

# On the intensities of electron diffraction rings

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The intensities of the rings formed when a beam of fast electrons is sent through a polycrystalline film were first studied by G. P. Thomson (1929) in the case of thin films of gold. The intensities were found to fit very well (Mott 1929) with those calculated theoretically on the assumption that the Laue theory held for scattering of electrons by the crystallites. Results also in accordance with the theory were obtained by Mark and Wierl (1930). A recent investigation by Ornstein and his collaborators (1938) on polycrystalline films of copper and silver have led to results diverging widely from the theoretical in the sense that if the (222) ring were fitted to the theoretical value the (111) ring, which is the strongest, had an intensity too low by a factor of two to three.

It had also been pointed out by Kirchner (1932) that the amount of scattering by atoms of the heavy elements (Au, Ag) is so large that the Laue theory can hardly be expected to hold, and he discounted the significance of the agreement between theory and experiment.

In view of the results of Ornstein and his co-workers, a consideration of the theoretical aspect of the scattering by small crystals seems to be necessary. In particular it is of interest to find out what size of crystal of a particular substance is compatible with the assumption of Laue scattering. In the following the scattering is regarded from the point of view of the dynamical theory in the form given by Bethe (1928). The dynamical theory is particularly applicable when the scattering is large, but there is no reason why the theory should not be used to discuss the case where the scattering is small, providing that it can be shown that the assumptions of the theory still hold. We shall consider the dynamical theory for thin crystals, and shall discuss the limiting case when it goes over into the kinematical (or Laue) form. In this way we obtain criteria as to when a crystal is sufficiently small to allow the Laue theory to be applied.

In applying this to the scattering by polycrystalline films, the results of the investigation are not quite as definite. The dynamical theory in its present form can be applied only to a parallel-sided slab; in a polycrystalline film the electrons entering through one face of a crystallite will, after reflexion, emerge from a face in general not parallel to the first. It seems

reasonable to assume, however, that where the dynamical theory in its present form shows large deviations from the Laue theory, these will also be found in a more exact theory.

§ 1. *Bethe's theory.* The Schroedinger equation for an electron in the periodic field of a lattice takes the form

$$\Delta\Psi + \frac{8\pi^2me}{h^2} (E + V) \Psi = 0, \tag{1}$$

where  $8\pi^2meV/h^2 = \sum v_g e^{2\pi i(\mathbf{g}, \mathbf{r})}$ , and  $V$  is the potential at a point in the crystal. The vector  $\mathbf{g}$  is a vector in the reciprocal lattice, i.e.

$$\mathbf{g} = g_1 \mathbf{b}_1 + g_2 \mathbf{b}_2 + g_3 \mathbf{b}_3, \tag{2}$$

where  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$  are the basis vectors of the reciprocal lattice, and  $g_1, g_2, g_3$  are whole numbers;  $v_g$  is written instead of  $v_{g_1 g_2 g_3}$  for convenience, and this convention will be used wherever feasible.

The solution of the Schroedinger equation can be expressed as a superposition of plane waves,

$$\Psi = \sum_g \psi_g e^{i(\mathbf{k}_0 + 2\pi\mathbf{g}, \mathbf{r})}, \tag{3}$$

where  $\mathbf{k}_0$  is a vector giving the direction of propagation of a representative wave, and having the magnitude  $2\pi/\lambda$ , where  $\lambda$  is the wave-length.  $\mathbf{g}$  is the vector defined above.

Inserting (3) in (1) we find that in order that the Schroedinger equation should be satisfied at all points, the following relation must hold between the amplitudes of the waves in the crystal

$$\psi_h (K^2 + v_0 - k_h^2) + \sum' v_g \psi_{h-g} = 0, \tag{4}$$

where  $K^2 = 8\pi^2meE/h^2$ .  $\sum'$  denotes that the term containing  $v_0$  is to be omitted;  $\mathbf{k}_h = \mathbf{k}_0 + 2\pi\mathbf{h}$  and  $k_h = |\mathbf{k}_h|$ .

The relations (4) show that the amplitudes of the waves are all inter-related. These equations can be reduced in number by considering only those waves for which the amplitude is large. It will be seen from (4) that, in general, a large amplitude is obtained only when the Laue condition

$$k_h^2 = K^2 + v_0 = \kappa^2 \tag{5}$$

holds either exactly or very nearly so.

