vector $\mathbf{k}$ might equally well be replaced by one of the second derivatives of E with respect to one of its components k_x, k_y, or k_z.

For the special case (VII.6.19), the evaluation of (VII.5.10) yields an equation

$$\mathbf{v} = \frac{1}{\hbar} \cdot E''(|\mathbf{k}_{\text{bound}}|) \cdot (\mathbf{k} - \mathbf{k}_{\text{bound}}) \tag{VII.6.20}$$

Differentiation with respect to time results in

$$\dot{\mathbf{v}} = \frac{1}{\hbar} \cdot E''(|\mathbf{k}_{\text{bound}}|) \cdot \dot{\mathbf{k}} \tag{VII.6.21}$$

which, with (VII.6.12), leads to

$$\dot{\mathbf{v}} = \frac{1}{\hbar^2} \cdot E''(|\mathbf{k}_{\text{bound}}|) \cdot \mathbf{F} \tag{VII.6.22}$$

Comparison of this relation (VII.6.22) for an electron in a crystal with Eq. (VII.6.18) for a free electron shows that for an electron in a crystal the electron mass is replaced, in acceleration processes, by an effective mass

$$m_{\text{eff}} = \frac{\hbar^2}{E''(|\mathbf{k}_{\text{bound}}|)} \tag{VII.6.23}$$

Before turning to the important physical consequences of this equation, we shall consider the case of a more general variation $E(\mathbf{k})$.

To this end we differentiate, e.g., the x component of (VII.5.10) with respect to time

$$\dot{v}_x = \frac{1}{\hbar} \frac{d}{dt} \left[\frac{\partial}{\partial k_x} E(k_x, k_y, k_z) \right] = \frac{1}{\hbar} \left[\frac{\partial^2 E}{\partial k_x^2} \dot{k}_x + \frac{\partial^2 E}{\partial k_x \, \partial k_y} \dot{k}_y + \frac{\partial^2 E}{\partial k_x \, \partial k_z} \dot{k}_z \right]$$

and combine this equation with the corresponding ones for $\dot{v}_y$ and $\dot{v}_z$ in the vector equation

$$\dot{\mathbf{v}} = \frac{1}{\hbar} \left(\frac{\partial^2 E}{\partial k_l \, \partial k_m} \right) \cdot \dot{\mathbf{k}} \tag{VII.6.24}$$

where the symbol $\partial^2 E / \partial k_l \, \partial k_m$ denotes the tensor

$$\left(\frac{\partial^2 E}{\partial k_l \, \partial k_m} \right) = \begin{bmatrix} \dfrac{\partial^2 E}{\partial k_x^2} & \dfrac{\partial^2 E}{\partial k_x \, \partial k_y} & \dfrac{\partial^2 E}{\partial k_x \, \partial k_z} \\ \dfrac{\partial^2 E}{\partial k_y \, \partial k_x} & \dfrac{\partial^2 E}{\partial k_y^2} & \dfrac{\partial^2 E}{\partial k_y \, \partial k_z} \\ \dfrac{\partial^2 E}{\partial k_z \, \partial k_x} & \dfrac{\partial^2 E}{\partial k_z \, \partial k_y} & \dfrac{\partial^2 E}{\partial k_z^2} \end{bmatrix} \tag{VII.6.25}$$

From (VII.6.24) and (VII.6.12) we now obtain as the desired analogue

to (VII.6.18) the equation

$$\dot{\mathbf{v}} = \frac{1}{\hbar^2}\left(\frac{\partial^2 E}{\partial k_l\, \partial k_m}\right) \cdot \mathbf{F} \qquad \text{(VII.6.26)}$$

We see that, in general, the reciprocal effective mass of an electron in a crystal has the character of a tensor. By the choice of suitable axial directions x, y, z, such a tensor may be transformed to principal axes or, in other words, the nondiagonal terms $\partial^2 E/\partial k_x\, \partial k_y$, $\partial^2 E/\partial k_y\, \partial k_z$, etc., can be made to vanish. Equation (VII.6.26) can then be replaced by three component equations

$$\begin{aligned} \dot{v}_x &= \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_x^2} \cdot F_x & \dot{v}_y &= \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_y^2} \cdot F_y & \dot{v}_z &= \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_z^2} \cdot F_z \\ \dot{v}_x &= \frac{1}{m_{x\,\mathrm{eff}}} F_x & \dot{v}_y &= \frac{1}{m_{y\,\mathrm{eff}}} F_y & \dot{v}_z &= \frac{1}{m_{z\,\mathrm{eff}}} F_z \end{aligned} \qquad \text{(VII.6.27)}$$

We see, then, that three effective masses determine the acceleration in the directions of the three principal axes

$$m_{x\,\mathrm{eff}} = \frac{\hbar^2}{\dfrac{\partial^2 E}{\partial k_x^2}} \qquad m_{y\,\mathrm{eff}} = \frac{\hbar^2}{\dfrac{\partial^2 E}{\partial k_y^2}} \qquad m_{z\,\mathrm{eff}} = \frac{\hbar^2}{\dfrac{\partial^2 E}{\partial k_z^2}} \qquad \text{(VII.6.28)}$$

For a force $\mathbf{F}$ pointing in an arbitrary direction, the acceleration $\dot{\mathbf{v}}$ will thus, in general, no longer have the same direction as the force $\mathbf{F}$.

What are now the physical consequences of Eqs. (VII.6.22) and (VII.6.23) and (VII.6.26) and (VII.6.28)? The most striking feature of these relations is perhaps that Eqs. (VII.6.23) and (VII.6.28) lead to a negative effective mass at the upper edge of the band, where $E(\mathbf{k})$ has a maximum[1] (see Figs. VII.3.10 to VII.3.12), so that the second derivative of the energy with respect to the wave number becomes negative. For a force acting in the direction of motion, an electron energetically close to the upper band edge is hence decelerated instead of accelerated.[2]

[1] This apparently so obvious statement does not apply with such generality. In three-dimensional lattices, the relations at the band edges can become very complex. We mentioned this already on p. 180 with reference to the face-centered cubic lattice.

[2] We should note that the transition from positive effective masses in the lower part of the band to negative effective masses in the upper part of the band does not take place by way of $m_{\mathrm{eff}} = 0$, but by way of $m_{\mathrm{eff}} = \infty$. This applies, however, only for one coordinate direction at a time, e.g., the x direction. In the three-dimensional case an electron with the particular energy pertaining hereto will fail to react only to a force acting purely in the x direction because of $m_{\mathrm{eff}} = \infty$, whereas for the y and z directions the effective masses will remain finite. Thus,

This statement ceases to be objectionable as soon as it is remembered what almost absurd procedure was followed in defining the effective mass. An electron in a crystal is subject, first of all, to very strong forces exerted by the lattice. In defining the effective mass by the equation $\dot{\mathbf{v}} = \mathbf{F}/m_{\text{eff}}$, we in effect disregard the lattice forces and act as though the added external force $\mathbf{F}$ alone were present. It must not surprise us if, in this procedure, strange values are obtained for the effective mass, since the lattice forces disregarded in the equation of definition $\dot{\mathbf{v}} = \mathbf{F}/m_{\text{eff}}$ express themselves in these anomalous values.

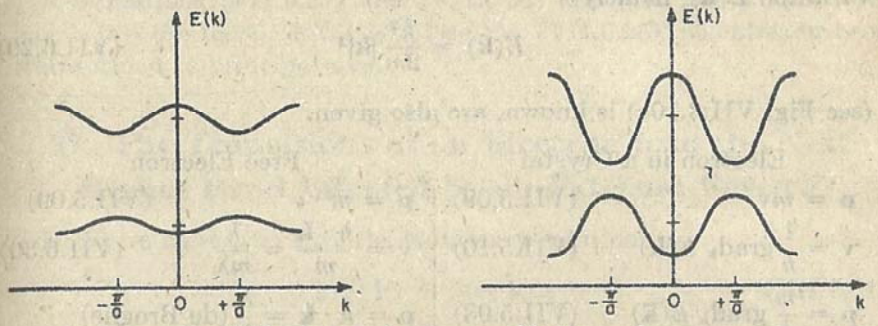

FIG. VII.6.3. Relation between binding and m_{eff}.

Strong binding	Weak binding
↓	↓
Narrow bands	Wide bands
↓	↓
$E''(k)$ small	$E''(k)$ large
↓	↓
m_{eff} large	m_{eff} small

In particular, for an electron lying energetically close below an upper edge of a band, the circumstances are such that a force acting in the direction of motion further increases the energy, so that the electron is brought still closer to the band edge. As a result, its eigenfunction becomes still more nearly a standing wave by increased Bragg reflection of the lattice and the mean velocity of the electron decreases. It is seen clearly how the action of the lattice, which is disregarded in the equation of definition $\dot{\mathbf{v}} = \mathbf{F}/m_{\text{eff}}$, is responsible for the seemingly strange behavior of the electron.

We had noted on page 200, item 6, that strong binding of the electrons to the atomic cores leads to narrow allowed energy bands. Now Fig. VII.6.3 shows that for narrow energy bands $E''(\mathbf{k})$ is small and

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the uppermost electrons of a half-filled band will never fail to react to forces of arbitrary direction; their inability to change their velocity exists at most for specific directions.

that for wide energy bands $E''(\mathbf{k})$ is large. Thus Eq. (VII.6.23) leads to large effective masses for strong binding and small effective masses for weak binding, a very plausible result.

d. Summary

At the close of this section we shall collect once more the relations between mean momentum $\mathbf{p}$, mean velocity $\mathbf{v}$, wave number $\mathbf{k}$, and force $\mathbf{F}$ which have been obtained in the last two paragraphs. The simplifications obtained for the case of the free electron, for which the variation $E(\mathbf{k})$, namely,

$$E(\mathbf{k}) = \frac{\hbar^2}{2m}|\mathbf{k}|^2 \tag{VII.6.29}$$

(see Fig. VII.3.10*a*) is known, are also given.

Electron in a Crystal		Free Electron	
$\mathbf{p} = m\mathbf{v}$	(VII.5.09)	$\mathbf{p} = m \cdot \mathbf{v}$	(VII.5.09)
$\mathbf{v} = \frac{1}{\hbar}\operatorname{grad}_{\mathbf{k}} E(\mathbf{k})$	(VII.5.10)	$\mathbf{v} = \frac{\hbar \cdot \mathbf{k}}{m} = \frac{h}{m\lambda}$	(VII.6.30)
$\mathbf{p} = \frac{m}{\hbar}\operatorname{grad}_{\mathbf{k}} E(\mathbf{k})$	(VII.5.03)	$\mathbf{p} = \hbar \cdot \mathbf{k} = \frac{h}{\lambda}$ (de Broglie)	(VII.6.31)
$\mathbf{F} = \hbar\dot{\mathbf{k}}$	(VII.6.12)	$\mathbf{F} = \hbar\dot{\mathbf{k}} = \dot{\mathbf{p}}$ (Newton)	(VII.6.32)
$m_{x\text{eff}} = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k_x^2}}$, $m_{y\text{eff}} = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k_y^2}}$, $m_{z\text{eff}} = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k_z^2}}$	(VII.6.28)	$m_{\text{eff}} = \frac{\hbar^2}{\frac{\hbar^2}{2m} \cdot 2} = m$	(VII.6.33)
$\dot{v}_x = \frac{1}{m_{x\text{eff}}} F_x$, $\dot{v}_y = \frac{1}{m_{y\text{eff}}} F_y$, $\dot{v}_z = \frac{1}{m_{z\text{eff}}} F_z$	(VII.6.27)	$\dot{\mathbf{v}} = \frac{1}{m}\mathbf{F}$	(VII.6.34)

Remarks: 1. Equation (VII.5.09) applies for the quantum-mechanical mean values $\mathbf{p}$ and $\mathbf{v}$ of the momentum operator $\hbar/j$ grad and the

velocity operator $\hbar/jm$ grad and is hence a simple consequence of the difference in the factor m of the two operators. For the sake of graphic interpretation, the quantum-mechanical mean value $\mathbf{v}$ of the velocity operator may then be identified with the group velocity both for the electron in a crystal and for a free electron.

2. From the analogy of Eqs. (VII.6.12) and (VII.6.32) we see that for an electron in a crystal the so-called lattice momentum $\hbar\mathbf{k}$ plays the same role as the ordinary momentum $\mathbf{p}$ for the free electron. In general, $\mathbf{p} = \hbar\mathbf{k}$ applies only for the free electron.

3. Equations (VII.6.27) and (VII.6.28) apply in this simple form only when the tensor $\partial^2 E/k_l\,\partial k_m$ [see Eq. (VII.6.25)] has already been transformed to principal axes.

§7. The Transitions of an Electron into the Next Higher Band Effected by an External Force F

In §6 we have seen that the stationary solutions

$$\psi(\mathbf{r};\mathbf{k}) = u(\mathbf{r};\mathbf{k})\,e^{j\mathbf{k}\cdot\mathbf{r}} \qquad \text{(VII.7.01)}$$

of the force-free problem have a certain significance also for the behavior of an electron under the influence of an external force $\mathbf{F}$. It was shown that even when acted upon by an external force $\mathbf{F}$ the electron was represented at any instance by a ψ function as given by (VII.7.01). At the same time, the wave vector $\mathbf{k}$ did not remain constant, but varied according to the law

$$\dot{\mathbf{k}} = \frac{1}{\hbar}\mathbf{F} \qquad \text{(VII.6.12)}$$

In treating, here, the transitions of an electron into another band under the influence of an external force $\mathbf{F}$ in a manner originally employed by Zener,[1] we utilize another significance which the stationary solutions of the force-free problem retain in the transition to the problem with an external force. To explain this significance we recall the well-known wave-mechanical calculations on the transmission of an electron through a potential barrier (tunnel effect). Here the potential barrier is not treated as an external force, and there is no attempt to seek solutions varying with time of the force-free problem; instead, a stationary solution is obtained of the problem with potential barrier. The solution in front of the barrier is then composed of two stationary solutions of the force-free problem, which may be

[1] C. Zener, *Proc. Roy. Soc. (London)*, **A145**: 523 (1934).

interpreted as incident and reflected waves and thus represent electrons which are moving toward the potential barrier and have been reflected by it, respectively.[1] In the space beyond the potential barrier the solution is identical with one stationary solution of the force-free problem and is interpreted as a transmitted wave. The desired probability of transmission of the electrons through the barrier is the ratio of the squares of the amplitudes of the transmitted and the incident wave, i.e., of two stationary solutions of the force-free problem.

Zener utilizes this significance of the stationary solutions of the force-free problem for the problem with an external force—a significance entirely different from that in Houston's procedure—for the treatment of the transition of electrons into another band. Just as in the treatment of the tunnel effect, we first obtain a stationary solution of the problem with external force. In one part of space this solution is identified with electrons in the lower band, in another part of space, on the other hand, with electrons which have passed over into the upper band.

Zener obtains the stationary solution of the problem with external force[2] $\mathfrak{F}$

$$-\frac{\hbar^2}{2m}\psi''(x) - (eU(x) + F \cdot x)\psi(x) = E\psi(x) \qquad \text{(VII.7.02)}$$

by the following consideration: Even field strengths of the order of the breakdown field strengths (e.g., 10^5 to 10^6 volts cm^{-1}) produce potential differences of only $3 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$ volt within a lattice constant (e.g., $3 \cdot 10^{-8}$ cm). On the other hand, the variations in the lattice potential U resulting from the atom cores within a lattice constant are of the order of 10 volts.[3] We see hence that in (VII.7.02) the term $F \cdot x$ is practically constant, as compared to the lattice potential $U(x)$,

[1] It should be recalled that an unlimited plane wave of finite amplitude is interpreted most simply, in view of normalization difficulties in infinite space, as a representation of a beam of many electrons of equal velocity rather than as a representation of a single electron. The square of the amplitude of this wave is then a measure for the intensity of this "cathode-ray beam."

[2] For simplicity we consider the one-dimensional problem. For the reason for employing $\mathfrak{F}$ in place of E, see p. 226.

[3] Along a straight line along which there lies a row of atom cores the variations of potential are even infinitely large since the potential energy of an electron becomes negatively infinite when it approaches the nucleus of an atom core arbitrarily closely. Since the valence electrons, which are here of interest, remain at a certain distance from the nuclei of the atom cores, the ionization potentials give a reasonable order of magnitude for the potential variations in question. These are, however, of the order of 10 volts. The Fourier coefficients of the threefold periodic function $U(x, y, z)$ are of the same order of magnitude. See H. A. Bethe in Geiger and Scheel, *op. cit.*, vol. XXIV, part 2, p. 423.

over a range of many lattice constants (see Fig. VII.7.1). For this reason, Zener claims that

$$\psi(x) = u(x; k(x))\, e^{j\int_{x=0}^{x} k(x)dx} \qquad \text{(VII.7.03)}$$

is a good approximate solution of (VII.7.02). Here the wave number $k(x)$ is now a function of x in so far as it depends in the same manner on $E + Fx$ as on E in the force-free case, i.e., as in Figs. VII.3.10 to

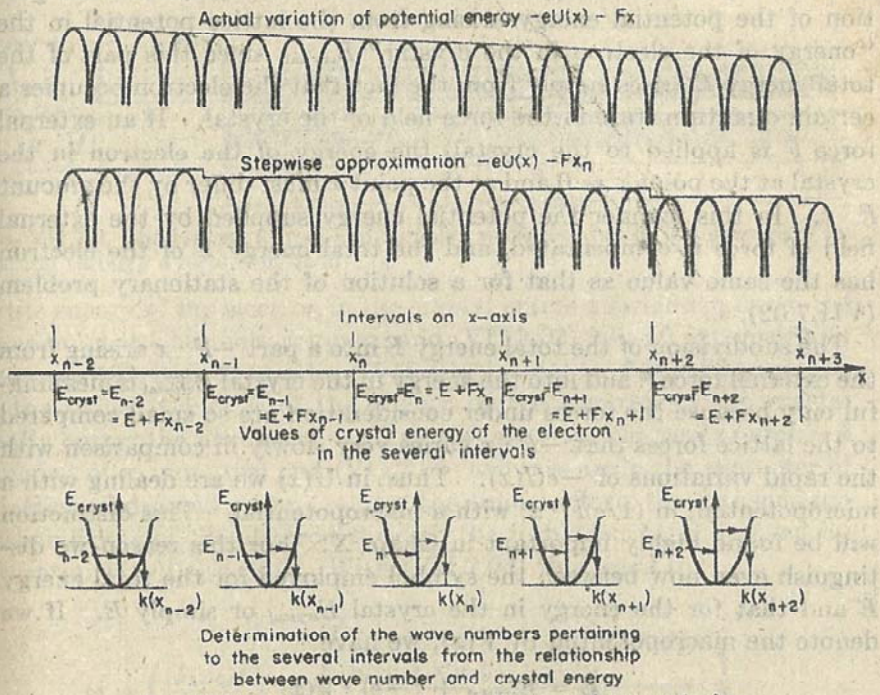

FIG. VII.7.1. The origin of Zener's approximate solution

$$\psi(x) = u(x; k(x))\, e^{j\int_{x=0}^{x} k(x)\,dx}$$

VII.3.12.[1] This is seen most simply by subdividing the x axis into intervals $x_1, x_2, \ldots x_n, x_{n+1}, \ldots$ and approximating Eq. (VII.7.02) within an interval $x_n < x < x_{n+1}$ covering several lattice constants by

$$-\frac{\hbar^2}{2m}\psi''(x) - eU(x)\psi(x) = E_{\text{crystal}}\,\psi(x) \qquad \text{(VII.7.04)}$$

[1] So far Figs. VII.3.10 to VII.3.12 have always been regarded as representations of the dependence of the energy in the crystal E on the wave number k. In quite the same manner they represent the inverse function, i.e., the dependence of the wave number k on the energy in the crystal E_{crystal}.

with $E_{\text{crystal}} = \boldsymbol{E} + Fx_n$, i.e., by the force-free Schrödinger equation with the value $\boldsymbol{E} + Fx_n$ for the energy of the electron in the crystal.

To explain the concept of the energy of the electron in the crystal E_{crystal}, we note that the energy of the electron in the crystal is in part kinetic, in part potential in nature. In the potential energy we can again distinguish between the part which arises from the lattice potential $U(x)$ and the part which arises from the external force F. We now combine the kinetic energy of the electron in the crystal with the portion of the potential energy arising from the lattice potential in the "energy of the electron in the crystal" E_{crystal}, since this part of the total energy $\boldsymbol{E}$ arises simply from the fact that the electron occupies a certain quantum state in the force field of the crystal. If an external force F is applied to the crystal, the energy of the electron in the crystal at the point $x = 0$ and at the point x must differ by the amount $F \cdot x$. In this manner the potential energy supplied by the external field of force is compensated, and the total energy $\boldsymbol{E}$ of the electron has the same value as that for a solution of the stationary problem (VII.7.02).

The subdivision of the total energy $\boldsymbol{E}$ into a part $-F \cdot x$ arising from the external force F and into the energy in the crystal E_{crystal} is meaningful only because the forces under consideration are so small compared to the lattice forces that $-F \cdot x$ varies very slowly in comparison with the rapid variations of $-eU(x)$. Thus, in $U(x)$ we are dealing with a micropotential, in $(1/e)F \cdot x$, with a macropotential. This distinction will be found highly important in Chap. X. For this reason we distinguish even now between the symbol employed for the total energy $\boldsymbol{E}$ and that for the energy in the crystal E_{crystal} or simply E. If we denote the macropotential by $V(x)$, we have

$$\boldsymbol{E} = E_{\text{crystal}} + (-e) \cdot V(x)$$

or, in the present case, $\boldsymbol{E} = E_{\text{crystal}} - Fx$. See also pages 336 to 338.

Zener's formulation (VII.7.03) may also be written in the form

$$\begin{aligned} \psi(x) &= u(x; k(x)) \cdot \mathrm{e}^{j\left[\int_{x=0}^{x_n} k(x)\,dx + \int_{x=x_n}^{x} k(x)\,dx\right]} \\ &= u(x; k(x)) \cdot \mathrm{e}^{j\int_{x=0}^{x=x_n} k(x)\,dx} \cdot \mathrm{e}^{j\int_{x=x_n}^{x} k(x)\,dx} \end{aligned}$$

In the interval considered this becomes, because of $k(x) \approx k(x_n)$,

$$\begin{aligned} \psi(x) &= u(x; k(x_n)) \cdot \mathrm{e}^{j\int_{x=0}^{x=x_n} k(x)\,dx} \cdot \mathrm{e}^{jk(x_n)(x-x_n)} \\ \psi(x) &= \text{const} \cdot u(x; k(x_n)) \cdot \mathrm{e}^{jk(x_n)x} \end{aligned} \qquad \text{(VII.7.05)}$$

This, however, is the solution of the substitute force-free problem[1] (VII.7.04) introduced for the interval $x_n < x < x_{n+1}$.

As long as the value $E + F \cdot x$ of the energy of the electron in the crystal falls into an allowed energy band of the force-free problem (VII.7.04) (see Fig. VII.7.2), the wave number k is real and (VII.7.03) has the usual character of a lattice-modulated plane wave, though with a wave number which is slowly variable in space. This applies, e.g., up to the point $x = x_B$. For a further increase in x, the value $E + F \cdot x$

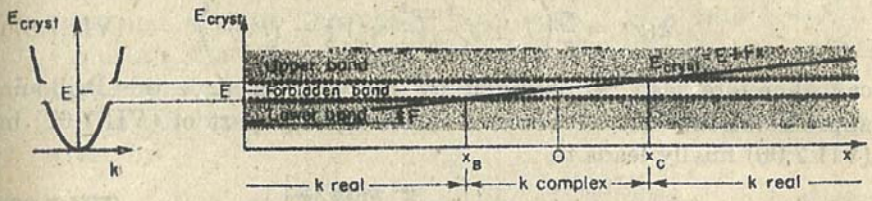

FIG. VII.7.2. The regions of real and complex wave number in the passage of an electron through a forbidden band.

of the energy of the electron in the crystal enters a forbidden band, the wave number k becomes complex, and (VII.7.03) falls off exponentially [see page 199, item 2, also Eq. (VII.7.05)]. As, for further increase in x, the value $E + F \cdot x$ of the energy of the electron in the crystal finally enters the next band, e.g., at $x = x_C > x_B$, the wave number k becomes once more real and (VII.7.03) assumes again the character of a lattice-modulated wave. As for the tunnel effect, the transmission probability w of the electron through the forbidden band is given by the ratio $|\psi(x_C)|^2/|\psi(x_B)|^2$. With (VII.7.03) this leads to

$$w = \left(\frac{|\psi(x_C)|}{|\psi(x_B)|}\right)^2 = \left(\frac{|u(x_C;\, k(x_C))| \cdot e^{-\int_0^{x_C} \mathrm{Im}\, k(x)dx}}{|u(x_B;\, k(x_B))| \cdot e^{-\int_0^{x_B} \mathrm{Im}\, k(x)dx}}\right)^2$$

$$= \left(\frac{|u(x_C;\, k(x_C))|}{|u(x_B;\, k(x_B))|} \cdot e^{-\int_{x_B}^{x_C} \mathrm{Im}\, k(x)dx}\right)^2$$

Zener writes, by way of approximation,

$$w \approx e^{-2\int_{x_B}^{x_C} \mathrm{Im}\, k(x)dx} \qquad \text{(VII.7.06)}$$

[1] Similar reasoning might justify the solution $u(x;\, k(x))\, e^{jk(x)\cdot x}$. As compared with Zener's formula (VII.7.03), this solution would have the drawback that the phase rotation between, e.g., an arbitrary point $x = x_1$ and the point $x = 0$ would

assuming that the lattice-periodic modulation factors $u(x_C; k(x_C))$ and $u(x_B; k(x_B))$ are immaterial for an estimate of the order of magnitude.[1]

To evaluate (VII.7.06), an explicit formulation of the dependence of the wave number k on the energy of the electron in the crystal E_{crystal} is required. Zener here utilizes papers by Hill and specializes Hill's results for a lattice potential $U(x) = 2V_1 \cos 2\pi(x/a)$ with a small amplitude V_1, thus coming within the range of the Brillouin approximation. The result given by him[2]

$$k(x) = \frac{\pi}{a}\left(1 \pm j\frac{4ma^2}{h^2}\sqrt{V_1^2 - (Fx)^2}\right) \qquad \text{(VII.7.07)}$$

can therefore also be obtained by carrying through the Brillouin approximation. Substitution of the imaginary part of (VII.7.07) in (VII.7.06) finally leads to

$$w = \exp\left[-\frac{\pi^2}{h^2}\frac{maE_{CV}^2}{F}\right] \qquad \text{(VII.7.08)}$$

Here $E_{CV} = 2V_1$ is the energy gap between the conduction band C and the valence band V, i.e., the width of the forbidden band traversed.[3]

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be determined by the wave vector at one point only, namely, $x = x_1$. In the Zener approximation (VII.7.03), the integral form of the exponent

$$\left[\int_{x=0}^{x_1} k(x)\,dx\right]$$

takes care that the wave vector appropriate to any one point of the interval $0 \cdots x_1$ enters into the progression of the phase at this point.

