THE ELECTRON THEORY OF METALS IN THE LIGHT OF NEW EXPERIMENTAL DATA.

BY P. W. BRIDGMAN.

SYNOPSIS.

Deviations from Ohm's Law at High Current Densities of 5×10^6 amp./cm.^{2} have been detected in the case of Au and Ag foils, of the order of 1 per cent. Details will be reported elsewhere.

Effect of Mechanical Tension on Electrical Resistance.—For Li, Ca and Sb, as in the case of most metals, the resistance increases with the tension, whereas for Bi and Sr the coefficient is negative. Details will be reported elsewhere.

Modified Electron Theory of Electrical Conductivity has already been suggested by the author. It is assumed that the number of free electrons is relatively small; that their mean free path is many times the atomic diameter and depends on the amplitude of atomic vibration; and that the natural velocity of the electrons has the equipartition value. It is here *discussed in the light of the above new experimental data.* The deviations from Ohm's law support the theory since they require long mean free paths. For normal atoms for which the resistance decreases with increasing pressure, the electrons must pass directly from atom to atom through intervening atoms; but for the abnormal atoms Li, Ca and Sb, with both pressure and tension coefficients positive, the electrons seem to pass in channels between the atoms, somewhat as in Wien's theory. Diagrams are given showing the relation of the channels to the crystal structure. This simple conception enables the various coefficients of resistance to be connected quantitatively. The tension and temperature coefficients are calculated in terms of the pressure coefficients and the elastic constants and are found to agree approximately with the observed values.

Pressure Coefficient of the Wiedemann-Franz Ratio has been found to be negative for nine out of the eleven metals tested; that is, the thermal conductivity increases with pressure less rapidly than the electrical conductivity. Details will be reported elsewhere.

Elastic Wave Theory of the Atomic Part of Thermal Conduction in Metals.—The above result for the pressure coefficient means that an important part, probably at least one third, of the thermal conduction in these metals is performed by atoms, a conclusion confirmed by a comparison of Lorentz's theoretical value of the Wiedemann-Franz ratio with the experimental value. As a crude *picture of the atomic conduction*, it is suggested that the atoms are arranged in coherent strings separated from each other by gaps which each shift in position by the diameter of an atom each time the string on either side is hit, just like gaps between strings of billiard balls. Thermal energy is transferred when the gap shifts. By calculation, the maximum rate of propagation of a gap comes out about half the speed of sound in the metal, much less than the electronic velocity. The theory of electrical conduction already presented suggests that the length of the coherent strings of atoms is the same as the free path of the electrons, thus making possible a connection between the electronic and atomic contributions to thermal conductivity. If the number of atoms is of the order of 20 times the number of free electrons, as is to be expected from the above theory of electrical conductivity, then atomic conductivity comes out of the proper order of magnitude. A discussion of the temperature and pressure coefficients of the atomic conductivity adds further evidence in favor of the probability of this theory. *Comparison with other theories.* It is similar to Debye's concept of thermal conduction in a crystal, but differs from Hall's ionization theory which, it is concluded, probably can account for only a small part of the conduction.

INTRODUCTION.

IN two papers in preceding numbers of this journal [1, 2] I have presented certain theoretical considerations with regard to the electron mechanism of electrical and thermal conduction in metals. Since writing these two papers, I have obtained three new sorts of experimental evidence bearing on the electron theory. In the first place, I have succeeded in detecting and measuring a departure from Ohm's law at high current densities in metallic gold and silver. In the second place, I have measured the effect of pressures to 12,000 kg./cm.^{2} on the thermal conductivity of eleven metals. And thirdly, I have measured the effect of mechanical tension on the resistance of those metals which are abnormal in that their resistance increases under hydrostatic pressure. It is the purpose of this paper to discuss the bearing of these new data on the electron theory of conduction as I have previously given it.

The theory which I have presented is a free path theory. It differs from the classical theory, which is also a free path theory, in the following respects: the number of free electrons is supposed small compared with the number of atoms, so that the free path is long compared with the distance between atomic centers, and the variations of resistance under changes of temperature or pressure are computed in terms of the variation of free path, which may be found from the variation of amplitude of atomic vibration, and in terms of the natural velocity of the electrons, for which the equipartition value is assumed, as in the classical theory. The evidence for the equipartition velocity is twofold: it is required to account for the universal value of the Wiedemann-Franz ratio, and it is also required to account for the universal value of the temperature coefficient of resistance.

The evidence seemed to be that there are two essentially different types of mechanism by which electrons pass through a metal. By far the most usual type is that of those metals whose resistance decreases with increasing pressure. In these metals it is probable that the electrons pass directly from atom to atom through the substance of the atom itself. There are a few metals, however, whose resistance increases under pressure. There are two possibilities in the way of mechanism for these abnormal metals. In the first place, the mechanism may be like that

[1] P. W. Bridgman, PHYS. REV., 9, 269–289, 1917.

[2] P. W. Bridgman, PHYS. REV., 17, 163–194, 1921.

above in that the electrons pass from atom to atom through the substance of the atom, but the law of force between atoms may be abnormal so that there are abnormalities in the way in which the amplitude changes with pressure (bismuth type), or the electrons may pass between the atoms in natural channels, much after the manner of the theory of Wien[3] (lithium type).

