THE ELECTRICAL RESISTANCE OF METALS.

By P. W. Bridgman.

Synopsis.

Electrical Resistance of Eighteen Elements.—The paper contains a brief summary of an extensive series of measurements which are to be published in detail elsewhere made to determine the *effect of pressures up to* 12000 *kg. per sq. cm. and of temperatures from* 0° *to* 275° *C.* on the resistance of *lithium, sodium, potassium, gallium, bismuth, mercury, calcium, strontium, magnesium, titanium, zirconium, arsenic, tungsten, lanthanum, neodymium, carbon (amorphous and graphitic), silicon, and black phosphorus.* The data for tungsten and magnesium are improvements on data previously published; the data for the other substances are new. The first six of these elements were studied in both the liquid and the solid states. The pressure coefficients of solid calcium, solid strontium, and both solid and liquid lithium are positive; the coefficient of bismuth is positive in the solid state, but negative in the liquid.

Modified Electron Theory of Metallic Conduction.—A previous theoretical discussion of measurements of the effect of pressure on resistance suggested most strongly that in metallic conduction the electrons pass through the substance of the atoms, and that the mechanism by which resistance is produced is *intimately connected with the amplitude of atomic vibration.* This view is here given quantitative form. The classical expression for conductivity, $\sigma = (e^2/2m)(nl/v)$, is retained; the number of free electrons is supposed to remain constant, their velocity is taken to be that of a gas particle of the same mass and temperature, and their mean free path is supposed to be many times the distance between atomic centers. The variations of path are then computed in terms of the variations of amplitude, and thus the variations of resistance are obtained and *checked with experimental results.* It is shown that the theory in this form explains Ohm's law, gives the correct temperature coefficient and the most important part of the pressure coefficient, avoids the difficulty of the classical theory with reference to specific heats, indicates a vanishing resistance at low temperatures, leaving open the possibility of super-conductivity, and retains the classical expression for the Wiedemann-Franz ratio. Besides these quantitative checks, the theory is shown to be entirely consistent qualitatively with all the new data; in fact, many of these new results, particularly the effect of pressure and temperature on the relative resistance of solid and liquid, seem to demand uniquely this conception of metallic conduction.

IN a forthcoming number of the Proceedings of the American Academy I shall give the results of measurements of the effect of pressure and temperature on the resistance of 18 elements and several alloys. This is additional to my previous results for 22 elements. The numerical data will be briefly summarized in the Proceedings of the National Academy. In a previous paper in this journal[1] I drew certain inferences

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[1] P. W. Bridgman, Phys. Rev., 9, 269–289, 1917.

with regard to the mechanism of electrical conduction from the previous data for 22 substances. In this paper I desire to extend this work in the light of the new data now available.

It will pay to briefly indicate the extent of the new data; the numerical results will be referred to in the following as the need arises. Previous to these measurements there were data for the effect of pressure on the resistance of no metal in both the liquid and the solid state, and the data were known for only one liquid metal, mercury. I have now obtained results for the variation of resistance under both pressure and temperature of the following six metals in both the liquid and the solid states: mercury, lithium, sodium, potassium, gallium, and bismuth. Previously none of the alkali or alkali earth metals had been measured; it is just these for which the largest pressure effects would be expected. I now have the data for lithium, sodium, potassium, calcium, and strontium. The effect of pressure was not known on any of the rare earth metals. I now have the data for La and Nd. The complete list of elements covered by the new work is: Li, Na, K, Mg, Ca, Sr, Hg, Ga, Ti, Zr, Bi, As, W, La, Nd, C, I, and P (black). Perhaps the most striking of the new results are as follows. Three more metals have been added to the list of those whose resistance increases with increasing pressure; these are Li, Ca, and Sr. Bi and Sb were the only ones previously known. Of these Li was a particular surprise, because its compressibility is so high. The resistance of liquid as well as solid Li increases under pressure. The resistance of liquid Bi, on the other hand, decreases under pressure, although that of the solid increases. I expected that the resistance of gallium would also increase under pressure, because this substance is abnormal in expanding on freezing, but its resistance decreases normally with pressure in both the solid and the liquid states. The effects of pressure on the resistance of Na and K are much larger than for any other metals, Na decreasing 40 per cent. in resistance under 12,000 kg., and K decreasing by 70 per cent. The decreases of these metals are insignificant compared with that of black phosphorus, however, which decreases to 3 per cent. of its initial resistance under the same pressure. The change is entirely reversible. The pressure coefficient of carbon has opposite signs in the amorphous and graphitic phases.

In my previous theoretical paper I directed especial emphasis to one fact brought out by the previous measurements, namely that the most important single factor in affecting the resistance of a metal is without doubt the amplitude of vibrations of the atoms. It turned out that the relative change of resistance under a change of either temperature or pressure was equal approximately to twice the corresponding change of amplitude of atomic vibration. The relation was fairly accurate for all metals with regard to the temperature coefficient (which is nearly the same for all metals and equal to the reciprocal of the absolute temperature), and was not so exact for changes of pressure, but nevertheless was somewhat more accurate than any other relation previously proposed for the pressure change. This fact seemed to me to indicate that the mechanism of conduction was by a passage of electrons from atom to atom through the substance of the atom itself. The atom is to be thought of as normally offering no resistance to the passage of the electron (super-conductivity at absolute zero), but resistance may be encountered in passing from atom to atom. The assumption of paths within the atom which are resistanceless need occasion no alarm in these days of non-radiating quantum orbits. In fact there may be an intimate connection between the two. I had called this theory the "gap" theory of resistance. Not only the quantitative fact that the resistance varies as the square of the atomic amplitude, but a large number of qualitative facts also, were in accord with this point of view. These qualitative facts were many of them brought into line by the conception that the "gap" may function in two ways. At large mean distances of separation of the atoms it may happen that passage of electrons from atom to atom is made easier by temperature agitation of unusual violence, which brings the surfaces of the atoms closer together than normal during part of their vibration, whereas at small mean distances of separation, the passage of electrons is on the average hindered by temperature agitation. Except for the deduction of the expressions for the variation of atomic amplitude with temperature and pressure, the theory as hitherto expounded was qualitative rather than quantitative. In particular, I did not attempt to give any detailed picture of the way in which the gaps between atoms might offer resistance to the passage of electrons, or what the character of the resistance might be. The theory as previously given also made no attempt to explain the Wiedemann-Franz ratio, although I pointed out that an explanation was not inconsistent with the elements of the theory.

It is now possible to cast this point of view into quantitative form, at least as far as temperature variations of resistance go; the pressure changes cannot be so easily dealt with for a reason that will appear later.

In the first place it is interesting to observe that the proportionality of resistance to the square of the amplitude of atomic vibration holds also at low temperatures; the previous considerations were entirely confined to ordinary temperatures. It has been noticed by Grüneisen,[1]

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[1] E. Grüneisen, Verh. D. Phys. Ges., 15, 186–200, 1913.

after an examination of the best data, that down to very low temperatures the quotient of resistance by absolute temperature is proportional to specific heat, the factor of proportionality being different for different metals. Let us compare this experimental variation of resistance with a variation as the square of the amplitude of atomic vibration at low temperatures. The specific heat formula which best fits the facts at low temperatures is that of Debye. This gives an energy content proportional to the fourth power of the absolute temperature, and of course a specific heat proportional to the third power, since the specific heat is obtained by differentiating the energy. We have, therefore, the expressions,

$$E = At^4 \qquad \text{and} \qquad C = 4At^3,$$

where E and C are the energy and the specific heat of the atom respectively. We may also express the energy of the atom in terms of its frequency and amplitude of vibration. This gives the equation

$$2\pi^2 m\nu^2\alpha^2 = At^4,$$

where α is the amplitude, and ν the frequency of atomic vibration. Now differentiate this expression logarithmically with respect to t, giving

$$\frac{2}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{4}{\tau} - \frac{2}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p.$$

The value of $1/\nu(\partial\nu/\partial\tau)_p$ was found in the previous paper. Substituting this value gives

$$\frac{2}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{4}{\tau} - 2\left(\frac{\partial v}{\partial\tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau.$$

An examination of the previous deduction of $1/\nu(\partial\nu/\partial\tau)_p$ shows that the connection between temperature and energy did not enter, so that the same expression is valid at low as well as high temperatures. But now it is an empirical fact that at low temperatures the compressibility approaches a constant value, and that the ratio of the thermal expansion to the specific heat also approaches a constant value. Hence in the limit, $(\partial v/\partial\tau)_p{}^2/C_v(\partial v/\partial p)_\tau$ becomes proportional to $(\partial v/\partial\tau)_p$, and hence vanishes. We have, therefore, at low temperatures,

$$\frac{2}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{4}{\tau}.$$

At high temperatures $2/\alpha(\partial\alpha/\partial\tau)_p$ was also proportional to $1/t$, but the factor of proportionality was 1 instead of 4.

