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*Proc. R. Soc. Lond. A* 1936 **156**, 368-382

doi: 10.1098/rspa.1936.0154

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## The Resistance and Thermoelectric Properties of the Transition Metals

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(Received 22 May, 1936)

1—In two recent papers\* the author has given for the transition metals a theory of electrical conduction which accounts for many of their peculiarities. In Paper I a reason was given for their relatively high resistivities and for the shape of the curves obtained when the resistivity of an alloy such as Ag-Pd is plotted against atomic composition; in Paper II the behaviour at high temperatures of Pd and Pt was discussed, and also of the resistance of ferromagnetic metals and of alloys such as constantan (Cu-Ni). In this paper it will be shown that the theory can give an account of some of the thermoelectric properties of these metals and alloys. The thermoelectric properties of ferromagnetic metals are of especial interest, because they have been cited as evidence that the same electrons are responsible for the ferromagnetism as for the conductivity.† We shall also give a further discussion of the electrical resistance both of paramagnetic and of ferromagnetic metals and a more detailed comparison with experiment than was attempted in Paper II.

In all metals the possible stationary states of an electron may be divided into zones‡ (the “ Brillouin zones ”); for cubic metals the first zone contains  $2N$  states per  $N$  atoms; Jones§ has shown that for the bismuth structure a zone exists containing  $5N$  electrons. Two zones may either be separated by a range of forbidden energies, or they may overlap. If all the states of a given zone are occupied, that zone can make no contribution to the conductivity of the metal. In the divalent metals or in bismuth the available electrons could just fill a zone; but, since these metals are conductors, we must assume that there are a certain number  $Nn_0$  of “ overlapping ” electrons in the second zone and an equal number

\* ‘ Proc. Phys. Soc. ’ vol. 47, p. 571 (1935); ‘ Proc. Roy. Soc. ’ A, vol. 153, p. 699 (1936), referred to as Papers I and II.

† Dorfman, Jaanus, and Kikoin, ‘ Z. Physik, ’ vol. 54, p. 277 (1929); the conclusions of these authors have been criticized by Stoner, ‘ Proc. Leeds Phil. Soc. ’ vol. 2, p. 401 (1933).

‡ Cf. Mott and Jones, “ The Theory of the Properties of Metals and Alloys, ” Oxford, 1936.

§ ‘ Proc. Roy. Soc. ’ A, vol. 147, p. 396 (1934).

of vacant places or "positive holes" in the first zone. The assumption that  $n_0$  is small compared with unity accounts for the fact that divalent metals and bismuth are poor conductors compared with monovalent metals; it is not necessary to assume that the mean free path is different for the two groups.

The explanation given in Paper I of the poor conductivity of the transition metals is different; here we have two zones to consider, which we called the  $s$  zone and the  $d$  zone. In nickel the number  $n_0$  of electrons per atom in the  $s$  zone and the equal number of positive holes in the  $d$  zone were shown to be about 0.6, and in palladium 0.55, which are not small compared with unity. These metals differ from the divalent metals in that the "effective mass"  $m$  of the positive holes is large compared with that of the electrons, because the  $d$  wave functions of the individual atoms overlap relatively little. This has two consequences: firstly, the positive holes make only a small contribution to the electric current in the metal, and secondly, the stationary states in the  $d$  zone are abnormally close together so that the density of states  $N_d(E)$  is large. The positive holes affect the resistance of a metal in the following way: under the influence of the lattice vibrations the  $s$  electrons may make transitions to unoccupied states of nearly the same energy in the  $d$  zone, as well as to other states in the  $s$  zone. The analysis appropriate to this case is given in Paper II, where it is shown that the probability of these  $s$ - $d$  transitions is proportional to the density of states  $N_d(E)$  in the  $d$  band. If  $N_d(E)$  is large we may expect this transition probability to be large and hence the mean free path to be small, which will lead to a small conductivity.

The most direct experimental evidence of the influence of the positive holes on the conductivity is provided by the behaviour of, for instance, the Pd-Au alloys. As gold is added to palladium the magnetic susceptibility of the alloys decreases and attains the small negative value of pure gold at about the composition 55 atoms per cent of Au, as is shown in fig. 1*a*; we may assume that at this composition the positive holes are all filled up (*cf.* Paper I). If now  $\rho_0, \rho_{100}$  denote the resistivities of these alloys at  $0^\circ$  and  $100^\circ$  C., then  $\rho_{100} - \rho_0$  is a measure of the part of the resistance which depends on the thermal vibration of the atoms of the metal and which is therefore proportional to the absolute temperature. This quantity is shown also in fig. 1*a*. It will be seen that  $\rho_{100} - \rho_0$  is much larger for Pd than for Au, but that it falls to nearly the value for pure gold at about the same composition as that at which the positive holes disappear.\*

\* The absolute value of the resistance, shown in curve III, increases as gold is added to palladium, because the increase in the "Restwiderstand" outweighs the decrease due to the filling up of the positive holes. Rosenhall ('Ann. Physik,' vol. 24, p. 297

