ELECTRIC CONDUCTIVITY AND OPTICAL ABSORPTION OF METALS

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In a paper on "Electron Free Path and Supraconductivity in Metals," printed in the Proceedings of the National Academy of Sciences for May, 1928, after calling attention to the fact that Sommerfeld's recently published "Electron Theory" requires "free paths" equal to some hundreds of times the "atomic distance," I suggested that we should regard the free path as terminated not in a collision of the electron with an atom but in its capture by a positive ion.

After this paper had been presented at a meeting of the National Academy of Sciences in April, 1928, Professor W. F. Durand of Stanford University called my attention to the fact that he had used the same conception of electron free path in a paper[1] printed many years before. I gladly make this acknowledgment, though I was entirely ignorant of the existence of Professor Durand's paper when I wrote my own. In fact, I rejoice to find occasional evidence that the views of electric conduction which I have been gradually evolving during the last fifteen years are not entirely singular and peculiar to myself.

Professor Durand's paper is an admirable discussion of free-electron conductivity and is well worth reading even now. It certainly contains the same general conception of free path that I have so recently proposed, though, as it does not emphasize this conception or dwell upon its advantages, it may well be that few readers of the paper have noticed that it departs from the ordinary theory of free-electron conduction in this particular.

In the paper referred to in my opening paragraph I have pointed out that a relatively small number of free electrons will be enough to account for the whole conductivity of metals, if free paths of several hundred "atomic distances" are supposed to prevail. A still smaller number will, of course, serve if, as I hold, the free electrons carry only a minor part of the current. Thus the specific-heat difficulty of which so much has been made, and which has done so much to discredit the natural view, originally held by every one, that the free electrons share the energy of the thermal agitation, may be abolished.

But it may be urged that the known optical properties of metals require us to suppose the existence within them of free electrons as numerous as, or even more numerous than, the atoms of the metals. The main purpose of the present paper is to examine the weight of this argument.

In the course of the discussion I shall make use of three alternative hypotheses concerning the mechanism of conduction:

Hypothesis A.—That the current is maintained entirely by free electrons sharing the energy of thermal agitation.

This was the hypothesis used by Lorentz in his "Theory of Electrons," published in 1909. In this book he says, on pp. 80 and 81, "It is well known that, in general, the optical properties of ponderable bodies cannot be deduced quantitatively with any degree of accuracy from the electrical properties. For example, though Maxwell's theoretical inference, published long ago in his treatise, that good conductors for electricity must be but little transparent for light, is corroborated by the fact that metals are very opaque, yet, if we compare the optical constants of a metal, one of which is its coefficient of absorption, with the formulae of the electromagnetic theory of light, taking for the conductivity the ordinary value that is found by measurements on electric currents, there is a very wide disagreement. This shows...that, in the case of the very rapid vibrations of light, circumstances come into play with which we are not concerned in our experiments on steady or slowly alternating electric currents. If this idea be right, we may hope to find a better agreement, if we examine the 'optical' properties as we may continue to call them, not for rays of light, but for infra-red rays of the largest wave-lengths that are known to exist. Now, in the case of the metals, this expectation has been verified in a splendid way by the measurements of the absorption that were made some years ago by Hagen and Rubens. These physicists have shown that rays whose wave-length is between 8 and 25 microns are absorbed to a degree that may be calculated with considerable accuracy from the known conductivity. We can conclude from this that, in order to obtain a theory of absorption in the case of these long waves, we have only to understand the nature of a common current of conduction."

Lorentz goes on, in Secs. 60 to 68, to show that, if we adopt the Drude-Lorentz theory of free-electron conductivity, make the free electrons as numerous as we please, and assume the time between collisions of a free electron with the atoms to be very small compared with the time of a light vibration, it is possible to account, by means of the free electrons, for Kirchhoff's law, Wien's law, and Planck's law in the form which it takes for long waves.