Apart from this, Zener's approximate solution is the proper application to the electron in the crystal of the method of Wentzel, Kramers, and Brillouin (W.K.B. method). Zener's solution corresponds to the zero step in the W.K.B. method. With regard to the W.K.B. method, see, e.g., W. Weizel, "Lehrbuch der theoretischen Physik," vol. II, p. 1010, Springer-Verlag OHG, Berlin, 1950.

[1] This has led to a criticism by F. Cernuschi, *Proc. Cambridge Phil. Soc.*, **32**: 276 (1936).

[2] Zener gives for the factor ahead of the root mistakenly $8ma^2/h^2$. Zener's final result is again correct, however.

[3] It was noted already on p. 217 that Houston's approach, as presented in §6, when carried further must also answer the question of Zener transitions. Houston himself has obtained in this manner a result which deviates from (VII.7.08) by the factor $(2\pi)^2$. In fact, this approach yields Zener's result (VII.7.08) except for the entirely immaterial factor $(\pi/3)^2$. This is particularly satisfying because Zener's calculation is not wholly convincing in several respects. Thus Zener's formula (VII.7.03), unlike Houston's formulas in §6, does not pass over into an exact solution in the transition to the limit from an electron in a crystal to a free electron (amplitude of the potential variations $\to 0$). An attempt at verification shows this immediately. The fact that, in Zener's considerations, a wave reflected at the upper band edge does not occur may be related to this.

This is, thus, the probability that an electron striking the upper edge of the band passes through the forbidden band into the next higher band. How often in unit time does an electron acted upon by the force F strike the upper edge of the band in which it happens to be? In §6 we saw that the wave number k changes at the rate $\dot{k} = F/\hbar$ under the influence of F. In this process the electron oscillates energetically back and forth between the upper and the lower band edge, as indicated by Figs. VII.3.10 to VII.3.12. A k interval $2\pi/a$ must be traversed for a full cycle from the upper band edge to the lower band edge and back to the upper band edge. At a rate $\dot{k} = F/\hbar$ this requires a time $(2\pi/a)/(F/\hbar) = h/aF$. Thus the electron strikes the upper band edge aF/h times in unit time.

The number of transitions per second into the upper band is thus given by

$$\frac{aF}{\hbar} w = \frac{aF}{h} \exp\left[-\frac{\pi^2}{\hbar^2}\frac{maE_{CV}^2}{F}\right] \qquad \text{(VII.7.09)}$$

In Fig. VII.7.3 this equation has been evaluated for $a = 3 \cdot 10^{-8}$ cm and three different widths E_{CV} of the forbidden band. We see that the effect is completely negligible up to a certain, very high, field strength $|E| = F/e$ and sets in here quite abruptly. This confirms the statement in §6 that, for normal field strengths, Zener transitions of a lattice electron into the next higher band are entirely negligible.

To complete the picture, it should be noted that the oscillation in energy of the electron is accompanied by an oscillation in space. Thus, for the states with $0 < k < +\pi/a$ we have in the lowest band of Fig. VII.3.10 and according to (VII.5.10) positive velocities $v = E'(k)/\hbar$, whereas for the states $+\pi/a < k < +2\pi/a$ the velocities are negative, etc. For the distance of oscillation we obtain, therefore,

$$l_{osc} = \int_{t_{bottom}}^{t_{top}} v\,dt = \int_{k=0}^{k=+\frac{\pi}{a}} \frac{1}{\hbar} E'(k) \cdot \frac{dt}{dk} \cdot dk$$

$$l_{osc} = \int_{k=0}^{k=+\frac{\pi}{a}} E'(k) \cdot \frac{dk}{\hbar \dot{k}}$$

With (VII.6.12) this becomes

$$l_{osc} = \int_{k=0}^{k=+\frac{\pi}{a}} E'(k) \cdot \frac{dk}{F}$$

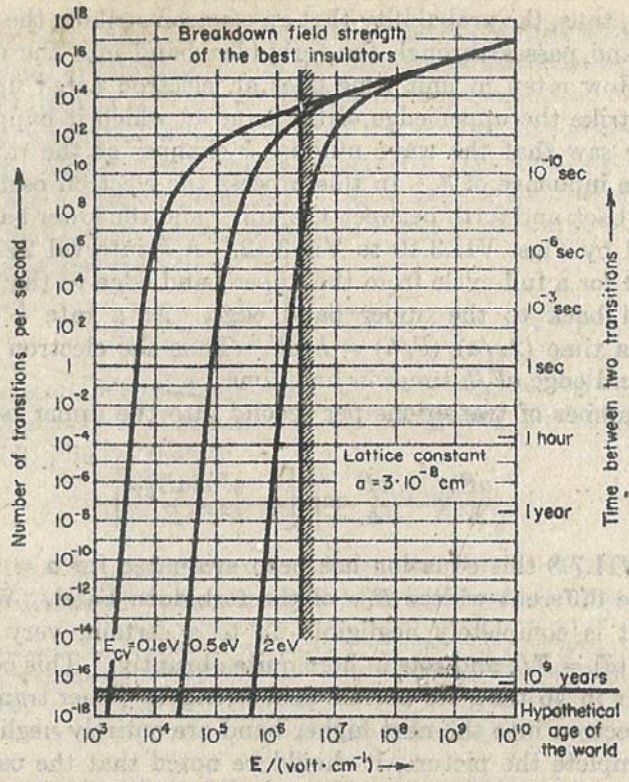

FIG. VII.7.3. Number of transitions per second of an electron in the crystal into the next band.

E_{CV} = width of forbidden band
E = field strength

Based on Eq. (VII.7.09) or (VII.7.13) with

$$m_{eff} = m\frac{2ma^2E_{CV}}{h^2} \text{ (Brillouin approximation)}$$

and furthermore, because of the constancy of F in time and space,

$$l_{osc} = \frac{1}{F}\int_{k=0}^{k=+\frac{\pi}{a}} E'(k)\,dk = \frac{E_{top} - E_{bottom}}{F} \qquad \text{(VII.7.10)}$$

If the external force F arises from an electrical field E, we have

$$l_{osc} = \frac{\frac{1}{e}(E_{top} - E_{bottom})}{|\mathbf{E}|} \qquad \text{(VII.7.11)}$$

With the aid of this equation we shall show on pages 257 to258 that, for normal field strengths E, a full realization of this oscillation is prevented by collisions of the electron with phonons and lattice defects.

Further discussion is needed to settle whether this remark is applicable to valence electrons. To begin with, it can be applied with safety only to the excess electrons in the conduction band and to the holes in the valence band. For a valence band which is fully occupied by electrons, it becomes meaningless to speak of collision processes. Since all states are occupied, a collision process could consist only of an exchange of states between two electrons; in view of the indistinguishability of the electrons, this cannot be regarded as a real effect. (The Schrödinger function for a many-electron system is a Slater determinant and merely changes its sign for an exchange of two rows.) By the same reasoning, only a formal significance can be attached to the oscillation of the valence electrons in the fully occupied valence band. We shall not discuss the question further to what extent the thermal loosening of the occupation of the valence band alters the situation and to what extent it may be meaningful, after all, to speak of thermal collisions in connection with the valence electrons at the upper edge of the valence band, i.e., just before the Zener transition into the next higher band.

In any case, we have here arrived at a point where we have the impression that the band model, with its electrons in various energy states (in the valence band) spread over the entire crystal, is no longer adequate to the facts. In viewing the totality of valence electrons in a germanium crystal, with two electrons accommodated in each of the tetrahedrally arranged valence bonds, we can scarcely escape the impression that the atomistic approach is more appropriate.

The atomistic treatment of the Zener effect could be carried out to a rough approximation by treating the liberation by a strong field through tunneling of an electron bound in a potential well. The work required to free the electron classically, i.e., without tunnel effect, would be, just as in the band model, E_{CV}; for, in such a liberation, a valence electron is converted into a conduction electron. We can get an idea of the results to be expected from the papers of W. Franz,[1] which, however, must be modified somewhat in detail. In any case, we obtain in this manner a law in which the exponential factor takes the form

$$\exp\left[-\frac{4}{3}\frac{\sqrt{2m_{eff}}}{\hbar F}(E_{CV})^{3/2}\right] \qquad \text{(VII.7.12)}$$

[1] W. Franz, *Ergeb. exakt. Naturw.*, 27: 16, Eq. (34) (1953).

A corresponding variation with

$$\exp\left[-\frac{4}{3}\frac{\sqrt{2m}}{\hbar F}(\Delta E)^{3/2}\right]$$

is obtained also for the field emission of electrons from cold metallic surfaces.[1]

It may seem at first sight that there are material differences between these variations and the Zener formula (VII.7.08). The occurrence of the bandwidth E_{CV} in the second power in the Zener formula, as contrasted with the $^3/_2$ power in the field emission laws, is particularly striking.

However, we can separate out, in the exponents of (VII.7.08) and (VII.7.09), the factor

$$2^{1/2}\frac{maE_{CV}^{1/2}}{h} = \sqrt{\frac{2m^2a^2E_{CV}}{h^2}}$$

and interpret it as $\sqrt{m_{eff}}$, where m_{eff} is the effective mass obtained in carrying through the Brillouin approximation.[2] Equation (VII.7.09) then takes on the following form:

$$\frac{\text{Number of transitions}}{\text{Number of valence electrons} \cdot \text{unit time}} = \frac{aF}{h}\exp\left[-\frac{\pi^2}{h}\left(\frac{m_{eff}}{2}\right)^{1/2}\frac{E_{CV}^{3/2}}{F}\right]$$

$$= \frac{aF}{h}\exp\left[-\frac{\pi}{4}\frac{\sqrt{2m_{eff}}}{\hbar F}(E_{CV})^{3/2}\right] \quad \text{(VII.7.13)}$$

In this form (VII.7.13) of the Zener formula (VII.7.09), the exponential factor is in fact very similar to that of the field emission laws. Thus, compared with (VII.7.12), the only difference in the exponent is the difference between the factors $^4/_3$ and $\pi/4$. The form (VII.7.13) is preferred by several authors[3] as being less tied to details and peculiar-

[1] See H. A. Bethe in Geiger and Scheel, *op. cit.*, vol. XXIV, part 2, p. 439, Eqs. (19.12) and (19.13).

[2] H. Fröhlich, "Elektronentheorie der Metalle," bottom of p. 44, Eq. (24), Springer-Verlag OHG, Berlin, 1936.

[3] See, e.g., K. B. McAfee, E. J. Ryder, W. Shockley, and M. Sparks, *Phys. Rev.*, 83: 650 (1951). In Eq. (1) of this paper the exponent is too large by a factor 2. This seems to be simply a printer's error, however, since in the numerical equation (3) of the same paper the exponent has again the right value.

ities of the Brillouin approximation than (VII.7.09). Hence we plot in Fig. VII.7.4 the results obtained from an evaluation of Eq. (VII.7.13) for the same data as those employed with Eq. (VII.7.09) in Fig. VII.7.3. We see that the principal characteristic of the effect, namely, the abrupt onset at a field strength of the order of 10^4 to 10^6 volts cm^{-1}, remains unaltered.

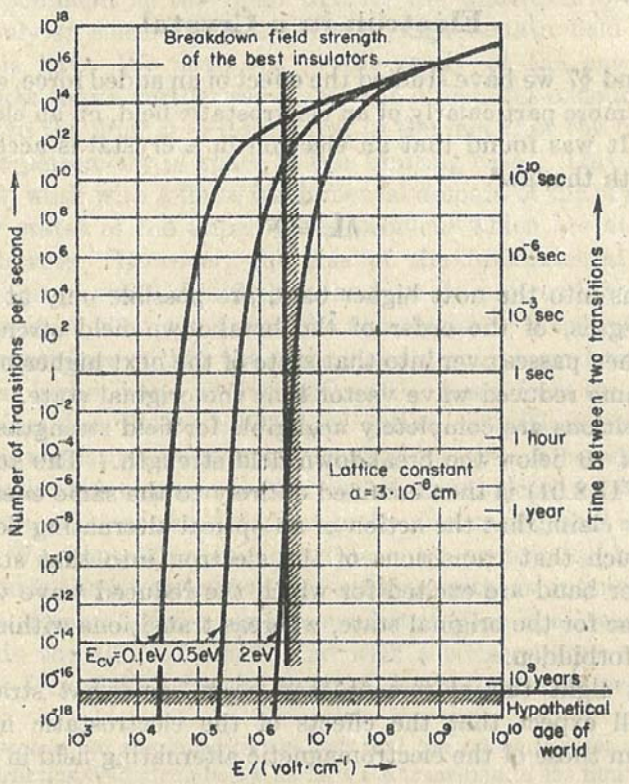

FIG. VII.7.4. Number of transitions per second of an electron in a crystal into the next band. E_{cv} = width of the forbidden band. E = field strength. Based on Eq. (VII.7.13) with $m_{eff} = m$.

Finally, we note that Zener himself was inclined to believe that the effect under consideration was of importance for the breakdown of insulators.[1] At present, there is some question as to whether break-

[1] We have seen on pp. 12 and 16 that an insulating crystal has a fully occupied and hence nonconducting valence band and empty conduction band (see also pp. 263 and 296). The insulating crystal can be made conducting only by introducing electrons into the empty conduction band. This could occur through the

down may not set in at lower field strengths as a result of other effects. However, the interest in the Zener effect has been materially increased recently, since McAfee, Ryder, Shockley, and Sparks have related to it the failure of rectifiers at high reverse voltages.[1]

§8. The Effect of an Optical Alternating Field on an Electron in a Crystal

In §6 and §7 we have studied the effect of an added force, constant in time, and more particularly of an electrostatic field, on an electron in a crystal. It was found that an electron in a crystal is accelerated in accord with the law[2]

$$\hbar\dot{\mathbf{k}} = \mathbf{F} \tag{VII.8.01}$$

Transitions into the next higher band are possible only at very high field strengths, of the order of the breakdown field strength. The electron then passes over into that state of the next higher band which has the same reduced wave vector $\mathbf{k}$ as the original state. However, such transitions are completely negligible for field strengths which lie a power of 10 below the breakdown field strength. The acceleration process (VII.8.01) is then confined entirely to the same energy band.

We now claim that the action of an optical alternating field is, conversely, such that transitions of the electron into that state of the next higher band are excited for which the reduced wave vector $\mathbf{k}$ is the same as for the original state, whereas transitions within the same band are forbidden.

At first sight this statement may seem somewhat strange. We might well expect that the effects of the electrostatic field would follow from those of the electromagnetic alternating field in passing to

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Zener effect above certain field strengths. Since the effect sets in very suddenly as the field strength is increased (Fig. VII.7.3), the crystal would suddenly become very highly conducting above a certain field strength, i.e., exhibit the phenomenon of "breakdown."

[1] See also G. K. McKay and K. B. McAfee, *Phys. Rev.*, **91**: 1079 (1953); and G. K. McKay, *Phys. Rev.*, **94**: 877 (1954).

[2] The quantity $\hbar\mathbf{k}$ thus assumes the role of a generalized momentum. For this reason it is frequently called the "crystal momentum" (Shockley, *op. cit.*, p. 143). For a free electron the quantum-mechanical mean value $\mathbf{p}$ of the momentum, for which we have derived the formula $\mathbf{p} = (m/\hbar)\cdot \operatorname{grad}_{\mathbf{k}} E(\mathbf{k})$, is, in fact, identical with the quantity $\hbar\mathbf{k}$. See Eq. (VII.6.31).

the limit

$$\text{Angular frequency} \to 0$$

An unbridgeable contradiction appears to separate the two statements "continuous acceleration within a band and no transitions into higher bands" and "no transitions within the same band, but only transitions to higher bands with conservation of the wave vector."[1]

We must comment on this point that for the transition to the limit $\omega \to 0$ not only an electrostatic but also a magnetostatic field of equal magnitude is left. We shall see in the study of the calculations reported below that a further reason for the difficulties encountered in the passage to the limit $\omega \to 0$ may rest in the fact that the perturbation loses its periodicity in space in this limiting case. This makes it impossible to work with a finite fundamental domain of the crystal and with energy states of the unperturbed problem which are at least in principle discrete. However, the size of the fundamental domain should have no physical significance, and we do not readily see how, from this point of view, we can arrive at a decision, below which frequency ω transitions within the same band dominate and transitions into the next higher band are insignificant.[2] Apart from this we have the impression that the prohibition of optical transitions within the same band is statistical in nature. In the following calculations only matter, namely, the electron in the crystal, is subjected to statistical quantum laws, whereas the electromagnetic alternating field is treated classically. We hope that the question may eventually be solved whether, under these circumstances, working with an infinitely large fundamental domain, with a continuous distribution of allowed energy values within the allowed bands, and with a consequently necessary wave-packet formulation for the electron, leads to a finite probability

[1] The situation is not simplified by the fact that the calculation for an electromagnetic alternating field given below permits the transition to the limit "angular frequency $\to$ 0" at least formally and that here transitions to neighboring states of the same band remain forbidden. In carrying through the calculation, we shall expressly indicate for what initial assumptions such a formal passage to the limit "angular frequency $\to$ 0" becomes inadmissible.

However, the contradiction is tempered to a certain extent by the fact that even a field which is constant in time effects transitions into higher bands; it is true that this has been noted so far only for strong external fields (Zener effect, §7). More recently it has been found, however, that these transitions into higher bands play a role in certain problems even for weak constant fields. [See D. Pfirsch and E. Spenke, *Z. Physik*, 137: 309 (1954).]

[2] Here a comparison of the angular frequency ω of the alternating field with the angular frequency $E_{CV}/\hbar$ pertaining to the transition "conduction band $\to$ valence band" may be more appropriate.

for transitions within the same band even for an alternating field in satisfactory manner, so that in the limit $\omega \to 0$ this probability for transitions within the same band dominates and the probability of transitions into the next higher band becomes of minor importance.

After these preliminary remarks, we reproduce the description of the action of an electromagnetic alternating field on an electron in a crystal which is now customary.[1] The electromagnetic field strengths $\mathbf{E}$ and $\mathbf{H}$ are derived from a vector potential[2]

$$\left.\begin{aligned} \mathbf{A} &= \{A_x, 0, 0\} \\ A_x &= -\frac{cF}{\omega\epsilon} \sin\frac{\omega}{c}(y - ct) \end{aligned}\right\} \qquad \text{(VII.8.02)}$$

with the aid of the equations

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \qquad \text{(VII.8.03)}$$

$$\mathbf{H} = \operatorname{curl} \mathbf{A} \qquad \text{(VII.8.04)}$$

The quantity F has here the meaning of a force amplitude, since $\mathbf{E}$ and $\mathbf{H}$ take the form

$$\mathbf{E} = \{E_x, 0, 0\}$$

with $$E_x = -\frac{1}{e}F \cos\frac{\omega}{c}(y - ct) \qquad \text{(VII.8.05)}$$

and $$\mathbf{H} = \{0, 0, H_z\}$$

with $$H_z = +\frac{1}{e}F \cos\frac{\omega}{c}(y - ct) \qquad \text{(VII.8.06)}$$

In the presence of a vector potential $\mathbf{A}$, the Schrödinger equation becomes[3]

$$-\frac{\hbar^2}{2m}\Delta\psi - eU(\mathbf{r})\cdot\psi - j\frac{e\hbar}{mc}\mathbf{A}\cdot\operatorname{grad}\psi = +j\hbar\frac{\partial}{\partial t}\psi \qquad \text{(VII.8.07)}$$

[1] See, e.g., Fröhlich, *op. cit.*, pp. 354 and 355.

[2] For simplicity, we have here assumed a crystal with $\varepsilon = 1$ and $\mu = 1$. Otherwise, a refractive index $n = \sqrt{\varepsilon\mu}$ would have to be introduced in (VII.8.02)

$$A_x = -\frac{cF}{\omega\epsilon}\sin\omega\cdot\frac{n}{c}\left(y - \frac{c}{n}t\right)$$

and (VII.8.04) would have to take the form $\mu\mathbf{H} = \operatorname{curl}\mathbf{A}$. Incidentally, c = velocity of light $= 3 \cdot 10^{10}$ cm-sec^{-1}.

[3] See, e.g., Weizel, *op. cit.*, vol. II, p. 881, Eq. (24).

or specifically for (VII.8.02)

$$-\frac{\hbar^2}{2m}\Delta\psi - eU(\mathbf{r})\psi + \frac{F\cdot\hbar}{2m\omega}\left[e^{+j\frac{\omega}{c}(y-ct)} - e^{-j\frac{\omega}{c}(y-ct)}\right]\frac{\partial}{\partial x}\psi = +j\hbar\frac{\partial}{\partial t}\psi \tag{VII.8.08}$$

To obtain a solution we write

$$\psi(\mathbf{r}, t) = \sum_l c_l(t)\psi_l(\mathbf{r}, t) \tag{VII.8.09}$$

where the $\psi_l(\mathbf{r}, t) = \psi_l(\mathbf{r})\, e^{-jE_l t/\hbar}$ are all the solutions (for all bands) of the unperturbed equation, i.e., of (VII.8.08) for $F = 0$. These solutions are periodic in space, with the fundamental domain of the crystal as period. The formula (VII.8.09) can hence represent a solution of the perturbed problem (VII.8.08) with $F \neq 0$ only if this solution is also periodic in the fundamental domain. However, for $\omega \to 0$ the perturbation term takes the form

$$+ j\frac{F\hbar}{mc}(y - ct)\frac{\partial}{\partial x}\psi$$

and ceases to be periodic. Under these circumstances the solution $\psi(\mathbf{r}, t)$ also cannot be periodic in space with a period constant in time, i.e., in a fixed fundamental domain. Hence the formula (VII.8.09), which is periodic in space, can no longer represent $\psi(\mathbf{r}, t)$.[1] Thus, with the formulation (VII.8.09) we renounce even now the possibility of a meaningful transition to the limit $\omega \to 0$.

Substitution of (VII.8.09) in (VII.8.08) and utilization of the fact that the $\psi_l(\mathbf{r}, t)$ satisfy the unperturbed equation [i.e., (VII.8.08) with $F = 0$] lead to

$$+\frac{F\hbar}{2m\omega}\sum_l c_l(t)\left[e^{+j\frac{\omega}{c}(y-ct)} - e^{-j\frac{\omega}{c}(y-ct)}\right]\frac{\partial}{\partial x}\psi_l = j\hbar\sum_l \dot{c}_l(t)\psi_l \tag{VII.8.10}$$

To determine the infinite number of unknown coefficients $c_l(t)$, we multiply from the left with $\psi_n^*(\mathbf{r}, t)$ and integrate over the fundamental domain. In view of the orthogonality of the $\psi_n(\mathbf{r})$, $\psi_l(\mathbf{r})$ we then

[1] The case of the free electron acted upon by an external field F, which is treated at the beginning of §6, is apparently an example to the contrary. Here also the Schrödinger equation (VII.6.06) contains an aperiodic term. Nevertheless, the verified solution (VII.6.07) is periodic at every instant of time t. However, this opposing example is not valid since the period is time dependent, whereas, as emphasized above, (VII.8.09) has the fundamental domain as a fixed, invariable period at all times.

obtain

$$\int_{V_{\text{fund}}} \psi_n^* \psi_l \, dV = \delta_{nl} = \begin{cases} 1 & \text{for } n = l \\ 0 & \text{for } n \neq l \end{cases} \quad \text{(VII.8.11)}$$

$$+ \frac{1}{j} \frac{F}{2m\omega} \sum_l c_l(t) \cdot \int_{V_{\text{fund}}} \psi_n^*(\mathbf{r}, t) \left[e^{+j\frac{\omega}{c}(y-ct)} - e^{-j\frac{\omega}{c}(y-ct)} \right] \frac{\partial}{\partial x} \psi_l(\mathbf{r}, t) \, dV$$

$$= \sum_l \dot{c}_l(t) \, \delta_{nl} \quad \text{(VII.8.12)}$$

On the right side of (VII.8.12), we utilize (VII.8.11). On the left side we place the time factors, which are constant in space, ahead of the integral and obtain

$$+ \frac{F}{2m\hbar\omega} \sum_l c_l(t) \cdot \left[e^{-\frac{j}{\hbar}(E_l - E_n + \hbar\omega)t} \cdot \int_{V_{\text{fund}}} \psi_n^*(\mathbf{r}) \, e^{+j\frac{\omega}{c}y} \cdot \frac{\hbar}{j} \frac{\partial}{\partial x} \psi_l(\mathbf{r}) \, dV \right.$$

$$\left. - e^{-\frac{j}{\hbar}(E_l - E_n - \hbar\omega)t} \cdot \int_{V_{\text{fund}}} \psi_n^*(\mathbf{r}) \, e^{-j\frac{\omega}{c}y} \cdot \frac{\hbar}{j} \frac{\partial}{\partial x} \psi_l(\mathbf{r}) \, dV \right] = \dot{c}_n(t) \quad \text{(VII.8.13)}$$

If we proceed from an initial state in which only one particular state $l = s$ is occupied, we must set for $t = 0$

$$c_l(0) = \begin{cases} 1 & \text{for } l = s \\ 0 & \text{for } l \neq s \end{cases}$$

As long as $c_s \approx 1$ and $c_{l \neq s}(t) \ll 1$, we can then write by way of approximation[1]

$$+ \frac{F}{2m\hbar\omega} \cdot \left[\pi_{ns}^{(+)} \cdot e^{-\frac{j}{\hbar}(E_s - E_n + \hbar\omega)t} - \pi_{ns}^{(-)} \cdot e^{-\frac{j}{\hbar}(E_s - E_n - \hbar\omega)t} \right] = \dot{c}_n(t) \quad \text{(VII.8.14)}$$

where we have used the abbreviations

$$\left. \begin{aligned} \pi_{ns}^{(+)} &= \int_{V_{\text{fund}}} \psi_n^*(\mathbf{r}) \, e^{+j\frac{\omega}{c}y} \frac{\hbar}{j} \frac{\partial}{\partial x} \psi_s(\mathbf{r}) \, dV \\ \pi_{ns}^{(-)} &= \int_{V_{\text{fund}}} \psi_n^*(\mathbf{r}) \, e^{-j\frac{\omega}{c}y} \frac{\hbar}{j} \frac{\partial}{\partial x} \psi_s(\mathbf{r}) \, dV \end{aligned} \right\} \quad \text{(VII.8.15)}$$

[1] These assumptions are certainly fulfilled for a while at the beginning of the process. The "smallness of the perturbation" remains valid longer in proportion as the force amplitude F is smaller.

