

The Theory of Electronic Semi-Conductors

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The Theory of Electronic Semi-Conductors.

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Introduction.

The application of quantum mechanics to the problem of metallic conduction has cleared up many of the difficulties which were so apparent in the free electron theories of Drude and Lorentz. Sommerfeld* assumed that the valency electrons of the metallic atoms formed an electron gas which obeyed the Fermi-Dirac statistics, instead of Maxwellian statistics, and, using in the main classical ideas, showed how the difficulty of the specific heat would be removed. He was, however, unable to determine the temperature dependence of the resistance, as his formulæ contained a mean free path about which little could be said.

F. Bloch† took up the question of the mechanics of electrons in a metallic lattice, and showed that if the lattice is perfect an electron can travel quite freely through it. Therefore so long as the lattice is perfect the conductivity is infinite, and it is only when we take into account the thermal motion and the impurities that we obtain a finite value for the conductivity. On this view all the electrons in a metal are free, and we cannot assume, as we do in the classical theory, that only the valency electrons are free. This does not give rise to any difficulty in the theory of metallic conduction, as the direct proportionality between the conductivity and the number of free electrons no longer holds when the Pauli principle is taken into account. If there is no external electric field, the number of electrons moving in any direction is equal to the number moving in the opposite direction. The action of a field is to accelerate or retard the electrons, causing them to make transitions from one set of energy levels to another. This can only happen if the final energy levels are already unoccupied, and therefore only those electrons whose energies are near the critical energy of the Fermi distribution can make transitions and take part in conduction, as it is only in the neighbourhood of the critical energy that the energy levels are partly filled and partly empty. These electrons are few in number compared with the valency electrons, and are what should be

* 'Z. Physik,' vol. 47, p. 1 (1928).

† 'Z. Physik,' vol. 52, p. 555 (1928).

called the conduction electrons. On the classical theory alone are the valency electrons, the free electrons and the conduction electrons the same.

Bloch has shown that for very tightly bound electrons the energy levels of the lowest states have the same distribution as for free electrons, the only difference being that the constants have different meanings in the two cases. This is not surprising if we rid ourselves of the false correlation between free electrons and conduction electrons, and it merely means that electrons in a metal have a dual aspect. For some phenomena the electrons behave as if they were bound, and for others as if they were free, corresponding to the particle and to the wave properties respectively of the electrons.

By applying these ideas Bloch arrives at a temperature dependence of the conductivity* which is in very satisfactory agreement with the measurements.† He finds that for high temperatures the resistance varies as T , the absolute temperature, and for low temperatures as T^5 . Here, however, certain difficulties arise. How are we to explain the non-conductivity of insulators and the temperature dependence of the resistance of electronic semi-conductors? On the classical theory the answer is quite simple. We merely postulate that there are no free electrons in an insulator, and that the number of free electrons in a semi-conductor varies rapidly with temperature. When we use quantum mechanics, we are no longer at liberty to take this easy way out, as all the electrons in a perfect lattice are free to move through the lattice, and it would seem at first sight that on Bloch's theory all substances should have infinite conductivity at absolute zero temperature. If this were a rigorous consequence of the theory it would be a very serious objection against it, and it is therefore necessary to see if we cannot find a place in the theory for insulators and semi-conductors.

It is not possible to maintain that the difference between good and bad conductors is one of degree only, the electrons in poor conductors being more tightly bound than in metals, and giving rise to a smaller current. There is an essential difference between a semi-conductor, such as germanium, and a good conductor, such as silver, which must be accounted for by any theory which attempts to deal with semi-conductors. In the first place there is the effect of impurities, which always increase the resistance of good conductors and generally decrease the resistance of poor conductors. Then there is the effect of temperature, which is still more marked. The resistance of a good conductor falls rapidly with falling temperature, while that of a poor

* 'Z. Physik,' vol. 59, p. 208 (1930).

† E. Gruneisen, 'Leipziger Vorträge' (1930).

conductor rises and becomes very large as the temperature approaches the absolute zero.

We have already seen that on the classical theory there is a confusion between free and conduction electrons, and it may be that we have allowed this confusion to slip once more into the theory. We shall therefore examine it more carefully. First of all we may ask how it is possible to obtain a model of an insulator or a semi-conductor. To do this it is necessary to have a perfect lattice in which all the electrons are free, and in which there are no conduction electrons at the absolute zero. Now, if we confine ourselves to Sommerfeld's picture of electrons moving in a region of uniform potential, it is impossible to obtain no conduction electrons. Fortunately, the model of a lattice is not quite so simple, and actually the potential in which the electrons move is periodic in three dimensions and not constant. The problem of an electron moving in a one-dimensional periodic potential has been studied by several authors,* and it appears that the energy levels break up into a number of bands of allowed energies, separated by bands of disallowed energies, which may be of considerable width. When we consider more than one dimension the problem is not quite so simple, for although there are discontinuities in the energy it is sometimes possible for the energy to take every value between a minimum value and infinity. This introduces a new complexity which is of importance for the theory of conduction. Leaving aside this complexity for the moment, it is possible to see from the one-dimensional case how we can have no conduction electrons at the absolute zero. Suppose the number of electrons is just sufficient to fill up the lowest band of allowed energies when all the electrons are in their lowest possible states. Then in the absence of an external field there is, of course, no resultant current. If a field is applied, it will be impossible on account of the Pauli principle for any electron to increase its stream without making a transition to the second band of allowed energies. This it will be unable to do provided the field is small enough, owing to the finite energy difference between the two bands.

In this case, therefore, we have no conduction electrons, and we have the rather curious result that not only is it possible to obtain conduction with bound electrons, but it is also possible to obtain non-conduction with free electrons.

When the temperature is different from zero there will be a few electrons in

* R. Peierls, 'Ann. Physik,' vol. 4, p. 121 (1930); P. M. Morse, 'Phys. Rev.,' vol. 35, p. 1310 (1930); L. Brillouin, 'J. Physique,' vol. 1, p. 377 (1930); R. Kronig and W. G. Penney, 'Proc. Roy. Soc.,' A, vol. 130, p. 499 (1931).

the second band and a few vacant places in the first band, and conduction can take place. The increase in the number of conduction electrons with rise of temperature will tend to increase the conductivity, while the excitation of the thermal vibrations of the lattice will tend to decrease it. At low temperatures the first effect must predominate, and so the resistance will have a negative temperature coefficient. At higher temperatures the effect of the thermal vibrations will be the more important, and the resistance will obey the normal law. This is just what is observed for semi-conductors.* The problem has to be formulated a little differently when we deal with three dimensions, but it is possible to construct a model which reproduces the properties of semi-conductors.

In the following sections these ideas are elaborated in some detail. We first discuss the energy levels of electrons in a lattice and show that, although the electrons are free in the sense that they can move from one atom of the lattice to another, yet there exist closed sub-groups which do not necessarily correspond to the closed sub-groups of the isolated atoms. Then the theory of the Fermi distribution is modified slightly so as to take account of possible discontinuities in the energy values, and applied to the problem of the paramagnetism of semi-conductors. Finally, the temperature dependence of the electrical resistance of semi-conductors is worked out. The calculations are very rough, and it is not pretended that anything more is done than to show that a place can be found in the theory for insulators and semi-conductors. The question as to why certain elements form metallic lattices, and others non-metallic lattices, is a difficult one, and would require much more elaborate calculations than are possible at the moment. At present only qualitative conditions can be given. It is, however, highly satisfactory that the same model should give the properties of both metallic conductors and semi-conductors.

The Motion of an Electron in a Lattice.

1. As is usual in the discussion of this problem, we only deal with a simple cubic crystal with lattice constant a . This means that we cannot properly apply our results to metals, that is to say quantitatively, as no metal or semi-metal has this crystal structure. However, any other assumption would make the calculations much more complicated, and, as we are only interested in general results, we may expect this simplifying assumption to give the broad outlines of the phenomena. Only in discussing the finer details of conduction, such as the anomalous thermoelectric and magnetic properties of certain

* Cf. E. Gruneisen, "Handbuch der Physik," vol. 13, p. 60.

metals, will it be necessary to include the effect of the actual crystal structure. If it is possible to obtain a division of the elements into metals and non-metals on the assumption of a cubic lattice, it is *a fortiori* possible when more complicated structures are considered.

Although the problem of the motion of an electron in a periodic field has been treated at length by the authors mentioned above, it has been thought advisable, on account of the importance of the results relative to the present problem, to review the subject once more. Exact methods are not used, perturbation methods being preferred as giving a much better insight into the problem. Two methods of approximation are employed, one starting from entirely free electrons, and the other starting from tightly bound electrons, the two methods giving very similar results. In this way it is possible to obtain the characteristics of the energy levels not only of the valency electrons but also of the inner, core, electrons.

Nearly Free Electrons.

1.1. It is not convenient to consider a finite crystal, and we therefore suppose an infinite crystal to be divided up into cubes whose sides are of length Ga , where G is a large number. All these cubes are supposed to have identical properties, which means that all the properties of the crystal have a three-dimensional periodicity with period Ga . The potential has the smaller period a .

Let the mean value of the potential energy of an electron be V_0 . Then the potential energy V can be expanded as a Fourier series

$$V = V_0 + \sum_{n_1 = -\infty}^{\infty} \sum_{n_2 = -\infty}^{\infty} \sum_{n_3 = -\infty}^{\infty} V_{n_1 n_2 n_3} e^{\frac{2\pi i}{a}(n_1 x + n_2 y + n_3 z)}, \quad (1)$$

where the axes are rectangular ones along the edges of the cube, and the combination $n_1 = n_2 = n_3 = 0$ does not occur. As zero approximation we consider an electron moving with the constant potential energy V_0 . The wave function characterising the motion is given by

$$\psi_{\xi\eta\zeta}^0 = (aG)^{-3/2} e^{\frac{i}{a}(\xi x + \eta y + \zeta z)}, \quad (2)$$

where the possible values of ξ , η , ζ are

$$2\pi/G (0, \pm 1, \pm 2 \dots). \quad (3)$$

If m is the mass of the electron, the corresponding energy values are

$$E_0 = \omega (\xi^2 + \eta^2 + \zeta^2) + V_0, \quad (4)$$

ω being

$$\hbar^2/(8\pi^2ma^2). \quad (5)$$

Treating the departure of the potential from uniformity as causing a small perturbation, it is easily seen that the diagonal elements of the perturbing energy are all zero, and that the non-diagonal elements ($\xi\eta\zeta | V | \xi'\eta'\zeta'$) are also zero unless ξ', η', ζ' differ from ξ, η, ζ respectively by multiples of 2π . These non-diagonal elements are only of importance in the first approximation provided E_0 is nearly equal to E_0' , and in this case the unperturbed state is nearly degenerate. Accordingly we put

$$\psi = c\psi_{\xi\eta\zeta}^0 + c'\psi_{\xi'\eta'\zeta'}^0 \quad (6)$$

and

$$E = \frac{1}{2}(E_0 + E_0') + \varepsilon. \quad (7)$$

The secular equation to determine ε is easily found to be

$$\begin{vmatrix} \frac{1}{2}(E_0 - E_0') - \varepsilon & (\xi | V | \xi') \\ (\xi | V | \xi') & \frac{1}{2}(E_0' - E_0) - \varepsilon \end{vmatrix} = 0$$

giving

$$\varepsilon^2 = \frac{1}{4}(E_0 - E_0')^2 + (\xi | V | \xi')^2. \quad (8)$$

This makes E a multivalued function of ξ , which is due to the fact that the state given by (6) is a mixture of the (ξ, η, ζ) state and the (ξ', η', ζ') state. It is convenient to have single valued functions, and we therefore adopt the convention that E is an increasing function of each of ξ, η, ζ , which suffices to fix E completely.

