

The Electrical Conductivity of Transition Metals

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1—In a recent paper* certain properties of the transition metals Ni, Pd, and Pt and of their alloys with Cu, Ag, and Au have been discussed from the point of view of the electron theory of metals based on quantum mechanics. In particular, a qualitative explanation was given of the relatively high electrical resistance of the transition metals. It was shown from an examination of the experimental evidence that the conduction electrons in these metals have wave functions derived mainly from s states just as in Cu, Ag, and Au, and that the effective number of conduction electrons is not much less than in the noble metals. On the other hand, the mean free path is much smaller, because under the influence of the lattice vibrations the conduction electrons may make transitions to the unoccupied d states, and the probability of these transitions is several times greater than the probability of ordinary scattering. Since the unoccupied d states are responsible for the ferromagnetism or high paramagnetism of the transition elements, there is a direct connexion between the magnetic properties and the electrical conductivity.

The purpose of this paper is as follows: in §§ 2, 3, and 4 we develop a formal theory of conductivity for metals, such as the transition metals, where *two* Brillouin zones are of importance for the conductivity; in § 5 we apply the theory to show why, at high temperatures, the temperature coefficient of the paramagnetic metals Pd and Pt falls below the normal value; and in § 6 we discuss the resistance of ferromagnetic metals, and show in § 7 qualitatively why constantan (Cu-Ni) has zero temperature coefficient at room temperature.

2—The element nickel has in the lowest state the electronic configuration $(3d)^8(4s)^2$, but states with the configurations $(3d)^9(4s)^1$, $(3d)^{10}$ are separated from it by energies of only a few electron volts. In our theory we shall use essentially a "one-electron" picture, *i.e.*, we treat the electrons, in the first approximation, as moving independently of one another in an electrostatic field. We must therefore suppose that, for a single electron

* Mott, 'Proc. Phys. Soc.,' vol. 47, p. 571 (1935), referred to as paper A.

moving in the field of the nickel atom, the $3d$ and $4s$ states have energies near together.

In the field of the crystal, instead of quantized energy values for the electron, we have bands or "zones" of allowed energies, a zone (or group of zones) corresponding to each state of an electron in the isolated atom. For nickel the $3d$ and $4s$ zones must overlap (otherwise the $3d$ band would be full, containing all the electrons, and the metal would not be a conductor). Thus, in the language of the electron theory of metals, the surface of the Fermi distribution lies in two zones—as also is the case for divalent metals. As explained in paper A, in nickel there are about 0.6 electrons in the $4s$ and $10 - 0.6 = 9.4$ in the $3d$ band. Similar results hold for the $5s$ and $4d$ states of palladium and the $6s$, $5d$ states of platinum.*

The theory already put forward in paper A to account for the high resistance of Ni, Pd, Pt is as follows. In the classical theory of Lorentz the conductivity of a metal is

$$\sigma = \frac{ne^2}{\mu} \tau, \quad (1)$$

where n is the number of electrons per unit volume, μ the mass of an electron, τ half the time between collisions or "time of relaxation." In the quantum theory of conduction, as developed for the monovalent alkali and noble metals,† this formula remains true with the following modifications; for μ we must understand the "effective" mass of an electron in the crystal lattice, which will in general be greater than the actual mass μ_0 of a free electron. Secondly, τ must be calculated by the methods of quantum mechanics, so that $1/\tau$ is proportional (for $T > \Theta_D$) to:

(1) The mean square displacement, due to thermal motion, of the atoms from their mean positions. This is proportional to $T/M\Theta_D^2$, where M is the mass of an atom, Θ_D the characteristic temperature.

(2) The density of states $N(E)$ at the surface of the Fermi distribution, *i.e.*, for the occupied states of highest energy.

