

The Reflection of Electrons From Crystals
and
The States of Divalent Crystals

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Summary

In the first part, the reflection of electrons from crystals is considered. We here treat this problem when the potential of the crystal is a completely general three dimensional Fourier series, whereas previously only very special cases were treated. Also our method is quite transparent while the previous methods were obscured by involved numerical computations. Also, we show quite generally what had been inferred from very special cases, including the Bragg law of reflection. The relation of the Fourier components of the potential of the crystal to the optical planes is clearly shown. How the potential of the crystal is to be obtained from the experimental data is discussed, and a formula for the width of the bands of total reflection is given.

In the second part the energy states of divalent crystals are considered. The two limiting cases of weak and strong coupling between the two valence electrons of each atom are shown to lead to energy expressions of the same form, and we conclude that there should be no difference in the ferromagnetism of monovalent and divalent crystals except as due to differences in the constants of the energy.

The Reflection of Electrons From Crystals

The reflection of electrons from crystals, an experiment which was performed by Davisson and Germer,¹ has been considered quantum mechanically by Strutt,² Zwicky,³ Bethe,⁴ Morse,⁵ de Kronig and Penney,⁶ and Hill.⁷ A crystal is defined as a medium in which the potential along any line is periodic. Such a potential can therefore be described analytically by a three dimensional Fourier Series. However, these authors were not able to treat this general case, and very severe restrictions were imposed on the potential in order to render the problem soluble.

Perhaps the most detailed treatment is that of Morse. He takes the potential as essentially

$$\cos \alpha x + \cos \beta y + \cos \gamma z \quad (1)$$

What this potential means in terms of optical planes of the crystal, we shall see later. At any rate, Morse treats the differential equation of the problem which results in forming the usual Schrodinger equation, by Hill's method. This method is perfectly rigorous and converges for all values of the energy of the incident electrons, but the solution cannot be exhibited in explicit form. Moreover, the essential conclusions arrived at have to be obtained through very involved numerical computations. Thus, aside from lack of generality, the solution is somewhat obscure.

Strutt, de Kronig and Penney, and Hill get very explicit solutions by making their potential a one dimensional square tooth and valley form. In passing to three dimensions, however, they resort to the same restriction as does Morse.

As we shall see later, complete generality is essential to revealing certain important characteristics of the various orders of reflection from a given set of planes.

Our treatment of the differential equation of the problem is merely that of Mathieu⁸ slightly generalized. This method is nothing more or less than the ordinary perturbation theory, but whereas usually difficulties are encountered in the first approximation, the n^{th} approximation is as easily solved as the first in our case, because of the purely periodic potential.

It should be mentioned that this method does not converge for all values of the energy of the incident electrons, but only when the energy is sufficiently high. Fortunately, this represents the experimental condition we are interested in, and in the limiting case arrive at our conclusions with complete rigor.

I. Wave Equation and Its Solutions

In order to treat the case of charged particles incident on a semi-infinite crystal (Davisson Germer experiment) it is necessary for us to consider solutions of the Schrodinger equation inside the crystal

$$\nabla^2 \Psi + \frac{8\pi^2\mu}{\hbar^2} (E - V) \Psi = 0$$

$$\text{where } V = -\frac{\hbar^2}{8\pi^2\mu} V_0 - \frac{\hbar^2}{8\pi^2\mu} \lambda \sum_{l,m,n=-\infty}^{\infty} A_{l,m,n} e^{i\left(\frac{l}{a}x + \frac{m}{b}y + \frac{n}{c}z\right)} \quad (2)$$

and μ is the mass of the particle, \hbar is Planck's constant, and E is the energy of the particle. Also, in order to make the potential real we take $A_{l,m,n} = A_{-l,-m,-n}^*$, where $A_{l,m,n}^*$ indicates the complex conjugate of $A_{l,m,n}$, and l, m, n take on all positive and negative integral values. We also take $A_{000} = 0$, so that $-\frac{\hbar^2}{8\pi^2\mu} V_0$ is the average potential of the crystal below that of the outside which is taken to be at zero potential, and λ is the perturbation parameter which must be made small enough so that the solution converges.

If $W = \frac{8\pi^2\mu}{\hbar^2} E + V_0$, then Eq.(2) becomes

$$\nabla^2 \Psi + (W + \lambda U) \Psi = 0$$

$$U = \sum_l A_{l,m,n} e^{i\left(\frac{l}{a}x + \frac{m}{b}y + \frac{n}{c}z\right)} \quad (3)$$

Now let

$$\Psi = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \dots$$

$$W = W_0 + \lambda W_1 + \lambda^2 W_2 + \dots \quad (4)$$

Substituting these expansions into Eq.(3) we obtain the following set of equations.

$$\nabla^2 \psi_0 + W_0 \psi_0 = 0 \quad (5)$$

$$\nabla^2 \psi_1 + W_0 \psi_1 = -\psi_0 (W_1 + U) \quad (6)$$

$$\nabla^2 \psi_2 + W_0 \psi_2 = -W_2 \psi_0 - \psi_1 (W_1 + U) \quad (7)$$

We stop at the second approximation equation merely for simplicity. As we shall see, we can easily solve the n'th approximation equation, but the above are enough to give us a clear idea of what takes place in the general case.

First let us take as the solution of Eq.(5)

$$\psi_0 = e^{i \left(\frac{\alpha}{a} x + \frac{\beta}{b} y + \frac{\gamma}{c} z \right)} \quad (8)$$

where $W_0 = \left(\frac{\alpha}{a} \right)^2 + \left(\frac{\beta}{b} \right)^2 + \left(\frac{\gamma}{c} \right)^2$. There are, of course, an infinity of solutions of Eq.(5) which we might have combined for ψ_0 . However, if none of these solutions are required by the succeeding approximations to meet conditions of finiteness, as will occur in certain cases which we shall investigate, then we reject these arbitrary terms since physically we know that if the crystal is behaving as though there were no periodic potential, a plane beam in the crystal proceeds practically unchanged.