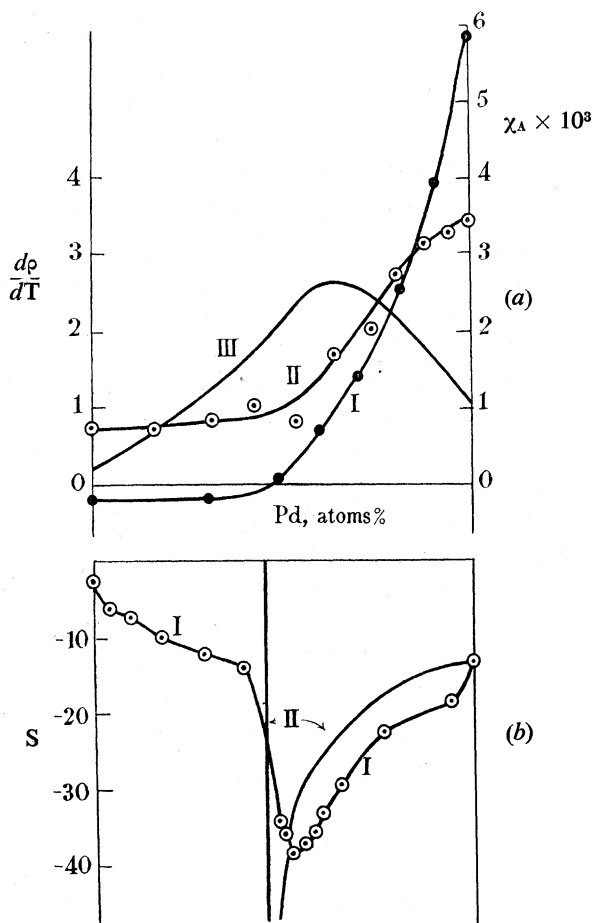


FIG. 1—Properties of gold-palladium alloys. (a) Curve I: atomic susceptibility\*  $\chi_A$  at  $-183^\circ\text{C}$ .; curve II:  $\rho_{100} - \rho_0$  in arbitrary units;† curve III: resistivity  $\rho_0$  in arbitrary units.† (b) Absolute thermoelectric power  $S$ , microvolts per degree. Curve I: observed‡ at  $0^\circ\text{C}$ .; curve II: theoretical, fitted to the observed curve for 100% Pd.

\* Vogt, 'Ann. Physik,' vol. 14, p. 1 (1932).

† Geibel, 'Z. angew. Chem.,' vol. 69, p. 38 (1910).

‡ Sedstrom, 'Diss.,' Lund (1924).

(1935)), however, has shown that if hydrogen is added to the similar Pd-Ag alloys, then, if the concentration of Pd is greater than 40%, the resistance at first decreases. It is known (*cf.* Paper I) that the addition of hydrogen decreases the magnetic susceptibility of these alloys, and thus that the electrons from the hydrogen atoms are effective in filling up the holes in the  $d$  shells of Pd. For these alloys, then, the effect of the protons on the already high residual resistance must be less than the effect of filling up the holes.

2—We denote by  $N_d(E)$ ,  $N_s(E)$  the densities of electronic states in the  $d$  and  $s$  bands respectively. At the absolute zero of temperature all states are occupied up to a maximum energy  $E = \zeta_0$ . According to quantum mechanics, the heat capacity of the electrons at temperature  $T$  is proportional to  $N(\zeta_0)T$ . Since for palladium\* the atomic heat in cal. per degree at low temperatures is  $0.0032T$  and for nickel†  $0.00169T$ , while for silver‡ ( $d$  band full,  $N_d(\zeta_0) = 0$ ) it is only  $0.00015T$ , we may deduce that for the former two metals  $N_d(\zeta_0)$  is 10 to 20 times bigger than  $N_s(\zeta_0)$ , which should be about the same as for silver.

Since the  $d$  band is nearly full, we shall take for  $N_d(E)$  in the neighbourhood of the highest occupied state

$$\begin{aligned} N_d(E) &= C\sqrt{E_0 - E} & E < E_0 \\ &= 0, & E > E_0 \end{aligned} \quad (1)$$

this formula being valid near the head of any band.

The two functions  $N_s$  and  $N_d$  are shown in fig. 2 for values of the energy in the neighbourhood of  $\zeta_0$ . If the number  $n_0$  of positive holes per atom is known, we may estimate  $E_0 - \zeta_0$  from specific heats at low temperatures from formulae (1), (1.1): the results are, with  $n_0 = 0.6, 0.55$  respectively,

	Ni§	Pd
$T_0 = \frac{E_0 - \zeta_0}{k}$	3470°	1940°

We may take  $N_s(E)$  to be sensibly constant, as shown in fig. 2*a*, over a range of  $E$  comparable with  $kT$  even at high temperatures.

