

# ELECTRONIC STATES AT THE SURFACES OF CRYSTALS

## I. THE APPROXIMATION OF NEARLY FREE ELECTRONS

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*Received 27 January 1939*

### INTRODUCTION

1. In the electron theory of metals as first developed the assumption is made that the "free" electrons of a crystal can be considered as moving in a field that is constant throughout the interior of the crystal. A better approximation is to consider this field to be periodic with the periodicity of the lattice. The major effect of this lattice periodicity is to divide the energy range into bands of allowed levels, or "Brillouin zones", separated by gaps within which there are no electronic levels, the "forbidden bands"<sup>†</sup>.

At first it was found necessary to assume a perfect periodicity with a consequent disregard of the presence of the surface. Subsequently, however, it has been found possible to study simultaneously the effect of both the periodic field within the crystal and the surface bounding it. It is found that from the bands of allowed levels there separate out "surface states" in which the electrons are bound to the surface of the crystal and may be pictured as rippling tangentially along it. The existence of these states was first realized by Tamm<sup>‡</sup>, who represented the metal by a one-dimensional Kronig potential field. Subsequently they were found by Rijanow<sup>§</sup> in a consideration of the eigenfunctions of a thin metal strip. Finally Maue<sup>||</sup>, using a Fourier expansion for the lattice field and applying the approximation of nearly free electrons, was able to indicate the effect of these states on the electrical conductivity of a metal.

Of this work that of Maue is the most recent and the most general, but even the results of his paper, particularly in the case of a real three-dimensional crystal, are not given in a form readily applicable to further work. The important role of the surface in present-day problems suggested that such a form should be obtained. By a suitable extension of Maue's method of approach I have been able to obtain explicit formulae for the wave functions and the corresponding

<sup>†</sup> See, for example, Mott and Jones, *The theory of the properties of metals and alloys* (Oxford, 1936), chap. II. For convenience, future references to this work are written in the form "M.J."

<sup>‡</sup> Tamm, *Phys. Z. Sowjet.* 1 (1932), 732.

<sup>§</sup> Rijanow, *Z. Phys.* 89 (1934), 806.

<sup>||</sup> Maue, *Z. Phys.* 94 (1935), 717.

energies of the surface states in terms of the constants of the crystalline field and, moreover, the method is applicable to any type of crystal lattice. We employ the approximation of nearly free electrons and consider first a simple cubic crystal, subsequently extending the results to a general crystal lattice. Though this method involves a slight expansion and some repetition of the work, on grounds of clarity it appears preferable to a direct consideration of the more general problem and a subsequent deduction of the simpler one as a particular case. We may add that a certain amount of Maué's work is repeated here but that this appears to be necessary for the sake of completeness.

### THE SIMPLE CUBIC CRYSTAL

2. The potential field of a simple cubic crystal, bounded by a surface in the  $yz$ -plane, may be represented by the triple Fourier series

$$\left. \begin{aligned} V(\mathbf{r}) &= \sum_{\mathbf{n}} V_{\mathbf{n}} e^{2\pi i \mathbf{n} \cdot \mathbf{r}/c} & (x < 0), \\ &= 0 & (x > 0), \end{aligned} \right\} \quad (1)$$

where  $\mathbf{r} = (x, y, z)$  is the position vector of the electron and  $c$  is the lattice constant. Also we assume that  $V_{\mathbf{n}}$  is real and accordingly that  $V_{\mathbf{n}} = V_{-\mathbf{n}}$ , since  $V(\mathbf{r})$  must also be real.

The wave equation of the electron is then

$$\nabla^2 \psi + \kappa^2 [W - V(\mathbf{r})] \psi = 0, \quad (2)$$

where

$$\kappa^2 = 8\pi^2 m / \hbar^2.$$

Following Bloch, we assume that the wave functions within the crystal have the form

$$\left. \begin{aligned} \psi &= e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}), \\ \text{where } u(\mathbf{r}) &= \sum_{\mathbf{n}} u_{\mathbf{n}} e^{2\pi i \mathbf{n} \cdot \mathbf{r}/c}, \end{aligned} \right\} \quad (3)$$

that is,  $u(\mathbf{r})$  is a Fourier series similar to that representing the potential function. It should be noted that the summations extend over all possible values of the vector  $\mathbf{n}$ , the components  $n_1, n_2, n_3$  taking all positive and negative integral values.

Substituting (1) and (3) into (2), multiplying by  $e^{-2\pi i \mathbf{n} \cdot \mathbf{r}/c}$  and integrating over the unit cell, we obtain the following series of relations between the coefficients  $u_{\mathbf{n}}$

$$\left[ - \left( \mathbf{k} + \frac{2\pi}{c} \mathbf{n} \right)^2 + \kappa^2 (W - V_{000}) \right] u_{\mathbf{n}} - \kappa^2 \sum_{\mathbf{n}' \neq \mathbf{n}} V_{\mathbf{n}-\mathbf{n}'} u_{\mathbf{n}'} = 0, \quad (4)$$

which hold for all possible values of  $\mathbf{n}$ .

Eliminating the  $u_{\mathbf{n}}$ , we obtain the determinantal equation

$$|| D_{\mathbf{n}'\mathbf{n}''} || = 0, \tag{5}$$

where

$$\left. \begin{aligned} D_{\mathbf{n}'\mathbf{n}'} &= - \left( \mathbf{k} + \frac{2\pi}{c} \mathbf{n}' \right)^2 + \kappa^2 (W - V_{000}), \\ D_{\mathbf{n}'\mathbf{n}''} &= - \kappa^2 V_{\mathbf{n}'-\mathbf{n}''} \quad (\mathbf{n}'' \neq \mathbf{n}'). \end{aligned} \right\} \tag{5a}$$

For given  $W, k_2, k_3$ , (5) may be regarded as an equation for  $k_1$ .

Now it is well known that the energy  $W$ , as a function of  $k_1, k_2, k_3$ , is discontinuous across certain planes in  $\mathbf{k}$ -space, namely, those whose equations are

$$n_1 k_1 + n_2 k_2 + n_3 k_3 = \frac{\pi}{c} (n_1^2 + n_2^2 + n_3^2). \tag{6}$$

The energies are thus divided into "Brillouin zones" by forbidden bands within which there are no electronic states. The forbidden band corresponding to (6) consists of the energy range

$$\left. \begin{aligned} W_k - |V_{n_1 n_2 n_3}| < W - V_{000} < W_k + |V_{n_1 n_2 n_3}|, \\ W_k &= \frac{1}{\kappa^2} (k_1^2 + k_2^2 + k_3^2). \end{aligned} \right\} \tag{6a}$$

where

We refer to this as the  $(n_1, n_2, n_3)$  forbidden band or, simply,  $(n_1, n_2, n_3)$  band.