The Evidence from Ohm's Law.—The data are to be presented in detail in another place. The experimental fact is that the resistance of gold and silver in the shape of thin leaf has been found to increase by something of the order of one or two per cent. at current densities of the order of $5 \times 10^{\circ}$ amp./cm^2. Now J. J. Thomson[4] showed long ago on the basis of the classical theory that the resistance would be expected to increase at very high current densities, because the velocity of drift imparted to the electrons by the external field would no longer be small compared with the natural velocity of the electrons. It is evident that the velocity of drift imparted by the external field will be greater the longer the free path, that is, the longer the time in which the field has a chance to act on the electron without interference. On the basis of the length of free path assumed by the classical theory, which is equal to or less than the distance between atomic centers, the departures from Ohm's law would not begin to play an important rôle at currents below 10^{11} amp./cm^2. Since I am also assuming a free path mechanism, the fact that I find departures from Ohm's law at densities so much lower than predicted by the classical theory must mean that the free paths are much longer than the distance between atomic centers. Now this is exactly the kind of free path that other kinds of evidence have already made seem probable to me, so that this new experimental fact affords confirmation of the theory.

It is unfortunate that I can see no way of calculating exactly what the free path is in terms of the departures from Ohm's law. Such a computation involves a knowledge of the small departures from Maxwell's distribution law for the electrons at high fields, and this again I believe involves a detailed knowledge of the whole atomic structure. I am compelled therefore at present to leave this new experimental evidence with the bare statement that it makes exceedingly probable a long free path, and is in so far in accord with my theory.

Effect of Pressure on Thermal Conductivity.—The data for eleven metals are to be published in another place, to which reference must be made for the details. Only normal metals, whose electrical resistance decreases

---

[3] W. Wien, Columbia Lectures, 1913, 29–48.

[4] J. J. Thomson, The Corpuscular Theory of Matter, 1907, p. 55.

under pressure, were measured. The broad facts are that the thermal conductivity may either increase or decrease under pressure. For only two metals was the increase of thermal conductivity greater than the increase of electrical conductivity; for these two metals (lead and tin) the Wiedemann-Franz ratio increases under pressure, for the other metals it decreases.

In my theory I took over without essential modification the classical picture of thermal conduction as performed by the same electrons that carry the current. The reason for this was that I could see no other way of accounting for the approximate constancy of the Wiedemann-Franz ratio for different metals, and this seemed to me the one most striking and outstanding fact with regard to thermal conduction. So far as the conduction of electrical current and heat is by the same mechanism, one may expect the effect of pressure on the electrical and thermal conductivity to be the same, and hence the pressure coefficient of the Wiedemann-Franz ratio to be zero. The new experimental evidence requires therefore a reconstruction of our previous picture of the mechanism of thermal conduction. The modification is not very serious, however, and does not require us to abandon anything of our previous position. It has of course always been known that the picture of thermal conduction offered by the classical theory is not complete in that it neglects the part of the heat carried by the atoms. We now have to inquire what the probable magnitude of this neglected part of the thermal conductivity is, and whether it is not capable of explaining the new facts.

With regard to the probable magnitude of the atomic part of thermal conduction, it is well known that the original value of the Wiedemann-Franz ratio deduced by Drude from elementary considerations agrees with the experimental facts much better than the more rigorous value deduced by Lorentz,[5] Bohr,[6] and others. Lorentz's value is only two thirds that of Drude, and Drude's is slightly less than the experimental value. If we accept Lorentz's value as the one properly to be deduced from the theory, and his work has been abundantly checked by others, this would mean that the atomic part of the electrical conductivity may be at least half as large as the electronic part. This is a fairly large part to have at our disposal.

Now the electronic part of the thermal conductivity must increase under pressure at the same rate as the electrical conductivity. But the atomic part may conceivably either increase or decrease, and so the pressure coefficient may be either positive or negative. The only absolute requirement here is that the total decrease of conductivity under

[5] H. A. Lorentz, The Theory of Electrons, p. 65.

[6] N. Bohr, Studier over metallernes Elektrontheori, Copenhagen, 1911.

pressure must never be so great as to more than use up the initial atomic contribution, because the atomic contribution must always remain positive. In the experimental paper this question is examined in detail, and I have shown that there is never any trouble on this score.

We now have to consider more in detail what the nature of the atomic part (more specifically, the part not determined by the classical electron free path mechanism) of the thermal conductivity may be, and what may be expected as to the sign of its pressure coefficient. The following picture seems to satisfy the requirements as far as order of magnitude goes, and has the advantage of using part of the same mechanism that we have invoked to explain electrical conductivity. In the normal metal I have thought of the electron as passing through the substance of the atom, with a free path a good many atomic diameters long. A crude picture of this state of affairs is that the atoms in a metal are separated into many coherent strings, one string separated from the next by a distance greater than the normal, that is, by a "gap." These strings are in a constant state of flux, as the position of the gaps is continually changing. The length of the string is the free path of the electrons for electrical conduction. The mechanism by which the gap wanders about in the metal is an elastic mechanism; we imagine the head of the string being struck by the rear atom of the string ahead of it; the impacting atom sticks to the string, an impulse travels along the string, and the rear atom flies off, exactly as when a row of billiard balls in contact is struck by a single ball head on. Under the most favorable conditions the gap cannot travel ahead by more than the diameter of an atom during the natural period of atomic vibration. Now the natural period is known for a number of metals, and a numerical calculation shows that for all metals this maximum velocity of propagation of the gap is about one half the velocity of sound. This is much less than the velocity of free flight of the electrons. At 0° C. this latter is about 1.7×10^7 cm./sec., and the maximum velocity of sound for any metal is about 5×10^5. This means that for the electrons the gaps are practically stationary, so that our former picture of conduction is not at all affected by the motion of the gaps.

