Equation (26) is suitable for use in computations for low temperatures. The expanded form for $\chi(0)$ analogous to (24) is suitable for use with high temperatures and is more immediately intelligible than (26). This form is

$$\chi(0)=2\pi\nu\Pi(\sigma)\sum_{n=1}^{\infty}\frac{(2j\Pi(\sigma))^{n-1}}{n!}\times\left\{\frac{1}{3}\sigma^3+\frac{(d-\sigma)d^2}{n+1}-\frac{2(d-\sigma)^2d}{n+2}+\frac{(d-\sigma)^3}{n+3}\right\}. \quad (27)$$

and the corresponding form of the second virial coefficient is

$$B=NkTb-2\pi N^2\Pi(\sigma)\sum_{n=1}^{\infty}\frac{(2j\Pi(\sigma))^{n-1}}{n!}\times\left\{\frac{(d-\sigma)d^2}{n+1}-\frac{2(d-\sigma)^2d}{n+2}+\frac{(d-\sigma)^3}{n+3}\right\}. \quad (28)$$

XCII. *The Reflexion of X-Rays from Imperfect Crystals.* *By* C. G. Darwin, *Fellow and Lecturer of Christ's College, Cambridge* *.

1. *Introduction.*

THE recent work of Bragg, James, and Bosanquet †, on the reflexion of X-rays from rock-salt crystals is of extreme importance in that it promises more directly than any other method to supply information about the actual positions which the electrons occupy in the atom. The method consists in a study of the intensity with which the various faces of the crystal reflect a given wave-length, and is based on the theoretical formulæ given by the present writer ‡. These formulæ showed that such experiments should determine a certain quantity, which is, roughly speaking, the amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam. A study of the various faces of a crystal gives this amplitude as a function of the angle of scattering, and from that the positions of the electrons can be inferred—with this second half of the problem I shall not be here concerned. But the deduction of the amplitude from the experiments encountered certain peculiar difficulties; for the absorption

* Communicated by the Author.

† Bragg, James, and Bosanquet, Phil. Mag. vol. xli. p. 309, and vol. xlii. p. 1 (1921).

‡ Darwin, Phil. Mag. vol. xxvii. p. 315 and p. 675 (1914).

coefficient of the crystal is involved in the formula, and there were indications that the actual absorption was a good deal stronger than usual. This was especially the case in the reflexions at small angles, and these small angles are particularly important, for by them is tested the truth of the hypothesis that in rock-salt the sodium atoms have passed one electron over to the chlorine. The difficulty was overcome—at any rate, partially—by finding the actual absorption coefficients for the various directions in the crystal, by a study of the reflexions of the internal planes of a set of plates of rock-salt. But even this method has an unsatisfactory feature; for it was only possible to arrive at a definite result by rejecting the observations from certain of the plates. It is true that the discrepancy was explained by the fact that these had had much rougher treatment than the rest, but still it suggests a certain measure of doubt as to the soundness of the method, or at any rate the necessity for an inquiry into it. It appeared to me therefore to be worth while to re-examine theoretically the reflexion from crystals in general, in the hope of clearing up the difficulties, and also in the hope that theory would indicate some way of obviating them. The whole point evidently lies in the imperfections of the crystals, and this introduces many complications. I am afraid I have not succeeded in welding the parts of the argument rigorously together, but in spite of certain gaps in the theory it seems unlikely that there is serious error in the general views to which it leads. The work has been rather heavy, but the trouble will have been justified, if it helps in determining the positions of the electrons in the atom, one of the supremely important problems in the present condition of physics.

There will be frequent occasion to refer to the two papers of Bragg, James, and Bosanquet*. When mentioning them in the text, I shall, for short, use only the name of the first of the authors. The papers themselves will be called B.J.B. i. and B.J.B. ii. Similarly, my own former papers† will be denoted D. i. and D. ii.

2. *Previous Theories.*

The theory of the reflexion of X-rays by crystals was discussed by the present writer in the papers D. i. and D. ii. In D. i. it was assumed that each atom scattered X-rays just as though it was alone, and the solution of this interference

* *Locc. citt.*

† *Locc. citt.*

problem led to a formula for the intensity of reflexion. The experimental arrangements to which the calculations were adapted were those in vogue at that time—that is, with crystal fixed during each observation. This was the arrangement used in the experiments of H. G. J. Moseley with the present writer*, and it was to them that the theoretical calculations were applied. In the course of those experiments a single, but a fairly good, measure was made of the absolute intensity of the reflexion of "white X-rays" and also the curve of reflexion against angle was found. By means of a quadrature it was therefore possible to measure the effect of a single atom, and the result was of the right order for the number of electrons anticipated. Yet it was apparent that the theory was defective, for it was calculated that the diffraction pattern of the reflexion could at most be a few seconds across, and that even if all the available radiation in this breadth were reflected the total would still be far short of the observed amount.

Now, if the reflexion was perfect over any region, it could not be legitimate to treat of the atoms as all scattering independently. In D. ii. therefore the mutual influence of the successive planes was included. It was found that over a breadth of a few seconds the reflexion was perfect, and that in this region the ordinary absorption of the rays by the crystal was swamped by a far more powerful special *extinction*. These principles led to a modified reflexion formula, but one which could explain the magnitude of the reflexion no better than the old. A way was found out of the difficulty by supposing the crystal to be a conglomerate of small blocks of perfect crystal all orientated approximately in the same direction, for such a conglomerate would reflect the radiation at many of its blocks, internal as well as external, and this would much increase the total amount reflected. No attempt was made to treat the problem at all fully, but a general line of argument suggested that the effect would be approximately to reinstate the formula of D. i. without the objections that had before attached to it.

All the calculations of these papers were based on experiments in which the crystal was fixed. A. H. Compton† carried out a somewhat similar process quite independently, but based it on the experimental arrangement which has, in fact, proved more convenient in the study of monochromatic

* Moseley and Darwin, Phil. Mag. vol. xxvi. p. 1024 (1913).

† Compton, "The Intensity of X-Ray Reflexion," etc., Phys. Rev. vol. ix. p. 29 (1917).

radiation—that in which the crystal turns during the experiment with a constant angular velocity, so as to integrate the effect of the crystal. His results were substantially the same as those of the present writer, though naturally in a form more convenient for comparison with recent experiments. From a mathematical point of view his method has the advantage that he had no need to consider Fresnel integrals, whereas in my method they were necessary in order to secure convergence. I think the identity of results depends on the fact that if an integral nearly converges, and is made to converge by the introduction of a slight convergency factor, then the consequent value is independent of the form of that factor. My factor was the Fresnel term, Compton made his expression converge by cutting it off at the end. As the present paper deals only with small crystals, the case will be analogous to Compton's, the convergence will be assured, and therefore no use will be made of the Fresnel terms.

The same reflexion formula is worked out in B.J.B. i. It is designed to meet the exact requirements of the work, and, though implicitly using the Fresnel integrals, it is free from much of the mathematical complication of the earlier derivations.

3. *General Exposition of the Problem.*

The imperfection of crystals may take either of two forms, warping or cracking. Either the atoms may be arranged on surfaces which are not quite flat, or else they may be arranged in blocks, each block a perfect crystal, but adjacent blocks not accurately fitted together. An examination of the surfaces of rock-salt crystals suggests that the first is probably more the nature of its imperfection, but the second is much more tractable to mathematics and so has been adopted here.

The whole question turns on the phenomenon of extinction, which may be roughly described as the diminution in the reflected beam due to the fact that when one part of a crystal has reflected some of the radiation, there is less for the parts behind it to reflect. In Bragg's work observation was made on the total ionization as the crystal turns through the reflecting angle. Now, at each instant of the rotation there will be a different amount reflected and therefore a different extinction, and consequently it will not suffice to treat of the mean effect of extinction, without first determining it at every setting of the crystal. As will be

seen, this complicates the mathematics of the problem considerably.

With regard to the extinction itself it is found that it exerts two effects, which may be called primary and secondary. The primary extinction consists in the reduction of the beam reflected from a *perfect* crystal, owing to the defect in the radiation which reaches its lower layers. As shown in D. ii. it may be deduced by considering the multiple reflexions between the planes of the crystal, and for a deep crystal it leads to perfect reflexion in a region near the reflecting angle. At first sight this is a little paradoxical, but it is easy to see that the simpler formula, which neglects extinction, gives an amount reflected greater than the amount of the incident beam.