Substituting into Eq.(6), we have

$$\begin{aligned} \nabla^2 \psi_1 + W_0 \psi_1 &= - e^{i \left(\frac{\alpha}{a} x + \frac{\beta}{b} y + \frac{\gamma}{c} z \right)} (W_1 + U) \quad (9) \\ &= -W_1 e^{i \left(\frac{\alpha}{a} x + \frac{\beta}{b} y + \frac{\gamma}{c} z \right)} - \sum_{l,m,n} A_{l,m,n} e^{i \left(\frac{\alpha+l}{a} x + \frac{\beta+m}{b} y + \frac{\gamma+n}{c} z \right)} \end{aligned}$$

$$\text{Let } \Psi_1 = \sum B_{lmm} e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+n}{c}z\right)} \quad (10)$$

$$\text{Then } B_{lmm} = \frac{A_{lmm}}{\left(\frac{\alpha+l}{a}\right)^2 + \left(\frac{\beta+m}{b}\right)^2 + \left(\frac{\gamma+n}{c}\right)^2 - W_0}$$

and $W_1 = 0$.

In general, if α, β, γ are non-integral numbers, the denominator of B_{lmm} will not vanish. Of course, α, β, γ may be chosen so that this happens, but we postpone discussion of this for the moment.

Substituting Ψ_0 and Ψ_1 into Eq. (7) we have

$$\begin{aligned} \nabla^2 \Psi_2 + W_0 \Psi_2 = -W_2 e^{i\left(\frac{\alpha}{a}x + \frac{\beta}{b}y + \frac{\gamma}{c}z\right)} \quad (11) \\ - \sum_{lmn} \sum_{pqr} A_{pqr} B_{lmm} e^{i\left(\frac{\alpha+l+p}{a}x + \frac{\beta+m+q}{b}y + \frac{\gamma+n+r}{c}z\right)} \end{aligned}$$

Again we have

$$\Psi_2 = \sum_{lmn} \sum_{pqr} C_{l+p, m+q, n+r} e^{i\left(\frac{\alpha+l+p}{a}x + \frac{\beta+m+q}{b}y + \frac{\gamma+n+r}{c}z\right)} \quad (12)$$

$$C_{l+p, m+q, n+r} = \frac{A_{pqr} B_{lmm}}{\left(\frac{\alpha+l+p}{a}\right)^2 + \left(\frac{\beta+m+q}{b}\right)^2 + \left(\frac{\gamma+n+r}{c}\right)^2 - W_0}$$

Note that the denominator of C_{000} vanishes. We take care of this by letting $C_{000} = 0$ and making

$$W_2 = - \sum_{lmn} A_{-l-m-n} B_{lmm} \quad (13)$$

At this point we shall draw some conclusions from our series representation of the solution. These conclusions can be justified only by showing that we can meet the proper boundary conditions at the surface of the semi-infinite crystal, but it is more transparent to draw them here. We have in the solution a principal term $e^{i(\frac{\alpha}{a}x + \frac{\beta}{c}y + \frac{\delta}{c}z)}$ which is a plane beam representing largely the incident beam. There are in addition, weak secondary beams (since λ is small) which represent reflections from various planes of the crystal. These secondary beams are of little interest, however, except in the case when $\xi \rightarrow 0$ where

$$\left(\frac{\alpha+\xi}{a}\right)^2 + \left(\frac{\beta+m}{c}\right)^2 + \left(\frac{\delta+m}{c}\right)^2 - W_0 = \xi \tag{14}$$

We see at once that as ξ decreases, $B_{\xi m m}$ increases, and if ξ is not too small, $\lambda B_{\xi m m}$ will outweigh all the other terms except ψ_0 . Hence we may infer that $\lambda B_{\xi m m}$ is a strongly reflected beam, and that $\xi=0$ is the condition for a strong reflection. This, is of course, merely an indication of what to look for, and we proceed to discuss rigorously in the next section the case of $\xi=0$. In Section 6 we shall discuss rigorously the case of ξ a small quantity, for the solution as thus far given fails to converge for ξ in the region of 0.

2. First Type of Solution-Exact Resonance

We assume the same series development as before, given by Eq.(4), but now let

$$\Psi_0 = A e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+n}{c}z\right)} + B e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+n}{c}z\right)} \quad (15)$$

where $\left(\frac{\alpha+l}{a}\right)^2 + \left(\frac{\beta+m}{b}\right)^2 + \left(\frac{\gamma+n}{c}\right)^2 - W_0 = 0$

Substituting into Eq.(6) we obtain

$$\begin{aligned} \nabla^2 \Psi_1 + W_0 \Psi_1 = & - \left(A W_1 + B A_{-l-m-n} \right) e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+n}{c}z\right)} \\ & - \left(A A_{lmm} + B W_1 \right) e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+n}{c}z\right)} \\ & - \sum_1 \end{aligned} \quad (16)$$

The \sum_1 indicates the remaining terms which do not interest us since they do not offer any trouble. We now take care of the two resonance terms by setting their coefficients equal to zero, and we obtain the usual secular equations

$$\begin{aligned} A W_1 + B A_{-l-m-n} &= 0 \\ A A_{lmm} + B W_1 &= 0 \end{aligned} \quad (17)$$

From these we obtain the two solutions

$$\begin{aligned} \frac{A}{B} &= \frac{A_{lmm}^*}{|A_{lmm} A_{lmm}^*|} ; W_1 = - |A_{lmm} A_{lmm}^*| \\ \frac{A}{B} &= \frac{A_{lmm}}{|A_{lmm} A_{lmm}^*|} ; W_1 = |A_{lmm} A_{lmm}^*| \end{aligned}$$

We could now solve for Ψ_1 without being troubled by infinite coefficients or lack of convergence, but this is not

necessary. The important thing to note is that we now have two terms of consequence, the incident beam $e^{i(\frac{\alpha}{a}x + \frac{\beta}{b}y + \frac{\gamma}{c}z)}$ and a reflected beam $e^{i(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+n}{c}z)}$ of the same intensity as the original one, since $|\frac{B}{A}| = 1$.

