XXXIV. The theory of X-ray reflexion

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XXXIV. *The Theory of X-Ray Reflexion. By* C. G. DARWIN, *M.A., Lecturer in Mathematical Physics in the University of Manchester* *.

1. THE formulæ developed by Prof. Laue† in connexion with the interference of X rays in crystals are competent to show the positions in which the interference maxima occur, but do not give the intensities at the maxima. For it is readily calculated that it is impossible experimentally to get a crystal so small that the spherical waves coming from a source at any manageable distance can be regarded as plane. If, following Bragg‡, we regard the phenomenon as due to reflexion in a set of parallel planes of atoms, the extreme shortness of the waves makes the Fresnel zones in these planes very small (in Friedrich and Knipping's§ experiments they would be about 2×10^{-7} sq. cm.), and this vitiates the application of Laue's formula for the intensity. In a later paper Laue ‖ has made use of the Fresnel diffraction principles to account for the shapes of the spots on the interference photographs, but a complete theory must regard the whole problem as one of spherical waves.

In working out such a theory there is great advantage in taking as model that experimental arrangement which has in fact proved most fruitful, reflexion from the planes parallel to an external face of a crystal. This gets rid, both for theory and experiment, of a great deal of rather complicated geometry, which is useful in investigating the structure of crystals, but has nothing to do with the nature of the reflexion.

2. *Assumptions.*

We shall assume simply that X-ray phenomena are a branch of optics. The optical theories of diffraction, and also of dispersion, etc., work out correctly on principles depending on a simple vibration theory, although some of the phenomena of light can only be reconciled with this theory with difficulty. Thus the photoelectric effect depends on Planckian considerations which seem contradictory to the wave theory. In the same way we shall suppose that X rays obey the ordinary laws of the electromagnetic theory, in

* Communicated by Sir Ernest Rutherford, F.R.S.
† M. Laue, *Kön. Bay. Ak.* 1912, p. 303.
‡ W. L. Bragg, Proc. Camb. Phil. Soc. vol. xvii. i. p. 43.
§ W. Friedrich & P. Knipping, *Kön. Bay. Ak.* 1912, p. 311.
‖ M. Laue, *Annal. d. Phys.* Bd. xli. p. 1003 (1913).

spite of the well-known fact that their absorption occurs by means of the emission of high-speed electrons. But a somewhat less satisfactory assumption must also be made. The observed exponential absorption of homogeneous rays is probably a statistical effect, but it is here assumed that the *amplitude* of a wave passing through matter diminishes exponentially with an absorption coefficient half that observed for the intensity. This assumption brings out the correct form for the absorption, and is to a certain extent justified by one of the experiments of Mr. Moseley with the present writer*. It was found that the intensity of reflexion from a crystal was cut down by exactly the same amount by a given piece of aluminium, whether it was placed so as to intercept the whole radiation before reflexion, or the selected radiation after reflexion. This experiment proves that the absorption of a heterogeneous beam can be calculated by Fourier analysis.

It should be said at once that part of the quantitative discussion in the present paper is inadequate and can only be regarded as a first approximation, but several points of interest have emerged. It is hoped to treat of a more complete theory in a future paper.

3. *The Structure of a Reflected Line.*

The first point we shall consider is employed in Moseley's† method for discovering the characteristic X-ray spectra of the elements. A crystal reflects waves of given length λ only at the angles given by the equation $n\lambda = 2a \sin \theta$, where n is an integer, a the distance between successive planes in which the atoms of the crystal are arranged, and θ is the "glancing" angle between the incident beam and the crystal face. If homogeneous radiation coming from a fine source falls on a crystal it is only reflected in the neighbourhood of a certain line on the crystal, this line being such that the incident beam there makes the proper angle with the crystal face. The reflected beam falls on a photographic plate and produces a fine line on it. Our present object is to discuss the structure of this line, which is of course not infinitely narrow. This can be done without calculation. First consider the effect of the outermost plane of the crystal on radiation coming from a point source. Each atom scatters a certain amount of radiation into a small spherical wave. These scattered wavelets reconstruct themselves into

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* Moseley & Darwin, Phil. Mag. vol. xxvi. p. 210 (1913).

† Moseley, Phil. Mag. vol. xxvi. p. 1024 (1913).

a single wave coming as though from I_1 the image of the source O in the plane (see fig.). The second plane similarly gives a wave coming from I_2 the image of O in the second plane. This wave is a little weaker than the first, because the radiation is absorbed in passing twice through the first plane. The same argument applies to all the lower planes. Thus the effect at any point P is simply that of a set of spherical waves starting in phase together from $I_1I_2 \ldots$. But this is the same as the effect when a plane wave falls perpendicularly on a plate in which small holes are made at I_1I_2, etc. The intensity at any point P is simply the intensity of the lateral spectra of the point grating. Observe
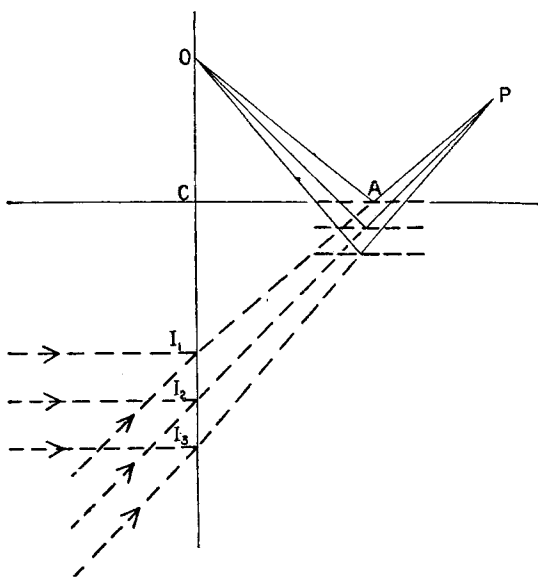
that the glancing angle is now the angle measured in the usual way from the normal. Let us now suppose the radiation to be monochromatic, and find the diffraction pattern in the neighbourhood of the nth lateral spectrum. The simplest way of seeing its nature is as follows. The waves from $I_1I_2 \ldots$ will produce the same effect if, instead of starting in phase together, each starts at phase $2n\pi$ behind the last. Thus the incident wave on the left of I_1I_2 may be imagined to be turned round through an angle θ where $n\lambda = 2a \sin \theta$ ($2a$ is the distance between adjacent holes). The phase difference between the waves going from two neighbouring holes in any direction near P is now small, so that the holes may be

