

VI

TRANSPORT PHENOMENA

6.1. General considerations. Collision time

ACCORDING to Chapter IV an electron in the field of force of a perfect lattice has stationary states in which the mean velocity and hence the mean transport of charge and of energy do not vanish. This means that we can set up an electric current and an energy flux without an electric field or a temperature gradient to maintain them. In other words, the electric and thermal resistivities are zero for a perfect lattice. The actual resistivities therefore depend on disturbances which, for the equilibrium problems of Chapter IV, are usually negligible. The main sources of such disturbances are (a) lattice vibrations, (b) impurities and lattice imperfections, and (c) the interaction between the electrons. For a good and pure crystal the first of these effects is the most important, and this explains at once the qualitative fact that the resistance of an ideal metal decreases with decreasing temperature, and tends to zero at $T = 0$. This was one of the major difficulties in the classical electron theory of metals.

The problem of treating these disturbances is similar to the calculation of transport phenomena in the kinetic theory of gases, but the nature of the interactions and the importance of quantum effects brings in a number of essentially new points.

The usual approach to the problem is based on calculating the probability, per unit time, of an electron making a transition from one given state to another, and obtaining from this the rate of change with time of the number of electrons in any given state. This rate of change depends on the distribution of the electrons over the various levels, and the stationary distribution is then determined as that for which there is no change with time. In some cases the lattice vibrations will also be affected by the presence of a current. In that case we must also require that the number and distribution of phonons do not change with time, and thus obtain two simultaneous sets of equations which determine both the electron and the phonon distribution.

In using this approach, which is taken over from gas theory, we are making certain assumptions which are sometimes hard to justify. We shall therefore be careful to note these assumptions in our derivation, and

we shall later return to the possible refinements that could come from a more rigorous approach.

For preliminary orientation, we shall first obtain the equations which are analogous to the assumption of constant mean free path in gas theory. However, since the electron velocity is not a convenient variable, we shall use the concept of collision time instead of that of mean free path.

The simple picture is then based on the following assumptions:

The electrons suffer only elastic collisions. The probability per unit time of an electron making a collision is $1/\tau$, where τ is called the collision time. This may depend on the energy of the electron, but for given energy is constant (independent of the direction of motion). After the collision the electron is found with equal probability on any part of the energy surface.

Then the average number of electrons making a transition from some state \mathbf{k} to some other state \mathbf{k}' is proportional to the probability of the state \mathbf{k} being occupied, and to the probability of the state \mathbf{k}' being empty (we consider only electrons of a given spin direction), say

$$An(\mathbf{k})\{1-n(\mathbf{k}')\}. \quad (6.1)$$

The probability of the inverse transition from \mathbf{k}' to \mathbf{k} is obtained by interchanging \mathbf{k} and \mathbf{k}' , but the coefficient A is the same (law of detailed balancing). The difference between the two rates gives us the net rate of transfer of electrons from \mathbf{k} to \mathbf{k}' , which is

$$A[n(\mathbf{k})\{1-n(\mathbf{k}')\}-n(\mathbf{k}')\{1-n(\mathbf{k})\}] = A\{n(\mathbf{k})-n(\mathbf{k}')\}. \quad (6.2)$$

This last result is the same as would have been obtained without the exclusion principle. In the present case we need not consider the exclusion principle in counting collisions.

Consider now all the states with energies between E and $E+dE$. For simplicity of notation we shall assume these all to be part of the same band, and suppress the suffix l , though this is not essential. Their number near an element $d\sigma$ of the energy surface is

$$dz = \left(\frac{L}{2\pi}\right)^3 \frac{d\sigma}{|\text{grad } E|} dE, \quad (6.3)$$

where L^3 is the volume of the crystal, $\text{grad } E$ is the gradient of $E(\mathbf{k})$ in \mathbf{k} space, and $d\sigma$ is the element of area of the energy surface. We write this as

$$dz = \rho d\sigma dE, \quad (6.4)$$

where ρ is the surface density of states, which in general varies over the surface, and we call

$$\int \rho d\sigma = S(E) = \frac{dZ}{dE}, \quad (6.5)$$

the last expression being the total number of states per unit energy, as in § 4.6.

Then the loss, per unit time, of electrons from the state \mathbf{k} due to collisions is

$$\frac{1}{\tau} n(\mathbf{k}),$$

whereas the gain from transitions into state \mathbf{k} is, since these cover all states in the energy shell with equal probability,

$$\frac{\int n(\mathbf{k}') \rho' d\sigma'}{\tau S} = \frac{1}{\tau} \bar{n}, \quad (6.6)$$

where \bar{n} is the average number per state on the energy shell. The net rate of change of the number of electrons in state \mathbf{k} is

$$\frac{dn(\mathbf{k})}{dt} = -\frac{1}{\tau} \{n(\mathbf{k}) - \bar{n}\}. \quad (6.7)$$

The solution of this equation in the absence of an external field is

$$n(\mathbf{k}, t) = \bar{n} + \{n(\mathbf{k}, 0) - \bar{n}\} e^{-t/\tau}. \quad (6.8)$$

Any initial deviation from uniformity over the energy shell decreases exponentially with time.

In an electric field in the x -direction the electrons move in k space according to the law (4.42), and hence the rate of change of n due to the field is

$$-\frac{eF}{\hbar} \frac{\partial n(\mathbf{k})}{\partial k_x}. \quad (6.9)$$

Combining the effect of the field with that of the collisions and requiring the electron distribution to be stationary, we obtain the 'Boltzmann equation'

$$\frac{1}{\tau} \{n(\mathbf{k}) - \bar{n}\} + \frac{eF}{\hbar} \frac{\partial n(\mathbf{k})}{\partial k_x} = 0. \quad (6.10)$$

The fields that can be maintained in a metal are weak and we may neglect terms proportional to the square of the field intensity. Otherwise we should include the Joule heat, and should not obtain stationary conditions at all unless we also included explicitly the mechanism by which the heat is disposed of. We therefore assume that

$$n(\mathbf{k}) = f(E) + n_1(\mathbf{k}), \quad (6.11)$$

where f is the Fermi distribution and n_1 is small of first order. Then (6.10) becomes, to first order,

$$\frac{1}{\tau} \{n_1(\mathbf{k}) - \bar{n}_1\} + \frac{eF}{\hbar} \frac{\partial f}{\partial E} \frac{\partial E}{\partial k_x} = 0, \quad (6.12)$$

or, using the expression (4.41) for the velocity,

$$\frac{1}{\tau}\{n_1(\mathbf{k}) - \bar{n}_1\} = -eFv_x \frac{df}{dE}. \quad (6.13)$$

If we average this equation over the energy surface, the left-hand side vanishes identically. The right-hand side also gives zero, since by (4.12) the energy is an even function of \mathbf{k} , hence the velocity an odd function, so that its average over the energy surface must vanish.

The constant \bar{n}_1 is therefore not determined. This is to be expected since, with only elastic collisions, the total number of electrons of each energy remains unchanged. We may therefore add to n_1 an arbitrary function of the energy. This will not contribute to the current, and is therefore unimportant for the present purpose. One can however show that, if also some inelastic collisions are allowed for, \bar{n}_1 has to be zero.

Now the electric current density is, if we choose the volume of the metal to be unity,

$$J_x = 2e \int n_1 v_x \rho dE d\sigma = -2e^2 F \int \bar{v}_x^2 \tau \frac{dZ}{dE} \frac{df}{dE} dE. \quad (6.14)$$

The factor 2 allows for the two spin directions, \bar{v}_x^2 is the average over the energy surface.

Now df/dE vanishes except in a region of width kT near $E = \eta$, the other factors in the integral vary slowly over that region. We may therefore replace them by their values at η ; the integral of df/dE is -1 . Then

$$\frac{\partial J_x}{\partial F_x} = 2e^2 \left(\tau \bar{v}_x^2 \frac{dZ}{dE} \right)_\eta,$$

and, by an obvious generalization to other components, the conductivity tensor $\sigma_{\mu\nu}$ is

$$\sigma_{\mu\nu} = \frac{\partial J_\mu}{\partial F_\nu} = 2e^2 \left(\tau v_\mu v_\nu \frac{dZ}{dE} \right)_\eta. \quad (6.15)$$

For cubic symmetry this may be replaced by

$$\sigma = \frac{1}{3} e^2 \left(\tau v^2 \frac{dZ}{dE} \right)_\eta.$$

In the particular case of free electrons, Z is proportional to $E^{3/2}$; hence $dZ/dE = 3Z/2E$. Using also the fact that $N = 2Z$ is then the total number of electrons per unit volume, and that v^2 is then constant over the energy surface and equal to $2E/m$, we obtain the well-known result

$$\sigma = \frac{e^2 N \tau}{m}. \quad (6.16)$$

Subject to the assumption about the collision time, this result is

evidently valid for the electrons near the bottom of a band, if m is replaced by the effective mass, and also for a nearly full band, if N then denotes the number of vacant places.

