sin \theta \cos \theta} \cdot e^{-B \sin^2 \theta}} \right\}^{1/2},$$

the accuracy of the assumed distribution may be tested.

For the cases of rock-salt and calcite the values of E/E_1 have been determined experimentally by Professor Bragg.^{2, 8} His results are given in Tables I. and II., columns 3. In the case of calcite the reflection at

TABLE I.

Rock-Salt.

Crystal Face.	$\frac{\sin \theta}{\sin \theta_1}$	$\frac{E}{E_1}$	U_{obs}	U_{calc_1}	U_{calc_2}
100	1.00	1.00	1.00	1.00	1.00
110	1.41	.41	.79	.83	.81
111	1.73	.244	.69	.75	.695
100	2.00	.187	.67	.70	.63
110	2.83	.0705	.55	.58	.56
100	3.00	.0625	.55	.56	.55
111	3.46	.042	.54	.51	.50

TABLE II.

Calcite.

Crystal Face.	$\frac{\sin \theta}{\sin \theta_1}$	$\frac{E}{E_1}$	U_{obs}	U_{calc_1}	U_{calc_2}
$\bar{1}\bar{1}\bar{1}$.80	1.44	1.05	1.12	1.03
100	1.00	1.12	1.03	1.00	1.00
111	1.07	.95	.98	.97	.98
$\bar{1}\bar{1}\bar{0}$	1.24	.67	.88	.90	.95
110	1.59	.46	.86	.78	.87
$\bar{1}\bar{1}\bar{1}$	1.60	.48	.88	.78	.87
100	2.00	.257	.72	.70	.79
211	2.12	.286	.78	.68	.76
111	2.14	.297	.80	.68	.76
$\bar{1}\bar{1}\bar{0}$	2.46	.164	.65	.62	.69
100	3.00	.113	.61	.56	.60
110	3.22	.091	.57	.54	.58
$\bar{1}\bar{1}\bar{1}$	3.21	.108	.62	.54	.58
100	4.00	.034	.41	.48	.44
111	4.28	.036	.42	.46	.42
110	4.78	.021	.37	.43	.36
$\bar{1}\bar{1}\bar{0}$	4.91	.013	.30	.42	.35

different angles is produced by layers of different kinds of atoms, but the values here given have been corrected according to the method explained by Professor Bragg⁸ for the effect of the differences in the atomic layers, so these figures may be taken as due to a crystal all of whose atoms are similar and whose atomic layers are uniformly spaced. In these tables

θ_1 is taken as the angle of the first order reflection from the (1, 0, 0) face of the crystal. The values of U calculated from the observed values of E/E_1 are given in columns 4, and are plotted in Fig. 3 against the corresponding values of $\sin \theta/\sin \theta_1$.^{*} The open circles in this figure represent the experimental values of U for rock-salt, and the solid ones for calcite. The agreement between the results of successive experiments indicates that these data may be taken as accurate within a probable error of

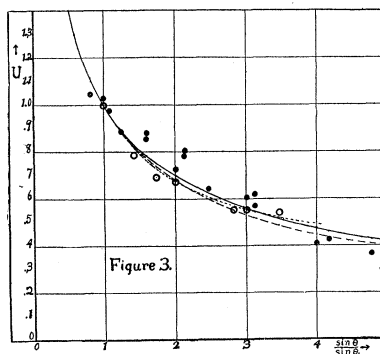


Fig. 3.

about one or two per cent., although consistent errors of considerably greater magnitude may occur due to various causes.

