THEORETICAL CONSIDERATIONS ON THE NATURE OF METALLIC RESISTANCE, WITH ESPECIAL REGARD TO THE PRESSURE EFFECTS.

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IN a recent number of the Proceedings of the American Academy[1] I have given data for the effect of pressures to 12,000 kg. and temperatures between 0° and 100° C. on the electrical resistance of 22 metals. A detailed discussion of the nature of the results and methods of measurement and calculation will be found in that paper. The most important results follow. (1) The temperature coefficient of resistance is nearly independent of pressure; this holds for pressures high enough to compress the metal in many cases to less than its volume at 0° Abs. Another way of stating the same fact is that the pressure coefficient is independent of temperature. (2) The relative pressure coefficient of resistance becomes less at higher pressures. (3) The curvature of the resistance-pressure curves is in most cases greater at lower temperatures. (4) Two metals, bismuth and antimony, show an abnormal positive pressure coefficient of resistance. The anomaly of bismuth was known before, but that of antimony is new.

The purpose of this paper is to present a view of the nature of metallic conduction which had its origin in an attempt to bring into line the facts at high pressures, but which also accounts for other facts not intimately connected with the pressure effects. In brief, this view of the nature of conduction regards all metals as naturally perfect conductors in the sense that the electrons may pass without resistance from atom to atom when the atoms are in contact at rest. The precise mechanism of this free transfer need not be further specified for our purposes; we may if we like suppose the electrons capable of freely penetrating the substance of the atom, in much the same way as recently suggested by Professor Hall.[2] If the atoms become too much separated, however, the electrons encounter difficulty in passing from atom to atom, and if the separation is too great, are almost entirely unable to pass. In a solid at absolute zero the electrons pass freely from atom to atom, thus giving perfect conductivity, but as the temperature is raised, the atomic centers become separated, and if the separation passes a certain critical value, the electrons encounter

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[1] P. W. Bridgman, Proc. Amer. Acad., 52, 571–646, 1917.

[2] E. H. Hall, Proc. Amer. Acad., 50, 67–103, 1914.

difficulty, and electrical resistance makes its appearance. In a solid under given conditions there must be a certain number of pairs of atoms separated by more than the critical distance, or we may say, there are a certain number of "gaps." The resistance is proportional to the number of gaps. Now the number of gaps evidently is closely connected with the mean amplitude of oscillation of the atoms. Our first task, in attempting to cast this view of the nature of conduction into quantitative form, is to find how the amplitude changes with pressure and temperature.

The following deduction of the variation of amplitude and frequency is valid only at moderate temperatures, where the classical statistical mechanics and quantum theory are not essentially in conflict. For these temperatures, everything may be obtained from three equations. We assume in the first place that the vibration of an atom is simple harmonic, and that the energy of a degree of freedom is equal to the energy of a degree of freedom of a gas atom at the same temperature. This gives as a first equation

$$\nu^2\alpha^2 = \text{const } \tau, \tag{1}$$

where ν is the average frequency of atomic vibration, and α is the average amplitude. The second assumption concerns the nature of the restoring force under which the atoms execute their harmonic vibrations. If the volume remains unaltered, it is natural to suppose that in most cases the average restoring force for a given displacement will not be affected by such changes as changes of temperature. We therefore write as the second equation

$$\left(\frac{\partial \nu}{\partial \tau}\right)_v = 0. \tag{2}$$

These two relations are not enough to completely determine ν and α as functions of pressure and temperature. As the third equation I will adopt Grüneisen's relation[1]

$$\frac{1}{\nu}\left(\frac{\partial \nu}{\partial p}\right)_s = \frac{1}{C_p}\left(\frac{dv}{\partial \tau}\right)_p. \tag{3}$$

These three relations must all be recognized as only approximate. At low temperatures $\nu^2\alpha^2$ increases more rapidly than τ, and at high temperatures there may be further increase. The frequency cannot be a function of volume only unless at constant volume the average restoring force on an atom is a linear function of atomic displacement. But it seems inevitable that as the amplitude of oscillation becomes greater the restoring force, due to contact between atoms, must increase more

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[1] E. Grüneisen, Ann. Phys., 39, formula 23, p. 276, 1912.

rapidly than the displacement, resulting in an increase of frequency as temperature is increased at constant volume. The existence of an effect of this nature is demonstrated by the existence of a positive thermal expansion. For if the restoring force were truly linear, the expansion must probably vanish, as I have suggested in connection with effects found in liquids at high pressures, and as Debye[1] has suggested more recently. Equation (2) is, therefore, only a first approximation. Grüneisen's relation, equation (3), is in accordance with an equation of quantum theory, obtained by assuming Planck's relation between energy and entropy. Planck finds that the entropy is a determinate universal function of ν/τ. Grüneisen's assumption is more general than the relation obtained from quantum theory, in that he assumes entropy a function only of ν/τ without assuming anything at all about the special form of the function; in fact he does not even assume that the function is of the same form for different substances. Since the particular form of the function demanded by quantum theory seems to suit the facts at atmospheric pressure fairly well, we are reasonably safe in assuming Grüneisen's less restricted form.