We may note that the number of positive holes is, per unit volume,

$$n_0 \propto 2 \int_0^{\zeta_0} N_d(E) dE = \frac{4}{3}C(E_0 - \zeta_0)^{3/2}. \quad (1.1)$$

Hence from (1) 
$$N_d(\zeta_0) \propto n_0^{2/3}. \quad (2)$$

As shown in Paper II, if  $\tau(E)$  is the time of relaxation for electrons of energy  $E$ , so that  $1/\tau$  is the probability per unit time that an electron is scattered by a lattice wave, then||

$$\frac{1}{\tau} = \frac{T}{M\Theta_D^2} [AN_s(E) + BN_d(E)], \quad (3)$$

\* Simon and Pickard, unpublished; I wish to thank Professor Simon for allowing me to quote these results.

† Keesom and Clark, 'Physica,' vol. 2, p. 513 (1935).

‡ Keesom and Kok, 'Physica,' vol. 1, p. 770 (1934).

§ The figure given is for ferromagnetic nickel; for paramagnetic nickel we must take  $T_0 = 3470/2^{2/3} \simeq 2200$ ; cf. Mott, 'Proc. Roy. Soc.,' A, vol. 152, p. 42 (1935).

|| Cf. Paper II, equation (15), in which, since  $\mu_d \gg \mu_s$  and  $a_{ss} \gg a_{sd}$ , the last term on the left-hand side may be neglected.

where  $A$  and  $B$  depend on the wave functions of the initial and final states, and  $\Theta_D$  is the Debye temperature. To calculate the conductivity and thermoelectric properties we need to know  $\tau$  only for values of the energy near the surface of the Fermi distribution, *i.e.*, for  $E \simeq \zeta_0$ . The only

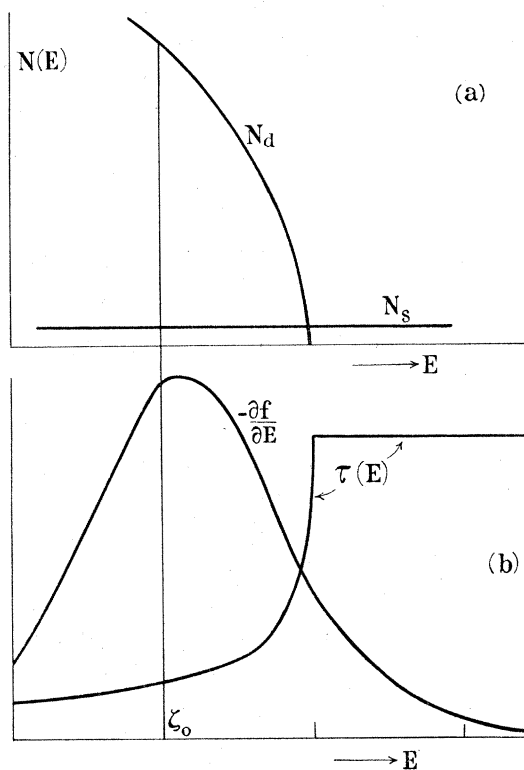


FIG. 2—(a) Density of states in  $d$  and  $s$  bands as functions of  $E$  in the neighbourhood of  $E = \zeta_0$ . (b) Time of relaxation  $\tau(E)$  and the function  $-\partial f/\partial E$  plotted for  $T/T_0 = 0.413$ , both in arbitrary units.

term in (3) which varies *rapidly* with the energy is  $N_d(E)$ ; we may therefore take for  $1/\tau$  near the surface of the Fermi distribution

$$\frac{1}{\tau} = \text{const.} \left[ \alpha + \sqrt{\frac{E_0 - E}{E_0 - \zeta_0}} \right] \frac{T}{M\Theta_D^2}, \quad (4)$$

where  $\alpha$  is the ratio of the probability of  $s$ - $s$  transitions to that for  $s$ - $d$  transitions for electrons with the energy  $\zeta_0$ .

Fig. 1a, curve II, shows that at room temperature the filling up of the positive holes in Pd decreases the part of the resistance which depends on temperature about fivefold. In our subsequent work, therefore, we shall assume

$$\alpha \simeq 0.25,$$

which, according to formula (4), gives this fivefold difference between the values assumed by  $1/\tau$  when  $E = E_0$  (no positive holes) and when  $E = \zeta_0$ .

With this value of  $\alpha$ ,  $\tau(E)$  according to formula (4) is illustrated in fig. 2*b*.

### 3—RESISTANCE OF PALLADIUM AND PLATINUM AT HIGH TEMPERATURES

In calculating the resistance we shall neglect the contribution to the current actually made by the positive holes. The conductivity  $\sigma$  is then given by\*

$$\sigma = - \int \sigma(E) \frac{\partial f(E)}{\partial E} dE.$$

Here  $\sigma(E)$  is the conductivity for electrons of energy  $E$ , defined by

$$\sigma(E) = N_{\text{eff}} e^2 \tau(E)/m, \quad (5)$$

where  $N_{\text{eff}}$  is the effective number of  $s$  electrons per unit volume,  $\tau(E)$  the "time of relaxation" (time between collisions) of an  $s$  electron of energy  $E$ .  $f(E)$  is the Fermi distribution function defined by

$$f(E) = \frac{1}{e^{(E-\zeta)/kT} + 1}.$$

The function  $\partial f/\partial E$  is small except in the range  $\zeta - kT < E < \zeta + kT$ . We may take  $N_{\text{eff}}$  to be constant in this range, but, at high temperatures, owing to the rapid change of  $\tau$  with  $E$  shown in fig. 2*b*, this is not legitimate for  $\tau$ . We therefore take for the conductivity

$$\sigma = - \frac{N_{\text{eff}} e^2}{m} \int \tau(E) \frac{\partial f}{\partial E} dE. \quad (6)$$