Carrying out the integration with respect to the time then yields

$$c_n(t) = \frac{F}{2m\hbar\omega}\left[\pi_{ns}^{(+)}\frac{e^{-\frac{j}{\hbar}(E_s-E_n+\hbar\omega)t}-1}{-\frac{j}{\hbar}(E_s-E_n+\hbar\omega)}\right.$$

$$\left. - \pi_{ns}^{(-)}\frac{e^{-\frac{j}{\hbar}(E_s-E_n-\hbar\omega)t}-1}{-\frac{j}{\hbar}(E_s-E_n-\hbar\omega)}\right]$$

$$= \frac{F}{2m\hbar\omega}\left[\pi_{ns}^{(+)}\cdot\frac{e^{-j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)t}-e^{+j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)t}}{-2j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)}\cdot e^{-j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)t}\right.$$

$$\left. - \pi_{ns}^{(-)}\cdot\frac{e^{-j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)t}-e^{+j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)t}}{-2j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)}\cdot e^{-j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)t}\right]$$

$$= \frac{F}{2m\hbar\omega}\left[\pi_{ns}^{(+)}\cdot\frac{\sin\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)t}{\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)}\cdot e^{-j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}+\omega\right)t}\right.$$

$$\left. - \pi_{ns}^{(-)}\cdot\frac{\sin\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)t}{\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)}\cdot e^{-j\frac{1}{2}\left(\frac{E_s-E_n}{\hbar}-\omega\right)t}\right]$$

$$c_n(t) = \frac{F}{2m\hbar\omega}\left[\pi_{ns}^{(+)}\frac{\sin\frac{1}{2}\left(\omega-\frac{E_n-E_s}{\hbar}\right)t}{\frac{1}{2}\left(\omega-\frac{E_n-E_s}{\hbar}\right)}\cdot e^{-j\frac{1}{2}\left(\omega-\frac{E_n-E_s}{\hbar}\right)t}\right.$$

$$\left. - \pi_{ns}^{(-)}\cdot\frac{\sin\frac{1}{2}\left(\omega+\frac{E_n-E_s}{\hbar}\right)t}{\frac{1}{2}\left(\omega+\frac{E_n-E_s}{\hbar}\right)}\cdot e^{+j\frac{1}{2}\left(\omega+\frac{E_n-E_s}{\hbar}\right)t}\right] \quad \text{(VII.8.16)}$$

We shall now compare the absolute value of the two terms in the brackets. The exponentials in the two terms are immaterial in this respect since their exponent is imaginary, so that they are simply phase factors with absolute value 1. We consider below an absorption process in which the energy E_n of the electron after the process is greater than that before the process (E_s)

$$E_n > E_s \quad \text{(VII.8.17)}$$

and write

$$\omega = \frac{E_n - E_s}{\hbar} + \delta\omega = \omega_{ns} + \delta\omega \qquad \text{(VII.8.18)}$$

Then the time factor of the first term in brackets is

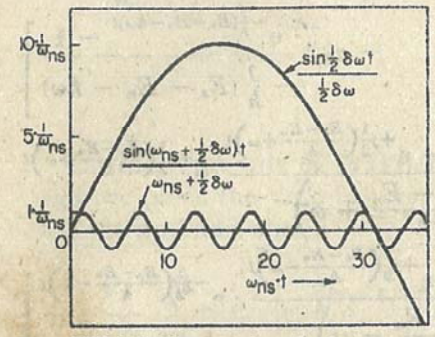

FIG. VII.8.1. Concerning the interpretation of Eq. (VII.8.16).

$$\frac{\sin \tfrac{1}{2}\delta\omega \cdot t}{\tfrac{1}{2}\delta\omega}$$

and that of the second term in brackets is

$$\frac{\sin\,(\omega_{ns} + \tfrac{1}{2}\delta\omega)t}{\omega_{ns} + \tfrac{1}{2}\delta\omega}$$

Figure VII.8.1 shows the time variation of the two factors for $\delta\omega = \omega_{ns}/5$. Both factors increase initially in proportion to t. After a short time the second factor bends over, whereas the first factor rises to much higher values. Hence we can neglect the second term in (VII.8.16) and obtain for the probability of occupation of the state n after a time t

$$|c_n(t)|^2 = \left(\frac{F}{2m\hbar\omega}\right)^2 (\pi_{ns}^{(+)})^2 \left[\frac{\sin \tfrac{1}{2}(\omega - \omega_{ns})t}{\tfrac{1}{2}(\omega - \omega_{ns})}\right]^2 \qquad \text{(VII.8.19)}$$

Furthermore, we see from Fig. VII.8.1 that the time factor in (VII.8.19) attains increasingly high values as ω approaches

$$\omega_{ns} = \frac{E_n - E_s}{\hbar}$$

i.e., as the law of conservation of energy

$$E_n = E_s + \hbar\omega \qquad \text{(VII.8.20)}$$

Final energy of the electron = initial energy of the electron
+ energy of the light quantum

is more nearly satisfied. Apart from the fulfillment of the law of conservation of energy, we also demand a relation concerning the momentum. This follows from the factor $(\pi_{ns}^{(+)})^2$ in (VII.8.19). From (VII.8.15), we have

$$\pi_{ns}^{(+)} = \int_{V_{\text{fund}}} \psi_n^*(\mathbf{r})\, e^{+i\frac{\omega}{c}\nu} \frac{\hbar}{j}\frac{\partial}{\partial x}\psi_s(\mathbf{r})\, dV \qquad \text{(VII.8.15)}$$

If we substitute the form $u(\mathbf{r};\mathbf{k})\,e^{j\mathbf{k}\cdot\mathbf{r}}$ for the eigenfunction $\psi(\mathbf{r})$ of the electron in the crystal, we obtain

$$\pi_{ns}^{(+)} = \hbar \int_{V_{\text{fund}}} u^*(\mathbf{r};\mathbf{k}_n)\left(k_{sx}u(\mathbf{r};\mathbf{k}_s) - j\frac{\partial}{\partial x}u(\mathbf{r};\mathbf{k}_s)\right) e^{j(\mathbf{k}_{\text{field}}+\mathbf{k}_s-\mathbf{k}_n)\cdot\mathbf{r}}\,dV \tag{VII.8.21}$$

Here

$$\mathbf{k}_{\text{field}} = \left\{0, \frac{\omega}{c}, 0\right\} \tag{VII.8.22}$$

is the wave vector of the electromagnetic wave propagated in the y direction, so that $\mathbf{k}_{\text{field}}\cdot\mathbf{r} = (\omega/c)y$.

Since the modulation factors $u(\mathbf{r};\mathbf{k})$ have lattice periodicity, this is true also of their derivatives. Hence the entire factor in the integrand ahead of the exponential also has lattice periodicity. If now the fundamental domain is so chosen that its edges are integer multiples of the wavelength of the electromagnetic wave, which is possible in view of the arbitrary choice of the fundamental domain, the exponential factor in the integrand is periodic in the fundamental domain and the theorem of Appendix I may be applied. Hence the integral $\pi_{ns}^{(+)}$ and, with it, the transition probability from state s to state n vanish completely unless the exponent

$$\mathbf{k}_{\text{field}} + \mathbf{k}_s - \mathbf{k}_n = 0 \tag{VII.8.23}$$

This means that the crystal momentum $\hbar\mathbf{k}$ of the electron after the absorption process is equal to the sum of the momentum of the light quantum $\hbar\mathbf{k}_{\text{field}}$ and of the crystal momentum of the electron before the absorption process:

$$\hbar\mathbf{k}_n = \hbar\mathbf{k}_{\text{field}} + \hbar\mathbf{k}_s \tag{VII.8.24}$$

Thus the law of conservation of momentum (VII.8.23) or (VII.8.24) must be satisfied in addition to the law of conservation of energy (VII.8.20).

For an emission process we have $E_n < E_s$. Then the second term in the brackets of (VII.8.16) is the critical term. The law of conservation of energy takes the form

$$E_n = E_s - \hbar\omega$$

Final energy of electron = initial energy of electron
− energy of emitted light quantum

An examination of the coefficient $\pi_{ns}^{(-)}$ yields the law of conservation of momentum

$$\hbar \mathbf{k}_n = \hbar \mathbf{k}_e - \hbar \mathbf{k}_{\text{field}}$$

Final value of crystal momentum
= initial value of crystal momentum
− momentum of emitted light quantum

If the electromagnetic wave is a light wave, the wave number $\mathbf{k}_{\text{field}}$ is of the order of 10^5 cm^{-1} since the wavelength is of the order of 10^{-5} cm. Compared with the range $2\pi/a \approx 2 \cdot 10^8$ cm^{-1} of the wave number $\mathbf{k}$ of the electron in the crystal, the change in the electron wave vector $\mathbf{k}$ by the light wave vector $\mathbf{k}_{\text{field}}$ is thus very slight.[1] If the transition of the electron would take place between two states of the same band, this would be a transition between closely adjoining states, and the laws of conservation of energy and momentum, (VII.8.20) and (VII.8.24), respectively, could be written in the form

$$\Delta E = \hbar\omega$$
$$\hbar|\Delta \mathbf{k}| = \hbar \cdot |\mathbf{k}_{\text{field}}| = \hbar \frac{\omega}{c}$$

Division of the first equation by the second

$$\frac{1}{\hbar} |\text{grad}_{\mathbf{k}} E| = c$$

and application of Eq. (VII.5.10) lead to the value of the electron velocity $\mathbf{v}$

$$|\mathbf{v}| = c$$

Thus the velocity of the electron in the two closely adjoining states, between which a transition would be effected by collision with a light quantum, would have to be equal to the velocity of light c. In fact, the electrons are much slower than this,[2] both in metals and in semiconductors [see Eqs. (VIII.4.09) and (VIII.4.27)]. For these slow electrons a collision with a light quantum cannot possibly lead to a transition to a neighboring state in the same band; instead, in an optical absorption process, the electron must pass over into another band effectively with conservation of its wave vector.

This theorem is of great importance in the theory of crystalline phosphors. Here we are concerned with an understanding of the experimentally established fact that an electron raised by the absorption of a light quantum from the valence band into the conduction

[1] This does not apply for the absorption of X-rays in view of their short wavelength.

[2] Apart from this the, simple Schrödinger equation employed in the discussion up to now would not be adequate for electron velocities of the order of that of light. All relations which have been derived would have to be modified relativistically.

band cannot simply return to the valence band with the emission of light.

This impossibility is made plausible by the fact that the requirement of conservation of the wave vector **k** permits only a single state of the valence band to serve as final state for the transition. It is extremely improbable that just this state is unoccupied. The combination of the two requirements for an emission process, namely, (1) final state unoccupied and (2) conservation of the **k** vector, makes an emission process in the ideal crystal practically impossible. The theory of crystal phosphors concludes from these considerations that optical emission processes in these solids are tied to the presence of defects in the ideal lattice. However, we cannot enter into details on this point.[1]

§9. The Influence of Atomic Imperfections and of Thermal Lattice Vibrations on the Motion of an Electron in a Crystal

a. Four Different Types of Deviations from Ideal Lattice Periodicity

In our past discussions, exact lattice periodicity was assumed for the potential energy of an electron in a crystal. This assumption applies only for an ideal occupancy of the lattice sites in the crystal under consideration. In real crystals, such an ideal occupation of lattice sites is out of question. We must expect vacancies at lattice sites and occupation of interstitial sites as well as the substitution of foreign atoms for lattice atoms. We have discussed such atomic imperfections[2] or lattice defects in greater detail in Chap. II.

Apart from these atomic imperfections, we find in a real crystal so-called structural defects, such as mosaic structures and dislocations. Furthermore, a material may frequently be available only in polycrystalline form. Then the complete crystal is traversed by an infinite number of crystallite boundaries.

We must also note that, apart from these perturbations of ideal lattice periodicity which are constant in time, the atoms, ions, or molecules composing the crystal vibrate about their positions of rest

[1] See, e.g., N. Riehl and M. Schön, *Z. Physik*, 114: 682 (1939), in particular p. 687; or N. Riehl, "Physik und technische Anwendung der Lumineszenz," pp. 103ff, Springer-Verlag OHG, Berlin, 1940.

[2] With regard to the concepts of dislocations and lattice defects see, e.g., H. G. F. Winkler, "Struktur und Eigenschaften der Krystalle," Springer-Verlag OHG, Berlin, 1950.

with an amplitude depending on the temperature of the crystal. These thermal lattice vibrations also have a strong influence on the motion of the electron in the crystal.

Of the deviations from ideal lattice periodicity which have been named, the first and the last have been investigated more closely with respect to their effects on the motion of an electron in a crystal. However, we shall not report here on the results obtained, much less give their derivation. These matters are too complicated for that, at least for this introductory treatment. We are rather concerned with clarifying the concepts which are commonly employed in this connection, such as the collision mean free time τ, the mean free path l, and the electron mobility μ.

These concepts originated in the classical electron theory of Riecke, Drude, and H. A. Lorentz at the beginning of this century and were carried over into the modern electron theory, which was developed on a wave-mechanical basis around 1930. In this process, the concepts in question lost much of their original graphic meaning. Hence an outline of the original classical reasoning seems necessary just for an understanding of the terminology used. After this, we shall indicate the concrete meaning of the collision time τ, the mean free path l, and the electron mobility μ from the presently accepted quantum-mechanical point of view.

b. Collision Time τ, Mean Free Path l, Electron Mobility μ, and Conductivity σ in Classical Electron Theory

The classical electron theory of metals proceeds from the hypothesis that, in a metal, many electrons—of the order of 1 per atom—are so freely mobile that they behave like a classical Maxwell-Boltzmann gas. Thus, a particular electron moves with uniform velocity $\mathbf{v}_1$ through the lattice until it suffers, after a time τ_{tr_1}, a collision and hence changes its velocity abruptly into $\mathbf{v}_2$.[1]

The electron retains this new velocity for a time interval τ_{tr_2}, up to the next collision, at which the velocity is changed to $\mathbf{v}_3$, etc. We now make the crude simplifying assumption

$$\tau_{tr_1} = \tau_{tr_2} = \tau_{tr_3} = \cdots = \tau_{tr} = \text{collision time}^2 \quad \text{(VII.9.01)}$$

[1] The lattice atoms and the remaining electrons were naturally regarded as collision partners. We shall see later, on p. 250, what difficulties arose herefrom.

[2] This unfortunately widely accepted designation is not very apt. After all, we are concerned with the time which elapses between two collisions and not with the duration of a collision itself. A designation such as "free time of flight" or "mean free time" appears more appropriate in view of its parallelism with "mean free path."

Furthermore, only the direction, but not the magnitude, of the velocity will be assumed to be changed in a collision:

$$|\mathbf{v}_1| = |\mathbf{v}_2| = |\mathbf{v}_3| = \cdots = v_{th} \qquad \text{(VII.9.02)}$$

Then, between two successive collisions, the electron always travels the distance

$$\tau_{tr} \cdot v_{th} = l = \text{mean free path} \qquad \text{(VII.9.03)}$$

Figure VII.9.1 shows the path of an electron under these circumstances.

So far, we have assumed the absence of external forces. We now imagine a voltage applied to the crystal, so that an electrostatic field $\mathbf{E}$ exists within the crystal. This exerts a force $\mathbf{F} = -e\mathbf{E}$ on the electron.

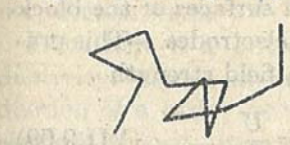

FIG. VII.9.1.

Every one of the originally straight paths between two collisions is now distorted into a parabola (see Fig. VII.9.2) since the external force effects an acceleration

$$\dot{\mathbf{v}} = \frac{1}{m}\mathbf{F} = -\frac{e}{m}\mathbf{E} \qquad \text{(VII.9.04)}$$

and hence a velocity increment

$$\mathbf{v}_{incr} = -\frac{e}{m}\mathbf{E}t \qquad \text{(VII.9.05)}$$

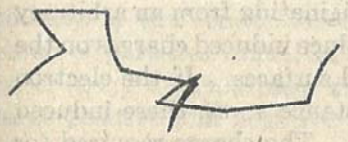

FIG. VII.9.2
Path of an electron with and without external force for the simplifying assumption of constant free path length.

As long as

$$|\mathbf{v}_{incr}| \ll v \qquad \text{(VII.9.06)}$$

during the entire time between two collisions, there is practically no change in the collision time τ_{tr} and the velocity increment (VII.9.05) increases in a single free flight from 0 to $(e/m)\mathbf{E}\tau_{tr}$. Its mean value is hence

$$\mathbf{v}_{incr} = -\frac{1}{2}\frac{e}{m}\mathbf{E}\tau_{tr} = -\mu\mathbf{E} \qquad \text{(VII.9.07)}$$

The proportionality factor

$$\left.\begin{aligned} \mu &= \frac{e}{m}\tau \qquad \text{with}^1\ \tau = \tfrac{1}{2}\tau_{tr} \\ \text{or} \quad \left(\frac{\mu}{\text{cm}^2/\text{volt-sec}}\right) &= 1.76 \cdot 10^{15}\left(\frac{\tau}{\text{sec}}\right) \end{aligned}\right\} \qquad \text{(VII.9.08)}$$

[1] The "mean" collision time τ would thus be equal to half the arithmetic mean value of the individual collision times $\tau_{tr_1}, \tau_{tr_2}, \tau_{tr_3}, \ldots \tau_{tr_n}$. The factor $\frac{1}{2}$ obtained in this crude consideration must not be taken too seriously, however. In actuality, much more complex averaging processes lead finally to a mean col-

is called the electron mobility. The reason for this will become plainer presently, on page 248. Its dimension cm²/(volt-sec) follows from the ratio of velocity cm-sec^{-1} and field strength volt-cm^{-1}.

We might be satisfied with this digression into classical electron theory. However, for much that follows it will be advantageous to proceed on this classical basis to the conductivity formula.

To this end we shall make our notions somewhat more concrete (see Fig. VII.9.3). Let the crystal volume under consideration be a block with a cross section Q and a length L. A voltage U is applied by a battery and an external metallic circuit to the end surfaces of the block by means of large surface electrodes. This produces within the crystal a field strength

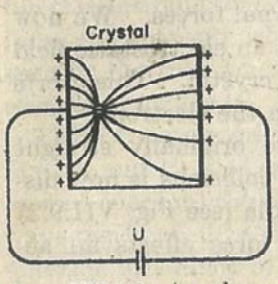

FIG. VII.9.3. An electron and the charges induced by it on the electrodes of the crystal. These induced charges change with a displacement of the electron and a corresponding current occurs in the external circuit.

$$\mathbf{E} = \frac{U}{L} \qquad \text{(VII.9.09)}$$

The lines of force originating from an arbitrary selected electron produce induced charges on the electrodes at the end surfaces. If the electron is displaced by a distance $\mathbf{v} \cdot dt$, these induced charges are changed. The charge required for this is supplied or withdrawn by the metallic circuit. Thus, for every motion $\mathbf{v}$ of a single selected electron there exists a current I_{single} in the external circuit. Its magnitude follows simply from the law of conservation of energy. The field $\mathbf{E}$ within the crystal does an amount of work

$$\mathbf{v} \cdot \mathbf{F} \cdot dt = -e\mathbf{v} \cdot \mathbf{E} \cdot dt \qquad \text{(VII.9.10)}$$

on the electron in question and thus increases, e.g., the kinetic energy of the electron. This energy must ultimately be supplied by the battery, from which the energy $U \cdot I_{\text{single}} \cdot dt$ is withdrawn for a current I_{single} in a time dt. Hence we must have

$$-e\mathbf{v} \cdot \mathbf{E} \cdot dt = U \cdot I_{\text{single}} \cdot dt \qquad \text{(VII.9.11)}$$

and hence

$$I_{\text{single}} = -e \cdot \mathbf{v} \cdot \frac{\mathbf{E}}{U} \qquad \text{(VII.9.12)}$$

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lision time τ, and this involves many modifications in numerical factors. For the sketchy considerations which follow, it is sufficient to identify τ simply with the arithmetic mean value τ_{tr}.

For the simple geometry assumed we have, according to (VII.9.09),

$$I_{\text{single}} = -ev_x \cdot \frac{1}{L}$$

if the x direction corresponds to the longitudinal dimension of the crystal. The mean current density referred to the cross section Q of the crystal is

$$i_{\text{single}} = -ev_x \frac{1}{L}\frac{1}{Q} = -\frac{e}{V} v_x \qquad \text{(VII.9.13)}$$

Herewith Eq. (VII.5.13) found on page 208 has been derived on a corpuscular basis.

From here it is but a short step to the basic formula for the conductivity. Since all the conduction electrons contribute to the conduction of a body, we shall—at least for this digression into classical electron theory—pass briefly beyond the bounds established by the "behavior of the single electron" even for this §9 and deal with the totality of the conduction electrons. The electron gas represents a cloud of particles which, in the absence of an external field, pass each other along the rectilinear zigzag paths of Fig. VII.9.1. Here equally large positive and negative x components of the velocity are, on the average, equally frequent so that the current contributions (VII.9.13) of the individual electrons cancel each other on the average. Hence there is no current. However, if an external field is applied, the zigzag paths are made up of parabolic arcs as in Fig. VII.9.2. According to Eq. (VII.9.07) every particle receives on the average a velocity increment $-\mu\mathbf{E}$, and since this average velocity increment is the same for all particles of the cloud, the cloud as a whole drifts slowly with the common drift velocity

$$\mathbf{v}_{\text{drift}} = -\mu\mathbf{E} \qquad \text{(VII.9.07)}$$

The contributions (VII.9.13) of the individual electrons no longer cancel, but add to lead to a total current density

$$\mathbf{i} = N \cdot \left(-\frac{e}{V}\right) \cdot \mathbf{v}_{\text{drift}} = \left(-e\frac{N}{V}\right) \cdot (-\mu\mathbf{E})$$

Introducing the concentration of the electrons

$$n = \frac{N}{V}$$

we obtain

$$\mathbf{i} = e\mu n\mathbf{E} \qquad \text{(VII.9.14)}$$

Comparison with Ohm's law

$$\mathbf{i} = \sigma \cdot \mathbf{E}$$

leads to an expression for the conductivity σ

$$\sigma = e\mu n$$

$$\text{or} \quad \left(\frac{\sigma}{\text{ohm}^{-1}\,\text{cm}^{-1}}\right) = 1.6 \cdot 10^{-19} \left(\frac{\mu}{\text{cm}^2/\text{volt-sec}}\right) \cdot \left(\frac{n}{\text{cm}^{-3}}\right) \quad \text{(VII.9.15)}$$

The meaning of the designation "mobility" for the proportionality factor μ becomes here particularly plain, since (VII.9.15) shows that the conductivity σ of the crystal increases with the "mobility" of the n conduction electrons of the crystal. For the concentration n of the conduction electrons in metals we may in general substitute the number of valence electrons, i.e., approximately $4 \cdot 10^{22}$ cm^{-3}, which corresponds to 1 per atom. For a metallic conductivity of about $4 \cdot 10^{5}$ ohm^{-1} cm^{-1}, we then obtain a mobility[1] $\mu \approx 60$ cm^2 volt^{-1} sec^{-1}. For this mobility Eq. (VII.9.08) yields a collision time $\tau = 3.6 \cdot 10^{-14}$ sec and (VII.9.03) a mean free path $\tau_{\text{fr}} v_{\text{th}} = 2\tau v_{\text{th}} = 7 \cdot 10^{-6}$ cm if we write for the thermal velocity in metals $v_{\text{th}} = 10^8$ cm sec^{-1}.[2] For a lattice constant $3 \cdot 10^{-8}$ cm, this mean free path is equal to 200 lattice constants! We shall discuss presently, on page 250, the difficulties which arose for the classical theory out of these large values of the mean free path.