From equations (2) and (3) above we obtain immediately $(\partial\nu/\partial p)_\tau$ and $(\partial\nu/\partial\tau)_p$. These are the derivatives which we want, because in this work p and τ are taken as the independent variables. We have, from (2)

$$\left(\frac{\partial\nu}{\partial\tau}\right)_v \equiv \left(\frac{\partial\nu}{\partial\tau}\right)_p + \left(\frac{\partial\nu}{\partial p}\right)_\tau \left(\frac{\partial p}{\partial\tau}\right)_v = 0,$$

and from (3)

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_s \equiv \frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_\tau + \frac{1}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p \left(\frac{\partial\tau}{\partial p}\right)_s = 0.$$

But

$$\left(\frac{\partial p}{\partial\tau}\right)_v = -\left(\frac{\partial v}{\partial\tau}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau, \quad \text{and} \quad \left(\frac{\partial\tau}{\partial p}\right)_s = \frac{\tau}{C_p}\left(\frac{\partial v}{\partial\tau}\right)_p.$$

Substituting and solving, we obtain

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p = \left(\frac{\partial v}{\partial\tau}\right)_p^2 \Big/ C_v \left(\frac{\partial v}{\partial p}\right)_\tau, \tag{4}$$

and

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_\tau = \left(\frac{\partial v}{\partial\tau}\right)_p \Big/ C_v. \tag{5}$$

Now differentiating (1) logarithmically, and eliminating $(1/\nu)(\partial\nu/\partial\tau)_p$ and $1/\nu)(\partial\nu/\partial p)_\tau$ we have immediately

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau = -\left(\frac{\partial v}{\partial\tau}\right)_p \Big/ C_v, \tag{6}$$

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[1] P. Debye, Wolfskehl. Conference, Göttingen, 1914, p. 19–60.

and

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \tau}\right)_p = \frac{1}{2\tau} - \left(\frac{\partial v}{\partial \tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau . \tag{7}$$

These equations give, therefore, the variation of both ν and α in any direction in terms only of quantities of thermodynamic nature.

The numerical magnitudes of these quantities first claim attention. The relative pressure coefficient of amplitude is negative, and its magnitude is in general six to nine times the linear compressibility. The amplitude increases with increasing temperature, approximately as $1/2\tau$, since the term $(\partial v/\partial \tau)_p^2/(C_v(\partial v/\partial p)_\tau)$ is small. The frequency increases with increasing pressure, the rate of increase being the same as the rate of decrease of the amplitude, and the frequency decreases with increasing temperature, but the rate of decrease is small compared with the rate of increase of amplitude.

TABLE I.

Metal.	$-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$.	$\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p$.	C_v Kg. Cm. per Cm³.	$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \tau}\right)_p$.	$-\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\tau$.	$-\frac{1}{\nu}\left(\frac{\partial \nu}{\partial \tau}\right)_p$.
In......	(?)2.0×10^{-6}	$.0_313$	15.2	2.39×10^{-3}	8.6×10^{-6}	55.5×10^{-5}
Sn......	1.86	$.0_451$	16.8	1.92	3.03	8.3
Tl......	2.26	$.0_492$	15.4	2.06	5.96	24.3
Cd......	2.06	$.0_490$	19.2	2.04	4.7	20.4
Pb......	2.28	$.0_4879$	14.0	2.07	6.27	24.3
Zn......	1.66	$.0_478$	26.8	1.97	2.91	13.7
Mg.....	2.84	$.0_478$	17.7	1.96	4.4	12.1
Al......	1.44	$.0_474$	23.1	2.00	3.19	16.5
Ag......	.99	$.0_455$	24.1	1.96	2.30	12.9
Au......	.628	$.0_4429$	24.8	1.95	1.73	11.8
Cu......	.735	$.0_451$	34.2	1.94	1.49	10.3
Ni......	.42	$.0_4375$	40.0	1.88	.94	8.4
Co......	? .50	$.0_437$	37.0	1.91	1.00	7.5
Fe......	.58	$.0_4375$	34.6	1.90	1.08	7.0
Pd......	.53	$.0_4355$	29.4	1.92	1.21	8.1
Pt......	.272	$.0_4292$	28.5	1.94	1.02	10.9
Mo.....	.45	$.0_4108$	24.7	1.84	.44	1.13
Ta......	.52	$.0_4237$	22.8	1.88	1.04	4.85
W......	.265	$.0_4101$	27.6	1.84	.37	1.39

In Table I. are collected the numerical values of the changes of amplitude and frequency for the metals whose pressure coefficient I have measured. In the table are also included the fundamental thermodynamic data used in the calculations. There is often considerable uncertainty as to the best experimental values to choose. I have in general used for thermal expansion the most consistent values from the last edition of Landolt and Börnstein and for compressibility the values of

Richards. A more detailed discussion of the manner of choice of these data may be found in the American Academy paper.

With the numerical values of the changes of amplitude at hand, we are now in a position to search for a connection between the changes of resistance and amplitude. It turns out that there is a very simple approximate relation between these two quantities, which I offer as the most important result of this paper. The relation is that the change of resistance with temperature or pressure or any other thermodynamic variable is twice the relative change of amplitude under the same conditions. It is perhaps worth mentioning that I was led to search for a relation between resistance and amplitude by the view I have outlined of the nature of resistance, and that the view was not suggested by observing the relation.

Consider first the variation of resistance with temperature. In order to simplify this first discussion, we consider the temperature coefficient at constant volume, thus avoiding a very small correction for changing volume. From the formulas already given, it follows immediately that

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

Now the temperature coefficient of most metals is nearly the reciprocal of the absolute temperature, so that we have here an approximate expression for the change of resistance in terms of the change of amplitude. The temperature coefficient as ordinarily given, however, is the coefficient of the observed resistance at constant pressure. The coefficient at constant volume is more nearly equal to $1/\tau$ than is the coefficient at constant pressure. In Table II. are shown the temperature coefficients at constant volume of the specific resistance at 0° C. In comparing these values with others it must be remembered that we are giving here the specific resistance, and not the observed resistance, and also that we are listing the instantaneous coefficient at 0° and not the average coefficient between 0° and 100°.