Mathematically this implies that, given an energy  $W$  satisfying the inequality (6a), it is not possible to find a corresponding wave number  $\mathbf{k}$  with all its components real and such that the equation (5) is satisfied. At least one of the components,  $k_1$  say, must be complex of the form  $p \pm iq$ . This would yield wave functions proportional to  $e^{\mp qx}$  which could not represent physically possible states for an infinite crystal, since they would be unbounded either at  $+\infty$  or at  $-\infty$ .

For a crystal bounded on the right by the plane  $x=0$ , however, a wave function proportional to  $e^{qx}$  within the crystal (i.e.  $x < 0$ ) is physically possible. If we represent such a wave function by  $\psi_i$  and let  $\psi_0$  be the wave function of a state of the same electronic energy for  $x > 0$  then, provided that we can satisfy the boundary conditions at  $x=0$ , the wave function

$$\left. \begin{aligned} \psi &= \psi_i \quad (x < 0) \\ &= \psi_0 \quad (x > 0) \end{aligned} \right\}$$

represents a possible electronic state. Moreover,  $\psi$  decreases exponentially as we leave the surface in the direction of either the inward or the outward normal, that is, the electron is bound to the surface and  $\psi$  represents a surface state.

The boundary conditions for the smooth fitting of the wave functions are

$$(\psi_0)_{x=0} = (\psi_i)_{x=0}, \quad (\partial\psi_0/\partial x)_{x=0} = (\partial\psi_i/\partial x)_{x=0},$$

which, since we may multiply either wave function by an arbitrary constant, reduce to the single condition

$$\left(\frac{\partial\psi_0}{\partial x}\bigg/\frac{\partial\psi_i}{\partial x}\right)_{x=0} = \left(\frac{\psi_0}{\psi_i}\right)_{x=0}. \quad (7)$$

2.1. *Restrictions on the available bands.* In this section we show that such surface states exist within the  $(n_1, n_2, n_3)$  band only when  $n_2 = n_3 = 0$ , i.e. within the forbidden bands which correspond to those planes of energy discontinuity (6) in the  $\mathbf{k}$ -space that are perpendicular to the  $k_1$ -axis. The particular form of this result depends, of course, on our choice of the  $yz$ -plane as the crystal boundary.

Since we are considering a crystal of infinite extent in the  $y, z$ , directions the components  $k_2, k_3$  of the wave number  $\mathbf{k}$  must both be real. Given such real components, denote by  $k'_1$  the value of  $k_1$  given in terms of them by the equation (6). Then we have seen that, for an energy  $W$  lying in the range

$$\left. \begin{aligned} W'_k - |V_{n_1 n_2 n_3}| < W < W'_k + |V_{n_1 n_2 n_3}|, \\ \text{where } W'_k = \frac{1}{\kappa^2} (k_1'^2 + k_2^2 + k_3^2) + V_{000}, \end{aligned} \right\} \quad (8)$$

the corresponding solutions of (5) for  $k_1$  are complex of the form  $p \pm iq$ . Accordingly, employing the approximation of nearly free electrons, we seek to determine a solution in the form†

$$\psi_i = e^{(ip+q)x+ik_2y+ik_3z} \{ \alpha + \beta e^{-2\pi i(n_1x+n_2y+n_3z)/c} \} \quad (x < 0). \quad (9)$$

Substituting in the wave equation and neglecting all the Fourier coefficients  $V_n$  other than  $V_{000}$  and  $V_{n_1 n_2 n_3}$ , that is, proceeding exactly as in the usual analysis for the determination of the Brillouin zones, we obtain the two equations

$$\left. \begin{aligned} \{ -(p-iq)^2 - k_2^2 - k_3^2 + \kappa^2(W - V_{000}) \} \alpha - \kappa^2 V_{-n_1 - n_2 - n_3} \beta &= 0, \\ \left\{ - \left( p - iq - \frac{2\pi n_1}{c} \right)^2 - \left( k_2 - \frac{2\pi n_2}{c} \right)^2 - \left( k_3 - \frac{2\pi n_3}{c} \right)^2 + \kappa^2(W - V_{000}) \right\} \beta \\ - \kappa^2 V_{n_1 n_2 n_3} \alpha &= 0. \end{aligned} \right\} \quad (10)$$

Thus

$$\begin{aligned} & \{ \kappa^2(W - V_{000}) - k_2^2 - k_3^2 - (p - iq)^2 \} \\ & \times \left\{ \kappa^2(W - V_{000}) - \left( k_2 - \frac{2\pi n_2}{c} \right)^2 - \left( k_3 - \frac{2\pi n_3}{c} \right)^2 - \left( p - iq - \frac{2\pi n_1}{c} \right)^2 \right\} = \kappa^4 V_{n_1 n_2 n_3}^2, \end{aligned} \quad (11)$$

since

$$V_{-n_1 - n_2 - n_3} = V_{n_1 n_2 n_3}.$$

† See, for example, M.J. pp. 59 *et seq.*

This equation may be considered as a quadratic for  $\kappa^2(W - V_{000})$ . We require its roots to be real and hence it follows that

$$\left[ \kappa^2(W - V_{000}) - \left(k_2 - \frac{2\pi n_2}{c}\right)^2 - \left(k_3 - \frac{2\pi n_3}{c}\right)^2 - \left(p - \frac{2\pi n_1}{c}\right)^2 + q^2 \right] / \left(p - \frac{2\pi n_1}{c}\right) = -[\kappa^2(W - V_{000}) - k_2^2 - k_3^2 - p^2 + q^2] / p = S. \quad (12)$$

Substituting from (12) into (11), we obtain

$$(S^2 + 4q^2)p \left(p - \frac{2\pi n_1}{c}\right) + \kappa^4 V_{n_1 n_2 n_3}^2 = 0.$$

Thus  $0 < p < \frac{2\pi n_1}{c}$  and  $S^2 = \frac{\kappa^4 V_{n_1 n_2 n_3}^2 - 4q^2 p (2\pi n_1 / c - p)}{p(2\pi n_1 / c - p)}. \quad (13)$