The secondary extinction is due to the reduction in intensity of the transmitted beam on emerging from the lower side of a small crystal in which some reflexion has taken place. Its effect is practically to increase the absorption coefficient of the crystal by an amount that can be calculated from the amount of the reflexion. The methods used in B.J.B. ii. remove the secondary extinction, but are without influence on the primary. In fact, it will appear that no experiments of the present type can possibly remove it; indeed, to do so would require the measurement of the actual sizes of the small blocks of perfect crystal. This is a serious difficulty in the problem of determining with certainty the positions of the electrons in the atom; but it should be said that it seems probable that in rock-salt the secondary extinction is far more important than the primary: for, if the imperfection is due to warping rather than cracking, there will be very little primary extinction (which depends on the depths of the perfect crystals), whereas the secondary extinction will be as effective as ever.

A confusing circumstance of the problem has lain in the different physical dimensions of the quantities that occur. For example, it is natural to measure the incident beam by its intensity, erg.cm.$^{-2}$sec.$^{-1}$, whereas the *whole* reflexion is required, and this is of dimensions erg.sec.$^{-1}$. This type of difficulty is illustrated in Bragg's formulæ, which involve a superficially irrelevant angular velocity. I have found it very helpful to adopt the terminology of dimensions for the various quantities occurring. Thus we shall denote the whole ionization produced in the electroscope in a given time as *energy*. Then, following the dynamical usage, *power* will signify energy per time. *Intensity* will be power per area,

and *amplitude* will be the square root of intensity. In the example above we should thus speak of the "reflected power." This necessitates a slight alteration from Bragg's terminology. He calls a certain quantity (of zero dimensions) the "reflecting power." To avoid confusion we shall here call it the "integrated reflexion."

The course of the paper is as follows :—

§ 4 treats of the reflexion from a small perfect crystal of any shape and belonging to any of the crystal classes. In § 5 there is found the reflexion from a conglomerate composed of a large number of small crystals orientated nearly in the same direction. In both these sections the crystals are supposed so thin that absorption and extinction are negligible. In § 6 there is a discussion of extinction. In § 7 all the results are combined so as to give the reflexion formula for a deep conglomerate, and in § 8 the same processes are applied to reflexion through a plate—the method of B.J.B. ii. In § 9 there is a short discussion of the rather few experimental results by which the theory can be tested. For the sake of completeness, the formula for reflexion from a powder of crystals is worked out in § 10. The paper concludes with a short general discussion and a summary.

4. *Reflexion from a Small Perfect Crystal.*

We shall first consider the reflexion from a single perfect crystal which is so small that absorption and extinction may be completely neglected. Apart from this condition there is no restriction on its size or shape, and it may belong to any of the crystal classes. Let it be divided into its fundamental lattice. Call the group of atoms in each element of the lattice a molecule. We are not here concerned with symmetry, and there is a certain amount of arbitrariness about the choice of lattice and molecule. For example, in rock-salt it is indifferent whether we take the face-centred cubic lattice, with molecules composed of a sodium atom and one of its chlorine neighbours, or the cubic lattice, containing four atoms of each kind. According to the choice the answer will take a different form, but it is an elementary matter to reconcile the difference.

Take an origin in the crystal, and draw the z axis perpendicular to the planes of which the reflexion is to be studied. Let xz be the plane of incidence of the rays, and let the positive directions of x and z be away from the source. The three primitive translations of the lattice may then be taken as a_x, a_y, a; $b_x, b_y, 0$; $c_x, c_y, 0$. The determinant of

the translations is the volume occupied by the molecule and this is 1/N, where N is the number of molecules in a cubic centimetre. If an incident beam with amplitude Ae^{ikct} falls on the molecule, let the amplitude of the scattered beam at distance r be $fAe^{ik(ct-r)}/r$. Here f is of the dimensions of a length, and, apart from the fact that it applies to molecules instead of atoms, is the same as Bragg's $(e^2/mc^2)\,\mathrm{F}$. It will depend on the orientation of the incident and scattered rays and on the wave-length. It will also vary from one molecule to another, according to the chance positions of the electrons, both on account of heat vibration and of the internal motions of the atoms.

Let the incident beam come from an anti-cathode at distance R, and let its amplitude at the crystal be A and its glancing angle of incidence be ζ. Consider the beam scattered to a direction with glancing angle χ and azimuthal angle ψ measured about Oz. Then the source is at $-\mathrm{R}\cos\zeta$, 0, $-\mathrm{R}\sin\zeta$, and the point of observation at $r\cos\chi\cos\psi$, $r\cos\chi\sin\psi$, $-r\sin\chi$. The position of a molecule is

$$\left.\begin{aligned} x &= \alpha a_x + \beta b_x + \gamma c_x \\ y &= \alpha a_y + \beta b_y + \gamma c_y \\ z &= \alpha a \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (4{\cdot}1)$$

where α, β, γ are three integers. For an incident beam $Ae^{ik(ct-\mathrm{R})}$ the wave scattered by this molecule is

$$\mathrm{A}(f_{\alpha\beta\gamma}/r)\exp ik(ct-\mathrm{R}_{\alpha\beta\gamma}-r_{\alpha\beta\gamma}). \quad . \quad . \quad (4{\cdot}2)$$

Expanding $\mathrm{R}_{\alpha\beta\gamma}$ and $r_{\alpha\beta\gamma}$, the amplitude of the total scattered wave is

$$(\mathrm{A}/r)e^{ik(ct-\mathrm{R}-r)}\sum_{\alpha\beta\gamma} f_{\alpha\beta\gamma}\exp ik[x(\cos\chi\cos\psi-\cos\zeta) + y\cos\chi\sin\psi - z(\sin\chi+\sin\zeta)].$$

To find the intensity multiply by the conjugate imaginary. If $\mathrm{J}=\mathrm{A}^2$ is the intensity of the incident beam, this gives

$$(\mathrm{J}/r^2)\sum_{\alpha\beta\gamma}\sum_{\alpha'\beta'\gamma'} f_{\alpha\beta\gamma}f'_{\alpha'\beta'\gamma'}\exp ik[(x-x')(\cos\chi\cos\psi-\cos\zeta) + (y-y')\cos\chi\sin\psi-(z-z')(\sin\chi+\sin\zeta)]\ldots., \quad (4{\cdot}3)$$

where $x'=\alpha' a_x+\beta' b_x+\gamma' c_x$, etc. f and its conjugate f' will vary from one molecule to another. We must take the mean of (4·3), allowing for the chance variations of f. This will be done by a double averaging of all possible

values of α, β, γ and α', β', γ', and as all pairs of molecules occur in the sum this is the same as taking the mean of f and squaring its modulus. This quantity will be denoted by f^2; it is different from the mean intensity scattered by a single molecule*.

Suppose that the crystal is set so that ζ is near θ, where θ is given by the equation $ka\sin\theta=n\pi$, which determines reflexion in the nth order. For angles far from this the reflexion is insignificant, so we may put

$$\zeta=\theta+u, \quad \chi=\theta+v,$$

and treat u, v, ψ as small. This approximation excludes all the other reflexions from consideration. The reflected intensity is then

$$(\mathrm{J}/r^2)f^2\sum_{\alpha\beta\gamma}\sum_{\alpha'\beta'\gamma'}\exp ik\{(x-x')(u-v)\sin\theta+(y-y')\psi\cos\theta -(z-z')(u+v)\cos\theta\}. \quad . \quad . \quad (4{\cdot}4)$$

From this a factor $\exp -2ik(z-z')\sin\theta$ has been rejected, as it is equal to unity. Now on account of the smallness of u, v, ψ the exponential terms only vary slowly with α, β, γ, and so it will be legitimate to replace the summations by integrations. The number of terms contained in a volume $d\mathrm{V}$ is $\mathrm{N}d\mathrm{V}$ and so the intensity becomes

$$(\mathrm{J}/r^2)\mathrm{N}^2f^2\int^{(6)}d\mathrm{V}\,d\mathrm{V}'\exp ik\{\mathrm{F}(x-x')+\mathrm{G}(y-y')+\mathrm{H}(z-z')\}, \quad . \quad . \quad . \quad (4{\cdot}5)$$

where $\mathrm{F}=(u-v)\sin\theta$, $\mathrm{G}=\psi\cos\theta$, $\mathrm{H}=-(u+v)\cos\theta$, and the volume integrations are each taken over the whole crystal.

