

## XIV. Conduction of electricity through metals

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is a consequence of a change in the mechanism of the discharge, as the high speed cathode rays make their appearance with a consequent increase in the amount of Röntgen radiation in the tube, that an unknown factor which is of small importance at high pressure predominates at the lower pressure, causing the length of the field to be independent of pressure.

I have much pleasure in recording my thanks to Professor Sir J. J. Thomson for suggesting this work to me.

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#### XIV. *Conduction of Electricity through Metals.*

By Sir J. J. THOMSON, O.M., F.R.S.\*

THE investigations of Kamerlingh Onnes on the resistance of metals at the temperature of liquid helium have led to results which are of vital importance in the theory of metallic conduction; they have shown, for example, that some metals can exist in a state where their specific resistance is less than one hundred thousandth millionth part of that at  $0^{\circ}\text{C}$ . The transition from the state in which the resistance is diminishing normally with the temperature to the one where they possess this super-conductivity takes place abruptly at a definite temperature, and the difference in the electrical properties of the metal above and below this temperature are as well marked as the difference in elastic properties when a solid melts, or in the magnetic ones when a piece of iron passes through the temperature of recalescence. One of the most remarkable effects discovered by Kamerlingh Onnes is that when a current was started in a small ring of lead at a temperature of about  $4^{\circ}$  absolute, by bringing a magnet close to it, the current instead of dying away, as it would have done at  $0^{\circ}\text{C}$ ., as soon as the magnet was stopped, went on with practically undiminished intensity, its rate of decay being so slow that Kamerlingh Onnes estimated that it would take four days to fall to half its initial value.

This power of transmitting a current for long periods when no external electromotive force acts on the metal is one that has to be accounted for by any theory of metallic conduction: any such theory must indicate that in certain metals a change of electrical state takes place at a definite temperature, that above this temperature the current dies away almost instantaneously after the electromotive force is

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removed, while below it the current may persist for days without undergoing any considerable diminution. It seems to me that this is another, and fatal objection to the theory that metallic conduction is due to the presence in the metal of free electrons which drift under the electric force, for no permissible increase in the number of free electrons or in the mean free path would explain the difference between the ordinary and super-conducting state. In the case of the lead ring the maximum free path (equal to the longest chord that can be drawn in the ring) cannot be more than a few millimetres.

It is the object of this paper to show that the effects discovered by Kamerlingh Onnes are in accordance with the theory of Metallic Conduction which I gave in 'The Corpuscular Theory of Matter' (page 86), and which, with the substitution of an electron for a charged atom, is substantially the same as that given in my 'Applications of Dynamics to Physics and Chemistry,' 1888.

On this theory, the atoms of some substances, including the metals, contain electrical doublets, *i. e.* pairs of equal and opposite electrical charges at a small distance apart. In the normal state of a body the axes of the large number of doublets occurring in even a small volume are uniformly distributed in all directions: when, however, an electrical force acts on the body, the axes of the doublets tend to point in the direction of the force and the moments of the doublets have a finite resultant in this direction. If the axes of the doublets were quite free to set in any direction, the smallest electrical force would be able to pull the axes of all the doublets into line and thus produce the maximum polarization. There are, however, several influences at work which limit the number of doublets which point in the direction of the electric force.

In the case of gases, for example, there are collisions between the various molecules which tend to knock the axes of the doublets out of line as fast as they are brought into it by the electric force. Langevin has calculated from the principles of the Kinetic theory of Gases the magnitude of this effect, and has shown that if  $M$  is the moment of each doublet,  $N$  the number of doublets in unit volume,  $I$  the resultant of these moments parallel to  $x$ , and  $X$  the force on a doublet in this direction,

$$I = NM \left\{ \frac{\epsilon^x + \epsilon^{-x}}{\epsilon^x - \epsilon^{-x}} - \frac{1}{x} \right\}$$

when

$$x = MX/R\theta,$$

$\theta$  being the absolute temperature and  $R\theta$  the mean kinetic

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energy of a molecule at this temperature ; when  $x$  is very small,  $I = \frac{1}{3}NMx$ , when it is very large,  $I = NM$ .

