should vanish over a certain range of current. Curves of both types were obtained in the experiments, and the slopes of the linear portions of the curves are in good quantitative agreement with the theoretical slopes.

It may, therefore, be concluded that the results of these experiments can be completely accounted for by the assumption of a critical magnetic field, without making use of the concept of critical current.

* Published by permission of the Director, Bureau of Standards, Department of Commerce. A more extended paper on this subject will appear as a scientific paper of the Bureau of Standards.

[1] *J. Franklin Inst.*, **201**, p. 379, April, 1926.

[2] *Bur. Standards Sci. Paper*, No. 307, 1917.

ON THE REFLECTION OF ELECTRONS FROM CRYSTAL LATTICES

BY F. ZWICKY*

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated May 31, 1927

(*a*) *Introduction.*—Davisson and Germer[1] have recently published their very interesting results on reflection of electrons from a single crystal of nickel. These results have been interpreted by analogy with the reflection of X-rays from crystals. This analogy, however, is not complete. The purpose of this short note is to point out the differences between the two phenomena. For the mathematical treatment use is made of the recent development of quantum mechanics (wave mechanics).

It is easy to see that a very important difference between the scattering of X-rays, as compared with the analogous phenomena for electrons, lies in the following fact. The scattering of slow electrons (of the order of 100 volt) is, crudely expressed, much more intense than that of X-rays. Indeed, one layer of atoms on the surface of a crystal may already deflect so considerable a part of an impinging beam of electrons that the effect can easily be observed. For ordinary X-ray scattering the effect produced by one layer is negligible and does not give an observable interference pattern. Only the coöperation of a large number of layers produces interference under the proper circumstances (Laue spots, Bragg reflection). We thus have the following difference. The interference pattern for X-rays is due to the action of a great number of lattice planes of a crystal, because of the small scattering coefficient of one layer. For the electrons, on the other hand, we have to expect that the action of a few layers on the

surface of the crystal already produces the whole effect. This is due to the high scattering coefficient of one lattice plane. From this point of view the pattern obtained by Davisson and Germer has been explained by Dr. Eckart.[2] There is also hope to provide in this way a reason for the hypothetical contraction of the lattice which Davisson and Germer have to introduce in order to establish the Bragg reflection law for their results.

In the following lines a derivation is given for the diffraction of an electron beam by a single lattice plane. A pattern is obtained similar to that for the reflection of light by a ruled crossed grating. The resolving power for a finite lattice is calculated. Finally it is shown that the reflecting power of a single plane is so large that it is not permissible to treat this case by analogy with X-rays. The interference pattern cannot be computed by assuming that the rays penetrate a great number of layers. On the contrary the whole phenomenon is produced by a few layers on the surface only.

The method which we apply is that given by M. Born[3] in a paper on periodic phenomena treated from the standpoint of wave mechanics. For its justification we refer to this paper.

The impinging beam of electrons of constant velocity, v, is represented by a wave function in space

$$\psi_0 = e^{ik(x\xi_0 + y\eta_0 + z\zeta_0)}. \tag{1}$$

ξ_0, η_0, ζ_0 are the components of a unit vector indicating the direction of the beam. If m and E are the mass and the energy of an electron, λ the wave-length of the associated wave, then we have (de Broglie)

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{h}\sqrt{2mE} = 2\pi\frac{mv}{h} \tag{2}$$

h = Plancks constant.

What we have to calculate then is the effect of a certain distribution of potential energy $V(x, y, z)$ in space on the primary beam as described by the equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0.$$

Born developed for this purpose the following method of approximation. Suppose

$$\psi = \psi_0 + \psi_1 + \psi_2 + \ldots\ldots$$

Then the successive approximations are given by

$$\psi_1(x, y, z) = -\frac{2\pi m}{h^2}\int dt' V(x', y', z')\psi_{i-1}(x', y', z') \frac{e^{ik\sqrt{(x-x')^2+(y-y')^2+(z-z')^2}}}{\sqrt{(x-x^1)^2+(y-y')^2+(z-z')^2}}. \quad (3)$$

The integral is to be taken over all space. The different function ψ_i satisfy these equations

$$\nabla^2\psi_0 + k^2\psi_0 = 0$$
$$\nabla^2\psi_i + k^2\psi_i = \frac{8\pi^2 m}{h^2} V.\psi_{i-1}. \quad (4)$$

According to Born the intensity of the electron stream is measured by the expression $|\psi|^2$. The intensity of the scattered beam, in the first approximation, is given by $|\psi_1|^2$.

