THE MOTION OF ELECTRICITY IN METALS[1])

When I had the honour to be invited to deliver this *May Lecture* I, of course, thought that it would be appropriate to choose for my subject some of the phenomena that occur in metallic substances. However, as I know much less than you of the constitution of metals, and of the properties which depend on it, I felt that I should have to confine myself to questions of a somewhat general character. Fortunately, in the remarks which I am going to make about the motion of electricity in metals, my ignorance — so, at least, I hope — will not become too apparent.

To begin with, I may say that, whenever physicists have tried to form a picture of a current of conduction, there has been a tendency to consider it as the motion of something material, comparable to the flow of water through a tube. It is true that some had doubts about this point, and we read, for example, in MAXWELL's Treatise: „It appears to me that, while we derive great advantage from the recognition of the many analogies between the electric current and a current of a material fluid, we must carefully avoid making any assumption not warranted by experimental evidence, and that there is, as yet, no experimental evidence to show whether the electric current is really a current of a material substance or a double current, or whether its velocity is great or small as measured in feet per second." This was very cautious indeed. Other physicists, however, less prudent than MAXWELL or more anxious to understand what goes on in the interior of a conductor, had not shrunk from developing a truly „material" theory. According to them a metal contains, in the interstices between its atoms, one or two electric fluids, and it was supposed that, under the action of an electric or electromotive force, the electricity can move forward, overcoming the resistance that is

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caused by the atoms, and that is similar to the force which the walls of a tube oppose to a current of fluid. In those old theories there was no question of any definite assumption as to the constitution of the atoms themselves. If the two electricities were thought to be free, the atoms were considered as small neutral particles, and if one movable fluid only was preferred, the other electricity was supposed to be fixed to the atoms, giving them a definite charge.

Further, in order to account for the electrodynamic and electromagnetic actions, different laws, such as those of WILHELM WEBER, RIEMANN and CLAUSIUS, had been proposed, all agreeing in so far as the mutual action of two particles of electricity was made to depend not only on their relative position, in the way expressed by COULOMB's law, but also on their state of motion. The consequences that can be drawn from these laws were worked out to a considerable extent, and many attempts were made to decide between the conflicting views and to ascertain whether in a current both electricities are moving, or one of them only. It should be noted also that the conception of a granular or atomic constitution of electricity was not wholly wanting. The theories to which I referred always spoke of the mutual action between two „particles" of electricity, but the magnitude of their individual charges was left wholly undeterminate.

Now, since WILHELM WEBER's days great and rapid progress has been made, and our present ideas about the constitution of a metal and the phenomena of which it is the seat are incomparably more definite and detailed than these old views which I recalled to you. I dare say that nowadays no physicist has any doubts about the structure of the atom; we have become quite familiar with the positively charged nucleus and the electrons surrounding it. The number of these electrons is known with certainty for all atoms. In the case of copper 29, for iron 26, for silver 47; it is simply what we call the „atomic number" of the element, i.e. the number that determines its place in a natural arrangement such as is given in MENDELEJEFF's table.

This number also determines the positive charge of the nucleus. For, since the electrons all have equal negative charges, say, each a unit of negative electricity, and since in its natural state with 29 electrons the copper atom as a whole has no charge, the charge of the nucleus must be 29 positive units. Similarly for other metals. I must add that nearly the whole mass of a body is concentrated in the nuclei and that, in the solid state, they occupy definite positions, in which they are maintained by certain forces which manifest themselves in the elastic properties of the metal. We may further be sure that over ranges many times longer than the molecular distances, the arrangement of the nuclei is perfectly regular. In other words, the metal is made up of crystals, very minute in most cases, but yet each containing millions and millions of atoms. The special features of this crystalline structure are found out by means of X-rays, but we need not speak of this now. It will be sufficient to know that the nuclei form, so to speak, the rigid framework of the metal. The motion of heat may slightly displace them from their positions of equilibrium, but the progressive motion of electricity which we call a current can only be a motion of the negative electrons. In this sense modern theory has decided in the old dilemma of one or two movable electricities.

To complete our picture I must remark that in the natural state of the metal, and apart from the agitation of heat, the electrons may already perform very rapid motions. You all know BOHR's theory, according to which the electrons of an atom are revolving about the nucleus with speeds that may be an appreciable fraction of the velocity of light. It is true that other models of the atom, with a static arrangement of the electrons, have been proposed by LEWIS and LANGMUIR, and that these have been found very serviceable for the understanding of chemical phenomena; but, especially in the fields of spectral lines and RÖNTGEN rays, the success of BOHR's theory has been so wonderful that I think we may safely trust to it.

The intensity and further peculiarities of the internal motions which we have now to imagine are inexorably determined by the conditions imposed by the theory of quanta; so these motions constitute an unalterable and fundamental feature of the chemical element, and without them our nucleus with its charge 29 and its 29 electrons would not form a system having the properties of a copper atom. Compared to these „constituent" motions heat is only a slight tremor of the nuclei, and the strongest electric current is probably but a comparatively unimportant additional phenomenon. It should finally be noted that metals belong to the electro-positive elements whose atoms easily lose one of their outer electrons. So we can understand that a certain number of these particles — a small fraction, however, of the total number — are set free; these may serve as the vehicle for the electric current.