In the case of solids and liquids, though there may not be collisions between the molecules, the rotation of the molecules endows them with a quasi rigidity, making each molecule behave very much as if its axis of rotation were acted on by a restoring couple proportional to the angle through which the axis is displaced and proportional also to the kinetic energy possessed by the body in virtue of its rotation : it behaves in fact very much like a spring whose stiffness is proportional to its kinetic energy. The value of  $I$  will be a function of the ratio of  $XM$ , the deflecting couple acting on the doublet, to the restoring couple brought into play when the axis is deflected through unit angle ; as this couple is proportional to  $w$ , the average kinetic energy of the molecules, we have

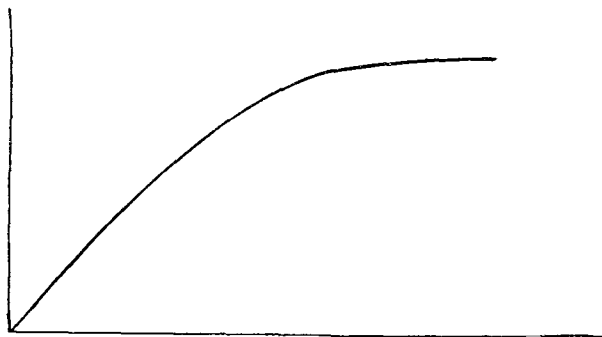
$$I = NMF(XM/w).$$

Thus we see that for solids and liquids, as well as for gases,  $I$  is a function of  $MX/w$ .

We need not here go into the question whether the form of the function depends on whether the body is in the solid, liquid, or gaseous state. It is sufficient to notice that whatever the state, when  $x=0$ ,  $F(x)=0$ , and when  $x=\infty$ ,  $F(x)=1$ .

Thus  $F(x)$  will be represented by a curve of the type shown in fig. 1. The force  $X$  which occurs in this expression

Fig. 1.



for  $x$  is not merely the external electric force acting on the system, the polarized doublets will themselves give rise to strong electric forces, and  $X$  is the resultant of such forces and the external electric force. We shall take the force due to the polarization of the doublets as proportional to  $I$  and

put it equal to  $kI$ . Thus, if  $X_0$  is the external electric force

$$X = X_0 + kI,$$

and

$$x = \frac{M(X_0 + kI)}{w}$$

or

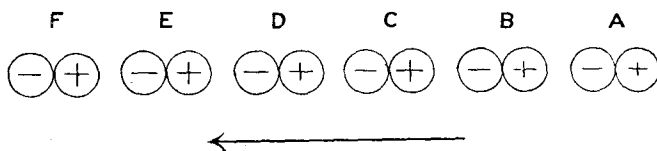
$$I = \frac{w}{Mk} x - \frac{X_0}{k}.$$

This relation between  $I$  and  $x$  is represented graphically by a straight line, and the value of  $I$  corresponding to any value of  $X_0$  can be determined by finding where this line intersects the curve

$$I = NM F(x).$$

The effects corresponding to any finite value of  $I$  will be the same as if  $I$  doublets per unit volume pointed in the direction of the electric force, while the axes of the rest were uniformly distributed in all directions; and we may picture the substance as containing a number of chains of polarized atoms whose doublets all point in the direction of the electric force as in fig. 2.

Fig. 2.



So far as we have gone there has been nothing to differentiate between insulators and metals; in each of these the doublets set under the electric field and give to the substance specific inductive capacity, the value of which is proportional to the value of  $I$  when  $X_0$  is unity.

It will be noticed that the electrons in the atoms of the substance will be under the influence of forces excited by neighbouring polarized atoms. Thus in the case represented in the figure these forces tend to make the electrons in A move towards B, and those in B to C and so on. On this theory the peculiarity of metals is that electrons, not necessarily nor probably those in the doublets, are very easily abstracted by these forces from the atoms when these are crowded together. Thus we may suppose that under these forces an electron is torn from A and goes to B, another from B going to C, and so on along the line,—the electrons passing along the chain of atoms like a company in single file passing over a series of stepping-stones. Let us suppose

that  $p$  electrons pass along each of these chains per second, then if there are  $n$  of these chains passing through unit area at right angles to the electric force, the current  $i$  through unit area will be  $epn$ ,  $e$  being the charge on an electron. If  $d$  is the distance between adjacent atoms in the chain, there will be  $1/d$  atoms per unit length of chain, and  $I$  the number of doublets per unit volume pointing in the direction of the electric force will be equal to  $n/d$ .