This method has been applied by Wentzel[4] to the case of scattering of α particles by nuclei. He obtained Rutherford's law as a first approximation.

(*b*) *Positions of the Maxima of Reflection.*—The potential energy of an electron in relation to a single lattice plane may generally be expressed by a double Fourier series in the two coördinates x and y for instance. As we only need the first approximation ψ_1, we may consider for simplicity the effect given by one member of this series only, without sacrifice of any essential features of the problem. This is indeed justified by the possibility of superposition of our solutions in the first approximation.[5] We, therefore, put

$$V(x, y, z) = A\cos\frac{2\pi mx}{l_1}\cos\frac{2\pi ny}{l_2}e^{-\alpha z^2-\beta(x^2+y^2)} \quad (5)$$

where l_1 and l_2 indicate the spacings between the atoms. The factor $e^{-\alpha z^2}$ has to be introduced as a means of giving the layer the required thickness (of one atomic diameter, approximately). Adjusting the constant β in a proper manner means that we make use of a finite portion of the crystal only. In this way we shall obtain an estimate as to the resolving power of a definite experimental arrangement.

For a beam of electrons in the direction z, normal to surface, we assume the expression (1) mentioned above, namely

$$\psi_0 = e^{ik\zeta_0 z}.$$

Assuming that the point (x, y, z) at which the reflected beam is observed is very distant we can write

$$\psi_1 = -\frac{2\pi m A e^{ikr}}{h^2 r}\int_{-\infty}^{+\infty}\int dx'dy'dz' \cos\frac{2\pi m x'}{l_1}$$

$$\cos\frac{2\pi n y'}{l_2}\exp[ik(\xi x' + \eta y' + \zeta z') - \beta(x'^2 + y'^2) - \alpha z'^2].$$

In this formula the following notations are used

$$r^2 = x^2 + y^2 + z^2$$

$$\xi = -\frac{x}{r} \qquad \eta = -\frac{y}{r} \qquad \zeta = -\frac{z}{r} + 1.$$

The integral is easily evaluated with the help of the following relations.

$$\int_{-\infty}^{+\infty} e^{ikz\zeta - \alpha z^2}\, dz = \sqrt{\frac{\pi}{\alpha}}\, e^{-\frac{k^2\zeta^2}{4\alpha}}.$$

The integrals with respect to x and y are similar, namely,

$$\int_{-\infty}^{+\infty} dx \cos\frac{2\pi m x}{l_1}\, e^{ik\xi x - \beta x^2}$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{\beta}}\left[e^{-\frac{1}{4\beta}\left(\frac{2\pi m}{l_1} + k\xi\right)^2} + e^{-\frac{1}{4\beta}\left(\frac{2\pi m}{l_1} - k\xi\right)^2}\right] = \sqrt{\frac{\pi}{\beta}}\, F_m(\xi_m, \beta).$$

For the wave function of the scattered radiation, this expression then follows

$$\psi_1 = -\frac{2\pi^2\sqrt{\pi}A e^{ikr}}{h^2\beta\sqrt{\alpha}\, r} e^{-\frac{k^2\zeta^2}{4\alpha}} F_m(\xi,\beta)F_n(\eta,\beta). \qquad (6)$$

For an infinitely extended plane and an infinitely wide homogeneous beam of impinging electrons ($\beta = 0$) we thus get the following result. ψ_1 will be zero (in spite of the factor $1/\beta$) on account of the functions F_m and F_n becoming zero exponentially. There are, however, some exceptional cases, namely those when the brackets in the exponential functions are zero. In this case ψ_1 will be infinitely large. If the ξ and η satisfy the two equations

$$\begin{aligned} m\lambda &= \mp\xi_m l_1 \\ n\lambda &= \pm\eta_m l_2 \end{aligned} \qquad (7)$$

a maximum of intensity of the beam is obtained. These conditions for the appearance of maxima are analogous to those for diffraction of ordinary

light on a plane crossed grating. Giving m and n independently all integral values, the whole interference pattern is obtained.