According to the theory, the electrons in all states belonging to zones

* It is possible that in one band there may be wave functions derived from a mixture of s and d wave functions (Jones, Mott, and Skinner, 'Phys. Rev.,' vol. 45, p. 379 (1934)). For our theory it is only necessary that at the top of the lower band the wave functions shall be mostly d , and at the bottom of the upper band mostly s . Cf. a paper on the wave functions of copper by Krutter, 'Phys. Rev.,' vol. 48, p. 664 (1935).

† Cf. the report by Sommerfeld and Bethe, 'Handb. der Physik,' vol. 24 (2), p. 499 (1933).

which are not fully occupied can contribute to the electric current; therefore the d as well as the s electrons must be classed as conductivity electrons. The effective masses, however, will be very different; the conductivity electrons of copper and silver have been investigated by Fuchs* by the method of Wigner and Seitz†; he finds that they behave approximately as free electrons. The same should be true for similar fields of Ni and Pd; we shall thus assume for the s electrons

$$\mu_s \simeq \mu_0,$$

where μ_0 is the actual mass of a free electron. For the d electrons, on the other hand, owing to the small overlap of one d wave function with another, we must assume

$$\mu_d \gg \mu_0.$$

In other words, the d electron takes longer to move from atom to atom under the influence of an applied field than does the s electron.

The conductivity of a transition metal will therefore be

$$\sigma = \frac{n_s e^2}{\mu_s} \tau_s + \frac{n_d e^2}{\mu_d} \tau_d, \quad (2)$$

where τ_s , τ_d are the times of relaxation for s and d electrons, μ_s , μ_d the effective masses, and n_s the number of s electrons per unit volume. n_d , as we shall see below, should be taken to be the number of *positive holes* in the d band rather than the number of electrons.

The low conductivity of the alkaline earths is usually explained as being due to the small overlap from the first Brillouin zone to the second, and thus to small values of n_s and n_d in a formula such as (2). For Ni and Pd we know from a variety of evidence (paper A) that $n_s = n_d \simeq 0.6 N_A$, where N_A is the number of atoms per unit volume; thus the high resistance of these metals must be due to a small value of τ_s . As we shall see, τ_s and τ_d are of the same order of magnitude, and hence the conductivity is almost entirely due to s electrons.

It is essential to the theory of the high paramagnetism‡ of Pd, and the ferromagnetism‡ of Ni that the d band should be narrow compared with the s band, of the order of magnitude of one electron volt or less. Since, moreover, the number of electronic states in the d band is 10 per atom,

* 'Proc. Roy. Soc.,' A, vol. 151, p. 585 (1935).

† 'Phys. Rev.,' vol. 43, p. 804 (1933).

‡ Paper A; cf. also Peierls, 'Ergebn. exakt. Naturw.,' vol. 11, p. 264 (1932); Slater, 'Phys. Rev.,' vol. 36, p. 57 (1931).

it follows that the density of states per unit energy range is much larger in the d band than for free electrons. The recent determination of the specific heats of nickel by Keesom and Clark† and of silver by Keesom and Kok‡ shows that the density of states at the surface of the Fermi distribution is about 20 times larger in nickel, where the d band is not full, than in silver, where it is.§

The large density of states is, of course, connected with the large effective mass; under certain assumptions to be discussed in the next section we may write

$$N(E) dE = 4\pi \frac{\sqrt{(2\mu^3)}}{h^3} \sqrt{E} dE. \quad (3)$$

Now the time of relaxation τ_s for s electrons is given by

$$1/\tau_s = P,$$

where P is the probability of scattering. An s electron can be scattered in two ways: either to another s state or to a d state. The transition probabilities are proportional to the squares of matrix elements of the type

$$\int \psi_2^* \Delta V \psi_1 d\tau,$$

where ΔV is the perturbing potential due to the lattice waves, and ψ_1 , ψ_2 the initial and final states of the electron. In the present state of the theory it is exceedingly difficult to evaluate these matrix elements in any way which seems physically significant; there is, however, no reason to believe that they are much smaller when the final state lies in the d band than when it lies in the s band. On the other hand, the transition probabilities for the two processes, as already stated, are proportional to the densities of states $N_s(E)$ and $N_d(E)$ for the two final states considered; N_d is much greater than N_s , and hence we conclude that transitions from the s to the d band are important for the determination of τ_s , and that τ_s will be much less than for the noble metals, where the d band is full, and only s — s transitions are possible.

