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The Theory of Electronic Semi-Conductors.—II.

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Introduction.

In a previous paper* it was shown that the quantum theory of conduction leads naturally to a division of crystals into conductors and insulators, and various properties of insulators were worked out. Since that paper was written, experimental material has come to my notice which necessitates an extension of the theory to include the effect of impurities, as it appears that impurities dominate the electrical properties of the semi-conductors. As the substances which show a negative temperature coefficient of the electrical resistance fall into two main classes, it will be as well to define what we mean by an electronic semi-conductor. In the first place, there are substances such as silicon which show a negative temperature coefficient in the impure state, but which are good metallic conductors in the pure state and are therefore to be classed as metals. The negative temperature coefficient is probably due to surface effects caused by the presence of oxide, and a tentative theory in this direction has been recently proposed by Frenkel.† Secondly, there are substances such as cuprous oxide which always show a negative temperature coefficient and which become much worse conductors when the amount of impurity present is reduced. Only these latter substances are to be regarded as semi-conductors, and it is with them that we shall deal in this paper. Lastly, there are some substances such as germanium which probably belong to both classes. That is, in some modifications they are metallic and in others insulating.

* 'Proc. Roy. Soc.,' A, vol. 133, p. 458 (1931), referred to as *loc. cit.*

† 'Phys. Rev.,' vol. 36, p. 1604 (1930).

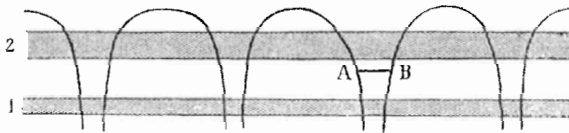
The treatment of semi-conductors given in the previous paper depends on the fact that the energy spectrum of an electron moving in a perfect lattice splits up into bands of allowed and disallowed energies, and if there are just sufficient electrons present to fill up one of the allowed bands there can be no conductivity at absolute zero temperature. Under these conditions it was shown that if ΔW is the minimum energy required to remove an electron into the next higher band of allowed energies, then for low temperatures the conductivity σ is given by $\sigma = \sigma_0 \exp(-\Delta W/2kT)$. The experimental results* on cuprous oxide can be expressed by such a formula with $\frac{1}{2}\Delta W = 0.3$ volt approximately. On the other hand, the inner photo-electric absorption in cuprous oxide† shows that for the pure substance ΔW is about 2 volts, and in general it seems that for all substances ΔW is of the order of a few volts, except for metals where it is, of course, zero. If this is true, then no pure non-metallic solid can ever have a significant natural electronic conductivity at ordinary temperatures, and the observed conductivity of semi-conductors must be due to the presence of impurities. This view is put forward by Gudden and analysed in some detail in the paper quoted above. The evidence seems convincing, and we shall here work out some of the consequences of this hypothesis. Of course, if there should be substances for which ΔW is small, the previous results will apply, but for the substances so far examined ΔW is about 2 volts.

It is easy to obtain a qualitative view of the effect of impurities. Consider first a perfect lattice and a single electron. If the electron is in the neighbourhood of a particular lattice point it can jump to a state of equal energy in the neighbourhood of the next lattice point even although it has to pass through a region where its kinetic energy is negative. In this way an electron can move through the lattice and act as a free electron. This description is correct so long as the lattice is perfect, since the electron can always jump from one state in the neighbourhood of a lattice point to a state of equal energy in the neighbourhood of the next lattice point, as all the lattice points are equivalent. When, however, there are impurities, the case is altered if the electron is originally attached to a foreign atom. For the electron to be free it must be able to jump to a state of equal energy, and this it can only do by jumping to a similar atom, except in the event of the energy level of the foreign atom coinciding with that of the pure substance. Since the transition probability falls off exponentially with distance the probability of an electron jumping from one foreign atom to

* W. Vogt, 'Ann. Physik,' vol. 7, p. 183 (1930).