The temperature coefficient at constant pressure involves a correction for changing volume, as already suggested. If the view of conduction given above is justified, we would expect that decreasing the number of atoms would, other things being equal, increase the resistance. The increase is proportional to the change of linear dimensions, that is to $\frac{1}{3}(1/v)(\partial v/\partial\tau)_p$, because an increase of length and an increase of one of the cross sectional dimensions work in opposite directions on the resistance. It turns out that to the same degree of approximation to which $(1/w)(\partial w/\partial\tau)_v$ is equal to $2(1/\alpha)(\partial\alpha/\partial\tau)_v$, $1/w(\partial w/\partial\tau)_p$ is also equal to

$2(1/\alpha)(\partial\alpha/\partial\tau)_p + \frac{1}{3}(1/v)(\partial v/\partial\tau)_p$. It is hardly worth while to give a special table for this other temperature coefficient. The correction for volume averages about $\frac{1}{2}$ per cent.

TABLE II.

Metal.	$\frac{1}{w}\left(\frac{\partial w}{\partial\tau}\right)_v$.	$\gamma\equiv\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau$.		**Ratio of γ calc. by Grüneisen's Formula to γ Obs.**	$\frac{\left(\frac{\partial\tau}{\partial p}\right)_w}{\left(\frac{\partial\tau}{\partial p}\right)_\alpha}$.
		$\gamma_{\text{Obs.}}$	$\frac{\gamma_{\text{Calc.}}}{\gamma_{\text{Obs.}}}$.		
In........	.00360	-12.9×10^{-6}	1.39	1.063	0.875
Sn........	402	11.1	0.597	0.420	1.62
Tl........	463	13.9	0.91	0.813	0.932
Cd........	357	11.3	0.894	0.643	1.21
Pb........	350	15.2	0.875	0.671	1.23
Zn........	389	5.95	1.066	0.718	0.99
Mg.......	380	6.4	1.547	1.094	0.72
Al........	409	4.64	1.48	1.157	0.665
Ag........	384	3.83	1.288	0.973	0.800
Au........	369	3.33	1.132	0.877	0.949
Cu........	414	2.45	1.315	0.985	0.738
Ni........	605	1.72	1.09	1.197	0.568
Co........	358	1.10	1.975	1.328	0.573
Fe........	545	2.60	0.905	0.807	0.815
Pd........	308	2.16	1.205	0.792	1.057
Pt........	367	2.07	1.030	0.865	1.007
Mo.......	432	1.48	0.601	0.338	1.443
Ta........	290	1.66	1.356	0.814	1.007
W........	313	1.37	0.598	0.305	1.354

We next compare the pressure coefficient of resistance at constant temperature with the change of amplitude with pressure at constant temperature, corrected for the effect of changing volume as just explained. The pressure coefficient computed in this way is given by the formula

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau = 2\,\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau + \frac{1}{3}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau.$$

The last term, which is the correction factor for changing volume, amounts to from 5 to 10 per cent. of the total effect. In Table II., Column 4, the ratio of the observed value of the pressure coefficient of specific resistance at 0° C. and 0 kg. to the value computed as above is shown.

The agreement is not as good as could be desired, but it should be remembered that the classical free electron theory did not give even the right sign to the pressure effect, to say nothing of the numerical magnitude, and that there has been only one other theory proposed which has attempted to account for the pressure effect. This other theory is that of Grüneisen,[1] who modifies the theory of Wien,[2] who regards the electrons as moving with constant velocities independent of the temperature. The formula of Grüneisen is

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau = \frac{1}{u}\left(\frac{\partial u}{\partial p}\right)_s - \frac{1}{N}\left(\frac{\partial N}{dp}\right)_s - \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s - \frac{1}{C_p}\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p\left[1 + \frac{1}{w}\left(\frac{\partial w}{\partial \tau}\right)_p \tau\right],$$

where u is the velocity of the free electrons, and N is their number per cm^3. In column 5 of Table II. the ratio of the values computed by Grüneisen's formula to the observed values are listed for purposes of comparison. It will be seen that on the whole the new formula agrees better with experiment than does that of Grüneisen. Grüneisen has discrepancies amounting to a factor of three for both Mo and W, whereas the greatest discrepancy of the new formula is by a factor of two for Co, which was known to be impure. There is also this difference between the new formula and that of Grüneisen, apart from its much greater simplicity. Grüneisen's formula does not give the pressure coefficient in terms only of other quantities of non-electrical nature, but, besides the first two terms which are small, introduces the temperature coefficient of resistance, which must be determined by experiment. It is of course true that the temperature coefficient is approximately equal to $1/\tau$, so that the last factor in Grüneisen's formula might have been written 2, but the formula would then have lost its theoretical significance, and become merely empirical. Furthermore, the agreement with observation would not have been so good if this simplification had been made, the departures of the temperature coefficients from equality with $1/\tau$ playing a real part in the numerical values given by the formula.

It is interesting to notice that by a combination of Grüneisen's formula with that suggested above, an empirical relation may be obtained much better than either. The relation is

$$\gamma_G/\gamma_{\mathrm{Obs}} + \gamma_{\mathrm{Obs}}/\gamma_B = \text{Const.}$$

where $\gamma = (1/w)(\partial w/\partial p)_\tau$ and the subscripts indicate whether the coefficient is observed or calculated according to Grüneisen's or my formula. The "constant" varies for the 19 normal metals from 1.54 to 1.97, or a range of 14 per cent. about the mean, whereas the variation in Grüneisen's formula, omitting Co, is 53 per cent., and that of the proposed formula above, omitting Co, is 37 per cent. It is curious, however, that the formula cannot be reversed, that is solved for γ_{Obs} to give an approxi-

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

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

mately correct value. It will be found, if one tries to operate with a fixed average value of the constant, that some substances give imaginary values for γ_{Obs}.