In the next two sections we shall investigate in greater detail the scattering probability P , and shall give a proof of (2).

† 'Physica,' vol. 2, pp. 230, 513 (1935).

‡ 'Physica,' vol. 1, p. 770 (1934).

§ Cf. Mott, contribution to discussion on Supraconductivity, 'Proc. Roy. Soc.,' A, vol. 152, p. 42 (1935).

3—THE SCATTERING PROBABILITY

In the quantum theory of metals, each electron has a wave function of the form

$$\psi_k = e^{i(\mathbf{k}\mathbf{r})} u_k(x, y, z),$$

where u_k is periodic with the period of the lattice. The corresponding energies will be denoted by $E(k)$.

In the usual quantum theory of conduction, a Debye model for the crystal is used; the electron is considered as interacting with a lattice wave of frequency ν , and gaining or losing a quantum of energy $h\nu$. For our purposes, since we are only interested in temperatures above the characteristic temperature Θ , we may simplify the whole theory by using an Einstein rather than a Debye model for the crystal; we shall consider every atom as vibrating independently of the others with frequency ν , where $h\nu = k\Theta$, and we shall calculate the probability that an electron is scattered by a single atom, and shall then sum for all atoms. Moreover, since the vibrating atom moves slowly compared with the electron, we shall treat it as though it were momentarily at rest, and therefore neglect altogether the change in the energy of the electron during the scattering process. These assumptions are not in the least necessary for our theory, but they simplify its exposition considerably.

Let $V(r)$ be the potential in the neighbourhood of any one ion in the crystal. Then, if that ion is displaced a distance ξ in the x direction, say, the perturbing potential which causes electronic transitions is

$$\Delta V = \xi \frac{\partial V}{\partial x}.$$

By the ordinary methods of quantum mechanics, one finds that if the electron is initially in the state k , the probability that at time t it is in the state k' is

$$\frac{1}{\hbar^2} \left| \int \psi_{k'}^* \Delta V \psi_k d\tau \right|^2 \frac{2(1 - \cos \lambda t)}{\lambda^2}, \quad (4)$$

where

$$\lambda = [E(\mathbf{k}') - E(\mathbf{k})]/\hbar.$$

This expression has a strong maximum for $E(\mathbf{k}') = E(\mathbf{k})$, and to obtain a physically significant result one must integrate over it. The transition probability may then best be expressed as follows: we draw in k -space the surface having the same energy as the state \mathbf{k} (*cf.* fig. 1), and take an area dS on this surface, and a cylinder of volume $d\zeta dS$ as shown.

To obtain the probability that after time t an electron has made a transition to any state in this volume element, we must multiply (4) by the number of states in the volume $d\zeta dS$, namely,

$$d\zeta dS / (2\pi)^3.$$

We now integrate over ζ ; since we may write

$$E(\mathbf{k}') - E(\mathbf{k}) = \zeta \frac{dE(\mathbf{k}')}{dk'_n},$$

the differentiation being normal to the surface, we obtain for the prob-

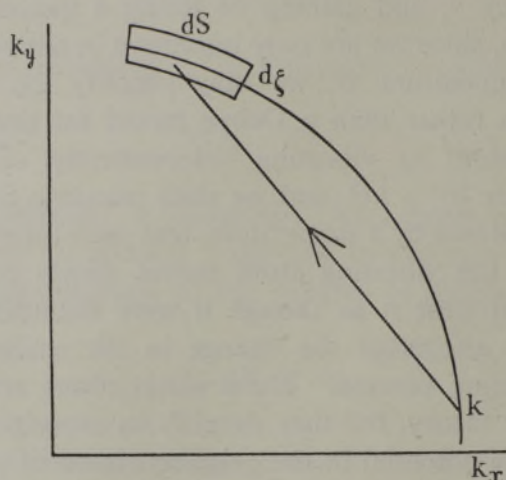


FIG. 1—Part of surface of Fermi distribution in k -space.