In the case of spherical symmetry, the work of this section can be extended to cover the case in which the electrons are not uniformly spread over the energy surface after each collision, but in which the probability of a deflexion through a given angle varies with the angle. In that case we may write, instead of (6.7),

$$\frac{dn(\mathbf{k})}{dt} = \int d\Omega' w(\Theta) \{n(\mathbf{k}') - n(\mathbf{k})\}, \quad (6.17)$$

where the integration is to be taken over a sphere of radius k . $d\Omega$ is the element of solid angle, and Θ is the angle between \mathbf{k} and \mathbf{k}' . $w(\Theta)$ is the differential scattering probability.

We expand n and w in spherical harmonics:

$$\left. \begin{aligned} n(\mathbf{k}) &= \sum n_{lm} Y_{lm} \\ w(\Theta) &= \sum \frac{w_l}{2l+1} P_l(\cos \Theta) \end{aligned} \right\}, \quad (6.18)$$

where the coefficients n_{lm} and w_l may still depend on the magnitude of \mathbf{k} . Inserting in (6.17) and using the properties of spherical harmonics,

$$\frac{dn_{lm}}{dt} = 4\pi(w_l - w_0)n_{lm}. \quad (6.19)$$

A deviation from uniformity in the angular distribution of the electrons still decays exponentially with time if it consists of spherical harmonics of a given order. However, its decay period now depends on the order. We may write

$$\left. \begin{aligned} \frac{dn_{lm}}{dt} &= -\frac{1}{\tau_l} n_{lm} \\ \frac{1}{\tau_l} &= 4\pi(w_0 - w_l) = \int \{1 - P_l(\cos \Theta)\} w(\Theta) d\Omega \end{aligned} \right\}. \quad (6.20)$$

Now in the isotropic case the right-hand side of (6.13) depends on angle only through v_x , which is proportional to a component of \mathbf{k} and therefore a spherical harmonic of first order, and (6.13) and all subsequent equations are still valid if we replace τ by τ_1 , which according to (6.20) gives

$$\frac{1}{\tau_1} = \int (1 - \cos \Theta) w(\Theta) d\Omega. \quad (6.21)$$

This shows in particular that the importance of small-angle scattering is proportional to the square of the angle, a result which is valid beyond the isotropic case discussed here.

In the general anisotropic case one may still look for the characteristic deviations which decrease exponentially with time, but in that case the disturbance caused by an external field will be a mixture of different characteristic disturbances, and the discussion becomes more complicated.

The equations of this section may be retained even in this general case, provided we interpret the quantity τ again as a mean value. This will now depend on the variation of the right-hand side of (6.13) over the energy surface, and also on the weight factor used in any averaging process like (6.14) for which the distribution is required.

6.2. Thermal conductivity

If, besides the electric field, there is also a temperature gradient, we obtain in the rate of change of the electron number the further contribution

$$-v_x \frac{\partial n(\mathbf{k})}{\partial x}. \quad (6.22)$$

The use of distribution functions depending on the coordinates as well as on the wave vector has to be understood in terms of wave packets, in the sense explained in § 2.4. Using again (6.11) and neglecting terms of second order in the temperature gradient, one finds, in place of (6.13),

$$\frac{1}{\tau} \{n_1(\mathbf{k}) - \bar{n}_1\} = -eFv_x \frac{\partial f}{\partial E} - \frac{dT}{dx} v_x \frac{\partial f}{\partial T}. \quad (6.23)$$

Obtaining again the electric current density as in (6.14) and the energy transport

$$S_x = 2 \int v_x E n_1 \rho dE d\sigma, \quad (6.24)$$

we find the equations

$$\left. \begin{aligned} J_x &= -2 \int \bar{v}_x^2 \tau \frac{dZ}{dE} \left(e^2 F \frac{\partial f}{\partial E} + e \frac{dT}{dx} \frac{\partial f}{\partial T} \right) dE \\ S_x &= -2 \int \bar{v}_x^2 E \tau \frac{dZ}{dE} \left(eF \frac{\partial f}{\partial E} + \frac{dT}{dx} \frac{\partial f}{\partial T} \right) dE \end{aligned} \right\}. \quad (6.25)$$

Although we have used the collision time concept in deriving these equations, they are, in fact, valid quite generally, as can be seen from the fact that the variation of the two terms on the right-hand side of (6.23) over the energy surface is the same, and that the weight factors used in (6.14) and (6.24) differ only by a function of the energy. Equations (6.25) may therefore be used, with τ having the same meaning in both, as long as we deal only with elastic collisions, so that the electrons of each energy must separately form a stationary distribution.

In evaluating the second terms in (6.25) some care is needed, since the

integral of $(dZ/dE)(\partial f/\partial T)$ over energy vanishes (the total number of electrons does not change with temperature). The contribution to (6.25) would therefore vanish if the other factors were constant, and it comes entirely from the variation of these factors over the boundary region of f . For these terms the temperature dependent part of (4.50) is therefore essential.

A simple calculation then gives the result

$$\left. \begin{aligned} J_x &= 2e^2 F \left(\tau \bar{v}_x^2 \frac{dZ}{dE} \right)_\eta - \frac{2e}{3} \frac{dT}{dx} \pi^2 k^2 T \left(\frac{dZ}{dE} \frac{d}{dE} (\bar{v}_x^2 \tau) \right)_\eta \\ S_x &= 2e F \left(\tau E \bar{v}_x^2 \frac{dZ}{dE} \right)_\eta - \frac{2}{3} \frac{dT}{dx} \pi^2 k^2 T \left(\frac{dZ}{dE} \frac{d}{dE} (\tau E \bar{v}_x^2) \right)_\eta \end{aligned} \right\}. \quad (6.26)$$

For the problem of thermal conductivity we have $J_x = 0$. Eliminating F from this condition, we find

$$S_x = -\frac{2}{3} \frac{dT}{dx} \pi^2 k^2 T \left(\frac{dZ}{dE} \bar{v}_x^2 \tau \right)_\eta = -\kappa \frac{dT}{dx}. \quad (6.27)$$

Comparing the thermal conductivity κ with the electric conductivity σ from (6.15)

$$\frac{\kappa}{\sigma} = \frac{\pi^2 k^2 T}{3e^2}. \quad (6.28)$$

This is known as the Wiedemann-Franz law.

This law can also be derived, with a different numerical factor, from a theory using classical, rather than Fermi-Dirac, statistics. It had therefore appeared surprising that the Wiedemann-Franz law was, apart from the factor, well confirmed by experiment, since this looked like a confirmation of the classical statistics, according to which the electron gas obeyed the equipartition law for the specific heat. In fact, from a simple dimensional argument one can see that, for given electron number and collision time, thermal conductivity depends on the product of the mean square velocity and the specific heat per electron. In the case of a degenerate Fermi gas the first is much larger than the classical value $3kT/m$, and the second correspondingly smaller than the classical specific heat, so that the product is about the same.

From the equations (6.25) one can also calculate the thermoelectric coefficients, but one must then include in (6.26) a correction to the first term, since the variation of the integrand over the energy interval near the edge of the Fermi distribution is then of importance.

6.3. Static obstacles. Impurities and imperfections

Turning now to the discussion of the mechanism of the collisions, we discuss first the case in which the cause of the scattering is an irregular

static potential. This assumption evidently covers the case of foreign atoms replacing atoms of the lattice or filling interstices, and other faults in the lattice. The effect of the lattice vibrations will require separate consideration.

Let the disturbing potential be $W(\mathbf{r})$ and assume it to be the combined effect of a large number of similar scattering centres, so that

$$W(\mathbf{r}) = \sum w(\mathbf{r} - \mathbf{R}_\nu). \quad (6.29)$$

Assume further that the disturbance caused by each centre is weak enough, and their number small enough, to regard W as a small perturbation.