Consider fixed values of η and ζ lying between $\pm \pi$, and not being nearly equal to either of these values. Then if the difference $(E_0 - E_0')$ is to be small it is necessary that $\eta = \eta', \zeta = \zeta'$ and ξ must be nearly $\pm \pi$. Putting $\xi = \pi - u$, then ξ' must be given by $\xi' = -\pi - u$, and then

$$(\xi\eta\zeta | V | \xi'\eta'\zeta') = V_{100}.$$

Also

$$E_0 = V_0 + \omega \{(\pi - u)^2 + \eta^2 + \zeta^2\}$$

and

$$E_0' = V_0 + \omega \{(\pi + u)^2 + \eta^2 + \zeta^2\},$$

giving

$$E = V_0 + \omega(\pi^2 + u^2 + \eta^2 + \zeta^2) \pm (\pi^2\omega^2u^2 + V_{100}^2)^{\frac{1}{2}}. \quad (9)$$

On expanding the square root we have approximately

$$E = V_0 + \pi^2\omega - V_{100} - u^2\left(\frac{\pi^2\omega^2}{V_{100}} - \omega\right) + \omega(\eta^2 + \zeta^2) \quad (10A)$$

by taking the negative sign, and

$$E = V_0 + \pi^2\omega + V_{100} + u^2\left(\frac{\pi^2\omega^2}{V_{100}} + \omega\right) + \omega(\eta^2 + \zeta^2) \quad (10B)$$

by taking the positive sign. The expression (10A) is valid when u is positive, and (10B) when u is negative, since this satisfies the convention that E is an increasing function.

If we plot the variable part of E against ξ , keeping η and ζ constant, we obtain a curve of the type given below. At the points $\xi = \pm \pi$ the energy is discontinuous, and in addition the derivative of E becomes zero. These discontinuities were first noticed by Peierls (*loc. cit.*), whose treatment we have given here. It is often convenient to treat ξ as a continuous variable. This is equivalent to making G tend to infinity, and when there is no ambiguity caused by this process we shall talk about ξ as if it were continuous.

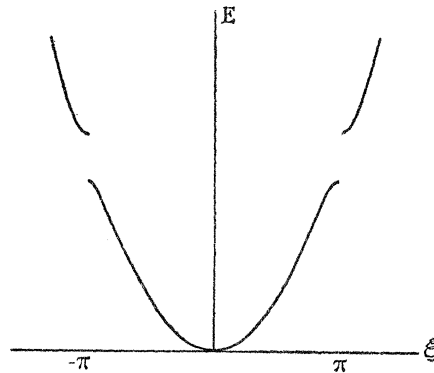


FIG. 1.

1.11. It is obvious that there will be similar discontinuities whenever one of ξ , η , ζ passes through a multiple of π . In this way we get zones of energies, which have been exhaustively studied by Brillouin (*loc. cit.*). The first zone occurs when each of ξ , η , ζ lies between $-\pi$ and π , giving G^3 energy levels in all. The second zone consists of six separate portions in which two of ξ , η , ζ lie between $\pm\pi$, while the third is either greater than π or less than $-\pi$. These six portions together give G^3 energy values. The third and higher zones are more complicated, and reference may be made to Brillouin's paper. They all have the property of comprising exactly G^3 energy levels.

As soon as we deal with more quantum numbers than one, there appears a property which is not brought out in the figure, but which may be readily seen by drawing a similar diagram for two independent variables. The highest energy levels in the first zone are given by $\xi = \pm \pi$, $\eta = \pm \pi$, $\zeta = \pm \pi$, all of which have the same energy, while the lowest energy levels in the second zone are given by $\xi = \pm \pi$, $\eta = 0$, $\zeta = 0$, and $\xi = 0$, $\eta = \pm \pi$, $\zeta = 0$ and $\xi = 0$, $\eta = 0$, $\zeta = \pm \pi$. Now there is no need for E_{\min} (2) to be greater than

E_{\max} (1), where (1) and (2) denote that the energies belong to the first and second zones respectively. Of course, E_{\min} (2) must be greater than $E(\pi, 0, 0)$, (1), but $E(\pi, \pi, \pi)$ (1) is also greater than $E(\pi, 0, 0)$ (1), and so E_{\min} (2) may be either greater or less than E_{\max} (2), depending on the magnitude of the discontinuities. In fact, for nearly free electrons the coefficients $V_{n_1 n_2 n_3}$ will all be small, and in this case E_{\min} (2) will certainly be less than E_{\max} (1), the condition for this being that $\pi^2 \omega$ is greater than V_{100} . The assumption of nearly free electrons, therefore, leads to the result that the energy does not show the forbidden ranges which appear in the one-dimensional case, the discontinuities only playing a rôle when we consider the energy as a function of one quantum number, the other two being considered fixed.

Tightly Bound Electrons.

1.2. We shall now consider the problem starting from the opposite limiting case of tightly bound electrons. This has already been partly treated by Bloch (*loc. cit.*). This method of treatment is more logical than that just given, in that it enables the assumptions to be clearly seen, and, though at the moment it is impossible to obtain any better or more detailed results from this model, any further advance in the theory of conduction will have to be made by taking into account the various effects here neglected.

Bloch has shown by a general argument that the wave function of an electron in a cubic lattice must have the form

$$\psi_{klm} = e^{\frac{2\pi i}{K}(kx + ly + mz)} u_{klm}(xyz), \quad (11)$$

where $K = aG$; k, l, m are positive or negative integers, but not zero, and $u_{klm}(xyz)$ is a periodic function of x, y, z with period a . It is not possible to obtain a general formula for the corresponding energy levels.

If we suppose that the potential energy of an electron in the crystal is very large and negative in the neighbourhood of each lattice point, and is elsewhere nearly constant, it is possible to derive approximate formulæ for the energy levels. As zero approximation we consider the electron to be in the neighbourhood of a lattice point, and we neglect the influence of the other atoms. The energy is then that of the free atom. This state is degenerate, as placing the electron in a similar orbit round any other lattice point gives a state with the same energy. The degeneracy is of order G^3 , and is removed when we introduce the forces due to the neighbouring atoms. Here we meet a difficulty. It is not possible even in the zero approximation to neglect entirely the interactions of the electrons, as the Coulomb forces due to the nuclei would then

give an infinite potential at every point. We must suppose that the lattice is electrically neutral, and that the interactions of the electrons are partly taken into account in some way by a "self-consistent field," so that the potential, expressed as a sum over the lattice points, converges to a finite value. The exchange forces between the electrons are, however, neglected, as it is only in this case that the electrons can be treated independently of one another. With these assumptions, together with the further one that the presence of the neighbouring atoms causes an energy change small compared with the energy differences between the various energy levels of the isolated atom, it is possible to solve the problem.

Using Bloch's notation, let the integers g_1, g_2, g_3 characterise the various lattice points, and let the potential energy of an electron due to one lattice point be

$$U_{g_1 g_2 g_3}(xyz) = U(x - g_1 a, y - g_2 a, z - g_3 a), \quad (12)$$

which is a function of the distance of the electron from the lattice point only. The potential energy of an electron in the crystal is then given by

$$V(xyz) = \sum_{g_1 g_2 g_3 = -\infty}^{\infty} U_{g_1 g_2 g_3}(xyz), \quad (13)$$

and the Schrödinger equation is

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0, \quad (14)$$

while the Schrödinger equation for an isolated atom is

$$\nabla^2 \phi_{g_1 g_2 g_3} + \frac{8\pi^2 m}{h^2} (E - U_{g_1 g_2 g_3}) \phi_{g_1 g_2 g_3} = 0. \quad (15)$$

This last equation has various solutions which may or may not be degenerate, and the subsequent work differs slightly in the two cases.

1.21. First let us consider an s state, which is the only case treated by Bloch. In this case $\phi_{g_1 g_2 g_3}$ is spherically symmetrical. If E_1 is the corresponding energy value, we solve equation (14) by setting

$$E = E_1 + \epsilon_1 \quad \text{and} \quad \psi = \sum_{g_1 g_2 g_3} a_{g_1 g_2 g_3} \phi_{g_1 g_2 g_3}. \quad (16)$$

The equations determining ϵ_1 and the a 's to the first order are easily found to be

$$\sum_{g_1 g_2 g_3} a_{g_1 g_2 g_3} \int_0^K \int_0^K \int_0^K (\epsilon_1 - U'_{g_1 g_2 g_3}) \phi_{g_1 g_2 g_3} \phi_{h_1 h_2 h_3} dx dy dz = 0 \quad (17)$$

for all integral values of h_1, h_2, h_3 , and where

$$U'_{g_1 g_2 g_3} = V - U_{g_1 g_2 g_3}.$$

For tightly bound electrons we assume

$$\int \phi_{g_1 g_2 g_3} \phi_{h_1 h_2 h_3} d\tau = \delta_{g_1}^{h_1} \delta_{g_2}^{h_2} \delta_{g_3}^{h_3},$$

and also since ϕ and U are both spherically symmetrical we put

$$\int U'_{g_1 g_2 g_3} \phi_{g_1 g_2 g_3} \phi_{h_1 h_2 h_3} d\tau$$

equal to α_1 if g and h are the same, equal to β_1 if g and h refer to lattice points which are nearest neighbours, and zero otherwise. The assumption of tightly bound electrons means that α_1 and β_1 are essentially positive.

