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THE QUANTUM MECHANICS OF ELECTRONS IN CRYSTALS

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ABSTRACT

A general solution is developed for the motion of electrons in the potential field of the nuclei in a crystal lattice. As usual the energy interaction terms due to nuclear vibration and to the presence of other electrons are neglected; they are to be included later by approximation methods.

It is shown for low energies the wave function becomes a linear combination of the atomic wave functions, the allowed energies approximating the discrete atomic levels; and for high energies the wave function approaches that of the free electron, with the allowed energies a nearly continuous range. However, for electrons coming into the crystal from outside, the crystal becomes impenetrable for those electronic wave-lengths and directions analogous to the beams producing Bragg and Laue beams in x-rays.

The solution is computed for a simple form of potential lattice, and the results are shown to be in quantitative agreement with the experimental results of Davisson and Germer. The phenomenon they call anomalous dispersion is shown to be a natural consequence of the characteristics of the wave function.

INTRODUCTION

THE problem of determining the behavior of electrons in crystals has applications in several types of phenomena: in the scattering of electrons from metal surfaces, instanced by the experiments of Davisson and Germer,[1] of G. P. Thomson and others; and in the behavior of metallic conductors.

The first problem in the study of the theory of any of these phenomena is the study of a single electron in a crystal lattice made up of atomic nuclei fixed at their equilibrium centers. The perturbation terms due to nuclear vibration and to the presence of other electrons must then be dealt with by approximation methods.

The simplest possible assumption for the unperturbed electron is that used by Sommerfeld,[2] the wave function being approximately like that of a field-free electron:

$$\psi_e(W) = N_e \exp i(W)^{1/2}(ax + by + cz) \tag{1}$$

where W is $8\pi^2\mu/h^2$ times the electronic kinetic energy inside the crystal, and a, b and c are the direction cosines of the electronic motion. This type

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[1] This work was begun under the supervision of Dr. Davisson, at the Bell Telephone Laboratories. The writer wishes to express his appreciation of the help the Laboratories in general, and Drs. Davisson and Germer in particular, have given him. He also has obtained many helpful suggestions from Professor E. Wigner.

[2] Sommerfeld, Zeits. f. Physik **47**, 1, (1928).

of wave function is most nearly correct for the most loosely bound electrons, but is not sufficiently correct, even for them, to explain the experiments of Davisson and Germer.

The other type of approximation is to consider the electron behavior as primarily determined by the electric fields of the crystal nuclei. Since the potential wall between the atoms is not infinite, there is a finite probability of an electron belonging originally to one nucleus to change to any other nucleus. This means that in equilibrium the wave function for the electrons in the crystal will be any one of the large number of linear combinations of terms, each term representing the electron in the nth quantum state about the sth nucleus.[3] This is an example of equivalence degeneracy similar to the simple case of the hydrogen molecular ion, and as a result the energy level corresponding to the nth quantum state of a free atom will be split into a large number of very slightly separated levels; in fact, if the crystal is considered infinite in extent, the levels of the free atom will be spread into bands of allowed energies which may or may not be separated from their neighbors by bands of forbidden energies. Of course the wave functions for the electron will be somewhat modified by this proximity of other nuclei, and Bloch[4] has used a wave function which becomes, for an infinitely large crystal:

$$\psi_e(E) = N_e \exp i(W)^{1/2}(ax + by + cz)\cdot u(W_a)$$

where E is a function of W and W_a, and u is a linear combination of wave functions representing the electron about the various nuclei with an energy W_a.

This assumption is fairly good for the more tightly bound electrons, in the inner orbits, but for the loosely bound ones, the ones contributing most to the electric conductivity, the field due to the nucleus is so greatly distorted by the neighboring atoms that the undisturbed atomic functions are not particularly good approximations.

At any rate, whatever the potential function happens to be, it can always be represented by the three dimensional Fourier series of the type

$$V = -\frac{h^2}{8\pi^2\mu}\sum_{l,m,n=-\infty}^{\infty} A_{lmn} \exp i(l\alpha x + m\beta y + n\gamma z) \qquad (2)$$

where $\alpha, \beta, \gamma = 2\pi/(d_x, d_y, d_z)$, where the d's are the lengths of sides of the unit lattice cell in the x, y and z directions respectively. The A's are chosen so that V is real and $A_{000} = 0$. This series is applicable to the cubic, tetragonal and orthorhombic systems of lattices, and the generalization to the other systems is obvious. The wave function for such a potential will be obtained, and its properties investigated, in this paper.[5]

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[3] Heisenberg, Zeits. f. Physik **49,** 619 (1928). A very good resumé of the subject is given by Slater, Phys. Rev. **35,** 509 (1930).

[4] Bloch, Zeits. f. Physik **52,** 555 (1928).

THE WAVE FUNCTION

A somewhat less general, but considerably simpler form of potential function

$$V = -\frac{h^2}{8\pi^2\mu}\left[\sum_{l=-\infty}^{\infty}\alpha^2 A_{xl}e^{il\alpha x} + \sum_{m=-\infty}^{\infty}\beta^2 A_{ym}e^{im\beta y} + \sum_{n=-\infty}^{\infty}\gamma^2 A_{zn}e^{in\gamma z}\right] \tag{3}$$

will first be considered. The crystal will at first be considered as infinite in extent, and the average potential as zero, so that $A_{x0}=A_{y0}=A_{z0}=0$. If the electronic energy is $h^2W/8\pi^2\mu$ then the Schroedinger equation which must be satisfied can be separated into three equations of the type

$$\Xi'' + \left(W_x\alpha^2 + \alpha^2\sum_l A_{xl}e^{il\alpha x}\right)\Xi = 0 \tag{4}$$

where $W_x\alpha^2+W_y\beta^2+W_z\gamma^2=W$. The complete wave function is $\Psi=\Xi(x)H(y)\cdot\Omega(z)$, where the equations for H and Ω are similar to Eq. (4).