Now the mechanism of translation of the gaps, that is, the sticking of an atom to the head of the string and the flying off of one from the rear, is evidently one that is capable of conducting heat, if there is a temperature gradient in the metal. Precisely the same analysis may be applied to this case as to the ordinary kinetic problem of heat transfer. The important feature is that the free path for heat transfer is the same as the free path for electrical conduction. In my theory of conduction I have assumed that there is equipartition of energy between the atoms and electrons. Let us call $f(\theta)$ the energy of either atom or electron as a function of temperature. Then for the part of the thermal conductivity due to the atoms, the ordinary transport analysis will give the formula

$$\mu_a = nl\frac{df}{d\theta},$$

and for the part due to the electrons the same analysis will give

$$\mu_e = \frac{1}{3}N_e v_e l\frac{df}{d\theta}.$$

Here N_e is the total number of free electrons (that is, electrons which take part in the conduction process) per cm.^{3}, v_e is the velocity of the electrons, l is the free path, and n is the number of atomic transfers of energy per second across unit section. Of these quantities n is the only one requiring further discussion. Its exact value will depend to a high degree on the structure of the crystal and the perfection of the fit between neighboring atoms, but we can at least set an upper limit. The maximum number of transfers of energy down each string of atoms is evidently the frequency of atomic vibration, ν, for this is the maximum number of collisions of the head of the string with the rear of the next. The number of strings crossing unit section is the number of atoms in unit section, or $N_a^{2/3}$, where N_a is the number of atoms per cm^3. Hence an upper limit for n is $\nu N_a^{2/3}$. If now we substitute this upper limit for n in the formula for μ_a, and take the ratio of the atomic to the electronic conductivity, we get

$$\frac{\mu_a}{\mu_e} = \frac{N_a}{N_e}\left(\frac{3\nu}{v_e N_a^{1/3}}\right).$$

The reasonableness of this may be checked as far as order of magnitude goes as follows. In the first place, μ_a/μ_e must be in the neighborhood of 0.5, for the actual Wiedemann-Franz ratio is usually about 50 per cent. greater than Lorentz's theoretical value. In the second place, my theory of electrical conduction demands that N_a/N_e be large, perhaps of the order of 100 or 1,000. If the velocity of migration of the gaps through the metal is the maximum, then N_a/N_e given by the above formula must also be of the same order, but since the migration velocity may well be much below the maximum, we may expect N_a/N_e to be smaller than the above, but still materially larger than unity. I have made the calculation in this way, putting $\mu_a/\mu_e = 0.5$, for the metals Al, Cu, Zn, Ag, and Pb. Nernst[7] gives the value of the frequency of these, and the other

---

[7] W. Nernst, Wolfskehlstiftung Vorträge, Göttingen, 1914, p. 77.

constants are well known. I find the following values respectively for N_a/N_e; 10, 15, 15, 15, 30. The order of magnitude of these is hence about what would be expected.

Another check as to the probability of this point of view is afforded by the variation of thermal conductivity with temperature. My theory of electrical conductivity gives a variation of electrical resistance as the absolute temperature, which of course agrees very approximately with the facts. Now theoretically the Wiedemann-Franz ratio is proportional to the absolute temperature; this means that that part of the thermal conductivity due to the electrons is independent of the temperature. This enables us to find at once the temperature coefficient of the atomic part of the thermal conduction. To find this, differentiate μ_e logarithmically, obtaining

$$\frac{1}{\mu_e}\frac{d\mu_e}{d\theta} = \frac{1}{N_e}\frac{dN_e}{d\theta} + \frac{1}{v_e}\frac{dv_e}{d\theta} + \frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right).$$

We suppose, as always, that N_e is constant, and since $d\mu_e/d\theta$ is to be zero, this gives

$$\frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right) = -\frac{1}{v_e}\frac{dv_e}{d\theta} = -\frac{1}{2\theta},$$

since v_e^2 is proportional to θ. Now differentiate μ_a logarithmically, obtaining

$$\begin{aligned}\frac{1}{\mu_a}\frac{d\mu_a}{d\theta} &= \frac{1}{n}\frac{dn}{d\theta} + \frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right)\\ &= \frac{1}{n}\frac{dn}{d\theta} - \frac{1}{2\theta}.\end{aligned}$$

Now assuming that n is a fixed fraction of its maximum value, the variation of n with temperature is small, since that of its factors N_a and ν is small, and may be neglected. (I have previously discussed the variation of ν with temperature.)[8] Hence finally,

$$\frac{1}{\mu_a}\frac{d\mu_a}{d\theta} = -\frac{1}{2\theta}.$$

If now we attempt to allow for a change with temperature of the fractional part of its maximum value which n assumes, the probability seems to me that this fractional part will increase with rising temperature, since the change in amplitude of atomic vibration with rising temperature is large compared with the change in the distance of separation of atomic centers. This would mean that the temperature coefficient of the atomic part of thermal conductivity is more nearly positive than $-1/2\theta$.

---

[8] Reference 1, equation (4), p. 271.

We have now found that the atomic part of the thermal conductivity decreases with rising temperature. The other part remains constant, and hence we would expect the temperature coefficient of thermal conductivity of all metals to be negative, and to be largest numerically in those metals in which the atomic share in conductivity is largest. Now a large Wiedemann-Franz ratio means a larger proportional atomic conductivity. Hence if we plot Wiedemann-Franz ratio against temperature coefficient of thermal conductivity, we would expect the high values of the one to go with the high values of the other. I have plotted these values in Fig. 1 for most of the metals of this paper. It is known that the temperature coefficient is extremely subject to experimental error, and different observers do not always agree. I have used the data of Jaeger and Diesselhorst,[9] by far the best, who made all the different sorts of measurements on the same samples of metal. Only for nickel do Jaeger and Diesselhorst not give the coefficient, and I have taken the temperature coefficient of conductivity from another observer.[10] All the metals of my pressure study are here included except antimony. With the exception of platinum, whose temperature coefficient of thermal conductivity is + 0.0005, and hence is entirely out of the class of the other metals, the correlation is strong between Wiedemann-Franz ratio and temperature coefficient, and hence lends probability to our view. With regard to platinum it may be said that its electrical resistance also behaves abnormally with regard to temperature, since it is one of a very few metals for which the curve of resistance against temperature is concave toward the temperature axis.