The past discussions permit us to check from what field strengths on Ohm's law (VII.9.14) must fail (apart from the deviations which may result at lower field strength from experimental imperfections, such as boundary resistances between individual crystallites). As soon as the drift velocity (VII.9.07) becomes comparable with the thermal velocity v_{th}, the condition (VII.9.06) is violated and the time of free flight of an electron is no longer determined primarily by its initial velocity after its last collision. The simple proportionality (VII.9.04) between mean velocity increment and field strength is then lost, and Ohm's law is no longer valid.

The critical field strength is thus obtained from[3]

$$|\mathbf{v}|_{\text{drift}} = \mu \cdot |\mathbf{E}| \approx v_{\text{th}}$$

$$|\mathbf{E}_{\text{crit}}| \approx \frac{v_{\text{th}}}{\mu} \quad \text{(VII.9.16)}$$

[1] The metallic mobilities lie in fact in the range from 10 to 100 cm^2 volt^{-1} sec^{-1}. See, e.g., F. Seitz, "The Modern Theory of Solids," p. 183, McGraw-Hill Book Company, Inc., New York, 1940.

[2] For this value, see Eq. (VIII.4.09).

[3] The condition $\mu E \ll v_{\text{th}}$ may be multiplied with the concentration n and states then that the particle current density $\mu n E$ in the field must be very small compared with the unidirectional thermal particle current density $v_{\text{th}} \cdot n/\sqrt{6\pi}$. (With regard to the unidirectional thermal current, see p. 82, footnote 1. The factor

We shall make plausible on pages 301 and 307 that we may write for the order of magnitude of the thermal velocity in metals 10^8 cm sec^{-1} (independently of temperature!) and in semiconductors 10^7 cm $sec^{-1}\sqrt{T/300°K}$ (see also page 256).

For the metallic mobilities[1] between 10 and 100 cm^2 $volt^{-1}$ sec^{-1} estimated on page 248, we thus obtain for metals critical field strengths between 10^6 and 10^7 volt cm^{-1}. These are values whose experimental realization is out of question.

For semiconductors and insulators, the range of mobilities is much larger. Thus, for germanium with $\mu = 3.6 \cdot 10^3$ cm^2 $volt^{-1}$ sec^{-1}, the critical field strength at room temperature would be about $3 \cdot 10^3$ volt cm^{-1}. In fact, we observe true deviations from Ohm's law for germanium even at $6 \cdot 10^2$ volt cm^{-1}.[2] Only a much more careful study of the collision processes makes possible an understanding of these phenomena.[3]

Even within the scope of classical theory the past considerations have merely created a formal basis on which a theory might be constructed. In particular, the collision processes must be investigated, and this demands a statement regarding the collision partners. As already mentioned in footnote 1, page 244, from a classical point of view the lattice atoms and the remaining electrons come here primarily into consideration.

In the absence of more precise views regarding the structure of atoms at the time in question (1900–1910), studies of the collisions of electrons with hard, immobile spheres were carried out. For this model the magnitude of the electron velocity after the collision is exactly equal to that before the collision, and for the direction of the electron after the collision every direction is equally probable, regardless of the direction of the electron before the collision.

Thus, in this model, the electron has no "memory of its past before the collision" with respect to its direction. We shall see presently what basic objections can be raised against this collision model. Before this, we shall sketch briefly a consequence of this model, which will be of importance for what follows.

In the calculation of the electrical conductivity to be discussed in §10, we shall have to answer the question how many electrons of a group of uniform velocity and direction are eliminated by collision

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$1/\sqrt{6\pi}$ can be added on the right since we are at any rate dealing only with order-of-magnitude considerations.)

[1] See Seitz, *op. cit.*, p. 183.

[2] E. J. Ryder and W. Shockley, *Phys. Rev.*, **81**: 139 and 140 (1951).

[3] W. Shockley, *Bell System Tech. J.*, **30**: 990 (1951).

processes in a time interval dt. If, on the average, a time τ elapses between two collisions of an electron, dt/τ terminal points of such times fall on the average into the time interval dt. Thus an electron suffers in the interval dt on the average dt/τ collisions, and N electrons suffer $N\,dt/\tau$ collisions. Thus collisions eliminate in an interval dt on the average

$$dN = N \cdot \frac{dt}{\tau} \qquad \text{(VII.9.17)}$$

electrons from a group with uniform velocity and direction. The number N of the electrons of this group with uniform velocity hence decreases exponentially with time:

$$N = N(0)\, e^{-\frac{t}{\tau}} \qquad \text{(VII.9.18)}$$

The mean collision time τ, which was first thought of as the arithmetic mean of a series of times of free flight $\tau_{tr_1}, \tau_{tr_2}, \ldots \tau_{tr_n}$, thus attains the meaning of a relaxation time which controls the decay in time of an electron group of uniform velocity. At a later point (page 252) it will prove very important that the mean collision time τ enters the calculation of the conductivity not as an arithmetic mean of successive free times of flight, but as a relaxation time.

We now turn to the already mentioned basic difficulties which arise for the classical electron theory from the fact that the observed values of the metallic conductivities lead to mean free paths of the order of 10^2 lattice constants,[1] as we have seen on page 248.

Since the classical electron theory had to regard the lattice atoms themselves (as well as the remaining electrons) as collision partners, it became incomprehensible how an electron could fly freely through some hundred closely packed collision partners without suffering a change in direction.[2]

Nothing was changed in this respect when first W. Pauli[3] and then A. Sommerfeld,[4] in 1927, applied Fermi statistics in place of Maxwell-Boltzmann statistics to the gas of the free conduction electrons and were thus able to overcome other basic difficulties of the classical elec-

[1] For germanium, even up to 500 lattice constants.

[2] An effort to evade the difficulty by assuming that the range of interaction of the atoms with their neighbors, which determines lattice binding, is much greater than the effective cross section for high-speed conduction electrons is simply another formulation of a situation which is incomprehensible from a classical standpoint.

[3] W. Pauli, *Z. Physik*, **41**: 81 (1927).

[4] A. Sommerfeld, *Naturwiss.*, **15**: 825 (1927); **16**: 374 (1928).

tron theory.[1] It is true that Sommerfeld demanded even at the end of his first paper: "To perfect the theory it would be necessary to introduce the mean free path in a more physical manner, e.g., in the sense of wave mechanics, by studying the scattering of the de Broglie waves at the lattice of the metal atoms, taking at the same time due account of the thermal agitation of this lattice."

This was accomplished by F. Bloch.[2] It then became clear that an ideal lattice constituted no obstacle whatsoever for electrons of suitable wave number so that the observed mean free paths of hundreds of lattice constants were in no sense incomprehensible. Bloch showed, furthermore, that deviations from exact lattice periodicity constituted the real obstacles to electron motion and considered in this connection thermal lattice vibrations in particular. At a much later date, Conwell and Weisskopf[3] investigated the effect of another type of deviations from lattice periodicity, namely, the scattering of electrons by charged atomic impurities. We shall defer the consideration of the lattice vibrations and consider first impurity scattering. With these spatially defined collision partners, it is of course more nearly possible to establish a relationship with classical notions than for the infinitely extended thermal lattice vibrations.

c. Scattering of an Electron in a Crystal by a Charged Imperfection

It is after all our objective to translate the concepts of collision time τ and mean free path l which have been elucidated on a classical corpuscular basis into present-day wave-mechanical terms. Hence we shall consider impurity scattering first from a classical corpuscular standpoint. The problem is here the same as that of the familiar Rutherford scattering of particles by heavy atomic nuclei. The negative electron, e.g., moves about the positively charged impurity on a hyperbolic path (Fig. VII.9.4) or turns away from a negatively charged impurity along a hyperbolic path (Fig. VII.9.5).

From a mathematical treatment of these circumstances, we obtain the so-called transition probabilities, i.e., the probabilities that an

[1] Pauli explained the temperature independence and weakness of the paramagnetism of the alkali metals, Sommerfeld the absence of a contribution to the specific heat of a solid from the conduction electrons (apart from other results).

[2] F. Bloch, *Z. Physik*, **52**: 555 (1928); **57**: 545 (1929). Shortly before then, Sommerfeld's student W. V. Houston had treated the scattering of electron waves in analogy with Debye scattering of X-rays at thermal density variations in the crystal, see *Z. Physik*, **48**: 449 (1928).

[3] E. Conwell and V. F. Weisskopf, *Phys. Rev.*, **69**: 258 (1946); **77**: 388 (1950).

electron have a velocity v′ after "collision" with the charged impurity, if it had the velocity v before the collision. Once again, we shall not enter into details, but indicate merely that the results for Rutherford scattering are quite different from those for the collision of electrons with hard spheres, where all directions of motion were equally probable after the collision. For Rutherford scattering the electron does not lose its memory of its original direction, but continues to show a definite preference for it. Deviations by small angles are more probable than deviations by large angles. This has an important consequence in the transition from the arithmetic mean value of successive free times of flight to a relaxation time.

If we now define a relaxation time by the decay of a current carried initially by a group of N electrons with uniform velocity and direction, the decay of this current is identical with the decay of the number N

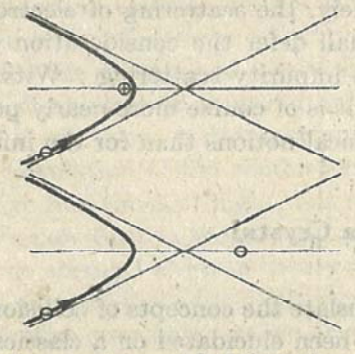

FIG. VII.9.4. The negative electron flies around a positive lattice defect.

FIG. VII.9.5. The negative electron is deflected away from a negative lattice defect.

of the electrons, provided that the collisions blot out memory. In this case, the velocities of the electrons which have been removed from the group by collisions are equally distributed over all directions and do not contribute to the current. However, as soon as the original direction is preferred (or discriminated against) after the collisions, the electrons which have been removed from the group continue to contribute to the current and the current decays more slowly (or more rapidly) than the number N of the electrons which have remained in the group.

We must, therefore, distinguish between the relaxation time of the number N of the electrons of uniform velocity and direction, on the one hand, and the relaxation time of the current carried by them, on the other. The relaxation time of the number N continues to be identical with the arithmetic mean τ of the successive times of free flight. This is not true, however, of the relaxation time of the current contribution when the collisions do not blot out memory, as, e.g., for impurity scattering.

This current relaxation time is of primary importance for the calculation of the conductivity. Even so, it is commonly designated as mean collision time. We see how the simple graphic meaning as an arithmetic mean value of successive free times of flight has gradually evaporated. We see furthermore that, for the calculation of the mean collision time as relaxation time of a current contribution, we are concerned only with the knowledge of certain transition probabilities between a state before the "collision" and the states after the "collision." This is important because the wave-mechanical treatment of scattering processes does not readily lead to the picture of the thermal zigzag path in Fig. VII.9.2.

The scattering of an electron at a charged impurity has also been treated with the aid of the Schrödinger equation for a point charge.[1] This exact treatment on a wave-mechanical basis has given the same values for the transition probabilities as the previously described classical corpuscular treatment with the hyperbolic paths of an electron particle. This is not too surprising since we know from general quantum mechanics that, by the formation of wave packets, we can demonstrate the corpuscular traits of particle behavior in so far as this is consistent with the uncertainty relations. We shall make increasing use of the possibility of representing wave-mechanical results in particle language.

d. Scattering of an Electron in a Crystal by Thermal Lattice Vibrations

Apart from impurity scattering, the thermal vibrations of the lattice components about their positions of rest have claimed the special attention of the modern theory of solids as further obstacles to the motion of an electron in a crystal. The vibrations of the individual lattice components are coupled by the strong forces which lead to the formation of the lattice. Low frequencies among these vibrations can occur only when neighboring lattice components move approximately in phase. We are then dealing with elastic or acoustic vibrations. At high frequencies, neighboring lattice components will vibrate in phase opposition. If the neighbors have opposite electric charge (heteropolar ionic lattices, such as NaCl), such a vibration leads to a high-frequency electric dipole moment and an electromagnetic wave is emitted. We speak, then, of optical vibrations.

The distinction between acoustical and optical vibrations becomes mandatory when a lattice is made up of components of different

[1] W Gordon, *Z. Physik*, **48**: 180 (1928). N. F. Mott, *Proc. Roy. Soc.* (*London*), **A118**: 542 (1928). S. Temple, *Proc. Roy. Soc.* (*London*), **A121**: 673 (1928).

masses. Then the total spectrum of the characteristic oscillations of the crystal splits into several branches. Of these, the acoustical branch embraces the frequencies 0 up to a limiting frequency for which the heavy components alone are in oscillation, whereas the light components are at rest (Fig. VII.9.6). Finally, at the lowest optical frequency the heavy components are at rest and the light ones alone in oscillation.[1] The highest optical frequency is that at which the two sublattices oscillate in opposition without deformation (Fig. VII.9.6).

At a finite temperature, all these oscillations are excited to some degree. The exact lattice periodicity is perturbed. The perturbation potential which is superposed on the lattice potential $U(\mathbf{r})$ is also periodic, with the wavelength of the lattice wave in question as period. The potential energy of the electron depends on its position relative to the wave. Thus the coordinates of the lattice components and the coordinates of the electron enter into the perturbation potential. The perturbation potential couples the lattice wave and the electron wave.

In the treatment of this perturbation problem we find, as for the perturbation of an electron in a crystal by an electromagnetic wave (§8), that an electron with wave vector $\mathbf{k}$ is excited to transitions into another state $\mathbf{k}'$. Just as there, such a transition must satisfy the law of conservation of energy

$$E(\mathbf{k}') = E(\mathbf{k}) \pm \hbar\omega_{\text{lattice}} \qquad \text{(VII.9.19)}$$

and the "law of conservation of momentum"

$$\mathbf{k}' = \mathbf{k} \pm \mathbf{k}_{\text{lattice}} \qquad \text{(VII.9.20)}$$

Equations (VII.9.19) and (VII.9.20) show that the scattering process of an electron by a lattice wave can also be described in corpuscular terms by stating that an electron collides with a "phonon"[2] and absorbs or emits the energy and momentum of a phonon. It is plausible that, again, a mean collision time may be calculated as relaxation time with the aid of computed transition probabilities.

Figure VII.9.6 shows incidentally that the thermal lattice vibrations have wavelengths down to two lattice constants. Hence the wave

[1] In comparing the highest acoustical and the lowest optical oscillations, the distinction between acoustical and optical oscillations, which is still apparent in a comparison of low or median acoustical oscillations with optical oscillations, is thus effaced. For further detail regarding these types of oscillations see, e.g., Weizel, *op. cit.*, vol. II, p. 1385.

[2] See pp. 13 to 14 and Fig. I.2.9.

numbers $2\pi/a$ of these vibrations traverse the same interval $(-\pi/a, +\pi/a)$ as the k numbers of the electron waves [see Eq. (VII.2.08)]. This contrasts sharply with the wave numbers $2\pi/\lambda$ of light waves which, because of the relatively long waves of visible light, are small

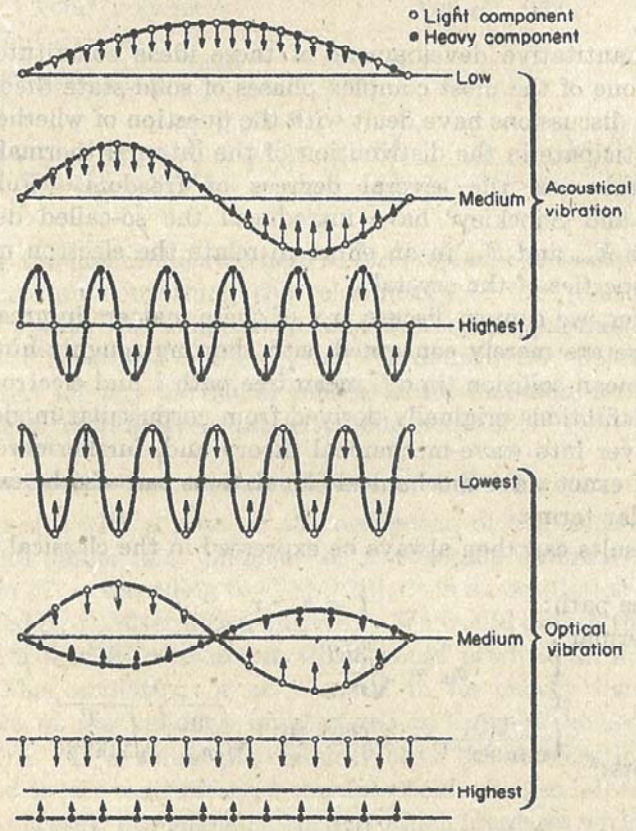

FIG. VII.9.6. Acoustical and optical vibrations of a diatomic lattice. Mass ratio $m_\bullet : m_\circ = 2:1$.

In principle, the heavy masses vibrate with larger amplitude than the light masses for all acoustical vibrations (i.e., also for the low and medium vibrations at the very top). This effect vanishes only for $\lambda = \infty$. For the wavelengths $\lambda = 24\,a$ and $\lambda = 48\,a$ assumed above it can no longer be demonstrated in a drawing, however. Similarly, for the medium optical vibration the amplitude ratio is practically already $-\frac{1}{2}$, though this value is attained exactly only for $\lambda = \infty$. a = equilibrium distance between ○ and ● = half the lattice constant.

compared to π/a. Thus the argument of page 242, which led to the conclusion that collisions with photons could result only in electron transitions into the next higher band with approximate conservation of the k numbers, does not apply for thermal lattice vibrations. In

collisions with phonons, transitions between quantum states of the same band are entirely possible. Transitions into the next higher band, on the other hand, do not occur in general for phonon collisions. The energy of the thermal lattice vibrations does not suffice for this—except in the special case of the intrinsic semiconductor (see pages 16 to 18).

The quantitative development of these ideas constitutes unquestionably one of the most complex phases of solid-state theory. Thus extensive discussions have dealt with the question of whether the electrons participate in the distribution of the internal thermal energy of the crystal over the several degrees of freedom.[1] Furthermore, Bardeen and Shockley[2] have introduced the so-called deformation potentials E_{1n} and E_{1p} in an effort to relate the electron mobility to other properties of the crystal.

However, we cannot discuss any of these matters in greater detail.

Here we are merely concerned with showing roughly how the concepts of mean collision time τ, mean free path l, and electron mobility μ, with definitions originally derived from corpuscular models, can be carried over into wave-mechanical theory and, furthermore, that the results of exact wave-mechanical calculations can also be expressed in corpuscular terms.

The results can then always be expressed in the classical form:

Mean free path:
$$l = v_{th} \cdot \tau \tag{VII.9.21}$$

Mean thermal electron velocity for semiconductors:[3]
$$v_{th} = \sqrt{\frac{3kT}{m_{eff}}}$$
$$\frac{v_{th}}{\text{cm sec}^{-1}} = 1.168 \cdot 10^7 \cdot \sqrt{\frac{m}{m_{eff}}} \cdot \sqrt{\frac{T}{300°\text{K}}} \tag{VII.9.22}$$

Thermal electron velocity for metals[4] (velocity at Fermi level):
$$v_{th} = \left(\frac{3}{8\pi}\right)^{1/3} \frac{h}{m_{eff}} n^{1/3} \quad \text{(independent of temperature)}$$
$$\left(\frac{v_{th}}{\text{cm sec}^{-1}}\right) = 7.71 \cdot 10^7 \left(\frac{m}{m_{eff}}\right) \cdot \left(\frac{n}{10^{22}\ \text{cm}^{-3}}\right)^{1/3} \tag{VII.9.23}$$

[1] The so-called Peierls reversal processes play here an important role. See H. A. Bethe in Geiger and Scheel, *op. cit.*, vol. XXIV, part 2, p. 536.

[2] W. Shockley and J. Bardeen, *Phys. Rev.*, 77: 407 (1950); Shockley, *op. cit.*, pp. 264ff.

[3] For derivation, see Eq. (VIII.4.27).

[4] For derivation, see Eq. (VIII.4.09).

Drift velocity: $$\mathbf{v}_{\text{drift}} = -\mu\mathbf{E} \tag{VII.9.24}$$

Electron mobility:
$$\mu = \frac{e}{m_{\text{eff}}}\tau$$
$$\left(\frac{\mu}{\text{cm}^2/\text{volt-sec}}\right) = 1.76 \cdot 10^{15} \cdot \left(\frac{m}{m_{\text{eff}}}\right) \cdot \left(\frac{\tau}{\text{sec}}\right) \tag{VII.9.25}$$

Mean current density of single electron: $$\mathbf{i}_{\text{single}} = -\frac{e}{V_{\text{fund}}}\mathbf{v}_{\text{drift}} \tag{VII.9.26}$$

Conductivity:
$$\sigma = e\,\mu\,n$$
$$\left(\frac{\sigma}{\text{ohm}^{-1}\,\text{cm}^{-1}}\right) = 1.60 \cdot 10^{-19}\left(\frac{\mu}{\text{cm}^2/\text{volt-sec}}\right) \cdot \left(\frac{n}{\text{cm}^{-3}}\right) \tag{VII.9.27}$$

Carrying the ideas indicated here to their logical conclusion will then give information concerning the relationship of the quantities l, τ, v_{th}, n, and μ with the temperature and the crystal parameters (such as the elastic constants of the crystal, the deformation potentials E_{1n} and E_{1p}, etc.) for any particular model, as for instance, a metal or a semiconductor with a given impurity concentration.

e. Zener's Oscillation and the Mean Free Path

We shall end with a note on the oscillation of the electrons in an energy band under the influence of a constant external force, as described in §7. According to (VII.9.26), such an oscillation would be accompanied by an alternating current. We would obtain the strange result that a field $\mathbf{E}$, constant in time, would produce an alternating current. The oscillation of an electron in its energy band was a consequence of the validity, unrestricted in time, of the acceleration law $\hbar\dot{\mathbf{k}} = \mathbf{F}$. If, according to classical ideas, the acceleration process is permitted to last indefinitely, a constant field will also fail to produce a constant current, but instead a current which increases without limit. In fact, this is prevented by collisions, and similarly, collisions prevent the full development of the Zener oscillations. We have seen in §7, page 230, that the oscillation is not limited to the energy band, but that the electron would also oscillate back and forth in space over a distance $(E_{\text{top}} - E_{\text{bottom}})/(e|\mathbf{E}|)$. For a width of the energy band

$$E_{\text{top}} - E_{\text{bottom}} \approx 1 \text{ ev}$$

and at a field strength of 1 volt cm^{-1} this distance would be 1 cm. Since the mean free paths are of the order of 10^{-5} to 10^{-6} cm, the electron is deflected by collisions long before it can traverse a full cycle of oscillation. Only for field strengths of 10^5 to 10^6 volt cm^{-1} would the oscillation amplitude become smaller than the mean free path so that

the oscillation may take precedence over the disordered thermal motion. However, at these field strengths there is a rapid increase in the probability that the electron leaves its band and passes over into the next band (see §7). Thus, even if such field strengths could be realized experimentally, a constant field would not produce alternating current. Thus we are still left with the form of motion of an electron under the simultaneous influence of a field and of collisions with phonons and impurities which was represented in corpuscular terms in Fig. VII.9.2.

§10. The Transition to the Many-electron Problem and the Calculation of the Conductivity

a. Introduction

Even in the introductory paragraph (page 166) we have pointed out that the transition from the one-electron problem treated in preceding paragraphs to the many-electron problem existing in reality need not involve the construction of suitable many-electron eigenfunctions. For many purposes it suffices to specify how the electrons of the solid body are distributed over the energy states of the one-electron problem, i.e., the quantum states of the band model.

This question is in part answered by the Pauli principle, which states that a quantum state can be occupied by only two electrons, which must have opposite spins. From this it follows that the state of lowest energy, i.e., the normal state, is realized when the electrons of the crystal occupy the system of levels of the band spectrum from the bottom up with just two[1] electrons per state. It is true that this normal state is realized only at absolute zero temperature. At finite temperatures, that macroscopic state will be observed for which the number of microscopic states realizing it is a maximum. The determination of the number of microscopic possibilities of realization and the finding of the macrostate with the maximum number of these possibilities is a problem of statistics. Because of the Pauli principle, an electron ensemble is governed by Fermi statistics. Fermi statistics teach that at finite temperatures there occurs, as compared with the normal state in which the quantum states are occupied from the bottom up with two electrons apiece, a loosening up which is described by the function

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \qquad \text{(VII.10.01)}$$

[1] Two because of the spin!