We shall now suppose that the crystal is put through one of Bragg's experiments. An instrument is placed so that it can catch all the reflected radiation. The element of area at r is $r^2\cos\chi\,d\chi\,d\psi$ or $r^2\cos\theta\,dv\,d\psi$, and so (4·5) must be multiplied by this and integrated over all values of v and ψ. Further, the crystal is made to rotate with angular velocity ω about the y axis, and the total energy E received by the instrument is measured. This is equivalent to an integration $\int du/\omega$ taken over all values of u. Then

$$\mathrm{E}=\int_{-\infty}^{\infty}du/\omega\iint_{-\infty}^{\infty}r^2\cos\theta\,dv\,d\psi\times(4{\cdot}5).$$

* See Bragg, James, and Bosanquet, *Zeitschrift für Physik*, vol. viii. p. 77 (1921).

To perform the integrations change variables from u, v, ψ to F, G, H ; the latter will all go from $-\infty$ to ∞, and

$$du\,dv\,d\psi = d\mathrm{F}\,d\mathrm{G}\,d\mathrm{H}\,\mathrm{cosec}\,2\theta\,\sec\theta,$$

and so

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{N}^2 f^2\,\mathrm{cosec}\,2\theta \iiint_{-\infty}^{\infty} d\mathrm{F}\,d\mathrm{G}\,d\mathrm{H} \int^{(6)} d\mathrm{V}\,d\mathrm{V}'$$
$$\exp ik\{\mathrm{F}(x-x') + \mathrm{G}(y-y') + \mathrm{H}(z-z')\}. \quad . \quad (4{\cdot}6)$$

This expression can be evaluated by an inversion of the order of integration ; I shall not attempt to justify the process rigorously. First, take the F, G, H integrations between the large limits $\pm \mathrm{F}_\infty$, etc. Then

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{N}^2 f^2\,\mathrm{cosec}\,2\theta\,(2/k)^3\,\mathrm{Lt} \int^{(6)} d\mathrm{V}\,d\mathrm{V}'$$
$$\frac{\sin k\mathrm{F}_\infty(x-x')}{x-x'}\,\frac{\sin k\mathrm{G}_\infty(y-y')}{y-y'}\,\frac{\sin k\mathrm{H}_\infty(z-z')}{z-z'}.$$

Now in the x' integration, which is to follow next, the presence of F_∞ implies that the only important part is near $x'=x$. Similarly, for y' and z'. Hence it will be valid to take these three integrations over all space instead of only over the crystal, for the parts outside will contribute nothing. We now have

$$\int_{-\infty}^{\infty} \frac{\sin k\mathrm{F}_\infty(x-x')}{x-x'}\,dx' = \pi, \text{ etc.}$$

The final three integrations then simply yield

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{N}^2 f^2\,\mathrm{cosec}\,2\theta\,(2/k)^3 . \pi^3 . \mathrm{V}.$$

Now $2\pi/k$ is the wave-length λ. Also we shall adopt the notation of B.J.B. ii. and write

$$\mathrm{Q} = \mathrm{N}^2 f^2 \lambda^3\,\mathrm{cosec}\,2\theta. \quad . \quad . \quad . \quad . \quad (4{\cdot}7)$$

Then

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{QV}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}8)$$

Q is of the dimensions of the reciprocal of a length. This equation is the same as B.J.B. i. p. 326 (4). A little care is needed in considering it, because its physical dimensions are different from those of other equations which will occur later, though it is similar to them in appearance.

The factor Q will include the special peculiarities of the crystal, such as the weak (1, 1, 1) reflexion of rock-salt.

The averaging process will introduce the temperature factor $e^{-B\sin^2\theta}$ and, if desired, the meaning of this may be modified so as to include the relative motions of the atoms in the molecule. There will also be the usual polarization factor $\frac{1}{2}(1+\cos^2 2\theta)$. If these are put in explicitly

$$Q=N^2f^2\lambda^3 \operatorname{cosec} 2\theta\, e^{-B\sin^2\theta}\tfrac{1}{2}(1+\cos^2 2\theta). \quad . \quad (4{\cdot}9)$$

Here f will represent the mean scattering in the equatorial plane of the emergent spherical wave from a molecule ; it is the right quantity for determining the distribution of the electrons. In this paper we shall only be concerned in the deduction of the value of Q and nothing further will be said about the other half of the problem.

The result of this section has been proved without allowance for the fact that the incident waves are really spherical and that the Fresnel zones are exceedingly small in X-ray work. It is easy to carry out the whole process, retaining the squares of x, y, z ; but the formulæ are much more cumbrous. As they lead to precisely the same result, it is not necessary to give them.

5. *Reflexion from a Conglomerate.*

The next problem to be considered is the reflexion from a small imperfect crystal. It is supposed to be made up of a number of perfect crystals differing slightly in their orientations, and the whole is to be so thin that extinction and absorption are negligible. We shall describe it as a *conglomerate* and the component perfect crystals as *blocks*. Suppose that such a conglomerate is put through the same experiment as in § 4. At every point of the observing instrument the intensity will be the sum of the intensities from the separate blocks. Hence the integrated energy will be given by (4·8), where now V is the volume of the whole conglomerate. But this is not enough; it is also necessary to find the actual reflexion when the crystal is fixed at any angle of incidence—a much more difficult matter. However, Bragg's experiments showed that there was reflexion for settings of the crystal differing by as much as a degree, which is very much larger than the breadth of the diffraction pattern of a single block, and this fact makes it possible to approximate. We defer the discussion of the size of blocks required for the approximation to be valid.

Consider a block of volume W which has normal l, m, -1 (it is convenient to take it in the negative direction), where

l, m are small and are measured with reference to some standard direction in the conglomerate, not necessarily the mean direction of the blocks. The intensity of the beam reflected by a single block is then given by (4·5) provided that $u-l$ is put for u, $v+l$ for v, and $\psi-2m\tan\theta$ for ψ. To specify the distribution of the blocks let

$$\mathrm{VF}(\mathrm{W}, l, m)d\mathrm{W}\,dl\,dm \quad . \quad . \quad . \quad . \quad (5{\cdot}1)$$

be the number of blocks in the volume V of the conglomerate which are themselves of volumes between W and $\mathrm{W}+d\mathrm{W}$ and have normals between l, m and $l+dl$, $m+dm$. It follows that

$$\int d\mathrm{W} \iint_{-\infty}^{\infty} dl\,dm\,\mathrm{WF}(\mathrm{W}, l, m)=1. \quad . \quad . \quad (5{\cdot}2)$$

The intensity of reflexion in the direction v, ψ is therefore obtained by taking (4·5) for a volume W (modified as above), multiplying it by (5·1) and integrating over all values of W, l, m that occur. To obtain the reflected power we multiply by $r^2\cos\theta\,dv\,d\psi$ and integrate over all values of v, ψ. The result is

$$\mathrm{JN}^2f^2\cos\theta\,.\,\mathrm{V}\iint_{-\infty}^{\infty} dv\,d\psi\int^{(3)}\mathrm{F}(\mathrm{W}, l, m)d\mathrm{W}\,dl\,dm\int_{\mathrm{W}}^{(6)}d\mathrm{V}\,d\mathrm{V}'$$

$$\exp ik\{(x-x')(u-v-2l)\sin\theta+(y-y')(\psi\cos\theta-2m\sin\theta)$$

$$-(z-z')(u+v)\cos\theta\}. \quad . \quad . \quad . \quad (5{\cdot}3)$$

This is a function of the angle of incidence, that is of u, and the fact that we are not to integrate for u alters the procedure. We must use the assumption that the diffraction pattern of each block extends over a much narrower angle than the distribution of the blocks. Now, if the shape of the blocks were known, it would be possible to carry out the six last integrations, and, regarding the result as a function of l, the l integrand would then consist of the product of two functions, one of which vanishes except for a narrow peak. It would then be correct to substitute in the rest of the integrand the value of l given by the maximum of the narrow peak—that is, to substitute $\frac{1}{2}(u-v)$ for l in F. We may make the same change, even when the order of integrations is altered so as to do that for l first. The same argument also applies for ψ and m. If l_∞, m_∞ denote quantities which

are to be made infinite later, the result of the l and m integrations is

$$\frac{\mathrm{J}\mathrm{N}^2 f^2 \cos\theta}{k^2 \sin^2\theta} \cdot \mathrm{V} \iint dv\, d\psi \int \mathrm{F}\left(\mathrm{W}, \frac{u-v}{2}, \frac{\psi \cot\theta}{2}\right) d\mathrm{W} \int_{\mathrm{w}}^{(6)} d\mathrm{V}\, d\mathrm{V}'$$

$$\frac{\sin k(x-x')\sin\theta \,.\, 2l_\infty}{x-x'} \frac{\sin k(y-y')\sin\theta \,.\, 2m}{y-y'}$$