The independent variables are now changed to ξ, η, $\zeta=\alpha x$, βy, γz and then all three equations have the form

$$\Xi'' + \left(W_x + \sum A_{xl}e^{il\xi}\right)\Xi = 0. \tag{5}$$

The solution of this equation was given by Hill,[6] and is

$$\Xi = N\cdot e^{ik_x\cdot\xi}\cdot\sum_{r=-\infty}^{\infty} b_{xr}(k_x)\cdot e^{ir\xi} \tag{6}$$

where k_x and the b's are to be determined. k_x is given by the equation

$$\sin^2\pi k_x = \sin^2\pi(W_x)^{1/2}\cdot\square(0) \tag{7}$$

where $\square(0)$ is the infinite determinant

$$\left|\begin{array}{cccccccc}
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \frac{-A_{x,-1}}{1-W_x} & 1 & \frac{-A_{x,1}}{1-W_x} & \frac{-A_{x,2}}{1-W_x} & \frac{-A_{x,3}}{1-W_x} & \frac{-A_{x,4}}{1-W_x} & \cdots \\
\cdots & \frac{-A_{x,-2}}{-W_x} & \frac{-A_{x,-1}}{-W_x} & 1 & \frac{-A_{x,1}}{-W_x} & \frac{-A_{x,2}}{-W_x} & \frac{-A_{x,3}}{-W_x} & \cdots \\
\cdots & \frac{-A_{x,-3}}{1-W_x} & \frac{-A_{x,-2}}{1-W_x} & \frac{-A_{x,-1}}{1-W_x} & 1 & \frac{-A_{x,1}}{1-W_x} & \frac{-A_{x,2}}{1-W_x} & \cdots \\
\cdots & \frac{-A_{x,-4}}{4-W_x} & \frac{-A_{x,-3}}{4-W_x} & \frac{-A_{x,-2}}{4-W_x} & \frac{-A_{x,-1}}{4-W_x} & 1 & \frac{-A_{x,1}}{4-W_x} & \cdots \\
\cdots & \frac{-A_{x,-5}}{9-W_x} & \frac{-A_{x,-4}}{9-W_x} & \frac{-A_{x,-3}}{9-W_x} & \frac{-A_{x,-2}}{9-W_x} & \frac{-A_{x,-1}}{9-W_x} & 1 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{array}\right|$$

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[5] Equations similar to those considered here were discussed by Bethe, Ann. d. Physik **87,** 55 (1928), but no solution was obtained, Peierls, Ann. d. Physik **4,** 121 (1930) gets an approximate solution, Strutt, Ann. d. Physik **86,** 319 (1928) discussed a one-dimensional case.

[6] Hill, Acta Mathematica **8,** 1 (1886).

This determinant can be expanded into a convergent series of the form

$$\begin{aligned}\square(0) = 1 &- (C_{11}A^2_{x1} - C_{12}A^4_{x1} + C_{13}A^6_{x1} \cdots) \\ &- (C_{21}A^2_{x2} \cdots) \cdots \\ &+ (C_{121}A^2_{x1}A_{x2} - C_{122}A^4_{x1}A_{x2} + \cdots) \\ &- (C_{131}A^3_{x1}A_{x3} \cdots) + \cdots \\ &+ (C_{1231}A_{x1}A_{x2}A_{x3} \cdots) + \cdots .\end{aligned} \tag{8}$$

The values of some of the C's as functions of W_x are given in Fig. (1).[7] When the series of A's converge at least as rapidly as $A_{xn} = 1/2^n$, this expansion

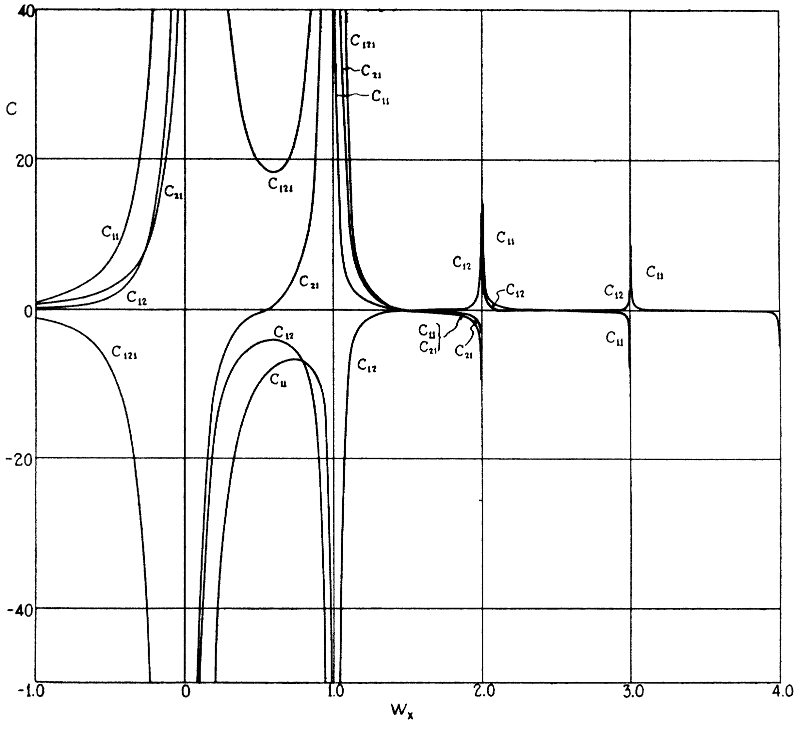

Fig. 1. Values of some of the coefficients in the expansion of $\square$ (0).

is accurate to one part in a thousand if only the terms written above are used.