The values of U calculated from Bragg's law, equation (1), are given in columns 5 of the tables and are shown on Fig. 3 by the solid line. If the function $F(z)$ is assumed to have the form bz^{-p} , U has the values observed for the first and second order reflections from rock-salt when

* In calculating the values of U here given, the constant B in equation (16) has been evaluated by Debye's formula,³

$$B = \frac{1.142 \times 10^{-12} \phi(x)}{A\theta\lambda^2 x},$$

where A is the atomic weight, θ is Debye's "characteristic temperature," $x = \theta/T$, where T is the absolute temperature, and $\phi(x)$ is a function which Debye evaluates. The value of B thus calculated has been found by Bragg² to account with considerable accuracy for the observed changes of the intensity of reflection with temperature. For rock-salt $\theta = 260^\circ \text{K.}$, $A = 29$, $x = .89$, $\phi = .80$, and using rhodium rays of wave-length $\lambda = .614 \times 10^{-8}$ we obtain $B = 3.6$. In the case of calcite $\theta = 910^\circ$ (determined from the specific heat at 298°K.), and taking $A = 20$, $x = 3.10$ and $\phi = .473$ we find $B = 0.25$. It is these values which have been used in calculating U . If a "Nullpunktenergie" is assumed, Debye shows that the value of B is

$$B = \frac{1.142 \times 10^{-12}}{A\theta\lambda^2} \left(\frac{\phi(x)}{x} + \frac{1}{4} \right).$$

In this case for rock-salt $B = 4.6$ and for calcite $B = .67$. This makes no very large difference in the values of U . In any case the effect of the temperature factor is not large at the angles at which these measurements are made, so that any slight error in the value of B will not greatly affect the results.

$p = 0.425$, which gives $U = (\sin \theta_1 / \sin \theta)^{.575}$. This expression is plotted in the broken line of Fig. 3, and is about as accurate an expression for the reflected energy as can be obtained with this type of function. Professor Bragg has suggested⁸ the use of a function of the form $F(z) = be^{-cz}$ to express the distribution of the electrons. The coefficient b in this case has a finite value, so although this function also implies an atom of infinite radius it is not *a priori* impossible. It can be shown, however, that the values of U obtained with such a distribution are considerably too large at moderately small angles, and decrease much too rapidly at large angles. Better agreement is obtained if a distribution of this type is combined with a certain concentration $F(0) = a$ of the electrons at the middle of the reflecting layers. In this case

$$U = \frac{a/b + c / \left\{ c^2 + \left(\frac{4\pi \sin \theta}{\lambda} \right)^2 \right\}}{a/b + c / \left\{ c^2 + \left(\frac{4\pi \sin \theta_1}{\lambda} \right)^2 \right\}}.$$

In order to make the values of U thus calculated agree with the observed values for the second and third orders of reflection from rock-salt we must put $a/b = 0.274 \lambda$ and $c = 1.51/\lambda$. The values of U thus obtained are plotted in the dotted curve of Fig. 3, and are seen to be in better agreement with the experiments on rock-salt than is the empirical law expressed by the solid curve. A comparison of the experimental data for rock-salt and calcite as shown in Fig. 3 shows at once that a curve which corresponds to the observed values of U for rock-salt cannot fit accurately the data for calcite. Professor Bragg has suggested⁸ the possibility of the existence of such a difference, but it was a difficult thing to detect on account of the many disturbing factors. Since by equation (15) U is a function only of the distribution of the electrons in the atomic layers and of $\sin \theta/\lambda$, any observed differences in U for a given value of $\sin \theta/\lambda$ can be explained only by differences in the distributions of the electrons in the layers of atoms which do the reflecting. Thus we may conclude that the distribution is not the same in the atoms of calcite as it is in the atoms of rock-salt.* It appears, therefore, that

* Note added December 9, 1916: A more striking example of the difference in the value of U for different crystals is afforded by Vegard's recent determination of the intensity of X-ray reflection from silver (Phil. Mag., 32, 94, July, 1916). He finds the intensity of the first three orders of reflection from the (111) plane to be in the ratio of 1.00 : 0.45 : 0.11, respectively. The corresponding values of U are 1.00 : 1.03 : 0.73. In the case of rock-salt we have found the values of U for the first three orders of reflection from the (100) plane to be 1.00, 0.67 and 0.55. The difference is too great to be accounted for by experimental error. Since, as pointed out above, U depends only upon the distribution of the electrons in the atoms of the crystal, these differences must be taken as a strong confirmation of our

instead of considering the electrons to be distributed according to some general law such as we have been discussing, one should rather consider every atom to possess a finite number of electrons, each placed at a definite distance from its center.