In figure 1,  $O$  and  $P$  are two lattice points in the reciprocal lattice.  $PO$  represents the direction of the incident wave modified by refraction and

$|PO| = 1/\lambda$ , where  $\lambda$  is the wave-length in the crystal. The condition which would give a very large amplitude for the reflected wave is

$$|PO| - |PH| = 0,$$

and hence the difference  $|PO| - |PH|$  plays an important part in the theory. In Bethe's notation it is put equal to  $\zeta/2\pi$ ;  $\zeta$  is called the "excitation error".

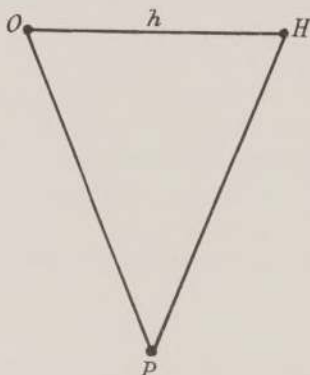


FIGURE 1. Vectors in reciprocal lattice space fulfilling the Laue conditions.

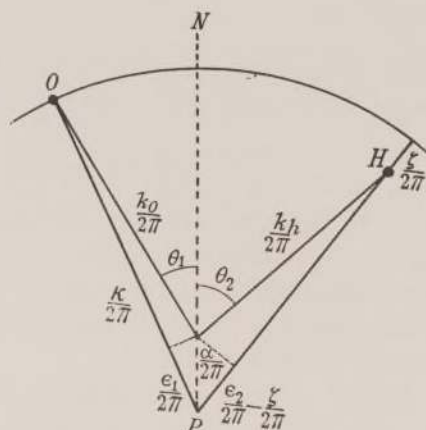


FIGURE 2. The representation in the reciprocal lattice of the "excitation error"  $\zeta$  and the resonance error  $\epsilon$ .

In the simplest case where we have only one reflected wave, the relations (4) reduce to a set of two. The condition for a solution is that the determinant of the coefficients of the  $\psi$  functions vanish. If we put  $\kappa - k_0 = \epsilon_1$ ,  $\kappa - k_h = \epsilon_2$ , where  $\mathbf{k}_0$  and  $\mathbf{k}_h$  represent a primary and a secondary wave respectively (figure 2), then  $\epsilon_2$  can be shown to depend on  $\epsilon_1$  and  $\zeta$ . Inserting these expressions into the reduced form of (4), a quadratic equation for  $\epsilon_1$  will be found to result from the condition that the determinant of the coefficients of  $\psi_0$  and  $\psi_h$  should vanish. There are hence two different sets of values of  $k_0$  and  $k_h$ .

To fix the waves uniquely, it is necessary to take the boundary conditions into account. These may be summed up by stating that the components of the wave vectors of the primary waves tangential to the surface must be the same as those of the incident wave. Assuming that the normal to the surface, the incident ray and the normal to the reflecting planes lie in the same plane, we can arrange for the boundary conditions to be satisfied by a construction given in figure 2. The vector  $PO$  represents the original wave incident on the crystal modified by refraction, i.e.  $|PO| = 1/\lambda$ .

Through  $P$  a line  $PN$  is drawn parallel to the normal to the surface of the crystal. Then the primary waves in the crystal are obtained by joining two points on  $PN$  to  $O$ , since the vectors representing these waves will have the correct projection on the surface. The secondary waves are obtained by joining the points to  $H$ . The actual position of these points is determined from (4) by transforming the equation for  $\epsilon_1$  into one for  $d$ , where  $d$  is the distance from  $P$  along the line  $PN$ . In this way the solution for the sets of waves inside the crystal is fixed completely.

§ 2. *The intensity of the reflected waves.* The theory as outlined in § 1 can be applied directly to the case of a parallel-sided slab, because in that case the two secondary waves will fit together at the lower surface to form a single wave outside the crystal. The direction in which the waves travel can be found from the condition that the secondary wave outside the crystal should have the same wave-length as the incident wave.

The calculations show that completely different results are obtained (a) when the electrons emerge from the surface on which they fall, (b) when they emerge from a different surface. Case (a) is known as the Bragg case, case (b) as the Laue case. The Bragg case is of little importance for the purpose of this paper, and we confine ourselves to the Laue case.