Then if we write the wave function of an electron at time t as

$$\psi(\mathbf{r}, t) = \sum_{\mathbf{k}, l} a_{\mathbf{k}, l}(t) \psi_{\mathbf{k}, l}(\mathbf{r}) e^{-iE_{\mathbf{k}} t / \hbar}, \quad (6.30)$$

where the $\psi_{\mathbf{k}, l}$ are the solutions for the perfect lattice, in the absence of the disturbance, the wave equation leads to the equation

$$i\hbar \dot{a}_{\mathbf{k}} = \sum_{\mathbf{k}', l'} (\mathbf{k}, l | W | \mathbf{k}', l') e^{i(E_{\mathbf{k}}(\mathbf{k}) - E_{\mathbf{k}}(\mathbf{k}')) / \hbar} a_{\mathbf{k}'}, \quad (6.31)$$

where $(\mathbf{k}, l | W | \mathbf{k}', l') = \int \psi_{\mathbf{k}, l}^*(\mathbf{r}) W(\mathbf{r}) \psi_{\mathbf{k}', l'}(\mathbf{r}) d\mathbf{r}$ (6.32)

is the matrix element of the perturbing potential. To first order we may regard the a on the right-hand side of (6.31) as constant; hence

$$a_{\mathbf{k}, l}(t) = - \sum_{\mathbf{k}', l'} (\mathbf{k}, l | W | \mathbf{k}', l') a_{\mathbf{k}', l'}(0) \frac{e^{i(E - E')t / \hbar} - 1}{E - E'}, \quad (6.33)$$

where E and E' will be understood as abbreviations for the energies occurring in the exponent of (6.31).

If, therefore, the electron is known to have been at $t = 0$ in a state \mathbf{k}, l , then the probability of finding it in the state \mathbf{k}', l' at time t is

$$|(\mathbf{k}', l' | W | \mathbf{k}, l)|^2 \frac{1 - \cos(E' - E)t / \hbar}{(E' - E)^2} = |(\mathbf{k}', l' | W | \mathbf{k}, l)|^2 D(t). \quad (6.34)$$

This expression is then, in a sense, the transition probability from state \mathbf{k}, l to \mathbf{k}', l' . However, it is strictly valid only if the electron was initially in a single stationary state. Had we taken more than one of the $a(0)$ into account in (6.33), we should have obtained cross products in the square (6.34). Now we shall use such a formula to test the stationary property of the electron distribution, and hence the time $t = 0$ should be an arbitrary instant, after the disturbances have already been acting for some time. It is obvious from (6.33) that, even if at $t = 0$ only one coefficient is non-zero, this will in general no longer be true at time t . This may result in phase relationships between the expansion coefficients

a_k . For example, if the disturbance W consisted of a repulsive potential in some region, the effect would no doubt be to reduce the electron density in that region, and this has to be expressed by means of standing waves, or phase relations between the coefficients of the progressive waves which we have used for the expansion.

If we are to neglect such phase relations, this needs justification. We state therefore

Assumption 1. The nature of the perturbing potential is such that we may obtain the statistical ensemble of electrons by distributing electrons over the stationary states of the perfect lattice with suitable probabilities, but without cross terms.

This assumption is justified if the scattering centres are numerous, and distributed at random, so that in the final probability (6.34) we may average over their positions. Then the square of the diagonal element in (6.34) is, from (6.29),

$$|(k', l' | W | k, l)|^2 = \sum_{\mu, \nu} |k', l' | w | k, l)|^2 e^{i(k-k') \cdot (R_\mu - R_\nu)}. \quad (6.35)$$

If we average over the positions R_μ independently, all terms cancel except those with $\mu = \nu$. The effect is therefore proportional to the number of scattering centres, which is reasonable. In addition, if we had taken a cross product instead of (6.34), we would have found the sum

$$e^{i(k-k') \cdot R_\mu - i(k-k') \cdot R_\nu}, \quad (6.36)$$

which, after averaging over the R_ν , gives zero, unless $k' = k$. There might still be phase relations between states of the same k and different l , but, since these will always have different energies, they will not be connected by elastic collisions. We have therefore reduced Assumption 1 to the randomness of the positions of the scattering centres, a requirement closely related to the 'Stosszahl-Ansatz' of the kinetic theory of gases.

Accepting (6.34), the change in the number of electrons in state k , between time 0 and time t , becomes, similarly to (6.2),

$$n(k, l, t) - n(k, l, 0) = \sum_{k', l'} |(k', l' | W | k, l)|^2 \{n(k', l') - n(k, l)\} D(t), \quad (6.37)$$

where D is the function defined by (6.34).

The function D , considered as a function of E' , has a steep maximum at $E' = E$. The width of this maximum is of the order of \hbar/t . It is therefore customary to assume that the variation of the other factors in (6.37)

with E' is slow, so that we may insert their values for $E' = E$, and carry out the integration on D . Since the integral of D is

$$\int D dE = \frac{2\pi t}{\hbar}, \quad (6.38)$$

the number of transitions is then proportional to the time, and we may write (6.37) as

$$\dot{n}(\mathbf{k}, l) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}', l'} |(\mathbf{k}', l' | W | \mathbf{k}, l)|^2 \{n(\mathbf{k}', l') - n(\mathbf{k}, l)\} \delta(E' - E). \quad (6.39)$$

However, in the expression (6.37), the factor $n(\mathbf{k}', l)$ may also be a rather quickly varying function of the energy. This happens when E' lies near η , which is the most important region. In that case, n changes by a large amount over an interval of kT . The approximation which underlies (6.39) is therefore valid only if this is larger than the width of the peak D , i.e. if

$$kT > \frac{\hbar}{t}. \quad (6.40)$$

On the other hand, we cannot make the time interval t too large, since we have used first-order perturbation theory, and this must certainly break down if the time interval is long enough for the electron to have made a second collision. Therefore t must be less than the collision time τ , and therefore we have

$$\text{Assumption II.} \quad \frac{\hbar}{\tau} < kT. \quad (6.41)$$

For times shorter than (6.40) we would have to replace the δ function in (6.39) by a wider maximum. Since the δ function expresses the conservation of energy, this looks as if, with small time intervals, the energy might not be conserved. This is not correct. We have to remember that the total energy includes the interaction energy as well as the unperturbed energy $E(\mathbf{k}, l)$. It follows from general principles that the total energy is always exactly conserved, but it equals the unperturbed energy only after a long time when the collision is certain to have ceased. In this sense we can interpret \hbar/kT as the duration of a collision, and (6.41) is the condition that the duration of a collision be shorter than the time between successive collisions.

One typical kind of disturbance is the replacement of a few atoms in the lattice by foreign atoms. In that case the use of first-order perturbation theory is not strictly permissible, unless the substituted atoms are very similar to the ones they replace. We should use, instead of (6.39), a more exact expression for the scattering probability of a single centre.

This would not alter the form of (6.39), nor the proportionality of the scattering probability with the number of centres.

The angular distribution of the scattered electrons will be complicated. However, since the size of the scattering centre is of the order of an atomic radius, and the effective electron wavelength ($2\pi/k$) of the same order, unless we are dealing with a nearly empty or nearly full band, we expect large-angle deflexions to be about as common as small-angle ones, so that it is reasonable to average over the energy surface, and use the collision time concept of § 6.1. A more accurate treatment would involve the solution of an integral equation, but our knowledge of the energy surfaces and of the scattering probability is not usually good enough to warrant this.

The situation is similar when we are dealing with atoms added to the lattice in interstitial positions, or with atoms missing from the lattice. These last two occur always in limited numbers, but the substitution can in suitable cases be carried to a point where an appreciable fraction of the atoms has been changed. If in a crystal of atoms A more and more atoms are replaced by B , we shall eventually approach a pure B lattice (assuming that no change of structure occurs) and then the electrons move again without resistance. This problem was treated by Nordheim (1931), who suggested using as the starting-point a perfect lattice in which the potential was an average of the potentials for either type of atom, weighted with their concentrations. Then it is easy to show that, taking the deviation from this mean as a small perturbation, the scattering probability is proportional to $c(1-c)$ where c is the concentration. This law agrees well with experiment in many cases. Typical exceptions were shown by Mott (1936) to be due to a change in the electron number, and the occupation of the different bands, with concentration.

Other lattice imperfections, such as grain boundaries and dislocations, present greater difficulties for a quantitative treatment.