$$\times \exp -ik(z-z')(u+v)\cos\theta.$$

In this x' has been equated to x and y' to y in all the terms that do not involve l_∞, m_∞. Next integrate for v. With exactly the same argument, we may put $-u$ for v in F, and this makes the integration possible. The result is

$$\frac{\mathrm{J}\mathrm{N}^2 f^2}{k^3 \sin^2\theta} \cdot 2\mathrm{V} \int_{-\infty}^{\infty} d\psi \int \mathrm{F}(\mathrm{W}, u, \tfrac{1}{2}\psi \cot\theta)\, d\mathrm{W} \int_{\mathrm{w}}^{(6)} d\mathrm{V}\, d\mathrm{V}'$$

$$\frac{\sin k(x-x')\sin\theta \,.\, 2l_\infty}{x-x'} \frac{\sin k(y-y')\sin\theta \,.\, 2m_\infty}{y-y'}$$

$$\times \frac{\sin k(z-z')\cos\theta \,.\, v_\infty}{z-z'}.$$

The argument of § 4 now shows that the double volume integration is equal to $\pi^3\mathrm{W}$. Thus the whole effect is

$$\mathrm{J}\mathrm{N}^2 f^2 \lambda^3 \operatorname{cosec} 2\theta \,.\, \mathrm{V} \int d\mathrm{W} \int_{-\infty}^{\infty} \mathrm{W}\mathrm{F}(\mathrm{W}, u, m')\, dm'.$$

Let

$$\mathrm{Q} \int d\mathrm{W} \int dm'\, \mathrm{W}\mathrm{F}(\mathrm{W}, u, m') = \mathrm{G}(u). \quad . \quad . \quad (5{\cdot}4)$$

Then, using (4·7), the power reflected is

$$\mathrm{J}\mathrm{V}\mathrm{G}(u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}5)$$

and by (5·2)

$$\int_{-\infty}^{\infty} \mathrm{G}(u)\, du = \mathrm{Q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}6)$$

The relation (5·5) is practically equivalent to saying that the incident beam is reflected by those blocks which are at the proper angle and no others*.

In order to test the validity of the assumptions made in this work, we shall simplify the problem by supposing that all the blocks are rectangular of sides ξ, η, ζ and orientated

* With a little modification the same argument proves the result deduced in general terms in D. ii, p. 686.

according to the error law. Let σ be the *scatter* of the blocks—that is, the departure of mean square of the normal of a block from that of the conglomerate. Then for (5·1) we must write

$$\frac{V}{\xi\eta\zeta}\frac{\exp-(l^2+m^2)/2\sigma^2}{2\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad (5{\cdot}7)$$

It is now possible, though still tedious, to work out (5·3) down to the last integration, which involves an error function. Approximating for this when u is small we find

$$JVQ\frac{e^{-u^2/2\sigma^2}}{\sqrt{2\pi}\sigma}\left\{1-\frac{1-u^2/2\sigma^2}{\sqrt{2\pi}\sigma\,.\,k\sin\theta\,.\,\xi}\right\}, \quad . \quad (5{\cdot}8)$$

as the expression corresponding to (5·5); so the validity of (5·5) depends on neglecting the second term in the bracket. Thus for a first-order reflexion a/ξ must be small compared to σ. In Bragg's experiments σ was of the order of 1°; so to get an accuracy of 1 per cent. ξ/a must be of the order of 10^4. For spectra of higher orders the conditions are less exacting.

From the general appearance of the work one may hazard a guess that the approximation will be true over a much wider range of values, and would cover the case of a crystal imperfect by warping. It is, of course, possible always to define a function $G(u)$ so as to satisfy (5·5) and it will probably be always true that $\int_{-\infty}^{\infty} G(u)du=Q$; but the important point is that $G(u)/Q$ should depend only on the structure of the conglomerate, for only so will it be possible to pass from reflexion of one order to one of another and from one set of crystal planes to another.

6. *Extinction.*

The calculations have so far dealt with crystals which are so thin that absorption and extinction can be neglected. It is now necessary to inquire to what extent this is justified. In D. ii. a study was made of the reflexion from an infinitely deep perfect crystal, and it was shown that the reflexion is practically perfect when the glancing angle differs from θ by less than $q/ka\cos\theta$, where $q=N\mathcal{f}\lambda a\,\mathrm{cosec}\,\theta$ is the coefficient of reflexion for a single plane (a quantity of zero dimensions); while on either side of this band it falls

off rather rapidly to zero. Inside the crystal the transmitted beam was found to be extinguished at a rate depending on the exact angle, the greatest factor being $e^{-2qz/a}$ at the central point. Now if we take the numerical value which q would have in Bragg's experiments, using rhodium K_α rays and the (1, 0, 0) planes of rock-salt, we find that $q=2\times10^{-4}$ and $2q/a=14000$. The ordinary absorption, measured by depth, is $\mu\operatorname{cosec}\theta=100$; so it is quite clear that extinction will be of far greater importance. Moreover, if we suppose the crystal only a thousand layers thick we have $2qz/a=2q\times1000=0{\cdot}4$, so in even quite a thin layer the extinction may be expected to become considerable, and its influence must be examined. We shall see that it cannot be neglected, but that there is a considerable modification in the formulæ.

In D. ii. the phenomenon was studied for an infinitely broad and infinitely deep crystal. The latter condition is to be altered, but to give up the infinite breadth would lead to great difficulty and we shall therefore retain this condition. It requires, however, an alteration in the type of observation, for an infinite plane will always reflect the rays from *some* point of its surface and so there will be no definite reflecting position. We therefore take a fixed crystal and find the total power reflected for a point source.

Take a crystal composed of m planes, and first consider its effect on plane waves. The equations of D. ii. p. 678 are applicable. They deal with the multiple reflexions in the successive planes of the crystal, allowing, of course, for their phase relations. The difference equations connecting T_r, the amplitude of the transmitted wave at the rth plane, with S_r, that of the reflected, take the form *

$$\left.\begin{aligned} S_r &= -iq\,T_r+(-)^n(1-h-ika\cos\theta\,.\,u)\,S_{r+1}\\ T_{r+1} &= (-)^n(1-h-ika\cos\theta\,.\,u)\,T_r-iq\,S_{r+1}\end{aligned}\right\}, \qquad (6{\cdot}1)$$

where $h=\frac{1}{2}\mu a\operatorname{cosec}\theta$ is the absorption factor for amplitude. The form of the solution will differ from that in D. ii., as the

* It has not been possible to retain completely the same notation as D. ii. The following are the chief differences:—

D. ii.	θ	ϕ	v
Here	$\theta+u$	θ	$ka\cos\theta\,.\,u$.

I am afraid that in D. ii. ϵ was used in two senses; on p. 679 it has the same meaning as here, but on p. 681 it is the same as u here.

end condition now is $S_m=0$. The solution is found to be

$$\left.\begin{aligned} S_0&=-iq\,T_0/(h+ika\cos\theta\,.\,u+\epsilon\coth m\epsilon)\\ T_m&=\epsilon\,\mathrm{cosech}\,m\epsilon\,.\,T_0/(h+ika\cos\theta\,.\,u+\epsilon\coth m\epsilon)\end{aligned}\right\},\quad(6\cdot2)$$

where
$$\epsilon^2=q^2+(h+ika\cos\theta\,.\,u)^2.\quad(6\cdot3)$$

Now, as we saw, h is very much smaller than q. If we neglect it altogether we have

$$\left.\begin{aligned}&\epsilon=\sqrt{q^2-(ka\cos\theta\,.\,u)^2}\quad\text{for}\quad|u|<q/ka\cos\theta\\ \text{and}\quad&\epsilon=i\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\quad\text{for}\quad|u|>q/ka\cos\theta\end{aligned}\right\}.\quad(6\cdot4)$$

It is then easy to verify that for all values of u

$$|T_m|^2+|S_0|^2=|T_0|^2.$$

Further, if h is not quite zero, it may be verified that to a first approximation

$$|T_m|^2+|S_0|^2=|T_0|^2(1-2mk).\quad(6\cdot5)$$

Thus we can always calculate the intensity of the transmitted beam by reducing the incident by an amount corresponding to ordinary absorption and subtracting from it the intensity reflected. This will play an important part in the next section, as it gives rise to the secondary extinction.