Lorentz does not evaluate definitely the number, n, of free electrons per unit volume needed for his purpose, but in Note 42 he calls attention to a discussion of this matter given by J. J. Thomson, at the end of Chapter 4 in his "Corpuscular Theory of Matter." On page 84 of this book we find the following passage, coming after a reference to the experiments of Hagen and Rubens:

"We can easily show that if k is the conductivity under steady forces, then when the forces vary as sin nt the conductivity will be proportional to $k\,\frac{\sin^2 nT}{n^2\,T^2}$, where $2T$ is the interval between two collisions [of a free electron with the atoms]. Thus, unless this interval be small compared with the period of the electric force the conductivity will be very materially reduced. Thus if T were as great as one quarter of the period of the force, so that $nT = \pi \div 2$, the conductivity would be reduced to $1 \div (\pi \div 2)^2$, or 0.4 of its steady value. As the diminution of the conductivity for light waves whose length is 4μ is less than this, we conclude that [$2T$] the interval between two collisions is less than one quarter [half] of the period of this light, or less than [2×] 3.3×10^{-15} sec. Hence u the velocity [*net*, of the free-electron stream] under unit electric force, since it is equal to $^1/_2\,\frac{e}{m}\,[2]\,T$, will be less than $^1/_2$ [omit?] $\times\ 3.3 \times 10^{-15}\,\frac{e}{m}$, and since k the conductivity is $n\ e\ u$, n [here the number of free electrons per cu. cm.] will be greater than [equal to] $k \div eu$, i.e., [greater] than [$^1/_2$]$\cdot\,\frac{k10^{15}m}{1.6e^2}$."

"For silver k is about 5×10^{-4}, and since $e \div m = 1.7$ [7] $\times 10^7$ and $e =$ [1.59 ×]10^{-20}, we see that n for this metal must be greater than 1.8×10^{24} [5.5×10^{23}]."

Making the corrections indicated in [ ], I find $n = 5.5 \times 10^{23}$ approximately. The number of atoms in a cu. cm. of silver is about 6×10^{22}, so that, according to this calculation, the number of free electrons would be about 9 times as great as the number of atoms.[2,3] Such a ratio, with the free electrons sharing the energy of thermal agitation, is of course impossible. Accordingly, in spite of the admirable effort of Lorentz to account for the Hagen and Rubens observations by means of the Drude theory of free-electron conduction, it must, I think, be concluded that hypothesis A is unable to bear the burden proposed for it. We must either reject this hypothesis altogether or admit that the known facts of the optical behavior of metals tell us nothing definite concerning the mechanism of electric conduction.

Hypothesis B.—That the current is maintained entirely by free electrons which do not share the energy of thermal agitation.

This is the hypothesis toward which speculation in general on this subject appears to have inclined during recent years, against my protest. It is, for example, the hypothesis of Sommerfeld.

Sommerfeld has not, so far as I have seen, made any reference to the relation between electric conductivity and optical properties in metals. It seems to me, however, that the argument which I have quoted from Thomson depends not at all upon the underlying translatory energy of the free electrons. It does not assume that these electrons have or that they lack the energy of thermal agitation. It would appear, then, that the numerical conclusion arrived at above, regarding the ratio of free-electron number to atom number, holds under hypothesis B as well as under hypothesis A. Is B, then, tenable?

Apparently not. The specific-heat difficulty may not, to be sure, present itself here in troublesome form, though Sommerfeld makes the energy of his free electrons depend, to some slight extent, on the temperature. But on other grounds the assumption that the free electrons are several times as numerous as the atoms seems inadmissible. For example, the "atoms" in such a case would not be atoms proper but the great majority of them would be multiply charged positive ions.

Hypothesis C.—That the electric current is maintained in part by free electrons sharing the energy of heat agitation, but mainly by an interchange of electrons in encounters between atoms and positive ions, the latter being, naturally, just as numerous as the free electrons. This is the dual theory of conduction which I have been advocating and illustrating for some years.