From (12) and (13) it is then possible to obtain the two roots for  $\kappa^2(W - V_{000})$  in the alternative forms

$$\begin{aligned} \kappa^2(W - V_{000}) &= k_2^2 + k_3^2 + p^2 - q^2 \\ &\pm \sqrt{\left[ \left\{ \kappa^4 V_{n_1 n_2 n_3}^2 - 4q^2 p \left(\frac{2\pi n_1}{c} - p\right) \right\} \left\{ p / \left(\frac{2\pi n_1}{c} - p\right) \right\} \right]} \quad (14a) \end{aligned}$$

$$\begin{aligned} &= \left(k_2 - \frac{2\pi n_2}{c}\right)^2 + \left(k_3 - \frac{2\pi n_3}{c}\right)^2 + \left(p - \frac{2\pi n_1}{c}\right)^2 - q^2 \\ &\pm \sqrt{\left[ \left\{ \kappa^4 V_{n_1 n_2 n_3}^2 - 4q^2 p \left(\frac{2\pi n_1}{c} - p\right) \right\} \left\{ \left(\frac{2\pi n_1}{c} - p\right) / p \right\} \right]}. \quad (14b) \end{aligned}$$

From the equivalence of these expressions we deduce that

$$\sqrt{\left\{ p / \left(\frac{2\pi n_1}{c} - p\right) \right\}} = \sqrt{\left\{ \left(\frac{2\pi n_1}{c} - p\right) / p \right\}}, \quad \text{i.e. } p = \frac{\pi n_1}{c},$$

and also that

$$k_2^2 + k_3^2 + p^2 = \left(k_2 - \frac{2\pi n_2}{c}\right)^2 + \left(k_3 - \frac{2\pi n_3}{c}\right)^2 + \left(p - \frac{2\pi n_1}{c}\right)^2,$$

whence  $k_2^2 + k_3^2 = \left(k_2 - \frac{2\pi n_2}{c}\right)^2 + \left(k_3 - \frac{2\pi n_3}{c}\right)^2.$

Since  $k_2$  and  $k_3$  are unrestricted, this last equation leads immediately to the conclusion that we must have  $n_2 = n_3 = 0$  in order that a surface state of the type given by (9) should exist in the  $(n_1, n_2, n_3)$  forbidden band.

The proof just completed might at first sight seem to preclude the possibility of mathematical solutions of the equation (5) within a band for which  $n_2$  and  $n_3$  are not both zero, though such solutions must clearly exist. To determine them, however, we must combine the expression (9) with a similar one in which  $q$  has been replaced by  $-q$ . Such an expression would then correspond to an energy lying within the forbidden band as required but would not represent a physically possible state in view of the exponential increase as  $x \rightarrow -\infty$ .

2.2. *Surface states in the (l, 0, 0) bands.* We proceed to a detailed consideration of the  $(n_1, 0, 0)$  bands. For convenience we now write  $l$  in place of  $n_1$ ,  $V_l$  for  $-V_{n_1,0,0}$ † and  $V_0$  for  $-V_{000}$ .  $V_0$  is then positive since  $V_{000}$  is essentially negative for a real crystal.

Then, given  $k_2, k_3$  (real) and  $W$  lying in the range

$$\left. \begin{aligned} W''_k - |V_l| < W < W''_k + |V_l|, \\ W''_k = \frac{1}{\kappa^2} \left\{ \left( \frac{\pi l}{c} \right)^2 + k_2^2 + k_3^2 \right\} - V_0, \end{aligned} \right\} \quad (15)$$

where

the solutions of (5) are of the form  $p \pm iq$ .

We attempt to determine a wave function of the form

$$\psi_i = e^{(ip+q)x + ik_2y + ik_3z} (\alpha + \beta e^{-2\pi ilx/c}). \quad (16)$$

Then, as before,

$$\left. \begin{aligned} \{ -(p-iq)^2 - k_2^2 - k_3^2 + \kappa^2(W+V_0) \} \alpha + \kappa^2 V_{-l} \beta &= 0, \\ \kappa^2 V_l \alpha + \{ -(p-iq-2\pi l/c)^2 - k_2^2 - k_3^2 + \kappa^2(W+V_0) \} \beta &= 0. \end{aligned} \right\} \quad (17)$$

The reality condition is now  $p = \pi l/c$ ,

while the expressions (14) are replaced by

$$\kappa^2(W+V_0) - k_2^2 - k_3^2 = (\pi l/c)^2 - q^2 \pm \sqrt{\{\kappa^4 V_l^2 - 4q^2(\pi l/c)^2\}}, \quad (18)$$

both of which solutions for the energy  $W$  lie within the band (15). We have accordingly only to satisfy the boundary condition (7) in order to obtain a surface state.

Corresponding to the roots (18) we have, from (17),

$$\alpha = e^{i\delta}, \quad \beta = e^{-i\delta}, \quad \text{where} \quad \delta = \frac{1}{2} \sin^{-1} \left( \frac{2\pi lq/c}{\kappa^2 V_l} \right), \quad (19)$$

and thus

$$\psi_i \propto e^{qx + ik_2y + ik_3z} \cos(\pi lx/c + \delta). \quad (20)$$

Also, from (19), (18) and (17),

$$\{2\pi ilq/c \pm \sqrt{[\kappa^4 V_l^2 - 4q^2(\pi l/c)^2]}\} e^{i\delta} + \kappa^2 V_l e^{-i\delta} = 0,$$

whence, equating the real part to zero, we have

$$(2\pi lq/c) \tan \delta = \kappa^2 V_l \pm \sqrt{[\kappa^4 V_l^2 - 4q^2(\pi l/c)^2]}, \quad (21)$$

upper and lower signs of (21) corresponding to upper and lower signs of (18).

Now for the wave function outside the crystal we have

$$\psi_0 = e^{-\sqrt{(k_2^2 + k_3^2 - \kappa^2 W)}x + ik_2y + ik_3z} \quad (x > 0), \quad (22)$$

since the state is one of energy  $W$ .

The boundary condition (7) of smooth fitting for  $\psi_0, \psi_i$  then gives

$$-\sqrt{(k_2^2 + k_3^2 - \kappa^2 W)} = q - (\pi l/c) \tan \delta. \quad (23)$$

† N.B. Thus  $V_l$  here replaces  $-V_l$  in Maue's work.