A result of some interest to be deduced from the expressions above for temperature and pressure coefficient is that the resistance is approximately constant along a line of constant amplitude. Column 6 in Table II. shows the ratio of $(\partial\tau/\partial p)_w$ to $(\partial\tau/\partial p)_\alpha$. This ratio of course should be unity if resistance were strictly constant at constant amplitude.

We may summarize the results of these numerical calculations by the statement that the change of specific resistance with either pressure or temperature, and therefore with any other thermodynamic variable, is given by

$$\frac{1}{w}dw = 2\frac{1}{\alpha}d\alpha + \tfrac{1}{3}dv,$$

to at least as good a degree of approximation as that of any other formula. The term containing the change of volume is comparatively unimportant, so that we may say that *the relative change of specific resistance in any direction is approximately equal to twice the corresponding change of average amplitude of atomic vibration.* The agreement with the pressure coefficient is better than that of the only previously proposed formula, and the temperature coefficient is correctly reproduced in the majority of cases. I know of no attempt to account for the departures of the temperature coefficient from $1/\tau$ except that of Wien, and his attempt to bring the departures into connection with the average frequency of atomic vibration cannot be considered a success.

The theoretical significance of this general relation becomes immediately obvious from the viewpoint outlined above that the resistance is proportional to the number of gaps between atoms. If the number of gaps is proportional to the square of the mean amplitude, then the change in the relative resistance will be proportional to twice the relative change of mean amplitude, plus a correction term for changing volume. Now it is easy to see how the number of gaps may be proportional to the square of the mean amplitude. A gap is formed when two neighboring atoms each have an amplitude enough greater than the mean so that the maximum distance of separation, when they are at opposite parts of their swing, shall exceed a critical value. That is, a gap is only produced by the chance coincidence in two neighboring atoms of two amplitudes both larger than the mean. If we suppose the amplitudes are distributed at random, the chance that there be two such coincident large amplitudes in two neighboring atoms is evidently proportional to the square of the chance that a single atom have an amplitude large enough. If then, the chance that a single atom have an amplitude of the requisite magnitude be proportional to the mean amplitude of oscillation of all the atoms, and this is certainly the simplest assumption that can be made, the connection becomes at once obvious. Of course in any actual case the conditions are much more complicated than we have supposed above; the amplitude of a single atom need not exceed a definite critical value before it can under any conditions form a gap with a neighboring atom, but the amplitude necessary to form a gap will depend on the relative phases of the two atoms. Such modifying features as this will not change the general result that the number of gaps is proportional to the square of the number of atoms with amplitude above a certain value, but will only change the numerical value of the factor of proportionality.

It is evident that these general considerations must be modified by many factors that vary from substance to substance. Consider first the manner of distribution of amplitudes about the mean. This is a subject which has not yet been worked out, but which can perhaps be solved in the not too distant future by such methods as those initiated by Born[1] in his recent book. Whatever the precise manner of distribution will turn out to be, we may be sure that it will not be Maxwell's distribution. I have obtained independent evidence on this point from the time rate of transition of polymorphs.[2] If one does assume Maxwell's distribution, the variation of number of gaps with mean amplitude may be worked out, and will be found proportional to some higher power of the mean amplitude than the second. This is sufficient to show that the manner of variation of number of gaps depends on the manner of distribution of amplitudes about the mean. The manner of distribution may well be expected to vary from substance to substance.

It is obvious, if all amplitudes are concentrated in a narrow band about the mean, that as temperature is increased from 0° Abs. there will be a definite temperature at which a finite number of gaps will suddenly appear, and the metal will suddenly become conducting, as do tin, lead, and mercury. This suggestion as to the sudden appearance of resistance must not be taken too seriously at present until it has been settled that this discontinuity is not due to a polymorphic transition, but in any event the new point of view leaves open such a possibility. If, on the other hand, the distribution is not so sharp, the appearance of resistance will not be so sudden, but in any event it is pretty evident that the resistance will at first, after it has once appeared, increase more rapidly than the increase of temperature itself. This is of course true for most pure metals; at low temperatures the resistance increases approximately as the

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[1] M. Born, Dynamik der Krystallgitter, Teubner, 1915.

[2] P. W. Bridgman, Proc. Amer. Acad., 52, 80, 1916.

fourth power of the temperature. The fact that the manner of variation of resistance with temperature is much the same for all metals at low temperatures suggests that at low temperatures, at least, the manner of distribution of amplitudes must be much the same for all substances. At higher temperatures individual differences in the behavior of resistance appear, and it seems not unlikely that similar differences in the manner of distribution should also appear.

Another important consideration is that of frequency. We have entirely neglected this factor in the considerations above. If frequency has no effect, then the effective number of gaps is not changed by a change of frequency. This means that if we double the frequency of oscillation we have thereby halved the time during which two atoms are separated by the critical distance during a single encounter, or doubling the rapidity of mean oscillation doubles the rapidity of every stage of the motion. This seems the most natural hypothesis, but judging by analogy with the collisions of elastic systems, it is by no means a necessary hypothesis. If the law of action between atoms is different for different kinds of atoms, there may be differences in the proportional length of time occupied in a collision. It does not seem unlikely that there should be such variations, and probably some of the discrepancies are to be explained by this neglected factor. The fact, however, that we have obtained as good agreement as we have probably means that the atoms of all normal metals are much alike. It ought to be possible to obtain information about the law of force between atoms by considerations of this character.