replaced by the line joining them. Thus the pattern at P is simply the diffraction pattern from a fine line one end of which I_1 is sharp, while the effect on the other side falls off exponentially. In conformity with our assumption the amplitude of the wave coming from a depth z below I_1 is to be taken as $e^{-\mu z \cosec \theta}$ of that coming from I_1 (μ is the absorption coefficient for intensity). The structure that will be observed is thus a band, on one side of which is the diffraction pattern of a straight edge, while in the other direction the intensity falls off exponentially. In any manageable experiment the scale of the diffraction pattern would be only a few seconds, and would be entirely masked by the finite size of the source. For very hard rays the exponential diminution in intensity should be observed. It may easily be seen that at a distance $\sin \theta \cos \theta / \mu$ from the sharp edge, the intensity has fallen to $1/e$. Thus, for work with hard rays it would be essential to use a very dense crystal, or else to curtail the grating by using a thin one. The line on the photographic plate is, strictly speaking, a conic section and not a straight line.

It is convenient here to anticipate a future result (§ 6). We shall see that the X rays must be held to have a refractive index which differs from unity by about a millionth. On account of the refraction the position of the line on the photograph is slightly shifted. Let λ, θ be the external wave-length and glancing angle, λ', θ' the internal. Let $1 + p$ be the refractive index. Then $\lambda = (1+p)\lambda'$ and $\cos \theta = (1+p) \cos \theta'$ or $\theta - \theta' = -p \cot \theta$. The observed position of the line corresponds to $n\lambda' = 2a \sin \theta'$, while that which would be expected is given by $n\lambda = 2a \sin \theta_0$. So $(1+p) \sin \theta' = \sin \theta_0$, and so $\theta_0 - \theta' = p \tan \theta$. Thus the shift is

$$\theta - \theta_0 = -p \cosec \theta \sec \theta.$$

This result will be proved later *ab initio*.

4. *Quantitative Method.*

We next consider the case where the reflexion is measured electrically. For this, the information required is quantitative. We shall first find the total energy reflected into the electroscope when monochromatic radiation falls on a crystal without any slits. As would be the case in most experiments, we shall suppose the electroscope to be so wide that all the reflected radiation is included; it is then unnecessary to allow for the fact that the distance of the electroscope is

finite, and complicated operations with Fresnel integrals are avoided.

It is not necessary to carry through all the details strictly according to the electromagnetic theory. These can be introduced later. Let us suppose that when a wave of length $2\pi/k$ falls on an atom, the amplitude of the scattered radiation at unit distance bears to that of the incident a ratio $f(\psi, k)$, where ψ is the angle between the direction of observation and the incident beam. f is of the dimensions of a length. In accordance with §§ 11–13 it will be taken to be real, involving no change of phase. In addition to ψ and k it will depend on the direction of polarization of the incident beam. We shall suppose f so small that the wave scattered by one atom does not influence the amplitude of vibration of the radiating system in any other. As we shall see, there is an effect on the phase which can still be included. It will appear that there is definite experimental evidence that the scattering of one atom *does* affect that of others, because we shall find reason to believe that over a narrow range of angles of incidence the reflexion is nearly perfect; so we can only regard the present process as a first approximation. For simplicity we shall take a crystal composed of atoms of a single element, arranged in a single lattice, but this lattice may be cubic or parallelopipedal. We also neglect the temperature vibrations of the atoms. These omissions are very easily set right later.

5. *Reflexion from a Single Plane.*

We first find the reflexion from one plane of atoms. Let the incident beam be $e^{ik(Ct-R)}/R$, where R is the distance from O (see fig. p. 317). Taking C as origin, O is the point $(0, 0, h)$. To find the reflexion at angle θ we take as point of observation $\rho\cos\theta, 0, \rho\sin\theta - h$, so that ρ is the distance from I_1. Then the point of geometrical reflexion A is $(R\cos\theta, 0, 0)$ where $h = R\sin\theta$. Let there be an atom at $R\cos\theta + \xi, \eta, 0$. This atom will contribute a component

$$\frac{f(2\theta, k)}{R(\rho - R)} \exp ik(Ct - R_{\xi\eta} - r_{\xi\eta}),$$

where the quantities that do not vary rapidly have been replaced by their values at A, and $R_{\xi\eta}$, $r_{\xi\eta}$ are the distances of ξ, η from O and P respectively. By expansion we find that

$$R_{\xi\eta} + r_{\xi\eta} = \rho + \frac{1}{2} \frac{\rho}{R(\rho - R)} (\xi^2\sin^2\theta + \eta^2),$$

so that the whole effect is

$$\frac{f(2\theta, k)}{\rho} e^{ik(Ct-\rho)} \frac{\rho}{R(\rho-R)} \Sigma \exp - \frac{ik}{2} \frac{\rho}{R(\rho-R)} (\xi^2 \sin^2\theta + \eta^2).$$