Now, consider the reflected beam coming from a point source. Following the line of argument of D. ii., we may resolve the spherical wave into plane, and the whole reflexion is given by integrating the plane wave formula over all values of u. The exact form of the answer involves such matters as the length of the slit in the observing instrument, but here it will suffice to find a quantity that is proportional to it. This is

$$\int_{-\infty}^{\infty}|S_0|^2\,du=q^2|T_0|^2\int_{-\infty}^{\infty}du/|h+ika\cos\theta\,.\,u+\epsilon\coth m\epsilon|^2.\quad(6\cdot6)$$

The evaluation of the integral seems to be impossible in general, but our object can be achieved by taking advantage of the smallness of h and using (6·4). But there is a complication; for unless h actually vanishes, ϵ will have a small real part in the outer region, and therefore if m is large

enough $\coth m\epsilon$ will tend to unity. This will bring the denominator to the form it had in D. ii., viz. :

$$|ika\cos\theta\,.\,u+i\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\,|^2.$$

But if we put $h=0$ before allowing m to become large, the corresponding expression is

$$|ika\cos\theta\,.\,u+\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\cot m\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\,|^2.$$

The integral still converges, but to a different value. To avoid this difficulty we must suppose that the crystal is so thin that mh is small—it must be less than about 10^5 layers thick. For such a crystal the real part of ϵ will not matter and we may put $h=0$ and write the relations (6·4) straight into (6·6). In spite of its unpromising appearance the integral can be evaluated and leads to the remarkably simple result *

$$\int_{-\infty}^{\infty}|S_0|^2\,du=|T_0|^2\frac{q}{ka\cos\theta}\pi\tanh mq. \quad . \quad . \quad (6{\cdot}7)$$

If in this we allow m to become infinite the result is $|T_0|^2\pi\frac{q}{ka\cos\theta}$, whereas the true value from D. ii. should be $|T_0|^2\frac{8}{3}\frac{q}{ka\cos\theta}$; so even in this extreme case the error is only 18 per cent. for taking h zero before putting m infinite. This shows that the approximation may be expected to hold for quite deep crystals with considerable accuracy.

Now take the same problem and work it out on the principles of § 4. It is easily found that

$$S_0=-iqT_0\frac{1-\exp-2mika\cos\theta\,.\,u}{2ika\cos\theta\,.\,u},$$

which leads to the result

$$\int_{-\infty}^{\infty}|S_0|^2\,du=|T_0|^2\frac{q}{ka\cos\theta}\pi\,.\,mq. \quad . \quad . \quad (6{\cdot}8)$$

* This result was first discovered by obtaining an expansion in terms of mq. The complete proof may be constructed as follows. Write the denominator as the product of two conjugate imaginaries and split it into partial fractions. Next express it as a complex integral with argument ϵ.... necessitating a *cut* between $\pm q$ in the ϵ-plane. It may then be proved that the poles of either fraction in the integrand lie entirely on one or other side of the path of integration. Hence the path may be replaced by a circle at infinity which contributes nothing, together with a small circle round $\epsilon=q$ which introduces the hyperbolic tangent.

So we may represent the effect of extinction by introducing a correction factor

$$\frac{\tanh mq}{mq}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}9)$$

and this is quite accurate for crystals not so deep that the ordinary absorption would become important, and remains fairly good even for those much deeper.

Now consider a small block limited in breadth as well as depth and irradiated by plane waves. The multiple internal reflexions will give a complicated system, which will depend on the crystal's shape and will be irregular at its surfaces. But it seems reasonable to represent its effect by calculating the intensity of reflexion as though it were of infinite area, and then selecting from the reflected rays the cross-section which has met the actual crystal. Let d be the mean depth, then V/d is the area. The cross-section of the rays is therefore $(\mathrm{V}/d)\sin\theta$, and so the power reflected is

$$|\mathrm{S}_0|^2\,(\mathrm{V}/d)\sin\theta.$$

Then we have

$$\mathrm{E}=\int_{-\infty}^{\infty}|\mathrm{S}_0|^2\,(\mathrm{V}/d)\sin\theta\,du/\omega.$$

If we put $\quad |\mathrm{T}_0|^2=\mathrm{J},\ d=ma,\ q^2=2\mathrm{Q}a^2\cot\theta/\lambda,$

we thus get $\quad \mathrm{E}\omega/\mathrm{J}=\mathrm{VQ}\tanh mq/mq, \quad . \quad . \quad . \quad (6{\cdot}10)$

which shows that on these assumptions the same correction factor is applicable in (4·8) as in (6·8).

Exactly the same process may be applied to the argument of § 5. For though there the crystal was not rotating, yet the distribution of the blocks was such that there was an integration, equivalent in its effects to the u integration here. We may thus say that the reflexion of a conglomerate at angle $(\theta+u)$ is given by

$$\mathrm{JVG}(u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}11)$$

provided that

$$\mathrm{G}(u)=\mathrm{Q}'\int d\mathrm{W}\int_{-\infty}^{\infty}dm'\,\mathrm{WF}(\mathrm{W},u,m'), \quad . \quad (6{\cdot}12)$$

where $\quad \mathrm{Q}'=\mathrm{Q}\tanh mq/mq. \quad . \quad . \quad . \quad . \quad (6{\cdot}13)$

In consequence of this (5·6) becomes

$$\int_{-\infty}^{\infty}\mathrm{G}(u)\,du=\mathrm{Q}'. \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}14)$$

The extinction factor is perhaps more properly expressed in terms of the depth of the block, rather than the number of its planes, because this will be roughly the same in all directions and so will give rise to a formula suitable for comparing reflexions of different faces of the crystal. Then the extinction factor is

$$\frac{\tanh\sqrt{2Qd^2\cot\theta/\lambda}}{\sqrt{2Qd^2\cot\theta/\lambda}} = 1-\frac{2}{3}\frac{Qd^2\cot\theta}{\lambda}+\frac{8}{15}\frac{Q^2d^4\cot^2\theta}{\lambda^2}-\ldots\ldots \quad (6{\cdot}15)$$

Considering the numerical values in Bragg's experiments, it appears that for a block two thousand layers thick the correction will be about 5 per cent.

Thus we see that a conglomerate of crystals of size d will give rise to a Q modified by the extinction factor (6·15). This modification is the primary extinction, and as we shall see it is untouched by Bragg's method of eliminating extinction. The secondary extinction arises in considering the action of the transmitted beam on the lower blocks. It may be calculated by allowing for the ordinary absorption of the incident beam and in addition subtracting from it the amount of the reflexion. As this last depends on Q′ the secondary extinction will do so too.

7. *Reflexion from a Face.*

Now consider what happens when a beam strikes the face of a thick conglomerate at any angle near the angle of reflexion. Imagine the conglomerate divided into successive layers. In the first layer it will find a few blocks rightly placed, and from each of these a ray will be reflected. In § 6 we saw that extinction would reduce the intensity of the transmitted beam by an amount equal to the intensity of the reflected beam. After traversing the first layer the beam will thus be defective in a few patches, where particular blocks have been able to extinguish it; but in considering the effect of many layers it will be correct to average the intensity after traversing each and so treat it as uniform for the next. To obtain the power transmitted through a single layer, we shall therefore take the power reflected by it, subtract it from the incident and reduce the result by an amount given by the ordinary absorption.

The whole reflexion from a deep crystal results from the

multiple reflexions in the successive layers. The multiplicity is of a different type from that of (6·1) because the rays are not now coherent. The problem of these multiple reflexions would be exceedingly difficult if it were treated exactly; for each layer will, on account of diffraction, spread out incident parallel rays into a certain range of angles and so will continually change the angle at which they attack the successive layers. But, if (as assumed in § 5) the crystal is so imperfect that diffraction does not change the direction of the rays to an extent comparable with the scale of variation in the orientations of the blocks, then it will be legitimate to regard the reflected rays as coming plane parallel off the crystal (at an angle exactly 2θ to the incident beam). In consequence of this it will be possible to replace a highly complicated system of integral equations by differential equations of a simple type.