This case can be treated on lines indicated by Bethe (1928), and the ratio of the scattered intensity to the incident intensity for a film of thickness  $H$  can be shown to be

$$I = I_0 \sin^2 \{A(W^2 + 1)^{\frac{1}{2}}\} / (W^2 + 1), \quad (6)$$

where  $A = vH (\cos \theta_1)^{\frac{1}{2}} / 2\kappa \cos \theta_2 (\cos \theta_2)^{\frac{1}{2}}$  and  $W = \kappa\zeta/v$ . Here the angles  $\theta_1$  and  $\theta_2$  are those shown in figure 2. The suffix of the Fourier coefficient has been dropped because we deal with the case where there is only one reflexion. For fast electrons, with which we are concerned, the Bragg angle is small, and the ratio  $(\cos \theta_1 / \cos \theta_2)^{\frac{1}{2}}$  can, in general, be put equal to unity. Though the angle  $\theta_2$  has been defined in figure 2 in the particular case where the incident ray, the normal to the surface and the normal to the reflecting planes lie in the same plane, the above formula holds for fast electrons in the general case with  $\theta_2$  again the angle between the direction of the reflected wave and the normal to the surface.

We consider first the intensity of the reflected wave when the Laue conditions are exactly fulfilled, i.e.  $\zeta = 0$ . The intensity will depend on the thickness of the plate and the direction of incidence relative to the normal to the surface. Keeping this direction fixed, the intensity has a periodic character as a function of the thickness, an effect first pointed out by Ewald (1917) in the case of X-rays. For very small thicknesses it has a

value proportional to  $H^2$ , reaches a maximum when  $A = \pi/2$  and has its second zero value when  $A = \pi$ . Besides this the intensity will vary as the crystal is turned out of the Bragg angle. Except in the region near  $A = \pi, 2\pi$ , etc., the intensity will drop steadily to zero and then go through a series of secondary maxima, the intensity of which decrease steadily. In the region near  $A = \pi, 2\pi$ , etc., the intensity will first rise to a maximum and then decrease to zero. Typical curves are shown in figure 3.