We see immediately that if  $V_i < 0$  then, from (21),  $\tan \delta < 0$ , the right-hand side of (23) is positive, and so the equation cannot be satisfied and there is no surface state. If  $V_i > 0$ , however, it may be possible to satisfy the equation (23). Accordingly, from now on, only the case of  $V_i$  positive will be considered.

Squaring (23) and substituting from (18), we have

$$\kappa^2 V_0 - (\pi l/c)^2 + q^2 \mp \sqrt{[\kappa^4 V_i^2 - 4q^2(\pi l/c)^2]} = q^2 - 2q(\pi l/c) \tan \delta + (\pi l/c)^2 \tan^2 \delta,$$

$$\text{whence, by (21),} \quad (\pi l/c)^2 \sec^2 \delta = \kappa^2(V_0 + V_i). \quad (24a)$$

$$\text{Also, from (19),} \quad \sin \delta \cos \delta = \frac{1}{2} \sin 2\delta = \frac{q(\pi l/c)}{\kappa^2 V_i}. \quad (24b)$$

The equations (24) combine to give

$$\frac{q^2(\pi l/c)^2}{\kappa^4 V_i^2} = \sin^2 \delta \cos^2 \delta = \frac{(\pi l/c)^2}{\kappa^2(V_0 + V_i)} \frac{\kappa^2(V_0 + V_i) - (\pi l/c)^2}{\kappa^2(V_0 + V_i)},$$

and so, since  $q$  is positive,

$$q = \frac{V_i}{V_0 + V_i} \sqrt{[\kappa^2(V_0 + V_i) - (\pi l/c)^2]}. \quad (25)$$

The energies given by (18) are thus solutions of one of the equations

$$\kappa^2(W + V_0) - k_2^2 - k_3^2 = \left(\frac{\pi l}{c}\right)^2 \left(\frac{V_0}{V_0 + V_i}\right)^2 + \kappa^2 V_i \frac{V_0}{V_0 + V_i}, \quad (26a)$$

$$\kappa^2(W + V_0) - k_2^2 - k_3^2 = \left(\frac{\pi l}{c}\right)^2 \left(\frac{V_0 + 2V_i}{V_0 + V_i}\right)^2 - \kappa^2 V_i \frac{V_0 + 2V_i}{V_0 + V_i}. \quad (26b)$$

Direct substitution shows that only (26a) satisfies (23), both sides of that equation then reducing to  $-V_0 q/V_i$ . Equation (26b) actually arises through squaring, and it corresponds to the negative root for  $q$  in (25). The quantities  $\delta$ ,  $q$  and the energy  $W$  corresponding to the surface state are thus determined by the relations (24a), (25) and (26a) respectively.

2.3. *The normalization factor and summary of the results.* The results of the preceding paragraph may be summarized as follows. Corresponding to any given  $k_2$ ,  $k_3$  and any positive integer  $l$  such that  $V_i$  is also positive, there exists a surface state of energy  $W$  given by

$$\kappa^2(W + V_0) - k_2^2 - k_3^2 = \left(\frac{\pi l}{c}\right)^2 \left(\frac{V_0}{V_0 + V_i}\right)^2 + \kappa^2 V_i \frac{V_0}{V_0 + V_i}. \quad (27)$$

The corresponding wave function may be written in the form

$$\left. \begin{aligned} \psi_{k_2 k_3} &\equiv \psi_i = N e^{qx + ik_2 y + ik_3 z} \cos(\pi l x/c + \delta) & (x < 0), \\ &\equiv \psi_0 = N \cos \delta e^{-V_0 q x/V_i + ik_2 y + ik_3 z} & (x > 0), \end{aligned} \right\} \quad (28)$$

where

$$\left. \begin{aligned} q &= \frac{V_l}{V_0 + V_l} \sqrt{[\kappa^2(V_0 + V_l) - (\pi l/c)^2]}, \\ \delta &= \cos^{-1} \frac{(\pi l/c)}{\sqrt{[\kappa^2(V_0 + V_l)]}} \quad (0 < \delta < \frac{1}{2}\pi), \end{aligned} \right\} \quad (29)$$

and  $N$  is the normalizing coefficient.

For the determination of  $N$  there is the usual condition

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_{k_2' k_3'}^* \psi_{k_2 k_3} dx dy dz = \delta(k_2' - k_2) \delta(k_3' - k_3), \quad (30)$$

where  $\psi_{k_2' k_3'}$ ,  $\psi_{k_2 k_3}$  both correspond to the same value of  $l$ , and  $\delta(k' - k)$  denotes the Dirac  $\delta$ -function. Strictly  $\psi$ 's corresponding to different values of  $l$  should be orthogonal, and (30) should include the factor  $\delta_l$  on the right-hand side. Since the wave functions are obtained here by an approximate method, however, they are not quite orthogonal, which is of little importance, since any actual calculation will almost certainly be concerned with wave functions corresponding to the same value of  $l$ .

Equation (30) reduces immediately to

$$4\pi^2 |N|^2 \left[ \int_{-\infty}^0 e^{2qx} \cos^2(\pi l x/c + \delta) dx + \cos^2 \delta \int_0^{\infty} e^{-2V_0 q x/V_l} dx \right] = 1.$$

Carrying out the integrations and substituting for  $q$  and  $\delta$ , we obtain

$$|N|^2 = \frac{q[q^2 + (\pi l/c)^2]}{\pi^2 (\pi l/c)^2 (1 + 2V_l/V_0)}, \quad (31)$$

which completes the evaluation of the surface states in the case of a semi-infinite simple cubic crystal bounded by the  $yz$ -plane.

We note finally that the  $x$ -factors of the wave functions do not contain the numbers  $k_2$ ,  $k_3$  at all. This fact should simplify greatly calculations involving these wave functions, since such calculations almost always involve integration over ranges of these wave numbers.

2.4. *The distribution of the electronic states.* In most applications of the electron theory of metals it is necessary to know which states are occupied at the absolute zero of temperature and which are excited electronic states. The appearance of surface states within a forbidden band must coincide with the disappearance of an equal number of levels from the allowed bands on either side, and it is accordingly desirable to know from which of these bands the levels disappear.

With this end in view, Maue considered the simple case of a finite chain of  $2N$  atoms, equally spaced along the  $X$ -axis and terminated at the points  $x = \pm Nc$ . There is no lack of generality in considering such a case and we here reproduce his work in order to render our discussion complete.