Atoms with a Finite Number of Electrons.—If each atom of a certain kind has an electron at a distance a from its center, the average effect from a large number of such atoms will be the same as that due to a uniform distribution of the electrons over the surface of a sphere of radius a . The center of this equivalent spherical shell will be in the mid-plane of the atomic layer, and the probability that a given electron in the shell will be at a distance z from the middle of the layer may be shown to be

$$F(z) = c \quad [-a < z < a],$$

or, in virtue of the relation

$$\int_{-a}^a c dz = 1,$$

$$F(z) = \frac{1}{2a} [-a < z < a].$$

The value of ψ due to an electron in such a shell is therefore

$$(17) \quad \psi' = \frac{1}{2a} \int_{-a}^a \cos \left(\frac{4\pi z \sin \theta}{\lambda} \right) dz = \frac{\sin \left(\frac{4\pi a \sin \theta}{\lambda} \right)}{\frac{4\pi a \sin \theta}{\lambda}},$$

and the value of ψ for a whole atom is

$$(18) \quad \psi = \frac{1}{\nu} \sum_r \psi_r' = \frac{1}{\nu} \sum_r \sin \left(\frac{4\pi a_r \sin \theta}{\lambda} \right) / \left(\frac{4\pi a_r \sin \theta}{\lambda} \right),$$

where ν is the number of electrons in the atom, and the summation extends over all the r 's from 1 to ν . In any actual case this summation is most readily performed by plotting ψ' according to equation (17) and taking off its values corresponding to the desired values of $a \sin \theta / \lambda$. From the value of ψ thus obtained, the quantity U can be calculated as before by equation (15).

Attempts to obtain a suitable formula for U by thus adding the effects of a number of electrons placed at arbitrary distances a from the centers fundamental assumption that the intensity of X-ray reflection depends upon the distribution of the electrons in the atoms of the reflecting crystal. If the values of U for silver are calculated on the basis of the assumptions used below in the case of calcite, giving to each electron an angular momentum of h/π , we obtain the values of U for the first three orders of reflection as 1.00 : 0.93 : 0.82. Though the agreement is far from perfect, it is much better than that obtained with the values 1.00 : 0.70 : 0.56, assigned by Bragg's law.

of the atoms soon convince one that the form of the resulting curve is very sensitive to changes in the assumed values of a . The results obtained above indicate that there must be a rather strong concentration of the electrons near the centers of the atoms, but it is difficult to select a distribution of the outer electrons which will give a reflection formula that agrees with the experimental data.

In the case of calcite it was found that a fairly acceptable expression could be obtained if the atoms of calcium, carbon and oxygen were assumed to have a number of electrons equal to their positive valence, *i. e.*, 2, 4 and 6, respectively, placed at distances from the centers of the atoms inversely proportional to the valence, together with an arbitrary number of electrons placed at the centers of the atoms. The use of this number of electrons in the outer part of each atom was suggested by well-known theories of valence, while some such spacing as this seemed necessary in order to obtain a suitable formula for U . This assumption concerning the spacing is, however, very nearly what is to be expected if these valency electrons revolve in rings about the centers of their respective atoms, all the electrons having the same angular momentum. For according to classical mechanics,¹³ the centrifugal force $m\omega^2a$, where m is the mass and ω the angular velocity of the electron and a is the radius of its orbit, must be balanced by the centripetal force $(M - \sigma_n)e^2/a^2$ where e is the electronic charge, M is the total charge in electronic units on the part of the atom inside the ring considered, and σ_n is a term which depends upon the mutual repulsion between the electrons in the same ring. With one electron in the ring $\sigma_1 = 0$, for two $\sigma_2 = .25$, and similarly $\sigma_4 = .96$, $\sigma_6 = 1.83$, $\sigma_7 = 2.31$ and $\sigma_8 = 2.81$. But if the angular momentum is constant, *i. e.*, $ma^2\omega = c$, we may write