† B. Gudden, 'Ber. Phys. Soz. Erlangen,' vol. 62, p. 289 (1931).

another is quite negligible if the amount of impurity present is small, and so in general the electrons belonging to impurities are bound electrons and not free. Several cases now arise which may be illustrated by the figure below, which represents a linear lattice in which occurs one foreign atom.



The potential energy of an electron is drawn and the shaded bands represent some of the permitted energy bands of the perfect lattice, which are only altered to a negligible degree by the presence of the foreign atom. The foreign atom has a discrete energy level, denoted by the horizontal line AB, which is normally occupied by an electron.

(1) If there are not sufficient electrons per atom of the pure substance to fill up band 1, then the foreign atom will become ionised and its electron will pass over into band 1. In this case the substance is a metal and the only effect of the impurity is to contribute to the residual resistance by acting as a scattering centre for the free electrons.

(2) If there are just sufficient electrons to fill up band 1, then the foreign atom will retain its electron at absolute zero temperature and the whole substance will be non-conducting. At higher temperatures it is possible, owing to the thermal vibrations, for the electron in the state AB to jump to a neighbouring atom of the pure substance. It will then be in band 2 and will be able to act as a free electron. In this case the conductivity will have a factor of the form $\exp(-\lambda/kT)$, but λ is not here connected with the minimum energy difference between the bands 1 and 2, but between the state AB and the band 2. It is obviously possible for this latter energy difference to be much smaller than the first, so that the thermal motions can excite electrons from the foreign atoms while quite incapable of exciting those from atoms of the pure substance. It should be noted that electrons on a foreign atom do not take part directly in conduction. They must first be transferred by the effect of the lattice vibrations to an atom of the pure substance. In this case the main function of the impurities is to provide electrons for the upper unoccupied energy bands of the crystal, while acting as scatterers is only a secondary function.

(3) If there are sufficient electrons to fill up band 1 entirely and band 2,

either wholly or in part, then the foreign atom can only act as a scatterer contributing to the residual resistance.

Semi-conductors obviously fall under the second heading and the condition for their occurrence is the presence of impurities such that the minimum energy difference between AB and band 2 is small enough to give a measurable conductivity at ordinary temperatures. If this is the correct view then the occurrence of semi-conductors is purely accidental. This is not in disagreement with the facts as there seem to be no other properties distinguishing insulators from semi-conductors.

The Equilibrium Distribution.

1. The formulæ given in the previous paper have to be modified a little as some of the approximations used no longer hold. The effect of this is to modify the temperature dependence of the conductivity in a way which we shall now work out. We consider as model a simple cubic crystal containing G^3 atoms of which N_0 are foreign atoms. We shall assume that $(G^3 - N_0)/G^3$ is effectively unity, and we shall neglect the disturbing effect of the impurities on the lattice. This latter effect gives rise to a resistance analogous to the residual resistance in metals and could be easily included, as the necessary calculations have been carried out by Nordheim.* This resistance is the dominating factor at very low temperatures, but at ordinary temperatures it is outweighed by the resistance arising from the lattice vibrations, and in order not to complicate the equations too much we shall omit it. We assume that each of the N_0 atoms of impurity possesses a single electron in a discrete state of energy W_1 , and that the electrons belonging to atoms of the pure substance form closed shells of energy less than W_1 . The next band of allowed energies of the pure crystal is taken to be given by

$$E_{\xi\eta\zeta} = W_2 + 6\beta - 2\beta (\cos \xi + \cos \eta + \cos \zeta), \quad (1)$$

where the permissible values of ξ, η, ζ are $2\pi G$ ($0, \pm 1, \pm 2, \dots$), the notation being the same as in *loc. cit.* We shall only use this expression for small values of ξ, η, ζ , and it then becomes

$$E_{\xi\eta\zeta} = W_2 + \beta (\xi^2 + \eta^2 + \zeta^2). \quad (2)$$

We suppose that $W_2 > W_1$, and we shall neglect entirely the possibility of any electrons from the closed groups receiving sufficient thermal energy to be excited into these energy levels.