The b's are obtained by solving the equations

$$[(k_x + r)^2 - W_x]b_{x,r} - \sum_{l=-\infty}^{\infty} A_{xl}b_{x,r-l} = 0 \tag{9}$$

where r can have any integral value from plus to minus infinity.

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[7] The writer is very much indebted to Mr. B. L. Snavely for computing the values of a number of the functions discussed in this paper.

A generalization of Hill's arguments shows that a solution of the Schroedinger equation using the general potential function given in Eq. (2) will be of the form

$$\psi = N \exp i(\kappa_x x + \kappa_y y + \kappa_z z) \sum_{r,s,t=-\infty}^{\infty} B_{rst} \exp i(r\alpha x + s\beta y + t\gamma z) \tag{10}$$

where the relations between the κ's are given by the equation

$$S(\kappa_x, \kappa_y, \kappa_z; \alpha, \beta, \gamma) = S(aW^{1/2}, bW^{1/2}, cW^{1/2}; \alpha, \beta, \gamma) \cdot \Box(0,0,0,) \tag{11}$$

where $\Box(0, 0, 0,)$ is a determinant similar to $\Box(0)$. The function

$$S(x, y, z; \alpha, \beta, \gamma) = (x^2 + y^2 + z^2) \prod_{l,m,n=-\infty}^{\infty}{}' \left[1 - \frac{2l\alpha x + 2m\beta y + 2n\gamma z - x^2 - y^2 - z^2}{l^2\alpha^2 + m^2\beta^2 + n^2\gamma^2} \right]$$

where the infinite product does not include the term for which $l = m = n = 0$, and a, b and c are the direction cosines which the electronic motion would have if all the A's were zero. For a two-dimensional case $S(x, y; \alpha, \beta)$ is the product of the elliptic functions $H(x+iy) \cdot H(x-iy)$, where the periods of these functions are $K = \alpha/2$ and $K' = \beta/2$. For the one-dimensional case discussed by Hill, $S(x; \alpha)$ is $\sin^2(\pi x/\alpha)$ as given in Eq. (7). The B's are given by the equations

$$[(\kappa_x + r\alpha)^2 + (\kappa_y + s\beta)^2 + (\kappa_z + t\gamma)^2 - W] B_{r,s,t} + \sum_{l,m,n} A_{lmn} B_{r-l,s-m,t-n} = 0.$$

Expression (10) is of natural form; that of a free electron whose direction cosines of motion are proportional to κ_x, κ_y and κ_z, multiplied by a function representing the distortion of the wave function due to the periodic variation of the potential function. For low energies this distorting function will be a Fourier expansion of one of the linear combinations of atomic wave functions discussed earlier. In this case Eq. (9) is the form used by Bloch.

One property of (9) must be emphasized, however. The coefficients κ_x, κ_y, κ_z, in the "field-free-electron" factor are not equal to $W^{1/2}(a, b, c)$ as they would be if the A's all equalled zero, as for Eq. (1). For values of $a(W)^{1/2}$ near $l\alpha/2$, or $b(W)^{1/2}$ near $m\beta/2$, or $c(W)^{1/2}$ near $n\gamma/2$ (i.e., near the singular points of the determinant or near the maximum points of the function S) the κ's differ considerably from the values $(W)^{1/2}(a, b, c)$, and for certain ranges become complex.

In crystals of infinite extent, the values of W and a, b and c for which any of the κ's become complex are not allowed; for in these cases the wave function contains a real exponential factor which becomes infinite at plus or minus infinity. Even in the case of finite crystals, it is seen that the amplitude of wave functions for which a κ becomes complex is negligible in the interior of the crystal. Thus for crystals of size greater than, say, a thousand atoms along a side, electrons with energies for which a κ is complex are not present inside the crystal.

This means that the periodic variation of potential inside the crystal creates bands of forbidden energies inside the crystal, even for electronic energies greater than the maximum potential energy, a somewhat surprising result. However, this only means that when electrons outside a crystal have energies such that their wave-number components are integral multiples of the reciprocal lattice spacing, they are reflected strongly back at the surface of the crystal. That this is true experimentally has been shown by Davisson and Germer.

These bands of forbidden energies are very wide for low energies, but become very narrow for higher energies. In other words, the allowed bands of energy are very narrow for low energies, corresponding quite closely to the atomic levels; but for energies larger than the maximum potential energy nearly every energy is allowed. Thus the general solution shows a gradual transition from purely atomic states to states of the free electron, as general considerations have shown it should.

A Simple Example

It will be of interest to examine in detail the solution for a very simple form of potential variation. The form

$$V = -\frac{h^2}{8\pi^2\mu}[2\alpha^2 A_x \cos \alpha x + 2\beta^2 A_y \cos \beta y + 2\gamma^2 A_z \cos \gamma z] \tag{12}$$

is not a particularly good approximation to the lattice field, but its solution is not too difficult, and the quantitative check of the computed results with experiment leads one to believe that it is not too bad an approximation when dealing with electrons of high energy. It is, of course, a very poor approximation for the low energy, "bound" electrons, and care should be used in applying its results.

The three Schroedinger equations which must be solved are Matthieu equations

$$\Xi'' + (W_x + Ae^{i\xi} + Ae^{-i\xi})\Xi = 0. \tag{13}$$

The solution is the generalized Matthieu function,[8] of the form given in Eq. (6), where the values of k_x are given by Eq. (7) when $A_{x1} = A_{x-1} = A$, and $A_{xn} = A_{x-n} = 0$, for n greater than unity, in the determinant $\Box(0)$.