Let M be the number of atoms per unit area. Then the number in an area $d\xi\, d\eta$ is $M d\xi\, d\eta$. Since the phase variation between neighbouring atoms is small we can replace the sum by an integral, and get as the reflected wave

$$\frac{f(2\theta, k)}{\rho} e^{ik(Ct-\rho)} M \frac{\rho}{R(\rho-R)} \iint_{-\infty}^{\infty} \exp - \frac{ik}{2} \frac{\rho}{R(\rho-R)} (\xi^2 \sin^2\theta + \eta^2) d\xi\, d\eta$$

$$= \frac{f(2\theta, k)}{\rho} e^{ik(Ct-\rho)} \frac{M \cdot 2\pi e^{-\frac{i\pi}{2}}}{k \sin\theta}.$$

If N be the number of atoms per unit volume and a the distance between successive planes of the crystal, $M = Na$, and we have as reflexion coefficient,

$$f(2\theta, k) \frac{Na 2\pi e^{-\frac{i\pi}{2}}}{k \sin\theta} = -iq. \quad \ldots \quad (1)$$

This expression is not perfectly general since q might be made greater than unity by increasing N. This would violate the conservation of energy. In actual matter this would be prevented, because the vibration of each atom would diminish those of its neighbours, so that we should have to regard f as dependent on N. Numerical calculation shows that q is of the order 10^{-4}, so that the simple form probably stands. The factor $e^{-\frac{i\pi}{2}}$ is the converse of the quarter wave which has to be introduced into diffraction problems.

6. *The Refractive Index.*

If the factor $f(2\theta, k)$ is replaced by $f(0, k)$ the same radiation, represented by $-iq_0$, is scattered on the other side of the plane, so that the wave there is of the form

$$(1-iq_0) \frac{e^{ik(Ct-R)}}{R} \quad \text{or} \quad \frac{e^{ik(Ct-R)-iq_0}}{R},$$

since q_0 is small. This neglects the absorption in the plane

which cuts down the amplitude by a real factor b, so that the transmitted wave is

$$b \frac{\exp ik(Ct - R) - iq_0}{R}.$$

The effect in the second plane is due to the incident wave and to the wavelets scattered by the atoms of the first. We have above seen that these reconstruct themselves and produce a component in the primary wave. This reconstruction will not really be very perfect until four or five layers have been passed, but no great error is introduced by supposing that it happens at once. Taking into account the effect of the first plane on the emerging wave, we find that the second plane gives a reflexion

$$-iq\, b^2 \frac{\exp ik(Ct - \rho_2) - 2iq_0}{\rho_2},$$

where ρ_2 is the distance from I_2. Proceeding in this way, we find that the sth plane gives an emerging wave

$$-iq\, b^{2s} \frac{\exp ik(Ct - \rho_s) - 2iq_0 s}{\rho_s}$$

and that beyond it the transmitted beam is

$$b^s \frac{\exp ik(Ct - R) - iq_0 s}{R}.$$

The intensity corresponding to this is $\dfrac{b^{2s}}{R^2}$. But the rays have traversed a thickness $sa\,\mathrm{cosec}\,\theta$, so we take

$$b^2 = e^{-\mu a\,\mathrm{cosec}\,\theta}.$$

The presence of the term $iq_0 s$ implies a refractive index. For $s = \dfrac{z}{a}$, so that the wave is propagated in a new direction with a velocity different from that of light. The refractive index is

$$1 + \frac{q_0}{ka}\sin\theta \quad \text{or} \quad 1 + \frac{2\pi N f(0, k)}{k^2}. \quad . \quad . \quad (2)$$

It should be observed that in the forward direction the wavelets scattered by the atoms are in phase together, whether the latter are arranged regularly or not. So this refractive index applies equally well to amorphous substances.

7. *Reflexion of Monochromatic Radiation.*

Returning to the reflexion we get as the whole reflected amplitude

$$-iq\frac{e^{ik(Ct-\rho_1)}}{\rho_1}\Big(1+\exp\{-\mu a\ \text{cosec}\ \theta+ik(\rho_1-\rho_2)-2iq_0\}$$
$$+\exp\{-2\mu a\ \text{cosec}\ \theta+ik(\rho_1-\rho_3)-4iq_0\}+\ldots\ldots\Big),$$

where the slowly varying quantities have been replaced by their values for the first plane. As has been indicated, the *whole* radiation at a finite distance is the same as at an infinite, so that we may take the ρ's as large as we please. Thus $\rho_s=\rho_1+2as\sin\theta$ and the whole expression is

$$-iq\frac{e^{ik(Ct-\rho)}}{\rho}\Big(1+\overset{\infty}{\underset{1}{\Sigma}}\exp-s\ .\ \mu a\ \text{cosec}\ \theta-sika2\sin\theta-s2iq_0\Big)$$

$$=-iq\frac{e^{ik(Ct-\rho)}}{\rho}\Big/\Big\{1-\exp-(\mu a\ \text{cosec}\ \theta+ika2\sin\theta+2iq_0)\Big\}.$$

