

A THEORY OF ELECTRICAL CONDUCTION IN METALS

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ABSTRACT

The electrons are assumed to have kinetic energy corresponding to the thermionic work function W and to move on orbits which form a space lattice with a constant δ of the same order as that of the positive ions δ_1 . At each critical point of an orbit, each of the six directions are taken as equally probable. Treating the problem as a kind of Brownian motion and applying the virial theorem, the specific conductivity σ is found approximately equal to $0.6 \times Ne^2(\delta^2/h)eW/\bar{E}$, when \bar{E} is the mean heat content of one degree of freedom of the metal. The observed and calculated values of σ (taking $\delta = \delta_1$) are in fair agreement for Ag, Au and Cu. For Na, $\sigma(\text{obs.})$ is twice $\sigma(\text{calc.})$. Better agreement would be obtained if δ were taken as $1.5\delta_1$, but uncertainty as to the values of W and as to the error introduced by applying the virial theorem to discontinuous processes makes this of little significance.

THE theory of conduction in metals, here presented, is based on the properties of space lattices and the theory of Brownian motion.

Recently J. Frenkel¹ and Hojendahl² developed views somewhat similar to those to be given. There are differences in essential points between Frenkel's theory and that presented here, but some developments have been modeled on Frenkel's views.

We shall regard a metal as a space lattice of positive ions in fixed positions (except for heat motion) and electrons moving on definite orbits between these ions, their motions being subject to quantum conditions. The paths of electrons we shall assume to form a space lattice in the metal. On this lattice electrons move in a disorderly fashion, at least as far as direction of motion is concerned. The space lattice constant δ will be very closely related to the lattice constant of the metal δ_1 , e.g. $\delta = \delta_1$ or $\delta = 1.5\delta_1$. The quantum conditions for the electrons should be applied between critical points of the lattice.

According to a well known theorem of mechanics, the mean kinetic energy of the electrons at absolute zero will be equal to the energy necessary to remove an electron from the metal, which in turn is equal to eW , where W is the thermionic work function and e is the electronic charge. For a discussion of this assumption and numerical calculations, reference

¹ J. Frenkel, *Zeits. f. Phys.* **29** (1924).

² Hojendahl, *Phil. Mag.* **48** (1924).

may be made to an article of J. J. Weigle.³ At temperatures higher than the absolute zero we must have

$$\frac{1}{2}m\bar{v}^2 = eW + \alpha\bar{E} \quad (1)$$

where \bar{v}^2 is the mean square velocity of electrons, m the mass of an electron, and \bar{E} the mean heat content of one degree of freedom of the metal. The constant α will be of the order of unity, e.g. 1/4 or 1/8. Equation (1) should not be interpreted as giving an increase of the heat content of the metal over the value given by Debye's theory, but rather as an expression of the fact that there is additional potential energy between electrons and ions due to the heat content of the body. In the theory of electrical conduction the quantity $\alpha\bar{E}$ can be neglected as compared with eW .

Let τ be the time between instants of passing successive critical points by an electron. According to quantum conditions, we have $h/\tau = 2eW$ or $\tau = h/2eW$.

As soon as an electron reaches one of these critical points all the directions in which it can move become equally probable and assuming the number of directions to be six, the probability that it will move a distance 2δ in a single direction is 1/6. Similarly the probability of moving a distance $k\delta$ in a single direction will be $(1/6)^{k-1}$. The mean square distance that an electron will move in one direction is therefore,

$$\lambda^2 = \delta^2 \frac{1 + 4(1/6) + 9(1/6)^2 + \dots}{1 + 1/6 + (1/6)^2 + \dots}.$$

A different space lattice would change this expression only very slightly.

By employing a reasoning familiar from the theory of Brownian motion, we find that after crossing a critical point n times, the mean value of the square of the distance of an electron from its original position will be:

$$\overline{r_n^2} = n\lambda^2 = 1.8\delta^2 n \quad (3)$$

A type of reasoning similar to the above, but one which seems to the writer more rigorous, leads to a factor 1.4 in place of 1.8 in Eq. (3). In view, however, of the approximate nature of the assumptions involved, this alteration was neglected in the following. In the time t the electron crosses $n = t/\tau$ critical points and consequently $\overline{r_n^2} = 1.8\delta^2 t/\tau$ or, taking the component in one direction

$$\overline{x^2} = \frac{1}{3}\overline{r_n^2} = 0.6\delta^2 t/\tau. \quad (4)$$

³ J. J. Weigle, Phys. Rev. **25**, 187 (Feb. 1925).

According to an equation given by Einstein⁴ we also have

$$\overline{x^2} = 2Dt \quad (5)$$

where D is the coefficient of diffusion of electrons. No gradient of concentration of electricity can occur in a metal and the coefficient of diffusion assumes a meaning only if we distinguish between some class of electrons and the rest.

The action of an electric field on electrons will consist in imparting a certain momentum in the direction of the field at a uniform rate. If we consider the interaction of the electrons among each other it appears obvious that this momentum will be conserved. As however, from statistical and thermodynamic considerations, this increase of energy of electrons cannot be permanent, it must be transferred to the positive ions, thereby resulting in an evolution of heat. In an electric field therefore, the electrons will at first acquire a mean acceleration, but very soon the interaction with positive ions will cause them to give up as much momentum as they gain and their mean velocity in the direction of the field will then become constant in time.