Moreover, these two beams constitute a Bragg reflection from the plane

$$\frac{l}{a}x + \frac{m}{b}y + \frac{n}{c}z = 0 \quad (18)$$

In the first place it can be easily shown that they make equal angles with the normal to this plane. Also the Bragg law is satisfied, for if θ is the angle between the incident beam and the normal to the plane considered, then

$$\cos \theta = \frac{\frac{\alpha l}{a^2} + \frac{\beta m}{b^2} + \frac{\gamma n}{c^2}}{\sqrt{(\frac{\alpha}{a})^2 + (\frac{\beta}{b})^2 + (\frac{\gamma}{c})^2} \sqrt{(\frac{l}{a})^2 + (\frac{m}{b})^2 + (\frac{n}{c})^2}} \quad (19)$$

Now we also have the two relations

$$\begin{aligned} (\frac{\alpha+l}{a})^2 + (\frac{\beta+m}{b})^2 + (\frac{\gamma+n}{c})^2 - W_0 &= 0 \\ (\frac{\alpha}{a})^2 + (\frac{\beta}{b})^2 + (\frac{\gamma}{c})^2 - W_0 &= 0 \end{aligned} \quad (20)$$

Subtracting, we get

$$\frac{\alpha l}{a^2} + \frac{\beta m}{b^2} + \frac{\gamma n}{c^2} = -\frac{1}{2} \left[(\frac{l}{a})^2 + (\frac{m}{b})^2 + (\frac{n}{c})^2 \right] \quad (21)$$

So that

$$\cos \theta = -\frac{1}{2} \frac{\sqrt{(\frac{l}{a})^2 + (\frac{m}{b})^2 + (\frac{n}{c})^2}}{\sqrt{W_0}} \quad (22)$$

Or we have

$$2d \cos \theta = -\frac{1}{\sqrt{W_0}} = -\Lambda \quad (23)$$

where $d = \left[\left(\frac{l}{a} \right)^2 + \left(\frac{m}{b} \right)^2 + \left(\frac{n}{c} \right)^2 \right]^{-\frac{1}{2}}$ and Λ is the wavelength of the electron. This is precisely the Bragg law for the first order reflection. The minus sign merely means that the angle should be measured in the opposite sense.

3. The Higher Order Bragg Reflections

We have seen from the above that the potential term

$$A_{lmn} e^{i \left(\frac{l}{a} x + \frac{m}{b} y + \frac{n}{c} z \right)} + A_{-l-m-n} e^{-i \left(\frac{l}{a} x + \frac{m}{b} y + \frac{n}{c} z \right)} \quad (24)$$

alone was responsible for the first order reflection from the plane whose Miller indices were l, m, n (l, m, n are assumed to have no common factor). We are going to show that all the higher order Bragg reflections from this same plane also arise from this same potential term. The identification between this potential term and the corresponding optical term will therefore be complete.

Thus, for the second order reflection, we take

$$\Psi_0 = A e^{i \left(\frac{\alpha}{a} x + \frac{\beta}{b} y + \frac{\gamma}{c} z \right)} + B e^{i \left(\frac{\alpha+2l}{a} x + \frac{\beta+2m}{b} y + \frac{\gamma+2n}{c} z \right)}$$

$$\text{and} \quad \left(\frac{\alpha+2l}{a} \right)^2 + \left(\frac{\beta+2m}{b} \right)^2 + \left(\frac{\gamma+2n}{c} \right)^2 - W_0^2 = 0 \quad (25)$$

Upon substituting in Eq.(6) we get

$$\begin{aligned} \nabla^2 \Psi_1 + W_0 \Psi_1 = -W_1 & \left[A e^{i \left(\frac{\alpha}{a} x + \frac{\beta}{b} y + \frac{\gamma}{c} z \right)} + B e^{i \left(\frac{\alpha+2l}{a} x + \frac{\beta+2m}{b} y + \frac{\gamma+2n}{c} z \right)} \right] \quad (26) \\ & - A A_{lmn} e^{i \left(\frac{\alpha+l}{a} x + \frac{\beta+m}{b} y + \frac{\gamma+n}{c} z \right)} - A A_{-l-m-n} e^{i \left(\frac{\alpha-l}{a} x + \frac{\beta-m}{b} y + \frac{\gamma-n}{c} z \right)} \\ & - B A_{lmn} e^{i \left(\frac{\alpha+3l}{a} x + \frac{\beta+3m}{b} y + \frac{\gamma+3n}{c} z \right)} - B A_{-l-m-n} e^{i \left(\frac{\alpha+l}{a} x + \frac{\beta+m}{b} y + \frac{\gamma-n}{c} z \right)} \end{aligned}$$

If we make use of Eq.(25) we get

$$\left(\frac{\alpha+3\ell}{a}\right)^2 + \left(\frac{\beta+3m}{b}\right)^2 + \left(\frac{\gamma+3n}{c}\right)^2 = \left(\frac{\alpha-\ell}{a}\right)^2 + \left(\frac{\beta-m}{b}\right)^2 + \left(\frac{\gamma-n}{c}\right)^2 \quad (27)$$

We then find that

$$\Psi_i = \frac{(AA_{\ell mm} + BA_{-\ell -m -n})}{\left(\frac{\alpha-\ell}{a}\right)^2 + \left(\frac{\beta-m}{b}\right)^2 + \left(\frac{\gamma-n}{c}\right)^2 - W_0} e^{i\left(\frac{\alpha-\ell}{a}x + \frac{\beta-m}{b}y + \frac{\gamma-n}{c}z\right)} \quad (28)$$

$$+ \frac{1}{\left(\frac{\alpha-\ell}{a}\right)^2 + \left(\frac{\beta+m}{b}\right)^2 + \left(\frac{\gamma+n}{c}\right)^2 - W_0} \left[BA_{\ell mm} e^{i\left(\frac{\alpha+3\ell}{a}x + \frac{\beta+3m}{b}y + \frac{\gamma+3n}{c}z\right)} + AA_{-\ell -m -n} e^{i\left(\frac{\alpha-\ell}{a}x + \frac{\beta-m}{b}y + \frac{\gamma-n}{c}z\right)} \right]$$

If we now substitute into Eq.(7) we have a precisely similar equation as Eq.(16) and the final result will also be that $|\frac{\beta}{A}| = 1$.