Perhaps the most striking factor that has been neglected is the effect of change of volume, apart from the effect on the number of atoms in unit volume. If the atoms are of finite size, and if this size remains constant, it is evident that when volume is decreased at constant amplitude, for example, the number of gaps and therefore the resistance should decrease. If the total volume occupied by the atoms is a large fraction of the total volume of the solid, such an effect should be rather large. According to Wien's theory, on the other hand, the resistance should increase instead of decrease as volume is decreased at constant amplitude. As a matter of fact, there seems to be no such effect; for some metals the resistance decreases with decreasing volume at constant amplitude, and for others the resistance increases. In any event the effect is small; in fact, to a first approximation, resistance is constant for all normal metals at constant amplitude, as has been shown in Table II. The point is an important one, and seems to me to indicate that under pressure the atom undergoes some sort of distortion so as to become effectively smaller. The same conclusion is strongly suggested by the fact that at pressures high enough to compress the volume to less than its value at 0° Abs. the temperature coefficient is practically unaffected. This would seem to indicate that the solid in some way remains similar to itself as pressure is increased, and this might be brought about by such a decrease of volume of the atoms themselves as to keep pace with the change of volume of the entire solid.

Another possibility to be kept in mind is that the boundary of the atom which determines the elastic collisions may not be the same as the boundary which determines the gaps for the passage of electrons. The latter may be inside the former, much in the same way as the effective radius of the atom as determined from dielectric measurements has been found to be less than the effective radius as found from kinetic theory. In fact, this view of the nature of conduction demands fundamentally a certain amount of interpenetration of the outer parts of the fields of force surrounding the atoms when they are in contact under normal circumstances in a solid, or else a very considerable distortion of the atom under changes of temperature. Or again, the atoms may not be absolutely separated in order to form a gap, but may be merely in contact over a smaller area, thus affording less chance for the passage of electrons.

In view of all these neglected factors it does not seem strange that the variations from the formula are as large as they are, but rather that they are no larger. It must be one of the next tasks of this theory to attempt to bring the variations from agreement with the formula into connection with the neglected factors, and obtain if possible a closer approximation to the observed values.

This is as far as I have been able to get quantitatively according to this view point. Qualitatively, however, many other facts may be brought into line if we consider that at high temperatures the gaps begin to function in a new way. Consider a metal kept at constant volume as temperature increases. If the volume is initially small, the number of gaps will increase, as already explained, as the average amplitude of oscillation is increased. But if the initial volume is large, the atoms may be separated so far that the electrons cannot pass freely from atom to atom under ordinary conditions, but can pass only when two atoms are brought especially close together during a collision of unusual violence. The number of such favorable opportunities will evidently increase as the mean amplitude increases. An increase of amplitude functions in two ways, therefore; at small volumes it increases the resistance by increasing the number of gaps, and at large volumes it decreases the resistance. If the metal is heated at constant pressure, being allowed to expand, there will be a progression from the first state of affairs toward the second. We may represent this by saying that effectively the atoms of the metal are divided into two classes; those of the first class are the ones to which we have already applied our formulas, and their resistance increases with increasing amplitude, while those of the second class tend to decrease in resistance as mean amplitude increases. The atoms of the first class have a low specific resistance, and those of the second class a high resistance. As the metal is heated the resistance will be affected in three ways; there will be an increase of resistance of the atoms of the first class, an increase of resistance due to the passage of atoms from the first to the second class, and a decrease of resistance of the atoms of the second class.

We now enumerate the various kinds of effect that can be brought into line by these considerations. This enumeration will include the facts that have already received quantitative treatment. (1) The temperature coefficient of resistance of solid metals at constant pressure is very nearly equal to $1/\tau$. It is, however, greater than $1/\tau$, and for nearly all metals becomes increasingly greater at higher temperatures. (2) The temperature coefficient of most liquid metals, on the other hand, is much less than $1/\tau$, and for some metals (Cd and Zn) may actually be negative. (3) The only liquid metal for which measurements have been made, mercury, has a negative temperature coefficient of resistance at constant volume. (4) At constant volume the temperature coefficient of solid metals becomes increasingly less than $1/\tau$ as temperature is raised, and if the same tendency persists will eventually become negative. (5) At very low temperatures some metals show a sudden drop of resistance to sensibly zero. (6) The pressure coefficient of resistance at constant temperature of nearly all pure metals is negative. The pressure coefficient of the only liquid metal measured, mercury, is much larger than that of solids. (7) The relative pressure coefficient at constant temperature decreases with increasing pressure. (8) The decrease with pressure of pressure coefficient at constant temperature is less at higher temperatures for most metals, but for a few metals with low melting point is greater. (9) If a metal is stretched by a force in tension, the resistance along the line of stretch is increased, but is decreased at right angles. (10) Two metals, Bi and Sb, have a positive pressure coefficient. This may be brought into direct connection with their abnormally small thermal expansion and the fact that both expand on freezing. (11) The high specific resistance of alloys compared with that of their constituents is what one would expect. The negative temperature coefficient of some alloys may also be explained by the same mechanism, and possibly the positive pressure coefficient.

We now consider these points in detail. (1) The temperature coefficient of solid metals, both at constant pressure and constant volume has already been discussed. One would be tempted to explain the fact that the coefficient is greater than $1/\tau$ by the passage of atoms from the first to the second state on raising temperature, but this explanation is seen not to be justified on considering that the coefficient at constant volume is also too large, and that the discrepancy at constant pressure is no greater than at constant volume. An explanation of the variations of temperature coefficient is much to be desired; as yet there seems to be no suggestion as to any possible connection with other physical properties. As already remarked, Wien's attack does not seem fruitful. Possibly a suggestion may be found in a distortion of the atoms with increasing violence of vibration, even at constant volume, which effectively decreases their volume, and so increases the number of gaps and the resistance. The upward curvature of the resistance curves, on the other hand, is probably to be explained by the increasing number of atoms in the second condition.

(2) The temperature coefficient of liquid metals, which are to be thought of as largely in the second condition, would be expected to be less than that of a solid because the temperature coefficient of atoms in the second class is by themselves negative. In any actual liquid the negative temperature coefficient of the second-class atoms is modified by the atoms which are passing from the first to the second class, and which produce an effect of the opposite sign. If the total number of atoms in the second class is large enough to outweigh this other effect, the coefficient will be negative, as it is for liquid Cd and Zn. In any event, we expect the coefficient for the liquid to be less than for the solid, and in general to be less than $1/\tau$. The accompanying table shows this.