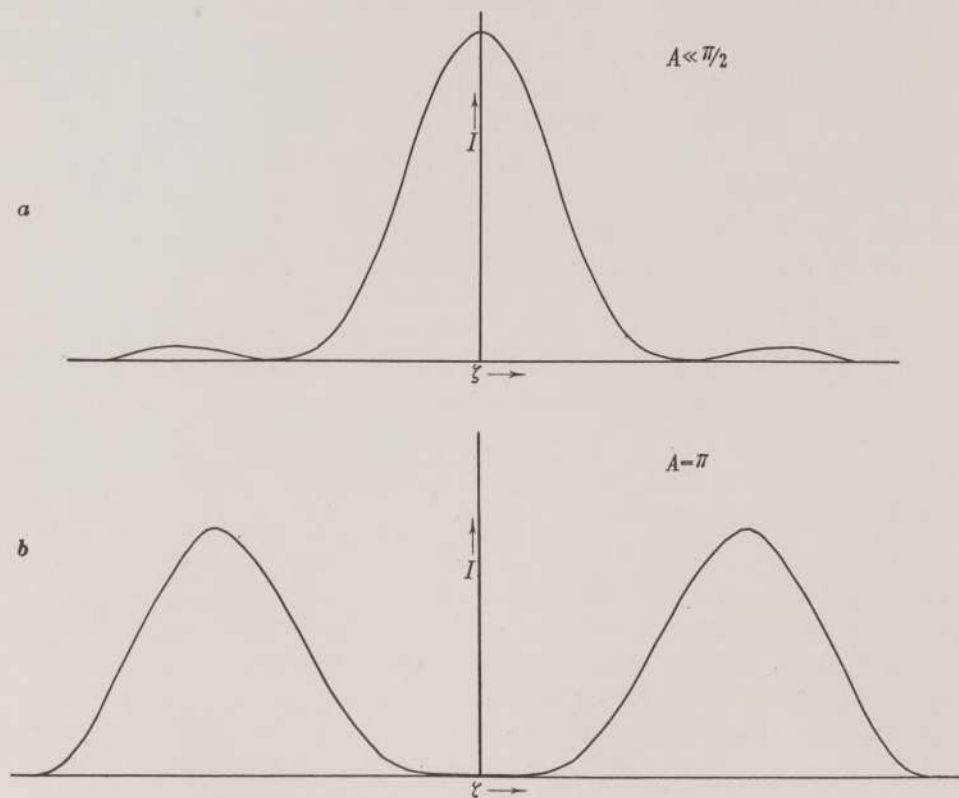


FIGURE 3. The reflected intensity as a function of  $\zeta$  for a thin plate (a) when  $A \ll \pi/2$ , (b) when  $A = \pi$ .

This behaviour will probably not be observable in the case of a polycrystalline film. It is, however, probable that thin coherent films, e.g. of mica or of molybdenite, may be sufficiently regular to show the effect on rotation or when they are bent. When such a thin film is rotated out of the position where it gives a strong reflexion ( $\zeta = 0$ ), it will come into a position where the reflexion is weak; on being further rotated the value of  $\zeta$  will change to one for which the intensity of reflexion is a relative maximum,

and these maxima will appear at regular intervals. Their position on a photographic plate exposed during the rotation will depend on the way the direction of the secondary wave is changed as a function of  $\zeta$ . This can be shown (Thomson and Blackman 1939) to depend on  $\zeta \tan \theta_1/\kappa$  in the above notation. The angular spacing of the secondary maxima would be  $\lambda \tan \theta_1/H$  if  $A \ll \pi/2$  for the case given in figure 2. In the general case the angle must be replaced by another; for the details, we refer to the paper by Thomson and Blackman (1939).

If such a film is bent and adjusted to give reflexion from a set of planes, there will be a large part of the area for which the incident beam does not make the correct angle with the planes, i.e.  $\zeta \neq 0$ . There will be a progressive change in the value of  $\zeta$  for the planes lying on each side of those for which  $\zeta = 0$ ; in that case there will be reflected rays corresponding to all values of  $\zeta$ , and these rays will emerge at slightly different angles and will have intensities determined by the particular value of  $\zeta$ . We can, therefore, obtain all the secondary maxima at one setting of the crystal, the angular spacing of these being practically identical with that given above.

For thin films ( $A \ll \pi/2$ ) the effect becomes indistinguishable from another, due to the small size of the crystal. When the thickness is very small the solution of the Schrodinger equation in the above form is no longer valid; the reason is that the mathematical point in the reciprocal lattice spreads out into a region and the reflected beam can show the secondary maxima given by the Laue theory. Such cases have been found by Finch and Wilman (1936) in the case of thin sheets of graphite.

It is hence extremely difficult to separate the two effects either in a rotation photograph or in a bent crystal photograph. There is, in addition, the question of the interaction of these very weak waves with other waves in the crystal, as the assumption of the dynamical theory, that the reflected waves considered are stronger than all the others, is no longer fulfilled. It should be possible to observe the split maxima in the region  $A \approx \pi$ , if the films are sufficiently regular in thickness.

The size of the periods referred to above is of some interest, especially as it can be shown to be of the order of 100 A, i.e. of the order of the size of the crystals and films used in electron diffraction work on transmission of electrons. The first maximum in the scattered intensity at the Bragg angle (i.e. at  $\zeta = 0$ ) considered as a function of  $v$  or  $H$  is reached for  $A = \pi/2$ , i.e.  $vH = \pi\kappa \cos \theta_2$ . Taking  $\cos \theta_2 = 1$ , which will give the value of  $H$  for direct transmission, we have  $vH = \pi\kappa$ . Now

$$v_{\theta_1\theta_2\theta_3} = 8\pi^2meV_{\theta_1\theta_2\theta_3}/h^2,$$

where  $V_{g_1 g_2 g_3}$  is the actual Fourier coefficient of the potential, and putting  $V$  in volts,  $H$  in angstroms and taking for  $\kappa$  a value  $100 \times 10^8 \text{ cm.}^{-1}$  (corresponding to an energy of 37.5 kV), this becomes

$$H = \frac{376\pi}{V_g}. \quad (7)$$

Taking the (111) reflexions of gold, silver and aluminium for which the values of  $V$  are 24.2, 17.3 and 6.6 V\* respectively, the values of  $H$  become 45.5, 70, and 180 angstroms respectively. It is hence clear that the kinematical theory is not applicable to a polycrystalline film of gold or silver of thickness a hundred angstroms, though it might be in the case of aluminium.