The values of k_x^2 as a function of A and W_x are shown by means of the contour map in Fig. 2. The shaded areas are the values of A and W_x where k_x is complex. It is to be noticed that these areas are larger the larger A is, and are smaller the larger W_x is. The area included between the diagonal dotted lines radiating from $A = W_x = 0$ represents the values of W_x less than the maximum and greater than the minimum potential energy. The values of the contours for k_x^2 are equal to the values of W_x when $A = 0$, as would be expected. The narrowing of the unshaded bands of energy as A increases

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[8] E. C. G. Poole, Proc. Lond. Math. Soc. **20**, 374 (1921); B. van der Pol and M. J. O. Strutt, Phil. Mag. **5**, 18 (1928).

illustrates the transition from the continuous allowed levels when $A = 0$ to the discrete levels when A is infinite.

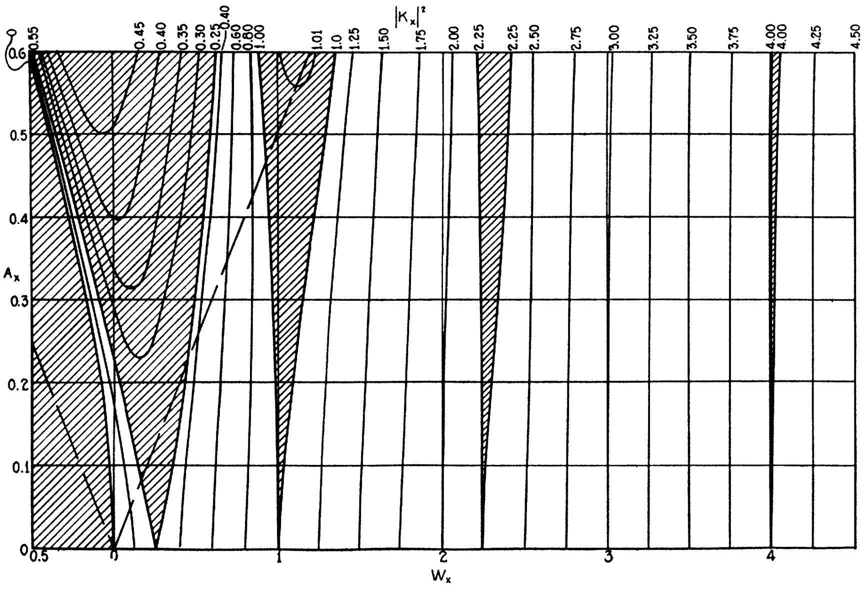

Fig. 2. Values of k_x^2 as a function of A and W_x. Shaded portions represent areas where k_x is complex and equals $(n/2)+ig(W_x)$, where g is real.

The difference between the character of the levels for one atom and for an infinite lattice is shown in Fig. 3. Curve (*a*) gives the potential energy cross section for a single "atom" with its discrete set of allowed levels, and curve (*b*) gives the potential function for an infinite lattice with its bands of allowed levels.

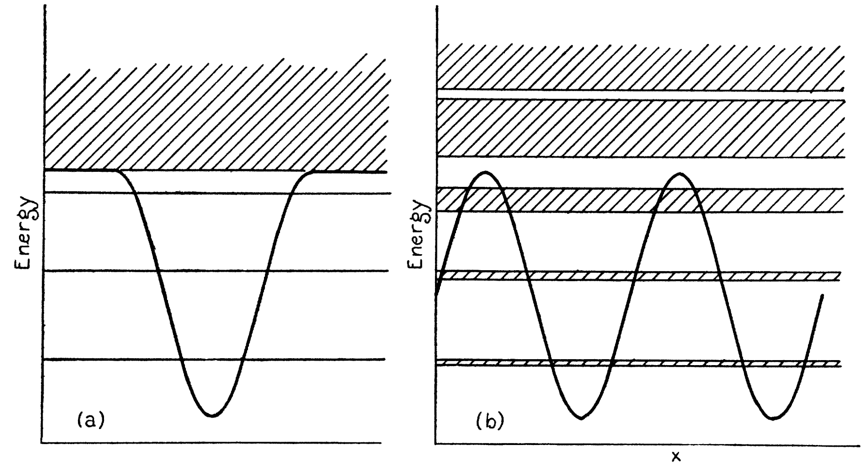

Fig. 3. Potential function and allowed energies for a single "atom" and for a crystal of infinite extent. Horizontal lines represent discrete levels, and shaded areas represent continuous allowed bands.

The difference between W_x and the real values of k_x for a given value of A can be given by considering W_x as a function of k_x and defining

$$f_x(k_x) = W_x(k_x) - k_x^2. \tag{15}$$

Values of f_x for real values of k_x are given in Fig. 4 for a particular value of A.

The value of A will be chosen to be 1/4 for the calculations below, since for this value, and for a lattice spacing of 3·5 Angstrom units, the difference between the maximum and minimum potential energy in the crystal will be about 36 electron volts, a reasonable variation.