Now our previous empirical observation was that $2/\alpha(\partial\alpha/\partial\tau)_p$ gives the variation of resistance with temperature. Compare this with

Grüneisen's empirical observation. He has

$$R/t = BC,$$
$$R = BCt$$
$$= 4ABt^4,$$

where R is the resistance and B a constant. Hence

$$\frac{1}{R}\frac{dR}{dt} = 4/t,$$

which checks precisely with the value of twice the variation of atomic amplitude.

Although we have found a variation at high and low temperatures proportional to the variation of the square of the amplitude, we cannot set the resistance at all temperatures equal to a constant times the square of the amplitude (that is if Grüneisen's observation is correct) for the factor of proportionality changes on passing from low to high temperature. The relation of proportionality must therefore fail at some intermediate temperature.

Returning now to the task of making the "gap" theory more definite, we in the first place make specific the action of the gap in imparting resistance by picturing precisely the same sort of mechanism as that operating during a collision of the classical theory. There cannot be any doubt that the electron encounters difficulty in getting free from the atom when the atoms are separated from each other as in a gas, for there is a definite ionizing potential, which involves an amount of energy large in comparison with that ordinarily available in the form of temperature energy of agitation. It is also evident that in some way the electrons do get free from the atoms in the solid state, because the solid is conducting for any E.M.F., no matter how small, and at low temperatures its Ohmic resistance vanishes. This means that under certain conditions forces may act on the electron when in the act of passing from one atom to another, whereas while the electron is passing through the interior of the atom no forces act. During the action of a force between electron and atom, there is a chance for the transfer of energy from one to the other, so that we have a tendency to equipartition. In other words, the "gap" produces resistance by interfering with or terminating the free path of the electron, precisely as did the "collision" in the classical theory. The amount of interference with the free path will depend on the amplitude of vibration, and so the resistance will depend on the amplitude. Such a picture as this enables us to carry over immediately much of the analysis of the classical theory. For instance, the classical expression for the resistance at once holds, namely,

$$R = \frac{2m}{e^2}\frac{v}{nl}, \tag{1}$$

where e is the charge on the electron, m the mass of the electron, n the number of electrons describing paths per cm.^{3}, l the mean free path of the electron, and v the undisturbed velocity of translation of the electron.

Ohm's law at once follows on the same basis as in the classical theory. Previously I had to leave Ohm's law unexplained, with only the remark that there was no inconsistency.

This picture of the mechanism of interference with the free path is so different physically from that of the classical theory, and yet gives such similar results when substituted into the mathematical expression, that it will pay to stop for a moment to inquire what is our justification for setting up so definite a picture. In particular, we may compare this picture with that of Wien,[1] who also has a free path mechanism of conduction and Ohm's law, but imagines the electrons interfered with in their flight by collisions with the centers of the atoms. Many facts are equally understandable from either point of view. There are a number, however, which are more naturally explained by supposing that the interference encountered is in passing through the surface from one atom to the next. Many of these facts will be given later; I mention only the two most striking. In the first place it is a universal fact that if a metal changes form, as by melting, or by a polymorphic transition, the phase with the smaller volume has the smaller resistance. This holds for all known normal meltings, in which the liquid has the larger volume, and also holds for the abnormal meltings of Bi, Sb, and Ga, in which the liquid has the smaller volume, and also the smaller resistance. It holds also for the normal polymorphic transitions of Zn and Ni, and for the abnormal transition of Tl, in which the high temperature phase has the smaller volume. Now this is difficult to understand from Wien's point of view, for it would seem that in the phase with the smaller volume there must be more chance of collision with the atomic centers, and so a higher resistance. The difficulty cannot be turned by supposing that the energy of temperature agitation is different in the two phases, for the specific heat of liquid bismuth is greater than that of the solid, and therefore in the liquid the atoms have more chance of terminating the free path both because they are more numerous, and because their amplitude of temperature agitation is greater, so that they effectively cover more territory. On the other hand, the fact that the resistance of the phase

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

with the smaller volume is the smaller is most naturally explained from the "gap" point of view simply by the observation that the atoms are closer together, and the electrons find it easier to pass from one to another. Another fact not readily understandable from Wien's point of view is that the temperature coefficient of resistance of the liquid is nearly always less than that of the solid. In some cases it may be very much less, or may even be negative, instead of positive. Now the increased violence of temperature agitation in the liquid, as shown by the higher specific heat, would seem to demand a higher temperature coefficient, according to Wien's view. There is a most natural explanation in terms of the gap theory, as has been explained in the preceding paper, or as will be elaborated further in the following.

So much for the mechanism by which resistance is produced, and the explanation of Ohm's law. To get further, we have to know the precise manner of variation of n, l, and v with temperature and pressure. The classical theory supposed that v was the value given by the equipartition of energy, treating the electron as a gas particle, that l was at least of the order of magnitude of the distance between atomic centers, and n could look out for itself, being determined by the necessities of the case. The weaknesses of the old theory are well known. One of the most serious is that the n needed to give the observed values of specific resistance is of the order of magnitude of the number of atoms itself, or even may be considerably in excess, which leads to the insuperable difficulty of the specific heat. An n of the same order of magnitude was indicated by the application of the theory to the optical theory of metals. Many attempts have been made to avoid this difficulty, but as yet without success. Nearly all attempts at replacing the classical theory have failed in the endeavor to give even an approximate explanation of the Wiedemann-Franz ratio. In order that the thermal conductivity of a metal shall have its high value, and in order that the Wiedemann-Franz ratio may have approximately its experimental value, it seems to be necessary to suppose not only that temperature energy is carried by the electrons, but that the amount so carried is precisely the amount which would be carried if the energy of the electrons were the equipartition energy on the old classical basis.

Apparently the most promising attempt at another explanation of the Wiedemann-Franz ratio is the recent theory of Borelius,[1] which does give a result of approximately the right magnitude. But although his explanation may be mathematically satisfying, I do not think that it can be considered satisfactory physically. His explanation is on the

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[1] G. Borelius, Ann. Phys., 57, 278–286, 1918.

basis of the Debye theory of heat conduction.[1] Debye's theory is that heat is conducted by elastic waves, which are dissipated by atomic irregularities. A quantity analogous to the mean free path may be defined in terms of the rate of dissipation, so that the higher the rate of dissipation the shorter the equivalent free path, and the less the conductivity. Debye has applied this theory to insulators, like rock salt, and has been able to account for the experimental fact that the conductivity varies inversely as the absolute temperature. Borelius has taken over this theory for metallic conduction, by means of the assumption that the amount of energy dissipated at each atom as the elastic wave passes over it is equal to the ratio of the thermal energy of the atom to that of the electron. This gives a thermal conductivity of the right order of magnitude. In combination with his theory of electric conduction he gets a Wiedemann-Franz ratio of approximately the right magnitude, and with the right dependence on temperature. But he has neglected the dissipation of the elastic waves due to the atoms. If Debye's analysis is correct, this should be present in the metal as well as in an insulator, and is very much larger than the dissipation supposed by Borelius. Hence, taking account of the neglected atomic dissipation, the thermal conductivity of a metal would turn out to be actually less than that of an insulator, for there is dissipation not only by the atoms but also by the electrons.

Compared with the classical conception of conduction as performed by a swarm of electrons playing in the free spaces between the atoms, the view at which we have arrived of conduction as performed by electrons passing freely through the substance of the atoms places us in a much more advantageous position, for it allows the possibility of very long free paths (in fact at absolute zero there is no resistance to the motion and the paths may be indefinitely long), and hence enables us to get along with many fewer electrons. In this way the specific heat difficulty may be avoided. But in order to account for the facts of thermal conduction, it seems necessary to take over the classical idea that the electrons are moving with the energy of gas particles at the same temperature.

The theory developed here proceeds on the following assumptions. We take over the classical expression (*I*) for resistance in terms of n, l, and v. We suppose that v is the same as that given by the classical equipartition theory, and we suppose l large enough to avoid the specific heat difficulty by allowing a small value of n. We try to deduce from our fundamental expression the variation of resistance with temperature

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[1] P. Debye, Wolfskehlstiftung Vorträge, B. G. Teubner, 1914, 17–60.

and pressure in terms of the variations of v, which are given by the classical expression, and the variations of l, which we get from our picture of the electrons jumping from atom to atom across a region capable of exercising interference with the path. The quantity n we suppose to stay constant. One reason for this supposition is that we do not need to assume any variation in order to account for the facts. However, it does not seem unplausible that n should stay approximately constant. As temperature is increased, the tendency to an increased n due to the increased chance of getting an electron out of an atom by increasing violence of collision is counterbalanced by the increasing difficulty of getting the electron out of the atom because of the increased distance of separation of atomic centers. Or again, it may be that the number of migrating electrons is determined by a sort of spontaneous atomic disintegration in the outer part of the atomic structure, over which changes of temperature or of pressure can have no control.