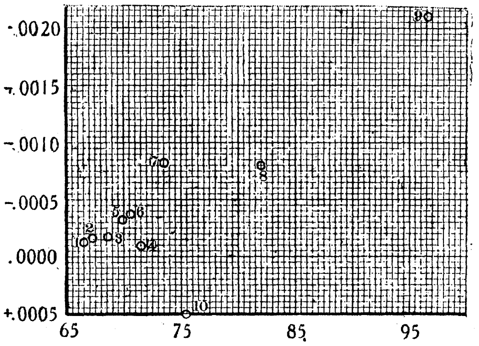

Fig. 1.

Temperature coefficient of thermal conductivity (ordinates) against Wiedemann-Franz ratio times 10^{-9} (abscissae). The metals shown are as follows: 1 Cu, 2 Zn, 3 Ag, 4 Pb, 5 Ni, 6 Cd, 7 Sn, 8 Fe, 9 Bi, 10 Pt.

---

[9] W. Jaeger und H. Diesselhorst, Phys. Tech. Reichsanstalt, Wiss. Abh. 3, 269–425, 1900.

[10] M. F. Angell, Phys. Rev., 33, 421–432, 1911.

This point of view imposes a limit on the possible temperature coefficient of thermal conductivity. This must not be so high that the coefficient of the atomic part alone gets numerically greater than $-1/2\theta$, or about -0.0018. This is true for all the metals above except bismuth, which of course is abnormal in other respects. The restriction is most exacting in the case of tin, but is still met with a few per cent. margin of safety.

So much for the inherent probability of our picture of the part of thermal conductivity done by the atoms. Now with regard to the effect of pressure on this part of the conductivity, we may recognize two opposing tendencies.

Differentiate μ_a and μ_e logarithmically at constant temperature, obtaining

$$\frac{1}{\mu_a}\left(\frac{\partial \mu_a}{\partial p}\right)_\theta = \frac{1}{n}\left(\frac{\partial n}{\partial p}\right)_\theta + \frac{\partial}{\partial p_\theta}\log\left(l\frac{df}{d\theta}\right)$$

and

$$\frac{1}{\mu_e}\left(\frac{\partial \mu_e}{\partial p}\right)_\theta = \frac{1}{N_e}\left(\frac{\partial N_e}{\partial p}\right)_\theta + \frac{1}{v_e}\left(\frac{\partial v_e}{\partial p}\right)_\theta + \frac{\partial}{\partial p_\theta}\log\left(l\frac{dt}{d\theta}\right).$$

We suppose that N_e remains constant, and our assumption with regard to equipartition also means that v_e is constant at constant temperature. Hence $(1/\mu_a)\ (\partial\mu_a/\partial p)_\theta$ differs from $(1/\mu_e)\ (\partial\mu_e/\partial p)_\theta$ only by the term $(1/n)\ (\partial n/\partial p)_\theta$. Now in general we may put $n = \beta\nu N_a^{2/3}$, where β is a factor which at the maximum can reach only unity. The variations of N_a with pressure are comparatively unimportant, so that if β does not change, the proportional change of n is determined by the proportional change of ν. This has been computed in a previous paper.[11] It is the negative of the proportional change of amplitude, which in turn is approximately one half the pressure coefficient of resistance. ν therefore increases under pressure, and at such a rate as to contribute to the atomic part of the conductivity an increase about one half as rapid as the increase of electrical conductivity. The other factor, β, however, is the one that is likely to be important. Our previous discussion of the order of magnitude of N_a/N_e shows that β is probably much below its maximum value of 1, so that there is plenty of room for variations in either direction. I do not believe that we can predict its precise manner of variation until we know a great deal about atomic structure and the arrangement of the atoms in the crystal. The factor β is a measure of the frequency with which energy is handed on from one string of atoms to the next, and it is also a measure of the speed of migration of the gaps through the metal. Now a gap is a joint or fissure in the atomic structure due to

---

[11] Reference 1, equation (5), p. 271.

temperature agitation. Its permanence, or its ease of migration, will obviously depend on the details of the structure. It seems quite plausible to me that the speed of migration or mobility might either increase or decrease under pressure, with the probability that in most cases it will decrease, because with increasing pressure a group of atoms must find it more difficult to escape from their lack of fit by handing it on to the neighbors. An escape from lack of fit would seem to involve a local and temporary increase of volume, which is against the urge of the external pressure. The mobility of the gaps may involve something analogous to the internal viscosity of the metal. This has never been measured under pressure, but it is known that the viscosity of liquids increases greatly with pressure, and that the increase is proportionally greater for those substances with a high absolute value of viscosity, so that it is not unreasonable to expect a comparatively large pressure effect on the internal viscosity of metals.

As a matter of fact, it does turn out in the majority of cases that the increase of thermal conductivity is smaller than the electrical conductivity, or else is negative, so that the atomic part of thermal conductivity in many cases must decrease. In the case of lead and tin only is the increase of thermal conductivity so large as to indicate that for them β may increase with pressure.