The function $f(E)$ indicates the probability that a quantum state with energy E is occupied. Figure VII.10.1 shows[1] that practically all states with energies below the "Fermi level" E_F are occupied and practically all states above the Fermi level E_F are unoccupied. The transition takes place within a few multiples of kT (k = Boltzmann constant) and hence becomes discontinuous for $T \to 0$. Quantum states whose

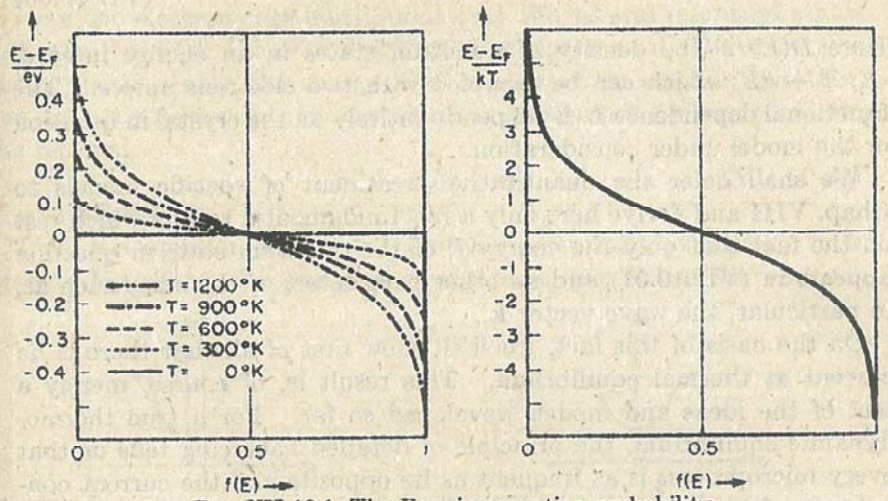

FIG. VII.10.1. The Fermi occupation probability

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

energy coincides with the Fermi level E_F are just half occupied and half unoccupied, since

$$f(E_F) = \frac{1}{e^0 + 1} = \frac{1}{1+1} = \frac{1}{2} \qquad \text{(VII.10.02)}$$

The position and the temperature dependence[2] of the Fermi level E_F depend on the distribution of the quantum states along the energy

[1] In graphic representations of the function $f(E)$, the energy E is commonly plotted as abscissa and $f(E)$ as ordinate. Since, however, in a later application of $f(E)$ in an energy-level diagram the energy is always plotted on the vertical axis, the same was done in the present representation of $f(E)$. We thus arrive directly at the horizontal Fermi level E_F, which will later become of great importance.

[2] The difference $E - E_F$ has been plotted instead of the energy E on the ordinate scale of the left graph of Fig. VII.10.1. This representation should not mislead us into thinking that the Fermi level is independent of temperature. It is true that this is approximately, but not strictly, so for metals. For semiconductors the Fermi level normally depends strongly on temperature.

scale, since E_F is determined by the requirement that the total number of electrons to be accommodated is fixed, e.g., equal to N:

$$2\int_{E=-\infty}^{E=\infty} D(E)\cdot f(E)\cdot dE = 2\int_{E=-\infty}^{E=\infty} D(E)\,\frac{1}{e^{\frac{E-E_F}{kT}}+1}\,dE = N \tag{VII.10.03}$$

Here $D(E)$ is the density of quantum states in an energy interval $(E, E + dE)$ which can be occupied with two electrons apiece. The functional dependence $D(E)$ depends entirely on the crystal in question or the model under consideration.

We shall defer the quantitative treatment of specific models to Chap. VIII and derive here only a few fundamental results which rest on the fact that only the energy E of the quantum state in question appears in (VII.10.01) and no other parameters of the state such as, in particular, the wave vector **k**.

On the basis of this fact, we shall show first of all that there is no current at thermal equilibrium. This result is, of course, merely a test of the ideas and models developed so far. For a true thermodynamic equilibrium, the principle of detailed balancing tells us that every microprocess is as frequent as its opposite and the current contribution from any one electron is balanced by an electron moving in the opposite direction. Hence, if the models and ideas developed so far would lead to a current even at thermal equilibrium, this would prove only the incorrectness of these models and ideas.

We then proceed to a brief consideration of fluctuations about the state of equilibrium and obtain thus a first proof that a crystal with only fully occupied bands must be an insulator.

We obtain two further proofs for this statement as we leave, subsequently, the study of the state of thermal equilibrium and consider the totality of the electrons under the influence of an external field. In this instance there may be a net current; it may be calculated in two ways.

First, the current contributions of the individual electrons may be summed. Second, the distribution of the electrons over the quantum states of the crystal in **k** space may be considered. For thermal equilibrium, this is centrally symmetric. An external force distorts it asymmetrically. This distortion results, in general, in a current.

Both methods yield the current zero for a fully occupied band and thus provide the two proofs mentioned regarding the dropping out of a fully occupied band with respect to the conductivity. We apply

the first method also to a partly occupied band. It yields then the relation for the conductivity which was already obtained in Eq. (VII.9.27) on the basis of classical electron theory:

$$\sigma = e\mu n$$

b. Thermal Equilibrium

Here the electrons are distributed over the several quantum states in accord with the Fermi probability of occupation (VII.10.01). The latter contains only the energy E of the quantum state in question, not its wave vector $\mathbf{k}$. It may now be shown that for every crystal the relation

$$E(\mathbf{k}) = E(-\mathbf{k}) \qquad \text{(VII.10.04)}$$

must be satisfied.

Thus the function $E(\mathbf{k})$ must always be centrally symmetric in $\mathbf{k}$ space. Hence, in the one-dimensional example, it cannot vary as

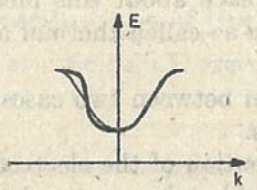

FIG. VII.10.2. Asymmetric $E(k)$-variation. Both $+k$ and $-k$ belong to specific eigenvalues E. However, this is not generally true.

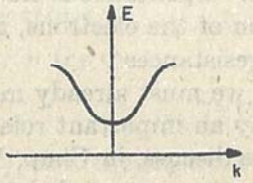

FIG. VII.10.3. Symmetrical $E(k)$-variation. Both $+k$ and $-k$ belong to every arbitrary eigenvalue E.

shown in Fig. VII.10.2, but must vary instead as shown in Fig. VII.10.3. Thus for every eigenvalue there must be apart from $\psi(x; k)$ with the wave factor e^{+jkx} a second eigenfunction with the wave factor e^{-jkx}. This follows quite generally from the fact that the Hamiltonian operator $-(\hbar^2/(2m))\Delta - eU(\mathbf{r})$ is real. For, if we pass from the normal Schrödinger equation

$$(H_{op} - E)\psi(\mathbf{r}; \mathbf{k}) = 0$$

to its complex conjugate

$$(H_{op} - E)\psi^*(\mathbf{r}; \mathbf{k}) = 0$$

we see that for the same eigenvalue E there is both an eigenfunction [i.e., $\psi(\mathbf{r}; \mathbf{k})$] with the wave factor $e^{j\mathbf{k}\cdot\mathbf{r}}$ and one [i.e., $\psi^*(\mathbf{r}; \mathbf{k})$] with the wave factor $e^{-j\mathbf{k}\cdot\mathbf{r}} = e^{+j(-\mathbf{k})\cdot\mathbf{r}}$, which was to be proved.

Thus it follows from Eqs. (VII.10.01) and (VII.10.04) that a state $+\mathbf{k}$ and a state $-\mathbf{k}$ are occupied with equal probability at thermal equilibrium. However, as a further consequence of central symmetry

(VII.10.04), their contributions to the current density

$$-\frac{e}{V_{\text{fund}}}\frac{1}{\hbar}\,\text{grad}_{\mathbf{k}}\,E(\mathbf{k})$$

[see Eq. (VII 5.13) on page 208] are equal and opposite. Thus, at thermal equilibrium, current contributions of opposite sign always occur with equal probability. Hence there is no current. In corpuscular terms we may say simply: At thermal equilibrium, electrons with equal, but oppositely directed, velocity occur with equal frequency and hence compensate each other with respect to the current.

c. Thermal Noise

The preceding statement, that at thermal equilibrium the probability of occupation of a quantum state by an electron depends only on its energy E and not on its wave vector $\mathbf{k}$, applies only for a time average. Spontaneous fluctuations take place about this mean distribution of the electrons, giving rise to the so-called thermal noise of ohmic resistances.

Here we must already make a distinction between two cases which will play an important role in what follows.

As we discuss, in Chap. VIII, the distribution of the electrons over the quantum states of the one-electron problem in greater detail, we shall encounter, as one possible case, the situation that all places in the uppermost energy band containing any electrons whatsoever are fully occupied. The next allowed band is empty. In another case, the uppermost allowed energy band containing electrons is partly occupied.

Since electrons can leave the band in which they find themselves only by the action of very strong fields (§7) or that of photon collisions (§8) and since we have excluded such external forces for the present, thermal fluctuations can lead only to transitions to other states in the same band. In a fully occupied band, these states are, however, occupied. Now it is immaterial whether we say that in a fully occupied band thermal fluctuations consist of an exchange of places between electrons or whether we say that in a fully occupied band thermal fluctuations are not possible. From the standpoint of quantum theory, electrons are indistinguishable. It matters only whether a state is occupied by any electron, not by which electron.[1] Hence there can be

[1] If two electrons exchange places, the eigenfunction of the many-electron problem (in zero approximation, the so-called Slater determinant) merely changes sign. This does not signify a change in the "physical situation" of the state of the many-electron problem.

The wave-mechanical equivalent of the "corpuscular" statement of the indis-

no thermal fluctuations in a fully occupied band. If a crystal has only fully occupied bands and no partly occupied band, it can exhibit no thermal noise. Otherwise, the mean-square fluctuation current $\overline{I^2}$ within a frequency band df for a short-circuited conductor at temperature T is related to the ohmic resistance R of the conductor according to the well-known theorem of Nyquist[1] by the relation

$$\overline{I^2} = \frac{4kT}{R} \cdot df \qquad \text{(VII.10.05)}$$

By this equation, thermal noise vanishes only for $R = \infty$, i.e., for an insulator. We have here a first indication that a crystal with only fully occupied bands is an insulator. This will be confirmed when, next, we consider the totality of the electrons in a crystal under the influence of an external force.

d. Calculation of the Conductivity by Summing the Contributions of the Individual Electrons

The electric field $\mathbf{E}$ exerts on every electron the force

$$\mathbf{F} = -e\mathbf{E} \qquad \text{(VII.10.06)}$$

We have seen on page 213, Eq. (VII.6.12), that the electrons change their state $\mathbf{k}$ in accord with the law

$$\hbar\dot{\mathbf{k}} = \mathbf{F} \qquad \text{(VII.6.12)}$$

In §9 we followed the fate of an individual electron under the simultaneous influence of an external force $\mathbf{F}$ and of collisions with phonons and impurities and determined its contribution to the current density. If we now sum over all the electrons, we must obtain the total current density.

In carrying out the summation, we shall limit ourselves to the "one-dimensional" case so as to avoid unnecessary mathematical

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tinguishability of the electrons is the axiom that among all the solutions of the Schrödinger equation of a many-particle problem only the symmetrical or the antisymmetric solutions have physical reality and, hence, need be considered. From this standpoint, the counting prescriptions of Bose and Fermi statistics represent simply the counting of the symmetrical and antisymmetric eigenfunctions, respectively, of a many-electron problem; see, e.g., L. Nordheim in Müller-Pouillet, "Lehrbuch der Physik," vol. IV, part 4, p. 251.

[1] H. Nyquist, *Phys. Rev.*, 32: 110 (1928). We prefer to introduce the mean-square current fluctuation $\overline{I^2}$ of a short-circuited conductor rather than the mean-square voltage $\overline{u^2}$ at the ends of a conductor in open circuit because in the latter case a spontaneous primary fluctuation produces a field within the conductor. We then no longer have the force-free case here under consideration.

complications. Thus the motion of the electrons has only one degree of freedom, namely, the x axis. Similarly, the field strength points in the x direction and the lattice potential $U = U(x)$ depends only on x. In order to be able to separate clearly the concepts of current and current density, we consider, in spite of the restriction of the direction of the force and the electron motion to the x axis, a crystal which has a cross section Q perpendicular to the x axis and has a length of G lattice constants a along the x axis, so that its volume is $Q \cdot Ga$. Then we obtain from (VII.9.26), (VII.9.24), and (VII.9.25)

$$\mathfrak{i}_{\text{single}} = \frac{1}{Q \cdot Ga} \frac{e^2\tau}{m_{\text{eff}}(k)} \mathbf{E}$$

The summation of the individual contributions follows, for the assumption that the quantum states are filled up to a k number k_{bound}:

$$\mathfrak{i} = \int \mathfrak{i}_{\text{single}}\, dN = \int_{k=-k_{\text{bound}}}^{k=+k_{\text{bound}}} \frac{1}{V_{\text{fund}}} \frac{e^2\tau}{m_{\text{eff}}(k)} \mathbf{E} \frac{dN}{dk} \cdot dk \qquad \text{(VII.10.07)}$$

The number dN of electrons which can be accommodated in the k interval $(k,\ k + dk)$ is equal to twice[1] the number of the quantum states in this interval. According to page 170, a quantum state claims an interval $2\pi/aG$ on the k axis. Thus there are $Ga \cdot dk/2\pi$ quantum states in the interval $(k,\ k + dk)$, and

$$dN = 2 \cdot \frac{Ga}{2\pi} dk \qquad \text{(VII.10.08)}$$

electrons can be accommodated. If we use Eq. (VII.6.28) for the effective mass in (VII.10.07), we obtain

$$\mathfrak{i} = e^2\mathbf{E}\tau \int_{k=-k_{\text{bound}}}^{k=+k_{\text{bound}}} \frac{1}{\hbar^2} E''(k) \cdot \frac{1}{Q \cdot Ga} 2 \frac{Ga}{2\pi} dk$$

$$= \frac{e^2\mathbf{E}\tau}{Q} \cdot \frac{1}{\pi} \frac{1}{\hbar^2} [E'(+k_{\text{bound}}) - E'(-k_{\text{bound}})]$$

In view of the general central symmetry (VII.10.04) of $E(k)$, we can conclude, furthermore, that

$$\mathfrak{i} = \frac{e^2\mathbf{E}\tau}{Q} \cdot \frac{1}{\pi} \frac{1}{\hbar^2} \cdot 2E'(+k_{\text{bound}}) \qquad \text{(VII.10.09)}$$

Let us consider first the case of the fully occupied band. Since at a band edge the $E(k)$ curve is horizontal (see Figs. VII.3.10c to VII.3.12),

[1] Because of the electron spin, a quantum state can be occupied by two electrons.

we have in this case $E'(k_{\text{bound}}) = 0$. We thus have the result that the fully occupied band supplies no current, in the presence of an electric field **E** as well as at thermal equilibrium. A fully occupied band does not contribute to the conductivity.

As our next example we consider a very slightly occupied band. Then only the states close to the bottom edge of the band are occupied. Here the approximation

$$E = E_C + \frac{\hbar^2}{2m_{\text{eff}}} k^2 \tag{VII.10.10}$$

is valid. Hence

$$E'(k_{\text{bound}}) = \frac{\hbar^2}{m_{\text{eff}}} \cdot k_{\text{bound}} \tag{VII.10.11}$$

On the other hand, k_{bound} may be expressed with the aid of (VII.10.08) in terms of the total number N of electrons in the volume $V = Q \cdot Ga$ of the crystal:

$$N = \frac{1}{\pi} Ga\,[(+k_{\text{bound}}) - (-k_{\text{bound}})] = \frac{2}{\pi} Gak_{\text{bound}} \tag{VII.10.12}$$

or

$$k_{\text{bound}} = \frac{\pi}{2} \frac{N}{Ga}$$

With (VII.10.11) and (VII.10.12), (VII.10.09) becomes

$$\mathbf{i} = \frac{e^2 \mathbf{E} \tau}{Q} \cdot \frac{1}{\pi} \cdot \frac{1}{\hbar^2} \cdot 2 \frac{\hbar^2}{m_{\text{eff}}} \cdot \frac{\pi}{2} \cdot \frac{N}{Ga}$$

or, introducing the concentration $n = N/(Q \cdot Ga)$ of the electrons,

$$\mathbf{i} = e \cdot n \cdot \frac{e}{m_{\text{eff}}} \tau \cdot \mathbf{E} \tag{VII.10.13}$$

For a slightly occupied band the conductivity, defined by

$$\mathbf{i} = \sigma \cdot \mathbf{E} \tag{VII.10.14}$$

thus becomes

$$\sigma = e \cdot n \cdot \mu. \tag{VII.10.15}$$

Here we have introduced the electron mobility

$$\mu = \frac{e}{m_{\text{eff}}} \cdot \tau \tag{VII.9.25}$$

which occurred in Eq. (VII.9.07) or (VII. 9.24) as a proportionality factor between the mean velocity increment of an electron and the field strength **E**. This leads to a purely corpuscular standpoint. It was shown on pages 246 to 248 how the conductivity formula (VII.10.15) is obtained from it.

c. The Distortion of the Equilibrium Distribution of the Electrons and the Calculation of the Conductivity

At the beginning of §10 we noted that we could obtain important results from general traits of the electron distribution over the several quantum states, without concerning ourselves with details. As one such trait we have utilized the fact that at thermal equilibrium the electrons occupy symmetrically the centrally symmetric pattern

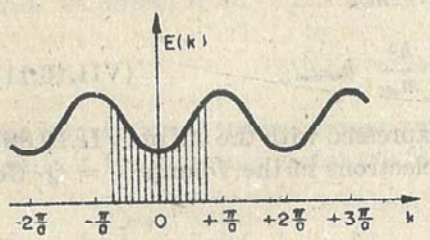


FIG. VII.10.4. In the absence of an external force the occupation of the $E(k)$-states is symmetrical.

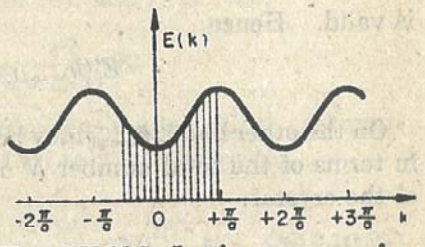


FIG. VII.10.5. In the presence of an external force the occupation of the $E(k)$-states becomes asymmetric.

$E(\mathbf{k})$ (see Fig. VII.10.4). Now, an external field perturbs the equilibrium distribution. All electrons uniformly seek, in accord with Eq. (VII.6.12),

$$\dot{\mathbf{k}} = \frac{1}{\hbar}\mathbf{F} \qquad \text{(VII.6.12)}$$

to occupy other $\mathbf{k}$ vectors, which point more nearly in the direction of $\mathbf{F}$. Since (VII.6.12) does not contain the quantum state $\mathbf{k}$ itself, we find that the equilibrium distribution of the electrons in $\mathbf{k}$ space tends to drift with uniform velocity without change in shape[1] or density.

At the same time, we have seen in connection with the treatment of the "oscillation" within a band of a single electron, on pages 257 to 258, that collisions with phonons and impurities prevent an actual development of this oscillation. In considering the totality of the electrons, we must similarly take account of the fact that, in fact, thermal equilibrium is attained through collisions of the electrons with phonons and impurities and that in case of a deviation from thermal equilibrium these collisions provide a retarding impulse which tends to reconvert the perturbed distribution into the equilibrium distribution.

Thus we see that the application of an external field $\mathbf{E}$ to the crystal results in a slightly perturbed distribution of the electrons over the

[1] For the one-dimensional example of Fig. VII.10.4, the "shape" of the $\mathbf{k}$ distribution is simply the width of the occupied k interval.

quantum states, of such nature that the equilibrium distribution is shifted slightly from its symmetrical position in the direction of larger k numbers (Fig. VII.10.5). The resulting current and hence the conductivity are derived from the magnitude of the shift.

We shall not carry this idea further at this point. Instead, we shall be satisfied with pointing out that, from this standpoint, the dropping out of a fully occupied band for the conductivity is easily recognized. In Fig. VII.10.6 we have shown the occupation of a full band with and without external field. Since the states in the k interval $+\pi/a < k < +3\pi/a$ are fully equivalent to the states in the interval $-\pi/a < k < +\pi/a$, the states which are missing in the interval $-\pi/a < k < +\pi/a$ after application of the field are exactly compensated by those which have been added in the interval $+\pi/a < k < +3\pi/a$. Thus the application of the field has actually made no change in the distribution of the electrons. Just as in the absence of a field, there is no current.

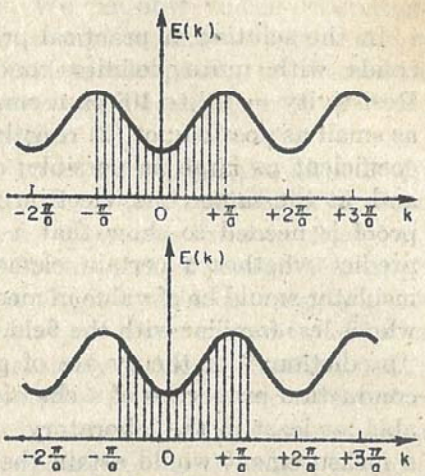


FIG. VII.10.6. The occupation of the $E(k)$ states for a fully occupied band. Upper figure: without external force. Lower figure: with external force.

f. Concluding and Summarizing Remarks

It must be emphasized repeatedly that the argument of §9 and §10 represents only a superficial outline of theories which are very complex in substance. Thus we have treated the collision time τ as independent of the quantum state $\mathbf{k}$, which is not generally correct. The statistical scattering of the free times of flight and, particularly, the coupling of the velocities before and after collision render very difficult the precise realization of the method first described, in which the current is calculated from the contributions of the individual electrons. Even in classical electron theory, this led H. A. Lorentz to abandon this method, which had been used by Riecke and Drude, and to replace it by considerations of the deviation from the equilibrium distribution. The second method is also tied less closely to the corpuscular picture and makes it possible to work directly with transition probabilities at a collision. Hence all authors have used it in effect for more precise wave-mechanical treatment of the ideas outlined here in §9 and §10.

§11. Conclusions from the Band Model Regarding the Conduction of a Particular Crystal Lattice

In the solution of practical problems we frequently seek electronic solids with quite definite conduction properties. [Examples: (1) Resistivity = 10^1 to 10^2 ohm-cm, temperature coefficient of resistance as small as possible; or (2) resistivity as small as possible, temperature coefficient as large as possible; or (3) resistivity as large as possible and, at the same time, electron mobility μ as large as possible.] No proof is needed to show that a theory of conductivity which might predict whether a certain element or compound is a conductor or insulator would be of value in meeting such requirements. The person who is less familiar with the field may be surprised, however, that such "predictions" of theory are of great value even in the study of the conduction properties of a chemical compound which is already available, at least in the laboratory. We might think that in such a case a measurement would attain the objective more quickly, and, in particular, with greater certainty than an application of theory.

However, a purely experimental procedure can lead to crude errors. In conductivity measurements, difficulties frequently arise simply from the fact that the contacts commonly introduce barrier layers. The measurement of voltages with zero-current probes proves helpful, but demands relatively large specimens. The main difficulty, however, arises from the fact that the conductivity of most semiconductors and insulators is extremely sensitive to minimal impurities or defects in structure and texture. Hence it is often extremely doubtful whether the measured specimens have those conduction properties of the material in question which are characteristic of it in a highly perfect state.

A historical example may show that this assertion is by no means contrived. For a long time it was undecided whether the elements silicon and germanium, in their purest form, were metals or insulators, and in 1930 reputable experimenters decided emphatically in favor of their metallic character. However, when these two elements, approximately ten years later, attained importance as materials for detectors, specimens of increasing perfection became available for measurements, and just the reverse was found to be correct. Today silicon and germanium are even regarded as prototypes of electronic semiconductors.

What potentialities does the theory have for determining the conduction properties of a solid? The nearest starting point is here, of course, the assertion of the band model that a fully occupied band does not contribute to the conductivity (see pages 263, 264, and 267) and

that a solid body can be a conductor only if its band model includes incompletely occupied bands. A very simple procedure, which, however, may frequently lead to erroneous conclusions, suggests itself for the application of this statement. We can observe the occupation of the individual electron levels of the atoms forming the lattice and conclude from the complete or incomplete occupation of these atomic levels regarding the complete or incomplete occupation of the "corresponding" bands of the crystal lattice.

From this point of view it is to be expected that the lattices of the condensed noble gases (Ne, Ar, Kr, X) with closed shells of eight in the individual atoms are insulators. This is so in fact. Also for the alkali metals Li, Na, K, Rb, and Cs this primitive argument applies. From the fact that there is here a single s electron outside a closed shell of eight, we deduce half-occupancy of a corresponding s band and hence metallic conductivity. It scarcely requires mention that for an ionic lattice (e.g., NaCl) the complete or incomplete occupation of shells in the ions Na^+ and Cl^- and not in the neutral atoms Na and Cl must be considered. In any case, in view of the shells of eight of Na^+ and Cl^-, we must regard the insulating character of the NaCl lattice as another confirmation of the elementary standpoint.

The alkaline earths Be, Mg, Ca, Sr, and Ba have two s electrons in their outermost shell. From the foregoing elementary point of view, their crystals should have a fully occupied s band and hence be insulators. The contrary is known to be true. The explanation may be sought in the fact that for these atoms an empty p term lies above the fully occupied s term. When the atoms are brought together in a crystal, these terms split up into bands and overlap apparently, so that the insulating gap between the s and p bands is closed.

A further failure of the primitive point of view occurs for the lattice of solid hydrogen. Like the alkali atoms, the hydrogen atom has a single s electron. Nevertheless, solid hydrogen is an insulator, in contrast with Li, Na, K, Rb, and Cs. We shall see that the explanation rests in the fact that hydrogen does not form an atomic lattice, but a molecular lattice,[1] i.e., a hexagonal close-packed lattice[2] in which the individual lattice points have a separation of 3.75 A and are occupied by H_2 molecules rather than by H atoms. Within the molecules, the two H atoms are known to have a separation of 0.74 A.[3]

In a molecular lattice (see, e.g., Fig. VII.11.1) we are no longer

[1] See, e.g., J. D'Ans and E. Lax, "Taschenbuch für Chemiker und Physiker," pp. 164 and 178, Springer-Verlag OHG, Berlin, 1943.

[2] See, e.g., P. P. Ewald, "Kristalle und Röntgenstrahlen," p. 150, Springer-Verlag OHG, Berlin, 1923.