ability $P(\mathbf{k}\mathbf{k}') dS'$ that after unit time the electron has made a transition to the state k'

$$P(\mathbf{k}\mathbf{k}') dS' = \frac{dS'}{4\pi^2\hbar} \left| \int \psi_{k'}^* \Delta V \psi_k d\tau \right|^2 \frac{dE}{dk'_n}. \quad (5)$$

We see, as stated in § 2, that the transition probability is proportional to $1/\frac{dE}{dk'_n}$, i.e., to the *density* of states in the neighbourhood of the final state.

The square of the matrix element in (5) is

$$\xi^2 \left| \int \psi_{k'}^* \frac{\partial V}{\partial x} \psi_k d\tau \right|^2.$$

Since we must sum over all atoms, we must take the mean value of ξ^2 , viz.,

$$\bar{\xi^2} = \frac{\hbar^2}{k} \frac{\mathbf{T}}{M\Theta^2}.$$

4—We must now prove formula (2), and hence give a more exact definition of τ_s, τ_d in terms of the transition probability (5). This can only be done if we make rather drastic simplifying assumptions. For the s electrons we set

$$E(\mathbf{k}) = \hbar^2 k^2 / 2\mu_s,$$

depending on the modulus k of \mathbf{k} only. μ_s is thus the effective mass of an s electron. We shall treat the atomic d state as non-degenerate (this can be allowed for afterwards), and shall denote the wave vector of a state in the d band by \mathbf{j} , \mathbf{j} being so defined that $j = 0$ corresponds to the state of *highest* energy. We shall assume also that the energy $E(\mathbf{j})$ of a d state depends only on the modulus j of \mathbf{j} , and shall write it

$$E(\mathbf{j}) = E_0 - \hbar^2 j^2 / 2\mu_d.$$

We must remember that $\mu_d \gg \mu_s$.

For the transition probability between one state and another we write, from (5)

$$P(\mathbf{k}\mathbf{k}') dS' = \mu_s A(\mathbf{k}\mathbf{k}') dS' / k', \quad (6)$$

where

$$A(\mathbf{k}\mathbf{k}') = \frac{1}{4\pi^2 \hbar^3} \left| \int \psi_{k'}^* \Delta V \psi_k d\tau \right|^2,$$

and similarly for the transition probability from an s to a d state of equal energy

$$P(\mathbf{k}\mathbf{j}) dS_j = \mu_d A(\mathbf{k}\mathbf{j}) dS_j / j. \quad (6.1)$$

We shall assume further that both $A(\mathbf{k}\mathbf{j})$ and $A(\mathbf{k}\mathbf{k}')$ depend only on the angle θ between \mathbf{k} and \mathbf{j} , or \mathbf{k} and \mathbf{k}' , so that we may write

$$A(\mathbf{k}\mathbf{k}') = A_{ss}(\theta) \quad A(\mathbf{k}\mathbf{j}) = A_{sd}(\theta).$$

Consider now the metal in the absence of a field. The probability that any electronic state is occupied is given by the Fermi function

$$f(\mathbf{k}) = f_0(\mathbf{k}) = \frac{1}{e^{(E - \zeta)/kT} + 1}, \quad E = E(\mathbf{k}).$$

If an external field F is applied, say in the x direction, the wave vector of each electron increases according to the equation $k_x = -eF/\hbar$; hence the rate of change of $f(\mathbf{k})$ is initially

$$\begin{aligned} \left(\frac{df}{dt} \right)_{\text{field}} &= - \frac{df_0}{dE} \frac{dE}{dk} \frac{k_x}{k} \frac{eF}{\hbar} \\ &= - \frac{df_0}{dE} \frac{\hbar^2}{\mu_s} k_x \frac{eF}{\hbar}, \end{aligned} \quad (7)$$

for s electrons, with a similar expression for the d electrons. These two expressions must be equated to the rate of change of f due to collisions.