If $ka\sin\theta$ is near $n\pi$ this has a strong maximum. Let $ka\sin\phi=n\pi$. Then $ka\sin\theta=n\pi+ka\cos\phi(\theta-\phi)$ and the amplitude is

$$-iq\frac{e^{ik(Ct-\rho)}}{\rho}\Big/\Big\{\mu a\ \text{cosec}\ \phi+i[2ka\cos\phi(\theta-\phi)+2q_0]\Big\}.$$

Corresponding to this we have an intensity

$$\frac{q^2}{\rho^2}\Big/\Big\{(\mu a\ \text{cosec}\ \phi)^2+[2ka\cos\phi(\theta-\phi)+2q_0]^2\Big\}.\quad.\quad(3)$$

This has its maximum at $ka\cos\phi(\theta-\phi)+q_0=0$. If q_0 is replaced by its value in terms of the refractive index, the expression at the end of § 3 can be recovered.

Suppose now that we measure the ionization in an electroscope of length l and sufficient breadth to include the whole beam. The effect then is

$$\frac{\mathrm{I}l}{\rho}q^2\int\frac{d\theta}{(\mu a\ \text{cosec}\ \phi)^2+4[ka\cos\phi(\theta-\phi)+q_0]^2},$$

where I is the intensity of the incident beam

$$=\mathrm{I}\frac{l}{\rho}q^2\frac{\pi}{\mu a\ \text{cosec}\ \phi\ .\ 2ka\cos\phi},$$

which reduces to

$$\mathrm{I}\frac{l}{\rho}\frac{f^2(2\theta,k)}{\mu}\mathrm{N}^2\ .\ \tfrac{1}{2}\lambda^3\ \text{cosec}\ 2\phi.\quad.\quad.\quad.\quad(4)$$

8. *Effect of a Slit.*

This expression, like that for reflexion from one plane, is not general because N may be so large that the reflexion would be greater than the incident beam and the energy would not be conserved. In reality, this would be avoided by the atoms influencing one another's scattering. The comparison with experiment (§ 14) shows that this is in fact the case, and we must see how. We have so far worked with an unlimited primary beam. Obviously the same result holds if a slit is introduced so broad that it does not cut out any of the radiation near the reflexion angle. The question arises, how narrow may this slit be before the reflexion suffers? This question may be answered by reference to the figure (p. 317). In front of each of the apertures I_1, I_2 ...... in the direction of P, supposed at infinite distance, must be introduced a slit. Each slit only has reference to its own aperture and is opaque to the waves from the others. In a direction near P the intensity will be given by the intensity in (3) multiplied by the intensity in this direction corresponding to a single slit. Suppose that the slit is placed symmetrically with regard to the spectral line. For any reasonable values the breadth of the diffraction pattern is much greater than that of the maximum in (3). Thus the condition to be satisfied is that the slit is to be of such a width that the intensity has its full value in the central line. Taking roughly the first maximum in a Cornu spiral we find $s^2 \cdot \dfrac{k}{\pi r} = 6$, where s is the slit's breadth and r its distance from the source. We can now deduce an upper limit to the reflexion. Taking $r = 30$ cm. and $k = 10^9$ for medium X rays, we find that all the reflexion occurs within an angular breadth of about $5''$. If the observed reflexion is more than the whole amount included within $5''$, it is a sign that the simple theory will not hold, and that in an improved theory which takes account of the influence between atoms, the reflexion must be spread out in a broader pattern than indicated above.

9. *Heterogeneous Radiation.*

The transition from monochromatic radiation to the general "white" radiation is simple. Let the amplitude be represented by

$$\int_0^\infty \left[\phi(k) + i\psi(k) \right] \frac{e^{ik(Ct - R)}}{R} dk.$$

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The intensity corresponding to this will be proportional to

$$\frac{1}{R^2}\int_0^\infty (\phi^2+\psi^2)dk \quad \text{or} \quad \frac{1}{R^2}\int_0^\infty u_k dk.$$

The reflected amplitude is

$$\int_0^\infty \left[\phi(k)+i\psi(k)\right](-iq)\frac{e^{ik(Ct-\rho)}}{\rho}\frac{dk}{1-\exp-(\mu a \cosec\theta+i\cdot 2ka\sin\theta+2iq_0)},$$

corresponding to which there is an intensity

$$\frac{1}{\rho^2}\int_0^\infty u_k q^2 \frac{dk}{|1-\exp-(\mu a \cosec\theta+i\cdot 2ka\sin\theta+2iq_0)|^2}.$$

We suppose that u_k only varies slowly. As k varies the integrand has strong maxima when $ka\sin\theta+q_0=n\pi$. Denote this value of k by k_n and near k_n put $k=k_n(1+x)$.