It can be seen from these, as also from more elementary considerations, that it is the product  $vH$  which determines whether the scattering is small or not. In the case of the outer rings, e.g. (531), the value of  $v$  is in general so low that the kinematical theory of Laue can be applied. To obtain a numerical estimate of the value of  $H$  below which the theory can be applied to all rings, we consider the intensity of the scattered wave (at  $\zeta = 0$ ) in the case of the strongest reflexion (111).† Table 1 shows these values when the ratio of the scattered intensity to the incident intensity is 5 and 10%. The error made in these two cases if the kinematical theory is assumed is 1.9 and 3.5% respectively.

TABLE 1

Ratio	Error %	Thickness of film (angstroms)		
		Gold	Silver	Aluminium
0.05	1.9	6.5	10	26
0.10	3.5	9	14	38

A more general method of treating the scattered intensity is to consider the integrated intensity, i.e. the total intensity scattered when the crystal is turned relative to the incident beam.

\* The data for calculating these Fourier coefficients were taken from a table of  $f_0$  values given by James and Brindley (1931). The method of calculation is given, for example, by Froehlich, *Elektronentheorie der Metalle*.

† In the above work the absorption of electrons (due to inelastic collisions) has been neglected. The absorption will, of course, materially reduce the intensity of the elastically scattered wave. The sizes of the crystals deduced above will, however, still be a rough measure of the point where the kinematical theory (with absorption) will go over into the dynamical theory.

The intensity reflected at any setting is

$$I = I_0 \sin^2 \{A(W^2 + 1)^{\frac{1}{2}}\} / (W^2 + 1),$$

where  $A = vH/2\kappa \cos \theta_2$ , and  $W = \kappa\zeta/v$ .  $\zeta$  is, of course, zero when the direction of incidence fulfils the Laue conditions. When the direction of incidence differs from this direction by an amount  $\alpha$  (in angular measure), the value of  $\zeta$  can be shown to be  $2\kappa\theta\alpha$ . The total reflected intensity when the crystal is rotated with angular speed  $\omega$  is

$$\begin{aligned} I_T &= \frac{I_0}{\omega} \int_{-\infty}^{+\infty} \sin^2 \{A(W^2 + 1)^{\frac{1}{2}}\} / (W^2 + 1) d\alpha \\ &= \frac{vI_0}{2\kappa^2\theta\omega} \int_{-\infty}^{+\infty} \sin^2 \{A(W^2 + 1)^{\frac{1}{2}}\} / (W^2 + 1) dW, \end{aligned} \tag{8}$$

where  $I_0$  is the intensity incident per unit time.

The above assumes that the angle through which the crystal can be turned relative to the incident beam while giving appreciable reflexion is sufficiently small to allow  $I_0$  to be treated as constant; it is further assumed that the intensity has dropped sufficiently when  $\alpha$  is large to allow the limits to be extended to infinity. This approximation is justified in all the applications made here.

The integral can be transformed into

$$I_T = I_0 \frac{v}{\omega\kappa^2\theta} \int_0^A J_0(2x) dx. \tag{9}$$

For small values of  $A$  the Bessel function  $J_0(2x)$  is practically a constant (unity), and hence

$$I_T = I_0 vA / \kappa^2\theta\omega = I_0 v^2 H' / 2\kappa^3\theta\omega,$$

where  $H' = H/\cos \theta_2$ . The integrated intensity has there the kinematical form; it is proportional to  $v^2$  and to the volume of the crystal as the intensity  $I_0$  intercepted from the main beam will be proportional to the area of the surface.