There is evidence as to the magnitude of n given by optical theories of metals. We shall for the present merely disregard this. We are much more justified in doing this now than we would have been several years ago, for quantum theory has made it exceedingly uncertain whether we are justified in keeping our old model of a vibrating electron as a source of light. Quantum theory has shown,[1] for example, that the success of the electron in giving the classical expression for the Zeeman separation was due to a quite accidental cancelling out of the factor h from the result, and that the factor h will not so conveniently cancel out in treating certain other phenomena, as the Stark effect. Furthermore, the number of electrons demanded by optical theory must now seem impossibly high in the light of our knowledge of the structure of the atom, so that we are probably justified in disregarding the line of attack from the optical side until quantum theory has become more developed.

Concerning our assumption of the equipartition value for v, putting it equal to $\sqrt{2(\kappa\tau/m)}$, there cannot be much question at moderate temperatures, so long as n is small enough to avoid the specific heat difficulty, but there may be question as to what the limit of temperature is to be. It is possible that the classical expression for the energy may hold to lower temperatures for the electron than for the atom. Hydrogen or helium at low temperatures in the gaseous condition in contact with the solid walls of the container continues to have the classical energy, although this is no longer the equipartition energy as compared with the atoms of the solid walls. However, the classical expression cannot continue to hold indefinitely to extremely low temperatures, for even a few

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[1] A. Sommerfeld, Atombau und Spektrallinien, Vieweg, 1919, 422–440.

electrons with the classical energy would ultimately make trouble with the specific heat. We will not concern ourselves further with the situation at extremely low temperatures except to remark that the assumptions of this theory will have to be modified, and to indicate that such a modification is not at all impossible. For instance, the electron in coming from the atom, leaves behind it a positively charged ion. As the electron wanders through the metal it must at some time come again in contact with an ion, and may recombine with it. Throughout the metal, therefore, there is going on a continuous process of emission of electrons by the atoms and reabsorption. Now the mechanism of the ejection of the electron by the atom within the solid is something which we do not understand, but it is not unlikely that it is determined from within the atom, and is not greatly affected by outside conditions, at least as far as the velocity of emission is concerned. The electron may, therefore, be expelled with a definite velocity independent of temperature. It then travels from atom to atom, and is jostled about, until it ultimately acquires the equipartition energy. The time required to accomplish equipartition may well be less the greater the violence of agitation. Presently, the electron recombines with an ion. At low temperatures, because of the feebleness of temperature agitation, it may be that the electron is absorbed before it has acquired the equipartition energy, or that it has possessed this energy for only a relatively short time. The specific heat difficulty will not then appear, and the conductivity will be even higher than that corresponding to Grüneisen's empirical observation, because the mean velocity will not decrease so rapidly with decreasing temperature. And it is of course a fact that some metals show superconductivity at extremely low temperatures, and that superconductivity is not covered by Grüneisen's formula.

So much for the assumptions with regard to v and n. Now for a deduction of the variation of l, the mean free path.

There is a point implied in our assumption of a long free path which may detain us for a moment. We have pictured the electron as passing through the substance of many atoms before its path is arrested. Now in a cubic crystal this means that the electronic paths may be confined to three directions mutually at right angles, along the crystalline axes. The classical deduction for the expression for conductivity assumes of course that the directions of the paths are distributed at random throughout space. Is a specialized distribution in only three directions consistent with the known fact that the resistance of a cubic crystal is independent of the direction? A simple analysis immediately shows that there is no inconsistency here. Imagine the applied electric force making the angles α, β, and γ with the crystal axes, and find the contribution made to the conductivity by the electrons moving along the X axis. The component of force along this axis is $E \cos \alpha$, so that the velocity imparted to the electron is smaller by the factor $\cos \alpha$ than it would be if the force were along the axis. And the component of this velocity in the direction of the force is further diminished by the factor $\cos \alpha$, so that the total contribution of the electrons moving along the X axis is diminished by the factor $\cos^2 \alpha$. Similarly the electrons moving along the other two axes contribute to the conductivity terms equal to $\cos^2 \beta$ and $\cos^2 \gamma$. The sum of the three terms is 1, which is thus independent of direction.

On the other hand, there is no necessity in supposing that a single free path is straight; the electrons may perform Virginia reels about the nuclei of the atoms in quantum orbits. Something of this sort probably has of necessity to take place in non-cubic crystals.

We return to the question of the variation of l. For the moment we consider that the solid is maintained at constant volume. As temperature is increased, the amplitude of vibration is increased, and it may be that during part of the vibration the atoms are so far separated that the electron cannot pass. That is, when the atoms are in vibration, there is a certain chance that the free path of the electron may be terminated in the passage from one atom to the next. This chance is a function both of the amplitude of atomic vibration, and of the mean distance of separation of atomic centers. Call β the chance that the path will be terminated, r the mean distance of separation of atomic centers and α the amplitude of atomic vibration. Then we may expand the unknown function in powers of α and write

$$\beta = f(r, 0) + \alpha \frac{\partial f(r, 0)}{\partial \alpha},$$

provided that α is small. α may be calculated, and it turns out that for ordinary temperatures α is a small fraction of r. Now it is our fundamental assumption that when the atoms are at rest no resistance is encountered in passing from atom to atom, provided that the distance of separation of atomic centers is not too great, as we suppose it is not for a solid. This means that $f(r, 0) = 0$, and we may write

$$\beta = \alpha \frac{\partial f(r, 0)}{\partial \alpha}.$$

That is, so long as the volume is kept constant, the chance that the path will be terminated in passing from atom to atom is proportional to α. In unit distance the chance that the path will be terminated is equal to β

multiplied by the number of atoms in unit length, again giving a constant times α. Now the probability definition of the mean free path is merely the reciprocal of the chance that the path will be terminated in unit distance, so that we have at once

$$l = \text{Const}/\alpha.$$

To compute the variation of l at constant volume it is sufficient to calculate the variation of α at constant volume.

Now the variation of α was already computed in the previous paper. The expressions there given were for the variation of α with pressure and temperature, but of course from these derivatives the derivative at constant volume may at once be found if we know the compressibility and thermal expansion of the substance.

The computation of the change of amplitude is the only place in the theory into which the quantum hypothesis explicitly enters. The assumptions at the basis of the computation were these. The energy of the atom is the classical amount, $\kappa\tau$ (so that the deduction does not hold for low temperatures), the frequency is a function of volume only (the forces on the atoms are on the average a function of volume only), and the entropy of the atom is the same as the entropy of an ideal linear oscillator at the same temperature, which by quantum considerations is shown to be a function of τ/ν only.

For convenience of reference the values previously found are reproduced here.

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau = -\left(\frac{\partial v}{\partial\tau}\right)_p\Big/ C_v,$$

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{1}{2\tau} - \left(\frac{\partial v}{\partial\tau}\right)_p^2\Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau.$$

The change of amplitude at constant volume may at once be found

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_v = \frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p + \frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau\left(\frac{\partial p}{\partial\tau}\right)_v.$$

But

$$\left(\frac{\partial p}{\partial\tau}\right)_v = -\left(\frac{\partial v}{\partial\tau}\right)_p\Big/\left(\frac{\partial v}{\partial p}\right)_\tau.$$

Substituting this value above gives at once the simple result

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_v = \frac{1}{2\tau}.$$

Now let us find the change of resistance at constant volume with temperature. Our formula for the specific resistance is

$$R = \frac{2m^{1/2}(2\kappa)^{1/2}}{e^2 n} \frac{\tau^{1/2}}{l}$$

$$= \text{Const} \frac{\tau^{1/2}}{l} .$$

Differentiating this logarithmically gives

$$\frac{1}{R}\left(\frac{\partial R}{\partial \tau}\right)_v = \frac{1}{2\tau} - \frac{1}{l}\left(\frac{\partial l}{\partial \tau}\right)_v .$$

Using the value found for l in terms of α gives

$$\frac{1}{l}\left(\frac{\partial l}{\partial \tau}\right) = -\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \tau}\right)_v ,$$

and substituting this gives

$$\frac{1}{R}\left(\frac{\partial R}{\partial \tau}\right)_v = \frac{1}{\tau} .$$

That is, the temperature coefficient of resistance at constant volume is the reciprocal of the absolute temperature. This of course, is in accord with the experimental facts. In my preceeding theoretical paper I gave the values of $1/R(\partial R/\partial \tau)_v$. The difference between $1/R(\partial R/\partial \tau)_v$ and $1/R(\partial R/\partial \tau)_p$ is not large, but is in the direction to make $1/R(\partial R/\partial \tau)_v$ even more nearly equal to $1/\tau$ than $1/R(\partial R/\partial \tau)_p$.