TABLE III.

Temperature Coefficient of Resistance of Liquid Metals.

Metal.	Temp. °C.	Temp. Coeff.	$\frac{1}{T}$.	Coefficient of Solid Extrapolated.
Na	100°	.00330	.00268	.00348
K	100	.00342	.00268	.00369
Al	657	.00051	.00107	
Cu	1100	.00037	.00073	
Sn	500	.00048	.00115	
Au	1100	.00045	.00073	
Hg	100	.00094	.00268	
Pb	500	.00044	.00115	
Bi	271	.00042	.00184	.0020±

Only two of the metals, K and Na which have low melting points, have a coefficient greater than $1/\tau$, and for all the metals the coefficient of the liquid is less than that of the solid at the same temperature. The coefficients of the solids listed in the table were obtained by an extrapolation; the coefficients of the solids not listed are in all cases greater than $1/\tau$.

(3) If a liquid metal is heated at constant volume, the relative number of atoms in the two classes is probably little affected, and we would expect the temperature coefficient to be negative, if the number of atoms in the second group is larger than those of the first, as we suppose it is for a liquid. This is verified by the only liquid metal for which the data exist, liquid mercury. This observation was first made by Barus.[1]

(4) One meaning of a pressure coefficient of resistance for solids independent of temperature is that as temperature is increased at constant pressure (say atmospheric) the temperature coefficient at constant volume becomes more nearly negative, and if the same tendency persists will ultimately become negative, as it is for liquid mercury. This indicates that at higher temperatures the solid metal approaches a condition in which most of its atoms are in the second group, and is exactly what one would expect.

The fact that there is a tendency toward the behavior of the liquid may be seen on considering that the thermal expansion and the compressibility of a metal are both little affected by temperature at constant pressure, and that the relation between temperature and resistance is to a first approximation linear. This means that at high temperatures the same increment of pressure and temperature will be required to maintain volume constant as at low temperatures. The same increment of temperature will produce the same increment of actual resistance, but the decrement of resistance under a constant increment of pressure will increase, because the relative pressure coefficient is constant, while the actual resistance, on which the coefficient is calculated, becomes higher.

(5) The sudden drop of resistance of some metals at low temperatures has already been touched on. It means, according to this view, a clustering of the amplitudes closely about the mean.

(6) The negative pressure coefficient has already been explained at some length. It is primarily due to a decrease of atomic amplitude brought about by an increasing frequency at higher pressures. Added to this effect must be another effect, in most cases considerably smaller, due to the crowding of atoms from the second condition into the first. We have already seen that under ordinary conditions the number of atoms in the second condition is small, but in the case of liquid metals the number in the second condition is relatively larger, and we should

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[1] C. Barus, Bull. U. S. Geol. Sur. No. 92, 1892, p. 74.

expect the decrease of resistance due to this cause to be higher. This is verified by the only liquid metal for which we have data, mercury.

(7) The decrease of relative pressure coefficient under increasing pressure is to be accounted for by the disappearance of atoms in the second class. This number is not large, and so the effect would be small, as it actually is. The rate of decrease of coefficient at rising pressures is a rough measure of the rate at which the atoms of the second group are being exhausted. If the rate of decrease of atoms of this group were constant at all pressures, we would, of course, have no decrease of the coefficient at higher pressures.

(8) The surprising fact that the decrease of coefficient with pressure is greater at low than at high temperatures is to be explained [by the fact that at low temperatures the atoms of the second group are being exhausted more rapidly, since there are fewer of them, and therefore they contribute a more rapidly decreasing term to the negative pressure coefficient. The more rapid decrease at higher temperatures of some of the metals with low melting points is, on the other hand, probably to be explained by the greater decrease of the thermodynamic quantities which enter the formulas for the amplitude. It is for just these metals that one would expect the greatest decrease, although such a decrease has not yet been proved by experiment.

(9) When a metal is stretched by a mechanical tension the atoms are separated along the line of tension, but are brought closer together in a direction at right angles to the tension. We would expect therefore the number of gaps to increase if the path of the electrons is along the tension, but to decrease if it is at right angles. This corresponds with the observed changes of resistance under tension.

(10) The positive pressure coefficient of resistance of Bi and Sb next engages us. A positive pressure coefficient, according to this view, means that the number of gaps increases as volume decreases at constant temperature. Such an increase may be accounted for by an increase in amplitude, or what is the same thing, a decrease in frequency at constant temperature. A decrease in frequency with decreasing volume is not what we would expect, but may be brought into immediate connection with two other abnormal features of the behavior of Bi and Sb. Both Sb and Bi contract instead of expanding when melted, and the thermal expansion of both is unusually small. If a diagram is plotted of thermal expansion against compressibility (or melting point) of all the metals of these experiments, Sb and Bi will be found to occupy a position apart from the others, with abnormally small expansions. Now it is a conclusion most strongly suggested by the analysis of Debye, and also by my

own examination[1] of the properties of a gas composed of only one atom already mentioned, that the thermal expansion is intimately connected with the law of force between atoms. The subject has by no means been worked through as yet to a satisfactory conclusion, but we may probably assume with safety that an abnormally high thermal expansion means a restoring force increasing with unusual rapidity as the atoms are brought together, and that a small expansion means that the restoring force increases less rapidly than normal with decreasing volume. If we admit the conclusion as justified by the results above that the restoring force in normal metals is linear and independent of the volume, then for a substance with small expansion the restoring force decreases as the volume decreases. Such a decrease of restoring force means a decrease of mean frequency with decreasing volume, and hence an increase of amplitude. It is not difficult to imagine a law of force which will lead to such an unusual result.