We must first find the distribution of electrons between the various levels

* 'Ann. Physik,' vol. 9, p. 607 (1931).

when there is thermal equilibrium. The statistics being Fermi statistics, the number of electrons on the foreign atoms is given by

$$\frac{N_0}{e^{\frac{W_1 - W_0}{kT}} + 1}, \tag{3}$$

and the number of electrons with quantum numbers 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

$$n_0 (\xi\eta\zeta) = \frac{1}{e^{\frac{E_{\xi\eta\zeta} - W_0}{kT}} + 1}, \tag{4}$$

as in *loc. cit.*, section 2. To determine W_0 we have

$$N_0 = \frac{N_0}{e^{\frac{W_1 - W_0}{kT}} + 1} + \frac{2G^3}{8\pi^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{d\xi d\eta d\zeta}{e^{\frac{E_{\xi\eta\zeta} - W_0}{kT}} + 1}, \tag{5}$$

corresponding to *loc. cit.*, equation (25). The work is exactly the same as before, and provided kT is small compared with $(W_2 - W_1)$ and with β , we have

$$W_0 = \frac{W_1 + W_2}{2} - \frac{kT}{2} \log \left\{ \frac{G^3}{4\pi^3 N_0} \left(\frac{\pi kT}{\beta} \right)^{3/2} \right\}, \tag{6}$$

approximately. To this degree of accuracy (4) becomes

$$n_0 (\xi\eta\zeta) = \sqrt{\left\{ \frac{4\pi^3 N_0}{G^3} \left(\frac{\beta}{\pi kT} \right)^{3/2} \right\}} e^{-\frac{W_2 - W_1}{2kT} - \frac{\rho^2}{kT}}, \tag{7}$$

where $\rho^2 = \xi^2 + \eta^2 + \zeta^2$. It is noteworthy that $(W_2 - W_1)/2$ occurs in the exponential factor, and not $(W_2 - W_1)$ as might have been expected. The formula (6) differs from *loc. cit.* (30) by having $(\pi kT/\beta)$ instead of (β_1/β_2) . This is because we have taken our lower levels as being sharply defined instead of being spread out into a band, and the approximations previously used do not apply to this case.

The total number of electrons in the upper band is obviously

$$N = \sqrt{\left\{ \frac{N_0 G^3}{4\pi^3} \left(\frac{\pi kT}{\beta} \right)^{3/2} \right\}} e^{-\frac{W_2 - W_1}{2kT}}, \tag{8}$$

and N/G^3 is "the number of free electrons per atom." The meaning of (8) is made clearer if we write it in the following form

$$\frac{N}{G^3} = \frac{(N_0/G^3)^{1/2}}{2\pi^{3/4}} \left(\frac{T}{T_0} \right)^{3/4} e^{-\frac{W_2 - W_1}{2kT}}, \tag{9}$$

where $\beta = kT_0$, and N_0/G^3 is the ratio of the number of atoms of impurity present to the number of atoms of the pure substance. This shows that the

number of "free electrons" per atom is proportional to $\sqrt{(N_0/G^3)}$, and not to N_0/G^3 , which is a very surprising result. Finally

$$n_0(\xi\eta\zeta) = 4\pi^3 \frac{N}{G^3} \left(\frac{\beta}{\pi kT}\right)^{3/2} e^{-\frac{\beta\rho^2}{kT}}, \quad (10)$$

which is equivalent to Maxwell's law.

The Calculation of the Conductivity.