The change from the point of view of the last paper is to be noticed. We previously thought of the change of α as the only significant feature, and noticed that $1/R(\partial R/\partial \tau)_v$ was equal to $2/\alpha(\partial \alpha/\partial \tau)_v$. We did not see any particular reason why the change of resistance should be proportional to twice the change of α, that is, why the resistance should be proportional to the square of the amplitude, although we advanced reasons which made it seem not improbable. Our present expression for R demands that we analyze the change of resistance into two effects; one is a temperature effect, due to the term $\tau^{1/2}$, and the other is an effect due to the change of l, which involves the change of α. Now it turns out that the change of l with α, which again changes with temperature, is of such a nature that the sum of the two effects is as before exactly equal to twice the change of α. Hence the previous analytical result stands, but our physical analysis is different.

We now let fall the condition that the volume be kept constant during the change, and consider the change of resistance with temperature at constant pressure, which is the coefficient usually directly determined by experiment. The formal work of differentiation of our fundamental expression for resistance may be carried through as before. We encounter difficulty in determining the variation of the mean free path with temperature, for the condition no longer holds that the volume is constant, and β, the probability of the termination of the path, can no longer be put equal to a constant times the amplitude, but the factor multiplying the amplitude is an unknown function of the volume. I have not found any universal assumption as to the dependence of β on the distance of separation of atomic centers which seems to be plausible, but it would seem that β might vary in any way with the structure of the particular atom. For instance, it is conceivable that as the distance of separation of atomic centers is increased the atoms acquire rotational movement with respect to each other, so that parts of the atomic surfaces are brought into opposition which are not so favorable for the passage of electrons. The magnitude of this effect will depend entirely on the structure of the particular atom. Or again, as the atoms are brought closer to each other, the ease of passage will be affected by the deformation of the atom, and this again varies in an unknown way from element to element. The only fact about this unknown effect of changing distance between atomic centers which it seems fairly safe to assume as common to most elements is the sign; it is likely that as the atoms are brought closer together at constant amplitude the ease of passage is increased, and so the mean free path is increased.

The unknown effect of changing volume will evidently be much greater for those changes of volume relatively large compared with the change of amplitude. This means that the unknown effect will be much larger for changes of pressure than for changes of temperature. The magnitude of these changes was considered in the previous paper. It was there shown that the pressure coefficient of amplitude is from six to nine times the pressure coefficient of distance of atomic separation (linear compressibility), whereas the temperature coefficient of amplitude was from 50 to 650 times as great as the temperature coefficient of atomic separation (linear dilatation). In view of the largeness of this latter ratio, it would seem that we are justified for most substances in neglecting the effect as far as variations of temperature at constant pressure are concerned. We will, as a matter of fact, make this assumption. We then have

$$\frac{1}{l}\left(\frac{\partial l}{\partial \tau}\right)_p = -\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \tau}\right)_p,$$

and analysis exactly like the preceding would give

$$\frac{1}{R}\left(\frac{\partial R}{\partial \tau}\right)_p = \frac{1}{\tau} - \left(\frac{\partial v}{\partial \tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau .$$

Now for all solid metals the second term is small compared with the first, and we may neglect it. We may now replace R, the specific resistance by ρ, the observed resistance (that is, the resistance of a piece of wire with fixed terminals), since the difference of the two coefficients is equal to the linear expansion, which may be neglected in comparison with $1/\tau$, and obtain as our final approximate result

$$\frac{1}{\rho}\left(\frac{\partial \rho}{\partial \tau}\right)_p = \frac{1}{\tau}.$$

This equation, of course, agrees with experimental fact. The usual temperature coefficients are always somewhat larger than $1/\tau$, which is the direction of variation which the above considerations would lead us to expect. I know of no theory which gives the departure of the temperature coefficient from $1/\tau$. Wien's theory is the only one which makes the attempt, and this cannot be regarded as successful. Of course the classical theory does not account for the temperature coefficient at all, but is driven to unplausible assumptions as to the variation of the free path with temperature in order to be consistent.

Now to find the pressure coefficient, we differentiate our expression for resistance with respect to pressure at constant temperature, getting

$$\frac{1}{R}\left(\frac{\partial R}{\partial p}\right)_\tau = -\frac{1}{l}\left(\frac{\partial l}{\partial p}\right)_\tau.$$

The only statement which we can make about $1/l(\partial l/\partial p)_\tau$ is that it is at least as large as $1/\alpha(\partial \alpha/\partial p)_\tau$, so that we expect the pressure coefficient of resistance to be at least as large numerically as $(\partial v/\partial \tau)_p/C_v$ (substituting the value found above for $1/\alpha(\partial \alpha/\partial p)_\tau$) and to be negative. In the previous paper it was shown that the pressure coefficient is given on an average for a large number of metals by $2/\alpha(\partial \alpha/\partial p)_\tau$. Our present theory leads us to replace this by the statement that there is a lower limit one half the value previously found. Now it is true that twice the amplitude represented a somewhat better approximation to the average of all the results than did the expression of Grüneisen, for example, which was the best of other theoretical expressions for the pressure coefficient of resistance, but there were deviations from it in both directions. It is on the other hand true that there are no cases known, either among the substances of the previous work or among the new elements of my more recent work, except those abnormal metals for which the coefficient is positive, and which will be dealt with separately later, in which the coefficient falls as low as $1/\alpha(\partial \alpha/\partial p)_\tau$. So that although our present theory is not complete because of the unknown element of atomic structure, it is at least more satisfactory than the former attempt in that it is true without exception.

So much for the formal expression of the theory with regard to temperature and pressure changes of resistance. The classical expression for thermal conductivity is to be taken over without change, and need not be written down explicitly. It gives the right order of magnitude for the Wiedemann-Franz ratio, but is not a complete expression of the facts because it neglects the part of conduction done by the atoms, and hence will be expected to fail particularly at low temperatures, where the atomic conduction becomes important.

The theory as outlined is not inconsistent with a retention of the classical expression for the Peltier heat. In particular the theory is in accord with the classical theory in at least two aspects of thermoelectric phenomena. The magnitude of the pressure coefficient of the thermoelectric force would mean, according to the classical theory, that the number of free electrons does not change much with increasing pressure. This is in exact accord with the assumptions of our theory. Furthermore, the small Peltier heat between a solid and a liquid metal makes it likely that the number of free electrons is not greatly different in solid and liquid. As will be seen in the following, our theory gives an account of the difference of resistance between solid and liquid in terms of a difference of free path only, without supposing a difference in the number of electrons. There was here a weak point of the classical theory, because to account for the great difference of conductivity between solid and liquid it had to suppose a number of electrons much greater in the solid than in the liquid, which was not consistent with the thermo-electric phenomena. At the same time I do not believe that it is desirable to take over entirely the whole classical picture of the mechanism of thermoelectric action. There are, of course ions as well as wandering electrons present in the metal, and these ions may play a part in thermo-electric action, although because of their relatively small translational velocity their part in conduction may be altogether insignificant. That some such modification is necessary is indicated by the fact that the classical expression for the Thomson heat demands that the number of free electrons increase as the square root of the absolute temperature, whereas we have assumed that the number is constant. However, the Thomson heat is relatively a small matter, and I have not attempted to bring it within the range of the present theory. If the above considerations are sound it ought to be possible to get it in without essentially modifying the mechanism which we have set up to account for conductivity.

This is as far as I have got at present with the quantitative development of the theory. Its advantages are obvious. It gives an unforced and inevitable description of the variation of resistance with temperature, predicts the right sign and an important part of the numerical magnitude of the pressure coefficient, avoids the difficulty of the classical theory with the specific heats while retaining the classical explanation of the Wiedemann-Franz ratio, and leaves open the possibility of much greater conductivity or even superconductivity at low temperatures, which was not possible to the classical theory. Further development of this theory seems to demand more intimate knowledge of atomic structure than we have at present.

But in addition to these quantitative facts, the theory is able to bring a very large number of facts qualitatively into line, as was emphasized in the preceding paper. In the following I give a survey of the new facts brought out by the new experimental work, and the relation of the theory to these facts.

1. The view of conduction as due to the passage of electrons from atom to atom through the substance of the atom receives confirmation from a group of phenomena not considered in detail in the previous paper, namely the phenomena of the resistance of alloys. Alloys fall into two main groups, according as they do or do not form mixed crystals. Those alloys which do not form mixed crystals solidify by the separation of the two components each in a pure condition, so that the solid alloy consists of a mechanical mixture of microscopic crystals of the two components. It would be expected that the resistance of a mixture of this sort would be the mean of the resistance of its components, and it is indeed the experimental fact that the resistance of such alloys can be computed by the rule of mixtures. The other class of alloys is one in which mixed crystals are formed, the atoms of the two metals entering side by side into the same crystal edifice. This is possible because of a certain degree of resemblance of the two kinds of atoms. The resemblance is not complete, however, and the indiscriminate use of either kind of atom in the crystal edifice is possible only with a certain amount of distortion in the final result. It is a fact that most mixed crystals will not accept an unlimited amount of the foreign ingredient, but the two atoms will crystallize side by side only up to certain limiting proportions. In the mixed crystal structure we would expect, therefore, a certain amount of imperfect fitting between adjacent atoms, with the result that the electrons encounter difficulty in passing from atom to atom, so that, because of the extra resistance of the "gaps" between the atoms, the resistance of the alloy is greater than that computed from the components. This is in exact accord with the experimental facts.