[3] See D'Ans and Lax, *op. cit.*, p. 118.

dealing with a "simple translation lattice" (commonly designated as Bravais lattice), but with a "translation lattice with basis." For these lattices we no longer obtain all[1] lattice points by giving the components l_1, l_2, l_3 of the number trio $\mathbf{l} = (l_1, l_2, l_3)$ in the equation for the radius vector $\mathbf{R}_l$ of a lattice point

$$\mathbf{R}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \quad \text{(VII.11.01)}$$

all positive and negative integer values; in this manner we obtain only the corners of the individual unit cell, and we must extend the "basis" of the unit cell, namely, the m vectors $\mathbf{r}_1 \ldots \mathbf{r}_m$ which lead from the corner of the unit cell to the m atoms in the cell, from these corners. A lattice can be described in infinitely many ways.[2] Thus the face-centered cubic and the body-centered cubic lattices (see Figs. VII.11.2 and VII.11.3) cease to be simple translation lattices if orthogonal axes of translation $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are employed, but become instead lattices with a basis of four and two atoms, respectively. With oblique axes of translation $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, they can be represented as simple translation lattices.

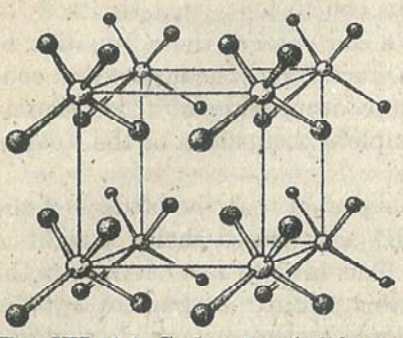


FIG. VII.11.1. Carbon tetraiodide as example of a molecular lattice. C atoms: white. I atoms: black.

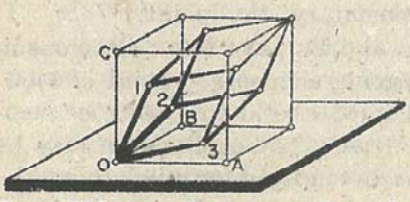


FIG. VII.11.2. Face-centered cubic lattice.

First representation: translation lattice with basis; orthogonal axes of translation: OA, OB, OC. Four atoms of basis: 0, 1, 2, 3.

Second representation: simple translation lattice; oblique axes of translation: 01, 02, 03.

From P. P. Ewald in Geiger and Scheel, vol. XXIII, part 2, p. 239, Fig. 46.

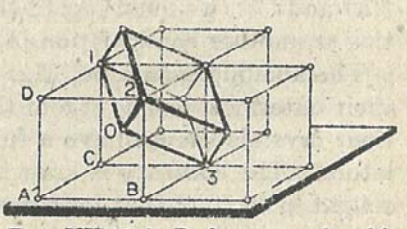


FIG. VII.11.3. Body-centered cubic lattice.

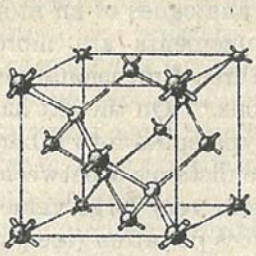
First representation: translation lattice with basis; orthogonal axes of translation: AB, AC, AD. Two atoms of basis: A, 0.

Second representation: simple translation lattice; oblique axes of translation: 01, 02, 03.

From P. P. Ewald in Geiger and Scheel, vol. XXIII, part 2, p. 239, Fig. 47.

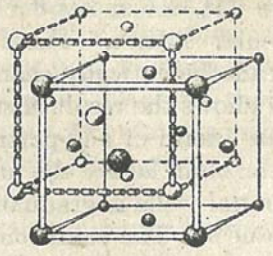
[1] More precisely, all and only all lattice points. In this connection, see the discussion on p. 271 on the diamond lattice and Fig. VII.11.4 corresponding to it.

[2] See Ewald, *op. cit.*, p. 272.



(a)

Every C atom has four neighbors placed at the corners of a tetrahedron.



(b)

Formation of the diamond lattice by two interlaced face-centered cubic lattices.

FIG. VII.11.4. Diamond lattice: all atoms C

Zinc blende lattice: black atoms Zn, white atoms S.

In a molecular lattice this cannot be done in any way; the geometrical relationships themselves prevent representation as a simple translation lattice (see Fig. VII.11.1). This is not true exclusively for a molecular lattice. The diamond lattice (see Fig. VII.11.4) also cannot be regarded as a simple translation lattice; it consists of two face-centered cubic lattices which are displaced by a quarter of a body diagonal. It is true that translation axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ can readily be indicated for which every C atom has a radius vector $l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$ with integer l_1, l_2, l_3. However, if we assign all positive and negative integer values to the l_1, l_2, l_3, we meet many points which are not occupied by C atoms. This cannot happen in a simple translation lattice, in whose definition on page 270 we should speak more precisely of "all and only all" lattice points rather than simply of "all" lattice points (see also footnote 1, page 270). Whereas for the molecular lattice and the diamond lattice purely geometrical circumstances prevent representation as a Bravais translation lattice, we find that for compounds such as NaCl the occupation of the lattice points by different kinds of atoms or ions forces us to regard them as translation lattices with basis (see Fig. VII.11.5), even when geometry alone would lead us to describe them as simple translation lattices.

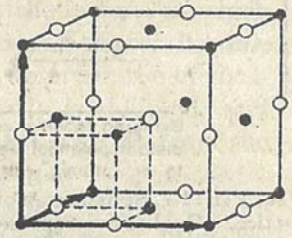


FIG. VII.11.5. The NaCl lattice might be regarded as a simple translation lattice with three orthogonal axes $a/2$ if the alternating occupation of the lattice points by Na and Cl atoms did not demand a different representation, e.g., as lattice with three orthogonal axes a and a basis of four Na and four Cl atoms.

Figure VII.11.6 shows one-dimensional analogues of an atomic and a molecular lattice. These linear arrangements are more easily handled mathematically than the actual three-dimensional ones; Fig. VII.11.7 shows the result of such calculations.[1] On the left half of the figure, an s term of one particular atom type splits into a band when in a linear atom lattice the identical lattice distance a between adjoining potential wells is gradually reduced from very large values to the small value b. The band contains two places per atom (see page 179).

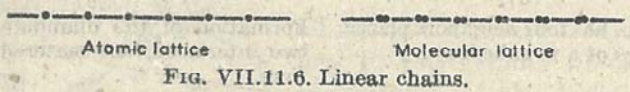


FIG. VII.11.6. Linear chains.

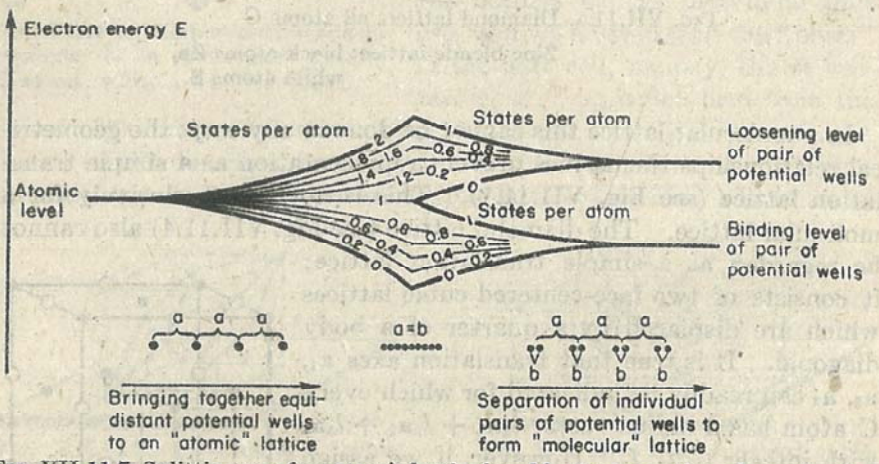


FIG. VII.11.7. Splitting up of an atomic lattice band in the formation of a molecular lattice. Qualitative representation. The thin lines within the band indicate the total number of states in the band lying below them. To the lower "molecular" level belongs a "binding" eigenfunction $\psi_+(\mathbf{r}) = \psi_{As}(r_a) + \psi_{As}(r_b)$. To the upper "molecular" level belongs a "loosening" eigenfunction $\psi_-(\mathbf{r}) = \psi_{As}(r_a) - \psi_{As}(r_b)$. See Eqs. (VI.2.01 and 2.02) and footnote on p. 155.

In the right half of the figure, the atoms are again separated. However, in this process the atoms retain the separation b in pairs and only the separation between adjoining pair centers is continuously increased. Thus, in the same right half of the figure, a linear molecular lattice is dilated until the molecules are practically separate. We see that the

[1] Since, as in the band model, we are here dealing with the one-electron problem (in a periodic potential field), the solution for the limiting case of separated molecules can also be compared only with the eigenfunctions of the molecular ion, from which the procedure of Hund and Mulliken can then construct the many-electron eigenfunctions of the molecule by linear combinations. See also the legend of Fig. VII.11.7.

continuous energy band of the atom lattice splits in the middle and that we obtain two separate bands with one place per atom. Thus, if the lattice points in such a linear molecular lattice are occupied by hydrogen atoms, electrons just fill completely all places of the lower band. The upper band remains empty. Thus we obtain an insulator. The transfer of these considerations to the three-dimensional H_2 lattice is certainly permissible.

In the example just described of a diatomic molecular lattice, there are two atoms in a unit cell. Each of the bands, therefore, has again two places per cell. Hence if we replace the phrase "two places per atom" with the phrase "two places per elementary unit cell of translation," we would seem to cover correctly both atomic and molecular lattices and might hope to arrive at a generally valid rule—eventually after introduction of a statistical weight ω for an atomic level with $(\omega - 1)$-fold degeneracy. However, this also is an illusion. A calculation for the case described—e.g., with the aid of Bloch's approximation—shows that the splitting between the two molecular bands vanishes when the distances of an atom from its two neighbors become just equal (we now traverse Fig. VII.11.7 from the right to the left). The fact that the rule "two places per elementary cell" applies also for the atomic lattice arises from the fact that at the instant at which the separations of an atom from its two nearest neighbors become equal the elementary cell becomes half as large as before in the molecular lattice. Thus the number of elementary cells is doubled, and hence the doubling of places in the one band which resulted from the closing of the gap between the molecular bands is just compensated.

Now the equalizing of the distances to the neighbors need not always be accompanied by the appearance of a smaller unit cell. Even so, two molecular bands can merge into a single atomic band. Thus if two face-centered cubic lattices are so placed that they are displaced relative to each other by a small fraction of a body diagonal, we have a molecular lattice. If the lattice points are occupied by atoms with an s electron, we have once more two molecular bands with two places in an energy band for each elementary unit cell (constructed with the surface diagonals! See Fig. VII.11.2). If, now, the lattices are displaced further, we reach the diamond lattice for a displacement by one-fourth of the body diagonal. The separations of an atom from its four neighbors become equal. The molecular bands merge into a single s band. However, no smaller unit cell is obtained, so that we have a band with four places per elementary unit cell in such a lattice.

The instructive example of the actual diamond lattice (atom with two $2s$ and two $2p$ electrons), which we shall discuss next, shows in

addition that the atomic states, which are split up in bringing the atoms together, can group themselves quite differently from the atom, so that the setting up of a more or less automatic rule for counting the places in the bands becomes entirely impossible. In the isolated C atom, the $2p$ level is occupied by only two electrons, although, by the Pauli principle, there is place for six electrons. Hence the primitive

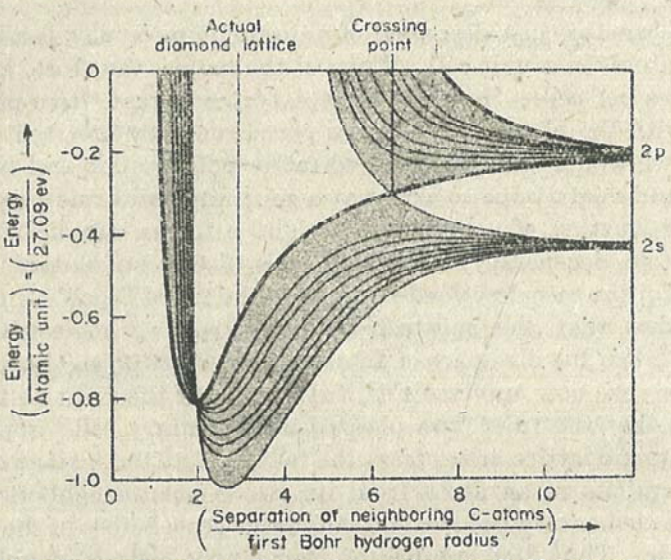


FIG. VII.11.8. Energy bands of diamond according to F. Hund and B. Mrowka. For large atomic separations the $2s$ band contains two states per atom. The $2p$ band contains 6 states per atom, of which, in the present approximation, only the central third splits up; the lower and the upper thirds of the $2p$ states are represented by the heavily drawn boundaries of the $2p$ band. See the text with respect to the behavior for smaller atomic separations.

standpoint might lead us to expect metallic conductivity for diamond. Such a consideration is valid, however, only for very widely separated C atoms; a calculation for diamond yields the system of levels shown in Fig. VII.11.8.[1] We have a $2s$ band with two places per atom and a $2p$ band with six places per atom only for very large values of the

[1] F. Hund and B. Mrowka, *Ber. Verhandl. sächs Akad. Wiss. Leipzig, Math-phys. Kl.*, 87: 185 and 325 (1935), in particular p. 192. Since in the isolated C atom there are not only two $2s$ electrons but also two $2p$ electrons, it seems reasonable to suggest that the Bloch approximation should be carried out with p functions. Hund and Mrowka have, however, carried out the Bloch approximation with s functions only and have utilized p functions only in the cellular method of Wigner and Seitz. Thus Eq. (VII.11.02) indicates only the band splitting of the atomic $2s$ level and says nothing regarding the band splitting of the atomic $2p$ level above it.

lattice constant. As the lattice constant is reduced continuously, retaining the tetrahedral arrangement of the individual C atoms—i.e., for geometrically similar reduction of the lattice dimensions—the lower edge of the $2p$ band and the upper edge of the $2s$ band cross. The decisive point is that, at the crossing, a fractional band of two places per atom leaves the upper band and merges with the $2s$ band below it, so that to the left of the crossing point the lower band has four places per atom and the band lying above it has also only four places per atom. Thus, to the left of the crossing the four electrons of the L shell of the C atom fill completely the lower band, which is followed by an insulating gap, and the band with four more places per atom lying above it remains empty.

Another surprising phenomenon occurring in the band theory of the diamond lattice may be related to this peculiar behavior of the $2p$ states. The Brillouin approximation, starting from free electrons, leads to a theorem regarding polyhedra in $\mathbf{k}$ space, the Brillouin zones (see page 189). In the Bloch approximation, starting from bound electrons, we also meet a polyhedron in $\mathbf{k}$ space, the periodicity polyhedron, outside of which the energy values repeat themselves periodically (see page 181). For the cubic, face-centered cubic, and body-centered cubic lattices treated in most textbooks, the Bloch periodicity polyhedron and the first Brillouin zone are identical. This is no longer true for the diamond lattice. According to Hund and Mrowka,[1] the Bloch approximation with atomic s functions yields for the diamond lattice

$$E = E^\circ + 4C \pm 2R\sqrt{1 + \cos\frac{a}{2}k_x \cdot \cos\frac{a}{2}k_y + \cos\frac{a}{2}k_y \cdot \cos\frac{a}{2}k_z + \cos\frac{a}{2}k_z \cdot \cos\frac{a}{2}k_x} \tag{VII.11.02}$$

whereas for a simple face-centered cubic lattice we have[2]

$$E = E^\circ + C + 4A\left(\cos\frac{a}{2}k_x \cdot \cos\frac{a}{2}k_y + \cos\frac{a}{2}k_y \cdot \cos\frac{a}{2}k_z + \cos\frac{a}{2}k_z \cdot \cos\frac{a}{2}k_x\right) \tag{VII.11.03}$$

The dependence on the components k_x, k_y, k_z of the wave vector $\mathbf{k}$ thus occurs for both lattices through the same expression $\cos ak_x/2 \cdot$

[1] *Ibid.*

[2] See, e.g., A. Sommerfeld and H. A. Bethe in Geiger and Scheel, *op. cit.*, vol. XXIV, part 2, p. 387, Eq. (12.15).

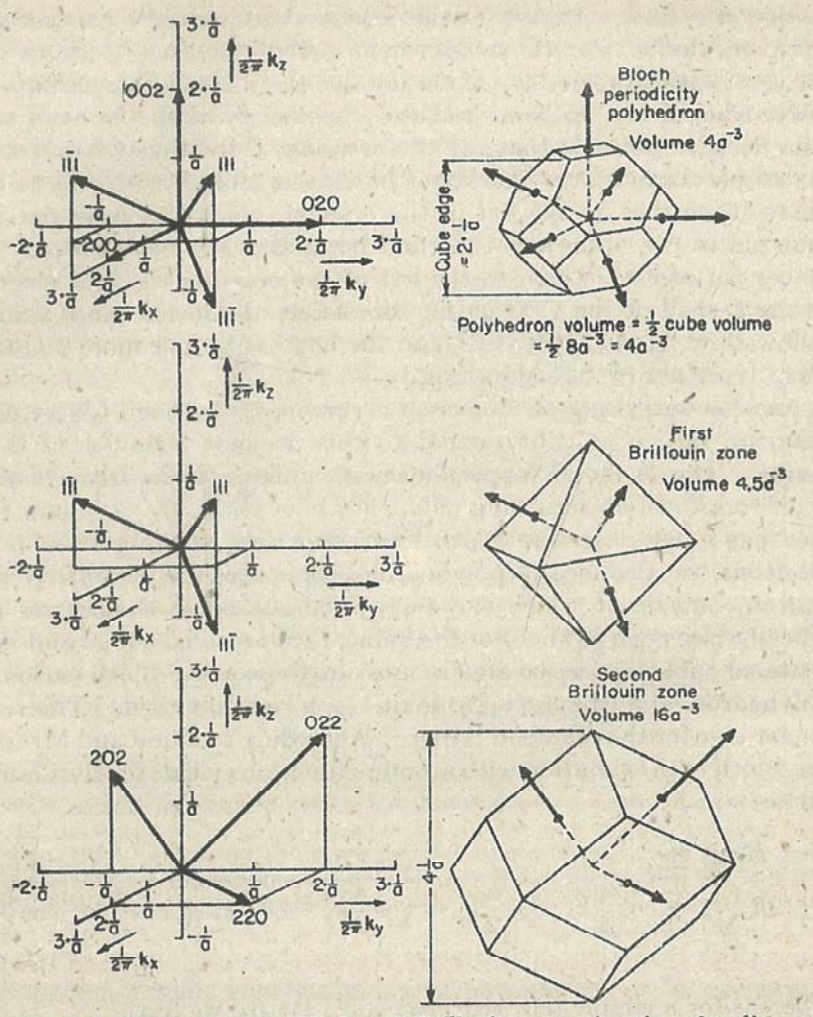


FIG. VII.11.9. Concerning the Bloch and Brillouin approximations for diamond.

$\cos ak_y/2 + \cos ak_y/2 \cdot \cos ak_z/2 + \cos ak_z/2 \cdot \cos ak_x/2$. Thus both lattices have the same Bloch periodicity polyhedron, i.e., the octahedron with the points cut off shown in Fig VII.11.9.

Concerning the first Brillouin zone of the diamond lattice, we know that it must be at least as large as that of the face-centered cubic lattice, since no additional Bragg reflections are produced by inserting into each other the two face-centered cubic lattices of which the diamond lattice consists (see Fig. VII.11.4).[1] On the other hand, certain

[1] Ewald, *op. cit.*, p. 91.

reflections can drop out, since the beams reflected by the two sublattices can cancel each other because of suitable phase differences.[1] In fact, for diamond the (200) planes, cutting off the points of the octahedron, drop out, so that the first Brillouin zone of diamond is the complete (111) octahedron. For the second Brillouin zone, a rhombic dodecahedron, formed by the (220) planes, is obtained (see Fig. VII.11.9).[2]

In the Bloch approximation, nothing is changed as compared with a face-centered cubic lattice in so far as we still obtain an s band with two places per atom. We recognize this as follows: According to Fig. VII.11.9, the Bloch periodicity polyhedron has, by elementary geometry, a volume $4a^{-3}$. According to §2, page 182, a $\mathbf{k}$ state requires a volume $(2\pi)^3/V_{\text{fund}}$ in $\mathbf{k}$ space and a volume $1/V_{\text{fund}}$ in the $\mathbf{k}/2\pi$ space used in Fig. VII.11.9 because the vector $\mathbf{k}/2\pi$ is also plotted in the construction of the Brillouin zones (see Figs. VII.3.5 and VII.3.6). We can hence accommodate $4V_{\text{fund}}a^{-3}$ different $\mathbf{k}$ states in the periodicity polyhedron with the volume $4a^{-3}$. On the other hand, the fundamental domain contains V_{fund}/a^3 elementary cubes with edge a. For the face-centered cubic lattice, every elementary cube contains four atoms. Thus there are $4V_{\text{fund}}a^{-3}$ atoms in the fundamental domain. Thus, for the face-centered cubic lattice the periodicity polyhedron provides space for $4V_{\text{fund}}a^{-3}$ different $\mathbf{k}$ states for $4V_{\text{fund}}a^{-3}$ atoms, or one $\mathbf{k}$ state per atom. Since by (VII.11.03) one energy value in the s band belongs to every $\mathbf{k}$ state, we obtain for the face-centered cubic lattice an s band with one energy value per atom or, because of the spin, two places per atom.

In the diamond lattice there are instead eight atoms in the elementary cube a^3. It would seem, hence, that we would obtain an s band with only one place per atom. However, according to (VII.11.02), the s band of the diamond lattice consists of two sub-bands, because of the two signs of the root; these merge, however, since the term under the radical vanishes, e.g., for $ak_x/2 = \pi$, $ak_y/2 = 0$, $ak_z/2 = \pi/2$.

[1] The condition for this is that the "structure factor"

$$S_{\mathbf{h}} = \sum_{t=1}^{t=m} e^{-2\pi i(\mathbf{h}\cdot\mathbf{r}_t)}$$

for the reflections at a family of planes $\mathbf{h}$ vanishes. The summation index $t = 1, 2, \ldots, m$ indicates the several sublattices in this expression; the m vectors $\mathbf{r}_t$ construct the basis within a unit cell. See, e.g., Ewald, *op. cit.*, p. 279.

[2] See N. F. Mott and H. Jones, "Properties of Metals and Alloys," p. 159, Clarendon Press, Oxford, 1936.

The complete s band formed by the two sub-bands thus contains twice as many places as for the face-centered cubic lattice. Hence the doubling of the number of atoms in an elementary cube is compensated, and we obtain once more an s band with two places per atom. This evidently corresponds to the conditions for a diamond lattice with very large lattice constant, i.e., the level system to the right of the crossing point in Fig. VII.11.8.

We can draw the following conclusion from the Brillouin approximation: Since the cubes with edge a contain four atoms in the face-centered cubic lattice and eight atoms in the diamond lattice, the number of places per atom in diamond is half as large as for the face-centered cubic lattice. Thus we would obtain one place per atom in the diamond lattice. Since, however, the points of the octahedron are not cut off for the diamond lattice, an exact calculation yields 1.125 places per atom, provided that we restrict ourselves to the first Brillouin zone. Only the next Brillouin zone, namely, the rhombic (220) dodecahedron, contains together with the first zone again a whole number of places per atom, namely, four. If we assume that there is band overlap between the first and second zone, but not between the second and the third zone, we obtain an energy band which is completely filled by the four valence electrons in the L shell of the C atom. This evidently corresponds to the circumstances for a diamond lattice with small lattice constant, i.e., the system of levels in Fig. VII.11.8 to the left of the crossing point. Thus, here the behavior of the valence electrons is to some extent covered by the Brillouin approximation, whereas the two strongly bound $1s$ electrons must be added to the nucleus.

Thus we see that the insulating character of diamond is by no means obvious from the standpoint of the band model and can be understood only with the aid of a more careful study of the splitting of the atomic states, in particular the $2p$ states. Whereas in this instance the "more careful study" has been carried out by Hund and Mrowka[1] on the one hand and by Kimball[1] on the other,[2] the same does not apply to cobalt monoxide, CoO. Yet here also the high resistance ($\rho \approx 10^8$ ohm-cm) found experimentally is rather difficult to understand. CoO crystallizes in a rock-salt lattice, whose lattice points are occupied by Co^{++}

[1] F. Hund and B. Mrowka, *Ber. Verhandl. sächs. Akad. Wiss. Leipzig, Math.-phys. Kl.*, **87**: 185 and 325 (1935); G. E. Kimball, *J. Chem. Phys.*, **3**: 560 (1935).

[2] Large-scale investigations of the band structure of the diamond lattice have been undertaken in the last few years by Herman (Radio Corporation of America). See F. Herman, *Phys. Rev.*, **88**: 1210 (1952); and **93**: 1214 (1954); F. Herman and J. Callaway, *Phys. Rev.*, **89**: 518 (1953); and F. Herman, J. Callaway, and F. S. Acton, *Phys. Rev.*, **95**: 371 (1954).

and O^{--} ions.[1] Whereas the O^{--} ions have a closed shell of 8 electrons, the 3*d* level of the Co^{++} ions is occupied by only 5 electrons, whereas it could accommodate 10 electrons. We, therefore, expect a half-occupied 3*d* band in the crystal and, hence, metallic conductivity, in contradiction with experiment. Hund[2] suggests as a way out that the 3*d* band is so narrow and consequently the effective mass of the electrons so large that, in spite of a normal mean free path of the conduction electrons, very small mobilities and, hence, very small conductivity are obtained. In this way we might "just about understand the insulating nature of these crystals."[3]

MnO represents a similar case. In fact, these compounds with incompletely filled 3*d* shells of the cations quite generally lead to difficulties. The existence of these "open-band semiconductors" has at times been regarded as a failure of the band model, and the conduction mechanism in these compounds has been treated on the basis of atomistic models.[4]

Finally, we note that simple conclusions from the occupation of the shells in isolated atoms or ions regarding the occupation of the bands in the crystal and, hence, the insulator or metal character of the lattice in question are quite unreliable in view of the phenomena which have been discussed—namely, band overlap, splitting of bands with the formation of molecules, branching off of a sub-band at a crossing point of band boundaries, and the possibility of very narrow bands with large effective masses and hence small mobility of the conduction electrons. This unreliability can be reduced only if, in the particular case in question, the level splitting is calculated by the methods of Wigner and Seitz[5] or of Slater.[6,7]

[1] See D'Ans and Lax, *op. cit.*, p. 180.