Our previous results show that, provided that the corresponding  $V_l$  is positive, there are two "surface states" with energies lying in the  $l$ th forbidden band, one for each "surface" or end of the chain. Maue found that corresponding to these states two normal electronic states disappear from the allowed bands; one from each side, namely the highest state of the lower ( $l$ th) allowed band and the lowest state of the upper ( $l + 1$ )th band. The method of procedure is as follows.

Assuming a wave function of the form

$$\psi_1 = e^{iqx}(\alpha + \beta e^{-2\pi ix/c}) \tag{32}$$

and substituting into the wave equation we obtain

$$\kappa^2(W + V_0) = \left(\frac{\pi l}{c}\right)^2 + \left(q - \frac{\pi l}{c}\right)^2 \pm \sqrt{\left[\kappa^4 V_l^2 + 4\left(\frac{\pi l}{c}\right)^2 \left(q - \frac{\pi l}{c}\right)^2\right]}, \tag{33}$$

together with the corresponding ratios of the coefficients

$$\frac{\alpha}{\beta} = \frac{\kappa^2 V_l}{2(\pi l/c)(q - \pi l/c) \mp \sqrt{[\kappa^4 V_l^2 + 4(\pi l/c)^2 (q - \pi l/c)^2]}}. \tag{34}$$

Here we have, as usual, neglected the effect of all but the  $l$ th Fourier coefficient  $V_l$ .

The complex conjugate wave function  $\psi_2 \equiv \psi_1^*$  gives rise to the same energies (33). The most general real wave function that can be formed by combination of  $\psi_1$  and  $\psi_2$  is

$$\begin{aligned} \psi &= \frac{1}{2}(e^{i\delta}\psi_1 + e^{-i\delta}\psi_2) \\ &= \alpha \cos(qx + \delta) + \beta \cos[(2\pi l/c - q)x - \delta]. \end{aligned} \tag{35}$$

That the wave function within the crystal should be real is required by the boundary conditions. These may be written as

$$\psi' / \psi = -\sqrt{(-\kappa^2 W)}, \quad \text{for } x = Nc, \tag{36a}$$

and either (i)  $\psi' = 0$  or (ii)  $\psi = 0$ , for  $x = 0$ . (36b)

(36a) is the condition for smooth fitting at one end of the chain, and (36b) corresponds either to symmetry or to antisymmetry about its midpoint. Thus

$$\begin{aligned} \text{(i)} \quad & \psi = \alpha \cos qx + \beta \cos(2\pi l/c - q)x, \\ \text{(ii)} \quad & \psi = \alpha \sin qx - \beta \sin(2\pi l/c - q)x, \end{aligned} \tag{37}$$

whence (36a) becomes

$$\begin{aligned} \text{(i)} \quad & -\left[ q - \frac{2\beta}{\alpha + \beta} \frac{\pi l}{c} \right] \tan qNc = -\sqrt{(-\kappa^2 W)}, \\ \text{(ii)} \quad & \left[ q - \frac{2\beta}{\alpha + \beta} \frac{\pi l}{c} \right] \cot qNc = -\sqrt{(-\kappa^2 W)}. \end{aligned} \tag{38}$$

In these expressions  $\sqrt{(-\kappa^2 W)}$  varies very little with  $q$  while  $\beta$  is small except in the neighbourhood of  $q = \pi l/c$ . Accordingly in general there is one root of each

equation within each range of  $q$  of length  $\pi/Nc$ . When  $q \sim \pi l/c$ , however, some of these roots disappear. Thus if  $q = \pi l/c - \epsilon$  the equations (38) reduce to

$$(i) \quad - \left[ \frac{(\pi l/c)^2}{\kappa^2 V_l} - 1 \right] \epsilon \tan \epsilon Nc = -\sqrt{(-\kappa^2 W)},$$

$$(ii) \quad \left[ \frac{(\pi l/c)^2}{\kappa^2 V_l} - 1 \right] \epsilon \cot \epsilon Nc = -\sqrt{(-\kappa^2 W)}.$$

The first of these has a solution within the range  $0 \leq \epsilon \leq \pi/Nc$ , but there is no corresponding solution of the second, since  $\epsilon \cot \epsilon Nc \rightarrow 1/Nc$  as  $\epsilon \rightarrow 0$ . Similarly if  $q = \pi l/c + \epsilon$  we obtain

$$(i) \quad - \frac{\kappa^2 V_l}{(\pi l/c)} \frac{1}{\epsilon} \tan \epsilon Nc = -\sqrt{(-\kappa^2 W)},$$

$$(ii) \quad \frac{\kappa^2 V_l}{(\pi l/c)} \frac{1}{\epsilon} \cot \epsilon Nc = -\sqrt{(-\kappa^2 W)},$$

and here there is one solution of (ii) but no solution of (i) in the range  $0 \leq \epsilon \leq \pi/Nc$ .

Thus we deduce that the surface states within any forbidden band arise one each from the allowed bands on either side, a result which may very readily be extended to the three-dimensional case. Finally we observe that the disappearing states are the symmetric lowest level from the upper band and the antisymmetric highest level from the lower band.

#### THE GENERAL CRYSTAL LATTICE

3. The previous theory, derived in the case of the simple cubic crystal structure, may now be extended to apply to a general lattice. This extension is immediate and the work runs parallel to that of § 2, differing from it only in analytical details.

Let  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  be the vectors forming the unit cell and  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$  those forming the reciprocal lattice. Thus

$$\mathbf{a}_m \cdot \mathbf{b}_n = \delta_{mn}.$$

Then the potential at any point  $\mathbf{r} = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3$  may be expanded as a Fourier series†

$$V(\mathbf{r}) = \sum_{\mathbf{n}} V_{\mathbf{n}} e^{2\pi i \mathbf{n} \cdot \mathbf{r}},$$

where

$$\mathbf{n} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3,$$

and thus

$$(\mathbf{n} \cdot \mathbf{r}) = n_1 x_1 + n_2 x_2 + n_3 x_3.$$

† In conformity with this expression we could have written (1) without the lattice constant  $c$  appearing in the denominator of the exponent. The methods here adopted, however, are so chosen to be as closely as possible in agreement with the notation of M.J.