Equations (17) reduce to the triply infinite set

$$(\epsilon_1 - \alpha_1) a_{g_1 g_2 g_3} + \beta_1 (a_{g_1+1, g_2, g_3} + a_{g_1-1, g_2, g_3} + a_{g_1, g_2+1, g_3} + a_{g_1, g_2-1, g_3} + a_{g_1, g_2, g_3+1} + a_{g_1, g_2, g_3-1}) = 0. \quad (18)$$

There is in addition the condition that ψ is periodic with period K . The equations (18) are satisfied by

$$a_{g_1 g_2 g_3}^{klm} = e^{\frac{2\pi i}{G}(kg_1 + lg_2 + mg_3)},$$

giving

$$\psi_{klm} = \sum_{g_1 g_2 g_3 = -\infty}^{\infty} e^{\frac{2\pi i}{G}(kg_1 + lg_2 + mg_3)} \phi_{g_1 g_2 g_3}, \quad (19)$$

and

$$E_{klm} = E_1 + \alpha_1 - 2\beta_1 \left(\cos \frac{2\pi k}{G} + \cos \frac{2\pi l}{G} + \cos \frac{2\pi m}{G} \right). \quad (20)$$

These results are only valid for values of k, l, m lying between $\pm \frac{1}{2}G$, higher values merely giving repetitions.

1.22. We next consider a p state. Here the level is triply degenerate, but it will not split up in a cubic crystal.* This is much more easily seen than in Bethe's paper if we use Cartesian co-ordinates instead of spherical polars. We then see immediately that the independent wave functions of the p state can be chosen to be $xf(r)$, $yf(r)$ and $zf(r)$, where $f(r)$ is a function of r only, and these three functions will give the same energy in a field with cubical symmetry. In view of Bethe's result we need only consider the levels derived from one of these wave functions, the others being obvious from symmetry.

Let $\chi_{g_1 g_2 g_3} = x_g f(r_g)$ be a wave function of the isolated atom corresponding to the energy value E_2 . Then we solve equation (14) as before by

$$E = E_2 + \epsilon_2 \quad \text{and} \quad \psi = \sum_{g_1 g_2 g_3} b_{g_1 g_2 g_3} \chi_{g_1 g_2 g_3}, \quad (16A)$$

* H. Bethe, 'Ann. Physik,' vol. 3, p. 133 (1929).

obtaining a set of equations similar to (17). Here, however, the equations involve more than two constants α and β , since χ is not spherically symmetrical. As before we set

$$\int U'_{g_1 g_2 g_3} \chi_{g_1 g_2 g_3} \chi_{h_1 h_2 h_3} d\tau$$

equal to α_2 if g and h refer to the same point. Among the other non-vanishing integrals we must distinguish two types. Firstly the type

$$\int U'_{g_1 g_2 g_3} \chi_{g_1 g_2 g_3} \chi_{g_1, g_2+1, g_3} d\tau.$$

This we set equal to β_2 , which is essentially positive, since the only factor which makes it differ in form from the integral for β_1 is $x_{g_2}^2$, which is positive. Then there is the type

$$\int U'_{g_1 g_2 g_3} \chi_{g_1 g_2 g_3} \chi_{g_1+1, g_2, g_3} d\tau.$$

This we set equal to $-\gamma_2$, where γ_2 is positive, since in the integrand there occurs a factor $x_{g_1} x_{g_1+1}$. Little can be said about β_2 and γ_2 except that they are both positive and of the same order of magnitude. The equations corresponding to (18) are

$$\begin{aligned} (\epsilon_2 - \alpha_2) b_{g_1 g_2 g_3} - \gamma_2 (b_{g_1+1, g_2, g_3} + b_{g_1-1, g_2, g_3}) \\ + \beta_2 (b_{g_1, g_2+1, g_3} + b_{g_1, g_2-1, g_3} + b_{g_1, g_2, g_3+1} + b_{g_1, g_2, g_3-1}) = 0. \end{aligned} \quad (18A)$$

This is solved as before by

$$b_{g_1 g_2 g_3}^{klm} = e^{\frac{2\pi i}{G}(kg_1 + lg_2 + mg_3)},$$

giving

$$E_{klm} = E_2 + \alpha_2 + 2\gamma_2 \cos \frac{2\pi k}{G} - 2\beta_2 \left(\cos \frac{2\pi l}{G} + \cos \frac{2\pi m}{G} \right). \quad (21)$$

This is valid for l and m lying between $\pm \frac{1}{2}G$, and k lying between either $\frac{1}{2}G$ and G or $-\frac{1}{2}G$ and $-G$. There are also two similar expressions obtained by permuting k , l and m .

1.23. Similar results could also be obtained for d and f states, but the work would be more complicated, not only on account of the larger degeneracy, but also because the degeneracy is partly removed by the crystalline field. For example, for d terms the harmonics may be taken to be xy , yz , zx , $x^2 - y^2$ and $y^2 - z^2$. The first three taken together will not split as they obviously give the same energy in a cubic field, but there will be an energy difference between these terms and the last two. As it is not the object of this paper to investigate the properties of special structures any further than is necessary

to explain the general outlines of semi-conduction, these questions will not be further discussed here.

1.24. In the expressions for the energy levels put

$$\xi = \frac{2\pi k}{G}, \quad \eta = \frac{2\pi l}{G}, \quad \zeta = \frac{2\pi m}{G}.$$

Then for small values of ξ , η , ζ equation (20) becomes

$$E_{\xi\eta\zeta} = E_1 + \alpha_1 - 6\beta_1 + \beta_1(\xi^2 + \eta^2 + \zeta^2),$$

which is of exactly the same form as (4) with β_1 instead of ω . Also putting $\xi = \pi - u$, and supposing u , η , ζ small, we have

$$E_{\xi\eta\zeta} = E_1 + \alpha_1 - 2\beta_1 - \beta_1 u^2 + \beta_1(\eta^2 + \zeta^2),$$

which is of the same form as (10A). We therefore conclude that the energy levels derived from an s state correspond exactly to those in the first zone of the free electron picture.

Further, treating η and ζ as small in the expression (21) and putting $\xi = \pi + u$, we have approximately

$$E_{\xi\eta\zeta} = E_2 + \alpha_2 - 4\beta_2 - 2\gamma_2 + \gamma_2 u^2 + \beta_2(\eta^2 + \zeta^2),$$

which is of exactly the same form as (10B). We conclude that the energy levels derived from p levels correspond to those in the second zone of the free electron picture. We therefore see that the discontinuities in the energy occur both for nearly free and for strongly bound electrons.

For our perturbation method to be valid it is necessary that the unperturbed energy levels of the isolated atom should be far apart. Therefore if (20) gives the states derived from a term ns , and (21) those derived from a term np it is necessary that the energy difference between these two systems should be large. Now the greatest of the energies (20) is given by putting $\xi = \eta = \zeta = \pi$ and is $E_1 + \alpha_1 + 6\beta_1$, while the least of the energies (21) is given by putting

$$\xi = \pi, \quad \eta = \zeta = 0 \quad \text{and is} \quad E_2 + \alpha_2 - 4\beta_2 - 2\gamma_2.$$

We must therefore have

$$E_2 + \alpha_2 - 4\beta_2 - 2\gamma_2 > E_1 + \alpha_1 + 6\beta_1. \quad (22)$$

In this case all the energies of the second zone lie above those of the first zone, and there are forbidden ranges of the energy, in contradistinction to the case of nearly free electrons, where, in spite of the discontinuities, the energy can take all values from V_0 to infinity.

The Internal State of a Metal.

1.3. By using the results established above for the two limiting cases of nearly free and of tightly bound electrons, it is possible to see qualitatively the energy levels in a metal, even of the inner electrons, in so far as the exchange forces can be neglected. This is a very serious restriction—how serious further investigation must show.

The innermost electrons in a metal must be in levels derived from the $1s$ state. The energy levels must therefore be given by a formula of the same form as (20), there being G^3 such levels in all. On account of the spin of the electron, these levels are double and can accommodate $2G^3$ electrons, that is two per atom, and so in a metal the $1s$ or K electrons will just fill up the lowest allowed band of energies. The $1s$ level is peculiar in that the next higher state is also an s level, and so the second band of allowed energies is also of the type (20). There is no doubt that in all metals the K electrons are strongly bound, and do not interfere with the $2s$ levels at all. They can therefore be omitted entirely from the discussion. The groups other than the first are not peculiar and it will be sufficient to discuss an element with $(n - 1)$ completed groups, but with the n th incomplete.

The states derived from the ns level are of the type (20), and these are the lowest states whether the electrons are nearly free or strongly bound. These levels can accommodate $2G^3$ electrons. For the alkalis which have a single ns electron we should expect that the G^3 valency electrons should all go into this level, half filling it. The alkaline earths having two ns electrons, we might expect that their $2G^3$ valency electrons would just fill up the band of states derived from the ns level. This is not necessarily true, since if the electrons are nearly free the lowest levels derived from the np state have lower energy than the highest levels derived from the ns state, as was pointed out in section 1.11. In this case not all the $2G^3$ levels in the first band would be filled, some electrons being in the second band. If, on the other hand, the electrons are strongly bound, then all the levels derived from the np state have higher energies than those derived from the ns state, and in this case all the $2G^3$ valency electrons would just fill up the $2G^3$ levels of the first band. In the first case the alkaline earths would be metals, and in the second case at most semi-conductors. We thus see that it might be possible for the alkaline earths to be non-metallic, while for the alkalis there is no such possibility. The fact that the alkaline earths are metallic shows that their valency electrons must be considered as nearly free, and that the first and second bands of energies

overlap. It therefore appears that electrons which form a closed sub-group in an atom need not necessarily do so in a metal.

The above discussion is sufficient to show the properties which are required to make an element a semi-conductor. It is necessary that the electrons which do not form a complete group should exactly fill up one of the bands of allowed energies, and further that these electrons should be tightly bound. The first condition is a qualitative one and involves the number of electrons per atom being even. If the crystal structure were the simple cubic one which is considered here, it would also be necessary that the number of electrons should be just sufficient to complete a sub-group of the isolated atom, but this is not necessary for more complicated structures, as in these the degeneracy of the p terms is removed by the crystalline field. Thus, electrons which form a closed sub-group in a metal do not necessarily do so in the isolated atom. This is the converse of the statement at the end of the last paragraph. It is to be noted that we define a closed group in a metal as consisting of the electrons occupying all those levels which belong to a band of allowed energies, irrespective of whether there are discontinuities or not, the only condition being that the energy takes all values between its upper and lower bounds. The second of the conditions for a semi-conductor is a quantitative one, and is the condition expressed by the inequality (22). The further investigation of this condition would necessitate the consideration of the actual crystal structure as well as the atomic levels, and would require calculations which are impossible at the moment.