In Fig. 1 is represented what we may suppose to be the action between three adjacent atoms. We suppose atom B to vibrate, and atoms A and C to remain at rest. The curve (1) shows the force with which A and B act on each other as a function of their distance apart. At infinite separation there is no force (indicated by the dotted horizontal line); as the atoms approach the force is at first an attraction, indicated by (1) lying above the horizontal line, but on closer approach the force rapidly becomes an intense repulsion. The law of force between B and C is precisely similar to that between A and B and is shown by the curve (2). The dotted part of curves (1) and (2) is what we may imagine for normal atoms, while the heavy curve is perhaps like that of Bi and Sb. The anomaly consists merely in a temporary acceleration of the rate of increase of the repulsive force followed by a retardation, as compared with the normal atom. The restoring force on B as it oscillates between A and C is evidently the difference of the forces exerted in opposite directions by A and C, and will therefore be proportional to the angle between (1) and (2) multiplied by the displacement of B from its equilibrium position. It is evident from inspection of the figure that as atoms A and C approach, that is as volume decreases, the angle of intersection between (1) and (2) decreases, and the restoring force therefore decreases. This decrease of restoring force means a small

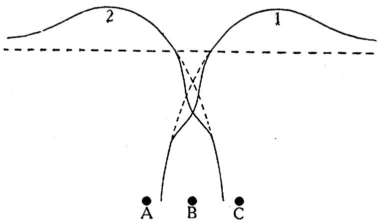

Fig. 1.

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[1] P. W. Bridgman, Proc. Amer. Acad., 49, 107, 1913.

thermal expansion, and at the same time a decrease of frequency, and so an increase of resistance.

The slight anomaly in the law of force shown in Fig. 1 is also consistent with the solid having a larger volume than the liquid. To simplify the argument on this point suppose that the solid is at 0° Abs. We will try to show that the atoms are in equilibrium in a position of abnormally large volume. Equilibrium is found in that configuration in which the work done by the attractive forces during a virtual decrease of volume is exactly equal to the work done on the repulsive forces. We may suppose that the repulsive forces act only between immediately adjacent atoms, whereas all the more distant atoms exert attractive forces. Equilibrium will therefore be found where the few repulsive forces balance the many attractive forces. If there is a region in which the repulsive forces are unusually intense at an unusually large distance from the center of the atoms, as we have supposed the case for Bi and Sb, the repulsive forces will balance the attractive forces when the atoms are separated more than usual, and we will have a solid of abnormally large specific volume. If we suppose that this particular law of force is valid only when the atoms have the regular orientation of the crystal, but that the average law of force for haphazard orientations is more nearly normal, we have immediately a suggestion as to why the metal contracts on melting.

The abnormality we have imagined to account for the pressure effect has little effect on the temperature coefficient. The reason for this is that the temperature axis is very nearly normal to the line of constant amplitude in any event, so that a relatively large change in the direction of the line of constant frequency will produce a relatively small change in the temperature derivative of frequency. It is true that the temperature coefficients of resistance of Bi and Sb are not at all abnormal.

(11) The fact that the resistance of an alloy is always greater than that of its components is simply explained by the failure of the atoms of the two metals to fit closely together. In an alloy there are, therefore, a greater number of gaps permanently present than in the pure metal, and consequently the resistance is greater. As far as I know the conductivity of every alloy is less than that of its best conducting component, and in many cases is less than that of either component. The positive pressure coefficient of some alloys may be explained by supposing some such effect as that imagined for Bi, which is plausible enough if we are dealing with molecules instead of atoms, or by supposing that under the constraint of increasing pressure the atoms assume less natural positions, in which the number of gaps is greater. This latter alternative would be suggested by all my experiments on polymorphic transitions, in which the applica-

tion of pressure at constant temperature drives the molecules ultimately into such a configuration that some other configuration is more stable.

In conclusion a few critical remarks are not out of place. I do not offer the view of conductivity here explained as the only *possible* one consistent with all the facts, but merely as the one which seems to me at present most probable in the light of the facts now at our disposal. In one essential particular it does seem to me likely, however, that this view is like that which will be finally adopted. In the mechanism of conduction the properties of the atomic framework play a preponderating part; the atoms are not merely the trees of a forest among which a breeze of electrons plays, as in the classical free electron theory. The new experimental justification for this broad requirement in any new theory is the observation that the change of resistance is intimately connected with the amplitude of atomic vibration. Even if one is still so unconvinced of the truth of quantum theory as to be unwilling to admit the validity of the fundamental equations (1), (2) and especially (3), the fact cannot be escaped that we have found an approximate relation between the change of resistance and certain quantities of a purely thermodynamic character, which are certainly intimately connected with atomic properties.

This theory of conduction is not complete in the sense of the old free electron theory because it does not at present explain Ohm's law. We merely postulate, without searching for a detailed mechanism, that the electrons encounter resistance when they jump a gap between atoms, and that the resistance of the gap is on the average a resistance which obeys Ohm's law. This point is, however, probably one that it will not be difficult to meet. If, for instance, the force encountered by an electron in jumping a gap is like an ordinary fluid frictional force, proportional to the velocity, the requirements are met. The assumption of such a force is already familiar in various branches of electron theory.

The picture which I have presented of conduction in a metal is of a chain of electrons, which are normally at rest, getting under way under an applied electromotive force down a coherent chain of atoms, and gaining in speed until suddenly the continuity of the chain is interrupted by a break which appears somewhere between two neighboring atoms of the chain. The chain of electrons is not entirely stopped by the formation of the gap, but drives itself across by its own electromagnetic momentum, using up some or all of its store of energy in so doing. The gap absorbs the energy by a mechanism not specified, just as a spark absorbs the energy of an interrupted circuit, and from the gap the energy is ultimately absorbed as heat energy.