$$ma \cdot \frac{c^2}{m^2a^4} = \frac{e^2}{a^2}(M - \sigma_n),$$

or

$$(19) \quad a = \frac{c^2}{me^2} \frac{1}{(M - \sigma_n)}.$$

Since for the outer ring of a neutral atom M is equal to the number of electrons in the ring, a is thus approximately inversely proportional to the number of valency electrons. This suggested, therefore, the assumption of the constancy of the angular momentum of the electrons in the atoms as a working basis.

It is of course possible to find any number of satisfactory arrangements unless the number of electrons in the atoms is defined. Barkla has shown¹³ that the number of electrons in an atom which are effective in

¹³ H. G. J. Moseley, *Phil. Mag.*, 26, 1032 (1913).

scattering X-rays is approximately equal to half the atomic weight. His work in connection with that of Rutherford on the scattering of alpha particles¹⁵ and of Moseley on the high frequency spectra of the elements¹⁴ makes it very probable that if N is the atomic number, there are N electrons distributed about the atomic nucleus, and that all these electrons are effective in scattering X-rays. This, together with the assumption used above concerning the valency electrons, determines the number of electrons in both rings of the first row of elements in the periodic table, including carbon and oxygen. For the second and third rows it has been assumed, in accordance with Moseley's interpretation of his X-ray spectra,¹³ that the inner ring contains 4 electrons. This leaves 6 electrons in the middle ring of the second row of atoms. There remain 8 electrons to be placed in the calcium atom, and it seemed reasonable to put these in a ring just inside of the valency electrons.

With the number of electrons in each ring thus determined, the relative distance of each electron from the nucleus can immediately be

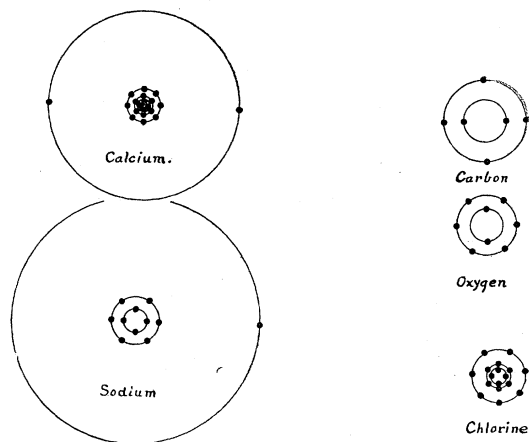


Fig. 4.

calculated by equation (19), and the corresponding values of U can be determined by equations (15) and (18). If the angular momentum of all the electrons is the same, their relative spacing in the atoms here used is as shown in Fig. 4. The value of U obtained for calcite on the basis of these assumptions is shown in the dotted curve of Fig. 5. Although the agreement is fair, it is evident that the theoretical values are too high in the low orders, and fall off too rapidly in the higher orders. It is to be noted that as there is but a single arbitrary constant, the

¹⁴ C. G. Barkla, *Phil. Mag.*, 14, 408 (1907).

¹⁵ E. Rutherford, *Phil. Mag.*, 27, 488 (1914).

angular momentum of an electron, in the equation for U , even this general agreement indicates that we are working along the right line. If the assumptions are modified to the extent of giving the electrons in the inner rings and in the second calcium ring half the angular momentum of those in the outer rings, the values of U given in column 6 of Table II. and shown in the solid curve of Fig. 5 are obtained. The equation for ψ is in this case,

$$\psi = \frac{I}{50} \left\{ \begin{array}{l} [4 \sin (.013k \sin \theta) / .013k \sin \theta + 6 \sin (.018k \sin \theta) / .018k \sin \theta] \\ + 8 \sin (.139k \sin \theta) / .139k \sin \theta + 2 \sin (.571k \sin \theta) / .571k \sin \theta \\ + [2 \sin (.043k \sin \theta) / .043k \sin \theta + 4 \sin (.329k \sin \theta) / .329k \sin \theta] \\ + 3[2 \sin (.032k \sin \theta) / .032k \sin \theta + 6 \sin (.240k \sin \theta) / .240k \sin \theta] \end{array} \right\}$$