Furthermore, the temperature coefficient of alloys is strikingly in accord with this view. The temperature coefficient of those alloys which do not form mixed crystals is the same as that of the pure metals, which is what we would expect, but the temperature coefficient of those alloys in which there are mixed crystals is very much less than that normal to a pure metal. A large number of binary alloys satisfy Matthiesen's rule in this regard. If we write the resistance of the alloy in the form

$$R_A = R_M + \Delta R,$$

where R_A is the resistance of the alloy, R_M the resistance which would be computed according to the rule of mixtures, and ΔR the resistance which must be added to the computed resistance to give the actual resistance, then Matthiesen's rule states that the temperature coefficient of the alloy is given by the expression

$$\frac{dR_A}{dt} = \frac{dR_M}{dt}.$$

This means that $d\Delta R/dt = 0$, or the additional resistance is not affected by changes of temperature. This is in precise accord with our point of view, for the additional resistance (ΔR) is due to the lack of perfect fit between adjacent atoms of different kinds, and this would be expected to be relatively little affected by changes of temperature.

It is also an experimental fact that the resistance of alloys tends to a finite value at 0° Abs., instead of vanishing like that of a pure metal. This merely means that the gaps between the different kinds of atoms persist to low temperatures, as we would certainly expect.

2. The fact that the resistance of a metal increases on hard drawing is consistent with this point of view. During hard drawing the crystal grains are broken up, and the fitting of the atoms is rendered less exact on the average. This is proved by the universal fact that during hard drawing the density of the metal decreases. But such a disarrangement of the fitting of the atoms means an increased chance of interference when the electrons pass from atom to atom, and consequently an increase of resistance.

Tammann[1] has given an explanation of this fact on the basis of a difference of resistance in different directions within the crystal grains. It would seem, however, that this explanation must be rejected, because the resistance of a cubic crystal is independent of direction (see Voigt, Krystal Physik, pp. 311, 313), whereas the phenomena of increase of resistance on hard drawing is shown by all metals, regardless of their crystal system.

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[1] G. Tammann, Lehrbuch der Metallographie, Leopold Voss, 1914, 117–125.

3. It has been observed that as the proportions of the components change through a series of alloys forming mixed crystals the electrical resistance increases in that direction in which the mechanical hardness also increases. Now an increased mechanical hardness means an increased staggering in the positions of the atoms in the crystalline grains, so that it is more difficult to produce sliding of one part of the crystal on another, and by the same token an increase in the difficulty of the electrons in making the leap from atom to atom.

4. In the previous paper a suggestion was made as to the possible explanation of the positive pressure coefficient of bismuth and antomony· The idea was that the amplitude might increase with increasing pressure instead of decreasing as normal. It was shown in that paper that the fact that both metals expand on freezing indicates that there is a certain relative position of the atoms in which the repulsive forces are unusually large at an unusual distance of separation, and that the atoms crystallize in this relative position. From a grossly material point of view this may be expressed by saying that the atoms have knobs, and that the metal crystallizes with the knobs in contact. On the average, except for these knobs, the bismuth atom may be much like that of other metals. The fact that the repulsive forces are unusually large at an unusual distance of separation of the atomic centers is compensated for by an unusually slow decrease of the repulsive force as the distance between atomic centers is decreased. This slow change of the repulsive force was shown in the preceding paper to be consistent with a decreasing frequency of atomic vibration as the centers are brought closer together, and hence consistent with an increasing amplitude with increasing pressure.

This view receives interesting numerical confirmation from recent work of Grüneisen[1] on the equation of state of solids. He has shown that it is possible to a good degree of approximation to explain the behavior of solids by supposing that at least over a small range the forces between atoms are represented to a sufficient approximation by the expression

$$f = \frac{A}{r^2} + \frac{B}{r^m},$$

where the first represents a force of attraction, and the second a force of repulsion. In general m will be much larger than 2. Its magnitude will give an idea of how rapidly the repulsive force increases as the atoms approach. Grüneisen gives an equation for m in terms of atomic volume, atomic heat, thermal expansion, and compressibility. It is not necessary

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[1] E. Grüneisen, Ann. Phys., 39, 257–306, 1912.

to reproduce the expression here. Grüneisen finds that m varies for normal metals from 7.5 for iron to 15.6 for gold. If we apply Grüneisen's formula to bismuth and antimony we find that m for the latter is 3.8, and for the former 4.5, both very much less than for normal metals. Our point of view is confirmed, therefore, that the repulsive forces in bismuth and antimony increase more slowly than normal as the distance between atomic centers is decreased, and therefore we have the possibility of an increasing amplitude with increasing pressure and so an increasing resistance.

5. The fact that the temperature coefficients of solid bismuth and antimony are normal is quite in accord with our view, for with rising temperature we have seen that the effect of temperature on increasing amplitude quite overshadows any pure volume effect, so that we would expect the temperature coefficients of all metals to be nearly the same, irrespective of the behavior of the pressure coefficient.

6. The fact that the pressure coefficient of liquid bismuth is normal in being negative is significant. It indicates that the positive coefficient of the solid is in some way connected with the crystalline structure. The picture which we have given of the mechanism of the positive coefficient of the solid has this property, for we have ascribed the increasing amplitude with increasing pressure in the solid to the fact that the atoms are held in fixed orientations with respect to each other, and that in this particular orientation the forces are abnormal in character. Such a fixity of orientation is possible only in the crystal. In the liquid there is no definite relation of orientation, the localities of abnormal force play a relatively unimportant part, and the liquid behaves normally. Not only is the pressure coefficient of liquid bismuth normal, but the temperature coefficient is also normal for a liquid, and is less than that of the solid, and less than the reciprocal of the absolute temperature.

7. It was shown in the previous paper that the abnormality of force between the atoms of bismuth made possible a crystal with abnormally large volume, and hence a crystal which expands on freezing. By analogy I was prepared for a positive pressure coefficient in gallium, which is also abnormal in expanding on freezing. The facts are the opposite, however, and the pressure coefficient of gallium is negative, as is normal. Our previous argument was entirely qualitative, however, and merely indicated the tendency toward an increasing amplitude with increasing pressure without setting up a criterion as to whether the tendency might be strong enough to counteract the normal tendency in the opposite direction or not. In the absence of a definite criterion therefore, we have only the right to expect the same tendency in gallium without

actually being sure whether the tendency will be strong enough to make the coefficient positive. Now as a matter of fact, if the expected magnitude of the pressure coefficient is calculated by the method of the previous paper, it will be found that the discrepancy for gallium is greater than for any other substance with negative coefficient, the calculated value being about twice the observed value. This means that the pressure coefficient is much less than we would expect from the behavior of normal substances, so that here we evidently have the tendency which we are looking for toward a positive coefficient.

In other respects the behavior of gallium is as we would expect. The temperature coefficient of the solid is normal, and the temperature coefficient of the liquid is also normal in being less than that of the solid. Furthermore, the pressure coefficient of the liquid is normal, and is greater numerically than that of the solid, as we would expect, because the tendency to abnormality in the solid is due to a particular orientation of the atoms, and this disappears in the liquid.

8. The behavior of lithium is of a type not shown by any other substance yet known. Its pressure coefficient is positive in both solid and liquid, and the coefficient of the liquid is greater than that of the solid. The temperature coefficient behaves normally. Furthermore, the melting of lithium is normal, in that the liquid has a larger volume than the solid. The data seem not to have been previously determined. In the paper on new resistance data will be found the melting data for lithium which I determined for this particular purpose. I have followed the melting curve up to 8,000 kg., and it seems normal in every respect. Our picture of the mechanism of conduction in lithium must probably, therefore, be different from that of bismuth or antimony or gallium. It is of course possible that the explanation of the abnormal coefficient follows on the same lines as for other metals, namely an increasing amplitude of atomic vibration with increasing pressure. If this explanation is adopted, the abnormality of the atom must not be thought of as confined to certain localities which function only in the crystalline phase, but the abnormality must be one of the atom as a whole, for the liquid as well as the solid is abnormal. This is not an impossible view, for if m be calculated for lithium by Grüneisen's formula, the value 5 will be found, which is low compared with most other metals, but is not low compared with bismuth and antimony. But now the question arises as to the interpretation to be put on the value of m. m itself merely is a measure of the rapidity with which the repulsive force increases as the atom is approached. A low value may be due either to an abnormality of a particular part of the atom, as we have supposed the case with bismuth

and antimony, or it may indicate that the atoms are separated by more than the usual distance, and the repulsive force is not important. We would expect the latter view to be more nearly correct for substances which are very compressible. This seems indicated by the fact that m is as small for the very compressible elements sodium and potassium as it is for lithium, and sodium and potassium have very large negative pressure coefficients of resistance. Now lithium is also one of the most compressible metals. It seems likely to me that the low value of m is more probably connected in some way with the high compressibility than with an abnormality which might result in an increasing amplitude of atomic vibration with increasing pressure.