2.1. We must now calculate the change in the distribution function of the free electrons under the combined influence of the lattice vibrations and a constant electric field, F , parallel to the axis of x . We set

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) - \xi\chi(E) \frac{dn_0}{dE}. \quad (11)$$

In *loc. cit.*, section 3, $\chi(\xi\eta\zeta)$ was used instead of $\xi\chi(E)$, but the latter choice is more convenient here. We then have the following integral equation for χ corresponding to equation (45) *loc. cit.*

$$\begin{aligned} \frac{2\pi aeF}{h} \frac{dn_0}{dE} = \frac{1}{kT} \sum_{\xi'} A_{\xi\xi'}^+ \frac{1}{(e^\epsilon + 1)(e^{-\epsilon'} + 1)(e^\epsilon - 1)} \left\{ \chi_{\xi'} \frac{\xi'}{\xi} - \chi_\xi \right\} \\ + \frac{1}{kT} \sum_{\xi'} A_{\xi\xi'}^- \frac{1}{(e^{-\epsilon} + 1)(e^{\epsilon'} + 1)(e^\epsilon - 1)} \left\{ \chi_{\xi'} \frac{\xi'}{\xi} - \chi_\xi \right\}, \quad (12) \end{aligned}$$

the notation being the same as in *loc. cit.* except for the difference in meaning of χ . The evaluation of the right-hand side is exactly the same as before and leads to the following result, as may be seen from equation (61) *loc. cit.*

$$\begin{aligned} \frac{T^3}{\lambda\rho} \int_0^{\frac{v\hbar}{\pi akT}(\rho+\rho_0)} \frac{x^2 dx}{e^x - 1} \left[\chi(\epsilon + x) \left\{ 1 + \frac{xkT}{2\beta\rho^2} - \left(\frac{\pi ak}{h\nu}\right)^2 \frac{2x^2 T^2}{\rho^2} \right\} - \chi(\epsilon) \right] \\ + \frac{T^3}{\lambda\rho} \int_0^{\frac{v\hbar}{\pi akT}(\rho-\rho_0)} \frac{x^2 dx}{e^x - 1} \left[\chi(\epsilon - x) \left\{ 1 - \frac{xkT}{2\beta\rho^2} - \left(\frac{\pi ak}{h\nu}\right)^2 \frac{2x^2 T^2}{\rho^2} \right\} - \chi(\epsilon) \right] \\ = -F, \quad (13) \end{aligned}$$

provided $\rho > \rho_0$, and provided $kT \ll (W_2 - W_1)$ and also $\ll \beta$. The notation is the same as in *loc. cit.* except that

$$\lambda = \frac{ea}{h} \frac{M}{G^3} \frac{16a\beta^2\nu\mu^2}{2\pi C^2} \left(\frac{h\nu}{ak}\right)^3. \quad (14)$$

We have also used the approximation (7) for n_0 , which is equivalent to ignoring the effect of the Pauli principle in limiting the transitions to those in which the final states are unoccupied. This is justified since the number of electrons in the upper band is so small that the free electrons are in a non-degenerate state,

and obey Maxwellian statistics. When $\rho < \rho_0$ the second integral in (13) disappears, and the bottom limit of the first integral is replaced by

$$(\rho_0 - \rho) \mathbf{v}h/\pi akT.$$

The limits of integration take a more familiar form if we introduce the Debye characteristic temperature Θ , defined by

$$\Theta = \frac{\mathbf{v}h}{ak} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}}.$$

Also

$$\rho_0 = \frac{\mathbf{v}h}{4\pi a\beta} = \frac{\Theta}{T_0} \left(\frac{1}{48\pi^2} \right)^{\frac{1}{3}},$$

where $kT_0 = \beta$. Writing therefore $\kappa = \mathbf{v}h/(\pi ak\Theta)$, which is a pure number of order unity—equal to $(4/3\pi^2)^{1/3}$ if our model is exact—equation (13) becomes