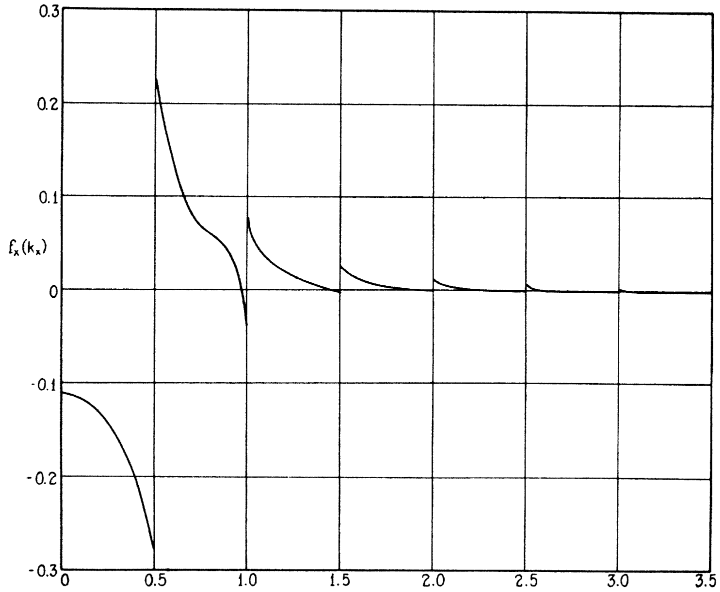

Fig. 4. Values of $f(k_x)$ for real values of k_x, for $A = 1/4$.

The Fourier coefficients, $b_{xn}(k_x)$, can next be computed by means of Eq. (9), which in this special case can be transformed[9] into one or the other of the following continued fractions

$$\begin{aligned} \frac{b_{x,r}}{b_{x,r+1}} &= \cfrac{A}{S_r - \cfrac{A^2}{S_{r-1} - \cfrac{A^2}{S_{r-2} - \cdots}}} \\ \frac{b_{x,r}}{b_{x,r-1}} &= \cfrac{A}{S_r - \cfrac{A^2}{S_{r+1} - \cfrac{A^2}{S_{r+2} - \cdots}}} \end{aligned} \tag{16}$$

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[9] E. C. G. Poole, Proc. Lond. Math. Soc. **20**, 382 (1921).

where $S_r=(k_x+r)^2-W_x$. Values of b_{xr} are computed in terms of b_{x0} and the value of b_{x0} adjusted so that $\sum_r b_{xr}^2=1$, for normalization purposes. Values of the b's for $A=1/4$ for various real values of k_x are shown in Fig. 5.

It can be shown in general, by symmetry arguments, that when $k_x=n/2$ (n an integer) $b_{x,r}=\pm b_{x,-n-r}$. In intermediate cases, as is seen in the curves, b_{x0} is very much larger numerically than any of the other b's.

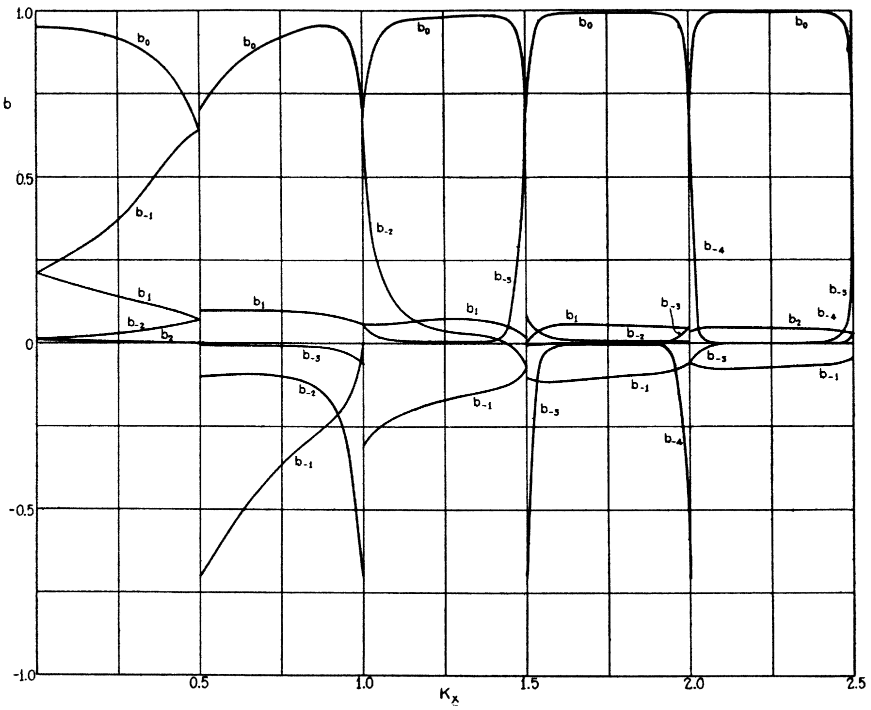

Fig. 5. Values of the Fourier coefficients $b_i(k_x)$ for real values of k_x, for $A=1/4$. Coefficients not shown in this figure are negligibly small.

SCATTERING FROM CRYSTAL SURFACES

Thus for this simple case it is possible to obtain an exact solution for the motion of electrons inside a potential lattice. Let us see how nearly these results check with experiments with electrons of high energies.

Such experiments have been chiefly concerned with the scattering of electrons from the surface of a crystal. A simple model of this experiment would be a plane electron wave of kinetic energy $h^2E/8\pi^2\mu$ outside the crystal. If the potential outside is zero, that inside will be $h^2V_0/8\pi^2\mu$ plus the V given in Eq. (12), since the average potential inside the crystal is less than that outside. The values of the W's used will then be such that $W_x\alpha^2+W_y\beta^2+W_z\gamma^2=W=E+V_0$.