Then the expression is approximately

$$\frac{1}{\rho^2}\sum_n u_n (q^2)_n\int_{-\infty}^\infty \frac{k_n\,dx}{(\mu_n a\cosec\theta)^2+(2n\pi x)^2},$$

where the n subscript denotes that the quantity has reference to k_n. Performing the integration and putting in the value of q, we have

$$\frac{1}{\rho^2}N^2a^2\,2\pi\sum_n\frac{f^2(2\theta,\,k_n)}{\mu_n}\frac{1}{n^2}u_n,$$

or in terms of the more usual E_λ where $E_\lambda\,d\lambda=u_k\,dk$,

$$\frac{1}{\rho^2}N^2a^2\sum\frac{1}{n^2}f^2(2\theta,\,k_n)\left(\frac{E_\lambda\lambda^2}{\mu}\right)_n. \quad . \quad . \quad . \quad (5)$$

By virtue of the assumption that u_k only changes slowly, the correction depending on the refractive index has been neglected. The expression would require a little modification for approximately monochromatic radiation.

It was by the above processes that the result quoted on pp. 230-231 of Moseley and Darwin was reached. Unfortunately there was made in that paper an assumption which cannot be maintained, viz. that the scattering and absorption are proportional. It would seem better to suppose them independent. The abbreviated proof there attempted cannot be maintained. In the first place, the area assigned for a Fresnel zone is incorrect and also the argument should be carried out with amplitude and not with energy. Amended in this way it gives the right result.

10. *Temperature Effect and Compound Crystal.*

We will next introduce an effect so far disregarded, the temperature correction. This, due to the fact that the atoms are at no time all in their planes, affects the reflexion from a single plane, but makes no further change. Of the displacements of the atoms, those in the plane produce no change of phase, and we only have to consider displacements out of the plane. The treatment here is rather different in detail from that of Debye [*]. Let us suppose that the potential energy for a displacement ζ is $\frac{1}{2}\sigma\zeta^2$. By the principle of equipartition out of the M atoms per sq. cm. a number

$$M\sqrt{\frac{\sigma}{2\pi kT}}\exp-\frac{1}{2}\frac{\sigma\zeta^2}{kT}d\zeta\dagger$$

are displaced a distance between ζ and $\zeta+d\zeta$. These atoms are wrong in phase to an extent expressed by $e^{-ik2\zeta\sin\theta}$. There are a great many atoms in any region over which the phases of the undisturbed atoms are sensibly constant. The temperature effect can be thus expressed as a factor in the value of q, and this factor is

$$\sqrt{\frac{\sigma}{2\pi kT}}\int_{-\infty}^{\infty}\exp-\frac{1}{2}\frac{\sigma\zeta^2}{kT}-ik2\zeta\sin\theta\,d\zeta$$

or $\quad\exp-\dfrac{1}{2}\dfrac{kT}{\sigma}(2k\sin\theta)^2\quad$ or $\quad\exp-\dfrac{1}{2}\dfrac{kT}{\sigma a^2}(2n\pi)^2.$

This is for the amplitude, and so for the intensity the temperature vibrations introduce a factor

$$\exp-\frac{kT}{\sigma a^2}(2n\pi)^2. \quad\quad\quad (6)$$

It is the same for a given order of reflexion, but diminishes rapidly with the higher orders.

We next deduce the reflexion for a crystal composed of several similar interpenetrating lattices. Let N_r be the number of atoms per c.c. of the rth lattice, f_r their scattering effect, and let the planes of this lattice be at distance $\alpha_r a$ from those of the first, let σ_r give the restraining force on the atoms. Then the expression

$$N^2 f^2 e^{-\frac{kT}{\sigma a^2}(2n\pi)^2}$$

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[*] Debye, *Ber. d. Deut. Phys. Ges.* 1913, p. 671.
† k is used in two different senses, but the difference will be clear.

must be replaced by

$$\left| \sum_r N_r f_r\, e^{-i2n\pi\alpha_r}\, e^{-\frac{kT}{2\sigma_r a^2}(2n\pi)^2} \right|^2 \quad . \quad . \quad . \quad (7)$$

This applies to both monochromatic and white radiation.

11. *The Scattering of a Single Atom.*

We must now discuss the form of the function f. When a light-wave in which the electric vector is along x falls on a system capable of vibration, a wave is scattered which is greatest in amplitude in the yz plane, vanishes in the line of x, and in any intermediate direction is proportional to the cosine of the angle between that direction and the yz plane. In this way we find that in $f^2(2\theta, k)$ there will be a factor $\dfrac{1 + \cos^2 2\theta}{2}$ due to the two polarized components of the incident beam. This gets rid of the polarization, and we need only consider the form of f in a plane perpendicular to the electric vector.

The atom consists of a positive charge and of electrons, but the former is much too heavy to scatter radiation and may be neglected. Though there can be little doubt that it does not represent the reality of the case, we shall proceed according to the ordinary electromagnetic theory, as applied to dispersion. In optics this gives satisfactory results, and it should do so here as well. Let e, m be charge and mass of an electron, and let the forces which hold it in equilibrium have a " stiffness " $mk_0^2C^2$, so that the emission wave-length is $2\pi/k_0$. Under the action of an electric force X the electron moves according to the equation

$$m\ddot{\xi} + mk_0^2C^2\xi - \frac{2}{3}\frac{e^2}{C^3}\dddot{\xi} = eX.$$

Then if $X = e^{ik(Ct-x)}$ we have

$$\xi = \frac{eX}{m(k_0^2 - k^2)C^2 + \frac{2}{3}e^2k^3 i}.$$

At a great distance r in the plane of yz this gives a wave of amplitude

$$\frac{e^2 X\, e^{-ikr}}{m(k_0^2 - k^2)C^2 + \frac{2}{3}e^2k^3 i}\frac{k^2}{r}. \quad . \quad . \quad . \quad (8)$$

If we take this expression and add together the terms for each electron in the atom, and substitute in (2) for the

refractive index, we get the Selmeyer dispersion formula. Since it is quite possible that k should be greater than k_0 for all the electrons, the refractive index may quite well be less than unity.