Suppose that a plane incident beam of total power I strikes a deep crystal at angle $\theta+u$ to the face, and let E_u be the total power reflected. Let $I_u(z)$ and $E_u(z)$ be the powers of the incident and reflected beams at a depth z inside the crystal. Suppose that the area of face they strike is B, and consider the effect of a layer of thickness δz. The incident beam has cross-section $B\sin(\theta+u)$ and so its intensity is $I_u(z)/B\sin(\theta+u)$. The power reflected by the volume $B\delta z$ will, by (6·11), be therefore $I_u(z)\,\delta z\,G(u)\operatorname{cosec}(\theta+u)$. The incident beam will lose the same amount through extinction, while through absorption it will lose $I_u(z)\,\delta z\,\mu\operatorname{cosec}(\theta+u)$. In the same way the reflected beam will be partly reflected back again. To treat of it we must regard the conglomerate upside down—that is, for $F(W, l, m)$ in (5·1) we must write $F(W, -l, -m)$ and also for u, $-u$. Thus $G(u)$ will be unaltered in form, and the beam $E_u(z+\delta z)$, which is coming outwards through the layer δz, throws an amount

$$E_u(z+\delta z)\,\delta z\,G(u)\operatorname{cosec}(\theta-u)$$

back into the incident direction. Corresponding to this there is an amount

$$E_u(z+\delta z)\,\delta z\,\{\mu+G(u)\}\operatorname{cosec}(\theta-u)$$

absorbed and extinguished. Balancing up the gains and losses we arrive at a pair of equations,

$$\left.\begin{aligned}\frac{\partial I_u(z)}{\partial z} &= -\frac{\mu+G(u)}{\sin(\theta+u)}I_u(z)+\frac{G(u)}{\sin(\theta-u)}E_u(z)\\ -\frac{\partial E_u(z)}{\partial z} &= -\frac{\mu+G(u)}{\sin(\theta-u)}E_u(z)+\frac{G(u)}{\sin(\theta+u)}I_u(z)\end{aligned}\right\}. \quad (7\cdot1)$$

These equations will be true even when the scatter of the blocks varies with the depth in the crystal, but to make progress we shall suppose it constant—that is, $G(u)$ is not a function of z. This makes the equations linear. The end conditions are that $I_u(z)$ and $E_u(z)$ should vanish for infinite z. There is no need to give the solution in detail—E_u the value at the surface is what is required. It is *

$$E_u/I = \frac{\sin(\theta-u)}{\sin\theta\cos u} G(u) \Big/ [\mu + G(u) + \sqrt{\{[\mu+G(u)]^2 - [G(u)]^2(1-\cot^2\theta\tan^2 u)\}}]. \quad (7{\cdot}2)$$

The first factor represents the influence of having a crystal face that is not the true reflexion plane—whether because the surface is covered by a vicinal face or because it has been badly ground. For the layers into which the crystal was divided were drawn parallel to the actual face, and if this is not the true reflexion face $G(u)$ will be unsymmetrical about $u=0$. Now suppose that the source and point of observation are interchanged—this is the same as observing on the other side of the spectrometer. We must then draw the x axis in the other direction, and so shall obtain a formula involving $-u$ instead of u. But if on this side we take $u'=-u$ we shall have

$$E'_{u'}/I = \frac{\sin(\theta+u')}{\sin\theta\cos u'} G(u') / \{\mu + G(u') + \text{ etc.}\}.$$

Thus if we compare together points where the u of one side is the same as the u' of the other, then clearly

$$E'_u/E_u = \sin(\theta+u)/\sin(\theta-u).$$

In the case of a fairly perfect vicinal face all the settings which give perceptible reflexion will be not far from $u=\alpha$, the inclination of the face, and so the ratio of all pairs of corresponding powers will be nearly $\sin(\theta+\alpha)/\sin(\theta-\alpha)$, and therefore the same will be true of the integrated reflexion. This factor may also be derived by simple consideration of the area of the crystal on which a limited beam would fall in the two cases. The difference of the reflexions was originally observed by Sir W. H. Bragg †, and

* *Mutatis mutandis* this is substantially the solution obtained by K. W. Lamson, Phys. Rev. vol. xvii. p. 624, by quite a different method. If (7·1) are treated as difference equations his exact form is obtained.

† W. H. Bragg, Phil. Mag. vol. xxvii. p. 888 (1914). At first I thought my explanation was different from his; but through correspondence it became evident that we were only regarding the matter from different points of view. I wish to express my thanks to him for his interest in the matter.

explained by considering the absorption of the emergent beams in the two cases. His argument leads to the same factor. The influence of the vicinal face can be completely eliminated by averaging for both sides, and we shall suppose this done. There is then no need to consider the first factor in (7·2) at all.

Bragg's "reflecting power" (which we are here calling the *integrated reflexion*) was defined by him as $E\omega/I$, where the crystal was turned with angular velocity ω through the reflecting angle and E was the total energy obtained, while I was the power of the incident beam. His I is the same as ours, his E is our $\int_{-\infty}^{\infty} E_u\,du/\omega$. So we have for the integrated reflexion

$$\rho = \int_{-\infty}^{\infty} G(u)\,du \Big/ \left\{ \mu + G(u) + \sqrt{[\mu+G(u)]^2 - [G(u)]^2(1-\cot^2\theta\tan^2 u)} \right\}. \quad (7\cdot3)$$

If $G(u)$ is small compared with μ for every value of u, then neglecting the small terms of the denominator and using (6·4) we have

$$\rho = Q'/2\mu.$$

Apart from the difference between Q' and Q, this is the equation used in B.J.B. i.

If $G(u)$ is not always small enough to justify this approximation, it may still be small enough to admit of expansion in powers of $G(u)/\mu$. Then we have

$$\rho = \frac{1}{2\mu}\int_{-\infty}^{\infty} G(u)\,du - \frac{1}{2\mu^2}\int_{-\infty}^{\infty} G^2(u)\,du + \frac{1}{\mu^3}\int_{-\infty}^{\infty} G^3(u)\left(\tfrac{5}{4} - \cot^2\theta\tan^2 u\right)du.$$

Let

$$\left.\begin{aligned} \int_{-\infty}^{\infty} G^2(u)\,du &= g_2 Q'^2 \\ \int_{-\infty}^{\infty} G^3(u)\,du &= g_3 Q'^3 \end{aligned}\right\}; \quad \ldots\ldots \quad (7\cdot4)$$

then g_2 and g_3 will be constants of the crystal. For most crystals it will be legitimate to neglect the term involving

$\tan^2 u$. Then

$$\rho = \frac{Q'}{2\mu} - g_2\frac{Q'^2}{2\mu^2} + g_3\frac{5Q'^3}{4\mu^3}$$

$$= \tfrac{1}{2}Q'/\left\{\mu + g_2Q' + (g_2^2 - \tfrac{5}{4}g_3)\frac{Q'^2}{\mu}\right\}. \quad . \quad (7{\cdot}5)$$

If the third term is neglected this is in the form used by Bragg, who calls g_2Q' the "extinction coefficient." If we had considered that every incident and every reflected beam had only a single reflexion, then we should have had instead of (7·2)

$$E_u/I = \tfrac{1}{2}G(u)/\{\mu + G(u)\},$$

and this would lead to the same first two terms in (7·5). This idea has been used by Sir W. H. Bragg *, and it is clear that there will be a wide region of values in which it will be a very good approximation.

It is evident that a knowledge of ρ by itself is not sufficient to determine the value of Q'; but (7·2) suggests that it may be possible to do so by a study of the shape of the reflexion curve. For if we know E_u for all values of u we may solve (7·2) for $G(u)$. If the first factor is omitted, we have

$$G(u) = \frac{2\mu(E_u/I)}{1 - 2(E_u/I) + (1 - \cot^2\theta\tan^2 u)(E_u/I)^2}. \quad (7{\cdot}6)$$

A quadrature will then lead to Q' by (6·14), and so the secondary extinction is eliminated.

It thus appears theoretically possible to determine Q' from observation on a single face. There is, however, a serious objection to the method. It is not reasonable to suppose that $G(u)$ is really independent of the depth; for grinding or even cleaving must necessarily act differently on the surface-layers and interior, and if G is an unknown function of z, the data are insufficient for a solution. If, in spite of this, the process should be valid, there would still be the difficulty that Q' may differ from Q. The only possibility of determining Q would appear to lie in finding Q' for several crystals, of which the blocks were scattered in various degrees. If then the results all came the same, there would be a presumption that primary extinction was not present. Of two discordant values the greater is to be

* W. H. Bragg, Phil. Mag. vol. xxvii. p. 881 (1914), and Proc. Lond. Phys. Soc. vol. xxxiii. p. 304 (1921).

preferred, and it would be expected that this greater value would be associated with a greater scattering among the blocks—that is, a broader region of reflexion.