The wave function inside the crystal (positive values of x) will be given by the product of three factors similar to Eq. (6). Then, since the wave function must be continuous in value and normal gradient at the crystal surface, the wave function outside must be

$$\begin{aligned}\Psi_0 = \sum_{m,n=-\infty}^{\infty} C_{mn} \exp i\{ [E - (k_y + m)^2\beta^2 - (k_z + n)^2\gamma^2]^{1/2} \cdot x \\ + (k_y + m)\beta y + (k_z + n)\gamma z\} \\ + \sum_{m,n=-\infty}^{\infty} D_{mn} \exp i\{ - [E - (k_y + m)^2\beta^2 - (k_z + n)^2\gamma^2]^{1/2} \cdot x \\ + (k_y + m)\beta y + (k_z + n)\gamma z\}\end{aligned} \tag{18}$$

where the C terms represent beams impinging on the surface and the D terms represent beams coming from the surface. But to fit the case we were considering, where there was only one incident beam with the direction cosines a, b and c, we must make all the C's equal to zero except, say, C_{00}, and then make $b^2E = k_y^2\beta^2$ and $c^2E = k_z^2\gamma^2$. To do this we must introduce other internal beams, due to the secondary internal reflections from the surface.

Then the complete wave function inside the crystal is

$$\begin{aligned}\Psi_i = \sum_{r,s=-\infty}^{\infty} F_{rs} \exp i[k_x(rs)\alpha x + (k_y + r)\beta y + (k_z + s)\gamma z] \\ \cdot \sum_{l,m,n} B_{lmn}(rs) \cdot \exp i(l\alpha x + m\beta y + n\gamma z)\end{aligned} \tag{19}$$

where $B_{lmn}(rs) = b_{xl}(k_x(rs)) \cdot b_{ym}(k_y + r) \cdot b_{zn}(k_z + s)$, and where F_{00}, the coefficient of the primary internal beam, can be taken as unity. The value of $k_x(rs)$ is determined by the value of $W_x(rs)$, where

$$\alpha^2 W_x(rs) = E + V_0 - (k_y + r)^2\beta^2 - (k_y + s)^2\gamma^2 - \beta^2 f_y(k_y + r) - \gamma^2 f_z(k_z + s).$$

No negative value of k_x is included, since the other boundary of the crystal is considered as being at x equals positive infinity, and no beams reflected from its surface are present.

The intensity of these secondary internal rays is determined by $|F_{rs}|^2$ and will be shown to be small compared to $|F_{00}|^2$. Since also the B's decrease rapidly (except for special cases considered later) for increasing l, m, n, to a good approximation we can neglect all except the $B_{l00}(rs)$ for every beam except the primary one, where $r = s = 0$.

Then the boundary conditions determining the relative magnitudes of the D's and F's for all C's equal to zero except C_{00} are, approximately

$$\begin{aligned}C + D_{00} &= \sum_l B_{l00}(00) \\ C - D_{00} &= \frac{\sum_l (k_x + l)\alpha B_{l00}(00)}{(E - k_y^2\beta^2 - k_z^2\gamma^2)^{1/2}}\end{aligned} \tag{20}$$

for the incident and primary reflected and refracted beams. Here $C = C_{00}$ and $k_x = k_x(00)$ for brevity. Also

$$D_{rs} = \sum_l \left[B_{lrs}(00) + F_{rs}\,B_{l00}(rs)\right]$$

$$-D_{rs} = \frac{\sum_l \left[(k_x + l)\,B_{lrs}(00) + F_{rs}\,(k_x(rs) + l)\,B_{l00}(rs)\right]\alpha}{(E - (k_y + r)^2\beta^2 - (k_z + s)^2\gamma^2)^{1/2}} \tag{21}$$

for the secondary beams outside and inside, since all the other C's are zero.

These equations will hold to a good approximation except in the special cases when F_{rs} becomes of the same order of magnitude as F_{00} (this can only happen when $B_{lrs}(00)$ is of the same order as $B_{000}(00)$, and then not necessarily). In this case the D's other than D_{rs} will be small anyhow, and the resulting inaccuracy in the determination of the reflected intensities will be small even in this special case.

Then the ratio between the incident current of electrons and the regularly reflected current is

$$\left|\frac{D_{00}}{C}\right|^2 = \left|\frac{\sum_r \left[(a(E)^{1/2}/\alpha) - k_x - r\right] b_{xr}(k_x)}{\sum_s \left[(a(E)^{1/2}/\alpha) + k_x + s\right] b_{xs}(k_x)}\right|^2 \tag{22}$$

When k_x is not near half integral values, it is nearly equal to $(a^2E + V_0)^{1/2}/\alpha$, and b_{x0} is the only not-negligible b_x. Then the formula reduces to

$$\left|\frac{D_{00}}{C}\right|^2 = \left[\frac{a(E)^{1/2} - (a^2E + V_0)^{1/2}}{a(E)^{1/2} + (a^2E + V_0)^{1/2}}\right]^2$$

which is the intensity of reflection when $A = 0$. That is, except for special values of k_x, the crystal behaves as though it were a hollow of uniform potential $-h^2V_0/8\pi^2\mu$ with no periodic potential variation at all.

When $k_x = n/2$, however, we have seen that $b_{x,s} = \pm b_{x,-s-n}$, and substituting $-(s+n)$ for r in Eq. (22) it is seen that

$$\left|\frac{D_{00}}{C}\right|^2 = \left[\frac{\pm\sum_s \left[(aE^{1/2}/\alpha) + (n/2) + s\right] b_{xs}}{\sum_s \left[(aE^{1/2}/\alpha) + (n/2) + s\right] b_{xs}}\right]^2 = 1.$$

For the complex values of k_x, $|D_{00}/C^2| = 1$, but there is a change of phase on reflection. That is, the crystal is perfectly reflecting for every value of electronic energy and direction of incidence which has a value of W_x for which k_x is a half integer or is complex. These values of W_x for any value of A are represented by the shaded areas in Fig. 2.