An interaction of this kind will be represented by a viscosity coefficient μ . In an electric field F the mean velocity will be $(e/\mu)F$ and the conductivity becomes $\sigma = Ne e/\mu = Ne^2/\mu$ where N is the number of valence electrons per unit volume of the metal.

Our object now will be to calculate μ . The rate at which momentum is lost by electrons being $\mu\dot{x}$, we have

$$-\mu \sum \dot{x} = \sum M \ddot{X} \quad (6)$$

where M and X refer to positive ions and the summation is extended to all positive ions and electrons.

As the transfer of momentum takes place in a disorderly fashion with regard to coordinates, we have also, by the virial theorem,

$$-\mu \sum x \dot{x} = \sum M X \ddot{X} \quad (7)$$

or

$$-\frac{\mu}{2} \frac{d}{dt} (\overline{x^2}) = \frac{M}{2} \frac{d^2}{dt^2} (\overline{X^2}) - M \overline{\dot{X}^2}. \quad (8)$$

Considering that no diffusion of positive ions takes place and with regard to Eqs. (4) and (5) we find

$$(0.38^2/\tau)\mu = \mu D = M \overline{\dot{X}^2} = \overline{E}. \quad (9)$$

⁴ Einstein, Ann. der Phys. (1905).

The mean heat content of one degree of freedom of the metal can according to Debye be written as

$$\bar{E} = RT \frac{3}{(\theta/T)^3} \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1}. \tag{10}$$

The equations (6) and (7) represent an application of the virial theorem to a discontinuous process and Eq. (9) can therefore be only approximately correct.

From (9) it follows that

$$\mu = 3.3 \tau \bar{E} / \delta^2 \tag{11}$$

and if we consider (2) the expression for conductivity σ becomes

$$\sigma = \frac{1}{3.3} N e^2 \frac{\delta^2}{\tau \bar{E}} = 0.6 N e^2 \frac{\delta^2}{h} \frac{eW}{\bar{E}}. \tag{12}$$

We shall now give a brief discussion of the limitations of the theory and compare the numerical values obtained from Eq. (12) with those actually observed.

In the first place as regards the variation of electrical conductivity with temperature it was shown above why (12) cannot be exact. Polarization of the ions and the quantity $a\bar{E}$ in Eq. (1) will, probably, be only of secondary importance. Qualitatively, however, the curve showing the heat content of solids is similar to that representing the resistivity of a metal and indeed formulas like $1/\sigma \sim TC_v$ or $1/\sigma \sim h\nu / (e^{h\nu/kT} - 1)$ have been proposed by various authors.⁵ Quantitatively, the agreement is not very good; even for temperatures as high as 0°C the theory gives a temperature coefficient of resistivity 20 percent higher than observed (Ag, Cu, Au).

As regards the actual value of conductivity there are difficulties in the numerical interpretation of the quantity δ in Eq. (12). For lack of any better value this was taken to be equal to the space lattice constant of the metal considered.

Below is given a table of observed and computed values for some univalent metals. The low calculated value of σ for Na will be explained below. W for Cu, Ag, Au was taken as 4 volts.

Metal:	Na	Cu	Ag	Au
$\sigma \times 10^{-4}$ (obs.):	22	64	67	45
(calc.):	10.6	61	50	47
$(1/\sigma)(d\sigma/dT)$ (obs.):	.0050	.0043	.0040	.0039
(calc.):	.0046	.0054	.0049	.0046

⁵ Wien, Berl. Ber. 1913 (Part 1);
 Grüneisen, Verh. Deutsch. Phys. Ges. **15** (1913) and **20** (1918);
 Wereide, Ann. der Phys. **55**, 589 (1918).

In view of the fact that the variation of resistivity with temperature is given only approximately, no exact agreement can be expected between the observed and calculated values of conductivity. If we consider that according to recent measurements the value of conductivity of a crystal of Cu is about 15 percent higher than that given above, we find that the order in which the metals Cu, Ag, Au are placed by the theory agrees with experiment.

There is one more point where the theory can be tested experimentally. According to Eq. (1) we have

$$\tau = \delta/\bar{v} = h/2eW \text{ or } \bar{v} = (2eW/h)\delta$$

and on the other hand

$$\sqrt{\bar{v}^2} = \sqrt{2eW/m}.$$

Metal:	Na	K	Cu	Ag	Au	
$\sqrt{\bar{v}^2}$:	.8	.7	1.2	1.2	1.2	($\times 10^8$)
\bar{v} :	.38	.39	.7	.8	.8	($\times 10^8$)

As a matter of fact we should have $\bar{v} < \sqrt{\bar{v}^2}$ but the difference between the calculated values seems rather too large to be explained by that alone. In particular in the case of Na it seems to indicate that δ is greater than the space lattice constant, a result which also explains the low value of σ obtained from Eq. (12).

It might seem at first sight that from the values of $\sqrt{\bar{v}^2}$ and \bar{v} given above we might calculate the value of δ and then substitute in the formula for conductivity. On account, however, of some uncertainty as to the numerical value of W only slight importance can be attached to that procedure.

In conclusion, it should be pointed out that an exact theory of conduction can probably be given only when the properties of the positive ions of the metal are taken into consideration. A considerable improvement could, however, be obtained by taking into account the discontinuous variation of momentum of electrons instead of using the virial theorem as has been done in this paper.

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