$$\begin{aligned} \frac{T^3}{\lambda\rho} \int_0^{\frac{\kappa\Theta}{T} \left(\rho + \frac{\kappa\Theta}{4T_0} \right)} \frac{x^2 dx}{e^x - 1} \left[\chi(\varepsilon + x) \left\{ 1 + \frac{x}{2\rho^2} \left(\frac{T}{T_0} \right) - \frac{2}{\kappa^2} \left(\frac{T}{\Theta} \right)^2 \frac{x^2}{\rho^2} \right\} - \chi(\varepsilon) \right] \\ + \frac{T^3}{\lambda\rho} \int_0^{\frac{\kappa\Theta}{T} \left(\rho - \frac{\kappa\Theta}{4T_0} \right)} \frac{x^2 dx}{e^x - 1} \left[\chi(\varepsilon + x) \left\{ 1 - \frac{x}{2\rho^2} \left(\frac{T}{T_0} \right) - \frac{2}{\kappa^2} \left(\frac{T}{\Theta} \right)^2 \frac{x^2}{\rho^2} \right\} - \chi(\varepsilon) \right] = -F. \end{aligned} \tag{13A}$$

Since the maximum value that x can have is Θ/T , the upper limits must be replaced by this value if $\rho > 1/\kappa$. Such values of ρ , however, play no significant part, and in fact for such large values of ρ the approximations are no longer valid. Now Θ is of order 10^2 degrees, while T_0 is probably of order 10^4 , so the most important range of temperatures from a practical point of view, and incidentally the range for which (13A) is most easily soluble, is given by $\Theta < T < T_0$. We shall endeavour to obtain a solution assuming that $\Theta \ll T \ll T_0$.

We first suppose that $\rho \gg \Theta/T_0$. Then ε being defined as $\beta\rho^2/kT$ is $T_0\rho^2/T$, while the maximum value of x is $\kappa\Theta\rho/T$ approximately. Therefore

$$\frac{x}{\varepsilon} = \frac{\kappa}{\rho} \frac{\Theta}{T_0} \ll 1.$$

It is therefore permissible to expand $\chi(\varepsilon + x)$ as $\chi(\varepsilon) + x\chi'(\varepsilon) + \dots$. We use this expansion in (13A) and retain only the lowest powers of Θ/T , treating T/T_0 as a small quantity of the same order as Θ/T . The terms of the integrals which are left after these approximations reduce to

$$-\frac{4T^3}{\lambda\rho} \int_0^{\frac{\kappa\Theta}{T} \rho} \chi(\varepsilon) \frac{1}{\kappa^2\rho^2} \left(\frac{T}{\Theta} \right)^2 \frac{x^4 dx}{e^x - 1},$$

and so we have

$$\chi = \frac{\lambda F}{\kappa^2 \Theta^2 T} \cdot \frac{1}{\rho}. \quad (14)$$

For values of ρ not large compared with Θ/T_0 , I have not been able to solve the equation. It is, however, to be expected that the use of (14) will not introduce a serious error. For values of $\rho < \rho_0$, (13A) becomes

$$\frac{T^3}{\lambda \rho} \int_{\frac{\kappa \Theta}{T} (\frac{\kappa \Theta}{4T_0} - \rho)}^{\frac{\kappa \Theta}{T} (\frac{\kappa \Theta}{4T_0} + \rho)} \frac{x^2 dx}{e^x - 1} \left[\chi(\varepsilon + x) \left\{ 1 + \frac{x}{2\rho^2} \frac{T}{T_0} - \frac{2}{\kappa^2} \left(\frac{T}{\Theta} \right)^2 \frac{x^2}{\rho^2} \right\} - \chi(\varepsilon) \right] = -F,$$

which can be solved exactly by

$$\chi = \frac{3\lambda F T_0}{2\kappa^3 \Theta^3 T}. \quad (14A)$$

It is doubtful how much physical significance is to be attached to this last result, as for such very slow electrons the lattice vibrations can hardly be treated as giving rise to a small perturbation. However, even when we give them their maximum importance, as here, their contribution to the conductivity is quite negligible.