There is a simple relation between the strength of a current and the mean velocity of the electrons, if by „mean velocity" we understand that of all the electrons together, free or otherwise. Indeed, we can fix our attention on an element of volume whose dimensions are a very small part only of a centimetre, but which nevertheless is large enough to contain an immense number of atoms. At a definite instant each electron present in it will have a definite velocity which we may decompose into components having the directions of the axes of coordinates. We may then take the mean value of all the components parallel to OX, with due regard to their positive or negative signs. Similarly, we may calculate the mean values of the velocities in the directions of OY and OZ. Finally, compounding the three results, we shall find, in direction and magnitude, the mean velocity of which I spoke. It will be zero, so long as there is no predominant direction of motion; this will be the case when the metal is in its natural state. On the other hand, the mean velocity will differ from zero whenever there is a general progressive motion, and then it will be a measure of the current of electricity. It is easily seen that the strength of the current, per unit area of a plane at right angles to it, is equal to the product of the mean velocity by the total charge of the electrons contained in unit of volume. This total charge is known, and so the mean velocity can be calculated for a given current intensity.

Take, for example, the case of a copper wire whose section is 1 mm^2 and in which there is a current of 1 amp. The number of atoms in a cm^3 may be taken to be $8{,}52 \times 10^{22}$, and the number of electrons is therefore $29 \times 8{,}52 \times 10^{22} = 2{,}47 \times 10^{24}$. The electronic charge being $1{,}59 \times 10^{-20}$ electromagnetic units, the total negative charge per unit of volume amounts to $3{,}93 \times 10^{4}$. On the other hand, expressed in the same electromagnetic units, the strength of the current per cm^2 is 10. From these data one finds for the mean velocity of the electrons $2{,}5 \times 10^{-4}$ cm per second.

Now, the mean distance between neighbouring atoms is about $2{,}3 \times 10^{-8}$ cm, and we see therefore that, if all the electrons had the mean velocity, each of them would pass along many thousands of atoms in a second. If the circuit had a length of 10 cm it would take the electrons eleven hours to go all round it. Of course, when the free electrons form only a small fraction of the total number, some individual particles must have performed the journey long before that time.

I do not mean to say that they have done so quite undisturbedly, nor that the same electrons remain free for a considerable length of time. In all probability the metal is the seat of a great variety of changes. While some electrons are set free, maybe by collisions of the atoms with moving particles, by a kind of dissociation due to the heat motion, or perhaps by radiations due to the transition of an atom from one stationary state to another, other electrons are recaptured by an atom; and if we could watch an individual particle we should probably see it freely moving for a short time, and then for a while imprisoned in an atom, moving in a BOHR orbit, until it is its turn again to be involved in the progressive motion.

Though all this may be extremely complicated, it is not difficult to account for OHM's law, the fundamental law of electrical conduction. To see this we may take the simplest case of all, a uniform steady current in a straight wire. As the state is stationary the resulting momentum G of all the electrons contained in the space between two sections S_1 and S_2 will not change in course of time, we may say so, even though the electrons that contribute to G are not the same at all instants, some particles leaving the space considered while others enter it. Hence, the different causes which tend to change the momentum G must counterbalance each other. As there is no reason why the transfer of momentum should be different at the sections S_1 and S_2, this means that the forces acting on the system of electrons must be in equilibrium. One force is due to the electric force acting along the wire, and there must therefore be another force equal and opposite to it; this action can only be exerted by the fixed nuclei.

It is clear that, so long as there is no mean velocity of progressive motion, a resulting force of this kind cannot exist. Though each electron belonging to an atom is attracted by its nucleus, and though there are similar forces acting on free electrons that come near a nucleus, yet these innumerable elementary actions will be directed indiscriminately towards all sides. So soon however as, in addition to these intrinsic motions, there is a small velocity of flow, it may well be that the actions of the nuclei on the electrons are somewhat stronger in one direction than in the other. It is natural to suppose that the force thus produced is opposed to the mean velocity of the electrons, so that it truly is a "resistance", and, inasmuch as we may expect that effects caused by small changes in the state of motion are proportional to these changes, we are led to a force of resistance proportional to the current, and thereby to an explanation of OHM's law. At all events it would be more difficult *not* to find this law.

The foregoing general considerations also suffice for the explanation of TOLMAN and STEWART's beautiful experiments on the currents produced by the acceleration or the retardation of a conductor, by which it was proved directly that the current consists in a motion of negative electrons. A similar experiment which we can make with a fluid may serve as an illustration. Let us take a closed circular tube filled with water and suddenly set it in rotation about its geometrical axis, the velocity becoming constant after a certain time. On account of the friction at the walls the fluid will at the end move with the same velocity as the tube; but it will require some time to be set in motion, so that at first the water will lag more or less behind. Conversely, when, beginning with a common motion of the tube and the water, the tube is suddenly brought to rest, the water will continue to move for a certain length of time.

It is very easy to calculate these relative motions of the water with respect to the walls. Let the tube be so narrow that all its points may be said to have the same velocity v, and let w be the relative velocity of the water in the tube. Both v and w are directed along the circle, and are positive or negative according to their direction. Now consider the force acting on the water per unit of length of the tube. Since all is the same at all points of the circle there can be no differences of pressure, and the only force will be the friction, which we may assume to be proportional to the relative velocity w and opposite to it, so that it may be represented by $-qw$, where q is a constant. Thus, since the velocity of the water is $v + w$ and its acceleration along the circle

$$\frac{d(v + w)}{dt},$$

we have the equation

$$m \frac{dv}{dt} + m \frac{dw}{dt} = - qw,$$

if m is the mass of the water per unit of length. By this formula the velocity w can be calculated for any instant, when v is given in function of the time.