For values of  $A$  which are not so small, the value of  $I_T$  deviates from the kinematical value. In figure 4 the function  $R(A) = \int_0^A J_0(2x) dx$  has been plotted as a function of  $A$ . From this curve the value of the integrated intensity  $I_T$  can be obtained immediately; the curve need only be multiplied by the factors given in (9), the most important of which is the term  $v$ . The characteristic feature is that the curve gives smaller values than would



be expected from an extrapolation of straight line which represents it for small values of  $A$ . For very large values of  $A$

$$\int_0^A J_0(2x) dx = \int_0^\infty J_0(2x) dx = \frac{1}{2},$$

and the value of  $I_T$  becomes

$$I_T = I_0 v / 2\kappa^2 \theta \omega, \quad (10)$$

i.e. the integrated intensity is proportional to  $v$ , which is one of the characteristic features of the dynamical theory for thick films.

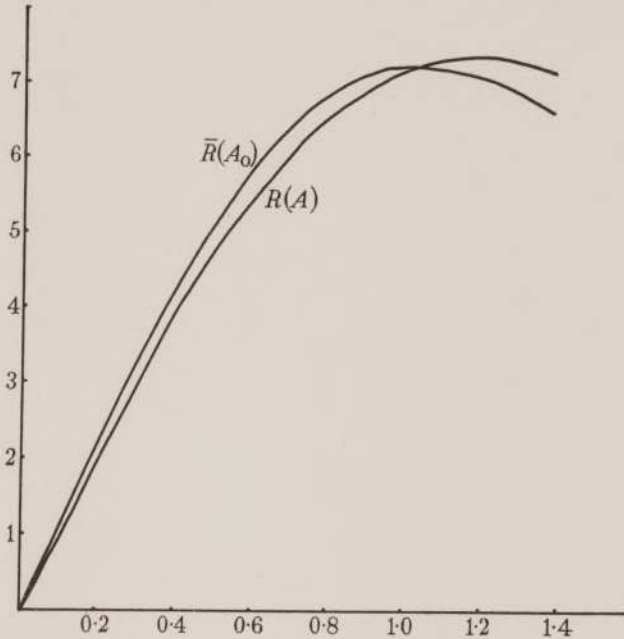


FIGURE 4. The intensity function  $R(A)$  and the averaged intensity function  $\bar{R}(A_0)$ ;  $A$  and  $A_0$  have been defined in the text. The ordinate is plotted in arbitrary units, but  $\bar{R}(A_0)$  from the values given in the above curve for  $R(A)$ .

The point at which the value of  $I_T$  differs appreciably ( $\sim 5\%$ ) from the  $v^2$  law can be obtained from the curve as well. The values found with data for the (111) reflexions of gold, silver and aluminium are 11.5, 18 and 46 angstroms respectively.

In the above considerations there are two points which require further investigations. The first is that the theory, as it stands, is an extrapolation of the theory for an infinite lattice: when one deals with films which may be as little as ten atoms thick, the relation between the rays in the crystal

as given by the Bethe theory is no longer valid. This can be expressed in the form that a point in the reciprocal lattice should be replaced by a region, which means that the intensity of the reflected waves would be changed. Though it would be impossible to treat this problem exactly, the effect of an extended region in the reciprocal lattice can be investigated by replacing the region by two points of suitable weight, and carrying through the Bethe theory for three waves instead of the usual two. An investigation was carried through in a case where the value of  $v$  was that for the (111) reflexion of gold, and the size of the crystal was taken to be 20 Å. The two points in the reciprocal lattice were chosen in weight (10 : 1) and distance, in such a way as to reproduce the features of the region as far as was possible with such an approximation. The calculation showed that the integrated intensity differed very little (less than 1%) from that found in the case where one point in the reciprocal lattice was taken and the whole weight attached to it.

In so far the extension to the region of small crystals seems to be satisfactory. There is, however, a second feature which needs consideration. A consideration of the kinematical theory shows that with the small wavelengths used, and with the small crystal size, there should be a number of reflected waves at each setting of the crystal. This must still be true in the dynamical theory for small crystals. These additional reflexions will change greatly in intensity as the crystal is turned, and will sometimes add to the intensity of the reflexion under consideration and sometimes reduce it. It is, therefore, probable that the effect when averaged will be small. An exact estimation will, however, be extremely complicated, and it is not thought worth while extending the investigation in this direction.

§ 3. *Application to a polycrystalline film.* The main object of the above investigation was to throw some light on the intensity of the electron diffraction rings from a thin polycrystalline film. The application of a theory based on a parallel-sided film can be regarded as justified only in so far as it can be considered to be a good approximation to the exact theory. Now the above theory does give all the features of the kinematical theory (in the same way that a more complete theory should do) when the scattering is small, and it seems reasonable to suppose that where the theory deviates a great deal from the kinematical theory, this deviation will be reproduced in the more exact theory. As will be shown below, the deductions as to the deviations do seem to fit in with the experimental facts.