12. *Mutual Action of the Electrons in an Atom.*

For the electrons which contribute the light spectrum k_0 is very much smaller than k and may be neglected. Sir J. J. Thomson* assumes this for all the electrons. The imaginary term is very much smaller than the real, so he puts $f = -\dfrac{e^2}{mC^2}$ for each electron, and uses this expression to estimate the number of electrons in the atom, from the known scattering of an amorphous substance.

But without further discussion this is not legitimate, even assuming that all the k_0's are negligible. For some of the electrons are crowded very close together, probably within a distance of about 5×10^{-10} cm.†, which is fairly small compared with the wave-length of the radiation. Now it is well known that a small body scatters light of short wave-length much more completely than long. We must make certain that this will not be the case here. Suppose we have ν electrons crowded together at points $x_1\, y_1\, z_1$ &c., the scale of their distances being measured by a length ρ. Let the external radiation be $X = e^{ikCt}$. This sets all the electrons in vibration, and the motion of each influences the others. Let ξ_1 be the displacement of the first electron. Then ξ_1 is of the form $\dfrac{A_1}{e}\exp ikCt$. At a near point this electron exerts a force

$$\frac{3\,\overline{x-x_1}^2 - r^2}{r^5}\,A_1\,e^{ikCt}.$$

Similarly for the others. The whole electric force on the first electron then is

$$\left(1 + \sum_{2}^{\nu}\frac{3\,(x_s - x_1)^2 - r_{1s}^2}{r_{1s}^5}\,A_s\right)e^{ikCt} = \frac{m\ddot{\xi}_1}{e} = -\frac{mk^2C^2}{e^2}\,A_1\,e^{ikCt}.$$

We are neglecting the restraining forces on the electrons,

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* J. J. Thomson, ' Conduction of Electricity in Gases,' p. 326.
† Calculated on Bohr's theory for a ring of 4 electrons in a sodium atom.

and also the reaction of their radiation on their motion. We thus get a set of equations

$$-A_1 = \frac{e^2}{mk^2C^2}\left(1 + \sum_2^\nu \frac{\beta_{1s}A_s}{\rho^3}\right),$$

where β_{1s} is a quantity depending on the arrangement and is of the order of unity. The whole amplitude of the radiation scattered to a distant point in the yz plane is

$$\frac{k^2}{r} e^{ik(Ct-r)} \Sigma A_s.$$

The character of the solution of the simultaneous equations depends on the magnitude of $\frac{e^2}{mk^2C^2}\frac{1}{\rho^3}$. If it is small we get $A_1 = -\frac{e^2}{mk^2C^2}$, so that the scattered radiation is proportional to $\nu \frac{e^2}{mC^2}$. On the other hand, if $\frac{e^2}{mk^2C^2}\frac{1}{\rho^3}$ is large we can neglect the terms on the left, and we have a set of equations of the form $1 + \sum_2^\nu \frac{\beta_{1s}A_s}{\rho^3} = 0$. Whatever the solution may be, it will give A_s independent of k and proportional to ρ^3, so that the scattered radiation will be proportional to $k^2\rho^3$. This is exactly the result found by Lord Rayleigh* in his theory of the light of the sky.

Thus the question turns on the value of $\frac{e^2}{mk^2C^2}\frac{1}{\rho^3}$. Taking light of wave-length 5×10^{-5} cm. and $\rho = 10^{-8}$ cm., we represent the effect of a molecule of the atmosphere. This gives $\frac{e^2}{mk^2C^2}\frac{1}{\rho^3} = 18$, which is probably large enough. For our inner ring of electrons we take $\rho = 5 \times 10^{-10}$ and for soft X rays $2\pi/k = 10^{-8}$. Then $\frac{e^2}{mk^2C^2}\frac{1}{\rho^3} = 6 \times 10^{-3}$. This is small enough, so that we may assume that an atom scatters long waves to the same extent as short.

13. *The "Excess" Scattering.*

The waves scattered by the electrons in an atom combine to a certain extent so as to give a scattered radiation greater in intensity than is simply proportional to their number. For example, the electrons at distances 5×10^{-10} cm. apart would exert an effect almost proportional to the square of

* *Cf.* Rayleigh, 'Sound,' vol. ii. p. 149.

their number. Consider the effect of an atom in a direction inclined to the incident beam at angle 2θ. Of the ν electrons, all in any plane at angle θ give waves in phase together. Let p_s be the distance of an electron from some plane drawn in this direction. The whole resultant amplitude is then proportional to $\Sigma \exp - ik \cdot 2p_s \sin \theta$. To find the corresponding intensity we multiply by the conjugate imaginary and get

$$\nu + 2 \, \Sigma\Sigma \cos 2k \sin \theta \, (p_s - p_t) \quad . \quad . \quad . \quad (9)$$

This expression accounts for the phenomenon of the "excess radiation" which is observed in the scattering at small angles by an amorphous substance*. For k is of the order 10^9 for medium rays and $p_s - p_t$ is at most 10^{-8}, so if θ is less than $5°$ every single electron in the atom contributes to the excess. At broader angles a few of the outermost electrons fail to help, but there will be still a number of contributors. Finally,

when $\theta = \dfrac{\pi}{2}$ only those contribute which are less than a

quarter wave apart. Moreover, the same excess will be exhibited at a broader angle for the softer rays†.