Of course in an actual crystal the reflected intensity for these values of W_x will be considerably less than unity, because a number of electrons will interact with the crystal atoms as they traverse the lattice. In any case, however, the maximum reflection intensity will be for values of W_x somewhere within the shaded areas in Fig. 2, and can be represented by the equation

$$W_{xn} = (n^2/4) + G_n(A) \tag{23}$$

where G is a small quantity compared to 1/4, except for the case $n = 1$.

When the incident electron stream is normal to the crystal surface, $W_y = f_y(0)$ and $W_z = f_z(0)$, since k_y and k_z must both equal zero. Equation (18) reduces to

$$W_x\alpha^2 = E + V_p$$

where $V_p = V_0 - \beta^2 f_y(0) - \gamma^2 f_z(0)$, which is larger than V_0 since the $f(0)$'s are negative quantities.

In this case the relative intensity of the reflected beam will be a maximum when

$$E_n = (n^2\alpha^2/4) + \alpha^2 G_n(A) - V_p \tag{24}$$

from Eq. (23). The ideal curve for a typical case is given in Fig. 6. In the actual case, as was previously pointed out, the maxima are less than unity and probably decrease in height for increasing n, since the peaks are narrower and the chance of losing energy is greater. The experimental curves of Davisson and Germer[10] for nearly normal incidence show just such characteristics.

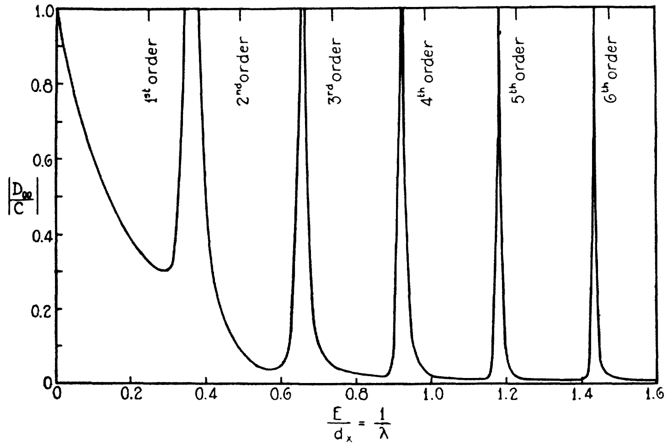

Fig. 6. Relative intensity of the regularly reflected beam as a function of the electronic wave number. The incident beam is normal to the 111 surface of a nickel crystal. Lines marked 1st order, etc., indicate positions of strong x-ray reflection for the same crystal.

There will also be the other scattered beams represented by the coefficients D_{mn} in Eq. (19) whose direction cosines will be $(E - m^2\beta^2 - n^2\gamma^2)^{1/2}/E^{1/2}$, $m\beta/E^{1/2}$ and $n\gamma/E^{1/2}$, whose relative intensities will vary with E, but will in general be much smaller than unity.

For an obliquely incident beam whose plane of incidence is parallel to the z axis we have

$$W_x\alpha^2 = E\cos^2\theta + V_a - \beta^2 f_y\left(\frac{E^{1/2}\cdot\sin\theta}{\beta}\right)$$

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[10] Davisson and Germer, Proc. Nat. Acad. Sci. **14,** 622 (1928).

where $V_a = V_0 - \gamma^2 f_z(0)$ is larger than V_0 but smaller than V_p, and where θ is the angle of incidence.

The values of θ and E for a regularly reflected beam of maximum intensity will be such that

$$W_{xn}\alpha^2 = (n^2\alpha^2/4) + \alpha^2 G_n(A)$$

similarly to Eq. (23). Substitution in the equation for $W_x\alpha^2$ gives

$$E_n \cos^2\theta_n = (n^2\alpha^2/4) - V_n + \beta^2 f_y\left(\frac{(E_n)^{1/2}\sin\theta_n}{\beta}\right) \tag{25}$$

where $V_n = V_a - \alpha^2 G_n$, and where E_n and θ_n signify the values of E and θ for maximum regular reflection. Since the quantity f_y is small for most values of its argument (see Fig. 4) we see that the wave-length $1/E_n^{1/2}$ plotted against $\cos\theta_n$ gives in general a straight line going through the origin. However since f_y is large and discontinuous for values of E_n and θ_n near where

$$E_n^{1/2}\sin\theta_n = m\beta/2 \tag{26}$$

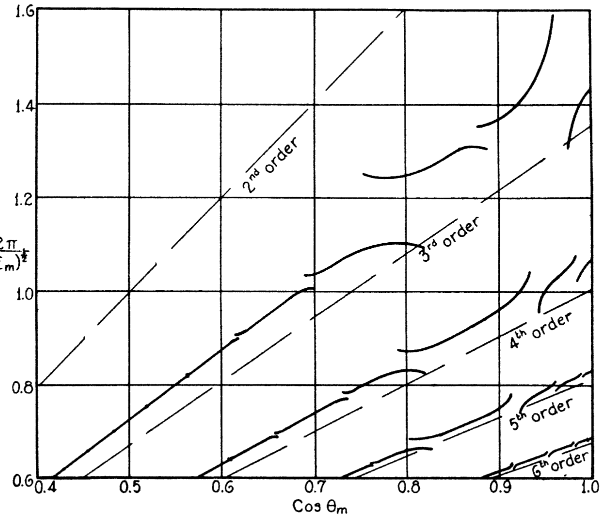

Fig. 7. Values of electronic wave number and angle of incidence of electron beam for strong regularly reflected beam. The crystal is nickel, the surface the 111 plane. Broken lines indicate positions of analogous x-ray reflection.