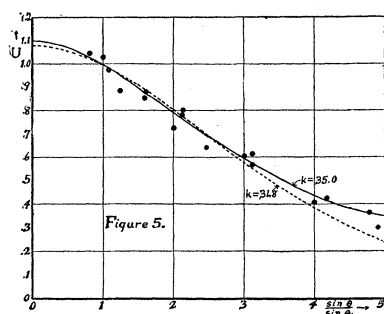


Fig. 5.

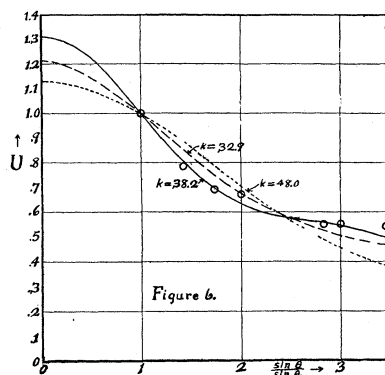


Fig. 6.

50 is the number of electrons in a molecule of calcium carbonate, and k is the constant $(4\pi/\lambda) \cdot (c^2/me^2)$ where c is the angular momentum of an electron in one of the outer rings. The agreement of the theoretical curve with the observed values is well within the probable experimental error, and is evidently better than that obtained with Bragg's empirical formula.

If the assumption that all the electrons have the same angular momentum is used in the case of rock-salt, a result is obtained which does not at all correspond with the observed intensities of reflection, as is shown in the dotted curve of Fig. 6. In order to account for the low value of U around the second order, it seems necessary that there shall be a ring of electrons about 1.00×10^{-8} cm. in radius which contains a considerable number of electrons, and that there shall be no other heavy ring of more than half as great diameter. This arrangement is obtained if we consider the electrons in the outer rings of chlorine to have $3/2$ as great angular momentum as those of sodium, and if, as before, we assume the

inner ring of each atom to have $\frac{1}{2}$ the normal angular momentum. According to the work of J. J. Thomson¹⁶ it appears probable that the valency electron of sodium goes over to the chlorine atom and becomes a part of its outer ring. This would give 8 electrons in the outer ring of chlorine and none in that of sodium. The values of U given in Table I. and shown in the solid curve of Fig. 6 have been calculated on this basis. If the valency electron of sodium is not thus transferred, the broken curve in this figure is obtained on the same assumptions concerning angular momentum. It will be seen that the former hypothesis yields the better results. Although the accuracy of the experimental values of U is not great enough at present to warrant any definite conclusions concerning such details, the difference in the curves obtained by thus shifting the position of a single electron indicates the extreme sensitiveness of this method for determining the distribution of the electrons in atoms.

CONCLUSIONS AND DISCUSSION.

Thus we see that if certain definite distributions of the electrons in atoms are assumed, it is possible to explain in a satisfactory manner the rapid decrease in the intensity of the higher orders of reflection of X-rays by crystals. Although it is not possible thus to derive Bragg's empirical formula, expressions for the intensity of reflection can be derived which agree better with experiment than does his law. We have shown from a theoretical standpoint that any equation which is to express adequately the relative intensity of the beam of X-rays reflected at different angles must be a function not only of the angle of reflection, as is Bragg's law, but must involve also the wave-length of the incident beam of X-rays. Professor Bragg has suggested that the observed values of the intensities of the reflection from different crystals actually show differences which do not depend upon the angle alone. These differences are usually masked by the large general variations of the intensity with the angle of reflection which is to be expected with any crystal grating; in the cases of rock-salt and calcite, however, these general variations can be accounted for, and it has been found above that there remain certain decided differences between the spectra from these crystals. It has been shown theoretically that any such differences must be due to differences in the distribution of the electrons in the atoms of the respective crystals, and the arrangements of the electrons which have been assigned to the different atoms have been found capable of accounting for these variations. Thus our fundamental hypothesis that the intensity of the reflected beam is a function of this distribution is strongly confirmed.