[2] F. Hund, *Physik. Z.*, **36**: 725 (1935), in particular, p. 728. Also reprinted in *Z. tech. Phys.*, **16**: 331 (1935), in particular p. 334.

[3] *Ibid.*

[4] J. H. de Boer and E. J. W. Verwey, *Proc. Phys. Soc.* (*London*), **49**: 59 (1935); W. Schottky, *Z. Elektrochem.*, **45**: 33 (1939), in particular, p. 57; H. Dressnandt, *Z. Physik*, **115**, 369 (1940); C. Wagner and E. Koch, *Z. physik. Chem.*, **B32**: 439 (1936); R. Peierls, *Proc. Phys. Soc.* (*London*), **49**: 72 (1937).

In the evaluation of past experimental results for these compounds, we should never forget that the preparation of satisfactory specimens is made very difficult by deviations from stoichiometric composition, by inhomogeneous structure of the specimens, and by polycrystallinity. We have already seen from the previously mentioned erroneous conclusions regarding the nature of conduction in Si and Ge what basic errors can result from measurements on imperfect specimens.

[5] E. Wigner and F. Seitz, *Phys. Rev.*, **43**: 804 (1933).

[6] J. C. Slater, *Phys. Rev.*, **45**: 794 (1934).

[7] The reader will find a compilation of more recent work in this field in G. V. Raynor, *Repts. Progr. Phys.*, **15**: 173 (1952).

Even when such generally extensive studies are carried out, there always remains an uncertainty regarding the justification of the band model itself. We must not forget that, as a one-electron approximation for a many-electron problem, the band model can at best take summary account of the interaction of the electrons through the potential curve employed in the approximation of Wigner, Seitz, and Slater. No final answer has as yet been given to the valid question as to whether this is always admissible or whether, in some cases, the failure of the remaining electrons to get out of the way of the reference electron may undercut the basis of the band model, namely, the periodicity of the potential field.

Thus the band model can only give some pointers regarding the likelihood that a particular crystal may be a conductor or an insulator or an intrinsic semiconductor. It will be advantageous here to employ methods which are largely empirical, such as comparisons with crystals of the same structure but different composition, utilization of regularities in the periodic system of elements, etc. This opens up the broad field of crystal chemistry, for which we shall merely indicate the reference texts.[1]

§12. Problems

Problems on One-dimensional Periodic Potentials

1. Many of the essential features of the band picture can be shown even by very simple one-dimensional models. Consider, for example, a one-dimensional lattice, consisting of (positive) delta functions, with a lattice constant l:

$$U(x) = +S \sum_{n=-\infty}^{+\infty} \delta(nl) \qquad \text{(VII.12.01)}$$

Between the δ functions the ψ functions are plane waves:

$$\psi(x) = A\,e^{ikx} + B\,e^{-ikx} \qquad k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \text{(VII.12.02)}$$

At the potential wells these waves have to be matched properly, as shown in Prob. 1 of Chap. VI, §5. This provides two equations for the relationship between the coefficients A and B in adjoining cells. Two additional equations follow from the

[1] U. Dehlinger, "Chemische Physik der Metalle und Legierungen," Akademische Verlagsgesellschaft, Leipzig, 1939; A. Eucken, "Lehrbuch der chemischen Physik," vol. II, part 2, 3d ed., Leipzig, 1949; F. Halla, "Kristallchemie und Kristallphysik metallischer Werkstoffe," J. A. Barth, Leipzig; W. Hume-Rothery, "The Structure of Metals and Alloys," Monograph and Report Series of the Institute of Metals, No. 1, London, 1950; L. Pauling, "The Nature of the Chemical Bond," 2d ed., New York/London, 1945; A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1945; H. G. F. Winckler, "Struktur und Eigenschaften der Krystalle," Springer-Verlag OHG, Berlin, 1950.

requirement that ψ multiplies itself simply with e^{ikl} in advancing by exactly one lattice spacing l. These, then, are four homogeneous linear equations for the four coefficients A and B in two adjoining cells. In order that these four equations be compatible, their determinant must vanish. This provides an equation for k as a function of $\varkappa$ and, therefore, as a function of the energy as well.

Set up the four equations mentioned, and show that their determinant vanishes if

$$\cos kl = \cos \varkappa l + \frac{mS}{\hbar^2 \varkappa} \sin \varkappa l \qquad \text{(VII.12.03)}$$

2. Plot the right side of Eq. (VII.12.03) as a function of $\varkappa l$ (qualitatively!) and show that it follows from Eq. (VII.12.03) that allowed and forbidden bands alternate up to the highest energies. Show that the forbidden bands correspond to a Bragg reflection. At what energy inside the forbidden band is the Bragg condition fulfilled exactly?

3. Give an approximation formula for the widths of the forbidden bands as a function of the band number and of the quantities S and l.

4.* Calculate the effective masses of the electrons near the upper and lower edges of the allowed bands. How do they depend upon the band number and upon S and l?

5. Assume that S in Eq. (VII.12.01) is negative. Show, then, that for $E > 0$, Eq. (VII.12.03) still holds, and give the corresponding equation for $E < 0$. Show that for $E < 0$ always one and only one allowed band exists.

6.* Show that each allowed band splits into two bands if the delta functions are no longer equidistant and equally strong, but when instead

a. Either their distance alternates between $l + \Delta l$ and $l - \Delta l$, or,

b. Their strength alternates between $S + \Delta S$ and $S - \Delta S$.

Explain this splitting in terms of Bragg reflections and of the structure of the Brillouin zone.[1]

7. In Prob. 1, replace the delta functions by regular square potential barriers of the width b and the height V_0. Show that Eq. (VII.12.03) is then replaced for $0 < E < V_0$ by

$$\cos kl = \cosh \lambda b \cos \varkappa a + \frac{\lambda^2 - \varkappa^2}{2\lambda\varkappa} \sinh \lambda b \sin \varkappa a \qquad \text{(VII.12.04)}$$

where $\varkappa$ has the same meaning as previously and

$$\lambda = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} \qquad \text{(VII.12.05)}$$

$$a = l - b \qquad \text{(VII.12.06)}$$

Answer the questions of Prob. 2 for this new case.

8.* It has been shown that the forbidden bands correspond to Bragg reflections of the electrons inside the crystal. This is most clearly demonstrated by the delta potential where the contribution of each atom to the reflected wave comes from a single point. When the atoms have a finite extension, the different parts of the individual atom all contribute separately to the reflected wave. For certain energies and directions, the contributions from the different parts of the same atom can destroy themselves mutually so that no reflection could occur even if the

[1] For a more general treatment, see Saxon and Hutner, *Philips Research Repts.*, 4: 81 (1949).

Bragg reflection condition were satisfied. For certain values of the lattice constant, the Bragg condition and the condition for zero amplitude of the scattered waves actually do coincide. The forbidden band will, then, have zero width.

Analyze this situation for the potential of Prob. 7. Show that the different forbidden bands vanish for certain lattice constants, and show that this happens when the waves reflected from the front of the square barriers interfere with those reflected from the back in such a way as to destroy each other.

Problems on Deviations from Ohm's Law

9. In Eq. (VII.9.06) it was assumed that the kinetic energy gained by an electron between two collisions is small compared to its thermal kinetic energy. This resulted in a proportionality between the drift velocity v and the electric field, that is, in a constant mobility. It was also shown in §9 that in high electric fields the initial assumption may no longer hold. While a rigorous treatment of this subject would be beyond the scope of this book, one can obtain a qualitative understanding from the following simplified model. Calculate the current-voltage relationship for fields E such that

$$e\mathbf{E}l \gg \tfrac{3}{2}kT$$

making the following assumptions: (*a*) the mean free path l is independent of both the field and the particle velocity, and (*b*) the electron loses all its kinetic energy during every collision.

Calculate the differential conductivity $d\mathbf{i}/d\mathbf{E}$ at an electric field of $\mathbf{E} = 10^4$ volt-cm^{-1} for n-type germanium of 1 ohm-cm low-field resistivity. Assume $\mu_n = 3{,}600$ cm^2 volt^{-1} sec^{-1} and $m_{eff} = \frac{1}{4}m$.

10. How is the result of the preceding problem modified if the mean free path is constant only for velocities below a certain velocity v_{max}, and if the electrons lose all their kinetic energy as soon as they have been accelerated up to v_{max}? This is the kind of assumption one would have to make if there existed a scattering mechanism that is inactive below a certain kinetic energy but has a very high scattering efficiency above. Shockley[1] has pointed out that the scattering of electrons by the so-called optical phonons would be such a process.

11. In the two preceding problems it was tacitly assumed that the electron is not accelerated to such high energies that the effective mass changes. Small mass changes would, of course, have no great influence upon the current-voltage relationship. But if the electron is actually driven into a region of negative mass, it will be decelerated and the Zener oscillations described in §7 and §9 will set in. As mentioned in §9e, for mean free path lengths l of about 10^{-5} cm, the fields necessary for this to happen lie above the breakdown fields. But at higher values of l, the oscillations could actually set in before breakdown.

It was also previously assumed that at every collision the electron loses all its energy. This again may not hold at very high fields since the maximum energy an electron can transfer to the lattice in a collision is equal to $h\nu_{max}$, where ν_{max} is the highest vibrational frequency of the lattice. One may, therefore, expect that in very high fields the average energy loss per collision will approach a limiting value.

What would be the current-field relationship for fields so high that Zener oscillations do occur (but not breakdown), assuming that both the collision frequency and the amount of energy lost per collision are independent of the field?

[1] W. Shockley, *Bell System Tech. J.*, **30**: 990 (1951).

CHAPTER VIII

Fermi Statistics of the Electrons in a Crystal

In this chapter, as mentioned on page 260, the connection between the position of the Fermi level E_F and the electron concentration n will be computed for a number of models. In §2 it will be shown that within a solid or within a system of solids in thermal equilibrium the Fermi level E_F has everywhere the same value. This statement is often formulated in the concise, though perhaps not rigorously correct, rule: "In thermal equilibrium, the Fermi level is horizontal." To begin with, the Fermi distribution and the Fermi level E_F are defined only for states of thermal equilibrium. However, if the relationship between concentration n and Fermi level E_F is established for non-equilibrium states, a Fermi level E_F is defined whose slope depends on the total current. This subject will be discussed in §3, together with the related subject of the identity of Fermi level E_F and electrochemical potential. In §4 we shall deal with the Fermi Statistics of electrons in metals and insulators. The simplest case of an impurity semiconductor will be examined in §5. Among the main results of these last two paragraphs will be the law of mass action (I.3.03) between electrons and holes and the law of mass action (II.6.04) between donors and conduction electrons.

§1. The Electron Gas in a Potential Well

On page 260 a method was indicated whereby the relationship between E_F and n is obtained. The first model to which we apply this method is an electron gas with concentration n, which is confined in a well because a high positive potential exists within the well so that the potential energy E_{pot} of the electrons is strongly negative while it is assumed to be zero outside the well (Fig. VIII.1.1). In this case the total energy E of an electron is

$$E = E_{pot} + \frac{1}{2m} p^2 \qquad \text{(VIII.1.01)}$$

In order to establish the density of states $D(E)$, we could determine the eigenfunctions and the energy eigenvalues E of an electron in the potential well under consideration. However, this treatment would be beyond the scope of this book, and it would also preclude a direct application of the results to the next model to be discussed, i.e., a crystal with metallic properties. We shall therefore use a treatment which can be applied directly to crystals, though it may seem very artificial in connection with the model of the electron gas in the potential well.

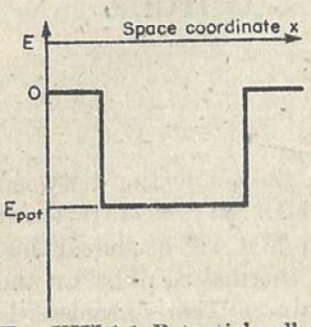


FIG. VIII.1.1. Potential well.

According to this treatment, we regard the constant potential within the well as a special case of a periodic lattice potential (i.e., the special case where the "amplitude" of the potential equals zero), and we introduce "unit cells" of arbitrary magnitude a. Further, we combine an arbitrary number G of unit cells in each axial direction to a "fundamental domain" of volume $V_{fund} = (Ga)^3$. We can then apply the result obtained on page 182: "A quantum state requires a volume $(2\pi)^3/V_{fund}$ in $\mathbf{k}$ space."[1]

The question now arises as to what volume in $\mathbf{k}$ space belongs to the energies between E and $E + dE$. To answer this we use (VII.6.04) and replace (VIII.1.01) by

$$E = E_{pot} + \frac{\hbar^2}{2m} |\mathbf{k}|^2$$

where $\mathbf{k}$ is the wave vector of the electron, or

$$|\mathbf{k}| = k = \frac{\sqrt{2m}}{\hbar} (E - E_{pot})^{1/2} \qquad \text{(VIII.1.02)}$$

Hence in the space of the wave vectors $\mathbf{k}$, $E = \text{const}$ represents spherical surfaces about the origin, and the condition

$$E < \text{energy of the states to be counted} < E + dE$$

defines a spherical shell of volume $4\pi k^2 \cdot dk$.

Now, according to page 182, a single quantum state requires a volume $(2\pi)^3/V$ in $\mathbf{k}$ space; hence the number $D(E)\,dE$ of the quantum

[1] The number N of the electrons which have to be accommodated in the arbitrary fundamental domain is nV; hence the arbitrary volume V of the fundamental domain will drop out on p. 285 and a result will be obtained which is free from these arbitrary assumptions (VIII.1.07).

states in the energy range $[E, E + dE]$ is given by the equation

$$D(E)\,dE = \frac{4\pi k^2\,dk}{(2\pi)^3/V}$$

or

$$D(E) = V \cdot \frac{1}{2\pi^2}\,k^2\,\frac{dk}{dE}$$

Finally, using (VIII.1.02), one obtains

$$D(E) = V \cdot \frac{1}{2\pi^2}\,\frac{2m}{\hbar^2}\,(E - E_{\text{pot}}) \cdot \frac{\sqrt{2m}}{\hbar}\,\frac{1}{2}\,(E - E_{\text{pot}})^{-1/2}$$

With $\hbar = h/2\pi$, the number of electrons that can be accommodated (equal to *twice* the number of the quantum states) is

$$2D(E)\,dE = V \cdot 4\pi \left(\frac{2m}{h^2}\right)^{3/2} (E - E_{\text{pot}})^{1/2}\,dE$$

$$2D(E)\,dE = V \cdot 2 \left(\frac{2\pi m\mathrm{k}T}{h^2}\right)^{3/2} \frac{2}{\sqrt{\pi}} \left(\frac{E - E_{\text{pot}}}{\mathrm{k}T}\right)^{1/2} d\left(\frac{E}{\mathrm{k}T}\right) \quad \text{(VIII.1.03)}$$

We now introduce an "effective density of states N" in the potential well:[1]

$$N = 2 \cdot \left(\frac{2\pi m\mathrm{k}T}{h^2}\right)^{3/2} = 2.5 \cdot 10^{19} \left(\frac{T}{300^\circ\mathrm{K}}\right)^{3/2} \mathrm{cm}^{-3} \quad \text{(VIII.1.04)}$$

and for the number $2D(E)\,dE$ of the electrons that can be accommodated in the energy range between E and $E + dE$ (equal to twice the number of the quantum states in this range), we finally obtain

$$2D(E)\,dE = V \cdot N \cdot \frac{2}{\sqrt{\pi}} \left(\frac{E - E_{\text{pot}}}{\mathrm{k}T}\right)^{1/2} d\left(\frac{E}{\mathrm{k}T}\right) \quad \text{(VIII.1.05)}$$

Hence the requirement (VII.10.03) established on page 260, in the case of the present model of the electron gas in the potential well, takes the form

$$V \cdot N \cdot \frac{2}{\sqrt{\pi}} \int_{E = E_{\text{pot}}}^{E = \infty} \frac{1}{e^{\frac{E - E_F}{\mathrm{k}T}} + 1} \left(\frac{E - E_{\text{pot}}}{\mathrm{k}T}\right)^{1/2} d\left(\frac{E}{\mathrm{k}T}\right) = N$$

Introduction of the integration variable

$$\eta = \frac{E - E_{\text{pot}}}{\mathrm{k}T}$$

[1] Here it must be mentioned that N is not a density of states in the same sense as the term $D(E)$. $D(E)$ represents a number of states per unit of the energy scale and hence has the dimension $(\text{energy})^{-1} = \text{cm}^{-2}\text{g}^{-1}\text{-sec}^2$. On the other hand, N has the dimension cm^{-3} and can therefore be regarded as a number of states per unit volume of the potential well (or, later, of the crystal). See footnote 1, p. 318.

and of the concentration of the electron gas

$$n = \frac{N}{V} \tag{VIII.1.06}$$

leads finally to the determining equation for E_F:

$$\frac{2}{\sqrt{\pi}} \int_{\eta=0}^{\eta=\infty} \frac{1}{e^{\eta - \frac{E_F - E_{pot}}{kT}} + 1} \sqrt{\eta}\, d\eta = \frac{n}{N} \tag{VIII.1.07}$$

A comparison of (VIII.1.07) with the defining equation (A.II.1) of the function $\zeta(n/N)$, which is treated in Appendix II, shows that in

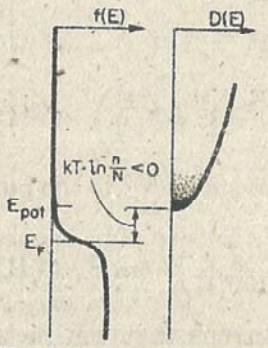


FIG. VIII.1.2. Few electrons in the potential well. $n \ll N$: no degeneracy. Maxwell-gas.

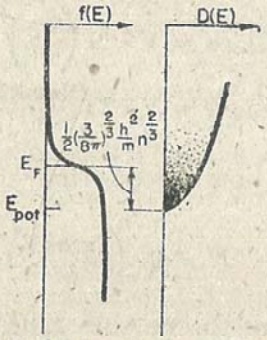


FIG. VIII.1.3. Many electrons in the potential well. $n \gg N$: strong degeneracy. Fermi-gas.

order to satisfy (VII.10.03) and (VIII.1.07) the Fermi level E_F must be formulated as follows:

$$E_F = E_{pot} + \zeta\left(\frac{n}{N}\right) \tag{VIII.1.08}$$

We now consider the two limiting cases of small and large concentration: According to Eq. (A.II.2), one obtains for $n \ll N$

$$E_F = E_{pot} + kT \cdot \ln \frac{n}{N} \tag{VIII.1.09}$$

In this case the Fermi level lies *below* the lowest available energy level E_{pot} because $\ln n/N < 0$ since $n \ll N$ (see Fig. VIII.1.2). In the energy distribution of the electrons

$$N(E)\, dE = 2D(E) f(E)\, dE$$
$$= VN \frac{2}{\sqrt{\pi}} \left(\frac{E - E_{pot}}{kT}\right)^{1/2} \frac{1}{e^{\frac{E - E_F}{kT}} + 1}\, d\left(\frac{E}{kT}\right) \tag{VIII.1.10}$$

we have $$e^{\frac{E-E_F}{kT}} = e^{\frac{E-E_{pot}}{kT}} \cdot e^{\frac{E_{pot}-E_F}{kT}} > e^{\frac{E_{pot}-E_F}{kT}} \gg 1$$

because $E - E_{pot}$ is positive in any case and $E_{pot} - E_F$ is strongly positive in the present case. Hence the general formula (VIII.1.10) applicable for the model under consideration can, in the limiting case of small concentration $n \ll N$, be simplified to

$$N(E)\,dE = VN\frac{2}{\sqrt{\pi}}\left(\frac{E - E_{pot}}{kT}\right)^{1/2} e^{-\frac{E-E_F}{kT}}\, d\left(\frac{E}{kT}\right)$$

$$N(E)\,dE = VN\, e^{\frac{E_F-E_{pot}}{kT}} \cdot \frac{2}{\sqrt{\pi}}\left(\frac{E - E_{pot}}{kT}\right)^{1/2} e^{-\frac{E-E_{pot}}{kT}}\, d\left(\frac{E}{kT}\right) \qquad \text{(VIII.1.11)}$$

Using (VIII.1.09) and (VIII.1.06), we finally obtain

$$N(E)\,dE = N \cdot \frac{2}{\sqrt{\pi}}\left(\frac{E - E_{pot}}{kT}\right)^{1/2} e^{-\frac{E-E_{pot}}{kT}}\, d\left(\frac{E - E_{pot}}{kT}\right) \qquad \text{(VIII.1.12)}$$

We see that the effective density of states N, in whose definition (VIII.1.04) the Planck constant appeared, has dropped out completely. The electron gas shows the classical Maxwell distribution. *If the electron gas is sufficiently diluted, it behaves like a Maxwell gas in a space with the potential energy* E_{pot}.

In the opposite limiting case of $n \gg N$, one obtains from equation (A.II.3)

$$E_F = E_{pot} + kT\left(\frac{3}{4}\right)^{2/3} \pi^{1/2}\left(\frac{n}{N}\right)^{2/3} \qquad \text{(VIII.1.13)}$$

or, using (VIII.1.04),

$$E_F = E_{pot} + \frac{1}{2}\left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{m}\, n^{2/3}$$

In other words, the Fermi level lies now *above* the lowest available level E_{pot} (see Fig. VIII.1.3). No general simplifications can be applied in the energy distribution of the electrons (VIII.1.10). The gas shows nonclassical behavior, and we talk of a *degenerate* or *Fermi gas*. We call the concentration above which degeneracy occurs the degeneracy concentration. It is approximately equal to the effective density of states N.

However, at high electron energies $E \gg E_F$, the exponential term in the denominator of the distribution function $f(E)$ predominates again and the equation (VIII.1.10) is simplified for the distribution of the high-energy electrons to

$$N(E)\,dE = VN\frac{2}{\sqrt{\pi}}\left(\frac{E - E_{pot}}{kT}\right)^{1/2} e^{-\frac{E-E_F}{kT}}\, d\left(\frac{E}{kT}\right) \qquad \text{(VIII.1.14)}$$

Comparison with (VIII.1.12) shows that this tail of the electron distribution in the direction of high energies $E \gg E_F > E_{pot}$ corresponds almost to a Maxwell gas of potential energy E_F and concentration N ("Maxwell tail"). The analogy would be complete if instead of the factor $[(E - E_{pot})/kT]^{1/2}$ we would have the factor $[(E - E_F)/kT]^{1/2}$. However, this difference is immaterial at the high energies which we are considering.

For the problem of surmounting potential barriers, for instance, for the question of how many electrons can leave the potential well, only the high-energy electrons are of importance. Hence in problems of this type a Fermi gas can be treated like a Maxwell gas with the concentration N and the potential energy[1] E_F.

§2. The General Condition for Thermal Equilibrium: E_F = const

The last remark makes the solution of the following problem relatively simple. Let two potential wells I and II be separated by a high potential barrier (see Fig. VIII.2.1). After a certain period of time, the electron concentrations in these will adjust themselves in such a way that as many electrons will surmount or tunnel through the potential barrier in unit time from left to right as from right to left. Thereafter, the concentrations n_I and n_{II} will not change any more, i.e., thermal equilibrium is established. It may now be asked what is the ratio of the concentrations n_I and n_{II} in this stationary final state?

We have just learned that the electron current emerging from potential well I can be computed as though the potential well contained a Maxwell gas of concentration N with the potential energy E_{F_I}. Correspondingly, the number of electrons emerging per unit time from well II is equal to the emission current which would be produced by a Maxwell gas of the same concentration N with the potential energy $E_{F_{II}}$. Hence the emission currents can be equal only if

$$E_{F_I} = E_{F_{II}} \qquad \text{(VIII.2.01)}$$

[1] This makes it plausible that the emission law for a Fermi gas is derived from the Richardson emission law for a Maxwell gas by inserting into the equation applicable for the Maxwell gas the value of N defined by (VIII.1.04) for the concentration of the gas and the difference between the potential energy outside the well and the Fermi level E_F for the depth of the potential well. Regarding the emission law for a Fermi gas see, e.g., A. Sommerfeld in H. Geiger and K. Scheel, "Handbuch der Physik," vol. XXIV, part 2, p. 350, Eq. (4.13), Springer-Verlag OHG, Berlin, 1933. In this equation one has to use $G = 2$ (*ibid.*, p. 337). Regarding the Richardson emission law for a Maxwell gas see *ibid.*, p. 351, Eq. (4.15).

If the electron concentration in both wells is so low that degeneracy has not yet set in and that therefore the thermal equilibrium between two Maxwell gases of different potential energy has to be determined, the Fermi levels E_{F_I} and $E_{F_{II}}$ are computed from (VIII.1.09) and (VIII.2.01) changes into

$$E_{\mathrm{pot}_I} + kT \ln \frac{n_I}{N} = E_{\mathrm{pot}_{II}} + kT \ln \frac{n_{II}}{N}$$

$$n_I = n_{II}\, e^{\frac{E_{\mathrm{pot}_{II}} - E_{\mathrm{pot}_I}}{kT}} \qquad \text{(VIII.2.02)}$$

This, however, is the well-known "Boltzmann equilibrium" between two Maxwell gases.[1]

If the electron concentrations are high enough for degeneracy, the equilibrium condition (VIII.2.01) is still valid, but it has now to be used with (VIII.1.13) instead of (VIII.1.09). However, we do not want to discuss this in detail but rather look once more at condition (VIII.2.01).