6.4. Effect of lattice vibrations. General

If the atoms are displaced from their ideal lattice positions, the potential $V(\mathbf{r})$ will be changed by an amount

$$W(\mathbf{r}) = \sum_{\mathbf{n}, j} W_j(\mathbf{r} - \mathbf{a}_{\mathbf{n}}) \cdot \mathbf{u}_{\mathbf{n}, j}. \quad (6.42)$$

Here $\mathbf{u}_{\mathbf{n}, j}$ is the displacement of the atom \mathbf{n} , j , as in Chapter I, W_j measures the effect on the potential of an infinitesimal displacement of the atom, and depends, as shown, only on the position of the point \mathbf{r}

relative to the cell \mathbf{n} . Terms of second and higher order in the displacements have been neglected.

It is convenient to express the displacements in terms of normal coordinates. Using (1.30),

$$W(\mathbf{r}) = \sum_{\mathbf{f}, s} \sum_{\mathbf{n}, j} W_j(\mathbf{r} - \mathbf{a}_{\mathbf{n}}) \cdot \mathbf{v}_j(\mathbf{f}, s) e^{i\mathbf{f} \cdot \mathbf{a}_{\mathbf{n}}} q(\mathbf{f}, s). \quad (6.43)$$

The normal coordinate $q(\mathbf{f}, s)$ is known to have matrix elements only between states differing by one unit in the quantum number $N(\mathbf{f}, s)$. Hence (6.43) can only cause transitions in which the electron is scattered and at the same time a phonon absorbed or emitted.

We consider, for definiteness, the case of absorption. Using the expression (1.63) for the matrix element of the normal coordinate, the matrix element of W for a transition from \mathbf{k} to \mathbf{k}' , and absorption of a phonon in the mode \mathbf{f}, s is

$$(\mathbf{k}', l' | W | \mathbf{k}, l; \mathbf{f}, s) = \sum_{\mathbf{n}, j} \int d^3\mathbf{r} \psi_{\mathbf{k}', l'}^*(\mathbf{r}) W_j(\mathbf{r} - \mathbf{a}_{\mathbf{n}}) \psi_{\mathbf{k}, l}(\mathbf{r}) \cdot \mathbf{v}_j(\mathbf{f}, s) e^{i\mathbf{f} \cdot \mathbf{a}_{\mathbf{n}}} \left(\frac{\hbar N(\mathbf{f}, s)}{2M^{(N)}\omega(\mathbf{f}, s)} \right)^{\frac{1}{2}}. \quad (6.44)$$

Changing the origin in the \mathbf{n} th term to $\mathbf{a}_{\mathbf{n}}$, and remembering the Bloch theorem (4.7), this becomes

$$\sum_j \int d^3\mathbf{r} \psi_{\mathbf{k}', l'}^*(\mathbf{r}) W_j(\mathbf{r}) \psi_{\mathbf{k}, l}(\mathbf{r}) \cdot \mathbf{v}_j(\mathbf{f}, s) \left(\frac{\hbar N(\mathbf{f}, s)}{2M^{(N)}\omega(\mathbf{f}, s)} \right)^{\frac{1}{2}} \sum_{\mathbf{n}} e^{i(\mathbf{f} + \mathbf{k} - \mathbf{k}') \cdot \mathbf{a}_{\mathbf{n}}}. \quad (6.45)$$

The last sum again vanishes, unless

$$\mathbf{f} + \mathbf{k} - \mathbf{k}' = \mathbf{K} \quad (6.46)$$

is a vector of the reciprocal lattice. In collisions between electrons and phonons, the wave vector is conserved, apart from vectors in the reciprocal lattice. Because of our restrictions of \mathbf{f} and \mathbf{k} to the basic cell, there is only one possible \mathbf{f} for given \mathbf{k}, \mathbf{k}' , and only one possible \mathbf{k}' for given \mathbf{k} and \mathbf{f} .

We now proceed, as in the derivation of (6.39), to find the transition probability per unit time:

$$|(\mathbf{k}', l' | A | \mathbf{k}, l; s)|^2 \delta\{E_l(\mathbf{k}') - E_l(\mathbf{k}) - \hbar\omega(\mathbf{f}, s)\} |N(\mathbf{f}, s)|, \quad (6.47)$$

where

$$(\mathbf{k}', l' | A | \mathbf{k}, l; s) = \sqrt{\left(\frac{2\pi}{\hbar}\right)} \sum_j N \int \psi_{\mathbf{k}', l'}^*(\mathbf{r}) W_j(\mathbf{r}) \psi_{\mathbf{k}, l}(\mathbf{r}) d^3\mathbf{r} \cdot \mathbf{v}_j(\mathbf{f}, s) \left(\frac{\hbar}{2M^{(N)}\omega(\mathbf{f}, s)} \right)^{\frac{1}{2}}, \quad (6.48)$$

and where \mathbf{f} is defined by (6.46). The same expression gives the probability of emission of a phonon with wave vector $-\mathbf{f}$, provided we

change the sign of ω in the argument of the δ -function in (6.47) and replace $N(\mathbf{f}, s)$ by $N(-\mathbf{f}, s) + 1$.

We can now use these results in a Boltzmann equation for the electron distribution, provided we are again prepared to accept Assumptions I and II of the preceding section. Then

$$\begin{aligned} \dot{n}(\mathbf{k}, l) = & \sum_{\mathbf{k}', l', \sigma} |(k', l' | A | \mathbf{k}, l, \sigma)|^2 \delta\{E_l(\mathbf{k}') - E_l(\mathbf{k}) - \hbar\omega(\mathbf{f}, \sigma)\} \times \\ & \times [N(\mathbf{f}, \sigma) + 1 |n(\mathbf{k}', l')\{1 - n(\mathbf{k}, l)\} - N(\mathbf{f}, \sigma)n(\mathbf{k}, l)\{1 - n(\mathbf{k}', l')\}]. \end{aligned} \quad (6.49)$$

Here we have again used the device introduced in (1.33) and (1.64) of separating positive and negative frequencies. The terms shown explicitly in (6.49) represent, for positive σ , the absorption of a phonon \mathbf{f}, s and the transition of the electron from \mathbf{k} to \mathbf{k}' and the inverse process. Negative σ means the emission of a phonon of wave number $-\mathbf{f}$ substituted for the absorption of \mathbf{f} , or vice versa. For given \mathbf{k}, \mathbf{k}' the δ -function will at most allow one or the other of these cases to be realized.

The change in the distribution of phonons is similarly given by

$$\begin{aligned} \dot{N}(\mathbf{f}, s) = & 2 \sum_{\mathbf{k}, l, l'} |(k', l' | A | \mathbf{k}, l, s)|^2 \delta\{E_l(\mathbf{k}') - E_l(\mathbf{k}) - \hbar\omega(\mathbf{f}, s)\} \times \\ & \times [\{N(\mathbf{f}, s) + 1\}n(\mathbf{k}', l')\{1 - n(\mathbf{k}, l)\} - N(\mathbf{f}, s)\{1 - n(\mathbf{k}', l')\}n(\mathbf{k}, l)], \end{aligned} \quad (6.50)$$

where, of course, \mathbf{k}, \mathbf{k}' , and \mathbf{f} are again assumed related by (6.46).

The expressions (6.49) and (6.50) vanish if we insert for the electron number the Fermi function $f(E)$, and for the phonon number the thermal mean value $N^0(\mathbf{f}, s)$ from (2.4). This follows because

$$\frac{N^0(\mathbf{f}, s)}{N^0(\mathbf{f}, s) + 1} = e^{-\hbar\omega(\mathbf{f}, s)/kT}; \quad \frac{f(E)}{1 - f(E)} = e^{-(E - \eta)/kT}. \quad (6.51)$$

One sees easily that the last bracket in (6.49) and in (6.50) is a difference between two terms whose ratio is unity by (6.51) whenever the energy condition is satisfied so that the δ -function does not vanish.

Under the influence of the collision the Fermi distribution for the electrons and the Planck distribution for the phonons therefore are seen to be stationary. This is, of course, ensured generally by the principles of statistical mechanics.