In Paper II, using formula (4) for  $\tau$  with  $\alpha = 0$ , we obtained from (6) an expansion in ascending powers of  $T/T_0$ :

$$\sigma = \frac{\text{const.}}{T} \left[ 1 + \frac{\pi^2}{6} \left( \frac{T}{T_0} \right)^2 \dots \right].$$

This expansion is, however, valid only for quite small values of  $T/T_0$ ; we have therefore evaluated (6) exactly. For this purpose it was necessary to calculate  $\zeta$  as a function of  $T$ . This was obtained by equating the number of  $s$  electrons to the number of positive holes:

$$\int_{-\infty}^{\infty} N_d(E) [1 - f(E)] dE = \int_{-\infty}^{\infty} N_s(E) f(E) dE.$$

\* Cf., for example, Mott and Jones, *loc. cit.*, chap. 7.

Between the temperatures zero and  $T$  the right-hand side cannot change by more than a term of the order  $kT/\zeta_0$  ( $\sim 0.02$ ) of its original magnitude; it was therefore taken as constant; we have, therefore, transforming the left-hand side by writing  $E' = E_0 - E$

$$\int_0^\infty C \sqrt{E'} \frac{dE'}{\exp\{(E' - E_0 + \zeta)/kT\} + 1} = \int_0^{E_0 - \zeta_0} C \sqrt{E'} dE' \\ = \frac{2}{3} C (kT_0)^{\frac{3}{2}}.$$

Using this equation  $E_0 - \zeta$  may be calculated for a series of values of  $T/T_0$  by using values already given by the present author.\*

We then integrated (6) numerically for a series of values of  $T/T_0$ . As fig. 2 shows, for  $T/T_0 \sim 0.4$ ,  $\tau(E)$  is by no means constant within the range in which  $-\partial f/\partial E$  is finite. We give in Table I the results for the ratio  $\phi$  defined by

$$\frac{1}{\phi} = \frac{-\int \tau(E) (\partial f/\partial E) dE}{\tau(\zeta_0)}, \quad (7)$$

which gives the decrease in the resistance due to the finite spread of the function  $-\partial f/\partial E$ .

TABLE I

$T/T_0$ . . . . .	0	0.1	0.2	0.3	0.4	0.5	0.6
$\phi$ . . . . .	1	0.98	0.92	0.78	0.65	0.54	0.47

To compare these results with experiment we plot in fig. 3 the observed and calculated values of  $\rho/T$  for Pd, where  $\rho$  is the resistivity. The theoretical values are obtained as follows: the following formula for the resistance of a "normal" metal can be derived from the theory subject to certain simplifying assumptions†:

$$\rho = \text{const.} \frac{T}{M\Theta_D^2} G\left(\frac{T}{\Theta_D}\right), \quad (8)$$

where  $\Theta_D$  is the characteristic temperature and

$$G = \left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}, \\ \rightarrow 1 \quad \text{as} \quad T/\Theta_D \rightarrow \infty.$$

The function  $G$  has been tabulated by Grüneisen,‡ and is in good agree-

\* 'Proc. Camb. Phil. Soc.,' vol. 32, p. 108 (1936).

† Cf. the article by Sommerfeld and Bethe, 'Handb. Phys.,' vol. 24/2 (1933), p. 530.

‡ 'Ann. Physik,' vol. 16, p. 530 (1933).



ment with experiment in the region  $T \sim \Theta_D$  for most normal metals (e.g., Cu, Ag, Au). For palladium, specific heat measurements give  $\Theta_D = 270$ , and we plot in fig. 3 the function  $G(T/\Theta_D)$  with this value of  $\Theta_D$  fitted