(*c*) *Resolving Power.*—It is easy to see now what the conditions will be for a crystal of finite size. ($\beta \neq 0$.) For not too large values of β the maxima will still be in the same places. But they will not be of infinite intensity. They also will be spread out over the whole range of angles. The intensity falls off rapidly with $\Delta\xi = |\xi - \xi_m|$ increasing. The value for $\Delta\xi$ at which the intensity is diminished by a factor e^{-1} is readily obtained by the condition

$$\frac{k^2\Delta\xi^2}{4\beta} = 1. \tag{8}$$

Now in the actual experimental arrangement we have to put $\beta = 100$ cm.$^{-2}$ because this corresponds to a width of the primary beam of approximately 1 mm.

Assuming electrons with an energy corresponding to 100 volts we have approximately

$$k^2 = 3 \times 10^{17} \text{ cm.}^{-2}$$
$$\Delta\xi = 3.5 \times 1\ 0^{-8}.$$

It is seen by this that the resolving power is very large. The width of the lines which is found experimentally is of quite another order of magnitude. This may be partly accounted for by the imperfection of the apparatus, as the authors mention. It is, however, probable that a considerable width of the reflected electron beam is due to the imperfections of the crystal surfaces and to temperature agitation. This will be true especially because of the fact that probably only a few layers on the surface of the crystal coöperate to produce the whole effect. To prove this point we shall give now a rough estimate as to the scattering power of a single lattice plane.

(*d*) *Reflection Power of One Plane of Atoms.*—For simplicity we assume a distribution of potential energy non-periodic in x and y, such as

$$V = A \exp[-\beta(x^2 + y^2) - \alpha z^2].$$

This non-periodic term is present in the practical case too, due to a general image force, for instance. In the numerical application we will identify it for $z = 0$ with the work function φ

$$A = e\varphi \qquad e = 4,77.10^{-10}\text{e.s.u.}$$

According to section (*b*) scattering will then only take place in the forward and in the backward direction. We have to put

$$m = 0 \qquad n = 0$$

which gives us (see formula 6)

$$\psi_1 = -\frac{2\pi^2\sqrt{\pi}mAe^{ikr}}{h^2\beta\sqrt{\alpha}r}\exp\left[-\frac{k^2}{4\beta}(\xi^2+\eta^2)-\frac{k^2\zeta^2}{4\alpha}\right].$$

The intensity of the scattered beam then, according to Born, is

$$|\psi_1|^2 = \frac{4\pi^5m^2A^2}{h^4\beta^2\alpha r^2}\exp\left[-\frac{k^2}{2\beta}(\xi^2+\eta^2)-\frac{k^2\zeta^2}{2\alpha}\right].$$

Denote the angle between the z axis and the direction of the reflected beam by θ. Then we have

$$\xi^2+\eta^2 = \sin^2\theta \qquad \zeta = 1-\cos\theta.$$

But $|\psi_1|^2$ is only appreciable for small values of θ. We may, therefore, use the following approximations

$$\xi^2+\eta^2 = \theta^2 \qquad \zeta^2 = \frac{\theta^4}{4} = 0$$

In order to get the total intensity I_1 of the beam scattered backwards we have to compute

$$I_1 = 2\pi\int_0^{\pi/2}|\psi_1|^2r^2\sin\theta d\theta.$$

This is with sufficient approximation for our purpose

$$I_1 = \frac{8\pi^6m^2A^2}{h^4\beta^2\alpha}\int_0^\infty e^{-\frac{k^2}{2\beta}\theta^2}\theta d\theta$$

$$I_1 = \frac{8\pi^6m^2A^2}{h^4\beta\alpha k^2}.$$

I_1 has to be compared with the intensity of the impinging beam integrated over the efficient part of the crystal, for which we have the expression

$$I_0 = \int_0^\infty|\psi_0|^2e^{-\beta r^2}2\pi r dr = 2\pi\int_0^\infty e^{-\beta r^2}r dr = \frac{\pi}{\beta}.$$