This picture of the atomic part of thermal conduction is in many respects like Debye's[12] concept of thermal conduction in a crystal. He has heat conducted by elastic waves, which are dissipated by the lack of perfect homogeneity of the material. The waves have an equivalent "free path" defined in terms of the distance between inhomogeneities. He finds the cause of the inhomogeneities in local chance variations from the mean density, which he calculates by the thermodynamic formulas for "Schwankungen." His local inhomogeneities evidently function as my gaps, and in fact may be the same thing physically. Debye did not discuss metallic conduction. My assumption that the free path of the elastic waves is the same as that of the electrons seems a most natural one, but so far as I know, has not been employed before. Notice in this connection that the purely atomic part of the conductivity in a metal is large compared with the total conductivity of such crystals as rock salt.

There are other possible factors to be taken into account. In the first place, the free path is not actually so cleanly defined a thing as we have supposed above. As the electrons pass from atom to atom they are subject to a certain amount of interference at every passage; there

---

[12] P. Debye, Wolfskehlstiftung Vorträge, Göttingen, 1914, 43–60.

is no catastrophic change every now and then as we have supposed, and the free path idea can only be a rough description of an average state of affairs. The same sort of thing must of course be recognized in applying kinetic theory to condensed gases or liquids. Kleeman has emphasized in his recent book[13] this indefinite character of the concept of a free path, and has shown that a great many kinds of free path must be recognized. For any particular sort of phenomenon, mean free path is defined in a corresponding particular way. The free path for viscosity, for example, is defined in terms of velocity transfer, and for heat conduction in terms of energy transfer. Kleeman has shown that different sorts of free path may differ in rare cases by factors of as much as 10. We would expect to find the same sort of thing in a metal, so that the free path of electrical conductivity (which is concerned with a velocity transfer) would not be the same as the free path of thermal conductivity (which is concerned with a kinetic energy transfer). This may account partly for the difference between the observed and computed Wiedemann-Franz ratio. It is also possibly conceivable that the two different kinds of path should be differently affected by pressure, so that the pressure coefficients might have opposite signs. The theory is not far enough advanced, however, to allow us to make any quantitative use of it. All that has hitherto been done is to calculate back from the experimental data to show that there must be different kinds of path if the kinetic formulas are correct. We cannot yet solve the direct problem of predicting in terms of the atomic structure what the relation between the different sorts of path will be, and it is the direct problem that must be solved for the present purpose.

There is a second possibility that I have considered. Professor Hall[14] has a theory of thermal conduction in terms of the heat of ionization of the atoms. This sort of a mechanism seems at first sight exactly what we need to explain the pressure coefficient of thermal conduction, because it is natural to suppose that the heat of ionization becomes less as the pressure becomes greater, and for this reason the thermal conductivity would decrease with rising pressure. But there is another factor to consider, namely, the number of ions per cm^3. If this number is connected with the heat of dissociation by the ordinary formula $n = n_0 e^{-(w/K\theta)}$, a decrease in the heat of ionization will be accompanied by an increase in the number of ions, so that for this reason the thermal conductivity will increase. A numerical discussion with probable values, for instance assuming such a heat of ionization that the atoms are 1/1,000 ionized, shows that the increase of numbers far overbalances the decrease of

[12] R. D. Kleeman, A Kinetic Theory of Gases and Liquids, Wiley and Sons, 1920.

[14] E. H. Hall, PHYS. REV., 11, 329, 1918.

heat of ionization, so that on the whole the conductivity will increase under pressure, instead of decrease. Another objection to Professor Hall's theory is that it gives no account of the Wiedemann-Franz ratio. Of course a mechanism like that of Professor Hall's theory must be present in the metal, simply because the presence of free electrons involves the presence of ions, but my own feeling is that this part of thermal conduction is not so important as some others.

Effect of Tension on the Resistance of the Abnormal Metals.—The experimental results are published at length in another place. Briefly, the essential facts are these. There are five metals known to be abnormal in that their resistance increases under pressure, Bi, Sb, Li, Ca, and Sr. Of these only two, Bi and Sr, are abnormal also with respect to the effect of tension, in that their resistance decreases under tension. The resistance of Li, Ca, and Sb increases under tension, as is normal. In the detailed paper I have shown that the metals with a "Bismuth mechanism" would be expected to act as Bi does under both tension and pressure, and that metals of the "Lithium mechanism" would be expected to act like Sb, Li, and Ca under tension and pressure. Considerations were given that made it likely that both sorts of mechanism were involved in Sr.

It is my purpose here to consider further the three metals Li, Ca, and Sb. The account which I have previously given of the effect of pressure and temperature does not apply to metals of this type. Further, the three metals are of particular interest in the apparently great simplicity of their mechanisms. This simplicity makes possible a deduction of expressions for the temperature and tension coefficients of resistance in terms of the pressure coefficient and other unrelated data.

In metals of the lithium type, the electrons are to be thought of as travelling in channels between the atoms. Under external changes, the channels change in dimensions, both because the centers of the atoms are changed in position and because the amplitude of atomic vibration is changed. For those changes which take place at constant temperature our problem is to deduce the changes of resistance in terms only of the changes in cross section of the channels; if the temperature changes also, the change of resistance involves both the change of dimensions of the channels and the changes of velocity of the electrons with temperature.

The details of the computation will involve a knowledge of the crystalline structure and the relation of the channels to that structure. The structure of lithium is known to be space centered cubic;[15] the structure of

---

[15] A. W. Hull, Phys. Rev., 10, 689, 1917.

calcium is face centered cubic;[16] the structure of antimony is complicated,[17] consisting of two interpenetrating lattices, but it is very approximately simple cubic in structure, and for our purposes it will be good enough to treat it as simple cubic.