¹⁶ J. J. Thomson, *Phil. Mag.*, 27, 757 (1914).

The scarcity and comparative uncertainty of the experimental data make it premature to arrive at any positive conclusions concerning the details of the distribution of the electrons in the atoms considered. In general, however, it may be said that a comparison of the different distributions of the electrons which have been found to give satisfactory results show that there is usually a rather strong concentration of the electrons near the centers of the atoms, but with a considerable number at appreciable distances from the atomic centers. The expression $F(z) = bz^{-3}$, which was found to give Bragg's law in a slightly modified form, implies that the volume of density of distribution of electrons is inversely proportional to the $5/2$ power of the distance from the center of the atom, and the satisfactory distributions in the case of a limited number of electrons have followed this rule approximately.

From the value of the constant k which is determined by the experimental data, it is possible to calculate the radii of the different rings of electrons according to the formula

$$a = \frac{k\lambda}{4\pi(M + \sigma_n)}$$

Using the values corresponding to the solid curve of Fig. 5 we thus find for the outer ring of calcium, $a = 0.97 \times 10^{-8}$ cm., for carbon, 0.56×10^{-8} cm., and for oxygen, 0.41×10^{-8} cm. The absolute magnitudes here given are of course subject to revision by further experiment, but if the number of electrons in the outer ring is taken equal to the positive valence of the atom, a number of unsatisfactory attempts to obtain expressions for U with other arrangements make it seem necessary that the ratio of the diameters of the rings shall be about that here given. This result is interesting in connection with the fact that while the carbon and oxygen atoms in calcite are only about 1.07×10^{-8} cm. apart, the calcium atom is about 2.95×10^{-8} cm. from its nearest neighbor. In the case of rock-salt, if the valency electron of sodium is in the outer chlorine ring, the radius of the next sodium ring is 0.36×10^{-8} cm., and of the outer chlorine ring is 1.00×10^{-8} cm. If the valency electron remains in the sodium atom, it is, according to our assumptions, 1.86×10^{-8} cm. from the center of the atom, and the chlorine ring is reduced to 0.89×10^{-8} cm. This is a possible arrangement, since the atoms are 2.81×10^{-8} cm. apart. As mentioned above, the diameter of the chlorine ring is probably determined with a fair degree of accuracy. The arrangement of the inner rings is by no means so definitely determined. A number of attempts were made, however, to fit the data for rock-salt assuming only 2 instead of 4 electrons in the inner rings, and this seemingly small change made the curve for U depart too far from the experi-

mental values to be acceptable. Results such as these make it reasonable to suppose that in the case of the lighter elements it may be possible, with a sufficient amount of accurate experimental data, to determine positively the distance of each individual electron from the center of its atom.

Bearing on Theories of Atomic Structure.—While it is difficult by any such “cut and try” method to find the only possible arrangement of the electrons in atoms, it is evident that a study of the intensity of X-ray spectra thus affords an extremely sensitive test of any theory which assigns a definite distribution to the electrons in atoms. From the experimental data now available it may be said, for example, that unless some important factor has been neglected in our formula for X-ray reflection, it seems impossible to account for the rapid diminution of the intensity of the higher orders on any theory, such as Crehore’s,¹⁷ which would confine the electrons of an atom within a distance less than 10^{-10} cm. from its center. Such a distribution would make the quantity ψ of equation (6) approximately equal to unity, and this equation would then differ from the experimental equation (1) by the factor $\tan \theta$, which is much greater than the experimental error. Even if such a factor were introduced into the theoretical equation, it would still be unable to account for the variations in intensity which are characteristic of the individual crystal used as a grating. It seems necessary, therefore, to reject Crehore’s theory of the atom as an impossible hypothesis.