When we come to consider the reflexion of a crystal we get the formula

$$\nu + 2 \, \Sigma\Sigma \cos \frac{2n\pi}{a} (p_s - p_t).$$

We may probably assume that the interiors of the atoms are oriented in all directions, since any forces which were strong enough to turn them into one direction, would probably show some optical effect, and this would mean that a cubic crystal should show double refraction. So we may suppose that the average of $p_s - p_t$ is independent of θ. Then the excess radiation contributes a constant factor to the reflexion in each order, but that factor is greater for the lower than for the higher orders.

Using the value of f as above, we arrive at the following formula for the reflexion of white radiation from a crystal composed of one lattice.

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* Barkla, Phil. Mag. vol. xxi. p. 270 (1911); Crowther, Proc. Roy. Soc. A. vol. lxxxv. p. 29 (1911).

† Various hypotheses have been put forward to account for the excess radiation, by J. A. Crowther (Proc. Camb. Phil. Soc. xvi. p. 534, 1913) and by D. L. Webster (Phil. Mag. xxv. p. 234, 1913). The last assumes it due to the cooperation between electrons. He does not distinguish between electrons in the same and in different atoms. Except in the region of the diffraction pattern of the primary beam, the latter are as likely to contribute a negative as a positive term to (9).

$$\frac{N^2 a^2}{\rho^2} \frac{1+\cos^2 2\theta}{2} \sum_n \frac{1}{n^2} \left(\frac{e^2}{mC^2}\right)^2 \left(\nu + 2 \Sigma\Sigma \cos\frac{2n\pi}{a}(p_s - p_t)\right) e^{-\frac{kT}{\sigma a^2}(2n\pi)^2} \left(\frac{E \cdot \lambda^2}{\mu}\right)_n \cdot$$

$$\dots \dots (10)$$

14. *Comparison with Experiment.*

We will now compare this result with experiment, and shall find that our formula gives more reflexion than is possible. The comparison is with the experiments on rocksalt in Moseley and Darwin[*]. The Braggs' work[†] has shown that Na and Cl both contribute to the reflexion, and for a rough comparison it will be good enough to take them as identical and deduce the average character of the two. They are then arranged on a simple cubic lattice. Using Millikan's[‡] most recent values, we find that the side of the lattice a is $2\cdot 81 \times 10^{-8}$ cm. and N is $4\cdot 50 \times 10^{22}$. The work of Moseley[§], combined with that of Barkla[||], shows that over a considerable range of the softer rays μ is exactly proportional to $\lambda^{5/2}$. For very much harder rays this is confirmed by a single experiment in Moseley and Darwin[¶]. We shall assume this relation to hold. Of the other quantities in (10) σ can be found from the infra-red absorption band of rocksalt. If M be the average mass of an atom $M\ddot\zeta + \sigma\zeta = 0$ expresses the vibration of an atom. The wavelength of the absorption band is $54\,\mu$[**]. From this σ can be found. The temperature factor is found to be $0\cdot96$ for the first order, $0\cdot86$ for the second. For the sixth it is $0\cdot27$. The smallness of the effect accounts for its not having been hitherto observed. The excess radiation factor is much in doubt until the structure of the atom is better known. The simplest process is to take the ratio of first to second order from the heights of the "peaks" in Bragg's experiments. Using this, it is a simple matter to disentangle the separate orders, and the work shows that a considerable error in estimating the strength of the second order will not change the result very much. No allowance can be made for the polarization of the rays coming from the tube, as it is not known which are the components polarized. Taking as standard wave-length λ_0, that reflected in rocksalt $(1, 0, 0)$ plane

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[*] *Loc. cit.* p. 219.
[†] W. L. Bragg, Proc. Roy. Soc. A. vol. lxxxix. p. 248 (1913).
[‡] R. Millikan, Phys. Rev. vol. ii. p. 109 (1913).
[§] H. G. J. Moseley, *loc. cit.*
[||] C. G. Barkla, Phil. Mag. vol. xxii. p. 396 (1911).
[¶] *Loc. cit.* p. 220.
[**] Rubens and v. Baeyer, *Berl. Ber.* 1913, p. 802.

at 4°, we have $\lambda_0 = 3 \cdot 92 \times 10^{-9}$ cm. We then get a curve of intensity given in the following table:—

λ/λ_0	$\frac{1}{2}$	$\frac{5}{8}$	$\frac{3}{4}$	$\frac{7}{8}$	1	$1\frac{1}{8}$	$1\frac{1}{4}$	$1\frac{1}{2}$	$1\frac{3}{4}$	2	$2\frac{1}{4}$
E_λ	3	10	32	68	100	104	99	79	48	22	11

By a rough quadrature it appears that about 7 per cent. of the radiation is contributed by the characteristic platinum radiations; and it happens that $\int E_\lambda d\lambda$ is very nearly equal to $E_0\lambda_0$, where E_0 refers to the value at λ_0. In deducing this result it is assumed that the ionization is proportional to the energy. This assumption is rather doubtful, as we should expect that the secondary electrons from the softer rays would be so appreciably absorbed by the gas that they produce less than their due share of ionization.