In Fig. 2 is shown a view of spheres piled in space centered cubic arrangement, the diameters of the spheres being such that they are in contact with each other. The dotted circles show the spheres in the layer below the full spheres. The diagram shows that there are open channels between the spheres through which the electrons may pass. Of course if the atoms are not large enough to be in mutual contact, the channels are even larger.

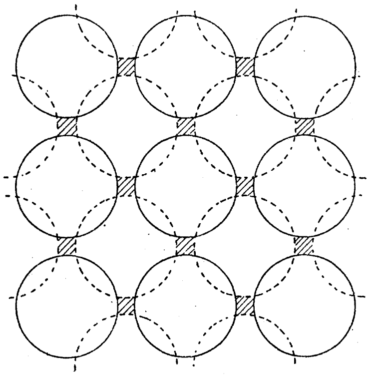

Fig. 2.

One view of spheres in contact in space centered cubic arrangement. The shaded areas indicate open channels.

In Fig. 3 is shown one view of spheres in mutual contact in face centered

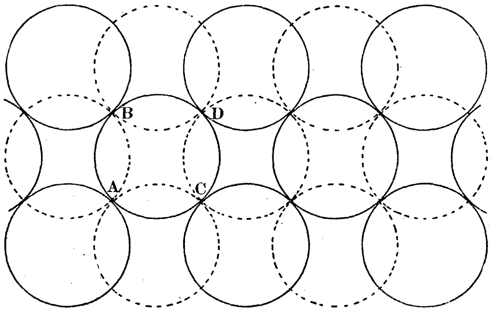

Fig. 3.

One view of spheres in contact in face centered cubic arrangement. Channels open where shown by the letters if the distance between atomic centers is slightly increased.

---

[16] A. W. Hull, PHYS. REV., 17, 42–44, 1921.

[17] R. W. James and N. Tunstall, Phil. Mag., 40, 233–239, 1920.

cubic arrangement. Now in this structure there are no open straight channels, but if the centers of the spheres are held fast, while their radii decrease, channels open in the locations indicated by the letters, and the plane section of the crystal becomes similar to that of the space centered crystal of Fig. 2. In fact Fig. 3 goes into Fig. 2 on rotation through 45°. (The distance of separation of the planes of the full and the dotted spheres does not become the same for the two kinds of crystal, however.) Now the crystallographic evidence proves that in the crystal of metallic calcium the atoms cannot be in contact,[18] and hence we assume the channels in metallic calcium to be in the place shown.

If the structure is simple cubic with the spheres in contact, the spaces between the full circles of Fig. 2 show the location of the channels. It seems more likely, however, that the atoms of Sb are not spherical, but are more nearly cubic, filling the space more completely. One reason why this seems probable is that spheres in simple cubic piling are exceedingly unstable, whereas cubes in simple cubic piling are as stable as possible. Fig. 4 therefore probably represents a closer approach to the case for antimony, the atoms having the shape of rounded cubes, and the channels being in the grooves between the edges, as shown.

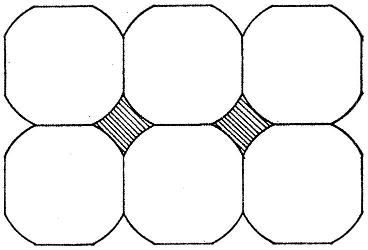

Fig. 4.

One view of approximately cubic atoms in simple cubic piling. The shaded regions show open channels.

We have now to consider the effect of temperature agitation on the size of the channels. The atom is to be thought of as of a fixed size, but at higher temperatures it occupies an effectively larger space in virtue of its temperature agitation. Under these conditions the section of the channel for all three types of crystal structure may be represented approximately as in Fig. 5. The full circles show the outlines of the stationary atoms, and the dotted circles the space effectively occupied by them in virtue of temperature agitation. If we call "a" the radius of the atom, α its amplitude of temperature vibration, c the width of the

---

[18] Reference 16, p. 44.

channel at the place shown, and L the distance between atomic centers in the direction indicated, then

$$L = 2a + 2\alpha + c.$$

Call δ the closest distance of approach of atomic centers. There is a relation between L and δ which is different for the different crystal systems.

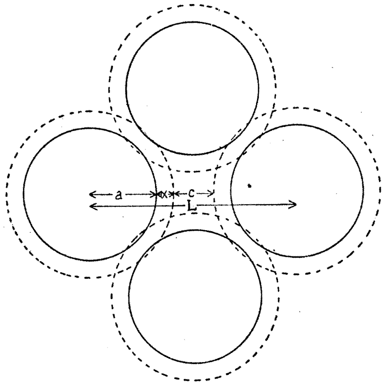

Fig. 5.

Shows the effective relations between the size of the atom, the space occupied by temperature agitation, and the open channels.

Simple cubic, $L = \sqrt{2}\delta$,
Face centered cubic, $L = \delta$,
Space centered cubic, $L = \frac{2}{\sqrt{3}}\delta$.

We now assume the free path of the electron, l, to be proportional to the section of the channel, which to a sufficient degree of approximation we may put equal to c^2. (The precise factor of proportionality between the area of the channel and c^2 does not enter the result so long only as it stays constant.) The resistance is inversely as l, and directly as v, the electronic velocity.

Our program calls in the first place for a computation of c in terms of the pressure coefficient of resistance, and then for a computation of the tension and temperature coefficients.