Consider now a small deviation from statistical equilibrium, which we shall take in the form

$$\left. \begin{aligned} n(\mathbf{k}, l) &= f(E) - g(\mathbf{k}, l) \frac{df(E)}{dE} = f(E) + \frac{1}{kT} \frac{g}{(1 + e^\epsilon)(1 + e^{-\epsilon})} \\ N(\mathbf{f}, s) &= N^0(\hbar\omega) - G(\mathbf{f}, s) \frac{dN^0}{d(\hbar\omega)} = N^0 + \frac{1}{kT} \frac{G}{(e^\gamma - 1)(1 + e^{-\gamma})} \end{aligned} \right\}. \quad (6.52)$$

Here we have used the abbreviations

$$\epsilon = \frac{E - \eta}{kT}, \quad \gamma = \frac{\hbar\omega}{kT}. \quad (6.53)$$

Inserting in (6.49) and (6.50) we then obtain, to first order in g and G , $n(\mathbf{k}, l)$

$$= \frac{1}{kT} \sum_{\mathbf{k}', l', \sigma} |(\mathbf{k}', l' | A | \mathbf{k}, l, \sigma)|^2 \delta(E' - E - \hbar\omega) \frac{g' - g - G}{(e^\epsilon + 1)(e^{-\epsilon'} + 1)|e^\gamma - 1|}; \quad (6.54)$$

$$N(\mathbf{f}, s) = \frac{2}{kT} \sum_{\mathbf{k}, l, l'} |(\mathbf{k}', l' | A | \mathbf{k}, l, s)|^2 \delta(E' - E - \hbar\omega) \frac{g' - g - G}{(e^\epsilon + 1)(e^{-\epsilon'} + 1)|e^\gamma - 1|}. \quad (6.55)$$

Here the arguments of E, g , etc., are not shown explicitly, but it will be obvious from the context that, for example, g means $g(\mathbf{k}, l)$ and g' means $g(\mathbf{k}', l')$.

We see now that the distributions (6.52) are still stationary if we choose

$$g = \text{constant}, \quad G = 0 \quad (6.56)$$

$$\text{or} \quad g = \lambda E, \quad G = \lambda \hbar\omega, \quad (6.57)$$

where λ is an infinitesimal constant. It is indeed evident from (6.52) that the first of these solutions amounts to an infinitesimal change in η , and hence to a change in the total number of electrons, and the second is an infinitesimal change in the temperature. These two parameters are, of course, connected with the conservation of the number of electrons and the conservation of energy. If the collisions were limited in such a way that the vector \mathbf{K} in (6.46) were always zero, as would be the case for free electrons interacting with an elastic continuum, then we should have a further solution in which

$$g = \lambda k_x, \quad G = \lambda f_x, \quad (6.58)$$

which then arises from the conservation of the total wave vector. It is obvious that the distribution modified by (6.58) carries a current, so that in those circumstances a current could persist in the absence of an electric field; we should have infinite conductivity. This shows that the presence of processes with $\mathbf{K} \neq 0$, or else of disturbances other than the electron-phonon collisions, is of vital importance for the electric resistance.

The situation is very similar to that in the thermal conductivity of non-metallic crystals, discussed in § 2.4.

Fig. 14 illustrates the possible collisions in a one-dimensional case. The full line indicates the $E(k)$ curve for one band, and the broken lines

show the frequency spectrum $\hbar\omega(f)$ for given polarization, plotted with some point on the electron energy curve as origin. Evidently an intersection of the two curves represents a solution of (6.46) and of the energy equation. The diagram is not to scale since, in most metals, the phonon

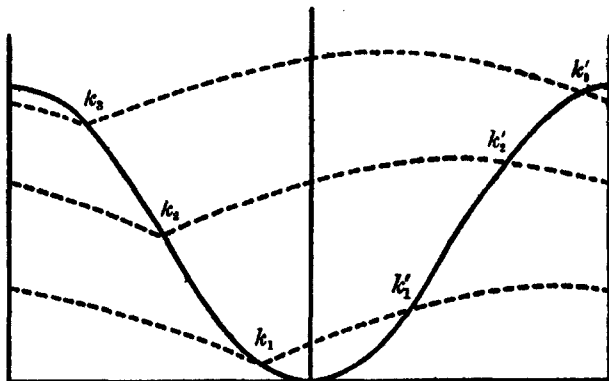


FIG. 14.

energies are much smaller in relation to electron energies than is convenient for a diagram.

Three cases are shown. If the electron is initially at k_1 , it can make a transition to k'_1 , and in that case the wave vector condition (6.46) is satisfied with $\mathbf{K} = 0$. In the cases labelled k_2 and k_3 , the difference $k' - k$ exceeds the limits of the basic cell, and in both cases

$$f = k' - k - \frac{2\pi}{a}.$$

In the third case, in particular, f is small. Remembering that the interval for k was chosen purely conventionally, it is more convenient to represent this last case in a diagram like Fig. 14 (a), in which the upper end of the previous figure has been replotted in terms of wave vectors lying between 0 and $2\pi/a$. This representation, which is particularly appropriate when we are dealing with a nearly full band, is quite equivalent to the previous one, but the reciprocal lattice vector \mathbf{K} in (6.46) takes

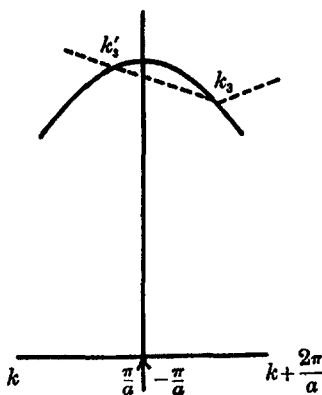


FIG. 14 (a).

in each case a different value. If it should happen that there are no collisions which require a non-zero \mathbf{K} in this representation (or in any

other definition of the k) we should still obtain an infinite conductivity. The stationary non-equilibrium distribution would then, of course, look like (6.58) in the new representation.

To conclude this section we require an estimate of the matrix element (6.48). This contains the quantity $W_j(\mathbf{r})$, the change of potential due to an infinitesimal displacement of an atom. It is reasonable to assume that the effect of such a displacement is simply to shift the whole potential field due to that atom bodily with the atom, and then

$$W_j(\mathbf{r}) = \text{grad } U_j(\mathbf{r}), \quad (6.59)$$

where U_j is the potential of the atom. Inserting this in the integral in (6.48), we recognize that this must vanish if $\mathbf{k} = \mathbf{k}'$, $l = l'$, since it then contains the factor

$$\sum_j \int |\psi_{\mathbf{k}l}(\mathbf{r})|^2 \text{grad } U_j(\mathbf{r}) d^3\mathbf{r}. \quad (6.60)$$

Because of the periodicity of the square of the wave functions (Bloch theorem), we may replace here the potential of one cell by the average over all cells, and (6.60) represents the change of energy of the electron upon an infinitesimal displacement of the whole lattice, which, of course, must be zero. Hence, for $l = l'$, the integral in (6.48) vanishes in the limit of long acoustic waves, for which with $\mathbf{f} = 0$, also $\omega(\mathbf{f}, s) = 0$. This will be of importance later. For $l \neq l'$, i.e. transitions from one band to another, the case $\omega = 0$ does not arise, since two states in different bands with the same wave vector will have different energies so that $\omega = 0$ would not be compatible with the energy equation.

It is therefore consistent to assume that the integral vanishes whenever $\omega(\mathbf{f}, s) = 0$, and that for small frequency it is proportional to ω . If we therefore write, in place of (6.48),

$$(\mathbf{k}', l' | A | \mathbf{k}, l, s) = (\mathbf{k}', l' | C | \mathbf{k}, l, s) \sqrt{\omega(\mathbf{f}, s)}, \quad (6.61)$$

then the new quantity C is likely to vary less in order of magnitude than A , and in any case tends to a constant limit as $\omega \rightarrow 0$, though this limit may in general depend on the direction of \mathbf{f} , the state \mathbf{k} , and the polarization s .

For a very crude estimate of order of magnitude, we may regard C as constant. The integral in (6.48) is of the dimension of an energy divided by a displacement, and since it represents only the effect of displacing the atoms in one cell out of N , we may expect it to be of order $D\omega/Na\omega_0$, where a is an atomic distance, and D an electronic energy of the order of

the band width. ω_0 is the maximum vibration frequency, as in § 2.1. This makes C have the order of magnitude

$$C \sim \frac{D}{a\omega_0\sqrt{M(N)}}. \quad (6.62)$$

6.5. Collisions between electrons

In the classical electron theory of metals the effect of collisions between the electrons was completely ignored on the grounds that in a collision between two free electrons the momentum is conserved, and, since the electric current is proportional to the resultant electron momentum, such collisions also do not alter the current. However, this argument is valid only for free electrons, and for those we have seen in the last section that we could use almost the same reasoning for the collisions with lattice waves. Leaving the lattice structure out of account, collisions with electrons or with elastic waves are insufficient to produce a resistance; allowing for the lattice structure, both will contribute.