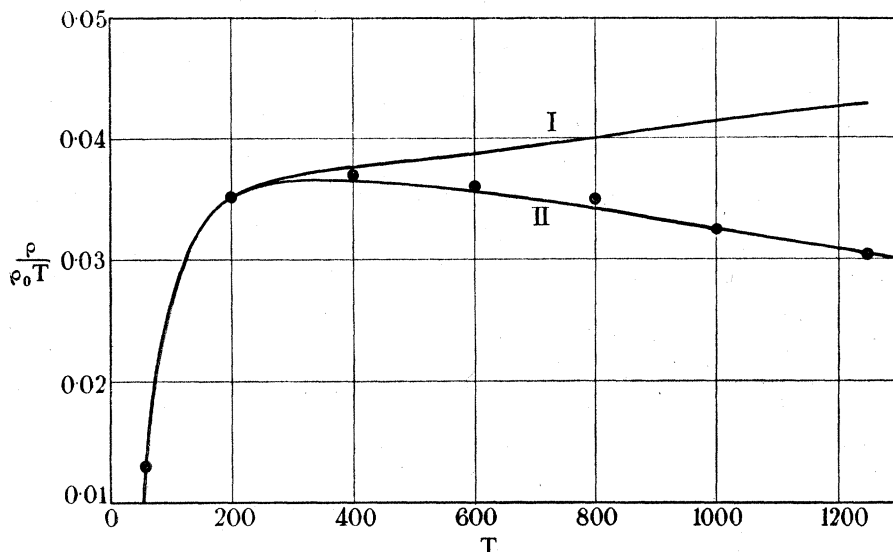


FIG. 3.—Resistance  $\rho/\rho_0$  of palladium divided by the absolute temperature  $T$ . I, Grüneisen function, allowing for thermal expansion; ● the same, multiplied by  $\phi$ ; II, observed.

to the experimental curve at low temperatures. For normal metals  $\rho/T$  increases slightly with temperature, and this may be accounted by the decrease in  $\Theta_D$  due to thermal expansion;\* this is given by†

$$-\frac{d(\log \Theta_D)}{dT} = \frac{\alpha_T^2 C_v}{V\chi_0}, \quad (9)$$

where  $\alpha_T$  is the thermal expansion coefficient,  $V$  the volume per gram atom, and  $\chi_0$  the compressibility at the absolute zero of temperature.

Curve I shows the value of  $\rho/T$  calculated from (8) with  $\Theta_D$  varying according to (9). The points marked ● show these same values with the ordinates multiplied by  $\phi$ , with  $T_0 = 3450$ , which gives the best fit with the experimental curve II.

#### 4—THERMOELECTRIC PROPERTIES OF PARAMAGNETIC METALS

Platinum and palladium have large negative thermoelectric powers; at  $100^\circ$  C. the values, in microvolts per degree, are  $-7.3$  and  $-9.5$ , compared with  $+2.0$  and  $+2.2$  for silver and gold.

\* Mott and Jones, *loc. cit.*, chap. 7, § 7.

† Cf. Herzfeld, "Wärmelehre," p. 250, or Mott and Jones, *loc. cit.*, chap. 1.

From the theoretical point of view, the thermoelectric power  $S$  depends on the rate of variation with  $E$  of the quantity  $\sigma(E)$  given by (5); the theoretical formula is\*

$$S = \frac{\pi^2 k^2 T}{3 e} \left\{ \frac{\partial (\log \sigma(E))}{\partial E} \right\}_{E=\zeta} \quad (10)$$

In  $\sigma(E)$  we shall neglect as before the variation with  $E$  of all factors except  $\tau(E)$ ; as fig. 2 shows,  $\tau(E)$  increases rapidly with  $E$ . The thermoelectric power will therefore be large and negative.

Substituting formula (4) in formula (10) we obtain, putting

$$E_0 - \zeta_0 = kT_0$$

$$S = \frac{\pi^2 k T}{3 e T_0} \frac{\frac{1}{2}}{1 + \alpha} \quad (11)$$

We shall calculate  $T_0$  from the observed values of  $S_{100} - S_0$ , assuming  $\alpha = \frac{1}{4}$ :

	$S_{100} - S_0$ microvolts per degree	$T_0$ degrees
Pd .....	-2.8	4100
Pt .....	-2.9	3900

These values will be correct only as to the order of magnitude, because we have neglected in deriving (11) all factors except the rapid decrease of the density of states in the  $d$  band, and thus the factors which produce the *whole* thermoelectric effect in, say, Cu or Au.

The derivation of (11) neglects the finite spread of  $\partial f/\partial E$  discussed in the last section, and will therefore be incorrect at high temperatures.

#### 5—ALLOYS OF PALLADIUM

As palladium is alloyed with copper or silver or gold, electrons are added and hence  $T_0$  decreases and the thermoelectric power becomes numerically greater as long as there remain any positive holes in the  $d$  band; when, however, the  $d$  band is full we should expect the thermoelectric power to fall to a value comparable with that for the noble metal. The quantity  $S$  plotted against atomic composition should thus show a discontinuity.

Denoting by  $\zeta_0$  the energy of the highest occupied state for pure Pd and by  $\zeta_0'$  that of the alloy, formulae (4) and (10) give for the thermoelectric power

$$S = \frac{\pi^2 k T}{3 e} \frac{\frac{1}{2} (E_0 - \zeta_0')^{-\frac{1}{2}}}{\alpha \sqrt{(E_0 - \zeta_0)} + \sqrt{(E_0 - \zeta_0')}}.$$

\* Cf. Mott and Jones, *loc. cit.*, chap. 7.