To determine the properties of a semi-conductor we shall consider a cubic lattice in which both the above conditions are satisfied. The model is a very rough one and is much simplified, but ought to give the broad outlines of the phenomena.

The Model of a Semi-Conductor.

2.1. We assume that we have a simple cubic lattice, consisting of atoms which have just enough electrons to fill up one of the zones discussed above, and that the electrons are tightly bound. For simplicity we shall only discuss the case when each atom has two s electrons outside a closed group. To obtain semi-conducting properties it is necessary to assume that all the energy levels derived from the p terms lie higher than those derived from the s terms.

The $2G^3$ levels derived from the s terms have energies given by

$$E_{\xi\eta\zeta} = E_1 + \alpha_1 - 2\beta_1 (\cos \xi + \cos \eta + \cos \zeta), \quad (20)$$

and the next terms are those derived from the p terms, having energies given by

$$E_{\xi\eta\zeta} = E_2 + \alpha_2 + 2\gamma_2 \cos \xi - 2\beta_2 (\cos \eta + \cos \zeta), \quad (21)$$

and by two other expressions obtained by permuting ξ , η , and ζ . The condition (22) must also be satisfied, so

$$E_2 + \alpha_2 - 4\beta_2 - 2\gamma_2 > E_1 + \alpha_1 + 6\beta_1.$$

At the absolute zero all the $2G^3$ valency electrons will be in the $2G^3$ levels given by (20), but at any higher temperature some of the electrons will be in the upper levels. The number of electrons with quantum numbers lying between (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ is given by $(2G^3/8\pi^3) n_0 (\xi\eta\zeta) d\xi d\eta d\zeta$, where $n_0 (\xi\eta\zeta)$ is the Fermi function and is given by

$$n_0 (\xi\eta\zeta) = \frac{1}{\frac{1}{A} \frac{e^E}{e^{kT}} + 1}. \quad (23)$$

The energy E is given by (20) for values of ξ , η , ζ lying between $\pm\pi$, and by (21) when two of ξ , η , ζ lie between $\pm\pi$ and the third lies either between π and 2π or between $-\pi$ and -2π . The higher levels are of no interest in the present discussion. Even with these simple forms for the energy levels the subsequent calculations are very complicated. A great simplification is introduced if we suppose $\beta_2 = \gamma_2$, and we therefore assume this. The two quantities are of the same order of magnitude and it would not be worth while treating them as unequal unless we also took into account the correct crystal structure of the semi-conductor. This assumption gives E a simple form in the neighbourhood of the critical energy of the Fermi distribution, and in this case alone has it so far been found possible to carry out the calculations completely.

It is first necessary to determine the value of the constant A , which is fixed by the number of electrons present. We set for convenience

$$E_1 + \alpha_1 + 6\beta_1 = W_1,$$

$$E_2 + \alpha_2 - 4\beta_2 - 2\gamma_2 = W_2 \quad (24)$$

and

$$\log A = W_0/kT.$$

In order that the effect of the discontinuity may be observable at ordinary temperatures it is necessary to assume that $(W_2 - W_1)$ is small compared with β_1 . The electrons are therefore to be thought of as neither tightly bound nor nearly free, but in an intermediate condition. For insulators $(W_2 - W_1)$ is

not small compared with β_1 , and the conductivity will only become appreciable for exceedingly high temperatures.

In the ordinary theory of the Fermi distribution W_0 is constant so long as T lies below the temperature of degeneracy, which is some thousands of degrees. Here, however, the theory is not so simple and W_0 is constant only if kT is not large compared with $(W_2 - W_1)$. In this case it is easily seen that W_0 must lie between W_1 and W_2 , for only if this condition is satisfied are all the levels in the first zone occupied at the absolute zero, and all those in the second zone unoccupied. Ordinarily W_0 is the null-point energy of the electrons, but this is no longer necessarily true if there are bands of forbidden energies, and if W_0 happens to be a forbidden energy the null-point energy is the highest allowed energy less than W_0 . If kT is large compared with $(W_2 - W_1)$ the effect of the discontinuity is negligible and the substance behaves as a metal. For a semi-conductor this temperature range usually lies below the temperature of degeneracy. To determine W_0 we have the equation

$$2G^3 = \frac{2G^3}{8\pi^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\xi d\eta d\zeta}{e^{\frac{E-W_0}{kT}} + 1}. \quad (25)$$

To evaluate the integral we split it up into parts. Consider first the contribution which is given by restricting all the variables of integration to lie between $\pm\pi$. The index of the exponential is then negative, and so the integrand is nearly unity, the deviation from unity being greatest near the points $(\pm\pi, \pm\pi, \pm\pi)$. The next contributions arise from restricting two of ξ, η, ζ to lie between $\pm\pi$, and the third to lie either between $-\pi$ and -2π or between π and 2π . Since there are three such ranges of integration there will be three equal contributions. The remaining contributions are negligible for small values of T . Equation (25) can therefore be written

$$\int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left(\frac{1}{e^{\frac{E-W_0}{kT}} + 1} - 1 \right) d\xi d\eta d\zeta + 3 \int_{-2\pi}^{-\pi} d\xi \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{d\eta d\zeta}{e^{\frac{E-W_0}{kT}} + 1} + 3 \int_{\pi}^{2\pi} d\xi \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{d\eta d\zeta}{e^{\frac{E-W_0}{kT}} + 1} = 0. \quad (26)$$

Taking the terms of the first integral together, the integrand is effectively zero except in the neighbourhood of the eight points $(\pm\pi, \pm\pi, \pm\pi)$. As the expression for E given by (20) is periodic in ξ, η, ζ with period 2π , we may replace the contributions from the regions in the neighbourhoods other than that near (π, π, π) by equivalent integrations in the neighbourhood of (π, π, π) ,

of course still using the expression (20) for the energy. Using new variables defined by

$$\xi = \pi - u, \quad \eta = \pi - v, \quad \zeta = \pi - w,$$

the integration takes place in a cube centre $u = v = w = 0$, the length of the sides being 2π . For small values of u, v, w the energy is given by

$$E = W_1 - \beta_1 (u^2 + v^2 + w^2), \quad (27)$$

and with this expression for the energy we may take the limits of integration to be infinite with negligible error, as the integrand vanishes exponentially for large values of the variables. The first integral therefore reduces to

$$-\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{du \, dv \, dw}{e^{\{W_0 - W_1 + \beta_1(u^2 + v^2 + w^2)\}/kT} + 1}. \quad (28)$$

The integrand of the second integral is only different from zero near $(-\pi, 0, 0)$ and that of the third integral near $(\pi, 0, 0)$. By substituting $\xi = -\pi - u$, $\eta = v$, $\zeta = w$ and $\xi = \pi + u$, $\eta = v$, $\zeta = w$ respectively, these two integrals may be combined together in much the same way as for the first integral, and they finally reduce to

$$3 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{du \, dv \, dw}{e^{\{W_2 - W_0 + \beta_2(u^2 + v^2 + w^2)\}/kT} + 1}. \quad (29)$$

Equating the sum of the expression (28) and (29) to zero gives an equation for W_0 . It is impossible to obtain an explicit value for W_0 which is valid for all values of T , but it is easy to do so if T is small. For other ranges of T the evaluation is more difficult.

For small values of T we expand the denominators of the integrands and retain only the first terms. This gives

$$(\beta_1)^{-3/2} e^{-\frac{W_0 - W_1}{kT}} = 3 (\beta_2)^{-3/2} e^{-\frac{W_2 - W_0}{kT}},$$

or

$$W_0 = \frac{1}{2} (W_1 + W_2) - \frac{1}{2} kT \log 3 (\beta_1/\beta_2)^{3/2}. \quad (30)$$

The last term may be either positive or negative since $\beta_1 < \beta_2$, the s electrons being more tightly bound than the p electrons. In general this term is negligible unless kT is comparable with $(W_2 - W_1)$.

The Specific Heat of the Electrons.

2.2. The specific heat of the electron gas has been calculated by Sommerfeld and by Bloch, the former using free electrons and the latter tightly bound electrons. Bloch assumes that the variable part of the energy is given by

$$E = -2\beta (\cos \xi + \cos \eta + \cos \zeta),$$

and finds that the specific heat is proportional to the temperature if $T < T_0$, and falls off as T^{-2} if $T > T_0$, where T_0 is the temperature $2\beta/k$, the maximum specific heat per gram-molecule of the metal being of the order R . For the model we are treating here the temperature dependence will be rather different, on account of the discontinuity in the energy, and for temperatures low compared with $(W_2 - W_1)/k$ the specific heat must fall off exponentially to zero.

If we choose $G^3 = L$, Loschmidt's number, the energy of the electrons per gram-molecule of metal is

$$U = \frac{2L}{8\pi^3} \iiint \frac{E d\xi d\eta d\zeta}{e^{\frac{E - W_0}{kT}} + 1}. \quad (31)$$

To evaluate this we split the integral up into parts, exactly as was done in the last section, and transform to the variables u, v, w . It is impossible to carry out the calculation exactly so we discuss two limiting cases.

(1) We first of all assume that T is very small, so small that $(W_2 - W_1)$ is large compared with kT .