We consider a semi-infinite crystal bounded by the face  $x_1 = 0$ . This restriction of assuming the surface to be one of the principal lattice planes is removed in § 4. The potential field is then

$$V(\mathbf{r}) = \left. \begin{aligned} \sum_{\mathbf{n}} V_{\mathbf{n}} e^{2\pi i \mathbf{n} \cdot \mathbf{r}} & \quad (x_1 < 0), \\ = 0 & \quad (x_1 > 0), \end{aligned} \right\} \quad (39)$$

and the wave equation, just as before, is

$$\left. \begin{aligned} \nabla^2 \psi + \kappa^2 [W - V(\mathbf{r})] \psi &= 0, \\ \nabla \equiv \mathbf{b}_1 \frac{\partial}{\partial x_1} + \mathbf{b}_2 \frac{\partial}{\partial x_2} + \mathbf{b}_3 \frac{\partial}{\partial x_3} & \end{aligned} \right\} \quad (40)$$

but where now

Assuming a solution of the form

$$\left. \begin{aligned} \psi &= e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}), \\ u(\mathbf{r}) &= \sum_{\mathbf{n}} u_{\mathbf{n}} e^{2\pi i \mathbf{n} \cdot \mathbf{r}}, \end{aligned} \right\} \quad (41)$$

where

$$\text{we again obtain} \quad || D_{\mathbf{n}'\mathbf{n}''} || = 0, \quad (42)$$

$$\left. \begin{aligned} \text{where now} \quad D_{\mathbf{n}'\mathbf{n}'} &= -(\mathbf{k} + 2\pi \mathbf{n}')^2 + \kappa^2 (W - V_{000}), \\ D_{\mathbf{n}'\mathbf{n}''} &= -\kappa^2 V_{\mathbf{n}'-\mathbf{n}''} \quad (\mathbf{n}' \neq \mathbf{n}''). \end{aligned} \right\} \quad (42a)$$

The planes of energy discontinuity are given by

$$\mathbf{n} \cdot \mathbf{k} = \pi n^2, \quad (43)$$

the corresponding forbidden band being

$$\left. \begin{aligned} W_k - |V_{\mathbf{n}}| < W - V_{000} < W_k + |V_{\mathbf{n}}|, \\ \text{where} \quad W_k &= \frac{1}{\kappa^2} |\mathbf{k}|^2. \end{aligned} \right\} \quad (43a)$$

The condition for smooth fitting of the wave functions is

$$\left( \frac{\partial \psi_0}{\partial x_1} / \frac{\partial \psi_i}{\partial x_1} \right)_{x_1=0} = \left( \frac{\psi_0}{\psi_i} \right)_{x_1=0}, \quad (44)$$

and we find again that surface states can exist only when  $n_2 = n_3 = 0$ . We proceed now to the proof of this.

3.1. *Restrictions on the available bands.* Given  $k_2, k_3$  (real) we denote by  $k'_1$  the corresponding value of  $k_1$  given by equation (43) and also write

$$W'_k = \frac{1}{\kappa^2} |k'_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3|^2 + V_{000}.$$

Then, if we are also given an energy in the range

$$W'_k - |V_{\mathbf{n}}| < W < W'_k + |V_{\mathbf{n}}|, \quad (45)$$

the corresponding solutions of (42) for  $k_1$  are complex of the form  $p \pm iq$ .

Attempting to determine a wave function of the form

$$\psi_i = e^{i(p+q)x_1+k_2x_2+k_3x_3}\{\alpha + \beta e^{-2\pi i(n_1x_1+n_2x_2+n_3x_3)}\} \quad (x_1 < 0),$$

we are led to an equation analogous to (11)

$$\begin{aligned} & [\kappa^2(W - V_{000}) - \{(p - iq)\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3\}^2] \\ & \times [\kappa^2(W - V_{000}) - \{(p - iq - 2\pi n_1)\mathbf{b}_1 + (k_2 - 2\pi n_2)\mathbf{b}_2 + (k_3 - 2\pi n_3)\mathbf{b}_3\}^2] \\ & = \kappa^4 V_{\frac{1}{2}}^2. \end{aligned} \quad (46)$$

In order that  $\kappa^2(W - V_{000})$  should be real we must have

$$\begin{aligned} & \frac{\kappa^2(W - V_{000}) - \{(p - 2\pi n_1)\mathbf{b}_1 + (k_2 - 2\pi n_2)\mathbf{b}_2 + (k_3 - 2\pi n_3)\mathbf{b}_3\}^2 + q^2\mathbf{b}_1^2}{\mathbf{b}_1 \cdot [(p - 2\pi n_1)\mathbf{b}_1 + (k_2 - 2\pi n_2)\mathbf{b}_2 + (k_3 - 2\pi n_3)\mathbf{b}_3]} \\ & = - \frac{\kappa^2(W - V_{000}) - (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 + q^2\mathbf{b}_1^2}{\mathbf{b}_1 \cdot (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)} = S. \end{aligned} \quad (47)$$

Substituting (47) into (46) we obtain

$$S^2 + 4q^2$$

$$= \frac{\kappa^4 V_{\frac{1}{2}}^2}{[\mathbf{b}_1 \cdot \{p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3\}][\mathbf{b}_1 \cdot \{(2\pi n_1 - p)\mathbf{b}_1 + (2\pi n_2 - k_2)\mathbf{b}_2 + (2\pi n_3 - k_3)\mathbf{b}_3\}]} \quad (48)$$

Substitution of (48) into (47) then yields alternative forms for  $\kappa^2(W - V_{000})$ , analogous to (14a) and (14b). The equivalence of these expressions requires that

$$\mathbf{b}_1 \cdot \{p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3\} = \mathbf{b}_1 \cdot \{(2\pi n_1 - p)\mathbf{b}_1 + (2\pi n_2 - k_2)\mathbf{b}_2 + (2\pi n_3 - k_3)\mathbf{b}_3\}$$

$$\text{and } (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 = \{(2\pi n_1 - p)\mathbf{b}_1 + (2\pi n_2 - k_2)\mathbf{b}_2 + (2\pi n_3 - k_3)\mathbf{b}_3\}^2.$$

These two conditions in turn give rise to the equations

$$\left. \begin{aligned} & \mathbf{b}_1 \cdot \{(p - \pi n_1)\mathbf{b}_1 + (k_2 - \pi n_2)\mathbf{b}_2 + (k_3 - \pi n_3)\mathbf{b}_3\} = 0, \\ & \{n_2\mathbf{b}_2 + n_3\mathbf{b}_3\} \cdot \{(p - \pi n_1)\mathbf{b}_1 + (k_2 - \pi n_2)\mathbf{b}_2 + (k_3 - \pi n_3)\mathbf{b}_3\} = 0, \end{aligned} \right\}$$

which cannot both be satisfied for arbitrarily chosen  $k_2$  and  $k_3$  unless  $n_2 = n_3 = 0$ .  $p$  is then given by

$$\mathbf{b}_1 \cdot \{p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3\} = \pi n_1 \mathbf{b}_1^2, \quad (49)$$

which we may note is the form taken by (43) with  $n_2 = n_3 = 0$ . There are thus the same restrictions as before on the bands available for real electronic surface states.