Thus we see that if we go out to the Nth approximation we get the Nth order Bragg reflection from the potential term of Eq.(24).

It should be noticed that we get the same Nth order Bragg reflection in the first approximation if the potential term

$$A_{N\ell, N_m, N_n} e^{iN\left(\frac{\ell}{a}x + \frac{m}{b}y + \frac{n}{c}z\right)} + A_{-N\ell, -N_m, -N_n} e^{-iN\left(\frac{\ell}{a}x + \frac{m}{b}y + \frac{n}{c}z\right)} \quad (29)$$

is present. We shall see later on how to decide experimentally between these two cases.

It is now obvious that the special potential of Eq.(1) used by Morse restricts the crystal to optical planes perpendicular to the principal axes of the crystal, with

no other cross planes possible.

Finally it should be remarked that in case α, β, γ are all integers, we have Laue beams present, for the incident beam is then normal to a set of planes in the crystal.

4. Second Type of Solution

In meeting the boundary conditions, an infinity of solutions inside the crystal will be found necessary. Physically this is because the solution given previously introduces inside the crystal an infinity of beaks which suffer internal reflection at the face of the crystal (we take this face to be the plane $x=0$).

Now if put $\lambda=0$ in Eq.(3) we have such an infinite set in

$$\psi_0^{(q,r)} = e^{i \left([q,r]x + \frac{\beta+\delta}{G}y + \frac{\gamma+\tau}{c}z \right)} \quad (30)$$

where $[q,r] = \sqrt{W - \left(\frac{\beta+\delta}{G}\right)^2 - \left(\frac{\gamma+\tau}{c}\right)^2}$, if we attribute to q, r all possible arbitrary values, although for our purposes they need take on only all integral values. However, if we use the same development in series as given previously, the energy of each solution corresponding to each function $\psi_0^{(q,r)}$ will be different from each other and the energy of the original solution W . We therefore assume a development

$$\begin{aligned} \psi^{(q,r)} &= e^{i \delta^{(q,r)} x} \cdot \left[\psi_0^{(q,r)} + \lambda \psi_1^{(q,r)} + \dots \right] \\ \delta^{(q,r)} &= \lambda \delta_1^{(q,r)} + \lambda^2 \delta_2^{(q,r)} + \dots \end{aligned} \quad (31)$$

Where $\delta^{(q,r)}$ is a parameter which we have introduced in order

to keep the energy fixed and equal to W . The reason we can do this is because if we substitute into Eq.(3) and obtain the successive approximation equations, the δ'_s occur in the same sort of way that the w'_s occurred previously. Thus for the first approximation we have

$$\nabla^2 \psi_1^{(\delta-r)} + W \psi_1^{(\delta-r)} = \psi_0^{(\delta-r)} \left\{ 2\delta_1^{(\delta-r)} [\delta-r] - \sum_{lmm} A_{lmm} e^{i(\frac{l}{a}x + \frac{m}{b}y + \frac{n}{c}z)} \right\} \quad (32)$$

So that

$$\psi_1^{(\delta-r)} = \sum_{lmm} B_{lmm} e^{i \left[(\delta-r) + \frac{l}{a} \right] x + \frac{\beta+l+m}{b} y + \frac{\gamma+r+n}{c} z} \quad (33)$$

$$B_{lmm} = \frac{A_{lmm}}{\left([\delta-r] + \frac{l}{a} \right)^2 + \left(\frac{\beta+l+m}{b} \right)^2 + \left(\frac{\gamma+r+n}{c} \right)^2 - W}$$

and $\delta_1 = 0$. We do not proceed any further since the remaining approximations are obvious.

5. The Boundary Problem

We take the face of the semi-infinite crystal to be at $x=0$ and the crystal to extend in the positive x direction. Suppose a plane beam $e^{i(\frac{\alpha_0}{a}x + \frac{\beta_0}{b}y + \frac{\gamma_0}{c}z)}$ incident on this face. If $\bar{\Phi}$ and $\bar{\Psi}$ are solutions outside and inside the crystal respectively, then we have the usual boundary conditions

$$\left. \begin{aligned} \bar{\Phi} &= \bar{\Psi} \\ \frac{\partial \bar{\Phi}}{\partial x} &= \frac{\partial \bar{\Psi}}{\partial x} \end{aligned} \right\} x=0 \quad (34)$$

Also the energies inside and outside the crystal are equal, so that $W - V_0 = \left(\frac{\alpha_0}{a} \right)^2 + \left(\frac{\beta_0}{b} \right)^2 + \left(\frac{\gamma_0}{c} \right)^2$. Since $\bar{\Phi}$ must consist of only one incident and the several reflected beams, it

must be of the form

$$\Phi = a_{00} e^{i\left(\frac{\alpha_0}{a}x + \frac{\beta_0}{b}y + \frac{\gamma_0}{c}z\right)} + \sum_{m,n} b_{mn} e^{i\left([mn]_0 x + \frac{\beta_0+m}{b}y + \frac{\gamma_0+n}{c}z\right)} \quad (35)$$

where $[mn]_0 = \sqrt{\left(\frac{\alpha_0}{a}\right)^2 + \left(\frac{\beta_0}{b}\right)^2 + \left(\frac{\gamma_0}{c}\right)^2 - \left(\frac{\beta_0+m}{b}\right)^2 - \left(\frac{\gamma_0+n}{c}\right)^2}$

The general expression for Ψ is

$$\Psi = \psi + \sum_{\beta, \gamma} c_{\beta\gamma} \psi^{(\beta\gamma)} \quad (36)$$