As explained in § 2, we may take  $\sqrt{(E_0 - \zeta'_0)}$  proportional to  $n_0^{\frac{1}{2}}$ , and thus for an alloy containing  $x$  parts of Cu or Ag to  $1 - x$  of Pd

$$\sqrt{(E_0 - \zeta'_0)} = \sqrt{(E_0 - \zeta_0)} \left( \frac{0.55 - x}{0.55} \right)^{\frac{1}{2}}.$$

Thus the formula for  $S$  becomes

$$S = \text{const. } T (0.55 - x)^{-\frac{1}{2}} \left/ \left\{ \alpha + \left( \frac{0.55 - x}{0.55} \right)^{\frac{1}{2}} \right\} \right. \quad x < 0.55.$$

The theoretical curve is shown in fig. 1*b*, and also the experimental points for Pd-Au due to Sedström.\* Similar results are obtained for Pd-Ag and Pd-Cu.

Heimburg† has shown that the numerical value of  $S$  for palladium charged with 900 volumes of hydrogen is more than twice as great as for the pure metal. Various workers have found that as palladium absorbs hydrogen the paramagnetism decreases and eventually disappears.‡ It would be interesting to know whether for Pd saturated with H the numerical value of  $S$  eventually decreases, as for the Pd-Ag alloys.

#### 6—RESISTANCE OF FERROMAGNETICS

We consider the metal nickel at a temperature  $T$  below the Curie point. In any one of the spontaneously magnetized domains there will exist a magnetization  $I$  in some definite direction,  $I$  being a function of the temperature and of the external field  $H$ . We denote by  $I_0$  the saturation intensity which  $I$  attains at the absolute zero of temperature, and by  $z$  the fraction given by

$$z = I/I_0.$$

Then at temperature  $T$  a fraction  $\frac{1}{2}(1 - z)$  of the unoccupied  $d$  states have their spins parallel to  $I$  and a fraction  $\frac{1}{2}(1 + z)$  will have their spins antiparallel.

Let now  $N_1(E)$  represent the density of states in the  $d$  band with spin parallel to  $I$  and  $N_2(E)$  that for antiparallel spins. We shall take, corresponding to (1)

$$N_1(E) = \frac{1}{2}C \sqrt{(E_1 - E)}$$

$$N_2(E) = \frac{1}{2}C \sqrt{(E_2 - E)}.$$

\* 'Diss.,' Lund (1924). See also 'Hand. Metallphysik.,' vol. 1 (1935).

† 'Phys. Z.,' vol. 24, p. 149 (1923).

‡ Cf. the discussion in Paper I.

$E_1$  and  $E_2$  represent the highest energies that electrons with the two spins can have; owing to the intramolecular field  $E_1$  and  $E_2$  will not be equal unless  $I = 0$ . We show  $N_1$  and  $N_2$  in fig. 4.

We now consider the time of relaxation  $\tau_1$  and  $\tau_2$  of  $s$  electrons with spins parallel and antiparallel to the magnetization. We set as before

$$\left. \begin{aligned} 1/\tau_1 &\propto N_1(E) + \beta \\ 1/\tau_2 &\propto N_2(E) + \beta \end{aligned} \right\}, \quad (12)$$

where  $\beta$  is the contribution to the scattering from  $s$ - $s$  transitions; thus  $\tau_1$  and  $\tau_2$  are unequal. As for Pd we shall assume that for paramagnetic

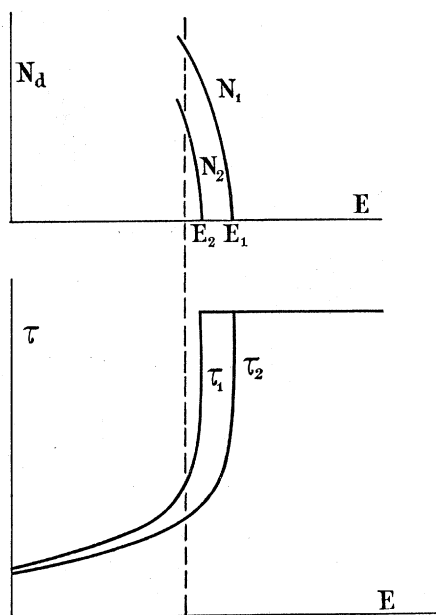


FIG. 4.

nickel (nickel above the Curie point)  $s$ - $s$  transitions are responsible for one-fifth of the resistance. If then above the Curie point  $E_1 = E_2 = E_0$ , and  $E_0 - \zeta_0 = kT_0$  as before, (12) becomes below the Curie point

$$\frac{1}{\tau_1} = \text{const.} \frac{T}{M\Theta^2} \left\{ \frac{\sqrt{(E_1 - E)}}{\sqrt{(E_0 - \zeta_0)}} + \alpha \right\} \quad \alpha \approx \frac{1}{4}, \quad (13)$$

with a similar expression for  $\tau_2$ . The two expressions for  $\tau$  as functions of  $E$  are shown in fig. 4.

If  $\zeta'_0$  represents the highest occupied state at  $T = 0$  for given  $H$ , and  $\zeta_0$  for vanishing field, then from (2) we see that

$$\sqrt{\frac{E_1 - \zeta'_0}{E_0 - \zeta_0}} = (1 - z)^{\frac{1}{2}}, \quad \sqrt{\frac{E_2 - \zeta'_0}{E_0 - \zeta_0}} = (1 + z)^{\frac{1}{2}}, \quad (14)$$

the two quantities giving the relative numbers of positive holes with given spin compared with the numbers in the paramagnetic state.