In the application of the theory, one has to consider first how the experimentally determined intensities of the various diffraction rings are

reduced to standard intensities for comparison with the theory. This is done by adapting the X-ray formulae (Compton and Allison 1935) for scattering by a polycrystalline film to the case of electrons. This scattering formula is based on kinematical considerations, but an examination of the method by which it was obtained shows that the same formula should apply, provided the kinematical atomic scattering factor is replaced by a dynamical one.

In equation (8), for example, we have a case in which the dynamical factor  $D = vR(A)$  goes over into the kinematical factor  $vA$  (which is proportional to  $v^2$ ) for a thin plate. In the case of a polycrystalline film we should again expect the  $v^2$  term for sufficiently small crystals; the dynamical factor will not be  $D$  but a suitable average value  $\bar{D}$ , as  $D$  contains the parameter  $A$  in which the angle between the reflected ray and the normal to the surface enters. An exact calculation of the average value would be very difficult and would, in any case, be impossible without an exact theory. We have, therefore, to use qualitative considerations.

In finding the average it is clear that, other things being equal, surfaces for which the angle between the incident ray and the normal to the surface is large will be less important than those for which it is small, since the area projected normal to the beam will be less in the former case.\* To allow for this the function  $D(A)$  (or  $R(A)$ ) has been averaged over the region  $+\pi/4 > \theta_2 > -\pi/4$ , equal weight being assigned to all angles in this region. It may be remarked that several other ways of arriving at the average were tried, all of which led to the same type of curve and gave practically the same results.

The averaged value of the function  $R(A)$  is shown in the upper curve of figure 4. The abscissa  $A_0$  differs from  $A$  in that the cosine term has been put equal to unity. As is to be expected from the method of averaging, the averaged function is not very different from the initial function  $R(A)$ .

It will be shown below that this function does represent with surprising success the intensities found by Ornstein and his co-workers when a reasonable value is assumed for the average size of the crystals.† The comparison for silver is given below

\* For the Bragg case the angle is always very large (for fast electrons); for this reason we are justified in neglecting the Bragg case and in confining ourselves to the Laue case.

† The effect of absorption has been neglected in the above considerations. As the intensities given by experiment are only relative ones, the formulae used above will still hold if the assumption is made that the intensity of each ring is affected in the same way by the absorption. In the case of polycrystalline films and transmission by fast electrons the deviation of the electrons in the scattering is a few degrees at

TABLE 2. SILVER

Ring	Experimental	Intensity functions	
		$\bar{D}$	$E$
(111)	113	117	166.3
(200)	93	105	132.7
(220)	66	66	66.0
(311)	51	47.7	45.1
(331)	27	24.2	21.1
(420)	24	22.4	19.5
(422)	20	17.4	15.0
(333)	11	14.6	12.6

In the above table the experimental intensity represents the intensity of the rings reduced to the form in which it can be compared directly with the theoretical function. The function  $E$  is that deduced on the assumption of kinematical scattering and is proportional to  $v_{hkl}^2$ . The function  $\bar{D}$  (which is the averaged value of  $D$ ) has been calculated from the upper curve given in figure 4 with the assumption of an average value of the size  $H = 50 \text{ \AA}$ , this value being chosen by trial. The values of the  $v_{hkl}$  which also enter into this calculation are the same as those used to find the values of  $E$ . The value of  $\kappa$  is determined, of course, from the voltage used in the experiments of Ornstein and his co-workers. As the experiment gives only relative values of the intensity, the values of  $\bar{D}$  and  $E$  are chosen so as to fit the experimental results at the (220) ring, which is the best as regards accuracy of measurement. In deciding on crystal size the main weight has been given to the first few rings, as the photometric estimation is much more accurate for the prominent rings and as the subtraction of the heavy background is attended by less error than in the case of the weaker rings. No correction has been applied for the effect of the heat motion; this correction would be quite important for the weaker rings and the theoretical intensities would have to be reduced. As the experimental accuracy is, however, only  $\pm 15\%$ , it is hardly worth while including the heat correction.