Denote the resistance by w. Then at constant temperature,

$$w = \frac{\text{const.}}{c^2},$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta = -\frac{2}{c}\left(\frac{\partial c}{\partial p}\right)_\theta,$$

whence

$$c = -\frac{2\left(\dfrac{\partial c}{\partial p}\right)_\theta}{\dfrac{1}{w}\left(\dfrac{\partial w}{\partial p}\right)_\theta}.$$

$(1/w)\,(\partial w/\partial p)_\theta$ is known experimentally. To find $(\partial c/\partial p)_\theta$ we have

$$\left(\frac{\partial L}{\partial p}\right)_\theta = 2\left(\frac{\partial \alpha}{\partial p}\right)_\theta + \left(\frac{\partial c}{\partial p}\right)_\theta.$$

$(\partial L/\partial p)_\theta$ may be found as follows. Obviously

$$\frac{1}{L}\left(\frac{\partial L}{\partial p}\right)_\theta = \frac{1}{3}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\theta,$$

and the cubic compressibility is known. We now need the absolute value of L. The absolute value of δ may be found in terms of the atomic volume, V, and the mass of the hydrogen atom by the formula

$$\delta = \gamma(m_H V)^{1/3},$$

where γ is a factor depending on the crystal system.

Simple cubic, $\gamma = 1$,
Face centered cubic, $\gamma = (2)^{1/6} = 1.123$,
Space centered cubic, $\gamma = \dfrac{\sqrt{3}}{2^{2/3}} = 1.09$.

Using the above equations for L in terms of δ, we can now find the absolute value of L, and hence can compute $(\partial L/\partial p)_\theta$.

Our next problem is to compute $(\partial \alpha/\partial p)_\theta$. In a previous paper[19] I have shown that

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\theta = -\left(\frac{\partial v}{\partial \theta}\right)_p \Big/ C_p.$$

Hence we can find $(\partial \alpha/\partial p)_\theta$ if we can find α. To get α, we use the equipartition law. In a solid, the atom has six degrees of freedom, and therefore its maximum kinetic energy is twice the energy of a gas molecule at the same temperature. If the atom executes simple harmonic vibrations of frequency ν, at 300° Abs. we have

$$\frac{m}{2}4\pi^2\nu^2\alpha^2 = 2 \times 300 \times 2 \times 10^{-16}.$$

The problem of determining α is reduced to determining ν. The best way would be from the specific heats at low temperatures, but the data

---

[19] Reference 1, equation (6), p. 271.

do not seem to have been obtained. In default of a better, we may use Lindemann's formula in terms of melting temperature, atomic weight, and atomic volume

$$\nu = 3.08 \times 10^{-12}\sqrt{\frac{T_s}{mV^{2/3}}}.$$

We now have all the material to compute the required quantities, eventually getting c, and also a, the atomic radius.

Our next task is to compute the changes of resistance under tension. Our general picture is as follows. When the metal is stretched longitudinally it contracts transversely, the channels becoming constricted, and the resistance increases. Since the tension is applied at constant temperature, we have as before $w = \text{const.}/c^2$, and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta = -\frac{2}{c}\left(\frac{\partial c}{\partial T}\right)_\theta,$$

where T denotes tension. $(\partial c/\partial T)_\theta$ can be found from the equation $L = 2a + 2\alpha + c$, provided we can get $(\partial \alpha/\partial T)_\theta$, for $(\partial L/\partial T)_\theta$ may be obtained in terms of the elastic constants. In fact

$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_\theta = -\frac{\sigma}{E},$$

where σ is Poisson's ratio, and E is Young's modulus. With regard to the changes of α under tension, we do not know much. In the first place, the substance becomes anisotropic under tension, so that changes of α are different in different directions. It is probable, however, that the changes of α are not important, and we shall neglect them. This may be approximately justified as follows. Neglecting anisotropy, a thermodynamic discussion of the changes of the average α with tension may be carried through on the same basis as the preceding discussion for the changes of α with pressure.[20] In that analysis we should have to replace p by T, and v (volume) by l (length). We would find for the final result

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial T}\right)_\theta = -\left(\frac{\partial l}{\partial \theta}\right)_T \Big/ C_T.$$

Now C_T, specific heat at constant tension, is very nearly the same as C_p, and $(\partial l/\partial \theta)_T = \frac{1}{3}(\partial v/\partial \theta)_p$. Therefore the proportional change of α under 1 kg./cm.^{2} tension is approximately one third of its change under 1 kg./cm.^{2} pressure. But on the other hand, the changes of dimensions under 1 kg. tension are considerably larger than under 1 kg. pressure, so that

---

[20] Reference 1, p. 271.

it is probable that under tension changes of α are relatively much less important than under pressure. But an examination of the figures above will show that even under pressure the changes of α are not important compared with the changes of dimensions (L), and we shall therefore neglect $(\partial\alpha/\partial T)_\theta$.

Hence we have

$$\left(\frac{\partial c}{\partial T}\right)_\theta = \left(\frac{\partial L}{\partial T}\right)_\theta = -\frac{L\sigma}{E},$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta = \frac{2}{c}\frac{L\sigma}{E}.$$

The tension coefficient is computed in this way and listed in the table. The computed value is 2/3 the observed value for Li, and 3/2 of it for Ca and Sb.

Finally we have to compute the temperature coefficient of resistance. According to our previous theory the changes of resistance with temperature depend on two factors; one of these is the change of the velocity of the electrons with temperature. This part of the change is $1/2\theta$, and is the same now as previously. The second part of the change of resistance is due to the change of free path. For normal metals I have shown that this change is also $1/2\theta$. The free path mechanism of these three abnormal metals is, however, entirely different from that of the normal metals, and the previous analysis fails. Our problem is to recompute the second part of the variation.