On the other hand, it seems possible to explain all the X-ray intensities on the basis of the type of atom suggested by Bohr.¹⁸ The working assumption that we have used, the constancy of angular momentum, is the fundamental hypothesis of Bohr’s theory. We may calculate the angular momentum of the electrons in the atoms here considered according to the relation

$$c = \sqrt{k \frac{\lambda m e^2}{4\pi}}.$$

Using the values $\lambda = 0.614 \times 10^{-8}$ cm., $m = 9.0 \times 10^{-28}$ gm. and $e = 4.77 \times 10^{-10}$ gm.^{1/2}cm.^{3/2}sec.⁻¹, for the outer rings of the atoms in calcite $k = 35.0$ and c becomes 1.87×10^{-27} gm. cm.² sec.⁻¹. For the inner rings our hypotheses make c half this value. According to Bohr the angular momentum of an electron in an atom is an integral multiple of $h/2\pi$, where h is Planck’s constant. Using the value $h = 6.57 \times 10^{-27}$

¹⁷ A. C. Crehore, *Phil. Mag.*, 26, 25 (1913) and elsewhere.

¹⁸ N. Bohr, *Phil. Mag.*, 26, pp. 1, 476, 857 (1913), 27, p. 506 (1914).

gm. cm.² sec.⁻¹, we find $c = 2(1 - .10) \cdot h/2\pi$. In the case of rock-salt it is the outer chlorine ring whose diameter is most definitely defined. In this case $k = 9/4 \cdot 38.2$, and $c = 2.93 \times 10^{-27} = 3(1 - .06) \cdot h/2\pi$. It may be only an accident that the angular momentum in these cases works out so nearly in accord with Bohr's hypothesis, but it is at least a most interesting accident. The difference between the coefficients of $h/2\pi$ and integers is probably too great to be due to experimental error in the determination of the radii of the electronic rings, but there are good reasons to believe that there may be forces acting on the electrons which have not been considered, and which would be sufficient to account for the difference.

SUMMARY.

In the first part of this paper an expression is derived for the energy of a beam of X-rays of definite wave-length which is reflected from a crystal. The result is in accord with that previously derived by Darwin, and shows that the intensity of the reflected beam depends not only upon the angle of reflection but also upon the arrangement of the electrons within the atoms of the reflecting crystal.

The form of the equation for the energy in the reflected beam is shown to be independent of the degree of perfection of the crystal and of the length of the wave-trains of which the X-rays consist.

In the latter part of the paper a study is made of the possible distributions of the electrons in atoms which will account for the observed energy in the reflected beam of X-rays. It is shown that there is no possible distribution of the electrons which will lead to Bragg's empirical law for the intensity of reflection; it is found rather that any formula for this intensity must depend not only upon the angle of reflection but also upon the wave-length of the incident rays.

Attention is called to the fact that Bragg's experimental data indicate differences in the reflection from certain crystals which can arise only from differences in the distribution of the electrons in the atoms of which the crystals are composed.

Assuming a number of electrons in each crystal equal to the atomic number, and making certain plausible assumptions concerning the arrangement of these electrons in rings, it is found possible to account in a satisfactory manner for the observed intensities of the X-ray spectra.

Although the particular distributions assigned to the electrons in the atoms of calcite and rock-salt may not be the only ones which will account for the observed intensities of the X-ray spectra, it seems probable that these distributions are not far from correct.

The results of this investigation seem to show conclusively that the

electrons are not concentrated within a very small distance from the center of the atom, as is assumed in Crehore's theory of atomic structure. On the other hand, the conclusions arrived at are in good accord with the theory of the atom due to Bohr.

My thanks are due to Professor H. L. Cooke for his helpful interest in this research.

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