3.2. *Surface states in the (l, 0, 0) bands.* Considering now the  $(n_1, 0, 0)$  bands in some detail, we again write  $l$ ,  $V_l$  and  $V_0$  for  $n_1$ ,  $-V_{l00}$  and  $-V_{000}$  respectively.

Given  $k_2, k_3$  (real),  $p$  in terms of them by (49), and  $W$  lying in the range

$$\left. \begin{aligned} & W''_k - |V_l| < W < W''_k + |V_l|, \\ & W''_k = \frac{1}{\kappa^2} (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 - V_0, \end{aligned} \right\} \quad (50)$$

where

then the solutions of (42) for  $k_1$  are of the form  $p \pm iq$ . We accordingly seek to determine a wave function of the form

$$\psi_i = e^{(ip+q)x_1+ik_2x_2+ik_3x_3}\{\alpha + \beta e^{-2\pi i l x_1}\}. \quad (51)$$

As in § 2.2 we find that

$$\kappa^2(W + V_0) - (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 = -qb_1^2 \pm \sqrt{(\kappa^4 V_i^2 - 4\pi^2 q^2 l^2 b_1^4)}, \quad (52)$$

while  $\alpha = e^{i\delta}$  and  $\beta = e^{-i\delta}$ , where  $\delta = \frac{1}{2} \sin^{-1} \left( \frac{2\pi q l b_1^2}{\kappa^2 V_i} \right)$ , (53)

and thus  $\psi_i \propto e^{i(p-\pi l+q)x_1+ik_2x_2+ik_3x_3} \cos(\pi l x_1 + \delta)$ . (54)

We also find that  $2\pi l q b_1^2 \tan \delta = \kappa^2 V_i \pm \sqrt{(\kappa^4 V_i^2 - 4\pi^2 q^2 l^2 b_1^4)}$ , (55)

upper and lower signs of (55) corresponding to upper and lower signs of (52). In the above equations we have written  $b_1$  for  $|\mathbf{b}_1|$ , etc., and thus  $\mathbf{b}_1^2 = b_1^2$ .

For the wave function outside the crystal we take

$$\psi_0 \propto e^{i(p-\pi l-\omega)x_1+ik_2x_2+ik_3x_3},$$

the corresponding energy being given by

$$\begin{aligned} \kappa^2 W &= \{(p - \pi l + i\omega)\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3\}^2 \\ &= (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 - (\omega^2 + \pi^2 l^2) b_1^2, \end{aligned}$$

by the relation (49). Thus

$$\psi_0 \propto e^{i(p-\pi l-\omega)x_1+ik_2x_2+ik_3x_3} e^{-\sqrt{[(p\mathbf{b}_1+k_2\mathbf{b}_2+k_3\mathbf{b}_3)^2-\pi^2 l^2 b_1^2-\kappa^2 W]/b_1} x_1}. \quad (56)$$

The condition (44) for smooth fitting is then

$$-\frac{1}{b_1} \sqrt{[(p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 - \pi^2 l^2 b_1^2 - \kappa^2 W]} = q - \pi l \tan \delta. \quad (57)$$

It follows as before that a surface state cannot exist in the  $(l, 0, 0)$  band unless  $V_i > 0$ . If we assume this to be the case, (55) and (57) combine to give

$$\pi^2 l^2 b_1^2 \sec^2 \delta = \kappa^2 (V_0 + V_i), \quad (58)$$

and hence, from (53),  $qb_1 = \frac{V_i}{V_0 + V_i} \sqrt{[\kappa^2 (V_0 + V_i) - \pi^2 l^2 b_1^2]}$ . (59)

Again, of the two energies given by (52) only one satisfies (57), and for this

$$\kappa^2 (W + V_0) - (p\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3)^2 + \pi^2 l^2 b_1^2 = \pi^2 l^2 b_1^2 \left( \frac{V_0}{V_0 + V_i} \right)^2 + \kappa^2 V_i \frac{V_0}{V_0 + V_i}. \quad (60)$$

To this energy corresponds, for any given  $k_2, k_3$  and positive integer  $l$  such that  $V_i > 0$ , a surface state whose wave function may be written

$$\begin{aligned} \psi_{k_2 k_3} &\equiv \psi_i = N e^{i(p-\pi l+q)x_1+ik_2x_2+ik_3x_3} \cos(\pi l x_1 + \delta) & (x_1 < 0), \\ &\equiv \psi_0 = N \cos \delta e^{i(p-\pi l-\omega)x_1+ik_2x_2+ik_3x_3} & (x_1 > 0), \end{aligned} \quad (61)$$

where  $N$  is the normalizing function,

$$\left. \begin{aligned} qb_1 &= \frac{V_l}{V_0 + V_l} \sqrt{[\kappa^2(V_0 + V_l) - \pi^2 l^2 b_1^2]}, \\ \text{and} \quad \delta &= \cos^{-1} \frac{\pi l b_1}{\sqrt{[\kappa^2(V_0 + V_l)]}} \quad (0 < \delta < \frac{1}{2}\pi). \end{aligned} \right\} \quad (62)$$

The normalizing condition (30) now takes the form

$$\int \psi_{k_2' k_3'}^* \psi_{k_2 k_3} dv = \delta(k_2' - k_2) \delta(k_3' - k_3),$$

where the element of volume  $dv = (\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3) dx_1 dx_2 dx_3$ ,  $(\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3)$  denoting the value of the triple product  $(\mathbf{a}_1 \cdot [\mathbf{a}_2 \wedge \mathbf{a}_3])$ , and the range of integration of each variable being from  $-\infty$  to  $+\infty$ . The evaluation of this integral leads to

$$|N|^2 = \frac{q^2(q^2 + \pi^2 l^2)}{\pi^2 (\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3) \pi^2 l^2 (1 + 2V_l/V_0)}, \quad (63)$$

thus completing the determination of the surface states for a semi-infinite crystal, of arbitrary lattice structure, the surface of which lies in one of the principal planes.