Using this quadrature and the experimental value $0 \cdot 0035$ for the efficiency of reflexion at 4°, we can estimate the value of $\nu + 2 \, \Sigma\Sigma \cos \dfrac{2n\pi}{a} (p_s - p_t)$. It is 26. But there is strong reason to believe that the efficiency was overestimated. We have seen that, assuming the independence of scattering from separate atoms, the whole reflexion really only takes place within a breadth of about $5''$. If we assume that the radiation in this breadth is completely reflected, we arrive at an efficiency $\dfrac{E_0 \dfrac{d\lambda}{d\theta} \delta\theta}{\int E d\lambda}$, where $\delta\theta$ is $5''$. Using the quadrature, this is $\cot\theta\,\delta\theta$ or $0 \cdot 0004$. It is possible that when the reflexion becomes strong it is spread over a broader angle, so that we cannot conclude that the overestimate of efficiency is as great as suggested by this figure. It may be observed that the disagreement cannot be due to the less ionization by the softer rays, since the efficiency is measured by comparison with the *ionization* of the whole beam. It seems possible that in comparing two effects one of which is 300 times the other, there should be incomplete saturation in the larger.

Unfortunately the fact that the reflexion must be regarded as nearly perfect vitiates the formulæ for reflexion. It does not even appear why the second order should be so much weaker than the first. It is hoped to discuss this aspect of the matter in a future paper.

15. *The Absence of Resonance.*

A very interesting question arises with regard to the natural periods of the electrons. If there are such periods in the X-ray region it should be possible to observe a marked change in the refractive index in their neighbourhood. It should also be found that a substance scatters a particular wave-length much more efficiently than any other. The early work on refraction was all with heterogeneous rays and so cannot be taken as evidence, and no one has worked at the scattering of characteristic radiation. In Moseley's experiments the reflexion of the iron rays by potassium ferrocyanide was not specially strong, but we know it in all cases to be nearly as good as it can be. But in spite of the absence of direct evidence, it seems almost incredible that an increase of about a million times (which is what would be expected from (8)) should not affect the apparent absorption. Barkla found no special absorption by a substance of its own radiation, but that it needed for example rays as hard as those from nickel, to be strongly absorbed in iron. Superficially this bears some resemblance to a resonance effect. Indeed, before anything was known about the wave character of the characteristic rays, it might be thought of as an example of the fact that a strongly damped vibration responds best to a different frequency from that of emission. Even without further information this explanation would hardly work, for whatever the damping it will be found that the response is always nearly as good to the emission frequency as to the optimum. But Moseley's work has shown that the characteristic rays are extremely homogeneous, so that this view becomes quite untenable. On the whole it is simplest to suppose that Barkla's results depend in some way on an intermediate secondary electron. With regard to there being some real resonance effect, we can only hold that it seems rather improbable that it exists. If it does not, we must conclude that a substance radiating its characteristic X-ray spectrum is in some abnormal state. It would be exactly analogous to the fact that the hydrogen lines from a spectrum-tube are not absorbed in hydrogen.

Summary.

(i.) The structure is discussed of the lines photographed by Moseley in his method of finding the X-ray spectra of the elements.

(ii.) Proceeding on a theory exactly analogous to that of light, the intensity of reflexion is found both for monochromatic and for heterogeneous radiation.

(iii.) The existence of a refractive index for both crystalline
and amorphous substances is indicated by the theory.

(iv.) The correction for the temperature vibrations is cal-
culated.

(v.) The effect of the several electrons in an atom is calcu-
lated, and is seen to account for the phenomenon of
" excess radiation " observed in the scattering of
X rays by amorphous substances.

(vi.) The results are compared with the experimental results
of Moseley and Darwin on rocksalt, and it appears
that the reflexion is so good that the formulæ on
which (ii.) is based must be inadequate in some parti-
culars. The wave scattered by one atom disturbs the
vibrations of the others.

My thanks are due to Prof. Rutherford for his kind
interest in this research. Also to Mr. H. G. J. Moseley;
several of the questions here considered arose from discus-
sions with him.

XXXV. *Anomalous Zeeman Effect in Satellites of Mercury
Lines. By* H. NAGAOKA, *Professor of Physics, and*
T. TAKAMINE, *Postgraduate in Physics, Imperial Uni-
versity, Tokyo* *.

[Plate V.]

I N the present stage of our knowledge of the Zeeman effect,
investigations as regards the separation of satellites of
spectrum lines in a magnetic field are very scanty. Gehrcke
and v. Baeyer † first measured the effect on the satellite of
the green line of mercury in weak magnetic fields ; similar
measurements were made by Lunelund ‡ on several satellites
of mercury lines, but as the strength of the field was limited
to a few thousand gauss, the separation was generally pro-
portional to the fields. Gmelin § was the first to notice an
anomalous effect in the satellite + 224 of the yellow line
5790, in which the separation was proportional to the square
of the field ; the observation was afterwards confirmed by
Lunelund. This singular case was of special interest, as
the principal line to which the said satellite belongs is,

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* Communicated by the Authors.

† Gehrcke and v. Baeyer, *Verh. d. Deutsch. Phys. Ges.* viii. p. 399
(1906).

‡ Lunelund, *Ann. d. Phys.* xxxiv. p. 505 (1911).

§ Gmelin, *Diss. Tübingen,* p. 41 (1909).