Consider the contribution to (31) coming from the first zone of allowed energies. It is

$$\frac{2L}{8\pi^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{E du dv dw}{e^{\frac{E - W_0}{kT}} + 1}$$

where

$$E = W_1 - 6\beta_1 + 2\beta_1(\cos u + \cos v + \cos w).$$

Since $W_0 > W_1$ the index of the exponential is always large and negative, and so the exponential term is small compared with unity. We may therefore expand the denominator and take the first two terms only. The first term gives

$$\frac{2L}{8\pi^3} \iiint E du dv dw = 2L(W_1 - 6\beta_1).$$

The second term is more difficult to evaluate. We shall, however, only make a very small error if we expand the cosines, and, instead of integrating through the cube, integrate through a sphere of the same volume. If, further, we integrate through an infinite sphere we make negligible error since the integrand vanishes exponentially. With these approximations the second term gives

$$- \frac{2L}{8\pi^3} \iiint \{W_1 - \beta_1(u^2 + v^2 + w^2)\} e^{-\frac{W_0 - W_1}{kT} - \frac{\beta_1}{kT}(u^2 + v^2 + w^2)} du dv dw,$$

which reduces to

$$- \frac{L\sqrt{\pi}}{8\pi^2} \left\{ 2W_1 \left(\frac{kT}{\beta_1} \right)^{3/2} - 3\beta_1 \left(\frac{kT}{\beta_1} \right)^{5/2} \right\} e^{-\frac{W_0 - W_1}{kT}}.$$

The contribution to (31) coming from the second zone of allowed energies is given by

$$\frac{6L}{8\pi^3} \iiint \frac{E \, du \, dv \, dw}{e^{\frac{E-W_0}{kT}} + 1},$$

where

$$E = W_2 + 6\beta_2 - 2\beta_2(\cos u + \cos v + \cos w).$$

Since $W_2 > W_0$ the index of the exponential is always large and positive, and so we need only retain the exponential term in the denominator and omit the 1. This gives on using the same approximations as before

$$\frac{3L\sqrt{\pi}}{8\pi^2} \left\{ 2W_2 \left(\frac{kT}{\beta_2}\right)^{3/2} + 3\beta_2 \left(\frac{kT}{\beta_2}\right)^{5/2} \right\} e^{-\frac{W_2-W_0}{kT}}.$$

Finally we have for U , after using (30) to combine the exponential terms,

$$U = 2L(W_1 - 6\beta_1) + \frac{L\sqrt{\pi}}{4\pi^2} \left\{ (W_2 - W_1) \left(\frac{kT}{\beta_1}\right)^{3/2} + 3\beta_1 \left(\frac{kT}{\beta_1}\right)^{5/2} \right\} e^{-\frac{W_0-W_1}{kT}}. \quad (32)$$

We now make the approximation $W_0 = \frac{1}{2}(W_1 + W_2)$, and, putting $k\Theta_u = W_0 - W_1$, and $kT_0 = \beta_1$, we have for the specific heat

$$C_v = \frac{\partial U}{\partial T} = \frac{R\sqrt{\pi}}{8\pi^2} \left(\frac{T}{T_0}\right)^{3/2} \left\{ 4 \left(\frac{\Theta_u}{T}\right)^2 + 12 \frac{\Theta_u}{T} + 15 \right\} e^{-\frac{\Theta_u}{T}}, \quad (33)$$

R being the gas constant.

(2) The second limiting case of interest occurs for values of T such that $(W_2 - W_1) \ll kT \ll \beta_1$. In this case the calculations are not so easy to carry out with any degree of accuracy, but it would seem a reasonable approximation to expand the integrals in powers of Θ_u/T , and neglect all terms but the first. This is equivalent to putting $W_1 = W_2 = W_0$. A calculation almost identical with the one above leads to the approximate result

$$C_v = \frac{R15\sqrt{\pi}}{16\pi^2} \left\{ 1 + 3 \left(\frac{\beta_1}{\beta_2}\right)^{3/2} \right\} \left(\frac{T}{T_0}\right)^{3/2}, \quad (33A)$$

the next term, involving Θ_u/T , being negative. This value is practically identical with (33) for large values of T ($< T_0$), and it is probable that in a more exact calculation the numerical factor in the bracket would be replaced by 2, which would render the two expressions (33) and (33A) identical for large values of T . We therefore see that the specific heat increases steadily from zero according to the exponential law (33) until T becomes of the same order as Θ_u . It then increases as $T^{3/2}$, there being no maximum in the curve. The order

of magnitude of the specific heat is the same as that calculated by Sommerfeld, and seems well below the limit of observation.

The Paramagnetism of the Electrons.

2.3. One of the first applications of the Fermi statistics was made by Pauli* to explain the small constant paramagnetism of the alkalis. For semi-conductors the paramagnetism will be constant at ordinary temperatures and will decrease exponentially to zero as the temperature is lowered.

The paramagnetic susceptibility is due to the effect of an external magnetic field in orienting the electrons, each electron possessing a magnetic moment of one Bohr magneton,

$$\mu_0 = \frac{eh}{4\pi mc}.$$

Under the influence of an external magnetic field H each electronic energy level is split up into two, the energies of the states being $E(\xi\eta\zeta) \pm \mu_0 H$. Since the degeneracy of the electronic states is removed we can no longer use (23) for the distribution function, and we must distinguish between the two directions of spin. The number of electrons with quantum numbers lying between (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ is now given by

$$(G^3/8\pi^3) n_0 (\xi\eta\zeta, \pm \mu_0 H) d\xi d\eta d\zeta,$$

where

$$n_0 (\xi\eta\zeta, \pm \mu_0 H) = \frac{1}{\frac{1}{A} e^{\frac{E \pm \mu_0 H}{kT}} + 1}.$$

The parameter A has the same value as before to the first order in H . The total magnetic moment is

$$\begin{aligned} M &= \frac{\mu_0 G^3}{8\pi^3} \iiint \left[\frac{1}{\frac{1}{A} e^{\frac{E - \mu_0 H}{kT}} + 1} - \frac{1}{\frac{1}{A} e^{\frac{E + \mu_0 H}{kT}} + 1} \right] d\xi d\eta d\zeta \\ &= \frac{2\mu_0^2 H G^3}{8\pi^3 kT} \iiint \frac{d\xi d\eta d\zeta}{\left(\frac{1}{A} e^{\frac{E}{kT}} + 1\right) \left(\frac{1}{A} e^{\frac{-E}{kT}} + 1\right)} \end{aligned} \quad (34)$$

to the first order in H . We split the integral up into parts as before, and a short calculation shows that the paramagnetic susceptibility κ is given by

$$\kappa = \frac{\mu_0^2 \sqrt{\pi}}{\pi^2 a^3 \beta_1} \left(\frac{T}{T_0}\right)^{\frac{3}{2}} e^{-\frac{\Theta_u}{T}}, \quad (35)$$

provided $T \ll \Theta_u$, a being the lattice constant.

* 'Z. Physik,' vol. 41, p. 81 (1927).

This is of the same order as the constant value found for the alkalis by Pauli, and also by Bloch,* the latter obtaining

$$\kappa \sim \frac{\mu_0^2}{a^3 \beta}.$$

It is doubtful whether there is any reliable experimental evidence with which to test the formula (35), though for some substances, notably carbon, an increase of diamagnetism with falling temperature has been observed, which might be attributed to the falling off of the paramagnetism of the outer electrons, the diamagnetism of the closed shells remaining constant.

The Calculation of the Conductivity.

3. The combined influence of a constant electric field and of the thermal motion of the lattice on the distribution of electrons in a metal has been studied in great detail by Bloch in the papers mentioned above. In the main we shall follow the same method here, but as we shall need to use some refinements later, it has been thought advisable first to give Bloch's calculations in a modified form and afterwards to apply them to a semi-conductor.

The problem is to determine the form of the distribution function $n(\xi\eta\zeta)$ under the combined action of a constant electric field \mathbf{F} , parallel to the x -axis, and the thermal vibrations. We assume that the elastic vibrations of the lattice are split up into their normal modes and that the vector displacement of a typical lattice point is given by

$$\mathbf{u}_{l_1 l_2 l_3} = \sum_{f', g', h'}^G \sum_{j=1}^3 a_{f' g' h' j} e^{\frac{2\pi i}{G}(l_1 f' + l_2 g' + l_3 h')} \mathbf{v}_{f' g' h' j},$$

where $\mathbf{v}_{f' g' h' j}$ is a unit vector giving the direction of the displacement, the $a_{f' g' h' j}$ being the normal co-ordinates, $j = 1$ giving the longitudinal vibrations and $j = 2, j = 3$ the transverse. The corresponding frequencies are given by

$$\nu_{f g h j} = \frac{v_j}{2\pi a} \sqrt{(f^2 + g^2 + h^2)}, \quad (36)$$

where v_j is the velocity of propagation and $f = 2\pi f'/G, g = 2\pi g'/G, h = 2\pi h'/G$. By the introduction of these normal co-ordinates the problem is reduced to the interaction of the valency electrons with a number of simple harmonic oscillators characterised by the integers f', g', h', j . Bloch shows that if an electron jumps from a state (ξ, η, ζ) to a state (ξ', η', ζ') , while the oscillator (f, g, h) emits or absorbs a quantum of energy, then it is necessary that,

$$\xi - \xi' = \pm f \pmod{2\pi}, \quad (37)$$

* 'Z. Physik,' vol. 53, p. 216 (1929).

with two similar conditions for g and h . He also shows that only the longitudinal vibration is of importance, and we shall therefore omit j in future.

3.1. The alteration in the distribution function $n(\xi\eta\zeta)$ due to the electric field is given by

$$-\frac{2\pi aeF}{h} \frac{\partial n}{\partial \xi}, \quad (38)$$

and the alteration due to collisions with the lattice is given by*

$$\begin{aligned} \sum_{\xi'f} A_{\xi\xi'f}^+ [n_{\xi'}(1-n_{\xi})(N_f+1) - n_{\xi}(1-n_{\xi'})N_f] \\ + \sum_{\xi'f} A_{\xi\xi'f}^- [n_{\xi'}(1-n_{\xi})N_f - n_{\xi}(1-n_{\xi'})(N_f+1)]. \end{aligned} \quad (39)$$

Only one of each set of quantum numbers has been written explicitly, but this will cause no confusion. The meaning of the various quantities is as follows.

$$A_{\xi\xi'f}^+ = \frac{hC^2(f^2+g^2+h^2)}{8\pi^2Ma^2\mu^2\nu} \frac{\partial}{\partial t} \frac{1 - \cos 2\pi t(E_{\xi} - E_{\xi'} + h\nu)/h}{(E_{\xi} - E_{\xi'} + h\nu)^2}, \quad (40)$$

where M is the mass of the crystal cube, C is a quantity of the order of the square of the reciprocal of the radius of the atom, and $\mu = 8\pi^2m/h^2$. $A_{\xi\xi'f}^-$ only differs from $A_{\xi\xi'f}^+$ by having $(E_{\xi} - E_{\xi'} - h\nu)$ in the time factor instead of $(E_{\xi} - E_{\xi'} + h\nu)$. Further, the three conditions (37) must be satisfied.

The expression for N_f varies somewhat with the assumptions we make. If we assume that the lattice vibrations are always in thermal equilibrium—a state of affairs which can be brought about by a minute quantity of impurity in the crystal—then we have

$$N_f = \frac{1}{e^{h\nu_f/kT} - 1}. \quad (41)$$

Otherwise N_f takes a slightly different form which has been discussed by Peierls. This question is of little importance for semi-conductors and we accordingly take N_f to be given by (41). In this case it is sufficient to consider transitions which satisfy

$$\left. \begin{aligned} \xi - \xi' &= \pm f \\ \eta - \eta' &= \pm g \\ \zeta - \zeta' &= \pm h \end{aligned} \right\}. \quad (37A)$$

The other transitions allowed by (37) would not change the temperature dependence of the resistance, but would only affect its magnitude.