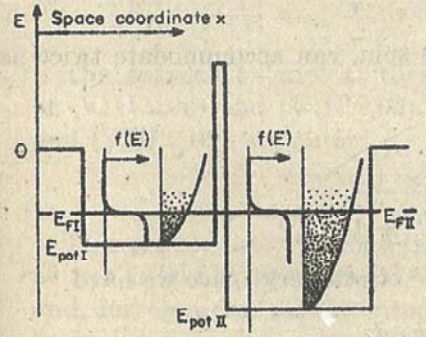


FIG. VIII.2.1. Two potential wells in thermal equilibrium: $E_{F_I} = E_{F_{II}}$.

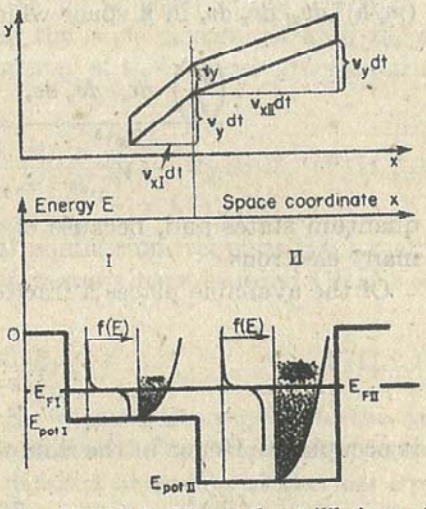


FIG. VIII.2.2. Thermal equilibrium of two spaces I and II with different potential energy E_{pot_I} and $E_{\mathrm{pot}_{II}}$.

The validity of this condition $E_F = \text{const}$ extends far beyond the particular example under consideration. In order to prove this, we start by dropping the high potential barrier between the two potential wells (see Fig. VIII.2.2). Furthermore, we think of the principle of detailed balancing, according to which every microprocess is as frequent as the reverse process if a real thermal equilibrium exists.

[1] See the very instructive discussion of the barometric altitude formula in R. Becker, "Vorstufe zur theoretischen Physik," p. 137, Springer-Verlag OHG, Berlin, 1950.

Therefore the condition of equality for the electron currents in the two directions has to be defined more rigorously by saying that this condition applies not only for the *total* currents through an imaginary separating plane between the two spaces I and II, but also for any arbitrary velocity group of a given magnitude and direction.

For a quantitative derivation we start from the fact that a group of electrons with velocities between $\{v_{xI}, v_y, v_z\}$ and $\{v_{xI} + dv_{xI}, v_y + dv_y, v_z + dv_z\}$ occupy the volume dv_{xI}, dv_y, dv_z in velocity space. The wave numbers k_x, k_y, k_z are connected with the velocities, according to (VII.6.31) and (VII.5.09), by

$$k_x = \frac{1}{\hbar} p_x = \frac{m}{\hbar} v_x \qquad k_y = \frac{m}{\hbar} v_y \qquad k_z = \frac{m}{\hbar} v_z \quad \text{(VIII.2.03)}$$

Hence the group of electrons under consideration occupies the volume $(m/\hbar)^3\, dv_{xI}\, dv_y\, dv_z$ in $\mathbf{k}$ space which[1] contains

$$\frac{\left(\frac{m}{\hbar}\right)^3 dv_{xI}\, dv_y\, dv_z}{\frac{(2\pi)^3}{V}} = V \cdot \left(\frac{m}{\hbar}\right)^3 dv_{xI}\, dv_y\, dv_z \quad \text{(VIII.2.04)}$$

quantum states and, because of the spin, can accommodate twice as many electrons.

Of the available places a fraction

$$\frac{1}{e^{\frac{1}{kT}[E - E_{F_I}]} + 1}$$

is occupied. Hence in the volume V of ordinary space we have

$$2 \cdot \left(\frac{m}{\hbar}\right)^3 \cdot \frac{dv_{xI}\, dv_y\, dv_z}{e^{\frac{1}{kT}\left[E_{\text{pot}_I} + \frac{m}{2}(v_{xI}^2 + v_y^2 + v_z^2) - E_{F_I}\right]} + 1} \cdot V \quad \text{(VIII.2.05)}$$

electrons of the velocity group under consideration.

During the time dt all those electrons of the velocity group under consideration which are within the parallelepiped of Fig. VIII.2.2 pass through a unit area $dy \cdot dz$ of an imaginary separating plane between the two spaces I and II. As the parallelepiped volume is $dy\, dz\, v_{xI}\, dt$, one obtains for the number of electrons, with the use of (VIII.2.05),

[1] According to p. 182, one quantum state requires the volume $(2\pi)^3/V$ in $\mathbf{k}$ space.

$$2 \cdot \left(\frac{m}{h}\right)^3 \cdot \frac{v_{x\mathrm{I}} \cdot dv_{x\mathrm{I}} \cdot dv_y \cdot dv_z}{e^{+\frac{1}{kT}\left[E_{\mathrm{pot_I}} + \frac{m}{2}(v_{x\mathrm{I}}^2 + v_y^2 + v_z^2) - E_{F_\mathrm{I}}\right]} + 1} \, dy\, dz\, dt \quad \text{(VIII.2.06)}$$

After entering space II, these electrons have the velocity $v_{x\mathrm{II}}$, v_y, v_z, because the tangential component does not change. The law of conservation of energy states that

$$E_{\mathrm{pot_I}} + \frac{m}{2}(v_{x\mathrm{I}}^2 + v_y^2 + v_z^2) = E_{\mathrm{pot_{II}}} + \frac{m}{2}(v_{x\mathrm{II}}^2 + v_y^2 + v_z^2) \quad \text{(VIII.2.07)}$$

Differentiation yields

$$v_{x\mathrm{I}}\, dv_{x\mathrm{I}} = v_{x\mathrm{II}}\, dv_{x\mathrm{II}} \quad \text{(VIII.2.08)}$$

The microscopic reverse process to an electron of group $\{v_{x\mathrm{I}}, v_y, v_z\}$ traversing the element of area $dy \cdot dz$ consists of an electron of group $\{-v_{x\mathrm{II}}, -v_y, -v_z\}$ traversing the same element of area $dy \cdot dz$. In analogy to (VIII.2.06), the frequency of this reverse process during the time dt is

$$2 \cdot \left(\frac{m}{h}\right)^3 \cdot \frac{v_{x\mathrm{II}}\, dv_{x\mathrm{II}}\, dv_y\, dv_z}{e^{+\frac{1}{kT}\left[E_{\mathrm{pot_{II}}} + \frac{m}{2}(v_{x\mathrm{II}}^2 + v_y^2 + v_z^2) - E_{F_\mathrm{II}}\right]} + 1} \, dy\, dz\, dt \quad \text{(VIII.2.09)}$$

The detailed balance at thermal equilibrium requires the equality of (VIII.2.06) and (VIII.2.09). If we now bear in mind (VIII.2.08) and (VIII.2.07), we obtain

$$E_{F_\mathrm{I}} = E_{F_\mathrm{II}} \quad \text{(VIII.2.10)}$$

This proves that the condition $E_F = \text{const}$ also applies to the case of two neighboring potential wells *without* a high separating barrier and, furthermore, that it ensures detailed balancing at thermal equilibrium. It is obvious that this result can be generalized by approximating continuous $E_{\mathrm{pot}}(x)$ curves[1] with stepped variations.

[1] Here we think in the first place of the space variation of the electrostatic macropotential which we have encountered in Chaps. IV and V in the barrier layers of rectifiers and p-n junctions.

Apart from this, Thomas and Fermi have regarded the electron shell of a heavy atom, by way of a model, as a highly degenerate electron gas which is contained in a potential well. The atomic nucleus as well as the electron shell contribute to the potential variation in space in accordance with the Poisson equation:

$$\Delta V = -4\pi\rho = +4\pi e n$$

Thomas and Fermi obtain a relation between local potential $V(x)$ and electron concentration $n(x)$ from the condition that the Fermi level $E_F = -eV + \zeta$ must be constant in space. For ζ they use the value applicable for the limiting case of

An electron gas filling a space in which the potential energy E_{pot} of an electron varies from place to place will in thermal equilibrium distribute itself in this space in such a way that the Fermi level E_F becomes independent of the position:

$$E_F = \text{const} \tag{VIII.2.11}$$

As the Fermi level E_F can be computed from the potential energy $E_{pot}(x)$ and the density $n(x)$ by (VIII.1.08), the condition (VIII.2.11) relates the change of concentration $n(x)$ and the spatial distribution $E_{pot}(x)$ of the potential energy of an electron by

$$E_F = E_{pot}(x) + \zeta\left(\frac{n(x)}{N}\right) = \text{const} \tag{VIII.2.12}$$

In the case of sufficient dilution

$$n(x) \ll N$$

the general equilibrium condition (VIII.2.12) changes with the aid of equation (A.II.2) into the well-known Boltzmann principle

$$n(x) \sim e^{-\frac{1}{kT}E_{pot}(x)} \tag{VIII.2.13}$$

of the Maxwell gas.

§3. The Significance of the Fermi Level $E_F = E_{pot}(x) + \zeta\left(\frac{n(x)}{N}\right)$ for Nonequilibrium States

We have seen in the last paragraph that the concentration $n(x)$ of an electron gas[1] adjusts itself at thermal equilibrium in a region with

---

a highly degenerate gas (VIII.4.07)

$$\zeta = \frac{1}{2}\left(\frac{3}{8\pi}\right)^{2/3}\frac{h^2}{m}n^{2/3}$$

They obtain thus

$$-eV(x) + \frac{1}{2}\left(\frac{3}{8\pi}\right)^{2/3}\frac{h^2}{m}n^{2/3} = \text{const}$$

At a great distance from the atom, the electron concentration $n = 0$. If we set here also the potential $V = 0$, the constant becomes zero and we obtain

$$n(x) = \frac{\pi}{3}\frac{8}{h^3}(2meV(x))^{3/2} \tag{VIII.2.131}$$

By using this expression for n in the Poisson equation, we obtain the Thomas-Fermi differential equation. [See A. Sommerfeld, "Atombau und Spektrallinien," vol. II, p. 693, Eq. (14), Vieweg-Verlag, Brunswick, Germany, 1944.] Equation (VIII.2.131) is the exact counterpart to the Boltzmann principle (VIII.2.13).

[1] With some changes in sign, the following discussion can also be applied to holes. See pp. 375 and 377.

potential energy $E_{pot}(x)$ varying in space, so as to fulfill the condition

$$E_{pot}(x) + \zeta\left(\frac{n(x)}{N}\right) = E_F = \text{const} \qquad \text{(VIII.2.12)}$$

We now assume that the potential energy E_{pot} is produced by an electrostatic potential $V(x)$ with field strength $\mathbf{E}(x) = -V'(x)$:

$$\frac{d}{dx}E_{pot}(x) = -eV'(x) = +e\mathbf{E}(x) \qquad \text{(VIII.3.01)}$$

If we differentiate (VIII.2.12) with respect to x, utilize (VIII.3.01), and finally multiply by the electron mobility μ_n and the concentration $n(x)$, we obtain

$$+ e\mu_n n(x) \cdot \mathbf{E}(x) + \mu_n \cdot n(x) \cdot \frac{d\zeta}{dn} \cdot n'(x) = 0 \qquad \text{(VIII.3.02)}$$

The thermal equilibrium therefore results from the mutual compensation of the field current $e\mu_n n(x)\mathbf{E}(x)$ and of a current component $+\mu_n n(x)(d\zeta/dn)n'(x)$, which is caused by a concentration gradient $n'(x)$ and which must consequently be regarded as a generalized diffusion current. Since the quantity ζ is a function of the concentration n only (see Fig. A.II.1 in Appendix II) the expression $\mu_n n(x)(d\zeta/dn)n'(x)$ does not contain the field strength $\mathbf{E}(x)$ at all and hence represents the diffusion current even in those cases where the electric field does not have exactly the value required for the compensation of the diffusion current. Therefore, even in nonequilibrium cases, one has to use for the diffusion current i_{diff} the equation derived from the equilibrium condition (VIII.3.02)

$$i_{diff} = +\mu_n n(x) \cdot \frac{d\zeta}{dn} \cdot n'(x) = +\mu_n \cdot \frac{d\zeta}{d\ln n} \cdot n'(x) \qquad \text{(VIII.3.03)}$$

or

$$i_{diff} = +\mu_n \cdot n(x) \cdot \frac{d}{dx}\zeta \qquad \text{(VIII.3.04)}$$

If one adds to this generalized diffusion current the field current $+e\mu_n n(x) \cdot (-dV/dx)$, one obtains for the total current under nonequilibrium conditions

$$i_{tot} = \mu_n n(x)\frac{d}{dx}[-eV(x) + \zeta(x)] = \mu_n \cdot n(x) \cdot \frac{d}{dx}[E_{pot}(x) + \zeta(x)]$$

or

$$i_{tot} = +\mu_n \cdot n(x) \cdot \frac{d}{dx}E_F(x) \qquad \text{(VIII.3.05)}$$

If we compare (VIII.3.04) and (VIII.3.05) with

$$i_{field} = e\mu_n n(x)\mathbf{E}(x) = \mu_n n(x) \cdot (-e) \cdot V'(x)$$

i.e., with

$$i_{\text{field}} = +\mu_n \cdot n(x) \cdot \frac{d}{dx} E_{\text{pot}}(x) \qquad \text{(VIII.3.06)}$$

we arrive at the following conclusion.

The Fermi level $E_F(x)$ and the function $\zeta(x)$ play the same role for the total current i_{tot} and the diffusion current i_{diff}, respectively, as does the potential energy $E_{\text{pot}} = -eV(x)$ for the field current i_{field}. Hence the function $\zeta(x)$ is called the chemical potential and E_F the electrochemical potential of the electron gas.[1]

If we compare Eq. (VIII.3.03) for the diffusion current with the form in which it is usually written

$$i_{\text{diff}} = (-e) \cdot (-D \cdot n'(x)) \qquad \text{(VIII.3.07)}$$

we obtain the following equation for the diffusion coefficient

$$D = \frac{\mu_n}{e} \frac{d\zeta(n)}{d \ln n} \qquad \text{(VIII.3.08)}$$

This means that the diffusion coefficient is, as a rule, a function of the concentration; for instance, in the Fermi limiting case $n \gg N$ of page 301, Eq. (VIII.4.07)

$$\zeta = \frac{1}{2}\left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{m_{\text{eff}}} n^{2/3} \qquad \text{(VIII.4.07)}$$

will result for the chemical potential. This leads to the following expression for the diffusion coefficient:

$$D = \frac{1}{3} \frac{\mu_n}{e} \left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{m_{\text{eff}}} n^{2/3} = \frac{2}{3} \frac{\mu_n}{e} \zeta(n) \qquad \text{(VIII.3.09)}$$

On the other hand, in the Maxwell limiting case $n \ll N$,

$$\zeta = kT \ln \frac{n}{N}$$

[see Eq. (A.II.2)] causes the diffusion coefficient to become *in*dependent of the concentration:

[1] In the use of these terms, one generally does not differentiate between "potential" and "potential energy." However, this is not done in mechanics either, so that the procedure in electrostatics constitutes an exception. Besides, the terms chemical and electrochemical potential are derived from thermodynamics where the equilibrium condition "electrochemical potential = const" is deduced from the second law. See W. Schottky and H. Rothe, Physik der Glühelektroden, in Wien and Harms, "Handbuch der Experimentalphysik," vol. 13, part 2, p. 18, Eq. (5), Akademische Verlagsgesellschaft, Leipzig, 1928.

$$D = \mu_n \frac{kT}{e} \qquad \text{(VIII.3.10)}$$

This is the well-known Nernst-Townsend-Einstein equation.[1]

The use of the electron mobility μ_n in the preceding discussion and the interpretation of the expression $e\mu_n n(x)\mathbf{E}(x)$ as field current indicate that only a negligible deviation from thermal equilibrium has been assumed. Ohm's equation

Field current density = conductivity × field strength

and the diffusion equation

Diffusion current density

= diffusion coefficient × concentration gradient

are justified only if the condition is fulfilled that the field and diffusion currents are small in relation to the thermal current in one direction (see page 248, footnote 1). This assumption is, in fact, contained in the word electron "gas." The typical example of the reverse case is represented by the electrons in a vacuum tube; here the thermal velocities are negligibly small compared with the common rush of the electrons from cathode to anode, and one therefore does not usually talk of an electron gas but rather of an "electron avalanche" or a similar term. Hence, if the concept of the electrochemical potential is to be used in nonequilibrium applications, one has to make sure that the resulting current is small compared with the unidirectional thermal current, i.e., that the deviation from thermal equilibrium is slight.

[1] W. Nernst, *Z. Phys. Chem.*, **2**: 613 (1888), particularly, p. 615. J. S. Townsend, *Trans. Roy. Soc. (London)*, **A193**: 129 (1900), particularly, p. 153. A. Einstein, *Ann. Physik*, **17**: 549 (1905), particularly pp. 554 and 555.

C. Wagner in *Z. physik. Chem.*, **B11**: 139 (1931), and, particularly, in *Z. physik. Chem.*, **B21**: 25 (1933), generalizes the ideas expressed in the above papers by leaving open the functional dependence of the chemical potential ζ on the concentration. For this reason, he obtains the relationship between current density (or migration velocity) and the gradient of the electrochemical potential in a *general* form [see *Z. physik. Chem.*, **B21**: 29 (1933), Eq. (6)]. W. Schottky, in *Wiss. Veröffentl. Siemens-Werken*, **14**: No. 2, 1 (1935), particularly p. 4, Eqs. (1), (1′), (2), (2′) and p. 12, Eq. (15), has also found in a general form the proportionality between current density and the gradient of the electrochemical potential. The same applies to C. Herring and M. H. Nichols in *Revs. Mod. Phys.*, **21**: 185 (1949), particularly p. 196, Eq. (I.6.2).

In *Bell System Tech. J.*, **28**: 435 (1949), W. Shockley discusses the case of the Maxwell gas and introduces the electrochemical potentials of the electrons and holes under the name of "quasi Fermi levels" or "imrefs" whereby he can prove the proportionality of the total current of the particle type concerned with the gradient of a generalized potential, i.e., the electrochemical potential [*ibid.*, p. 451, Eq. (3.5)].

§4. Fermi Statistics in Metals and Insulators

In the preceding paragraphs we have discussed the electron gas in the potential well as a first model and inserted, subsequently, considerations concerning equilibrium and nonequilibrium states in regions with space-varying potential. We shall now turn from the single-electron

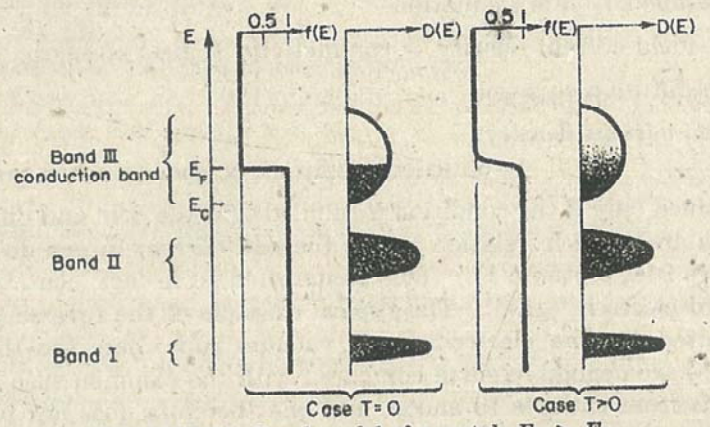


FIG. VIII.4.1. Band model of a metal: $E_F > E_C$.

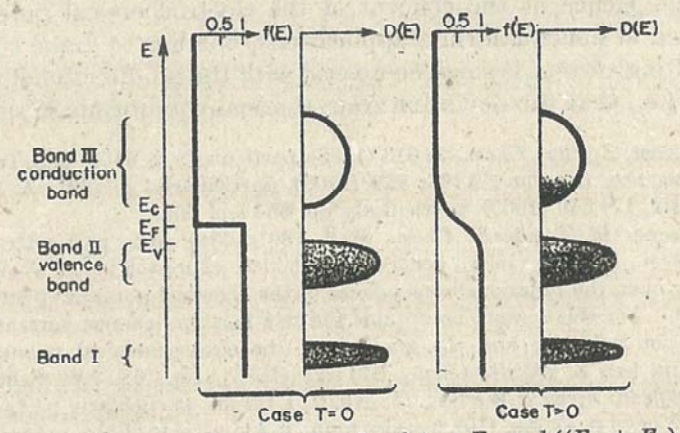


FIG. VIII.4.2. Band model of an insulator: $E_F \approx \frac{1}{2}(E_C + E_V)$.

problem to the many-electron problem, i.e., we shall carry out the distribution of the electrons among the quantum states of the single-electron problem in the case of a *crystal*, from the point of view of Fermi statistics. We have seen in Chap. VII, §2 to §4, that here the quantum states are arranged in bands so that we have to distinguish between two cases, namely, that in which the Fermi level at the

temperature $T = 0$ falls into an allowed band and that in which it falls into a forbidden band (see Figs. VIII.4.1 and VIII.4.2).

a. The Band Models of a Metal and of an Insulator at Temperature $T = 0$

We have seen on pages 263 and 267 that a fully occupied band cannot produce a current and therefore drops out for the conduction process. The case of Fig. VIII.4.1 with the Fermi level within an allowed band leads to a band that is only partially occupied; in other words, on applying an external field, a current is produced and we have the case of a metal. The partially occupied band is called the "conduction band." On the other hand, in the case of Fig. VIII.4.2 with the Fermi level E_F *between* two allowed bands, the bands below the Fermi level E_F are completely occupied and therefore drop out for the conduction process. The band above the Fermi level, however, in which conduction processes could take place if any electrons were present and which is therefore called the conduction band, is empty. Such a crystal does not carry any current when an external field is applied (at least at $T = 0$); we have the case of an insulator or of an "intrinsic semiconductor". (see pages 16 to 20).

During the last few years the lattices of Group IV of the periodic system which are insulators at $T = 0$, namely, carbon in the form of diamond, silicon, germanium, and gray tin, have gained particular importance. The four outer valence electrons of these elements just fill the last band below the Fermi level E_F completely at $T = 0$. Therefore this band is often called the valence band. A more general term is "bound electron band."[1]

If one is interested, beyond these general statements, in the exact position of the Fermi level E_F in a metal or in an insulator which is,

[1] If one explains the elimination of the "valence band" for conduction processes, not with the considerations of pages 263 to 267, but by the fact that the electrons occupying this band are tightly bound to the four neighboring atoms by homopolar pair formation, one leaves the whole concept of the band model (the Hund-Mulliken approximation) and passes over to the atomistic model (Heitler-London approximation). The same consideration applies, if, for instance, one explains the insulating nature of an NaCl crystal by the strong binding of the electrons in the M shell of the Cl ion (the L shell of the Na^+ which is also fully occupied lies at a lower level; hence the *highest* fully occupied band is not associated with it). See, for instance, F. Hund, *Z. tech. Phys.*, **16**: 333 (1935), Fig. 3.

One need not worry about this oscillation between the band model and the atomistic concept. On the contrary, one can have greater confidence in the result obtained from one concept if it is also derived from the other concept, as is the case here with the elimination of a fully occupied band from the conduction processes.

for instance, important for work-function problems as was mentioned above on page 287, information about the density of states $D(E)$ is essential. In discussing these problems, we shall consider temperatures $T > 0$ right from the start.

b. The Band Model of a Metal at Temperatures $T > 0$

In the case drawn in Fig. (VIII.4.1), bands I and II are practically completely occupied, not only at temperature $T = 0$, but also at higher temperatures. (Concerning the case of extremely high temperatures see page 300.) Hence, for the calculation of the position of the Fermi level E_F in accordance with condition (VII.10.03), one can use either all the electrons and all three bands I, II, and III or only the "conduction electrons" of the "conduction band III." In the second procedure, one reduces the number of available electron places and the number of electrons to be accommodated by the same number, i.e., the number of electron places in I and II. If we decide to make the computation only with the conduction electrons and only with the places available in band III, this is done mainly for reasons of simplicity. In this case, we require information only about the nature of the density of states $D(E)$ within the conduction band.[1] Furthermore, in view of the discussion in Chap. VI, the description of the behavior of the strongly bound electrons in the lower energy levels with the aid of the band model, i.e., with the Hund-Mulliken approximation, is of doubtful validity. Therefore, it is desirable for fundamental reasons, too, that the inner electron shells of each atom be added to the atom cores causing the periodic potential and that the band model be applied only to the electrons of the outermost shell.

In the determining equation (VII.10.03) for E_F, we now must use the energy E_C of the lower edge of the conduction band as the lower integration limit:

$$2 \int_{E=E_c}^{E=\infty} D(E) \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \, dE = N \qquad \text{(VIII.4.01)}$$

where N is now the number of conduction electrons in the conduction band. Naturally, a more or less explicit evaluation of (VIII.4.01) can be attempted only if more accurate information about the distribution of the density of states $D(E)$ in the conduction band is available. Here one starts frequently from the approximation (VII.4.04) or (VII.6.19) which, with the aid of Eq. (VII.6.23), $m_{eff} = \hbar^2/E''(|\mathbf{k}_C|)$, and with

[1] Concerning the shape of $D(E)$ which is shown only diagrammatically in Fig. VIII.4.1, see p. 299, footnote 1, and p. 303, footnote 3.