Thus  $n = Id$ , and therefore

$$i = epId.$$

The specific conductivity of the metal  $c$  is equal to  $i/X_0$ , so that

$$c = epdI/X_0.$$

The force exerted by the polarized atoms on the nearest electron in a neighbouring atom will be very large compared with that exerted by the external electric force, so that  $p$  will be determined by these inter-atomic forces and will not to an appreciable extent depend on the external electric force. The ratio of the current to this force will therefore follow the same laws as the ratio of  $I$  to the force.

We have seen that the value of  $I$  is determined by the intersection of the line

$$I = \frac{w}{Mk} - \frac{X_0}{k} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with the curve

$$I = NM F(x), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $w$  is the kinetic energy of a molecule; unless the temperature is very low  $w = R\theta$ , where  $\theta$  is the absolute temperature and  $R$  the gas constant: when the temperature falls to the stage where the specific heat diminishes with the temperature,  $w$  will be smaller than the value given by this equation.

When  $w/MK$  is considerable the line (1) will be steep and will intersect the curve near the origin, where it approximates to the straight line

$$I = NMx F'(0) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the intersection of (1) and (3) is given by

$$I = \frac{NM^2 F'(0) X_0}{w - NM^2 k F'(0)},$$

and  $i$  the current by

$$i = \frac{epdNM^2 F'(0) X_0}{w - NM^2 k F'(0)}.$$

Thus the current is proportional to  $X_0$  and Ohm's law holds ; the specific resistance  $\sigma$  is given by

$$\sigma = \frac{w - NM^2kF'(0)}{epdNM^2F'(0)}.$$

Now, except at very low temperatures,  $w$  is equal to  $R\theta$ , so that  $\sigma$  is expressed by an equation of the form

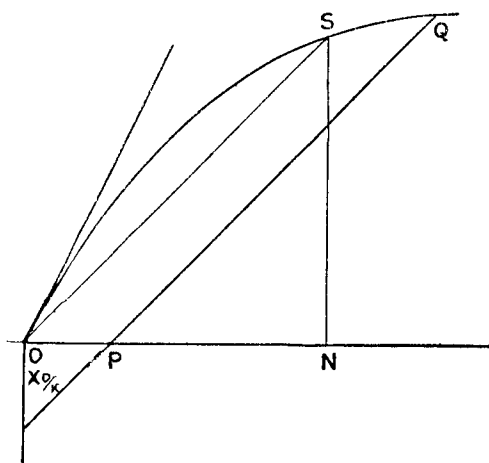
$$\sigma = a(\theta - b).$$

It is thus a linear function of the temperature, this is very approximately true for pure metals.

### Super Conductivity.

Let us now consider what happens when the temperature is diminished, the slope of the line (1) continually decreases and the intersection of this line with the curve gets further and further away from the origin; when the intersection comes on a part of the curve at an appreciable distance from the tangent at the origin, Ohm's law will no longer hold. Suppose that the slope of the line (1) has fallen so that, as in fig. 3, it is less than that of the tangent at the origin to

Fig. 3.



the curve  $I = NM^2F(x)$ , and after the application of a force  $X_0$  suppose the force is gradually removed, the value of  $I$  corresponding to the diminished force will be got by drawing parallels to  $PQ$  continually getting nearer to the origin, and its value when the force has been entirely removed by drawing a parallel through the origin itself. We see from the figure that in this case the line through the origin will

intersect the curve again at S, showing that I retains the finite value SN after the electric force has disappeared. From the point of view of this paper, however, the part played by the electric force in metallic conduction is to polarize the metal, *i. e.* to form chains; when once these are formed the electricity is transmitted along them by the forces exerted by the atoms on the electrons in their neighbours. Thus if the polarization remains after the electric force is removed the current will remain too, just as it did in Kamerlingh Onnes' experiment with the lead ring. The argument is similar to that by which Weiss explained the existence of permanent magnetism below a critical temperature.

We see that we shall have the current remaining after the removal of the electric force; *i. e.*, the metal will be in the super-conducting state as soon as the slope of the line is less than that of the tangent at the origin to the curve, *i. e.* when

$$\frac{w}{kM} \text{ is less than } NM'F'(0),$$

$$\text{or} \quad w \text{ less than } kNM^2F'(0).$$

Thus the temperature at which the metal passes into the super-conducting state is such that

$$w = NM^2kF'(0).$$

$NMk$  is the electrical force exerted by the doublets when they all point in one direction: if we denote this force by  $P$ ,

$$w = MPF'(0).$$

If the specific heat of the metal had not commenced to diminish at this temperature,  $\theta_0$  the temperature of transition into this state would be given by the equation