Under the combined influence of the electric field and of collisions with the

* R. Peierls, 'Ann. Physik,' vol. 4, p. 121 (1930), equation (12), corrected.

lattice, the distribution of electrons must be steady. We therefore obtain an integral equation for $n(\xi\eta\zeta)$ by equating to zero the sum of (38) and (39). We try to solve this by putting

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) + n_1(\xi\eta\zeta), \tag{42}$$

where $n_0(\xi\eta\zeta)$ is the Fermi distribution (23), and n_1 is small and proportional to F . We use the abbreviations

$$\frac{E_\xi - W_0}{kT} = \varepsilon, \quad \frac{E_{\xi'} - W_0}{kT} = \varepsilon', \quad \frac{h\nu_f}{kT} = x. \tag{43}$$

Owing to the presence of the time factor, the expression for $A_{\xi\xi'f}^+$ is only sensibly different from zero when $\varepsilon - \varepsilon' + x = 0$, and we may substitute this value for x in any terms multiplying $A_{\xi\xi'f}^+$. Similarly $A_{\xi\xi'f}^-$ is only different from zero when $\varepsilon - \varepsilon' - x = 0$. We now take as our unknown

$$\chi(\xi\eta\zeta) = n_1(\xi\eta\zeta)(e^\varepsilon + 1)(e^{-\varepsilon} + 1), \tag{44}$$

and then, neglecting squares of F , we have

$$\begin{aligned} \frac{2\pi aeF}{h} \frac{\partial n_0}{\partial \xi} = & \sum_{\xi'} A_{\xi\xi'f}^+ \frac{1}{(e^\varepsilon + 1)(e^{-\varepsilon'} + 1)(e^x - 1)} \{\chi_{\xi'} - \chi_\xi\} \\ & + \sum_{\xi'} A_{\xi\xi'f}^- \frac{1}{(e^{-\varepsilon} + 1)(e^{\varepsilon'} + 1)(e^x - 1)} \{\chi_\xi - \chi_{\xi'}\}. \end{aligned} \tag{45}$$

It is important to note that changing ξ into ξ' changes the factor by which $(\chi_\xi - \chi_{\xi'})$ is multiplied in the first term into the factor occurring in the second term, and *vice versa*. The variables f, g and h do not occur explicitly in (45), being given by (37A).

Now let us write the equation (42) for shortness in the following form

$$\begin{aligned} \chi(\xi\eta\zeta) \phi(\xi\eta\zeta) - \iiint K(\xi\eta\zeta, \xi'\eta'\zeta') \chi(\xi'\eta'\zeta') d\xi' d\eta' d\zeta' \\ = - \frac{2\pi aeF}{h} \frac{\partial n_0}{\partial \xi}. \end{aligned} \tag{45A}$$

We have here replaced the summation by an integration, which is allowable as we may make ξ, η, ζ continuous variables by allowing G to tend to infinity. As remarked above, $K(\xi, \xi')$ is symmetrical between the dashed and the undashed letters, and from the form of (45) we must have

$$\phi(\xi\eta\zeta) = \iiint K(\xi\eta\zeta, \xi'\eta'\zeta') d\xi' d\eta' d\zeta'. \tag{46}$$

To solve (45A) is very difficult, and we have to make approximations which will be better appreciated if we treat a special case first. The approximations are not easy to justify mathematically, and rest rather on physical arguments. Accordingly, in this section we treat the case of ordinary metals and assume that the variable part of the energy is given by

$$E_{\xi} = \beta (\xi^2 + \eta^2 + \zeta^2),$$

reserving the general case for consideration later.

The right-hand side of (45A) involves $\xi \partial n_0 / \partial E$, that is ξ multiplied by a factor which is symmetrical in ξ, η, ζ . This suggests that we try a function of the same form for χ . Further, in order that our expressions for $A_{\xi\xi'}$ may be correct, it is necessary to assume that the lattice vibrations are equivalent to a small perturbation of the electronic motion. Actually, unless the temperature is exceedingly high, an electron only loses a very small fraction of its energy or of its momentum in a collision, and we therefore suppose that $(\xi - \xi')/\xi'$ is small compared with unity. From these considerations we write (45A) in the form

$$\begin{aligned} \chi_{\xi} \phi_{\xi} - \int K(\xi, \xi') \frac{\xi}{\xi'} \chi_{\xi'} d\xi' d\eta' d\zeta' \\ = - \frac{2\pi a e F}{h} \frac{\partial n_0}{\partial \xi} - \int K(\xi, \xi') \frac{\xi - \xi'}{\xi'} \chi_{\xi'} d\xi' d\eta' d\zeta'. \end{aligned} \quad (47)$$

If we put the right-hand side of (47) equal to zero, the resulting homogeneous equation has the solution

$$\chi_{\xi} = \xi$$

on account of (46). We therefore solve (47) by successive approximations, putting

$$\chi_{\xi} = \alpha \xi + \chi_2,$$

where α is at present an arbitrary constant and χ_2 is supposed small compared with the first term. We then obtain the following equation for χ_2 , omitting terms of the order $\chi_2(\xi - \xi')/\xi'$.

$$\begin{aligned} \chi_2 \phi_{\xi} - \int K(\xi, \xi') \frac{\xi}{\xi'} \chi_2 d\xi' d\eta' d\zeta' \\ = - \frac{2\pi a e F}{h} \frac{\partial n_0}{\partial \xi} - \alpha \int K(\xi, \xi') (\xi - \xi') d\xi' d\eta' d\zeta'. \end{aligned}$$

The essential difference between this equation and (47) is that here the unknown function only occurs on the left-hand side of the equation, and the corresponding homogeneous equation can be solved exactly. In order that this equation

may be soluble it is necessary that the right-hand side should be orthogonal to the solution of the homogeneous equation obtained by transposing the left-hand side. This condition gives an equation for α . If we take $\chi_2\phi_\xi$ as a new unknown, it is easily seen that the solution of the homogeneous transposed equation is

$$\chi_2\phi_\xi = \xi^{-1},$$

and so the orthogonality condition is

$$\frac{2\pi aeF}{h} \int \frac{1}{\xi} \frac{\partial n_0}{\partial \xi} d\xi d\eta d\zeta + \alpha \iiint K(\xi, \xi') \frac{\xi - \xi'}{\xi} d\xi d\eta d\zeta d\xi' d\eta' d\zeta' = 0. \quad (48)$$

We therefore finally obtain an approximate solution of the form

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) + \frac{\alpha\xi}{(e^\epsilon + 1)(e^{-\epsilon} + 1)},$$

which is Bloch's solution. The equation (48) for α differs slightly from that given by Bloch, who did not formulate the orthogonality condition properly. However, within the accuracy to which we are working the two equations give the same final result.

3.11. We now evaluate the parameter α under the conditions which probably obtain in the alkali metals, the energy being given by $E = \beta(\xi^2 + \eta^2 + \zeta^2)$. The first term in (48) is

$$-\frac{2\pi aeF}{h} \frac{2\beta}{kT} \int \frac{d\xi d\eta d\zeta}{(e^\epsilon + 1)(e^{-\epsilon} + 1)} \quad (49)$$

and presents no difficulty. The sextuple integral is, however, extremely difficult to calculate, mainly owing to the presence of the time factor. The corresponding time factors which occur in dispersion or collision problems do not cause any trouble because there are no relations such as (37A) to be satisfied, and a simple integration over $E_{\xi'}$ suffices to eliminate the time factor. Here ν is not independent of ξ and ξ' , and this introduces a complication which renders the evaluation of the sextuple integral a matter of some delicacy.

We first of all use polar co-ordinates ρ, θ, ϕ and ρ', θ', ϕ' , so that we have $\xi^2 + \eta^2 + \zeta^2 = \rho^2$ and $\xi'^2 + \eta'^2 + \zeta'^2 = \rho'^2$, the axis of ξ being $\theta = 0$. Then instead of ρ', θ', ϕ' we use polar co-ordinates R, ϑ, ϖ in the f, g, h space, and finally instead of R we use the equivalent variable ν , which is connected with R by equation (36),

$$\nu = \frac{b}{2\pi a} R.$$

The line joining (ξ, η, ζ) to the origin is taken as $\vartheta = 0$, and ϑ is therefore the angle between the direction of propagation of the incident electronic wave

and that of the elastic vibration, the direction cosines being proportional to (ξ, η, ζ) and to (f, g, h) respectively.

First let us consider the factor involving the time. It is

$$\frac{2\pi}{h} \frac{\sin 2\pi t (\mathbf{E}_\xi - \mathbf{E}_{\xi'} \pm h\nu)/h}{\mathbf{E}_\xi - \mathbf{E}_{\xi'} \pm h\nu} = \frac{2\pi}{h} \frac{\sin 2\pi ty/h}{y},$$

where

$$y = \beta \left(\frac{4\pi^2 a^2}{b^2} \nu^2 + \frac{4\pi a}{b} \nu \cos \vartheta \right) \mp h\nu.$$

If t is large this expression oscillates very rapidly, and in any integral involving it the only effective contributions will be from small values of y . We therefore change variables from ϑ to y , and in any expression which varies slowly we put $y = 0$. Now

$$dy = - \frac{4\pi a \beta}{b} \nu \sin \vartheta d\vartheta$$

and so

$$\int_0^\pi \frac{\sin 2\pi t (\mathbf{E}_\xi - \mathbf{E}_{\xi'} \pm h\nu)/h}{\mathbf{E}_\xi - \mathbf{E}_{\xi'} \pm h\nu} \sin \vartheta d\vartheta = - \int_{y=0}^{y=\pi} \frac{b}{4\pi a \beta \nu} \frac{\sin 2\pi ty/h}{y} dy.$$

Further, putting $z = 2\pi ty/h$ the integral becomes

$$\frac{b}{4\pi a \beta \nu} \int_{y=\pi}^{y=0} \frac{\sin z}{z} dz,$$

the upper limit of integration being

$$z = \frac{2\pi t}{h} \left\{ \beta \left(\frac{4\pi^2 a^2}{b^2} \nu^2 + \frac{4\pi a}{b} \nu \right) \mp h\nu \right\}$$

and the lower limit being

$$z = \frac{2\pi t}{h} \left\{ \beta \left(\frac{4\pi^2 a^2}{b^2} \nu^2 - \frac{4\pi a}{b} \nu \right) \mp h\nu \right\}.$$

If these limits of integration are of opposite sign, then for large t the last integral is effectively

$$\int_{-\infty}^{\infty} \frac{\sin z}{z} dz,$$

that is π , and if the limits are of the same sign the integral is zero. It is therefore necessary to consider the limits of integration carefully.