It will be sufficient for our purpose to consider the transition during an interval of time extending from t_1 to t_2, from one steady state to another, in both of which the water has the velocity of the tube, so that at the beginning and at the end $w = 0$. Multiply the equation by dt and integrate from $t = t_1$ to $t = t_2$. The second term disappears and the first gives $m(v_2 - v_1)$, if v_1 and v_2 are the initial and the final velocity of the tube. Thus

$$m(v_2 - v_1) = - q \int_{t_1}^{t_2} w dt.$$

If the section of the tube is denoted by ω, the volume of water that has flowed through a section is given by

$$\omega \int_{t_1}^{t_2} w dt = - \frac{\omega m}{q} (v_2 - v_1).$$

We shall have the two cases of which I spoke, if we put either $v_1 = 0$ or $v_2 = 0$.

The electric currents observed by TOLMAN and STEWART can be calculated in nearly the same way, the only difference being that we have to introduce the force of self-induction. We now take a circular metallic wire rotating about its geometrical axis with the velocity v. Let w be the mean velocity relatively to the wire of the electrons, both free and otherwise. Then, if N is the total number of electrons per unit of volume, e the charge of each of them, and ω the section of the wire, the current will be

$$i = N\omega e w.$$

The forces acting on the electrons, per unit of length, are: first a resistance $-qw$, and in the second place a force due to the self-induction. It is well known that this latter force is proportional to $-di/dt$, so that we may write for it

$$-p\frac{di}{dt},$$

with a constant coefficient p. Thus, the equation of motion becomes

$$N\omega m\frac{d(v+w)}{dt} = -qw - p\frac{di}{dt},$$

where m is the mass of an electron.

Now, let the wire with the electrons contained in it first have the constant velocity v_1, and suppose that, after a certain time, the velocity of the wire is v_2, which again is kept constant. During the acceleration or retardation of the wire the electrons will have a velocity different from v, lagging behind or shooting forward, as the case may be; but, if we wait long enough, the „friction" will cause them again to move with the velocity of the wire. Thus, if the transition from one state to the other is made during the period from t_1 to t_2, we shall have, both for $t = t_1$ and for $t = t_2$, $w = 0$ and $i = 0$, and we find by the same integration which we used in the former case

$$N\omega m\,(v_2 - v_1) = -q\int_{t_1}^{t_2} wdt,$$

the terms with dw/dt and di/dt disappearing.

The total strength of the transient electric current that has been produced in the wire by the transition from the velocity v_1 to v_2 is given by

$$I = \int_{t_1}^{t_2} idt = N\omega e\int_{t_1}^{t_2} wdt,$$

so that we have

$$I = \frac{N^2\omega^2 em}{q}(v_1 - v_2).$$

In order to see the meaning of the coefficient we shall consider the constant current set up in the metal by an electric force E. There will be equilibrium between the forces $N\omega eE$ and $-qw$, if we denote again by w the mean velocity of the electrons. Thus

$$w = \frac{N\omega e}{q} E,$$

so that the current per unit of area of the section of the wire is given by

$$\frac{N^2\omega e^2}{q} E,$$

showing that

$$\sigma = \frac{N^2\omega e^2}{q}$$

is the coefficient of conductivity. Hence, if l is the length of the wire and r its resistance in the ordinary sense of the word,

$$r = \frac{l}{\omega\sigma} = \frac{ql}{N^2\omega^2 e^2}$$

and

$$I = \frac{lm}{re}(v_1 - v_2).$$

If the conductor is first moving with the velocity v and then brought to rest, the current will be

$$I = \frac{lm}{re} v.$$

The experiment was made with a coil of many windings (about 600), the ends of which were connected with a galvanometer, and whose motion of rotation about the axis was suddenly stopped by means of a brake. The direction of the current showed that the moving electricity really is the negative one, and that it is concentrated in electrons of the same kind as those that exist in cathode rays could be deduced from the value found for e/m, a ratio that can be calculated from the above formula if we take for l the total length of the coil and for r the resistance of the circuit, the galvanometer included. If the number thus obtained is divided by the value of e/m for cathode rays, the result is 0,89 for copper, 0,86 for aluminium, and 0,83 for silver.

It is interesting to apply to TOLMAN and STEWART's experiment the mode of reasoning set forth in the chapter on the „Dynamical theory of electromagnetism" of MAXWELL's Treatise, a chapter that will always remain remarkable for the way in which the general equations of dynamics were applied to electromagnetic phenomena. In these equations all is made to depend on the expressions for the potential and the kinetic energy, and MAXWELL showed how the laws of ponderomotive forces and induced currents can be derived on the assumption that the energy of the magnetic field plays the part of the kinetic energy. He remarks that, in the case of moving bodies carrying electric currents, the kinetic energy may be conceived as made up of three parts. The first of these, which he calls T_m, is the ordinary kinetic energy of the matter of the conductors, the second, T_e, is due to the electric currents taken by themselves, and the third part, T_{me}, arises from the combination of the motion of the conductors with the motion relatively to them of the electricity which they contain. MAXWELL was especially interested in the question whether this third part of the kinetic energy really exists, and he thoroughly discussed the effects that might be expected from it. He also tried to observe some of them, for which, however, his instruments were not sufficiently sensitive.