According to estimates, no doubt very fallible, which I published[4] in 1921, and which were based on a study of the electric conductivity, thermal conductivity and thermo-electric properties of many metals, the ratio of free-electron conductivity, k_f, to total conductivity, k, in these metals at 0°C. ranges from about 0.02 in iron to about 0.19 in bismuth. For copper, gold and silver it appears to be about 7%.

Let us consider the case of silver. At 0°C. its conductivity, k, is about 67×10^{-5} in absolute units, and so, according to my estimate, its value of k_f is about 4.7×10^{-5}. Taking the Drude formula for free-electron conductivity as

$$k_f = \frac{e^2lnu}{4\,RT},$$

we thus find, for 0°C., $ln = 2.46 \times 10^{15}$. If now we take l, the mean "path" of the free electrons, as 200 times the "atomic distance," the latter being about 2.5×10^{-8} cm., we find n to be 5×10^{20}, which is somewhat less than 1% of the number of atoms per cu. cm. of silver. I have taken this particular length of electron path because it agrees very nearly with the value arrived at by Sommerfeld in the recent statement[5] of his conduction theory; but I might well have taken a still greater length. If we once admit that the free-electron path can be several times the atomic distance, there is no obvious reason why it may not be hundreds or thousands of times this distance, and the estimated value of n decreases in proportion as l increases. In taking such a value of l as to make the number of free-electrons only 1%[6] of the number of atoms, I have perhaps gone far enough to meet, or rather to avoid, the specific-heat difficulty.

The absorptive power of such long-path free electrons, for radiations of any ordinary wave-lengths, would doubtless be negligible. We must now consider what possibilities lie in the other mechanism of conduction, the direct passage of electrons from atoms to ions.

Let us suppose that a current of 1000 amperes is to be carried in the direction x along a silver bar of 1 sq. cm. cross-section. The mean "atomic distance" in silver is about 2.5×10^{-8} cm. and the mean projection of the atomic distance in the direction of x is about 1.5×10^{-8} cm. It is reasonable to suppose that the transfer of an electron from an atom to an adjacent ion is in some way connected with the heat oscillations of the atoms and ions. These oscillations are of course very irregular and have no definite single frequency, but the Debye theory of the specific heat of a solid, applied to the available data in the case of silver, gives for v_m, the "maximum frequency," a value about 4.5×10^{12} per second.

Let us now suppose that once in q vibrations of an ion the potential gradient which is maintaining the electric current determines the passage of an electron from an atom to an ion in the general direction of x, or inhibits such a passage in the opposite direction, one of these effects being as good as the other for maintaining a net current along x. If each electron passage covers the distance 1.5×10^{-8}, and if we suppose the number of ions, equally numerous with the free electrons, to be 1 for each 100 atoms, we get as the resultant current along x, per sq. cm. of cross-section,

$$I = 6 \times 10^{20} \times 1.5 \times 10^{-8} \times (4.5 \times 10^{12} \div q)\, 1.6 \times 10^{-20}.$$

If the current is to be 1000 amperes, I, in electromagnetic measure, will be 100, and so $q = 6500$, approximately. This does not seem to be an impossible or absurd value, though I recognize the fact that my picture of the transfer process leaves much to be desired.

It may be, indeed, that this particular matter should be looked at from a different point of view. It is possible that the ions should be regarded as not merely charged but polarized also, and therefore subject to a certain net orientation by action of the imposed electromotive force that maintains the current, an orientation which the thermal agitation of the atoms and ions would oppose. The effectiveness of the electromotive force for conduction may conceivably lie in this directive power, controlling to some slight extent the net direction in which the transits of the electrons, from atoms to ions, occur. Sir J. J. Thomson, as we shall presently see, imagined something not unlike this as a possible mode of conduction.