Taking first the upper sign for $h\nu$, which corresponds to the absorption of a

“sound quantum” by the electrons, we see that the upper limit becomes negative if

$$\nu < \frac{h\nu^2}{4\pi^2 a^2 \beta} - \frac{\nu \rho}{\pi a}, \quad (50)$$

and the lower limit becomes positive if

$$\nu > \frac{h\nu^2}{4\pi^2 a^2 \beta} + \frac{\nu \rho}{\pi a}. \quad (51)$$

These ranges are therefore to be excluded.

Taking next the lower sign for $h\nu$, corresponding to an emission of a “sound quantum,” we see that the upper limit is always positive, but that the lower limit becomes positive if

$$\nu > \frac{\nu \rho}{\pi a} - \frac{h\nu^2}{4\pi^2 a^2 \beta}. \quad (52)$$

This range is therefore to be excluded, as giving zero contribution. Further, any other factors containing \mathfrak{D} are to be replaced by their values when $y = 0$, that is when

$$\cos \mathfrak{D} = \pm \frac{h\nu}{4\pi a \beta \rho} - \frac{\pi a \nu}{\nu \rho}. \quad (53)$$

We next carry out the integration over ϖ , which presents no difficulty as the only factor involving ϖ is $(\xi - \xi')/\xi$. From (37A) we have

$$\int_0^{2\pi} \frac{\xi - \xi'}{\xi} d\varpi = -\frac{R}{\rho} \int_0^{2\pi} \frac{\cos \theta_1}{\cos \theta} d\varpi,$$

where θ_1 is the angle which the line joining (ρ, θ, ϕ) and (ρ', θ', ϕ') makes with the line $\theta = 0$. The definition of \mathfrak{D} and ϖ gives

$$\cos \theta_1 = \cos \theta \cos \mathfrak{D} + \sin \theta \sin \mathfrak{D} \cos \varpi,$$

and so we have

$$\int_0^{2\pi} \frac{\xi - \xi'}{\xi} d\varpi = -\frac{R \cos \mathfrak{D}}{\rho}. \quad (54)$$

By these integrations the sextuple integral has been reduced to the following form, from which a constant multiplying factor has been omitted.

$$\begin{aligned} \int_{\rho^3} \frac{1}{\rho^3} d\xi d\eta d\zeta \int \frac{\nu^2 d\nu}{e^x - 1} \left[\left(\nu^2 - \frac{h\nu^2}{4\pi^2 a^2 \beta} \nu \right) \frac{1}{(e^\epsilon + 1)(e^{-\epsilon-x} + 1)} \right. \\ \left. + \left(\nu^2 + \frac{h\nu^2}{4\pi^2 a^2 \beta} \nu \right) \frac{e^x}{(e^\epsilon + 1)(e^{-\epsilon+x} + 1)} \right], \quad (55) \end{aligned}$$

the limits of integration being determined by (50), (51) and (52). With these limits of integration the integral is finite, as it must be, though, if we had taken

the limits of integration for ρ to be 0 and ∞ , the integral would have been logarithmically infinite at the lower limit. However, only small values of x contribute appreciably and from this it also follows that only values of ρ in the neighbourhood of the critical point of the Fermi distribution are effective, as was to be expected on physical grounds. The integrand is, therefore, only appreciable for small values of x and of ε , and in this case the exact limits of integration do not affect the result. We take ν to vary from 0 to ν_m , the maximum Debye frequency, or equivalently we take x to vary from 0 to Θ/T , where Θ is the Debye characteristic temperature. The integral over ρ need only be taken over a range including $\varepsilon = 0$, sufficiently large for the integrand to have become inappreciable. The equation (48) for α becomes

$$\left(\frac{T}{\Theta}\right)^3 \frac{\alpha}{\lambda} \int \frac{1}{\rho^3} d\xi d\eta d\zeta \int_0^{\Theta/T} \frac{x^2 dx}{e^x - 1} \left[\left\{ \left(\frac{T}{\Theta}\right)^2 x^2 - \gamma \left(\frac{T}{\Theta}\right) x \right\} \frac{1}{(e^\varepsilon + 1)(e^{-\varepsilon-x} + 1)} \right. \\ \left. + \left\{ \left(\frac{T}{\Theta}\right)^2 x^2 + \gamma \left(\frac{T}{\Theta}\right) x \right\} \frac{e^x}{(e^\varepsilon + 1)(e^{-\varepsilon+x} + 1)} \right] = \frac{2\beta F}{kT} \int \frac{d\xi d\eta d\zeta}{(e^\varepsilon + 1)(e^{-\varepsilon} + 1)}. \quad (56)$$

The definitions of the constants are

$$\gamma = \frac{1}{\beta k \Theta} \left(\frac{h\nu}{2\pi a} \right)^2$$

and

$$\lambda = \frac{4e\nu a^2 M \mu^2 \beta}{\pi^3 G^3 h C^2} \left(\frac{h\nu}{ak\Theta} \right)^5. \quad (57)$$

Since only small values of x contribute effectively to the integral we may, in terms involving both ε and x , expand in powers of x and invert the orders of integration. The terms involving γ disappear, and on changing the variable to E we obtain

$$\left(\frac{T}{\Theta}\right)^5 \frac{2\alpha\beta^{3/2}}{\lambda} \int \frac{dE}{E(e^\varepsilon + 1)(e^{-\varepsilon} + 1)} \int_0^{\Theta/T} \frac{x^4 dx}{e^x - 1} = \frac{2\beta F}{kT} \int \frac{\sqrt{E} dE}{(e^\varepsilon + 1)(e^{-\varepsilon} + 1)}. \quad (58)$$

The ratio of the two E integrals is found to be $W_0^{3/2}$ on using the formulæ given by Sommerfeld, while the x integral is easily evaluated in the two limiting cases of T very large or very small compared with Θ .

For $T \gg \Theta$ we develop the integrand in powers of x , obtaining for α

$$\alpha = \frac{4F\lambda}{\sqrt{\beta}} \frac{\Theta}{T} \frac{W_0^{3/2}}{kT}.$$

For $T \ll \Theta$ the integration may be taken to ∞ with negligible error, and we obtain

$$\alpha = \frac{F\lambda}{125\sqrt{\beta}} \left(\frac{\Theta}{T}\right)^5 \frac{W_0^{3/2}}{kT}.$$

The distribution function therefore takes the form

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) - F\lambda_1 \frac{\Theta}{T} \frac{\partial n_0}{\partial \xi} \quad \text{for } T \gg \Theta, \quad (59A)$$

and

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) - \frac{F\lambda_1}{500} \left(\frac{\Theta}{T}\right)^5 \frac{\partial n_0}{\partial \xi} \quad \text{for } T \ll \Theta, \quad (59B)$$

where

$$\lambda_1 = 2 \left(\frac{W_0}{\beta}\right)^{3/2} \lambda. \quad (57A)$$

This is equivalent to Bloch's result, and gives a conductivity which varies as T^{-5} for low temperatures and as T^{-1} for high temperatures.

3.2. We now consider the general case when we do not assume E to have the simple form used in the last section. The solution of equation (45), which is valid independent of the form assumed by E , is suggested by the way in which we have written the expressions (59). Instead of (47) we use the following equation, which reduces to (47) under the conditions assumed in section 3.1.

$$\begin{aligned} \chi_\xi \phi_\xi - \int \mathbf{K}(\xi, \xi') \frac{\partial E / \partial \xi}{\partial E / \partial \xi'} \chi_{\xi'} d\xi' d\eta' d\zeta' \\ = -\frac{2\pi a e F}{h} \frac{\partial n_0}{\partial \xi} - \int \mathbf{K}(\xi, \xi') \frac{\partial E / \partial \xi - \partial E / \partial \xi'}{\partial E / \partial \xi'} \chi_{\xi'} d\xi' d\eta' d\zeta'. \end{aligned} \quad (47A)$$

The argument follows exactly the same lines as before, a solution of the equation with the right-hand side replaced by zero being

$$\chi_\xi = \frac{\partial E}{\partial \xi}.$$

We therefore solve (47A) by putting

$$\chi_\xi = \alpha' \frac{\partial E}{\partial \xi} + \chi_2,$$

α' being given by an orthogonality condition, which is easily found to be

$$\begin{aligned} \frac{2\pi a e F}{h} \int \frac{1}{\partial E / \partial \xi} \frac{\partial n_0}{\partial \xi} d\xi d\eta d\zeta + \alpha' \iint \mathbf{K}(\xi, \xi') \frac{\partial E / \partial \xi - \partial E / \partial \xi'}{\partial E / \partial \xi} \\ d\xi d\eta d\zeta d\xi' d\eta' d\zeta' = 0. \end{aligned} \quad (48A)$$

3.21. It only remains to solve this equation for α' . In the general case it is not possible to carry out the integrations as completely as above, but there is little doubt that a similar result will be obtained. Here we shall carry out the calculation for our model of a semi-conductor. We shall only treat the case of low temperatures, as all theories give the same law for high temperatures, and so the interesting region is that of low temperatures.

Our model of a semi-conductor consists in having a large number of electrons in the first zone of energy values, and a few electrons in the second, there being a finite energy difference between the two zones. At low temperatures only the thermal vibrations of small energy will be excited, and the probability of the transition of an electron from the first to the second zone will be small. In calculating the conductivity we may therefore neglect such transitions as they form a very small fraction of the total number of transitions. Further in evaluating (48A) we restrict ξ, η, ζ and ξ', η', ζ' to lie between $\pm\pi$, that is in the first zone. If we restrict them to lie in the second zone we obtain a value for α' which is the same as the first one, as it must be, on account of the relation (30).