Now there is a picture of conduction offered by the theories of Wien[3] and Lindemann[1] which gives an alternative explanation, which may quite probably be correct for this particular substance. Their picture is of electrons as well as atoms located on a space framework, and of the space framework of electrons moving bodily through the framework of the atoms when an external force is applied. The mean free path of the electrons in this motion is interrupted by collisions with the nuclei of the atoms. This picture means a positive pressure coefficient of resistance for most substances, for as pressure is increased the channels of passage of the electrons become more restricted. The reason for this is that the closing in of the channels because of the decreasing distance between atomic centers more than neutralizes the opening of the channels because of decreasing amplitude of atomic vibration. This is in spite of the fact that the relative change in atomic amplitude is much greater than the relative change in the distance between atomic centers, because the distance between atomic centers is absolutely much greater than the amplitude. It will be found as a matter of fact that if the relative magnitudes of atomic distance and amplitude and of the changes of atomic amplitude and distance with pressure be calculated for lithium, Wien and Lindemann's picture would lead us to expect a positive pressure coefficient. Evidently the positive pressure coefficient suggested by this picture remains true for the liquid state so long as the electrons continue to move between the atoms.

Apart from the argument from the pressure coefficient, this picture of Wien and Lindemann seems to have a particular probability of being correct for lithium because of its atomic structure. The structure is a simple nucleus consisting of a central positive charge and two electrons rotating about it, and a single other electron connected in some way with the nucleus at a relatively large distance. If the superficial electrons of

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[1] F. A. Lindemann, Phil. Mag., 29, 127–140, 1915.

the atom are ever to arrange themselves into a space lattice, it would seem that here is their chance.

The fact that the pressure coefficient of liquid lithium is larger than that of the solid is simply explained as due to the greater compressibility of the liquid. The compressibility of the liquid has never been measured, but there is no case known in which the liquid does have a smaller compressibility than the solid, and furthermore the behavior of the melting curve, its direction of curvature, and the direction of the difference of volume between solid and liquid, makes it almost inevitable that the compressibility of the liquid be greater than that of the solid.

The fact that the pressure coefficient of resistance becomes greater at higher pressures is also intelligible from this point of view. The channels through which the electrons slip are the spaces which are left between atomic centers after the inpenetrable nucleus has been subtracted. Hence a given proportional decrease in the distance between atomic centers will mean a greater proportional decrease in the channel when the atoms are close together (high pressures) than when they are further apart.

9. On the other hand, the increase of the pressure coefficient of bismuth and antimony with increasing pressure is at least perfectly consistent with the picture presented of their conduction as performed by electrons passing through the atoms instead of between them. If reference is made to Fig. 1 of the previous theoretical paper it will be seen that it is quite possible that as the atomic centers approach the restoring force per unit displacement becomes weaker. In fact such a behavior is inevitable at some value of the volume, but we have no criterion for deciding whether this takes place at a volume greater or less than the volume at which the crystal is stable. Now such a weakening of the restoring force when the volume decreases means an amplitude of vibration becoming progressively larger at the higher pressures (smaller volumes), and hence a pressure coefficient increasing with increasing pressure.

10. The pressure coefficients of calcium and strontium were also found to be positive. It is difficult to decide from the data at hand whether this is more probably due to the lithium or the bismuth type of mechanism. The melting data are not known for either of these metals, so that we do not know whether the liquid or the solid has the greater volume. Neither are the data known for the effect of pressure on the resistance of the liquid. It is true that the value of the "m" of the atomic force calculated for calcium is somewhat lower than for the ordinary run of metals, being 6, but the compressibility of calcium is also high, and the m

for strontium is distinctly high, being 9.5. It is, of course, probable that the mechanisms of calcium and strontium are the same, because of their similar positions in the periodic table. I believe that at present the probability is in favor of the lithium rather than the bismuth type of conduction. The melting data would be a great help toward this decision.

11. There is an interesting relation between the temperature coefficients of solid and liquid lithium. At the melting point of lithium, 180°, the temperature coefficient of the solid is 0.00251 (obtained by a linear extrapolation of the resistances at 0° and 100° and therefore somewhat uncertain, but the best that we can do), and the coefficient of the liquid is 0.00150. The ratio of these two coefficients is 1.69, which is almost exactly the ratio of the specific resistance of the liquid to that of the solid at the melting temperature, for which I found the value 1.68.

This can be easily understood in the light of Wien and Lindemann's picture. The resistance of the liquid is higher than that of the solid because the regular channels between the atoms are broken up by the haphazard arrangement of the atoms in the liquid. Now this factor of random arrangement of the atoms in the liquid is one that will persist at all temperatures, producing a permanent difference of resistance between solid and liquid. This can be given mathematical expression. Write the equation

$$R_L = R_S + \Delta R,$$

where R_L is the resistance of the liquid, R_S the resistance of the solid, and ΔR the increment of resistance on passing from solid to liquid. Now differentiate with respect to the temperature

$$\frac{1}{R_L}\frac{dR_L}{dt} = \frac{R_S}{R_L}\cdot\frac{1}{R_S}\frac{dR_S}{dt} + \frac{\Delta R}{R_L}\cdot\frac{1}{\Delta R}\frac{d\Delta R}{dt}.$$

If the experimental relation

$$\frac{1}{R_L}\frac{dR_L}{dt} = \frac{R_S}{R_L}\cdot\frac{1}{R_S}\frac{dR_S}{dt}$$

is to hold, then we must have $d\Delta R/dt = 0$. That is, the increment of resistance when the solid passes to the liquid is independent of temperature, which is what our picture suggested.

12. The same relation between the temperature coefficient of the solid and the liquid holds for some other metals. Thus for sodium at the melting point at atmospheric pressure I found for the coefficient of the solid 0.00414, and for the liquid 0.00310. The ratio of these is 1.34, and I found experimentally the ratio of the resistance of the liquid to that of the solid to be 1.45. Mercury has the largest ratio observed for the

ratio of specific resistance of liquid to solid, and we would therefore expect an unusually small temperature coefficient for the liquid. It is in fact unusually small, being only 0.00090 at 0° C. If we assume that the coefficent of the solid is $1/\tau$, we find for its coefficient at the melting point (– 38.85°) 0.00409, and for that of the liquid at the same temperature 0.000934. The ratio of these is 4.38 and the ratio of the resistance of the liquid to the solid found by Onnes[1] is 4.22. On the other hand, the relation breaks down for solid and liquid potassium. I find that the temperature coefficient of the liquid is actually slightly greater than that of the solid at the melting point, which is abnormal, whereas the resistance of the liquid is 1.56 times greater than that of the solid. It might be mentioned that my figures for the temperature coefficients of solid and liquid do not agree with those of other observers. The values of Northrup[1] are most favorable to the hypothesis being urged here. He makes the coefficient of liquid potassium less than that of the solid, but the ratio of the two coefficients as found by him is only 1.27, whereas the ratio of specific resistances would demand 1.56.

The only other metals for which I have determined the coefficients, namely bismuth and gallium, cannot possibly satisfy the relation because the temperature coefficients of the solid are greater than those of the liquid, as is normal, but the resistance of the liquid is less than that of the solid. This is because of the abnormal volume relation, so that we are not surprised that the relation breaks down.

There are also some data of Northrup[3] for other metals. For gold his data give a ratio of the temperature coefficients at the melting point of 2.15, and he found for the ratio of the resistances 2.28.

Now with regard to the explanation of this relation between the temperature coefficients, our point of view would lead us to expect an invariable element, unaffected by changes of temperature, in the relative resistances of solid and liquid, and hence, according to the analysis, a ratio of the coefficients equal to the inverse ratio of the resistances. When the solid melts to the liquid the atoms lose their regular mutual arrangement, which becomes haphazard. In passing from atom to atom in the liquid the electrons cannot avail themselves of particularly favorable localities, but must use the average of the entire atom. This element will be a permanent difference between solid and liquid, unaffected by changes of temperature. However, the relations are so complicated that this can be only part of the picture, and in fact the relation

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[1] K. Onnes, Kon. Akad. Wet. Proc., 4, 113–115, 1911.

[2] E. F. Northrup, Trans. Amer. Elec. Chem. Soc., 20, 185–204, 1911.

[3] E. F. Northrup, Jour. Fran. Inst., 177, 287–292, 1914.

does not always hold. There is a specific effect due to the "τ" term in our formula for resistance. This may to some extent be neutralized by the tendency of the "gaps" in the liquid condition to function in the second way, decreasing instead of increasing the resistance with increasing amplitude. Furthermore, it is not certain to what extent our deduction of the variation of amplitude with temperature and pressure is valid for the liquid. We assumed that the energy of atomic vibration was either potential or else kinetic energy of to and fro motion. Now in the liquid there is probably some rotational energy as well. The exact relation between the translational and the rotational energies in the liquid is not yet clear, so that we do not know how large an effect to expect on this account. It seems evident, however, that the direction of the effect will be to decrease somewhat the temperature coefficient of amplitude, because part at least of the energy will be rotational, and therefore the translational energy, and so the amplitude, cannot increase as rapidly with increasing temperature as if we had supposed all the energy to be translational.