This second suggestion regarding the nature of associated-electron conductivity has the merit of indicating an explanation of the decrease of conductivity with rise of temperature. The first suggestion does not do this, but it is not necessarily to be rejected on that account. The passage of an electron out from an atom under such conditions that it will lodge immediately in an adjacent ion, instead of going "free," is an operation which may be interfered with by the turbulence of thermal agitation.

The difficulty encountered at present in the attempt to form a satisfactory conception of associated-electron conductivity appears to be one of kinematics rather than of dynamics. It seems probable that wave-mechanics will have something to say in this connection. Perhaps it will be found permissible to suppose that the electron which unites with an ion may come as if *through* a chain of several atoms in one leap.

Let us next consider how the atom to atom mode of electron progression might be expected to function in the field of optical phenomena. It is helpful here to remember that more than twenty years ago J. J. Thomson, in close connection with the passage which I have quoted from his "Corpuscular Theory—and largely because of the weakness which that passage discovered in the free-electron theory of conduction—proposed an alternative theory. On pp. 49 and 50 he says, after briefly outlining the free-electron method of conduction, "It is easy to see, however, that a current could be carried through the metal by corpuscles which went straight out of one atom and lodged at their first impact in another; such corpuscles would not be free in the sense in which the word was previously used and would have no opportunities of getting into temperature equilibrium with their surroundings."

It may appear for the moment that I am about to lay the whole responsibility for the dual theory of conduction on the broad shoulders of the dean of British physicists, but I shall stop short of that. Thomson did not, so far as I know, make any attempt to combine the two suggested modes of conduction. Moreover, and this I regard as a distinction of great importance, he did not make the same use of the positive metal ions that I have made. In fact, having abandoned, for the time being at least, the idea of free electrons within the metal, he naturally does not think of positive ions as existing there. On the other hand, he conceives of "a large number of doublets, formed by the union of a positively electrified atom with a negatively electrified one," and proceeds to discuss the possible conductive working of such a mechanism, oriented by an imposed electromotive force, both for electricity and for heat. The theory of heat conduction to which he is thus led is exceedingly different from the one which I have since hit upon, but I need not dwell further on such differences. The fact of importance for my present inquiry is this, that Thomson worked out, for his second mode of electric conduction, a theory of connection between conductivity and optical absorption, which I am disposed to make use of for my own purposes, believing that my "associated-electron conduction" and his "second method" of conduction are enough alike to justify this proceeding. He begins his discussion as follows, on p. 89: "We have seen (p. 61) that Lorentz has shown that the long wave radiation can be regarded as part of the electromagnetic pulses emitted when the moving corpuscles come into collision with the atoms of the substance through which they are moving, and he has given an expression for the amount of the energy calculated on this principle, which agrees well with that found by experiment. [It is to be remembered, however, that in the first quotation given above from Thomson the theory developed by Lorentz was found to require an improbably large number of free electrons.] But in the new theory, as in the old, we have the sudden starting and stopping of charged corpuscles and therefore the incessant production of electromagnetic pulses; these when resolved by the aid of Fourier's theorem [as Lorentz had resolved the pulses supposed to come from the accelerations of the free electrons] will be represented by a series of wave-lengths from zero to infinity. We must see if the energy in the long wave-length radiation at a given temperature would on the new theory be approximately equal to that on the old."

After several pages of mathematical discussion, in which, of course, certain arbitrary assumptions are made concerning the character and duration of the accelerations to which the conduction electrons are subject, in the two modes of conduction compared, Thomson gets, p. 97, for the first mode

$$W = \frac{2}{3} \frac{\alpha\theta\mu^2}{\pi^2 c^3} q^2 dq$$

and for the second mode

$$W = \frac{3}{4} \frac{\alpha\theta\mu^2}{\pi^2 c^3} \frac{b}{d} q^2 dq.$$

In each case W is the density of long-wave radiant energy, between the frequency limits q and $q + dq$, within the metal, $\alpha\theta$ is the kinetic energy per atom of the metal, μ is the refractive index, c is the velocity of light. In the second expression b is "the distance between the centers of the doublets" and d is "the distance between the charges in the doublet."