As in section 2 the integrands are only effectively different from zero in the neighbourhood of the points $(\pm\pi, \pm\pi, \pm\pi)$. We therefore transform to the variables, u, v, w used in section 2. The first term in (48A) then becomes

$$-\frac{2\pi aeF}{h} \frac{1}{kT} \int \frac{du dv dw}{(e^\epsilon + 1)(e^{-\epsilon} + 1)}, \quad (49A)$$

where

$$kT\epsilon = E - W_0 = W_1 - W_0 - \beta_1(u^2 + v^2 + w^2). \quad (W_0 > W_1) \quad (60)$$

The treatment of the second term follows exactly the same lines as in the last section and, omitting a constant multiplying factor, we again obtain the expression (55). There is, however, a great difference, since here ϵ is always negative and decreases as ρ increases, where $\rho^2 = u^2 + v^2 + w^2$. Small values of ρ are therefore the most important, and so the exact limits of integration must be used. From (50), (51), (52) and from the fact that neither ρ nor v can be negative we see that the expression (55) must be written

$$\begin{aligned} & 4\pi \int_0^{\rho_0} \frac{1}{\rho} d\rho \int_{\frac{\hbar}{\pi a}(\rho_0 - \rho)}^{\frac{\hbar}{\pi a}(\rho_0 + \rho)} \frac{(v - \mathfrak{b}\rho_0/\pi a) v^3 dv}{(e^\epsilon + 1)(e^{-\epsilon - x} + 1)(e^x - 1)} \\ & + 4\pi \int_{\rho_0}^{\infty} \frac{1}{\rho} d\rho \int_0^{\frac{\hbar}{\pi a}(\rho_0 + \rho)} \frac{(v - \mathfrak{b}\rho_0/\pi a) v^3 dv}{(e^\epsilon + 1)(e^{-\epsilon - x} + 1)(e^x - 1)} \\ & + 4\pi \int_{\rho_0}^{\infty} \frac{1}{\rho} d\rho \int_0^{\frac{\hbar}{\pi a}(\rho - \rho_0)} \frac{(v + \mathfrak{b}\rho_0/\pi a) v^3 dv}{(e^\epsilon + 1)(e^{-\epsilon - x} + 1)(e^x - 1)}, \end{aligned} \quad (61)$$

where $\rho_0 = \hbar\mathfrak{b}/4\pi a\beta_1$. To carry the integrations further is not easy, and we therefore make approximations which are valid when we use those numerical values of the various constants which actually occur. If we put $\mathfrak{b} = 10^5$ cm.

per second, $a = 10^{-8}$ cm. and $\beta_1 = 10^{-12}$ erg, ρ_0 comes out to be of the order 10^{-3} . Further, the integrand is negligible for values of ρ which are much greater than ρ_1 , where $\beta_1 \rho_1^2 = kT$. The value of ρ_1 is of the order $10^{-2} \sqrt{T}$, and this may be taken as the maximum value of ρ which occurs in the ν integrals. The corresponding value of $x (= h\nu/kT)$ is of the order $T^{-\frac{1}{2}}$. From these numerical results we see that except for extremely small values of T of the order of a fraction of a degree it is permissible to expand the integrand in powers of x , and we therefore replace the factor $(e^x - 1)$ by x . Also on account of its smallness we put ρ_0 equal to zero, the resulting error being negligible. We then have for (61)

$$\frac{2\pi kT}{h} \left(\frac{b}{\pi a}\right)^4 \int_0^\infty \frac{\rho^3 d\rho}{(e^\epsilon + 1)(e^{-\epsilon} + 1)}, \quad (62)$$

and so we have for α' the equation

$$\frac{\alpha'}{\lambda'} \cdot \frac{kT}{\beta_1} \int_0^\infty \frac{\rho^3 d\rho}{(e^\epsilon + 1)(e^{-\epsilon} + 1)} = \frac{F}{kT} \int_0^\infty \frac{\rho^2 d\rho}{(e^{-\epsilon} + 1)}, \quad (63)$$

where

$$\lambda' = \frac{2\pi Macb^2 \mu^2}{C^2 G^3}. \quad (64)$$

On integration by parts we find

$$\alpha' = \frac{\sqrt{\pi}}{2} \left(\frac{\beta_1}{kT}\right)^{3/2} \frac{F\lambda'}{kT}, \quad (65)$$

which gives for the distribution function

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) - \frac{\sqrt{\pi}}{2} \cdot F\lambda' \left(\frac{\beta_1}{kT}\right)^{3/2} \frac{\partial n_0}{\partial \xi}. \quad (66)$$

3.22. To evaluate the conductivity we use the general result that the stream of an electron is given by

$$s_s = \frac{2\pi ea}{h} \frac{\partial E(\xi\eta\zeta)}{\partial \xi}. \quad (67)$$

This has been proved by Bloch for tightly bound electrons by direct evaluation of the stream, and by Peierls* for the case when $u_{k,lm}(xyz)$, defined in equation (11), does not vary rapidly with k , that is, for nearly free electrons. This relation also holds in the neighbourhood of the discontinuities in the energy, as may be seen by writing equation (6) in the form

$$\begin{aligned} \psi &= c\psi_{\xi\eta\zeta}^0 + c'\psi_{\xi'\eta'\zeta'}^0 \\ &= c e^{i\xi x/a} + c' e^{i(\xi - 2\pi)x/a} \\ &= e^{i\xi x/a} (c + c' e^{-2\pi i x/a}). \end{aligned}$$

* 'Z. Physik,' vol. 53, p. 255 (1929).

The expression in the bracket is $u_k(x)$ and is independent of k , so Peierls' proof still holds.

The total current is

$$J_x = \int n(\xi\eta\zeta) s_x d\xi d\eta d\zeta,$$

and so depends on evaluating the expression

$$\int \frac{\partial E}{\partial \xi} \frac{\partial n_0}{\partial \xi} d\xi d\eta d\zeta. \quad (68)$$

This we do by splitting up the integral in the usual way and considering the contributions from the different regions.

Introducing the variables u, v, w used in section 2, $\partial E/\partial \xi$ for the first zone becomes $2\beta_1 u$ and the corresponding contribution to the integral (68) is

$$- \int 2\beta_1 u \frac{\partial n_0}{\partial u} du dv dw,$$

or

$$- \frac{4\beta_1^2}{kT} \int \frac{u^2 du dv dw}{(e^{\{W_1 - W_0 - \beta_1(u^2 + v^2 + w^2)\}/kT} + 1) (e^{-\{W_1 - W_0 - \beta_1(u^2 + v^2 + w^2)\}/kT} + 1)}.$$

If we write $kT\varepsilon_1 = \beta_1(u^2 + v^2 + w^2)$ this becomes

$$\begin{aligned} & - \frac{8\pi (kT)^{3/2}}{3 \beta_1^{1/2}} \int_0^\infty \frac{\varepsilon_1^{3/2} d\varepsilon_1}{(e^{\varepsilon_1 + (W_0 - W_1)/kT} + 1) (e^{-\varepsilon_1 - (W_0 - W_1)/kT} + 1)} \\ & = - \frac{4\pi (kT)^{3/2}}{\beta_1^{1/2}} \int_0^\infty \frac{\sqrt{\varepsilon_1} d\varepsilon_1}{e^{\varepsilon_1 + (W_0 - W_1)/kT} + 1}. \end{aligned} \quad (69)$$

For small values of T we may omit the 1 in the denominator since $W_0 > W_1$, obtaining

$$- \pi^{3/2} kT (kT/\beta_1)^{1/2} e^{-\frac{W_0 - W_1}{kT}}. \quad (70)$$

The second zone gives a similar contribution, and the two may be combined together by using (30) and we find

$$- \pi^{3/2} kT \left(\frac{kT}{\beta_1}\right)^{1/2} \left(1 + \frac{\beta_2}{\beta_1}\right) e^{-\frac{W_0 - W_1}{kT}}.$$

Introducing the temperature Θ_u defined in section 2.2, the conductivity σ is given by

$$\sigma = \sigma_0 e^{-\frac{\Theta_u}{T}}, \quad (71)$$

where σ_0 is a constant. This formula is only valid for $T \ll \Theta_u$. If $T \gg \Theta_u$ the discontinuity is unimportant, the substance behaves as a metal and for

sufficiently high temperatures must have σ inversely proportional to the temperature.

Comparison with Experiment.

4. The experimental results on semi-conductors are not easy to interpret. In the first place there are two main types of semi-conductors. The first type consists of ionic conductors in which heavy ions are transported through the crystal by a process akin to electrolysis. The second type consists of purely electronic conductors, while there is a third class in which the current is carried partly by ions and partly by electrons. The theory developed here only applies to electronic conductors. Further, we have considered the crystal to be atomic, and the theory must not be expected to apply to molecular crystals without considerable modification. The greatest difficulty in the interpretation arises, however, because there is no general agreement as to which substances are to be classified as metals and which as semi-metals. Gruneisen, in his article on conductivity in the "Handbuch der Physik," cites a number of elements as semi-conductors. Unfortunately, the resistance curves are often completely changed by the presence of small quantities of impurities. For example, titanium is cited by Gruneisen as a semi-conductor, and in certain states it shows a pronounced negative temperature coefficient, whereas recent measurements have shown that titanium is a superconductor. Germanium exhibits a very curious resistance curve with two minima, and impure silicon shows several discontinuities in resistance, with the result that silicon shows no minimum at ordinary temperatures. On the other hand, Gudden* is inclined to the view that no pure substance is ever a semi-conductor. This view is supported by the superconductivity of titanium and by the fact that a positive temperature coefficient has been found for silicon.† Recent measurements by Meissner‡ did not confirm the metallic character of silicon, though this is almost certainly due to the presence of oxygen in his single crystal. From the experimental side, therefore, the existence or non-existence of semi-conductors remains an open question, and neither the measurements of specific heat nor those of susceptibility are sufficiently accurate to supply additional evidence. Theoretically there is no reason why semi-conductors should not exist, the main difference between semi-conductors and insulators being that for the former Θ_u is so small that the substance has a measurable conductivity at ordinary temperatures, while

* "Ergebnisse der Exakten Naturwissenschaften," vol. 3, p. 116 (1924).

† H. J. Seemann, 'Phys. Z.,' vol. 28, p. 765 (1927) and vol. 29, p. 94 (1928).

‡ W. Meissner and B. Voigt, 'Ann. Physik,' vol. 7, pp. 761 and 892 (1930).

for the latter Θ_u is extremely large. Experimentally, however, the only substances which show undoubted semi-conducting properties are very impure, and it may be that they have no intrinsic conductivity. If this is so, the theory would have to be extended to take account of the effect of impurities in increasing the conductivity of poor conductors.* Under the circumstances the value of $\Delta W (= W_2 - W_1)$ cannot be fixed, not only because of the doubtful nature of the experimental evidence, but also because the formula for the resistance is not known over the whole range of temperature. However, a minimum resistance often occurs at a few hundred degrees absolute, and this must be due to ΔW and kT becoming of the same order. ΔW is therefore usually a few hundredths of a volt, while it may be as much as a few tenths of a volt. This seems quite reasonable, and indicates that, though there are many points still to be cleared up, the theory is on the right lines.

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* [*Note added in proof.*—It has been found possible to do this to a certain extent, and the results will be published in a further paper.]