The entire theoretical significance of this observation as to the ratio of the temperature coefficients of solid and liquid may therefore not yet be completely clear, but at any rate the observation itself is to be kept in mind. I am not aware that this relation has been previously noticed.

13. The considerations of the last section have an application to the temperature coefficient of resistance of the liquid at high temperatures. Write the formula for the resistance in the form

$$R_L = \text{const } \tau^{1/2}/l_L.$$

Now the free path, l_L, is inversely proportional to the chance, β, that the free flight of the electron will be terminated in passing from atom to atom. Let us analyze this chance of termination into two parts. One will depend on the haphazard orientation of the atoms with respect to each other, and will be independent of temperature, and the other will depend on the amplitude, and will, as before, be proportional to the amplitude, if we can neglect the pure volume effect, and the tendency of the gaps to function in the second way. Hence we may write

$$\beta = A_1 + A_2\alpha,$$

which gives

$$R_L = \text{const } \tau^{1/2}(A + \alpha).$$

Differentiate this with respect to the temperature, giving,

$$\frac{1}{R_L}\frac{dR_L}{d\tau} = \frac{1}{2t} + \frac{\alpha}{A + \alpha} \cdot \frac{1}{2\tau}.$$

Hence we see that at high temperatures, where α is large, the temperature coefficient again approaches $1/\tau$, although at lower temperatures it is less than $1/\tau$. These considerations apply only to those liquids for which the functioning of the gaps by decreasing resistance at large distances of separation may be neglected. Now there are liquids for which this last factor is certainly important, as zinc and cadmium, whose temperature coefficients immediately after melting are negative, but there are other liquids, as tin and lead, whose resistance in the liquid shows no peculiarity. The resistance of these liquids increases linearly with the temperature. In fact the linear increase of the resistance of tin is so striking that Northrup and Suydam[1] have proposed this as the basis of a resistance thermometer. Now it is evident that the temperature coefficient of any metal which increases linearly in resistance with temperature must eventually become equal to $1/\tau$, according to the above formula.

14. The very large difference of resistance between solid and liquid mercury is striking, particularly in view of the fact that the change of volume on melting is not larger than usual. This would suggest that the structure of the mercury atom is such that the element of haphazard orientation is particularly important. This element we saw has a tendency to constancy. Consider now the variation of resistance with pressure. I found experimentally that the pressure coefficient of the liquid is less numerically than that of the solid, a somewhat unexpected result. Write

$$R_L = R_S + \Delta R.$$

Differentiate with respect to the pressure

$$\frac{1}{R_L}\left(\frac{\partial R_L}{\partial p}\right)_\tau = \frac{R_S}{R_L}\cdot\frac{1}{R_S}\left(\frac{\partial R_S}{\partial p}\right)_\tau + \frac{\Delta R}{R_L}\cdot\frac{1}{\Delta R}\left(\frac{\partial \Delta R}{\partial p}\right)_\tau .$$

This equation shows at once that the experimental relation

$$\frac{1}{R_L}\left(\frac{\partial R_L}{\partial p}\right)_\tau < \frac{1}{R_S}\left(\frac{\partial R_S}{\partial p}\right)_\tau$$

demands that

$$\frac{1}{\Delta R}\left(\frac{\partial \Delta R}{\partial p}\right)_\tau < \frac{1}{R_S}\left(\frac{\partial R_S}{\partial p}\right)_\tau ,$$

which is what our picture led us to expect. Notice that we have disregarded the pure volume effect, so that these considerations would not be expected to apply to a highly compressible metal. Mercury, however, is relatively incompressible, and the considerations have a certain force.

15. A similar consideration applies to the pressure coefficient of alloys. The pressure coefficient of resistance of the alloys of the relatively in-

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[1] E. F. Northrup and V. A. Suydam, Jour. Fran. Inst., 175, 153–161, 1913.

compressible metals is usually less than that of the components. This is to be ascribed to a relative insensitiveness to pressure of the feature which is responsible for the increased resistance of the alloy. This feature is the failure of the exact register of the different kinds of atoms, and this feature will be insensitive to pressure unless the atoms themselves are highly deformable. The data for alloys are very restricted, and it is not known how the alloys of such very compressible metals as sodium and potassium would behave under pressure.

16. The same considerations also show why the ratio of resistance of solid to liquid is relatively constant along the melting curve. For the six substances which I measured this ratio suffered relatively little change, although the accuracy of the measurement was not as great as desirable in some cases. This constancy is to be ascribed to the fact that the effect of haphazard orientation in the liquid as opposed to the regular arrangement in the crystal is an intrinsic difference between solid and liquid, and is not affected by temperature and pressure changes.

17. In my previous paper some significance was attached to the fact that the temperature coefficient of liquid mercury at constant volume is negative. This was ascribed to the second manner of functioning of the gaps at the increased volume of the liquid. It was suggested that such might be found to be the case for all liquid metals. At the same time there was no necessity in the suggestion, and there was no criterion which could show whether the second manner of functioning of the gaps would be more important than the normal method for other metals or not. It appears that this is not the case for the new metals. The computation could be made only for sodium, potassium, and bismuth. The values of the thermal expansion are not known for liquid gallium. For lithium, because of the abnormal pressure coefficient of the liquid, the temperature coefficient of the liquid at constant volume is even larger than at constant pressure, and is of course positive. The computation for the three metals above is somewhat uncertain because the compressibility and thermal expansion of the liquids are not known with any great accuracy. A discussion will be found in the new American Academy paper. I find for sodium that the coefficient at constant pressure is 0.00325 against 0.00170 at constant volume; for potassium the respective coefficients are 0.0044 and 0.0025, and for bismuth they are 0.000475 and 0.000015. The uncertainty in the fundamental data is not so great but that there can be no doubt that the coefficients at constant volume of both liquid sodium and potassium are positive, but there may be considerable question in the case of bismuth.

Sodium and potassium are among the most compressible and expansible of the elements, and it is perhaps not surprising that for them the amplitude continues to function in the normal manner. The example of bismuth makes it not unlikely, however, that the coefficient at constant volume of the ordinary liquid metals may be negative, as it is for mercury, instead of positive. It is in any event significant that the difference between the coefficients at constant volume and constant pressure of all the liquid metals is greater than the difference for the solid, so that the tendency of the gap to function in the second way is manifest.

The second manner of functioning of the gap in liquid mercury may at first seem inconsistent with the relative constancy of the gap under pressure, which we invoked to explain the pressure coefficient of the liquid being less than that of the solid. But it is to be remembered that a change of temperature is always more effective than a change of pressure (compare the magnitudes of the compressibility and the dilatation) so that the two facts are not inconsistent. It is also to be kept in mind that the difference of compressibility between solid and liquid mercury is abnormally small.

18. The behavior of the alkali metals sodium and potassium is of interest because of the unusual magnitude of the effect, and demands special discussion.

In the first place I may mention in the interest of candidness that I had anticipated a possible positive pressure coefficient for potassium on the basis of the similarity of the structure of its atom to that of lithium. According to Langmuir's picture,[1] lithium consists of a positive kernel surrounded by one shell, with a single electron outside that shell, whereas potassium consists of a positive kernel, two surrounding shells, and a single electron outside the two shells. This similarity would seem to give some justification for the expectation of a positive pressure effect. However, the facts are the exact reverse. Not only is the pressure coefficient of potassium negative, as is normal, but it is larger than for any other metal as yet measured. It would seem, therefore, that the greater size of the central portion of the atomic structure of the atom of potassium prevents the arrangement of the superficial electrons in a space lattice, or at least is not favorable to the ready mobility of such a lattice, if it exists. The mechanism of conduction in the case of potassium is probably normal, in that the electrons pass through the substance of the atoms. It must be said, however, that potassium is abnormal in several respects. My measurements make the temperature coefficient of the liquid at the freezing point greater than that of the solid, and the pressure

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[1] I. Langmuir, Jour. Amer. Chem. Soc., 41, 868–934, 1919.

effects are abnormal in that the coefficient of the liquid decreases with increasing temperature. It is therefore not impossible that part of the mechanism of conduction of potassium is abnormal.