The author now remarks, "If, as we should expect in a good conductor, b is very nearly equal to d, the radiation on the new theory is to that on the old as 9 to 8. Thus the expressions are so nearly equal that in the present state of our knowledge [1907] we cannot say that in this respect the one theory agrees better with the facts than the other."

It is quite possible that Thomson would not today attach any great importance to the numerical similarity of the two expressions in question. So long as we are in doubt concerning the fundamental nature of radiation, we can hardly expect to have a completely satisfactory theory of the relation between metallic conduction and absorptive or emissive power of metals. The point which I wish to make here is merely this, that nothing which we know concerning the optical properties of metals forbids us to hold a theory which presents as the chief mechanism of metallic conduction the passage of electrons from particles to adjacent particles of the metal without entering the "free" state or sharing the energy of thermal agitation. Such a mechanism Thomson has imagined for his "second method" and such a method is my conception of "associated-electron conductivity." So far as the evidence thus far produced in the present paper goes, hypothesis *C* appears preferable to hypothesis *A* and to hypothesis *B* in this particular, that it does not require an inordinate number of free electrons in order to account for the experimental observations of Hagen and Rubens concerning the relation between metallic conductivity and absorptive power for long waves of radiation.

But everything which I have quoted from Lorentz or from Thomson was written some twenty years or more ago, before the advent of Bohr. How much should the Bohr theory of radiation change the aspect of the question before us? This theory has thus far had to do, almost entirely, with atoms in the gaseous state, and with changes of condition occurring *within* the atom. If metallic conduction is carried on solely by free electrons, whether sharing or not sharing the energy of thermal radiation, and if the "collisions" of these free electrons with atoms are such as to result in no unions of electrons with the atoms, it is not obvious that the Bohr ideas will have any very important bearing on the relations of metallic conductivity and absorptive power. If, however, every free-electron "path" begins with the issue of an electron out from an atom, leaving it an ion, and ends with the union of the electron with an ion, forming thus an atom, and if every "associated-electron" passage takes an electron out from an atom into union with an adjacent ion, it seems highly probable that what has been learned during the past fifteen years about the internal structure and behavior of atoms will have much to do in clearing up the mystery which now surrounds the relations in question.

From this point of view the beginning of a "free path" within a metal is a process similar to photo-electric emission, accompanied or produced by the absorption of some definite quantum of radiant energy; and the termination of the free path, by reunion of the electron with an ion, is a reverse process accompanied by the emission of a definite quantum of radiant energy. Naturally, the quantum of energy needed to free an electron *within* the metal may be much less than the quantum required to free it *from* the metal. Probably, too, the quantum of energy needed to release an electron from an atom in the neighborhood of a positive ion, into union with which the electron is about to pass, is much less than the amount needed to release an electron into a free path.

It seems to me, however, that such considerations leave hypothesis *A* and hypothesis *B* still open to the objection which I, on the basis of my first quotation from Thomson, have urged against them, that they require many more free electrons than there are atoms. On the other hand, hypothesis C, which puts the main burden of conduction on the associated-electron conductivity, appears still to be free from this objection.

The application of hypothesis C to the observations of Hagen and Rubens can be illustrated somewhat further as follows: An electron transit directly from an atom to an adjacent ion evidently can be effected in a much shorter time than that required for a "free path" covering several "atomic distances." Accordingly, associated-electron conductivity, k_a, will diminish less rapidly than free-electron conductivity, k_f, with increase of the frequency of electric-force alternations in radiation.