It is worthy of remark that the currents observed by TOLMAN and STEWART have their origin in this third part of the kinetic energy. Indeed, in addition to the ordinary kinetic energy of the coil, we have in the first place the energy of the electromagnetic field, for which we may write $\frac{1}{2}Li^2$, if L is the coefficient of self-induction, and in the second place the kinetic energy of the electrons. In order to find an expression for this latter energy we shall henceforth understand by N the number of *free* electrons only, and by w *their* mean velocity, and we shall suppose that each of them has this velocity w added to the velocity v of the wire. By this change of meaning of N and w their product is not altered.

We may now write for the kinetic energy of the free electrons

$$\frac{1}{2}Nl\omega m\,(v + w)^2,$$

or, using the relation between w and i,

$$\frac{1}{2}Nl\omega mv^2 + \frac{lm}{e}vi + \frac{lm}{2N\omega e^2}i^2,$$

so that the expression for the total kinetic energy takes the form

$$\frac{1}{2}Qv^2 + \frac{lm}{e}vi + \frac{1}{2}\left(L + \frac{lm}{N\omega e^2}\right)i^2.$$

Having got thus far one can easily deduce the formula for the TOLMAN-STEWART effect by means of LAGRANGE's equations, and then it is found to arise from the second term, which, as you see, is of the kind of MAXWELL's T_{me}.

I may perhaps mention here that the mass m of the electrons will also make itself felt when the conductor is left at rest. Our last formula shows that, on account of it, the coefficient of self-induction is augmented by an amount

$$\frac{lm}{N\omega e^2}.$$

If, in our measurements of the currents produced by self-induction and in the calculation of L in terms of the geometrical dimensions of the circuit, we could attain a sufficient precision, the influence of the additional term ought to become apparent. In one of the first papers of HEINRICH HERTZ, published in 1880, an account is given of an attempt he had made in this direction. But HERTZ was no more successful than MAXWELL. He could only fix an upper limit for the kinetic energy of the moving electricity. According to our equation this means a lower limit for the number N, and, indeed, applying the formula to the numbers given by HERTZ, I find that in his copper wire the number of free electrons per cm^3 must have been more than about $2{,}2 \times 10^{16}$. As the total number of electrons is $2{,}47 \times 10^{24}$, you will not object to this result.

Thus far we have followed rather general ideas only. One must go farther than this, and try to make more definite assumptions concerning the behaviour of the free electrons and their interactions with the metallic atoms, if one wants to understand the causes that determine the degree of conductivity of a metal and the relations between the electric current and other phenomena. A vast amount of experimental evidence has accumulated in this field, and many interesting and beautiful theories have been proposed; a full account of all this may be found in a report presented by Professor BRIDGMAN to the Solvay meeting of 1924.

It would be impossible for me now to speak of all this, and I think I had better confine myself to a small number of questions. Allow me therefore to devote the remaining part of my lecture to some considerations in connection with the theory that was developed a quarter of a century ago by DRUDE, and to a discussion of one of the experiments which Professor KAMERLINGH ONNES has made with supraconductive metals.

DRUDE's fundamental ideas were that the free electrons in a metal have their share in the thermal agitation, moving at such speeds that their mean kinetic energy is equal to that of the molecules of a gas, and that their paths of undisturbed motion are limited by their encounters with the atoms. I shall now show how a theory of electric conduction can be based on these assumptions. In doing so I shall begin without any special assumption concerning the mutual action of an electron and an atom near which it comes. Our general formula will hold whatever be the precise nature of this action. It may be applied, for example, when the atoms are considered as solid spheres from which the electrons rebound according to the laws of elastic impact, but also when the electrons can pass right through the atoms, suffering perhaps only a slight deflexion from their original path.

Let us consider a group of free electrons, possibly moving in many different directions, but having at a definite time t a certain mean or common velocity w; this group may, for example, consist of the N free electrons which are found in unit of volume. At all events, we shall suppose it to be so numerous that in an interval of time dt — that is but a very small fraction of a second — a great number of encounters take place. At the end of this lapse of time we may again fix our attention on the velocities of the particles and take the mean of them all; we may do so even when not exactly the same electrons constitute the group at the two instants, i.e. if some free electrons have been captured by the atoms and have been replaced by an equal number of new ones.

Now, I think you will find no difficulty in making the following assumptions:

1. The new mean velocity w' has the same direction as the original one w; indeed, there is no reason why, of two directions equally inclined to w, one should predominate over the other.

2. The new velocity w' is smaller than w. This means that the irregular actions exerted by the atoms tend to obliterate a common progressive motion of the electrons.

3. The change $w - w'$ is proportional to the time dt.

4. It is likewise proportional to w itself. This follows from the remark already made, that the progressive motion of the electrons constitutes only a very slight departure from the natural state of things. Inasmuch as small deviations of this kind generally obey linear equations, we may say that w, w', and therefore also their difference, may be altered in the same ratio.

What precedes leads us to the equation

$$w' - w = - \alpha w dt,$$

where α is a constant. Or, if we write dw instead of $w' - w$,

$$dw = - \alpha w dt,$$

and on integration

$$w = w_0 e^{-\alpha t},$$

where w_0 is the mean velocity of the group at the instant $t = 0$. This velocity is thus seen to die out at a rate determined by the factor $e^{-\alpha t}$.

Now, let the metal be subjected to an electric force E, so that in unit of time a velocity eE/m is communicated to each free electron, and let us try to determine the mean velocity of flow of a numerous group at a definite instant t_0. For this purpose we have only to see what are at this instant the parts that remain of the velocities acquired by the electrons in the intervals of time previous to t_0.