8. *Reflexion through a Plate.*

To overcome the difficulty of the unknown extinction Bragg sent X-rays through a crystal plate and observed the reflexion from the interior planes. In this case the equations for the multiple reflexions take quite a different form from (7·1). Suppose the crystal cut into layers parallel to its faces, the breadth of a layer being δx. Let $I_u(x)$ be the power of the incident beam at depth x from the front face, $E_u(x)$ of the reflected beam. Let B be the area of the face on which the rays fall. The incident beam now makes angle $\theta+u$ with the *normal* to B, and so the intensity is $I_u(x)/B\cos(\theta+u)$. The power reflected in the volume $B\delta x$ is $I_u(x)\,\delta x\,G(u)\sec(\theta+u)$ and the incident ray is reduced by an amount

$$I_u(x)\,\delta x\{\mu+G(u)\}\sec(\theta+u).$$

Similarly for the reflected rays. The differential equations now are

$$\left.\begin{aligned}\frac{\partial I_u(x)}{\partial x} &= -\frac{\mu+G(u)}{\cos(\theta+u)}I_u(x)+\frac{G(u)}{\cos(\theta-u)}E_u(x)\\ \frac{\partial E_u(x)}{\partial x} &= -\frac{\mu+G(u)}{\cos(\theta-u)}E_u(x)+\frac{G(u)}{\cos(\theta+u)}I_u(x)\end{aligned}\right\}. \quad (8\cdot1)$$

The end condition is that $E_u(x)=0$ for $x=0$. If E_u is the power of the emerging reflected beam, the solution gives

$$E_u/I=\frac{G(u)}{\cos(\theta+u)}\,\frac{\sinh\tau x}{\tau}\exp-\frac{x\{\mu+G(u)\}\cos\theta\cos u}{\cos(\theta+u)\cos(\theta-u)}, \quad (8\cdot2)$$

where

$$\tau=\frac{\sqrt{G^2\cos(\theta+u)\cos(\theta-u)+(\mu+G)^2\sin^2\theta\sin^2 u}}{\cos(\theta+u)\cos(\theta-u)}.$$

Apart from the first factor in (8·2), u only occurs as a square. So, as in § 7, an averaging with the reversed beam will eliminate the effect of untrue faces. In most cases this will be far less important than it was in § 7, because the factor occurs as a cosine and in the important cases θ will be fairly small.

The exponential and hyperbolic functions can always be expanded, and if $G(u)/\mu$ is not large the series will converge rapidly. It will usually be right to omit the terms involving $\sin^2 u$, etc., even though some of these are multiplied by μ and are being compared with others only multiplied by $G(u)$. Then

$$\tau = G(u) \sec\theta$$

and

$$E_u/I = e^{-\mu x'}[x'G(u) - x'^2G^2(u) + \tfrac{2}{3}x'^3G^3(u)], \quad . \quad (8{\cdot}3)$$

where x' is written for $x \sec\theta$. As in § 7, if the form of E_u/I is found experimentally, it is possible to solve (8·3) and so to obtain $G(u)$, and consequently Q', from observation of a single crystal. In this case the process will be free from the objection raised in § 7 about non-uniform distribution of the blocks; for, in reflecting, the surface does not now receive preferential treatment over the interior. The primary extinction is again untouched by the process.

Bragg adopted a method which assumed that he could get a series of plates of various thicknesses, for all of which the distribution of the blocks was the same. He took the integrated reflexion of them, and found for each set of reflecting planes the thickness which gave maximum reflexion and the height of the maximum. Now by (7·4) the integrated reflexion may be written as

$$\rho = \int_{-\infty}^{\infty} (E_u/I)\, du = e^{-\mu x'}[Q'x' - g_2 Q'^2 x'^2 + \tfrac{2}{3}g_3 Q'^3 x'^3]. \quad (8{\cdot}4)$$

This has maximum at

$$x' = \frac{1}{\mu} - g_2\frac{Q'}{\mu^2} + \tfrac{4}{3}g_3\frac{Q'^2}{\mu^3}, \quad . \quad . \quad . \quad . \quad . \quad (8{\cdot}5)$$

and the value there is

$$\frac{Q'}{\mu e}\left[1 - g_2\frac{Q'}{\mu} + (\tfrac{1}{2}g_2^2 + \tfrac{2}{3}g_3)\frac{Q'^2}{\mu^2}\right] \quad . \quad . \quad . \quad (8{\cdot}6)$$

$$= Q'\Big/e\left\{\mu + g_2Q' + (\tfrac{1}{2}g_2^2 - \tfrac{2}{3}g_3)\frac{Q'^2}{\mu}\right\}. \quad (8{\cdot}7)$$

Thus Bragg's work determines g_2Q', and if the distribution of the blocks is the same as in the crystal used for the work of § 7, it follows that his correction for secondary extinction is correct to the second order, and from the magnitudes of the quantities involved it is improbable that the third order is sensible.

9. *Comparison with Experiment.*

There is not a great deal of material suitable for testing these formulæ, and the result of the test is not very satisfactory. The first point of comparison is the curve in B.J.B. ii. p. 12, which relates the modified absorption coefficient to the integrated reflexion of a face. The ordinate of the curve is given by (8·7) and its abscissa by (7·5). The linear form of the curve means that

$$\left\{ g_2+(\tfrac{1}{2}g_2^2-\tfrac{2}{3}g_3)\frac{Q'}{\mu} \right\} . 2(\mu+g_2Q') \quad . \quad . \quad (9\cdot1)$$

is practically constant, and this it will be, if g_2^2Q', g_3Q' are negligible compared with $g_2\mu$. Neglecting these terms we find

$$2g_2\mu=5\cdot6\div(5\cdot41\times10^{-4}),$$

whence $g_2=484$. This may be best interpreted by assuming an error law of distribution as in (5·7). Then

$$G(u)=Q'e^{-u^2/2\sigma^2}/\sqrt{2\pi}\sigma \quad \text{and} \quad g_2=\sqrt{\pi}/2\sigma,$$

which gives $\sigma=6'$. This is a good deal smaller than would be expected from the general description of the experiments; for it means that all the reflexion should take place within less than half a degree, whereas the paper implies that the band of reflexion was nearly a degree broad. A part of the discrepancy may be due to the neglect of the further terms in (9·1), for it is evident that the series is not very rapidly convergent, when, as here, $g_2Q'/\mu=5\cdot6/10\cdot7$.

A more detailed, but still less satisfactory, comparison may be made with the reflexion curves of B.J.B. ii. p. 13. The experiments dealt with the reflexion through two plates of the same thickness, of which the surfaces had been differently treated. The information about the curves is not quite complete, but can be supplied indirectly. It is first necessary to find the absolute values of E_u/I. The curves are drawn in arbitrary units, and a constant multiplier must be obtained for each from the observed value of its integrated reflexion (which is the area of the curve), in terms of that of a standard plate of the same thickness. The reflexion of the standard was calculated (p. 7) from that of a face, on the principle that for a surface the integrated reflexion is $Q'/2(\mu+g_2Q')$, while for a plate of thickness giving maximum reflexion it is $Q'/e(\mu+g_2Q')$. There is thus the assumption that the plate has the same scatter as the face.

However, from these data it is possible to get the numerical values of E_u/I for all values of u. It is found that the approximation of (8·3) is quite accurate enough, and this equation can be solved for $G(u)$. A quadrature then gives Q'. The results are rather disappointing, for the curve A gives $Q'=\cdot0119$, while B gives $Q'=\cdot0146$. Moreover, the extinction coefficients g_2Q' come out as 1·01 and 0·47 respectively, whereas values in the neighbourhood of 5 would have been expected. The discrepancy is exactly the same as in the evaluation of g_2 above. There it was found that the region of reflexion ought to be narrower for the observed extinction, here that the observed reflexion curve implies less extinction than is in fact found. It is, of course, possible that a part of the difference between A and B may be due to a difference of their primary extinctions, and the cause suggested at the end of § 7 may be another source of discrepancy.

Finally, our results may be applied to some experiments due to Davis and Stempel *. Here the perfection of the calcite crystal was enormously greater than in Bragg's rock-salt, and all the approximations are hopelessly wrong. If, nevertheless, we apply our formulæ to the actual curves we may obtain something of an idea of the perfection of the crystal. The data are directly in terms of E_u/I. They were dealing with white X-rays, but there was double reflexion in two crystals with parallel faces and it is easy to see that dispersion will play no part, so that the formulæ for monochromatic rays are applicable. Taking the most extreme case of all, their fig. 6 (p. 617), we use (7·6) to obtain $G(u)$ and from this we get a scatter $\sigma=4''\cdot8$. Now this is only a little greater than what should be the region of complete reflexion in a perfect crystal, and the most remarkable thing about it is that not more than half the incident beam is reflected. This suggests that a part of the breadth of the reflexion is really due to imperfection. It does not appear worth while to carry further the comparison with these experiments, both because our methods are not applicable rigorously, and because there must certainly be a great deal of primary extinction in crystals that are so nearly perfect, so that they would be of little use in a determination of Q.