Thus, long-path free-electron conductivity may be regarded as negligible in the observations referred to. There is, however, no apparent reason why k_a should not continue nearly unimpaired under the radiation frequencies for which Hagen and Rubens found the Maxwell formula for absorption to hold, frequencies corresponding to wave-lengths between 8 μ and 25 microns, with vibration periods of 2.7×10^{-14} seconds and 8.3×10^{-14} seconds, respectively. But it may begin to fail with somewhat shorter wave-lengths. As I have already said, it seems probable that the k_a transits of electrons are conditioned in some way by the thermal vibrations of the atoms, the maximum frequency of which in silver is, according to Debye's theory of specific heat, about 4.5×10^{12}, with a vibration period of 2.2×10^{-13} second. If we assume the time occupied in an electron transit to be a hundredth part of this period, or 2.2×10^{-15} seconds, which is about 12 times the period of an 8-micron radiation-wave, we get a possible explanation of the fact that, according to Hagen and Rubens, the absorption of 8-micron radiation by metals agrees well with the formula of Maxwell (which uses the value of conductivity found with steady currents), while the rate of absorption of 1-micron radiation would not agree with this formula and would indicate a diminution of conductivity.

It should be remembered of course that radiant energy may be absorbed by means of operations occurring wholely within the atoms and having, therefore, nothing directly to do with the process of electric conduction. Lorentz plainly recognizes this fact in Sec. 120 of his "Theory of Electrons," written years before the Bohr theory of absorption and emission of energy, by means of changes of status within the atom, was formed. Accordingly, the suggestion which I have made[7] concerning supra-conductivity—that it may be due to very long free paths—does not imply that metals in the supra-conductive state should be incapable of absorbing radiant energy. But the optical qualities of metals in this state might be an interesting subject for experimental study. I should expect their absorptive power for long-wave radiation to be less than that of metals at ordinary temperatures.

[1] "The Interpretation of Electric Current Flow in Terms of the Electron Theory," *J. Elec., Power, Gas*, **February, 1914.**

[2] O. W. Richardson, on pages 430–432 of his *Electron Theory of Matter*, refers to the work of Schuster, Jeans, and H. A. Wilson in dealing theoretically with free-electron conductivity under periodic forces. These authors derive a diminution formula which is different from the one used by Thomson. Schuster, applying his formula to the optical data accumulated by Drude, finds that "for all the commoner metals the number of free electrons in a given volume is from one to three times as great as the number of atoms present."

[3] Schuster, whose paper appeared in 1904, does not refer to the work of Hagen and Rubens and of course does not deal with the 4 micron wave-lengths of which Thomson makes so much. The difference between Thomson's estimate and Schuster's estimates of n does not materially affect the force of the argument I am making.

[4] *Proc. Nat. Acad. Sci.*, **7**, pp. 98–107.

[5] *Zeits. Physik*, **47**, February, 1928.

[6] Owing to the rate of increase of both n and the heat of ionization with rise of temperature, according to my theory, the number of free electrons here indicated might involve a contribution of about 3% to the specific heat of silver.

[7] See the paper referred to in my opening paragraph.

A DESCRIPTION OF THE ONTOGENETIC DEVELOPMENT OF RETINAL ACTION CURRENTS IN THE HOUSE MOUSE

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Several investigations upon the eyes of lower vertebrates (Chaffee and Adrian and their collaborators, and others) have given us much information as to the nature of the retinal response elicited by the action of light. These studies were made almost entirely employing excised eyes. Technical difficulties make it almost impossible to apply these methods to mammals. All such attempts employing eyes of the highest class of vertebrates have failed since the excised mammalian eye, tested immediately after removal, shows evidence of degeneration.

In a recent communication[1] (Keeler, Sutcliffe and Chaffee, 1928) it was shown that it is possible to obtain from normal intact unanaesthetized adult house mice, action-current responses quite similar to those found in the excised eyes of lower forms, while "rodless" house mice exhibited no changes in potential.

Apparatus.—The apparatus employed has been described by us, and in more detail[2] by Chaffee, Bovie and Hampson, 1923. The changes in potential are detected by a delicate Einthoven string galvanometer