However, as we shall see, the electron collisions are in most cases quantitatively less important than the electron-phonon collisions, except perhaps at very low temperatures.

The matrix element of the electron interaction for a transition in which one electron changes from a state \mathbf{k}_1 to \mathbf{k}'_1 and another from \mathbf{k}_2 to \mathbf{k}'_2 (we omit the suffix l here for simplicity) is

$$\iint \psi_{\mathbf{k}'_1}^*(\mathbf{r}_1)\psi_{\mathbf{k}_1}(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{\mathbf{k}'_2}^*(\mathbf{r}_2)\psi_{\mathbf{k}_2}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (6.63)$$

It follows again from the Bloch theorem that this matrix element vanishes unless

$$\mathbf{k}'_1 + \mathbf{k}'_2 - \mathbf{k}_1 - \mathbf{k}_2 = \mathbf{K}. \quad (6.64)$$

For free electrons, when the wave functions are plane waves, \mathbf{K} must vanish, and the matrix element then becomes

$$\frac{4\pi e^2}{L^3(\mathbf{k}'_1 - \mathbf{k}_1)^2}, \quad (6.65)$$

where L^3 is the volume.

Strictly speaking, (6.65) is too large for small momentum difference, since it is a bad approximation to assume Coulomb's law to hold at very large distances. In a pure two-body problem this would be correct, but, if we remember that there are other electrons present besides the ones under consideration, and that they will neutralize the field of each electron at large distances, we see that it would be more realistic to take a screened Coulomb field in (6.63) and thus obtain a matrix element less strongly divergent than (6.65).

If the electrons are not free, a similar correction has to be applied, and we should also allow for the fact that the mean interaction between the electrons has already been allowed for in the definition of the wave functions. A precise definition of the matrix element is therefore not simple. However, it is reasonable to take its order of magnitude to be roughly equal to (6.65).

Denoting $\sqrt{(2\pi/\hbar)}$ times the matrix element (6.63) by

$$(k'_1, k'_2 | I | k_1, k_2),$$

the electron collisions contribute to the rate of change of the electron number a term

$$\dot{n}(\mathbf{k}) = 2 \sum_{\mathbf{k}', \mathbf{k}_2} |(k', k'_2 | I | k, k_2)|^2 \delta(E + E_2 - E' - E'_2) \times \\ \times \{n' n'_2 (1-n)(1-n_2) - n n_2 (1-n')(1-n'_2)\}, \quad (6.66)$$

where the arguments of n and E are indicated by the accent or suffix, and where k'_2 is defined by (6.64). It is again obvious that (6.66) vanishes if $n(\mathbf{k})$ is the Fermi distribution. For a small deviation of the form (6.52) we find

$$\dot{n}(\mathbf{k}) = \frac{2}{kT} \sum_{\mathbf{k}', \mathbf{k}_2} |(k', k'_2 | I | k, k_2)|^2 \delta(E + E_2 - E' - E'_2) \times \\ \times \frac{g' + g'_2 - g - g_2}{(e^{\epsilon'} + 1)(e^{\epsilon'_2} + 1)(e^{-\epsilon} + 1)(e^{-\epsilon_2} + 1)}. \quad (6.67)$$

It is of interest to estimate the frequency of collisions for each electron. We choose some state \mathbf{k} in the border region of the Fermi distribution, i.e. in the region in which $E - \eta$ is at most of the order of kT .

The number of collisions suffered by this electron is then given by the contribution to (6.66) of the second term in the bracket, putting $n = 1$. Now n_2 vanishes if E_2 lies above the border region, and $(1-n')$ and $(1-n'_2)$ vanish if E' or E'_2 lie below the border region. Hence all four energies must, in fact, lie within the border region.

Select, therefore, a value of k_2 in the border region. This can be done in

$$kT \left(\frac{dZ}{dE} \right)_\eta \quad (6.68)$$

ways. The number of ways of choosing \mathbf{k}' is now less than (6.68), because it is further restricted by the energy equation. If we let \mathbf{k}' vary over all the possible (6.68) values, the energy difference between initial and final states would range over some energy interval D , comparable with the width of an energy band. The δ -function will pick out from this region only one particular value for the energy change (namely, zero)

and this brings in a factor of the order of D^{-1} . Hence the number of terms that contribute is roughly

$$\frac{1}{D} (kT)^2 \left(\frac{dZ}{dE} \right)_\eta^2. \quad (6.69)$$

Using the estimate (6.65) for the matrix element, choosing unit volume, and putting for the difference of wave vectors in the denominator a mean value of the order π/a , we find for the number of collisions per unit time, apart from numerical factors:

$$\frac{e^4 a^4}{\hbar D \pi^4} (kT)^2 \left(\frac{dZ}{dE} \right)_\eta^2. \quad (6.70)$$

dZ/dE may be estimated as the electron density, which for a monovalent metal is of the order a^{-3} , divided by an electronic energy of the order of the band width D . Hence the collision frequency is

$$\frac{1}{\pi^4} \left(\frac{e^2}{a} \right)^2 \frac{(kT)^2}{\hbar D^3}. \quad (6.71)$$

With a of the order of $2 \cdot 10^{-8}$ cm., and $D = 2$ eV, this comes to $5 \cdot 10^{11}$ sec.⁻¹ at room temperature. We shall see later that this is rather less than the effective frequency of collisions due to other sources.

6.6. Collisions at high temperatures

If the temperature is well above the Debye temperature Θ , so that kT is large compared to $\hbar\omega$ for all elastic waves, the problem simplifies considerably. Firstly, it is then in general true that the collisions between phonons are frequent enough to keep the phonon distribution in equilibrium, as we shall verify later. We may therefore put $G = 0$ in (6.54) and ignore equation (6.55). Moreover, the phonon energy is always small compared to the electron energies, and we may regard the collisions as elastic. We may also treat γ as a small quantity in (6.54) so that we may replace ϵ' by ϵ and $\epsilon' - 1$ by γ . If we then allow for the effect of the external electric field (cf. (5.9)), and insert for the matrix element from (6.61), we find

$$\frac{2}{\hbar} \sum_{\mathbf{k}', l', s} |C|^2 \delta(E' - E) (g' - g) kT = eFv_x. \quad (6.72)$$

The factor 2 arises because we have combined the absorption and emission, so that the polarization index s now takes only positive values.

(6.72) is an integral equation over the energy surface of the kind discussed in § 6.1. We saw there, in particular, that the Wiedemann-Franz

law and other consequences of collision-time theory were valid provided all collisions could be regarded as elastic.

We see, moreover, that the temperature enters only through the factor kT on the left-hand side of equation (6.72) and that therefore the solution $g(\mathbf{k})$ of this integral equation is, for given field, inversely proportional to the temperature. This is a well-known empirical law for pure metals at high temperatures.

If impurities and imperfections are not negligible, we must allow for collisions with them on the left-hand side of the equation. The resistances due to either type of collision will be additive if the function g which solves the equation for either type of collision is the same. This is exactly true if the collision time concept is applicable to both types of collision, or in the case of isotropy. In general, deviations from this additivity are not likely to be large.

To estimate the order of magnitude of the conductivity, we take C to be a constant in (6.72). The integral equation is then solved by

$$g = eFv_x\tau,$$

which then makes the term in g' vanish by symmetry. The collision time τ is given by

$$\frac{1}{\tau} = \frac{2}{\hbar} kT \frac{dZ}{dE} |C|^2. \quad (6.73)$$

With the estimate (6.62) for C this becomes

$$\frac{2D^2 kT}{\hbar a^2 \omega_0^2 \rho} \frac{dZ}{dE},$$

where, for unit volume, we have replaced the mass $M^{(N)}$ of the metal by the density ρ . In order of magnitude, dZ/dE is Z/D , and ρ/Z is the atomic mass M . Since $Ma^2\omega_0^2$ is the potential energy for displacing an atom by a distance a , this is again of the order of an electronic energy, i.e. of D . This gives finally, and crudely,

$$\frac{1}{\tau} \sim \frac{kT}{\hbar}. \quad (6.74)$$

This gives the order of magnitude of the conductivity of a normal metal correctly. It also shows that the electron collisions are unimportant if we accept the estimate (6.71).