Consider an instant a time τ before t_0 and the element of time corresponding to $d\tau$, i.e. the interval that extends from $t_0 - (\tau + d\tau)$ to $t_0 - \tau$. The velocity imparted to the electrons during this time is

$$\frac{eE}{m} d\tau,$$

and this has decayed to

$$\frac{eE}{m} e^{-\alpha\tau} d\tau$$

at the instant t_0. Thus the mean velocity of the free electrons is

$$\frac{eE}{m} \int_0^\infty e^{-\alpha\tau} d\tau = \frac{eE}{\alpha m}.$$

The current is therefore

$$\frac{Ne^2E}{\alpha m}$$

and we find for the coefficient of conductivity

$$\sigma = \frac{Ne^2}{\alpha m}.$$

The mean velocity is the same as would be produced if the effect of the electric force had accumulated without being disturbed during a time $1/\alpha$. This interval $1/\alpha$ also has the meaning that, in the course of it, a mean velocity previously existing diminishes in the ratio of 1 to $1/e$.

The value of α will, of course, depend on the nature of the encounters.

Suppose, for example, that the atoms act as perfectly elastic spheres. Then, according to a theorem proved by MAXWELL in 1860, in his first paper on the kinetic theory of gases, the mean velocity of a group of electrons will be wholly lost as soon as each of them has experienced one encounter.

The part of our group of electrons N that strike against an atom between t and $t + dt$ may be represented by

$$\beta N dt,$$

where β is a coefficient depending on the size and the number of the atoms, and if we suppose that initially this sub-group $\beta N dt$ had exactly the same mean velocity as the general group N, we shall have, at the instant $t + dt$, $\beta N dt$ electrons deprived of their mean velocity, and $N(1 - \beta dt)$ particles for which it is still w. Thus, the new mean velocity is

$$w' = (1 - \beta dt)w,$$

showing that in this case α has the value β.

Introducing a properly chosen mean velocity of heat motion u, we may also say that in a time during which, in this motion, the electrons travel over a path ds,

$$\beta \frac{N}{u} ds$$

electrons, out of the whole number N, will hit an atom. From this we may infer that, if we first fix our attention on the positions of the electrons at some definite instant t_0, the mean length of the paths which they describe between this instant and the encounter following it will be u/β. Of course, the mean length of the paths described in the intervals of time between t_0 and the encounter preceding it has this same value, and the mean length of the paths, reckoned from one encounter to the next, which the electrons are describing at the moment t_0, is twice as great. Thus, if this latter mean length is denoted by l,

$$\frac{u}{\beta} = \frac{1}{2} l, \ \alpha = \beta = \frac{2u}{l}$$

and

$$\sigma = \frac{Ne^2 l}{2mu}.$$

This is DRUDE's formula for the electrical conductivity. We could have found it directly by remarking that, at a definite time, the velocities of the electrons, so far as they are due to the electric force, are those that have been acquired since the last encounter, i.e. during a lapse of time, the mean value of which is

$$\frac{l}{2u}.$$

If R is the radius of an atom, and if there are n of them in unit of volume, the length of l is given by

$$l = \frac{2(1 - \frac{4}{3}\pi n R^3)}{\pi n R^2}.$$

Comparing this with the distance λ of neighbouring atoms (the atoms being supposed to have a cubical arrangement) one finds

$$\frac{l}{\lambda} = 1{,}65 \times \frac{1-\delta}{\sqrt[3]{\delta^2}}$$

if δ is the part of the whole volume occupied by the atoms.

Drude was led to a most remarkable result by combining the above formula with a similar one for the thermal conductivity. The explanation which he gave of this latter phenomenon is much like that which is current in the theory of gases. Indeed, the free electrons in a metal may in a sense be considered as forming a gas, whose mobility, however, is limited, not by the mutual encounters between the particles, but by those with fixed obstacles; it is as if we had an ultra-rarefied gas enclosed in a porous substance. It is easy to calculate the kinetic energy carried by the electrons from a place of higher to one of lower temperature; this will give us the conductivity of the metal for heat if we assume that there is no other mode of conduction, and, in particular, no appreciable transfer of heat through the framework constituted by the atoms or the nuclei.

Drude finds that the coefficient of thermal conductivity $\varkappa$ depends in the same way as that of electrical conductivity σ on the mean length of free path l and on the number of electrons N, so that these quantities disappear from the ratio between the two conductivities. His formula for the ratio is

$$\frac{\varkappa}{\sigma} = 3\left(\frac{k}{e}\right)^2 T,$$

where T is the absolute temperature and k the well-known coefficient that determines the mean kinetic energy of a particle at the temperature T, this energy being $\frac{3}{2}kT$.

Thus Drude was able to account for the fundamental fact that metals are at the same time the best conductors for heat and for electricity, and for Wiedemann and Franz's law, according to which the ratio between the two conductivities is the same for all metals. The theoretical conclusion that the ratio should be proportional to the absolute temperature is verified fairly well by the experimental values. JAEGER and DIESSELHORST found that, when the temperature is raised from 18° C to 100° C, i.e. when the absolute temperature is changed in the ratio of 1 to 1,28, the value of $\varkappa/\sigma$ increases in a ratio varying for different metals between 1,25 and 1,12. Moreover, the absolute value of the ratio $\varkappa/\sigma$ as deduced from the observations, which in the case of silver, for example, at 18° C is 686×10^8 (electromagnetic units), is nearly equal to the theoretical number. If, in DRUDE's formula, we substitute the known values of k and e, viz. $k = 1{,}37 \times 10^{-16}$ and $e = 1{,}59 \times 10^{-20}$, we find

$$\frac{\varkappa}{\sigma} = 648 \times 10^8.$$

In a theory which has given results like these, there must certainly be a good deal of truth. Yet, there are serious difficulties which I must now, in part at least, point out to you.