Table 3 gives a comparison for the case of copper, the experimental intensities again being those found by Ornstein and his co-workers.

The value of the average size of the crystals of copper assumed above the most (in the case of the rings considered here); the sizes of the crystallites responsible for different rings can certainly be taken to be the same; so that the assumption that the absorption affects each ring similarly seems to be justified.

was 63 Å, which is appreciably larger than the size of the crystals of silver.

TABLE 3. COPPER

Ring	Experimental	Intensity functions	
		$\bar{D}$	$E$
(111)	127	126	216
(200)	93	111	154
(220)	66	66	66
(311)	50	46	43
(331)	26	22.4	19.5
(420)	26	21.2	18.3
(422)	21	16.7	14.1
(333)	12	13.9	11.8

The above agreement is very good on the whole, but it should not be taken as indicating more than the correctness of the general form of the intensity function  $\bar{D}$  which replaces the usual function  $E$ . It would be of some interest if the estimate of the size of the crystals could be checked as well.

The calculation of the Fourier coefficients is based on the Born theory of the scattering of fast electrons. In the evaluation the Thomas-Fermi atomic model is used so that the individual features of the electronic arrangement in the atom is neglected.\* Another factor of some importance is that the scattering of the electrons cannot be considered as small in the case of heavy atoms, so that the Born approximation is not strictly valid. This point has been investigated by Henneberg (1933), who finds discrepancies for mercury atoms but fairly good agreement for silver. The numerical values of the  $V_{hkl}$  are actually smaller by 10%, but the relative values are practically the same as before over the range used.

The case for gold is interesting as an example of a particularly heavy element. It was the first to be investigated (Thomson 1929) and the comparison with the theoretical values of  $E$  made by Mott (1929) seemed to give good agreement. A closer examination shows that there is a discrepancy in the same sense as that found by Ornstein and his co-workers (1938) for silver and copper. This can be seen in table 4.

\* The method given by Bethe (1928), using hydrogen-like wave functions, yields 13.4 V for  $V_{111}$  in the case of silver, whereas the method used above gives 16.5 V according to Trillat and Hautot (1938).

The theoretical calculations were made on the basis of the Born theory. It will be seen that the most important rings ((111), (200)) give a value which is too low if the curves are fitted to the (220) ring. The calculations of Henneburg show that this discrepancy should be even greater, and also that the agreement found above is to some extent accidental. The data given are not sufficient to allow a detailed comparison to be made for gold, but it would seem possible to fit the experimental results of Thomson (1929) with an average size of 30–35 Å. This value is a reasonable one, as the films used had a thickness of 70 Å in one case, and the rings themselves were not particularly sharp.

TABLE 4. GOLD

Ring	Intensity functions	
	Experimental	Theoretical ( $E$ )
(111) \	127	156
(200) /		
(220)	67	63.2
(311) \	42.2	43.5
(222) /		
(331) \	20.8	20.6
(420) /		
(422) \	10.2	13.9
(333) /		

The theory as outlined above cannot explain the experimental results obtained by Mark and Wierl (1930) who made a careful study of the scattering in the case of foils of silver, gold and aluminium. Since the rings they obtained were sharp, their crystals must have been comparatively large, but they found good agreement with the theoretical function  $E$ , which, on the above theory, should be the case only for very small crystals. Their results for silver do not, however, fit in with the later work of Ornstein, Brinkman, Hauer and Tol, and at present it is impossible to decide as to the cause of the discrepancy.

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## SUMMARY

The reflexion of electrons by a thin film is examined from the point of view of the dynamical theory in the Laue case. The formulae are used to

obtain a criterion which determines when the scattering is sufficiently small to allow the kinematical theory to be applied; it is found that this theory is not, in general, applicable to the thin films used in work with fast electrons. The total intensity scattered from a film when it is turned through its range of reflexion is also found, and the result is used to obtain an approximate intensity function showing how the intensities of the diffraction rings from a polycrystalline film will vary when the scattering is sufficiently large for the kinematical theory to be inapplicable. This intensity function is tested by comparing it with the experimental intensity function found for copper and silver. It is found possible to obtain a good fit with very reasonable assumptions as to the average crystal size.

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