It remains to justify the assumption that the lattice vibrations are kept in equilibrium by the phonon interaction. This means that a phonon collides more frequently with another phonon than with electrons.

We may estimate the mean collision time for a phonon from (6.50) in the way in which we derived (6.73) and the result is

$$\frac{1}{\tau_{pe}} \sim 2|C|^2 \omega k T \left(\frac{dZ}{dE} \right)_\eta \frac{1}{D}, \quad (6.75)$$

and hence, from (6.73),
$$\frac{\tau_{pe}}{\tau_e} \sim \frac{D}{\hbar \omega}. \quad (6.76)$$

With $\tau_e \sim 10^{-13}$, we therefore find for τ_{pe} a mean value of the order 10^{-11} . This should be compared with the collision time for phonons colliding with each other, which can be estimated from the thermal conductivity of non-metallic crystals, and, at room temperature, is also about 10^{-13} sec. It is therefore reasonable to suppose the phonons to be in equilibrium.

6.7. Low temperatures

The problem becomes much more involved when the temperature is comparable to the Debye temperature Θ , and we shall discuss only the limiting case when $T \ll \theta$. We may then no longer neglect the energy transfer in collisions, since, for the important collisions, this will turn out to be of the order of kT . The only contributions to (6.54) and (6.55) will now come from small values of \mathbf{f} for which $\hbar\omega$ is at most of the order kT . If ω is larger, then the absorption of such phonons does not occur because their number is negligible, and the emission does not occur because no electron can lose so much energy. This explains, as was first shown by Bloch, that the resistance of an ideal metal tends to zero at $T = 0$, in spite of the zero-point motion of the lattice, which is connected with the possibility of emitting phonons. In this respect the position differs radically from that in the scattering of X-rays (Chapter III), where we found the zero-point motion to give a finite random scattering even at $T = 0$. This difference arises because in the conduction problem the electrons themselves are nearly in equilibrium at a low temperature, so that processes with large energy transfer to the lattice are ruled out.

We can now estimate the collision time as follows:

For a given electron state \mathbf{k} , the energy equation may be written, using also the wave-vector condition (6.46) with $\mathbf{K} = 0$,

$$E(\mathbf{k} + \mathbf{f}) - E(\mathbf{k}) - \hbar\omega(\mathbf{f}, s) = 0,$$

or, to first order,
$$\hbar \mathbf{f} \cdot \mathbf{v}(\mathbf{k}) - \hbar\omega(\mathbf{f}, s) = 0. \quad (6.77)$$

If we disregard the energy condition, the number of values of \mathbf{f} with magnitude between f and $f+df$ is

$$\left(\frac{L}{2\pi}\right)^3 4\pi f^2 df.$$

These, however, will in general violate the energy condition (6.77) by an amount of the order $\hbar f v$, where v is the electron velocity, and therefore the effect of the δ function in (6.49) is to reduce the contribution to

$$\left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{v} f df.$$

Since by (6.61) the square of the matrix element contains a factor ω which, for small f , is also proportional to f , we see then that the contribution to (6.49) from the part in which phonons of wave vectors up to f are included, is proportional to f^3 . Now collisions in which $\hbar\omega(\mathbf{f}, s)$ exceeds kT are negligible, and therefore the collision frequency is seen to be proportional to T^3 .

This does not, however, mean that the resistance will be proportional to T^3 , since small f also means a very small deflexion of the electron. We have seen in (6.21) that the effectiveness of small-angle collisions is proportional to the square of the angle, and since in the present problem the angle is proportional to f , hence to kT , we expect the resistance to vary as T^5 .

A resistance formula in agreement with this asymptotic law was derived by Bloch, assuming the electron motion to be isotropic, using the elastic waves for an isotropic continuum with a maximum frequency as in the Debye model, and assuming the phonons always to be in equilibrium. Bloch also assumes the constant C of (6.61) to be constant for longitudinal elastic waves and zero for transverse waves. The result relates the coefficient of the T^5 law to that of the linear resistance law at high temperatures and the characteristic Debye temperature Θ . This relation seems in better agreement with experiment than, with the many approximations contained in it, one would expect.

This is brought out particularly by the fact that the collision time for phonon-phonon collisions increases very rapidly at low temperatures. The thermal conductivity of non-metallic crystals increases at least as fast as the $1/T$ law which is valid at high temperatures; since the specific heat decreases as T^3 , this means that the collision time varies at least as T^{-4} . On the other hand, the ratio of the number of phonons to the number of electrons in the border region is proportional to T^2 . We have seen that the frequency of phonon-electron collisions per electron was

proportional to T^3 , and the frequency of the same collisions per phonon is therefore proportional to T . (No factor arises here from the smallness of the deflexion; while the collision deflects the electron only slightly, it completely destroys or produces the phonon.)

An important point is that, as we saw in § 2.4, collisions in which the total wave vector of all the phonons changes (Umklapp collisions) are very rare at low temperatures. Unless the electron-phonon interaction leads to such Umklapp processes, the equilibrium is therefore dependent on the former, and we would expect the resistance to decrease exponentially at low temperatures.

It is therefore very important to consider Umklapp collisions, i.e. those with $\mathbf{K} \neq 0$ in (6.46). Since at low temperatures f must be small for all collisions, we see that $\mathbf{k} - \mathbf{k}'$ must nearly equal \mathbf{K} , i.e. the initial and final states of the electron must be nearly equivalent. This means therefore that \mathbf{k} must lie near a zone boundary, and \mathbf{k}' near the opposite face of the zone.

In the particular case of a band with its minimum energy near $\mathbf{k} = 0$, and containing only a small number of electrons, states near the zone boundary are practically empty, the occupation number being of the order $e^{-D/kT}$, where D is again an energy of the order of the band width. This exponential is quite negligible at room temperatures, and in such a case the rate of Umklapp processes, and hence the resistance, is limited by the phonon-phonon collisions and should vary exponentially with temperature.

The same is true for a few empty places in a nearly full zone, except that in that case we must change, in accordance with Fig. 14 (a), the convention about wave vectors and with it the definition of Umklapp processes.

We can visualize this situation by saying that, in the first case, the collisions between electrons and phonons cause a drift of the phonons in the same direction as the electrons. Once the drift velocities are equal, further collisions are as likely to accelerate as to decelerate the electrons.

The same is true for a nearly full band, except that the current is now carried by a few holes in the electron distribution which, like positive carriers, tend to set up a phonon drift in the opposite direction to that in the other case.

In a metal in which there is one nearly empty and one nearly full band, the electrons in the one tend to produce a phonon drift in one direction, the holes in the other one in the opposite direction. It is usually stated that in this case equilibrium can always be established, but in fact this is

true only if the number of electrons in the band equals that of the holes in the other.

It is likely that equilibrium can always be established if the energy surface $E(\mathbf{k}) = \eta$ intersects the zone boundary, since in that case a displacement of the whole electron distribution can be restored using up phonons of all directions.

It seems, however, unlikely that this is the case in the alkali metals, since these have body-centred cubic structures with one electron per atom. The zone is therefore just half full, and even on the simple approximation of § 4.2 (cf. Fig. 8) that energy surface which divides the zone in half is a cube which touches the boundary only with its corners. The real shape of the surface is likely to be more nearly spherical, and therefore clear of the boundary.

In such cases some other mechanism must be involved, and this is probably provided by the collisions between electrons. We have previously found these negligible at high temperatures; but since they give a collision time proportional to T^{-2} (cf. (6.7)) as compared to T^{-5} for the collisions with phonons, they must ultimately become dominant.

The condition for the existence of Umklapp collisions between electrons, i.e. collisions with $\mathbf{K} \neq 0$ in (6.64), is that the Fermi surface should extend at least half-way from the centre to the nearest zone boundary. For example, if the point half-way to the boundary (which is $\mathbf{K}/4$ if \mathbf{K} is the reciprocal lattice vector associated with that part of the boundary) lies on the energy surface, we can take the transition

$$\mathbf{k}_1 = \mathbf{k}_2 = -\mathbf{k}'_1 = -\mathbf{k}'_2 = \frac{1}{4}\mathbf{K},$$

which satisfies (6.64) as well as the energy equation. For a Fermi surface of larger size such cases are more easily arranged by including a small angle between \mathbf{k}_1 and \mathbf{k}_2 .