If we substitute into the boundary conditions, we see first of all that $\beta_0 = \beta$; $\gamma_0 = \gamma$ since y and z are arbitrary. Secondly, if we equate coefficients of each different Fourier component in y and z we obtain an infinite set of equations with an infinite set of unknowns for the determination of a_{00} , b_{mn} , c_{mn} . These equations are best solved by means of successive approximations, but we shall stop at the first approximation. For the case of non-resonance, for which the experimental data are most accurate, we have for the zero'th power of λ ,

$$\begin{aligned} a_{00}^0 + b_{00}^0 &= 1 \\ \alpha_0(a_{00}^0 + b_{00}^0) &= \alpha \end{aligned} \quad (37)$$

For the first power of λ we obtain

$$\begin{aligned} a'_{00} + b'_{00} &= \sum_l B_{l00} \\ \alpha_0(a'_{00} - b'_{00}) &= \sum_l (\alpha+l) B_{l00} \end{aligned} \quad (38a)$$

$$\begin{aligned} b'_{mn} &= \sum_l B_{lmm} + c'_{mn} \\ -[mn]_0 b'_{mn} &= \sum_l \frac{(\alpha+l)}{a} B_{lmm} + [mn] c'_{mn} \end{aligned} \quad (38b)$$

Where

$$\begin{aligned}
 a_{00} &= a_{00}^0 + \lambda a_{00}' + \dots \\
 b_{mm} &= b_{mm}^0 + \lambda b_{mm}' + \dots \\
 c_{mm} &= c_{mm}^0 + \lambda c_{mm}' + \dots
 \end{aligned}
 \tag{40}$$

We therefore find for the intensity of the reflected beams

$$\left| \frac{b_{00}}{a_{00}} \right|^2 = \left| \frac{(\alpha_0 - \alpha) + \lambda \sum_l (\alpha_0 - \alpha - l) B_{l00}}{(\alpha_0 + \alpha) + \lambda \sum_l (\alpha_0 + \alpha + l) B_{l00}} \right|^2
 \tag{41a}$$

$$\left| \frac{b_{mm}}{a_{00}} \right|^2 = \left| \frac{2 \alpha_0 \sum_l ([mm] - \alpha - l) B_{lmm}}{([mm]_0 + [mm]) (\alpha + \alpha_0 + \lambda \sum_l (\alpha_0 + \alpha + l) B_{l00})} \right|
 \tag{41b}$$

The relation between α_0 and α is

$$\left(\frac{\alpha}{a} \right)^2 = V_0 + \left(\frac{\alpha_0}{a} \right)^2
 \tag{42}$$

These intensity formulas are rather unwieldy in their explicit form, so we shall give them explicitly only when the single potential term Eq.(24) is present. We then obtain

$$\left| \frac{b_{00}}{a_{00}} \right|^2 = \left| \frac{\left(\frac{\alpha_0}{a} \right) - \sqrt{\left(\frac{\alpha_0}{a} \right)^2 + V_0}}{\left(\frac{\alpha_0}{a} \right) + \sqrt{\left(\frac{\alpha_0}{a} \right)^2 + V_0}} \right|^2
 \tag{43a}$$

$$\left| \frac{b_{mm}}{a_{00}} \right|^2 = \frac{2 \alpha_0 \lambda \left[\sqrt{E_0 + V_0 - \left(\frac{\beta_0 + m}{b} \right)^2 - \left(\frac{\delta_0 + m}{c} \right)^2} - \sqrt{\left(\frac{\alpha_0}{a} \right)^2 + V_0} - l \right] A_{lmm}}{\left[\sqrt{E_0 + V_0 - \left(\frac{\beta_0 + m}{b} \right)^2 - \left(\frac{\delta_0 + m}{c} \right)^2} + \sqrt{E_0 - \left(\frac{\beta_0 + m}{b} \right)^2 - \left(\frac{\delta_0 + m}{c} \right)^2} \right] \left[l \left(\frac{b}{a} + 2 \sqrt{\left(\frac{\alpha_0}{a} \right)^2 + V_0} + m \left(\frac{m + 2\beta_0}{b} \right) + m \left(\frac{m + 2\delta_0}{c} \right) \right) \right]}
 \tag{43b}$$

Where
$$E_0 = \left(\frac{\alpha_0}{a}\right)^2 + \left(\frac{\beta_0}{b}\right)^2 + \left(\frac{\gamma_0}{c}\right)^2$$

We will also recall that $E = \frac{h^2}{8\pi^2\mu} E_0$, E being the energy of the incident beam, while the work function of the crystal is $\varphi = \frac{h^2}{8\pi^2\mu} V_0$.

In comparing these formulas with experiment, it is perhaps most illuminating to take the experiment of Davisson and Germer in which they keep the direction of the incident beam fixed, and measure the intensity of the reflected beam as a function of the energy of the incident beam. This means that in our formulas, we must take the ratio of $\frac{\alpha_0}{a} : \frac{\beta_0}{b} : \frac{\gamma_0}{c}$ as constant, and vary them only by multiplying them by the same arbitrary parameter. In this way we pass through successive orders of Bragg reflection.

In the first place, it is clear that Eq.(43a) is of no interest to us, since it merely represents the reflection due to the potential drop of the crystal wall, and has nothing to do with the periodic potential of the crystal. Eq.(43b), however, gives us the intensity of the N'th order reflection from the plane (lmn) which is due to the presence of the term A_{Nl, Nm, N_m} in the potential. It is immediately obvious that all the orders of reflection as are due to these terms are of the same order in λ , and if we are given the coefficients A_{lmm} we can determine

the intensities. Practically, however, they are not given, and since they are unknown, no absolute fit is possible. In fact, they are to be determined by the experimental data.

As we have shown in Section 3, A_{lmm} alone gives rise to N 'th order reflections also given by $A_{Nl, Nm, Nn}$. Thus, to render the determination of the A_{lmm} directly, we must show when this effect can be neglected. Now in fact, it is easy to see that the intensity of the N 'th order will be of the order of λ^{2N} , and the ratio of two adjacent orders will be of the order of λ^2 .