$$R\theta_0 = NM^2kF'(0).$$

As, however, the transition takes place at very low temperatures, when the specific heats are variable and  $w$  no longer equal to  $R\theta$  we must use a more general expression for  $w$  in terms of  $\theta$  to determine the critical temperature. The persistence of the chains after the removal of the electric force is due to the disturbance due to thermal agitation being too weak to break up the chains when once they are formed. The chains are held together by the electric force due to the doublets in the chain itself as well as by the external electric force, and when we approach the critical temperature the



force due to the doublets is much greater than that due to the external field. We see this from the expression

$$I = \frac{NM^2F'(0)X_0}{w - kNM^2F'(0)}.$$

If  $w_0$  is the value of  $w$  at the critical temperature,

$$w_0 = kNM^2F'(0), \dots \dots \dots (4)$$

so that

$$I = \frac{1}{k} \frac{w_0}{w - w_0} X_0$$

or

$$\frac{kI}{X_0} = \frac{w_0}{w - w_0}.$$

Now  $kI$  is the part of the force on a doublet due to the other doublets, and we see from this expression that when  $w$  is nearly equal to  $w_0$   $kI$  is very large compared with  $X_0$ , so that the removal of  $X_0$  will not appreciably weaken the coherence of the chains. On the other hand, at temperatures considerably above the critical,  $kI$  is small compared with  $X_0$ , so that the external force is essential for the coherence of the chains.

If the disturbing effect on the chains is entirely due to the thermal energy and if this energy vanishes at the zero of temperature, it will always be possible to find a value of  $w$  which satisfies equation (4), and there will always be a critical temperature, *i. e.* the metal will be able to pass into the super-conducting state. It is probable, however, that the action of adjacent atoms may, independently of thermal agitation, tend to make the axes of the doublet take up a definite orientation, and that the doublets, when disturbed from this alignment, come under the action of couples tending to restore them to their original positions. We can easily take this into account, all that we have to do is to replace  $w$  in the preceding equation by  $w + D$ , where  $D$  is proportional to the restoring couple for unit angular displacement, due to the mutually directive action of the atoms. If  $L$  is the local electric force due to the action of the adjacent atoms,  $D = LM$ .

The equation to the straight line (1) is now

$$I = \frac{w + D}{Mk} x - \frac{X_0}{k}. \dots \dots \dots (5)$$

We should expect the directive force either to be independent of the temperature or to vary but slowly with it. In this case the slope of the line will not diminish indefinitely as

the temperature, but will reach a minimum value whose tangent is  $D/Mk$ . If this slope is greater than that of the tangent to the curve at the origin, whose tangent is  $NMF'(0)$ , there will be no critical temperature, hence the condition for a critical temperature is

$$\frac{D}{Mk} \text{ less than } NMF'(0),$$

or  $D$  less than  $w_0$  where  $w_0 = NM^2kF'(0)$ , this is equivalent to  $L$  less than  $PF'(0)$ . The value of  $w$  at the critical temperature is now  $w_0 - D$ .

When the slope of the line is considerable, we have from equations (3) and (5)

$$I = \frac{1}{k} \frac{w_0}{w + D - w_0} X_0,$$

or

$$X_0 = k \frac{(w + D - w_0)}{w_0} \frac{i}{epd} \dots \dots \dots (6)$$

and  $\sigma$  the specific resistance is equal to

$$\frac{k}{epd} \frac{(w + D - w_0)}{w_0} \dots \dots \dots (7)$$

Unless the temperature is very low we may put  $w = R\theta$ , and we have

$$\sigma = \frac{k}{epd} \left( \frac{R\theta + D - w_0}{w_0} \right).$$

If  $\sigma_0$  is the resistance at  $0^\circ$  C., and  $\alpha$  the temperature coefficient of the resistance

$$\sigma = \sigma_0(1 + \alpha t),$$

where  $t$  is the centigrade temperature; comparing this with the previous expression we see that

$$\alpha = \frac{1}{273 + \frac{D - w_0}{R}}.$$

The condition for the existence of a critical temperature is  $D < w_0$ , *i. e.* that the temperature coefficient of the resistance when the temperature is not very low should be greater than  $1/273$ .