We now take the conductivity to be given by

$$\sigma = -\frac{Ne^2}{m} \int \frac{1}{2} (\tau_1 + \tau_2) \frac{\partial f}{\partial E} dE. \quad (15)$$

In Paper II we took the *resistance* to be proportional to the sum of  $1/\tau_1$  and  $1/\tau_2$ . This would be correct if a conduction electron changed its spin direction during a mean free path. Formula (15), however, gives much better agreement with experiment, and is correct if the spin direction of a conduction electron remains unaltered during a mean free path, which we shall assume to be the case.

If we treat  $\partial f/\partial E$  as vanishing except at the point  $E = \zeta'_0$ , then (15) gives for the resistivity by (14)

$$\rho = \text{const.} \frac{T}{M\Theta^2} \left[ \frac{1}{(1-z)^{\frac{1}{2}} + \alpha} + \frac{1}{(1+z)^{\frac{1}{2}} + \alpha} \right]^{-1}. \quad (16)$$

We may consider this expression to be a function of two variables  $T$  and  $z$ ;  $z$  is a function of  $T$  and  $H$ . The two limiting cases,  $z = 1$  (saturated nickel) and  $z = 0$  (paramagnetic nickel) are of interest: comparing the two we have

$$\frac{\rho_{z=1}}{\rho_{z=0}} = \frac{2}{1+\alpha} \sqrt{\frac{1}{\alpha} + \frac{1}{\alpha+2^{\frac{1}{2}}}} \simeq 0.34, \quad (17)$$

if  $\alpha \simeq 0.25$ . Thus the dependence of  $\rho$  on the magnetization is large.

It will not be correct to use formula (16) at high temperatures because of the corrections discussed in § 3. Even at low temperatures, moreover, the *alteration* in the conductivity due to demagnetization cannot be calculated from (16), because when the demagnetization is small the corresponding value  $E_1 - \zeta$  is in fact always comparable with  $kT$ . We have therefore evaluated the integral (15), exactly for a series of values of  $T$ . For this purpose it was necessary to know  $E_1 - \zeta$ ,  $E_2 - \zeta$ ; these quantities were calculated from the equations

$$\int_0^\infty \frac{\sqrt{E} dE}{e^{(E-(E_1-\zeta))/kT} + 1} = \left(1 + \frac{I}{I_0}\right) \int_0^{E_0-\zeta_0} \sqrt{E} dE$$

$$\int_0^\infty \frac{\sqrt{E} dE}{e^{(E-(E_2-\zeta))/kT} + 1} = \left(1 - \frac{I}{I_0}\right) \int_0^{E_0-\zeta_0} \sqrt{E} dE.$$

The quantities on the right are proportional to the number of positive holes with the two spin directions. For  $I/I_0$  we took the *experimental*

values, and for  $T_0 = (E_0 - \zeta_0)/k$  we took the value  $2200^\circ$ , deduced from specific heat measurements at low temperatures.\*

Fig. 5 shows the values thus obtained. Curve I shows the observed resistance of nickel, in arbitrary units. Curve II is the calculated curve for  $I = 0$  (no magnetization). This curve was obtained as in § 3 for palladium, with  $T_0 = 2100$  and  $\Theta_D = 410$ , and was fitted to the observed values just above the Curie point. The three points marked  $\oplus$  are calculated, as described above, for the observed magnetization at the

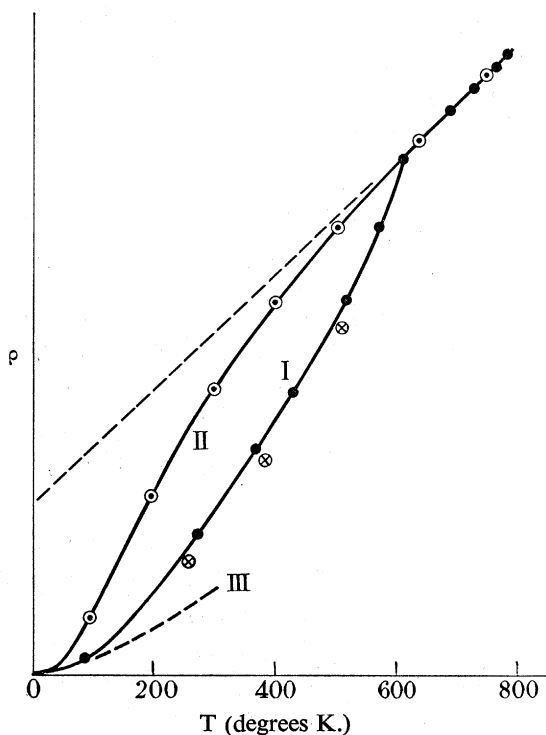


FIG. 5—Resistivity of nickel. ● observed; ○ calculated for zero magnetization (fitted to curve I at  $635^\circ$  K.); III calculated for  $I/I_0 = 1$ ;  $\oplus$  calculated for observed values of  $I/I_0$ .

temperatures  $275$ ,  $380$ , and  $515^\circ$  K. The agreement between theory and experiment is good.