Now experimentally, the energy of the incident beam was of the order of two hundred volts, while the work function was of the order of ten volts, so that λ^2 in this case would be approximately $1/100$. For this reason it is quite safe to make the neglect considered above. The distinction or recognition of these two effects does not seem to have been noticed before. Indeed, Morse takes the term of Eq.(1) to be generally a fairly good approximation to an actual crystal for high energies.

In actual shape, we find that Eq.(43b) is in fair agreement with the lower parts of the experimental curves. This should hardly be taken as a test, however, since neither theory or experiment are very sensitive in this region.

6. The Width of the Bands of Total Reflection

Strutt, Morse, and Hill show in their special cases that the energy for which total reflection occurs (which they call a forbidden energy) does not occur for single discreet values, but in a continuous range of values in certain regions. We thus have bands of total reflection, and moreover these bands become wider as the energy of the electrons approach that of the periodic potential.

We shall show all this quite generally, and also obtain explicitly the width of these bands for the case of perpendicular incidence of the beam. In the first place, we will notice in Section 2 that we obtained total reflection for two values of the energy. The reason we did there get a continuous range of values was that we obtained a less general solution than is possible.

Instead of expanding like Eq.(4) or like Eq.(31), we can combine the two, so that we assume a development

$$\begin{aligned}\psi &= e^{i\delta x} [\psi_0 + \lambda \psi_1 + \dots] \\ \delta &= \lambda \delta_1 + \lambda^2 \delta_2 + \dots \\ W &= w_0 + \lambda w_1 + \lambda^2 w_2 + \dots\end{aligned}\tag{44}$$

Also, since we are considering resonance, we take

$$\Psi_0 = A e^{i\left(\frac{\alpha}{a}x + \frac{\beta}{b}y + \frac{\gamma}{c}z\right)} + B e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+m}{c}z\right)}$$

$$\left(\frac{\alpha}{a}\right)^2 + \left(\frac{\beta}{b}\right)^2 + \left(\frac{\gamma}{c}\right)^2 = W_0 \quad (45)$$

$$\left(\frac{\alpha+l}{a}\right)^2 + \left(\frac{\beta+m}{b}\right)^2 + \left(\frac{\gamma+m}{c}\right)^2 = W_0$$

We then find that

$$\begin{aligned} \nabla^2 \Psi_0 + W_0 \Psi_0 &= \left[A \left(2\frac{\alpha}{a} \delta_1 - W_1 \right) A_{lmm} - B A_{-l-m-m} \right] e^{i\left(\frac{\alpha}{a}x + \frac{\beta}{b}y + \frac{\gamma}{c}z\right)} \\ &+ \left[-A A_{lmm} + B \left(2\frac{\alpha+l}{a} \delta_1 - W_1 \right) A_{-l-m-m} \right] e^{i\left(\frac{\alpha+l}{a}x + \frac{\beta+m}{b}y + \frac{\gamma+m}{c}z\right)} \\ &+ \sum \end{aligned} \quad (46)$$

The \sum indicates the remaining non-resonance terms.

The secular equations are now

$$\begin{aligned} A \left(2\frac{\alpha}{a} \delta_1 - W_1 \right) A_{lmm} - B A_{-l-m-m} &= 0 \\ -A A_{lmm} + B \left(2\frac{\alpha+l}{a} \delta_1 - W_1 \right) A_{-l-m-m} &= 0 \end{aligned} \quad (47)$$

and we have the condition

$$\begin{vmatrix} 2\left(\frac{\alpha}{a}\delta_1 - W_1\right) & -A_{-l-m-m} \\ -A_{lmm} & \left(2\frac{\alpha+l}{a}\delta_1 - W_1\right) \end{vmatrix} = 0 \quad (48)$$

Now w_1 can take on only real values and for a certain range of w_1 , δ_1 becomes complex throughout this region.

This means that we have total reflection, for then $\left|\frac{B}{A}\right| = 1$.

It is easily found that δ_1 is complex if $w_1^2 \left(\frac{b}{a}\right)^4 < \left\{ \left(\frac{a}{a}\right)^4 - \left[\left(\frac{m}{b}\right)^2 + \left(\frac{n}{c}\right)^2 \right]^2 \right\} A_{lmm} A_{lmm}^*$

and is real when w_1 lies outside this region. We thus

pass from a region of perfect reflection to only partial reflection.

To find the angular width of the bands, we must remember that the energy of the outside incident beam is kept constant and the angle varied. This means that in the Bragg formula, $4d^2 \cos^2 \theta = \frac{N^2}{W}$, which we have derived, N^2 varies, and $\Delta N^2 = \Delta W$.

Therefore, differentiating

$$4d^2 \cos \theta \sin \theta \Delta \theta = \frac{\Delta W}{W}$$

and we get
$$\Delta \theta = \frac{4d^2 \cos \theta \sqrt{\left(\frac{d}{a}\right)^4 - \left[\left(\frac{m}{a}\right)^2 + \left(\frac{m}{a}\right)^2\right]^2 A_{lmm} A_{lmm}^*}}{N^2 \sin \theta \left(\frac{d}{a}\right)^2} \quad (49)$$

Graphically, this formula can be represented as in Morse's paper, and it is also equivalent to Darwin's well known formula for x-rays.

Conclusion

The difference between this and previous treatments may be summed up as follows. We have shown quite generally what had been inferred from very special cases. The Bragg law was derived, and only relations analogous to it were previously derived. We have shown how the potential of a crystal can be determined from the experimental data, a problem not hitherto considered. Finally, we give a formula for the width of the bands of total reflection.

The States of Divalent Crystals

The problem of monovalent crystals in connection with ferromagnetism for tightly bound electrons was first treated by Bloch⁹ using a method due to Slater.¹⁰ Bloch, however, made several questionable assumptions which were corrected and their consequences investigated in a paper by Epstein.¹² In this latter paper it was surmised that if the crystal consisted of divalent atoms instead of monovalent atoms, then the analysis would hold good if the two electrons belonging to the same atom were in widely separated states; if, on the other hand, they were in nearly equivalent states this would not be true. It is this point which we shall investigate here.