* Davis and Stempel, Phys. Rev. vol. xvii. p. 608 (1921).

10. *The Powder Method.*

From the preceding sections it appears that the phenomenon of primary extinction is likely to make serious difficulty in determining Q by the method of reflexion, whether from a face or through a plate. The only way to ensure its absence is to use crystals so small that it is bound to be negligible. For example, from the numerical data of § 6, primary extinction would be absent, if the crystals were so small as to be just about invisible under a high-power microscope. The only practicable way of using such is by the powder method of Debye and Hull, which has recently been used quantitatively by Sir W. H. Bragg *. For the sake of completeness we shall apply our processes to this, adopting an arrangement which is probably not the most convenient, but which could easily be modified.

We shall suppose a speck of powder is illuminated by rays and shall find the total power thrown off into a cone (of half-angle 2θ), corresponding to one particular set of planes. Let the volume be V and let it be composed of small blocks, the typical block being of volume W with normal in the direction of colatitude and longitude ω, ϕ. Let the distribution of the blocks be given by

$$\mathrm{V F(W)}\, d\mathrm{W} \sin\omega\, d\omega\, d\phi. \quad . \quad . \quad . \quad (10{\cdot}1)$$

F is nearly the same as in § 5, but is now independent of ω, ϕ, as they are pointed equally in all directions. We have then

$$4\pi \int \mathrm{W\, F(W)}\, d\mathrm{W} = 1,$$

ω is the inclination of the normal to the incident beam, and so $\omega = \frac{\pi}{2} - \theta - u$. Multiplying (4·5) by the appropriate factors we have for the whole reflected power arising from this set of planes

$$\mathrm{J N^2} f^2 \cos^2\theta \,.\, \mathrm{V} \int^{(3)} \mathrm{F(W)}\, d\mathrm{W}\, du\, d\phi \int^{(2)} dv\, d\psi \int_{\mathrm{W}}^{(6)} d\mathrm{V}\, d\mathrm{V}'$$
$$\exp ik\{(x-x')(u-v)\sin\theta + (y-y')\psi\cos\theta$$
$$-(z-z')(u+v)\cos\theta\}. \quad . \quad (10{\cdot}3)$$

Here J is the incident intensity and of the factor $\cos^2\theta$ one term is due to the $\sin\omega$, the other to the $r^2\cos\theta\, dv\, d\psi$ integration. The integrations follow the same course as

* W. H. Bragg, Proc. Lond. Phys. Soc. vol. xxxiii. p. 222 (1921).

those in § 4. The result is *

$$\tfrac{1}{2}\mathrm{JV}\cos\theta\,.\,\mathrm{Q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10{\cdot}4)$$

This must then be multiplied by a numerical factor given by the symmetry of the crystal according to the following rule. If the crystal has no centre of symmetry, add one on to its symmetry elements. Now construct the "form" corresponding to the planes that are being studied. The number of its faces is the required numerical factor for (10·4); by virtue of the centre of symmetry it must always be an even number. For example, in rock-salt the form for (1, 0, 0) is a cube and the factor is 6; for (1, 1, 0) it is a rhombic dodecahedron and the factor is 12; for most planes the number is 48. It may sometimes be necessary to apply a correction for absorption. This will depend on the shape of the powder and is a matter of simple geometry. It should not be necessary to make any allowance for secondary extinction, but if it were needed it could be calculated on the principles of §§ 7, 8.

11. *Discussion of Results.*

The tests in § 9 were rather unsuccessful, but I do not think sufficiently so to condemn our theory out of hand. Should further tests prove that the discrepancy is real, it appears to me that it would throw doubt, not only on my own work, but also on the validity of the deduction of Q in B.J.B. ii.; for that deduction can only be founded on some theory which must be the same as the present one in principle.

It is of course possible that a crystal, imperfect by warping instead of cracking, should obey a different rule, but I should judge this to be very unlikely. For (5·5) may be used to define a function $\mathrm{G}(u)$ for such a crystal, though its expression in terms of the imperfection will not be so easy as for a cracked crystal. With this $\mathrm{G}(u)$, the work of §§ 7, 8 will all stand good, and will determine the relation between the extinction and the breadth of the reflexion region, without touching the question of the meaning of $\mathrm{G}(u)$. As to this last, it is a most natural conjecture that (5·6) will be true for it, in view of the generality which that equation has already been proved to possess, and so will lead to the right value for Q. If, as appears probable, rock-salt is warped rather than cracked, this will have the advantage that primary extinction is unlikely to be important, and so the

* The expression does not vanish for $\theta=\pi/2$ on account of the factor $\mathrm{cosec}\,2\theta$ in Q.

interpretation of experiments will be freed from a source of error, the amount of which must be very uncertain.

We therefore conclude that, to establish beyond doubt the validity of the work of Bragg, James, and Bosanquet, it is essential that the work of §§ 7, 8 should be verified by tests like those of § 9, and if it should be proved correct, then we may have great confidence in their results. Failing this verification, the theory on which they eliminated the extinction is without good foundation and the results must be regarded with some caution. In this case, it seems to me that the most satisfactory way of determining Q is by the powder method of § 10.

Summary.

The paper is a theoretical inquiry into the possibility of determining the arrangement of electrons in the atom from the intensities of the X-rays scattered by crystals. This problem falls into two stages: first from crystal to molecule, then from molecule to electrons—only the first stage is here treated.

Simple formulæ have been given by various writers, and the process has been carried out experimentally by Bragg, James and Bosanquet. They encountered the difficulty of "extinction." This extra absorption falsifies the formulæ, but they measured it directly and so obtained a correction. This paper is concerned with seeing whether their correction was valid. The point of the problem was known to lie in the imperfection of crystals.

After a general discussion (§§ 1, 2, 3), it is shown (§ 4) that if a small perfect crystal of any shape is turned through the reflecting angle for monochromatic rays, the amount of reflexion determines a quantity Q, which is what is required for the second stage of the problem.

The reflexion is worked out (§ 5) for a conglomerate of small blocks of perfect crystal all orientated nearly in the same direction, the conglomerate being so thin that absorption and extinction can be neglected.

Extinction—that is, the special absorption of rays at the reflecting angle—is shown (§ 6) to lead to two effects, primary and secondary. The primary diminishes the reflexion from a perfect crystal below the amount given by the simpler theory. It leads to a change in the value of Q depending on the depth of the crystal, and none of the experimental processes eliminate this change. The secondary extinction results from the reduction in the strength of the beam transmitted through the crystal.

The reflexion from the face of a deep imperfect crystal is evaluated (§ 7), and it is shown how the secondary extinction may be eliminated.

The same process for reflexion from the interior planes of a plate is worked out (§ 8), and the formulæ are justified whereby Bragg, James, and Bosanquet eliminated the extinction—but only the secondary extinction.

The theoretical results are compared with experiment (§ 9). The experimental data are rather inadequate and the agreement is not very good.

The corresponding calculations are done for the powder method of observation on crystals (§ 10).

The paper concludes with a short discussion (§ 11), suggesting the need of further tests.

XCIII. *Scattering and Dispersion of Light.* *By* U. Doi, *Research Student in the Institute of Physical and Chemical Research, Tokyo* *.

AUTHORS differ in their opinions as to the mechanism of scattering light by a medium through which the light travels. Schuster asserts, however, in his 'Theory of Light' (p. 325) that, if a molecule of the medium may be looked upon as a separate source of scattering, the scattering due to it follows undeviatedly the celebrated formula of Lord Rayleigh, whatever be the theory we adopt. It will not be without interest, for instance, to notice that Jakob Kunz †, indeed, derived exactly the same formula from an elementary theory of scattering of light by small dielectric spheres.

Ever since the electron theory of matter began its striding progress, and the well-known dispersion formula was deduced by H. A. Lorentz through his electronian analysis of atomic constructions, attempts have been made to interpret the absorption of light from the electronian standpoint of view. Thus, Drude ‡ and Voigt § attribute it to the damping of the oscillations of bound electrons in the atoms of the absorbing medium, the damping process being caused by a resisting force proportional to the velocity of the electrons. They insert consequently a term of this damping in the equation of motion of

* Communicated by the Author.
† Phil. Mag. xxxix. p. 416 (1920).
‡ P. Drude, *Lehrbuch der Optik*, p. 353.
§ W. Voigt, *Magneto- und Electrooptik*, p. 104.