The formula for the electrical conductivity shows that it depends on the number of free electrons and on the length of free path. Now, in our assumptions about N, we are limited by what we know about the specific heat of metals. At temperatures that are not too low the values found for the specific heat conform to DULONG and PETIT's law, and may be accounted for by attributing to each atom a mean kinetic energy $\frac{3}{2}kT$ and an equal amount of potential energy; we are justified to make this latter addition by the theorem that in a system performing harmonic vibrations about a position of equilibrium the mean values of the kinetic and the potential energy are equal. Now, it is clear that this explanation leaves no room for any appreciable contribution to the specific heat that could be due to the electrons.

If all the electrons contained in the copper had their share in the thermal agitation, it would be as if we had thirty atoms instead of one, and, even if for the 29 electrons we reckoned only with the kinetic energy, we should find for the specific heat a value about fifteen times too great. In so far as we are concerned with the electrons belonging to the constitution of an atom, we escape from this difficulty by the hypothesis that their motion relatively to the nucleus is inexorably prescribed by quantum conditions. No change of temperature can alter it, and in all questions of heat motion we may regard the nucleus with its system of electrons as a single particle having, as we say, no more than three degrees of liberty. For the free electrons, however, to which we have expressly assigned the kinetic energy $\frac{3}{2}kT$, the trouble remains. If the specific heat shall not become too great, the number of free electrons must be small in comparison with the number of atoms, and, as the conductivity depends on the product Nl, the smaller we make N, the longer must be the free paths. Suppose, for example, that N is the twentieth part of the number of atoms. I then find that l must be about 500 times the distance between neighbouring atoms, and our formula for l/λ would require a value of δ, the ratio between the volume of the atoms and the total volume, smaller than 0,0002. As the atomic volume is certainly much greater than this, we must give up the idea of atoms into which the electrons cannot penetrate and revert to the general formula for the conductivity which made it depend on the coefficient α. If we like, we may still use DRUDE's formula, but then we must define l by

$$l = \frac{2u}{\alpha},$$

meaning that it is the length of path corresponding to a time during which an initial mean velocity has fallen off in the ratio of 1 to $1/e^2$.

I may here remark that probably not only DRUDE's formula for σ, but also his equation for the thermal conductivity would remain valid, so that his conclusion about the ratio $\varkappa/\sigma$ would remain unchanged, if this new and longer „free path" were a straight line. This might be the case if an electron could pass through many atoms without having its velocity sensibly changed until it comes very near a nucleus. But when each encounter with, or passage through an atom is attended by an appreciable deflexion, our new path l is curved, and then it becomes very difficult to calculate exactly the conductivity for heat.

These remarks may suffice to show that we are still far from a satisfactory solution of these problems. Many modifications of DRUDE's theory have already been proposed, especially with a view to the phenomena observed at low temperatures. It may very well be that, when we come to these, the theorem of equipartition of energy, requiring the mean kinetic energy $\frac{3}{2}kT$ for each particle, which we had previously to abandon for the atoms, will also fail to hold for the free electrons, so that they also have to be subjected to the rules of the quantum theory. The great problem will be to reconcile the heat motion of the free electrons with the immunity for thermal agitation of the electrons inside the atoms, and clearly to understand the mechanism of the encounters and the partition of the energy of heat between the atoms and the free electrons.

I now come to the experiment with a supra-conducting metal to which I have previously alluded. You know the beautiful discovery made by KAMERLINGH ONNES in his cryogenic laboratory; several metals completely, or almost completely, lose their resistance when by means of liquid helium they are cooled below a certain temperature, 4,2° K in the case of mercury, 3° K for tin, and 7,3° K for lead.

Below this point of discontinuity currents can persist in the metal for hours and days, and it seems that practically the body may in many cases be regarded as a perfect conductor with no resistance at all.

The existence of the currents can be shown either by their action on a small magnet or by the ponderomotive forces exerted on the body by an external magnetic field. I choose an experiment in which this ponderomotive force was observed; it is particularly interesting, because it can give us some indications about the degree of freedom of motion which we may ascribe to the electrons.

Allow me, by way of introduction, to recall to you that an electromagnetic field is characterized by the electric force E and the magnetic force H, which in the cases to be considered we need not distinguish from the magnetic induction, and that between these forces there is always the connection that is expressed by MAXWELL's equations. If a unit of electricity is made to move around a closed line, the work of the force E acting on it is given by the rate of change, taken with the negative sign, of the magnetic induction through a surface having the line for its boundary. Instead of „work of the electric force" we may also say „line integral of the force", meaning by this that each element of the line is multiplied by the component of the force along it, and that the products thus obtained, with due regard to their signs, are added.

The action of the field on a charge e that is at rest is simply given by the product eE, but there is an additional force when the charge moves. This new force is perpendicular to the plane passing through the direction of the velocity v and that of the magnetic force H; in the case of a positive charge the force is directed towards that side of the plane from where a rotation from the direction of v towards that of H is seen as counter-clockwise. For a negative charge the force has the opposite direction and it is proportional in any case to the magnitude of the charge. The force acting on unit of electricity is determined by the product of the velocity v, the magnetic force H, and the sine of the angle between them.