When  $D$  is considerable the line (5) will be steep, so that at all temperatures the intersection of the curve and the line will be quite close to the origin; we may, therefore, use

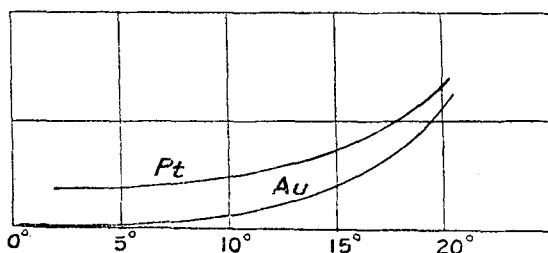
equation (3) even for very low temperatures, so that at all temperatures

$$\sigma = \frac{k}{cpd} \frac{(w + D - w_0)}{w_0}.$$

The temperature coefficient of the resistance is proportional to  $d\sigma/d\theta$ , and this as we see is proportional to  $dw/d\theta$ . This quantity, the rate of increase of the energy with the temperature, is proportional to the specific heat at the temperature.

As the specific heats of many substances are very much smaller at the low temperatures obtained by the use of liquid hydrogen or helium, than at normal temperatures, we see that on this theory the temperature coefficients of metals which have no critical temperature ought to be very small at low temperatures. The experiments of Kamerlingh Onnes, and Dewar and Fleming, show that this is in some cases a very well marked effect. Fig. 4 shows the variation

Fig. 4.



of resistance of gold and platinum suspected of not being quite pure : it will be noticed that at very low temperatures the resistance becomes almost independent of the temperature. Similar effects are shown by many alloys; they would on this theory be shown at low temperatures by any metal or mixture which had not too small a value of  $D$  and whose specific heat fell appreciably at low temperatures.

In fact the general behaviour of alloys seems to admit of a satisfactory explanation on the supposition that in them, or at any rate in those whose resistance is considerably greater than the value calculated from their percentage composition, the restoring couple  $D$  is much greater than in pure metals. This seems what we might expect when the alloy is not a mere mixture; for if it was a definite compound of the two metals, we should expect that there would be a tendency for the axes of the molecules of one metal to have definite orientation with reference to those of the molecules of the other. The same thing would also apply if the metals did

not form definite compounds with each other but did form mixed crystals, we should expect the local force  $L$  to be increased by anything analogous to chemical combination.

We see from the preceding equations that if  $D$  were large for these alloys, they would have (1) a small temperature coefficient at normal temperatures and a very small one indeed at temperatures low enough to diminish the specific heats, (2) they would not have a critical temperature and would never pass into the super-conducting state. These are characteristic properties of the resistance of alloys.

Again, if there are  $m$  molecules of the metal (1),  $n$  of the other (2) per unit volume, we should, from the expressions (7) for the specific resistance of a pure metal, expect that  $\sigma$  the specific resistance of the alloy would be given by a formula of the type

$$\sigma = \left\{ \frac{mk_1}{ep_1d_1} \frac{(w + D_1 - w_0)}{w_0} + \frac{mk_2}{ep_2d_2} \frac{(w + D_2 - w'_0)}{w'_0} \right\} / (m + n).$$

As this involves the restoring couples  $D_1$  and  $D_2$  it cannot be calculated from the resistances of the pure metals; we see, however, that  $\sigma_t - \sigma_T$  the difference between the specific resistances of the alloy at the temperatures  $t$  and  $T$ , is given by the equation

$$\sigma_t - \sigma_T = \left\{ \frac{mk_1}{ep_1d_1} \frac{(w_t - w_T)}{w_0} + \frac{nk_2}{ep_2d_2} \frac{(w_t - w_T)}{w'_0} \right\} / (m + n);$$

the  $D$ 's have disappeared from this equation, and it is exactly the value we should have calculated on the supposition that the alloy is a mechanical mixture. This is the result known as Matthiessen's rule, which states that even when the specific resistance of the alloys cannot, the difference between the resistances at two temperatures can, be calculated from its constituents; another way of stating it is that the difference between the observed and calculated value is independent of the temperature. We have supposed that  $D$  is independent of the temperature; if it changes appreciably with it, as it might be expected to do if the nature of the compounds, or mixed crystals formed by the two metals did so, the temperature coefficients would show anomalies such as those found in alloys which have negative temperature coefficients.

I have shown ('Corpuscular Theory of Matter,' p. 86) that the electric and thermal conductivities will on this theory bear a nearly constant ratio to each other if the electrons which take part in the conduction are in thermal equilibrium with the metal in their neighbourhood.