#### CRYSTAL SURFACE IN AN ARBITRARY CRYSTAL PLANE

4. In the previous sections we considered the case of crystals with a surface parallel to the  $x_2 x_3$  plane of the unit cell. We obtained surface states with energies lying in certain of the  $(l, 0, 0)$  forbidden bands, namely those for which  $V_l > 0$ , that is, for which the corresponding Fourier coefficient  $V_{l00}$  is negative. We may remark here that, if the corresponding structure factor† is zero, then  $V_l = 0$  and there can be no surface state, as is otherwise physically obvious since there is no  $(l, 0, 0)$  forbidden band.

We now consider the more general case and show that if the crystal surface consists of a section in the crystal plane

$$p_1 x_1 + p_2 x_2 + p_3 x_3 = 0, \quad (64)$$

$p_1, p_2, p_3$  being integers with no common factor, then we obtain surface states with energies lying in the  $(lp_1, lp_2, lp_3)$  forbidden bands,  $l$  being a positive integer, provided that  $V_{lp_1, lp_2, lp_3}$  is negative.

The property just asserted is most readily proved by a simple transformation of axes, which corresponds physically to making an appropriate different choice

† Cf. M.J. p. 154.

of the unit cell. We define the coordinates  $\xi_1, \xi_2, \xi_3$  in terms of the original  $x_1, x_2, x_3$  by the relations

$$\left. \begin{aligned} p_1 x_1 + p_2 x_2 + p_3 x_3 &= \xi_1, \\ q_1 x_1 + q_2 x_2 + q_3 x_3 &= \xi_2, \\ r_1 x_1 + r_2 x_2 + r_3 x_3 &= \xi_3, \end{aligned} \right\} \quad (65)$$

where the  $p$ 's are defined in (64) and the  $q$ 's and  $r$ 's are integers chosen so that

$$\begin{vmatrix} p_1 & q_1 & r_1 \\ p_2 & q_2 & r_2 \\ p_3 & q_3 & r_3 \end{vmatrix} = 1. \quad (66)$$

This choice is clearly possible, and in several ways. We may take, for example,  $q_1, q_2$  to be integers so that  $p_1 q_2 - p_2 q_1 = \omega_3$ , as in the usual process of determining the H.C.F.  $\omega_3$  of  $p_1, p_2$ , and similarly for  $\omega_1, \omega_2$ . We then require that

$$r_1 \omega_1 + r_2 \omega_2 + r_3 \omega_3 = 1.$$

This can easily be satisfied since no two of the  $\omega$ 's have a common factor which would, if it existed, be a factor common to all the  $p$ 's.

Expressing the potential function in terms of these coordinates, we have

$$V(\mathbf{r}) = \sum_{\mathbf{n}} V_{n_1 n_2 n_3} e^{2\pi i(n_1 x_1 + n_2 x_2 + n_3 x_3)} \quad (67)$$

$$= \sum_{\mathbf{v}} \mathcal{V}_{\nu_1 \nu_2 \nu_3} e^{2\pi i(\nu_1 \xi_1 + \nu_2 \xi_2 + \nu_3 \xi_3)}, \quad (68)$$

where

$$\left. \begin{aligned} \nu_1 p_1 + \nu_2 q_1 + \nu_3 r_1 &= n_1, \\ \nu_1 p_2 + \nu_2 q_2 + \nu_3 r_2 &= n_2, \\ \nu_1 p_3 + \nu_2 q_3 + \nu_3 r_3 &= n_3. \end{aligned} \right\} \quad (69)$$

We can solve the equations for the  $\nu$ 's, obtaining by (66),

$$\nu_1 = \begin{vmatrix} n_1 & q_1 & r_1 \\ n_2 & q_2 & r_2 \\ n_3 & q_3 & r_3 \end{vmatrix}, \quad \nu_2 = \begin{vmatrix} p_1 & n_1 & r_1 \\ p_2 & n_2 & r_2 \\ p_3 & n_3 & r_3 \end{vmatrix}, \quad \nu_3 = \begin{vmatrix} p_1 & q_1 & n_1 \\ p_2 & q_2 & n_2 \\ p_3 & q_3 & n_3 \end{vmatrix}.$$

It is clear that the numbers  $\mathbf{v}$  are integers in 1-1 correspondence with the integers  $\mathbf{n}$ . It follows that the summation of (68) is over exactly the same range as that of (67). Moreover in the new coordinate system the plane of the surface (64) has the equation  $\xi_1 = 0$ , which corresponds to  $x_1 = 0$  in the work of § 3. This work may now be taken over completely and we see that we now have surface states corresponding to the Fourier coefficients  $\mathcal{V}_{l,0,0}$  whose energies lie in the new  $(l, 0, 0)$  forbidden bands. From (69) we see that  $\mathbf{v} \equiv (l, 0, 0)$  corresponds to  $\mathbf{n} \equiv (lp_1, lp_2, lp_3)$  and so, reverting to the original nomenclature, we have surface states corresponding to the coefficient  $V_{lp_1, lp_2, lp_3}$  whose energies lie in the  $(lp_1, lp_2, lp_3)$  forbidden bands. The condition for their existence is  $V_{lp_1, lp_2, lp_3} < 0$ .

The wave function in the  $\xi$ -space is of exactly the same form as the previous wave function in the  $\mathbf{x}$ -space. Indeed all the previous results may be taken over directly in this form. If it is so desired they may then be written in terms of the original coördinates by means of the equations (65).

This completes the determination, on the nearly free electron approximation, of the formulae for the surface states in the most general case of a semi-infinite crystal bounded by one plane face.

#### SUMMARY

It is shown that in a crystal there exist states in which the electron is bound to a surface of the crystal and has an energy lying within a forbidden band. The wave functions and energies of these states are calculated, on the nearly free electron approximation, in terms of the constants of the crystalline potential field, which is represented by a triple Fourier series having the periodicity of the lattice. The method is shown to be applicable to a general crystal having a surface parallel to any one of the crystal planes.

In conclusion I wish to thank Prof. J. E. Lennard-Jones for his helpful interest in both this work and that of the subsequent papers of the series.

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