Now for changes of temperature, the conditions are the exact reverse for changes of tension. Here the changes of dimensions of the metal are unimportant compared with the changes of amplitude of atomic vibration. One may easily check this by a simple calculation. (I have already gone into the matter in connection with the pressure effects.)[21] In order to entirely get rid of the effect of changing dimensions, we will compute the temperature coefficient of resistance at constant volume instead of at constant pressure. The two coefficients differ by only a few per cent.; the exact formulas will be found in the place last cited.

For changes of resistance at constant volume we now have

$$\frac{1}{w}\left(\frac{\partial w}{\partial \theta}\right)_v = \frac{1}{2\theta} - \frac{2}{c}\left(\frac{\partial c}{\partial \theta}\right)_v.$$

To find $(\partial c/\partial\theta)_v$, we differentiate the equation $L = 2a + 2\alpha + c$, obtaining

$$\left(\frac{\partial c}{\partial \theta}\right)_v = -2\left(\frac{\partial \alpha}{\partial \theta}\right)_v.$$

---

[21] Reference 1, p. 272.

Metal.	$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta$.	$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\theta$.	ν.	δ.	L.	$\left(\frac{\partial L}{\partial p}\right)_\theta$.	α.	$\left(\frac{\partial \alpha}{\partial p}\right)_\theta$.
Li.......	6.8×10^{-6}	-10×10^{-6}	10.6×10^{12}	3.11×10^{-8}	3.60×10^{-8}	-10.8×10^{-14}	2.16×10^{-9}	-21.6×10^{-15}
Ca.......	10.6	-7.7	5.4	3.94	3.94	-7.5	1.77	-13.7
Sb.......	12.2	-2.26	3.23	3.18	4.46	-3.57	1.71	-3.86

	$\left(\frac{\partial c}{\partial p}\right)_\theta$.	c.	a.	$-\frac{2}{c}\left(\frac{\partial c}{\partial T}\right)_\theta$.	$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta$.	$\frac{1}{\theta}\left(\frac{1}{2}+\frac{2\alpha}{c}\right)$	$\frac{1}{w}\left(\frac{\partial w}{\partial \theta}\right)_v$.
Li...........	-6.5×10^{-14}	1.91×10^{-8}	0.62×10^{-8}	3.2×10^{-5}	4.8×10^{-5}	.0027	.0043
Ca...........	-4.8	0.905	1.34	1.24	0.84	.0033	.0030
Sb...........	-2.80	0.459	1.83	0.73	0.50	.0046	.0049

But we have already found that

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\theta}\right)_v = \frac{1}{2\theta}\cdot$$

Hence finally

$$\frac{1}{w}\left(\frac{\partial w}{\partial\theta}\right)_v = \frac{1}{\theta}\left(\frac{1}{2} + 2\frac{\alpha}{c}\right).$$

The results of computation by this formula are given in the table. The result is distinctly low for Li, but is as close to the experimental value as could be desired for Ca and Sb. The agreement would be expected to be closer for the temperature than for the tension coefficient, because there is here no assumption so questionable as our neglect of $(\partial\alpha/\partial T)_\theta$ in computing the tension coefficient.

Comment seems to be called for in one particular with regard to the values found for lithium. The calculated atomic radius is so small that the spheres of influence do not overlap, and the effective section of the channels is not in appearance like that shown in Fig. 5. I have therefore made a more exact computation for this case, putting as the fundamental equation

$$\text{Area of channel} = L^2 - 2\pi(a + \alpha)^2.$$

The analysis may be carried through on the exact lines of the above, except that instead of linear equations there are quadratics to solve. The result differs by only a few per cent. from that found by the simpler method, and it does not seem worth while to reproduce it. The essential feature in determining the result is the variation of the channel as c^2. It is also to be noticed that the values found for the radius of antimony justify our assumption of the rounded cube shape.

In connection with the small value of the effective radius of lithium as compared with the distance between atomic centers in the metal, it is interesting that Born[22] has recently arrived at a result of the same order of magnitude for the diameter of the lithium ion in solution. His value for the effective radius is 0.45×10^{-8} cm. against 0.62×10^{-8} cm. calculated above. Born states that the nature of his approximations is such that his result is small rather than large.

Our picture of the mechanism has been crude in the following particulars, among others. In the first place the assumption of the quantum theory of solids, which is at the basis of the formulas for the variations of α and ν, that the entropy is a function only of ν/θ, is probably not exact, and at any rate should have more careful verification. In the second place, Lindemann's formula for the frequency in terms of the melting

---

[22] M. Born, ZS. Elektrochemie, 26, 304, 1920.

temperature is known to be only an approximation for a number of substances. Thirdly, our assumption that the atoms act as if possessing a well-defined bounding surface of surface of definite shape can only be an approximation. In the case of lithium this approximation would seem to be particularly rough when one considers the atomic structure of lithium in terms of a nucleus and only three surrounding electrons. In fact, it is most difficult to see how the atom of lithium can have such a symmetry as to compel a crystal edifice of space centered cubic symmetry.

In view of the roughness of many of the assumptions it seems to me that the agreement of the observed with the computed values is as close as could be expected, and indicates that our picture of the mechanism is correct in the essential features. It is to be remembered that, so far as I know, there has been no previous attempt to account for the tension coefficient of resistance, and also that there has been no account given of the departure of the temperature coefficient from exact equality with $1/\theta$.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.