the curve deviates from a straight line near these values, and is discontinuous. A curve of $1/E_n^{1/2}$ against $\cos\theta_n$ for values of α, β and A corresponding to a nickel crystal is shown in Fig. 7.[11]

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[11] The analysis here has been for the case when the crystal surface is the 100 plane, perpendicular to a crystal axis. In the experiments of Davisson and Germer, the crystal surface was the 111 plane, oblique to the crystal axes. In this case, both f_x and f_y vary, and although the discontinuities are of the same character as that given above, their shape is more complicated. Eqs. (25) and (26) still hold, however, if α and β are now considered as the distance between atom planes parallel and perpendicular to the surface, respectively, and $\Phi(E_n{}^{\frac{1}{2}}\sin\theta_n/\beta)$, a function of f_x and f_y, be substituted for f_y in Eq. (25). Fig. 7 has been computed by means of these revised equations.

When the experimental curves[12] for this case are studied it is seen that not only is the general form of the curves similar, discontinuities and all, but that the positions of the discontinuities correspond. The shape of the curves near the discontinuities does not fit exactly, but if a better approximation to the actual potential function were used in the calculations, the correspondence would probably be better.

The physical explanation of these discontinuities is that for $E_n \sin^2\theta_n = m^2\beta^2/4$ there is resonance, and therefore strong damping, in the y direction, and nearly all the electrons are reflected back in a direction exactly opposite to the incident beam, leaving none to be regularly reflected. This phenomenon was given the tentative name of "anomalous dispersion" by Davisson and Germer, and in a way this term is correct, for it is due to a simultaneous resonance of the x and y components of the electronic wave number, and a consequent damping out of the wave function in the interior of the crystal.

The other scattered beams in the x, y plane come off at angles ϕ_m, where

$$\sin\phi_m = \sin\theta + m\beta/E^{1/2}. \tag{27}$$

It can be seen from Eq. (21) that their relative intensities will be

$$\left|\frac{D_{m0}}{C}\right| = \left|\frac{b_{ym}(E^{1/2}\sin\theta)}{b_{y0}(E^{1/2}\sin\theta)} \times \frac{\sum_{rs}(k_x' + s - k_x - r)\, b_{xr}(k_x)\cdot b(k_x')}{\sum_{ln}\left(k_x' + l + \dfrac{E^{1/2}\cos\Phi}{\alpha}\right)\left(k_x + n + \dfrac{E^{1/2}\cos\theta}{\alpha}\right) b_{xn}(k_x) b_{xl}(k_x')}\right|^2 \frac{E\cos^2\theta}{\alpha^2}$$

where k_x' is the $k_x(mo)$ of the beam reflected back into the crystal at the surface, and is a function of the energy W_x', where

$$\alpha^2 W_x' = E + V_a - (E^{1/2}\sin\theta + m\beta)^2 - \beta^2 f_y\left(\frac{E^{1/2}\sin\theta}{\beta} + m\right)$$

These secondary internal beams will make a slight change in the magnitude of the primary internal beam, but this can be neglected. The quantity b_{ym} is only large when $E^{1/2}\sin\theta$ is near the value $-m/2$, corresponding to reinforcement due to the y, z planes of atoms, and, when E and θ also satisfy Eq. (23), corresponding to the case of "anomalous dispersion" of the regularly reflected beam. The quantity $|D_{m0}/C|^2$ also shows other maxima analogous to the various Laue beams in x-ray scattering.

CONCLUSION

Thus it has been seen that for high energy electrons even the simple potential function used above gives results in good accordance with experiment. This accordance becomes less and less good as we consider electrons with less and less energy, and the results probably do not fit at all for the

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[12] Davisson and Germer, Proc. Nat. Acad. Sci. **14**, 624 (1928). Later (unpublished) curves show a more complete agreement.

tightly bound electrons in the inner atomic shells, where the allowed energies are narrow bands very slightly different from the simple discrete atomic levels. For these electrons, also, the interaction between electrons cannot be neglected.

However for those electrons whose energy is greater than $-h^2V_0/8\pi^2\mu$ it seems likely that the results of the simple case discussed above will be indicative. So that while this simple case will not tell us anything about ferromagnetism, for instance, or of any other crystal property which depends on the inner bound electrons, it may be of help in discussing those properties which depend primarily on the high energy free electrons, such as electric conductivity. We have seen that for the still higher energy electrons used in scattering experiments, the agreement with experiment is very good.

When the stationary states inside a crystal of finite size (say a rectangular one whose edges are Ld_x, Md_y, Nd_z respectively, where L, M and N are integers) are considered, it is seen that the wave functions are

$$\psi_{rst} = \frac{(2)^{1/2}}{(L^2d_x^{\,2} + M^2d_y^{\,2} + N^2d_z^{\,2})^{1/2}} \cdot \sum_{l,m,n} B_{lmn}(r,s,t) \sin\left[\left(\frac{r}{2L} + l\right)\alpha x + \left(\frac{s}{2M} + m\right)\beta y + \left(\frac{t}{2N} + n\right)\gamma z\right]$$

where the fractions $r\alpha/2L$, $s\beta/2M$ and $t\gamma/2N$ (r, s, t integers) replace the variables κ_x, κ_y and κ_z, and where the B's are normalized so that $\sum_{l,m,n} B_{lmn}^{\,2} = 1$. From this it can be seen that the distribution of electrons in terms of $r^2\alpha^2/L^2$, $s^2\beta^2/M^2$, $t^2\gamma^2/M^2$ is a normal Fermi one. But, since the energy is a complicated function of these quantities, the electron distribution in energy is different from that of the completely free electron.