Curve III is that calculated for  $I/I_0 = 1$ .

If one calculates the resistance from the simple formula (16) one gets very similar results, but with larger deviations from III for low temperatures.

\* Mott, 'Proc. Roy. Soc.,' A, vol. 152, p. 42 (1935).

## 7—THERMOELECTRIC PROPERTIES OF FERROMAGNETICS NEAR THE CURIE POINT

For the paramagnetic metals Pd and Pt,  $|S|$  increases linearly with  $T$  as for normal metals; for nickel, on the other hand,  $|S|$  is greater some way below the Curie point than at the Curie point itself, as shown in fig. 6. We believe this to be due to the same reason as the increase in  $|S|$  for Pd when Au is added in solid solution; for  $s$  electrons with their spins parallel to the direction of magnetization, the number of positive holes available for transitions decreases as the magnetization increases. As fig. 4 shows, this leads to a more rapid variation of  $\tau$  with  $E$  and hence to a larger value of  $|S|$ .

The thermoelectric power is given by

$$S = \frac{\pi^2 k^2 T}{3e} \left\{ \frac{\partial}{\partial E} \log (\tau_1 + \tau_2) \right\}_{E=\zeta}$$

From (13) this gives

$$S = \frac{\pi^2 k^2 T}{3e} \left[ \frac{\frac{1}{2} (E_1 - \zeta'_0)^{-\frac{1}{2}}}{\{(E_1 - \zeta'_0)^{\frac{1}{2}} + \alpha (E_0 - \zeta_0)^{\frac{1}{2}}\}^2} + \frac{\frac{1}{2} (E_2 - \zeta'_0)^{-\frac{1}{2}}}{\{(E_2 - \zeta'_0)^{\frac{1}{2}} + \alpha (E_0 - \zeta_0)^{\frac{1}{2}}\}^2} \right] \\ \div \left[ \frac{1}{(E_1 - \zeta'_0)^{\frac{1}{2}} + \alpha (E_0 - \zeta_0)^{\frac{1}{2}}} + \frac{1}{(E_2 - \zeta'_0)^{\frac{1}{2}} + \alpha (E_0 - \zeta_0)^{\frac{1}{2}}} \right].$$

Substituting for  $E$  from (14) this gives

$$S = \text{const. } T \left[ \frac{1}{(1-z)^{\frac{1}{2}}} \frac{\alpha + (1+z)^{\frac{1}{2}}}{\alpha + (1-z)^{\frac{1}{2}}} + \frac{1}{(1+z)^{\frac{1}{2}}} \frac{\alpha + (1-z)^{\frac{1}{2}}}{\alpha + (1+z)^{\frac{1}{2}}} \right] / [2\alpha + (1+z)^{\frac{1}{2}} + (1-z)^{\frac{1}{2}}].$$

This formula is derived on the assumption that  $\tau_1$  and  $\tau_2$  do not vary much in the range in which  $\partial f / \partial E$  is finite, which we have seen not to be the case; it should, however, give qualitatively correct results.

Using the same experimental values of  $z$  as a function of  $T$  as before, we plot in fig. 6 the theoretical values of  $S$  and the experimental values due to Grew.\* The experimental and theoretical values are fitted at the Curie point. The agreement is fair, and the deviation probably due to the reason mentioned above.

## SUMMARY

Explanations are given in terms of the quantum theory of metals of the following phenomena:

\* 'Phys. Rev.,' vol. 41, p. 356 (1932).

The decrease in the temperature coefficient of resistance of palladium and platinum at high temperatures.

The large negative thermoelectric power of palladium and platinum.

The increase in the absolute magnitude of the thermoelectric power of

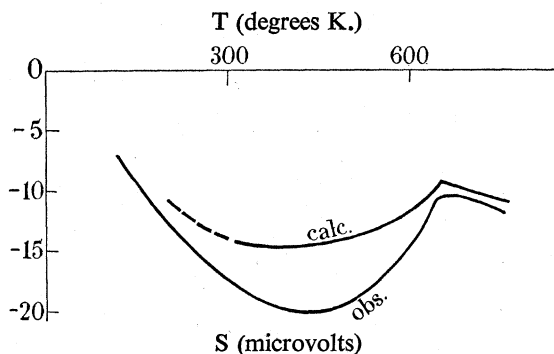


FIG. 6—Thermoelectric power of nickel; the dotted part of the theoretical curve is uncertain owing to the uncertainty in the experimental values of  $1 - z$  (the demagnetization).

palladium when it is alloyed with copper, silver, gold, or hydrogen, and the sudden drop for higher concentrations.

The sudden change in the temperature coefficient of resistance of ferromagnetic metals at the Curie temperature.

The behaviour of the thermoelectric power of nickel near the Curie temperature.

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