2.2. We must now calculate the current set up by the field, the stream in the x -direction per electron being

$$s_x = \frac{2\pi e a}{h} \frac{\partial E}{\partial \xi} = \frac{4\pi e a \beta}{h} \xi.$$

The total current is therefore

$$J_x = -\frac{4\pi e a \beta}{h} \int \frac{G^3 \xi^2}{4\pi^3} \chi(E) \frac{dn_0}{dE} d\xi d\eta d\zeta$$

parallel to the axis of x . For $\rho < \rho_0$, $\chi(E)$ is given by (14A), and for $\rho > \rho_0$ by (14), but since the contribution to the integral from the range $\rho < \rho_0$ is of order $(\Theta^2/TT_0)^2$ compared with the remaining contribution, we may use (14) for the whole range with negligible error. Hence the conductivity σ is given by

$$\begin{aligned} \sigma &= \frac{J_x}{F(Ga)^3} = \frac{16\pi^{1/2} \lambda e \beta^{5/2} (N/G^3)}{3h\kappa^2 a^2 \Theta^2 h^{3/2} T^{5/2}} \int_0^\infty \rho^3 e^{-\frac{\beta \rho^2}{kT}} d\rho \\ &= A(N/G^3) T^{-3/2} \end{aligned} \quad (15)$$

$$= B(N_0/G^3)^{1/2} T^{-3/4} e^{-\frac{W_2 - W_1}{2kT}}, \quad (16)$$

where A and B are complicated constants. Equation (15) gives the variation of σ with the number of free electrons, and equation (16) the variation of σ with the temperature and with the amount of impurity.

We may compare (15) with the classical formula

$$\sigma = \frac{4}{3} \frac{e^2 l}{(2\pi m k T)^{\frac{1}{2}}} \frac{N}{(Ga)^3}, \tag{17}$$

where l is the mean free path, and $N/(Ga)^3$ is the number of free electrons per unit volume. This is a purely classical result, and it gives no information about l . The quantum theory shows that l varies as T^{-1} for temperatures above the Debye temperature, and so (17) agrees with (15). In deriving (15) we have made no use of the Fermi distribution, which is only used to determine the variation in the number of free electrons with temperature, and which gives rise to the very surprising result expressed by (16). Formula (15) therefore holds for any semi-conductor, independently of whether the conduction is intrinsic or due to impurities, while (16) is different in the two cases. In fact, if the conduction is intrinsic

$$N \propto T^{3/2} e^{-\frac{\Delta W}{2kT}},$$

and so

$$\sigma = \sigma_0 e^{-\frac{\Delta W}{2kT}}, \tag{16A}$$

where ΔW is the minimum energy difference between the bands 1 and 2.

The Hall Effect.

3. As the Hall effect is very useful in determining the properties of semi-conductors, it is advisable to consider what the theoretical expression for the Hall coefficient should be. Classically the Hall coefficient only depends on the number of free electrons per unit volume and not on the mean free path. We must, therefore, have exactly the classical formula, as the only difference between the classical and quantum treatments of semi-conductors is that the quantum theory makes explicit evaluation of the free path. So the Hall coefficient R is given by

$$R = \frac{3\pi (Ga)^3}{8eN} \tag{18}$$

$$= \frac{3\pi^{7/4} a^{3/2}}{4e} \sqrt{\frac{G^3 a^3}{N_0} \left(\frac{\beta}{kT}\right)^{3/4} e^{\frac{W_2 - W_1}{2kT}}}. \tag{19}$$

We see from (19) that it is not possible to determine directly the number of atoms of impurity present from measurements of the Hall coefficient, as β is not known. However, it is found experimentally that $R\sigma$ is approximately the same for all substances, including semi-conductors, at the same temperature, and as this quantity is mainly determined by β we may assume that for semi-

conductors β is of the same order of magnitude as for metals, that is, about 1 volt. It must be admitted that the approximate constancy of $R\sigma$ is not a conclusive proof of the constancy of β , on account of the large number of ill-determined constants occurring in the theoretical formulæ, which are as follows:—