If the expected magnitude of the pressure coefficients of sodium and potassium is computed on the basis of the preceding paper from twice the pressure coefficient of amplitude, it will be found in both cases that the computed values are very much too small. The observed coefficient of sodium is 1.75 times the computed, and the observed value for potassium is 2.4 times that computed. According to our view, this means an unusually large volume effect in addition to the amplitude effect. Now not only are the compressibilities of sodium and potassium among the highest of the elements, but the change of atomic distance with pressure is an unusually large fraction of the change of amplitude, so that for this additional reason we would expect a large volume effect. If the ratio of the pressure coefficient of amplitude to the coefficient of linear compressibility be computed, by the use of formulas already given, the values 3.8 and 3.6 will be found for sodium and potassium respectively. This is unusually small, we have already seen that the run of values for the ordinary metals is from 6 to 9. Lithium is the only metal which is markedly lower, and for this the ratio is 0.95, but since its conduction mechanism is abnormal, we need not consider it further. It is, then, just for such metals as sodium and potassium that our picture would lead us to expect the largest discrepancy between the amplitude and the total effects, and it is just here that we find them.

Sodium and potassium are also unusual in the large decrease of the pressure coefficient with increasing pressure. Between atmospheric pressure and 12,000 kg. the instantaneous coefficient of sodium has decreased by a factor of 2.5, and that of potassium by 2.6. In the previous work the largest decrease was for lead, with a factor 1.38. The large decreases for sodium and potassium are evidently connected with the unusually high compressibilities. It is a universal result of experiment that those substances with a high compressibility show not only an unusually large absolute decrease of compressibility with rising pressure, but the relative decrease is also unusually high. The actual data have not been determined for sodium and potassium, but we have every reason to expect that the same will be found to hold for them also. This means that the volume effect becomes relatively less at high pressures, and that the pressure coefficient decreases by an unusually large amount.

In addition to the unusually large decrease of pressure coefficient with increasing pressure, there is an unusually large change of the coefficients with temperature. The pressure coefficient increases with rising temperature by an unusually large amount, whereas the metals of the previous paper showed relatively little change with temperature. The coefficients of sodium at atmospheric pressure increase by a factor of 1.18 between 0° and 80°. The corresponding comparison cannot be made for potassium, because it is not solid over a wide enough range, but a comparison of the results at higher pressures shows that the change for potassium is even more rapid than for sodium. Of course a mathematical consquence of a pressure coefficient changing rapidly with temperature is a temperature coefficient changing rapidly with pressure. This effect again can be explained on the basis of the volume effect. Sodium is unusually expansible at atmospheric pressure, and we would expect a temperature coefficient considerably greater than that computed on the basis of the amplitude effect alone, that is, a coefficient greater than $1/\tau$. And as a matter of fact, the average coefficient of sodium between 0° and 100° is 0.00475, larger than $1/\tau$ by an unusual amount. Now at higher pressures, although the actual measurements have not yet been made, it is exceedingly probable that the volume expansion will show an unusually large decrease, and that sodium will approach more nearly the behavior of the more staid metals. The behavior of the temperature coefficient is in entire accord with this expectation, at 12,000 kg. it has dropped from 0.00475 to 0.00408, a value still somewhat larger than $1/\tau$, but not any larger than for many of the other metals at atmospheric pressure.

These considerations would lead us to expect the temperature coefficient to become not less than $1/\tau$ for any pressure, no matter how high, as long as the atomic vibration continues to function in the normal way in decreasing the probability of an undisturbed flight of the electron. It is conceivable that at exceedingly high pressures the atom itself may become so much compressed that a moderate amount of temperature disturbance is not sufficient to interfere at all with the chance of passage of an electron from atom to atom. The kinetic energy of temperature agitation in such a solid would consist in a quivering of the nucleus within the outer structure of the atom, which is prevented from much superficial motion by the close packing of the adjacent atoms. This state of affairs demands an unusually small thermal expansion. If such a state of affairs should occur, we might expect the temperature coefficient of resistance to become less than $1/\tau$. Now this is actually what does occur with potassium. Its mean temperature coefficient between 25° and 60° decreases from 0.00454 at atmospheric pressure to 0.00184 at 12,000 kg., the final value thus being much less than $1/\tau$. This speculation is most attractive, but more weight cannot be attached to it until the dilation of potassium has been measured at high pressures. It may be said that if this effect is to exist anywhere, it has the best chance with potassium of the metals measured, since it is by far the most compressible. Potassium is a trifle more than twice as compressible as the nearest metal sodium. And in further support of this view it may be noticed that the temperature coefficient of potassium at 6,000 kg. has dropped only to 0.0034, and it is therefore still a little higher than $1/\tau$ ($\tau = 298°$ Abs.), so that the decrease of the temperature coefficient becomes increasingly rapid at higher pressures, a most unusual behavior for a pressure effect. In caution it may be said that the experimental accuracy in determining the variation of the coefficients of potassium was not so high as for some other substances. It will be most interesting to attempt the verification of this observation on cæsium, which is almost twice as compressible as potassium.

If this observation should be justified by the measurements of thermal expansion, it would be a further most important verification of the view that the free flight of the electrons is interferred with during the passage from one atom to another, and that the interference is not due to the vibration of the nucleus, for the temperature agitation of the nucleus must continue to exceedingly high pressures.

19. The new data cover the non-metallic elements carbon and phosphorus (black). It is probably too early to extend this theory to all non-metallic substances, but it is interesting that in two important particulars the behavior of carbon and black phosphorus is what we would expect. We have thought of the gaps between atoms as functioning in two ways. Normally in metals the electrons leap easily across the gaps, and their passage is made more difficult by temperature agitation. The gaps, when in this condition, have a low specific resistance. But when the atoms are separated by more than the usual amount the electrons usually find difficulty in leaping the gaps, which are thus of high specific resistance, but the passage may be made more easy by increasing violence of temperature agitation, which brings the atoms closer together during part of their vibration. If the gaps are on the average in this second condition, we expect a high specific resistance for the substance as a whole, and a negative temperature coefficient of resistance (at least at constant volume, and presumably at constant pressure). Now these are the facts for both carbon and black phosphorus. Their specific resistance is much higher than that of any metal, but their temperature coefficient is negative.

It is also natural to expect that in such a substance the effect of pressure will be to drive the gaps from the second condition to the first as the atoms are brought closer together. This means an unusually large decrease of resistance with pressure. This is the fact for black phosphorus. The pressure effect is larger than for any other substance, and is so large that at 12,000 kg. the resistance is only 3 per cent. of its value at atmospheric pressure. Even after this enormous decrease the resistance is still much higher than for metals. The specific resistance of black phosphorus normally is 1 ohm per cm. cube, and therefore at 12,000 kg. it is still 0.03. The temperature coefficient at 12,000 kg. is still negative, but has dropped numerically from 0.0058 to 0.0030, which is in the direction to be expected as the resistance approaches that of a metal in character. The pressure effect on black phosphorus is different in another respect from that of metals, in that the relative coefficient $1/R(\partial R/\partial p)_\tau$ is very nearly independent of pressure. We saw that for metals this coefficient decreases with increasing pressure, and we gave as the explanation the decreasing compressibility with increasing pressure. It is evident that the mechanism is different in the case of black phosphorus. A constant coefficient would mean that a constant increment of external pressure always drives the same fraction of the total number of gaps from the second into the first group. We would expect this condition to hold as long as the number of electrons in the second group is still large. That this number still is large, even under 12,000 kg., is shown by the fact that under 12,000 kg. the resistance is still very much higher than for metals.

Conclusion.

We have now considered a great many of the phenomena of the electrical resistance of metals, and found them all consistent with the view of the nature of electrical conduction previously advanced. The facts considered in this paper were nearly all not known when the view was first suggested and are different in character from any previously available, having largely to do with the pressure and temperature changes of resistance of both the liquid and the solid metal, particularly of the alkali metals, in which the effects are very large.

The view of conduction is that the free paths of the electrons are interfered with in jumping from atom to atom, but that throughout the interior of the atom there is no resistance to their motion. We have put this conception into quantitative form, partly on the basis of the classical theory. At ordinary temperatures we have assumed the equipartition velocity of the electrons, that their number is independent of the temperature, and that the free path varies with the amplitude in a way which may be computed. This gives Ohm's law, the correct temperature coefficient, the Wiedemann-Franz ratio, an important part of the pressure effect, vanishing resistance at 0° Abs., and avoids the specific heat difficulty. In addition there are certain features which can be discussed only qualitatively; there is a specific effect of changing volume of which we may be pretty sure of the sign, but which depends in an unknown way on atomic structure, and there is a second manner of functioning of the "gap" at large volumes. Within the restricted range open to quantitative discussion the facts are in accord with the theory, and throughout the much wider domain open to qualitative discussion I have not found a single fact which is inconsistent, and many which I believe demand this view uniquely.

The probability seems great that the view contains the most important elements operative in the phenomena of resistance and thermal conduction in metals. This theory does not exclude the presence of other factors which may be important for the thermo-electric and the Hall effects. In fact our theory has made it inevitable that there should be in the metal charged ions as well as the electrons, and there is no reason why these should not be important in certain phenomena, although because of their low velocity of translation they cannot be expected to play a large part in conduction.

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