In what follows I shall speak of E as the „electric force", and of the force depending on v and H as the „transverse" one, because it is at right angles to the line of motion.

The effect of the transverse force is observed in the magnetic deflexion of cathode rays and of other rays that consist of moving charged corpuscles. It also gives rise to the ponderomotive force acting on a wire through which a current is passed and which is placed in a magnetic field. This force, which is perpendicular to the length of the wire, must be understood to act primarily on the electrons moving in the wire; it is transmitted to the metal in a way which we can easily imagine in simple cases.

In the experiment made by KAMERLINGH ONNES a thin spherical shell of lead was used; it was suspended by a torsion spring, so that it could rotate about its vertical diameter. We shall suppose it to be so thin that we may think of currents flowing in a „surface".

It will be convenient in our discussion to consider the system as made up of two parts, viz. the free electrons or the „moving electricity" and the totality of nuclei with the electrons connected with them. This second part may be called the „framework", or simply the „metal"; it has a positive charge equal to the negative charge of the free electrons.

Some remarks may also be made here about the way in which currents can be set up in the sphere. You can easily imagine forces so distributed that they can produce no continual circulation of electricity, but only movements of short duration, giving rise to a distribution of electric charges by whose reaction the moving forces are soon counterbalanced. We have an example of an equilibrium of this kind when we suppose the electricity to be acted on by forces directed towards a fixed point P of the sphere along great circles passing through that point and having the same intensity at all points equally distant from P. Distributions of this kind are called „irrotational"; their line-integral is zero for any closed line on the sphere, and this is the reason why they do not tend to give a circulating motion to the electricity. In our problem any irrotational distribution of forces may simply be regarded as ineffective. We may add that the effect of forces that are not irrotationally distributed is wholly determined by their line-integrals for different closed lines. Two different distributions of such a kind, that, for any closed line on the sphere, the line-integral has the same value in the two cases, are equivalent, for one of them can be obtained from the other by compounding it with an irrotational distribution, for which the line-integral is zero and which is ineffective.

In the case of a body in which the electricity can move with absolute freedom there is a very simple rule. The slightest cause which tends to make the electricity circulate would produce a very strong current, and therefore things arrange themselves in such a way that the line-integral of the forces that are at play is zero for any closed curve.

I shall now, in the first place, try to explain in what way persistent currents can be set up in the supra-conducting shell. I shall next examine the action of an external field on these currents; we shall find that, even if the moving electrons are perfectly free, the transverse force which they experience is transferred to the metal, thus producing a deflecting ponderomotive couple such as has been observed. We shall be able to specify the way in which the transmission is effected. Finally, however, it will appear that, under the circumstances of the experiment, the transmission must have taken place by some more direct action between the free electrons and the framework.

1. Currents are set up in the sphere by exciting an external magnetic field H. If this be uniform, say, in the direction of a line

OL drawn from the centre, the lines of flow will be circles, having OL for their axis. The intensity of the current will be greatest at the equator, i.e. in a plane passing through the centre at right angles to OL, and it will decrease towards the poles, according to a simple law. In fact, you may get an idea of the system of currents by imagining the shell to be replaced by a spherical surface uniformly charged with negative electricity and free to move as a whole while the charge is fixed to it. If the external field is started such a sphere will be set rotating about OL, so that we have a system of convection currents. The currents produced in the perfectly conducting shell are distributed in exactly the same way as these convection currents; it is as if the movable electricity were attached to a spherical surface free to move *in* the metal.

All this may be inferred from the rule which I mentioned just now. The line-integral of the electric force along any closed line on the sphere must constantly be zero. This means that the magnetic induction through a part of the sphere must remain unaltered, and from this we deduce that at any point of the sphere the normal component H_n of the magnetic force does not change in course of time. In our experiment we began with $H_n = 0$, as, initially, we had neither currents in the shell nor an external field. Consequently, H_n must remain zero. If we excite an external magnetic force H in the direction of OL, having at any point P a normal component $H \cos \theta$, where θ is the angle LOP, the induced currents must be such that they give rise to a normal component of magnetic force opposite and equal to $H \cos \theta$. This is mathematically equivalent to the condition that at all internal points the field H is exactly compensated by the field arising from the induced currents, and from this the currents are found by an easy calculation. The result is that at any point P of the surface the electrons will move along the parallel circle with a velocity

$$-\frac{3c}{2Ne} H \sin \theta,$$

whose direction, when the coefficient is positive, corresponds (in the sense generally given to this word in electromagnetic theory) to the direction of the magnetic force H. By N I have now denoted the number of free electrons per unit area of the shell, e is again the charge of an electron and c the velocity of light; this latter factor appears in the formula because H and e have been expressed in so-called rational units.

It can further be shown that, in virtue of the currents produced in it, the sphere has become equivalent to a magnet of small size placed at the centre and having a moment

$$-2\pi R^3 H.$$

R is the radius of the shell, and the negative sign means that the moment has a direction opposite to that of the external field.

The induced currents will persist so long as the external field remains unaltered. Any change of the field, either in intensity or in direction, will, however, be attended by a new induction, and we have the theorem that, whatever be the course of these changes, the motion of electricity is at any moment exactly such as would have been produced if the field had at once been started with the direction and the intensity which it has at the instant considered. Thus, in a variable uniform field, the magnetic moment of the shell will at any time be such as we have specified.

When the field is made to disappear the currents vanish at the same time.