1. The Secular Equations

In our treatment we also use Slater's method, and, inasmuch as very clear expositions are given by the above authors, we shall suppose that they have been studied by the reader and therefore omit derivations given by them.

The essential difference between the divalent and monovalent cases is that in the former case we have to do with orbital degeneracy for the electron pair belonging to the same atom, whereas in the latter case

the valence electron is taken to in the S state, for which no degeneracy in orbit is present.

However, it is difficult enough to treat the orbital degeneracy of just a molecule formed by two divalent atoms, let alone a crystal. Instead, we shall proceed just as though no orbital degeneracy existed, but in place of the hydrogenic functions used for no orbital degeneracy we insert combination functions as indicated by Slater.¹¹ No discussion of how this function is to be formed will be given since it does not arise explicitly except in certain exchange integrals which cannot be evaluated anyway.

Suppose the crystal to contain $2N$ electrons. Each electron has either a positive or negative spin along a fixed axis. As in the notation of Epstein let r electrons have negative spins and $2N - r$ positive. Let the electrons be successively denoted by $1, 2, \dots, 2N$ and those electrons with negative spin by $\beta_1, \beta_2, \dots, \beta_r$. The anti-symmetric function corresponding to this arrangement is then denoted by $\Psi(\beta_1, \beta_2, \dots, \beta_r)$. The total eigenfunction is then given by

$$\Psi(\tau) = \sum_{\beta_1, \dots, \beta_r} a(\beta_1, \dots, \beta_r) \Psi(\beta_1, \dots, \beta_r) \quad (1)$$

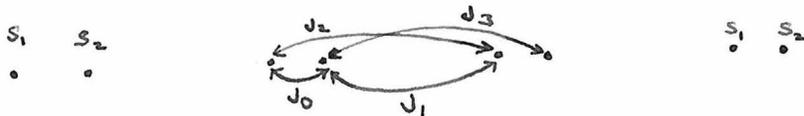
The coefficients $a(\beta_1 \dots \beta_r)$ are determined by the secular equations

$$E a(\beta_1 \dots \beta_r) - [k + (n+m) \sum J_{\beta\beta'}] + \sum_t \{ [a(\beta_1' \dots \beta_r') - a(\beta_1 \dots \beta_r)] J_{\beta\beta'} - E S_{\beta\beta'} a(\beta_1' \dots \beta_r') \} \quad (2)$$

The summation is extended over all pairs of electrons having opposite spins, the total number of negative spins being kept constant. Here $J_{\beta\beta'}$ is the Heitler and London exchange integral and $S_{\beta\beta'}$ is the same integral but without the interaction term in the integrand.

2. Solution In a Special Case

We are going to solve a special case as illustrative of the general procedure and take a linear chain with $r=2$. Furthermore, we shall suppose that all the interchange integrals, except those indicated by the diagram, are zero.



Here J_0 is the interchange integral between the two electrons belonging to the same atom, while J_1 is the interchange integral belonging to two electrons on different atoms and in different states (the states of the electrons are designated by s_1 and s_2). The meaning of the remaining integrals is self evident. We also suppose that only S_0 is significantly different from

zero (Bloch and Epstein suppose all the S'_i are zero).

It is convenient for us to divide the coefficients in the following four groups when $r = 2$:

$$\begin{array}{llll}
 \text{I} & f_1 = 2m_1 + 1 & ; & f_2 = 2m_2 + 1 & a(f_1, f_2) = a(m_1, m_2) \\
 \text{II} & f_1 = 2m_1 + 1 & ; & f_2 = 2m_2 & a(f_1, f_2) = b(m_1, m_2) \\
 \text{III} & f_1 = 2m_1 & ; & f_2 = 2m_2 + 1 & a(f_1, f_2) = c(m_1, m_2) \\
 \text{IV} & f_1 = 2m_1 & ; & f_2 = 2m_2 & a(f_1, f_2) = d(m_1, m_2)
 \end{array} \quad (3)$$

Whereupon we obtain from Eq.(2) the following four sets of equations corresponding to each of the four arrangements above

$$\begin{aligned}
 \text{I} \quad E a(m_1, m_2) & - [K + (m_1 + m_2) \sum J_{ff'}] a(m_1, m_2) \\
 & - E S_0 [c(m_1 + 1, m_2) + b(m_1, m_2 + 1)] \\
 & + J_0 [c(m_1 + 1, m_2) + b(m_1, m_2 + 1) - 2a(m_1, m_2)] \\
 & + J_1 [c(m_1, m_2) + b(m_1, m_2) - 2a(m_1, m_2)] \\
 & + J_2 [a(m_1 + 1, m_2) + a(m_1 - 1, m_2) - 2a(m_1, m_2) \\
 & \quad + a(m_1, m_2 + 1) + a(m_1, m_2 - 1) - 2a(m_1, m_2)] = 0
 \end{aligned} \quad (4)$$

$$\begin{aligned}
\text{II} \quad E \mathcal{G}(m_1, m_2) - [K + (m + m') \sum J_{\beta\beta'}] \mathcal{G}(m_1, m_2) \\
- ES_0 [d(m_1 + 1, m_2) + a(m_1, m_2 - 1)] \\
+ J_0 [d(m_1 + 1, m_2) + a(m_1, m_2 - 1) - 2\mathcal{G}(m_1, m_2)] \\
+ J_1 [d(m_1, m_2) + a(m_1, m_2) - 2\mathcal{G}(m_1, m_2)] \\
+ J_2 [\mathcal{G}(m_1 + 1, m_2) + \mathcal{G}(m_1 - 1, m_2) - 2\mathcal{G}(m_1, m_2)] \\
+ J_3 [\mathcal{G}(m_1, m_2 + 1) + \mathcal{G}(m_1, m_2 - 1) - 2\mathcal{G}(m_1, m_2)] = 0
\end{aligned} \tag{5}$$