An alternative picture is that the gaps are not of sporadic, isolated occurrence as above, but that between every pair of neighboring atoms there is a resistance which on the average is proportional to the square of the mean amplitude. An objection to this view is that we must assume the square law, without at present even attempting to make it plausible, as we have above.

Still another point of view is possible, connecting so closely with the old free-electron theory as to account for Ohm's law. When the atoms are at rest at 0° Abs. we may suppose that the electrons travel freely through the substance of the atoms, as the atoms of a gas freely traverse interatomic space, but as the amplitude of atomic vibration is increased, the electrons collide with the *gaps* between the atoms, precisely as they collided with the atoms on the old view. Ohm's law follows immediately, as on the old view. An objection to this viewpoint is that it brings up again the specific heat difficulty. We will have to suppose the electronic velocity independent of temperature, as does Wien. This does not seem to me a formidable difficulty; in fact such a constant velocity seems more plausible under the supposed circumstances than under the conditions imagined by Wien. For there must be some electrons always traversing the substance of the atoms as β-particles, continually emitted by the break-up of the outer ring of electrons in the atoms, and continually reabsorbed. Velocities from such a source as this must be independent of the temperature.

Wien's original picture of electrons passing freely through alley-ways between atoms is not a remote possibility consistent with a close connection between change of resistance and amplitude. The picture may contain much that is true, but probably the details of working out, as given by Wien, must be modified in any event. In particular Wien's assumption must be given up that at very low temperatures the quanta of energy are all located in a few isolated atoms, the rest of the atoms being at rest. It seems more probable now that the quanta are located in modes of elastic vibration. To explain the absence of any specific effect of a change of volume as such, we must suppose according to this view also that the atoms are distorted by pressure.

A combination of Wien's point of view with that advocated by this paper offers many attractive features: We may suppose that the electrons pass freely through the substance of the outer part of the atoms, encountering no resistance even when passing from atom to atom. The electron may, however, collide with the positive nucleus, which is so small that it acts like a point charge. The number of collisions will evidently be directly connected with the amplitude of oscillation of the nuclei.

According to this point of view the absence of any specific volume effect is not so serious a difficulty, because we would not expect it to be nearly as large. I do not at present, however, see the possibility of bringing into line with this view the wide range of facts dealt with qualitatively above.

The chief claim to consideration of the old free electron theory was that it offered an explanation for the Wiedemann-Franz ratio. Wien regretted as one of the weak points of his theory that he had to give up hope of explaining the Wiedemann-Franz ratio when he assumed electronic velocity independent of temperature. The view of conduction offered above does not attempt as yet to explain the Wiedemann-Franz ratio, but such an explanation does not seem to me beyond the bound of ultimate possibilities. In the first place, any mechanically consistent theory, irrespective of whether it assumes thermal conduction performed by electrons or not, must give a ratio involving the electronic charge in the correct way, simply by dimensional reasoning, but need not give the correct form for the coefficient of the charge. This is all the old theory does, the coefficient it predicts is not of the correct form. It is commonly held that because electrical conductors are so much better thermal conductors than electrical insulators the electron must play a large part in the thermal conduction of metals, and that therefore no theory can be correct which does not assign some part of the energy of temperature agitation to the electrons. This conclusion seems to me not necessary; all that is indicated is that the same mechanism which makes easy a transfer of electrons from atom to atom should also make possible an easy heat transfer. Now this is immediately indicated by the view above. Electrons pass freely from atom to atom without break of continuity when the outer parts of the fields of force of the atoms so merge that the effective individuality of the atom is lost. But when the atoms are so merged as to lose their individuality they will function as one large atom, and the energy of heat vibration will jump over whole ranks of atoms, as we know it must if the thermal conductivity of metals is to be accounted for by an atomic mechanism only.

SUMMARY.

The most important result of this paper is the observation that the variations of resistance of a normal solid metal are preeminently concerned with one factor only, the average amplitude of vibration of the atoms, irrespective of whether the change of amplitude is brought about by a change of pressure or of temperature. The proportional change of resistance is approximately twice the proportional change of amplitude.

This suggests that a successful theory of metallic conduction must discard the old viewpoint, which explained resistance in terms of the properties of an assemblage of electrons little affected by the inert framework of atoms, and substitute an explanation in terms of the properties of the atomic framework. There are several possible ways of giving such an explanation, of different physical complexions, all of them suggesting an intimate connection between resistance and amplitude. The view which I have adopted above seems to me that best adapted to bring into line the entire range of facts. This view is that the electrons normally pass freely from atom to atom, but if the atoms are separated beyond a critical distance, as by temperature agitation, gaps appear between the atoms which offer resistance. The resistance at ordinary temperatures is proportional to the number of gaps, and it is not unplausible to expect the change in the number of gaps to be twice the proportional change in the amplitude. At higher temperatures, however, that is large volumes, as in liquid metals, the passage of electrons from atom to atom is on the average difficult, but is facilitated by a collision of unusual violence. An increasing amplitude functions in opposite ways, therefore, at large and at small volumes. Under actual conditions there must be a combination of these two effects in varying proportions. I have shown in detail how the play against each other of these two different effects offers an explanation of the most important features of the behavior of both normal and abnormal metals.

Another point of extreme suggestiveness is that a pressure high enough to compress the metal to less than its volume at 0° Abs. is powerless to change its temperature coefficient of resistance. Consistency with the view advanced here seems to me to demand a distortion of the atom under pressure. Such a distortion has been suggested by many other aspects of my work on high pressures.

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[1] J. H. Jeans, Mathematical Theory of Electricity and Magnetism, Cambridge University Press, 1908, p. 133.