Thus far we had only systems of currents, for which the axis — i.e. the line around which the electricity is circulating — has the direction of the external field. By appropriate devices it may, however, be made to deviate from this direction. Suppose, for example, that *before* cooling the sphere we apply a magnetic field H_1, which is thereupon maintained constant. As the metal is still an ordinary conductor, the induction currents that have been excited by the introduction of the field will die out in a short time. Let the next step be to lower the temperature, so that the sphere becomes supra-conductive. This operation will not give rise to any motion of electricity, and after it we shall therefore have a sphere without currents placed in the field H_1. If, finally, we apply a field H_2 which makes an angle with H_1, we shall obtain circular currents whose axis does not coincide with the direction of the external field, which we find by compounding H_1 and H_2.

2. This, a spherical shell in which there are circular currents around an axis OL, and which is placed in a field H making an

angle with OL, is the case that has now to be examined. The motion of the free electrons will be determined not only by the electric force, but also by the transverse force, and the fundamental condition will be that for any closed line on the surface the line-integral of the two forces taken together must be zero.

Now, this condition would not be fulfilled if the system of currents for ever remained as it is at first. For then there would be no changes of magnetic force, and consequently no electric force E, whereas it is easy to find closed lines on the sphere for which the line-integral of the transverse force is not zero. So the problem is to determine the *changes* of the current system.

It is found that there is but one solution. The axis OL rotates with constant velocity about a diameter having the direction of the external field, and while it does so, the currents around it are at any moment such as they were first. In other terms, the system of currents has a precessional motion comparable to that of a spinning-top, whose axis is in an inclined position. The angular velocity of precession is given by the expression

$$-\frac{3}{2}\frac{c}{NeR}H.$$

As e is negative, the rotation has a direction corresponding to that of H.

The calculation is too long to be worked out here, but you can easily understand how it comes about that the fundamental condition is now fulfilled. When the system of currents rotates, the magnetic field belonging to it does so likewise. Thus at a point of the shell the normal component of this field changes, and this gives rise to inductive forces E, whose line-integral has a definite value, in general different from zero, for any closed curve. When the precession goes on in the direction and with the velocity just indicated, this line-integral is exactly equal and opposite to that of the transverse force. In this sense the inductive forces E and the transverse ones, acting on the movable electricity, may be said to counterbalance each other.

3. I have next to show you the origin of the ponderomotive forces acting on the substance of the sphere. This is speedily done. The transverse forces acting on the negative electrons produce a

certain resulting couple; let this be C. Similarly, the forces E acting on these same electrons give rise to a couple C', and from what we have just seen we infer that $C' = -C$.

As I have previously remarked, the framework of the metal has a positive charge equal to the negative charge of the electrons. Consequently, the forces E drive it forward in directions opposite to their action on the electrons, thus producing a couple C'' equal and opposite to C'. On the other hand, since the framework is at rest, it is insensible to the transverse forces, and so the couple C'' remains uncompensated. As it has the same direction and magnitude as C, we may say that this latter couple, resulting from the action of the transverse forces on the electrons, is transmitted to the metal. This is not done by any direct interaction, but this time the connecting-link is to be looked for in the variable magnetic field in which the inductive forces E have their origin.

As to the direction and magnitude of the ponderomotive couple, these are exactly such as they would be if the external field acted on the magnetic moment of which I previously spoke, and to which the shell is equivalent.

4. Professor Kamerlingh Onnes has observed and measured the ponderomotive couple, and so far all is satisfactory. But, unfortunately, there is the motion of precession, and on account of this the equivalent magnet also must be imagined to rotate.

In the experiments the external field had a horizontal direction, say OX, and the sphere could rotate about a vertical line, say OY. Under these circumstances the couple that is observed depends on the component of the magnetic moment in the direction OZ perpendicular both to the suspension and to the magnetic field. One sees immediately that, when a constant magnetic moment making an angle with OX turns about that line, its component along OZ changes continually, vanishing at certain instants and passing from one direction to the other. Thus, if the precession exists, there ought to be corresponding changes in the couple. Nothing of the kind has, however, been observed.

In order to account for this, one might think that perhaps the precession is so slow that in the course of the observations the direction of the axis of the currents is not sensibly altered. This is a supposition that can be tested by means of the expression which we found for the speed of rotation. If this is to be small, the number N must be sufficiently large, and the question is, whether the value that is required for it can be considered as admissible.

The couple was found not to change appreciably in about six hours. From this we may safely conclude that the angle over which the precession took place during this lapse of time has been smaller than, say, 20°. This means that the velocity of the precessional rotation,

$$-\frac{3}{2}\frac{c}{NeR}H,$$

has been less than $1{,}62 \times 10^{-5}$. From this I infer that the ratio between the number of free electrons and that of the atoms ought to be greater than

$$5{,}4\frac{H}{R\delta},$$

where H is the strength of the magnetic field in gauss and δ the thickness of the shell.

This condition has certainly not been fulfilled, for H has been some tens of gauss and the number of free electrons can be no more than a small fraction of that of the atoms.

So, after all, our conclusion must be that in the supra-conductive metal the electrons are not *wholly* free. It seems as if definite paths were prescribed them *along* which they can move without encountering a resistance, but which they cannot freely leave *sideways*. A precessional motion would be excluded by this, and the transverse actions would be transmitted to the metal by the intervention of the forces which prevent the electrons deviating from their prescribed trajectories.

I hope that I have given you the impression that the phenomena which we observe in supra-conductors are well worth close and careful examination. But we must not forget that a simple copper wire at ordinary temperatures, traversed by a current, is no less a world full of mystery.