$$\begin{aligned}
\text{III} \quad E \mathcal{C}(m_1, m_2) - [K + (m + m') \sum J_{\beta\beta'}] \mathcal{C}(m_1, m_2) \\
- ES_0 [d(m_1, m_2 + 1) + a(m_1 - 1, m_2)] \\
+ J_0 [d(m_1, m_2 + 1) + a(m_1 - 1, m_2) - 2\mathcal{C}(m_1, m_2)] \\
+ J_1 [a(m_1, m_2) + d(m_1, m_2) - 2\mathcal{C}(m_1, m_2)] \\
+ J_2 [\mathcal{C}(m_1, m_2 + 1) + \mathcal{C}(m_1, m_2 - 1) - 2\mathcal{C}(m_1, m_2)] \\
+ J_3 [\mathcal{C}(m_1 + 1, m_2) + \mathcal{C}(m_1 - 1, m_2) - 2\mathcal{C}(m_1, m_2)] = 0
\end{aligned} \tag{6}$$

$$\begin{aligned}
\text{IV} \quad E d(m_1, m_2) - [K + (m + m') \sum J_{\beta\beta'}] d(m_1, m_2) \\
- ES_0 [\mathcal{G}(m_1 - 1, m_2) + c(m_1, m_2 - 1)] \\
+ J_0 [\mathcal{G}(m_1 - 1, m_2) + c(m_1, m_2 - 1) - 2d(m_1, m_2)] \\
+ J_1 [\mathcal{G}(m_1, m_2) + c(m_1, m_2) - 2d(m_1, m_2)] \\
+ J_3 [d(m_1 + 1, m_2) + d(m_1 - 1, m_2) - 2d(m_1, m_2) \\
+ d(m_1, m_2 + 1) + d(m_1, m_2 - 1) - 2d(m_1, m_2)] = 0
\end{aligned} \tag{7}$$

We try to solve this set of four simultaneous difference equations by setting

$$\begin{aligned}
 a(m_1, m_2) &= e^{i\alpha(a_1 m_1 + a_2 m_2)} & c(m_1, m_2) &= e^{i\gamma(c_1 m_1 + c_2 m_2)} \\
 b(m_1, m_2) &= e^{i\beta(b_1 m_1 + b_2 m_2)} & d(m_1, m_2) &= e^{i\delta(d_1 m_1 + d_2 m_2)}
 \end{aligned}
 \tag{8}$$

Upon substituting, we immediately obtain four homogeneous linear equations in the unknown coefficients

$$a(m_1, m_2) ; b(m_1, m_2) ; c(m_1, m_2) ; d(m_1, m_2)$$

Now we know from the elementary theory of such equations that we get

$$a(m_1, m_2) ; b(m_1, m_2) ; c(m_1, m_2) ; d(m_1, m_2) = C_1 ; C_2 ; C_3 ; C_4 \tag{9}$$

where C_1, C_2, C_3, C_4 are independent of m_1 and m_2 .

We must therefore conclude that

$$\begin{aligned}
 \alpha a_1 &= \beta b_1 = \gamma c_1 = \delta d_1 = \alpha K_1 \\
 \alpha a_2 &= \beta b_2 = \gamma c_2 = \delta d_2 = \alpha K_2
 \end{aligned}
 \tag{10}$$

It is important that these conditions hold in order that the energy of the system, which we next determine, be real. We might have solved the equations with these conditions in the first place, but the reader might then suspect lack of generality.

In order that these four simultaneous equations have a solution, we must have the determinant of their coefficients vanish, giving us

The energy of the system is thus given us as the roots of this fourth degree equation. We shall not, however, solve it rigorously, but only approximately in the two limiting cases that interest us.

The first case is when the two electrons of each atom are in widely separated states and each electron interacts with neighboring electrons in the same state as itself. This means analytically that J_0, J_1, S_0 are small compared with J_2, J_3 . Also in Epstein's language, this means that each electron is in resonance with its own kind. Now we see immediately from the determinant that neglecting J_0, J_1, S_0 , it factors into four factors each of which is of the type obtained for the monovalent case by Slater. If we now treat J_0, J_1, S_0 as small quantities, we still get expressions of the same form, but with J_2 and J_3 changed slightly due to the inclusion of these small terms. We do not give the explicit expressions since only the form of the energy is important.

The second case is when the two electrons of each atom are in nearly equivalent states. This means that J_1, J_2, J_3 are small compared to J_0, S_0 . We solve by approximations, first setting $J_1 = J_2 = J_3 = 0$. We then find the following equation for E .

$$a_0 E^4 + a_1 E^3 + a_2 E^2 + a_3 E + a_4 = 0 \quad (11)$$

Where a_0, a_1, a_2, a_3, a_4 are constants independent of K_1, K_2 . This fact is important to us, for it means that in the first approximation ψ is independent of K_1, K_2 . We are thus enabled to find the dependence of E on K_1, K_2 , without solving a quartic equation, by introducing J_1, J_2, J_3 as small quantities and solving approximately. We then find that E is of the form

$$E = C_1 + C_2 \frac{\sin^2 \alpha K_1}{2} + C_3 \frac{\sin^2 \alpha K_2}{2} \quad (12)$$

where C_1 is a constant depending on J_0, J_0 , and C_2, C_3 are constants depending on J_1, J_2, J_3 .

Thus we see that in this limiting case, we also get an energy expression of the same form as the monovalent case.

3. The General Case

In general, when we have r spins, we get a determinantal equation of the $2r$ 'th order. We cannot, of course, solve this exactly, but if we carry out the same sort of approximation as before, we find an exactly analogous state of affairs as prevailed when $r=2$. For this reason the general energy expression remains of the same form as the monovalent case.

We have neglected to mention thus far degeneration of the electrons as a whole. In the first limiting case

for two valence electrons it is obvious that we have a double degeneration so that in order to obtain the total energy of the system from Eq.(12) we have to take twice the value obtained from this expression. Now this also holds in the other limiting case, and we conclude that since the discussions of ferromagnetism depend on the energy, there should be no difference in the ferromagnetism of monovalent and divalent crystals except what can be attributed to differences in the values of the energy coefficients.

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