For metals

$$R\sigma = 48\pi^5\kappa^5 \frac{ea^6\nu\beta^2\mu^2}{h^2C^2} \cdot \frac{M}{G^3a^3} \cdot \frac{\Theta}{T}, \quad (20)$$

while for semi-conductors

$$R\sigma = 8\pi^{7/2}\kappa \frac{ea^6\nu\beta^2\mu^2}{h^2C^2} \cdot \frac{M}{G^3a^3} \cdot \left(\frac{\beta}{kT}\right)^{1/2} \frac{\Theta}{T}. \quad (21)$$

The ratio of the numerical factors in the two formulæ is $6\pi^{3/2}\kappa^4$, which is about 2, and if we assume that the other characteristic constants are of the same order of magnitude for metals and semi-conductors, then for $R\sigma$ to be the same in the two cases we must have β^2 for a metal equal to $\beta^2 (\beta/kT)^{1/2}$ for a semi-conductor at ordinary temperatures. This is satisfied if we take β to be about 1 volt in the two cases. Theoretically we should expect β for a semi-conductor to be less than β for a metal, since β measures the "looseness of the binding of the electrons," and as we have no better evidence than the above to go on we shall take 1 volt as being an upper limit for β .

Numerical Results.

4. The only results which seem good enough to be used to test the theory are those of Vogt on cuprous oxide. He finds that the conductivity and the Hall coefficient can be well represented by

$$\sigma = \sigma_0 e^{-q/T} \quad \text{and} \quad R = R_0 e^{q/T}.$$

They can equally well be represented by the formulæ derived here, and the experiments are unable to decide which set is the more correct.

The value of q is about 3900, which corresponds to an energy of about 0.3 volt, and so $(W_2 - W_1)$ is twice this, that is, 0.6 volt. It is a most remarkable feature of the theory that conductivity measurements determine directly $\frac{1}{2}(W_2 - W_1)$, while the inner photoelectric effect determines $(W_2 - W_1)$. Unfortunately, an experimental verification of this point seems to be extremely difficult, since for pure substances for which the photoelectric effect is easily measurable the conductivity is infinitesimal, while for impure substances with a measurable conductivity the amount of impurity present is so small that the corresponding absorption cannot be detected with certainty.

Vogt finds that the Hall coefficient of one specimen can be expressed as

$$eR = 10^{-18} e^{3900/T},$$

and concludes that there are 10^{18} atoms of impurity per cubic centimetre. This is not true, since Boltzmann's law does not hold. Using equation (19) we may express R as

$$eR = 10^{-16} T^{-3/4} e^{3900/T},$$

and so

$$\sqrt{\frac{N_0}{G^3 a^3}} = \frac{3}{4} \pi^{7/4} a^{3/2} 10^{16} \left(\frac{\beta}{k}\right)^{3/4}.$$

Putting $a^3 = 10^{-22}$ c.c. and $\beta = 1$ volt, we obtain for $N_0/G^3 a^3$ about 10^{17} , and so there are about 10^{17} atoms of impurity per cubic centimetre, while there are about 10^{22} molecules of Cu_2O per cubic centimetre. This is a conclusive proof that the conductivity is due to impurities and is not intrinsic.

To sum up, we may say that the experiments do not contradict the theory, but this can hardly be taken as a proof of the correctness of the latter, since the assumptions made by Vogt are also adequate to explain the known facts. However, the advantage of the present theory is that it gives a definite meaning to the idea of a "free electron," and the number of these is not arbitrary but is definitely fixed by the arrangement of the energy levels. The most important point in the theory—the occurrence of $\frac{1}{2}(W_2 - W_1)$ in the expression for the conductivity—does not seem capable of being tested at the moment.