The desired ratio between the impinging and the scattered intensity is, therefore,

$$I_1/I_2 = \frac{8\pi^5m^2A^2}{\alpha k^2h^4}.$$

Substituting the expression for k^2 we obtain

$$I_1/I_0 = \frac{\pi^3 m A^2}{h^2 \alpha E}. \qquad (9)$$

The numerical value will be computed on the assumption that our single layer has a thickness of approximately 2×10^{-8} cm. This corresponds approximately to

$$\alpha = 0.25 \times 10^{16} \text{ cm.}^{-2}.$$

As mentioned we identify A with a potential energy corresponding to the work function ($\varphi = 5$ volts). The energy E of the impinging electrons may correspond to 100 volts. With these data we have approximately

$$A = e\varphi = 8.10^{-12} \text{ ergs}$$

$$I_1/I_0 = 0.11.$$

The scattering will be increased still considerably by the effect of the higher harmonics in $V(x, y, z)$. From this estimate it follows, then, that only a few layers of atoms on the surface of the crystal produce the diffraction phenomenon discovered by Davisson and Germer. The exact numerical value obtained for I_1/I_2 cannot be taken too seriously. Its magnitude indicates indeed that the approximation method applied is no longer rigorous enough for the potential energies in consideration. The order of magnitude, however, will not be affected by a more adequate calculation. The opacity of the crystal then seems to be established both from the experimental and the theoretical point of view. The crystal behaves in relation to electrons as a dispersive medium (with complex index of refraction) does in respect to light. The change of wave-length at the boundary of the crystal cannot be neglected. This is possibly the reason for the necessity of the contraction factor introduced by Davisson and Germer in order to establish Bragg's reflection law. An adequate theory for this contraction factor might be given by studying the effect of a thin sheet of a crystal on the impinging beam. It is easy to see that the first approximation of our theory would yield Bragg's law without a contraction factor. This factor only might be obtained by taking into account the second approximation or by solving the Schrödinger equation rigorously.

The experiments yield three anomalous maxima of reflection which do not seem to have any relation to the crystal structure. They are indeed independent of the azimuth. This suggests that they might be due to some adsorbed gas molecules, oxygen for instance. These adsorbed gases on the surface may also cause the diffuse continuous scattering over all the angles, especially at low velocities.

* Research Fellow, International Education Board.

[1] Davisson and Germer, *Nature*, 1927, April 16.

[2] C. Eckart, these PROCEEDINGS, **13**, 460, 1927. I am indebted to Dr. Eckart for private communication of his results.

[3] M. Born, *Zs. Physik*, **38**, 803, 1926.

[4] G. Wentzel, *Ibid*, **40**, p. 590.

[5] The general case will be treated elswhere by Dr. P. S. Epstein.

DISPLACEMENT OF CERTAIN MULTIPLETS AND MULTIPLE LEVELS FOR ELEMENTS IN THE FIRST LONG PERIOD[1]

BY R. C. GIBBS AND H. E. WHITE

DEPARTMENT OF PHYSICS, CORNELL UNIVERSITY

Communicated June 7, 1927

In previous reports on the first long period of the periodic table we have shown how beautifully the regular and irregular doublet laws are found to hold not only for iso-electronic systems containing one[2] valence electron but also those containing two[3a] and three[3b] valence electrons. It has also been shown that the addition of 0, 1, 2 and 3 $3d$ electrons to the one-electron systems of K, Ca, Sc and Ti, respectively, cause not only a change in the multiplicity of the resultant terms but also a shift in radiated lines toward the longer wave-lengths. This regular displacement law of multiplets, as well as the irregular doublet law, has enabled us to locate approximately the position in the spectrum of certain characteristic multiplets of Cr III and Mn III, which multiplets arise from the electron transitions, $3d^34p$ to $3d^34s$ and $3d^44p$ to $3d^44s$, respectively. The data for these two multiplets are given in table 1. The regular doublet law in conjunction with Landé's interval rule was most effective in determining approximately the frequency differences between the terms of ${}^5F'_{1,2,3,4,5}$ $(3d^34s)$ and those of ${}^5G'_{2,3,4,5,6}$ $(3d^34p)$ for Cr III as well as between the terms of ${}^6D_{1,2,3,4,5}(3d^44s)$ and those of ${}^6F_{1,2,3,4,5,6}(3d^44p)$ for Mn III. These frequency intervals are so regular for both the initial and final states that the strong lines of each multiplet, i.e., the diagonal lines in table 1, were easily picked out before the lines were definitely identified by exact measurements.

Sufficient data is now available for elements in the first long period so that it is possible to extend the regular displacement law of multiplets, the nature of which has already been pointed out,[3b] through successively increasing iso-electronic systems as far as those of the Cu I, Zn II, etc., type. The wave-numbers given in table 2 and shown graphically in figure 1 were chosen in the following way. For the one-electron systems in the first column we have selected the strongest line of the principal doublet