This condition is certainly satisfied in the alkalis, and it is therefore easy to understand why their conductivity does not increase exponentially at low temperatures. It is, however, very hard to see why, in these circumstances, the T^5 law, which took only phonon-electron collisions into account, and even the factor resulting from the simple Bloch theory, should be in such good agreement with observation. It is also hard to see why, amongst more complex structures, there should not occasionally be a case where the effective number of conduction electrons is so small that even the collisions between electrons are insufficient to cause a reasonable resistance.

We end this section with a remark about the thermal conductivity.

For high temperatures this problem is already solved by the remark that the collisions are in fact elastic, so that, according to § 6.2, the law of Wiedemann and Franz applies.

At very low temperatures, we can obtain the temperature variation in a similar way to the arguments in the case of electric conductivity. However, whereas the low-temperature electron-phonon collisions are inefficient in stopping an electron drift, because they deflect electrons only through small angles, they are quite efficient in adapting electrons to the temperature of their surroundings, since in each collision the electron energy may change by an amount of the order of kT . This is all that is required to change the temperature of the electron gas. Therefore the effective collision time for this purpose is proportional to T^{-3} , and not to T^{-5} , as before.

Since the specific heat of the electron gas is proportional to T , the thermal conductivity comes out proportional to T^{-2} at low temperatures.

This law is not subject to any doubt about the existence of Umklapp processes. The reason for this is that the definition of thermal conductivity refers to a situation where there is no electric current, and, as in § 6.2, we have to assume the presence of an electric field which will ensure this. There is therefore no electron drift, and no tendency to set up a phonon drift.

The phonons contribute, in principle, to the heat transport, but we have seen that they collide much more frequently with electrons than with each other, and therefore their collision time is much shorter than it would be in an insulator. Since their specific heat is small, the amount they contribute to the total heat transport is quite negligible.

6.8. Validity of assumptions

I stressed in § 6.3 the importance of the two assumptions which were used in our basic arguments. Assumption II in particular was stated in the form of the inequality $\hbar/\tau < kT$. But at high temperatures our estimate (6.74) showed that these quantities are of the same order of magnitude. Taking more precise figures for τ from measured conductivities, Mott and Jones (1936) quote the following collision times for the alkalis:

Li	Na	K	Rb	Cs	
0.86	3.1	4.4	2.7	2.1	$\times 10^{-14}$

which are to be compared with $\hbar/kT \sim 2.5 \cdot 10^{-14}$. In general, Assumption II is therefore not well satisfied, and the position gets worse for impure specimens or alloys. Since $1/\tau$ is, at high temperatures, proportional to T , nothing is gained by changing the temperature in this

integral is to extend over the region in which $V > E$. In the present problem $V - E$ is equal to the work function at the surface, and from there decreases linearly to zero at x_1 . Hence the exponential factor becomes

$$e^{-\lambda W^{1/2}/E}, \quad \lambda = \frac{4(2m)^{1/2}}{3e\hbar}. \quad (4.66)$$

As in the previous case, there are factors depending on the field intensity multiplying the exponential, but again they are hard to isolate in practice because of minor variations of the exponent over the surface and in this case also because any geometrical irregularity of the surface may lead to a local increase of the electric field.

In this discussion of surface effects we have taken into account only the influence of the surface on the position of the main energy bands. In addition, the surface will cause changes in the electron states. One very obvious consequence of the presence of a surface is that, instead of progressive waves, we must introduce standing waves which do not carry any current in a direction normal to the surface. The phase of such a standing wave depends on the behaviour of the potential near the surface and, since this phase influences the electron density near the surface, will itself influence the potential.

A less obvious feature is the fact that in addition to wave functions which change periodically with a displacement by successive multiples of a lattice vector (4.7), we cannot now rule out wave functions which decrease exponentially as we pass from the surface into the metal. In other words, the component of \mathbf{k} in a direction at right angles to the surface may now be complex. This gives rise to surface waves. Their number is always small compared to that of the periodic solutions, and they are therefore always negligible in statistical arguments concerning the whole metal. For problems in which the surface is of special importance, they may, however, have to be taken into account.

region. However, at low temperatures, where the collision time increases more rapidly, the assumption is, in general, valid. For an imperfect specimen it may break down again at low temperatures, where the resistance is mainly due to impurities and tends to a constant limit.

It might therefore appear that all the theory of the transport phenomena stood on very shaky foundations. However, Landau has given an argument to show that, as long as one is dealing with elastic collisions only, one can obtain the results of the theory by a slightly different approach without using Assumption II.

In fact in all those cases in which the assumption is in doubt, namely at high temperatures and in conditions when the impurity resistance is dominant, we are dealing with elastic collisions, and they represent therefore the most critical case.

The argument by Landau (summarized by Peierls (1934*a*)) starts with the consideration of electrons in a static field. This is assumed to contain the periodic potential of the perfect lattice as well as the effect of irregular disturbances. In this combined field, energy is still conserved, and we can define the number of states per unit energy, which we shall again denote by dZ/dE . We consider a large number of electrons distributed over these states so that the number of electrons in an interval dE is

$$2 \frac{dZ}{dE} f(E) dE,$$

where $f(E)$ is an arbitrary function, not necessarily related to the Fermi function. Since we are not allowing for any processes which may change the energy, any such distribution will remain stationary.

Now imagine the same system in an infinitesimal electric field. We then conclude from the general principles of statistical mechanics that, provided the potential field contains a sufficiently irregular part, this will lead to a stationary state with a current proportional to the field. Moreover, since the electric field is capable of changing the electron energy by only infinitesimal amounts, the contribution to the total current from electrons of a particular energy will depend only on the distribution function $f(E)$ for that and immediately adjacent values of the energy.

We also know that the current must vanish if $f(E)$ is a constant, since a uniform distribution of electrons over all states in an energy band must behave like an insulator. Therefore the expression for the total current must be of the form

$$J = e^2 F \int Q(E) \frac{df}{dE} dE, \quad (6.78)$$

where $Q(E)$ is some function of the energy. This is of the same form as (6.14), and, in fact, most of the theory of § 6.1 can be reproduced in this manner.

The main point is now this: from the definition (6.78), $Q(E)$ is related only to the properties of electrons with energies very close to E , and, since this is to be valid for any distribution function $f(E)$, the concept of temperature has not yet arisen. We now ask for the dependence of $Q(E)$ on the strength of the irregular part of the potential. If this is very weak, undoubtedly our Assumption II will be satisfied, and we can accept the results of the preceding sections, so that then

$$Q(E) = 2\bar{v}_x^2 \tau \frac{dZ}{dE},$$

with the collision time τ inversely proportional to the square of the irregular potential and calculated according to § 6.3. That derivation is valid as long as $\hbar/\tau < kT$. But since the temperature appears neither in the mechanism nor in the definition of $Q(E)$, this inequality cannot represent the real limit of the proportionality between $1/\tau$ and the square of the potential. In fact, the only quantity of the dimension of an energy which occurs is the electron energy measured from the nearest band limit.

It follows from this that the real limit of the proportionality is given by the inequality

$$\frac{\hbar}{\tau} < \eta, \quad (6.79)$$

where η is measured from the nearest band limit. This is very much weaker than (6.41) and is practically always satisfied in metals.

It follows also that the work of § 6.6 is limited in validity only by (6.79), since in the high-temperature region the atomic displacements may be regarded as static (since the energy transmitted to the electrons is negligible) so that Landau's reasoning applies.

Some work is now in progress to illustrate this situation further. One result, contained in a recent paper by van Wieringen (1954), starts from the perturbation theory of § 6.3, but proceeds to include terms of fourth order, instead of only second order, in the potential W . It is found that no correction terms of the order $\hbar/\tau kT$ turn up, and the only corrections are of order $\hbar/\tau \eta$. While this, in itself, does not prove that the first approximation is adequate up to the limit (6.79), it provides a useful confirmation of Landau's reasoning.

It would seem, therefore, that in the ordinary theory of conduction the question of the limitation of the usual approach is a rather academic

one. It looks as if the usual methods can be applied with correct results to practically all cases in which we can separate the forces into those determining the 'unperturbed' motion of the electron and the 'collisions', the effect of the latter being limited by a condition of the type (6.79). There are, however, cases in which such a division is not possible, for example in the resistance of alloys, and of liquids, and I shall later refer to such a case in the magneto-resistance problem.