When a steady current is flowing, the probability that a state is occupied will no longer be given by $f_0(\mathbf{k})$ but by the "perturbed" Fermi functions $f_s(\mathbf{k}), f_d(\mathbf{j})$ for s and d electrons respectively. We shall write

$$f_s(\mathbf{k}) = f_0(\mathbf{k}) + g_s(\mathbf{k}), \quad f_d(\mathbf{j}) = f_0(\mathbf{j}) + g_d(\mathbf{j}).$$

Now, by the definition of the "time of relaxation" τ_s , we have

$$g_s(\mathbf{k}) = \frac{df}{dt} \tau_s,$$

which may be written

$$g_s(\mathbf{k}) = - \frac{df_0}{dE} \frac{\hbar^2}{\mu_s} k_x \tau_s \frac{eF}{\hbar}, \quad (8)$$

which gives the change of the distribution function due to the field F , in terms of the time of relaxation τ_s .

We now calculate the rate of change of f due to collisions, which has to be equated to (7).

We consider a volume element of k space in the s zone. Let the volume element be situated at the point \mathbf{k} , and let its volume be $d\mathbf{k} = dk_x dk_y dk_z$. Then for unit volume of the metal the number of electrons in states within the element is

$$2f_s(\mathbf{k}) d\mathbf{k}/(2\pi)^3.$$

Owing to the thermal vibrations of the atoms, electrons make transitions to states of practically equal energy; the number of such transitions in which an electron leaves the volume element $d\mathbf{k}$ is, per unit time,

$$2f_s(\mathbf{k}) \frac{d\mathbf{k}}{8\pi^3} \left[\int P(\mathbf{k}\mathbf{k}') \{1 - f_s(\mathbf{k}')\} dS' + \int P(\mathbf{k}\mathbf{j}) \{1 - f_d(\mathbf{j})\} dS_j \right]. \quad (9)$$

The integration is over all surface elements dS', dS_j in k, j space which have the same energy as the initial state.

Substituting from (6), (6.1), we have, for (9)

$$2f_s(\mathbf{k}) \frac{d\mathbf{k}}{8\pi^3} \left[\frac{\mu_s}{k} \int A(\mathbf{k}\mathbf{k}') \{1 - f_s(\mathbf{k}')\} dS' + \frac{\mu_d}{j} \int A(\mathbf{k}\mathbf{j}) \{1 - f_d(\mathbf{j})\} dS_j \right]. \quad (10)$$

Similarly, we obtain for the number of electrons entering the volume element $d\mathbf{k}$ per unit time

$$2 \{1 - f_s(\mathbf{k})\} \frac{d\mathbf{k}}{8\pi^3} \left[\frac{\mu_s}{k} \int A(\mathbf{k}\mathbf{k}') f_s(\mathbf{k}') dS' + \frac{\mu_d}{j} \int A(\mathbf{j}\mathbf{k}) f_d(\mathbf{j}) dS_j \right]. \quad (11)$$

Subtracting (10) from (11) we obtain for the decrease, due to collisions, in the number of electrons in the volume element $d\mathbf{k}$ per unit time,

$$2 \frac{d\mathbf{k}}{8\pi^3} \left[\frac{\mu_s}{k} \int A(\mathbf{k}\mathbf{k}') \{f_s(\mathbf{k}) - f_s(\mathbf{k}')\} dS' + \frac{\mu_d}{j} \int A(\mathbf{k}\mathbf{j}) \{f_s(\mathbf{k}) - f_d(\mathbf{j})\} dS_j \right]. \quad (12)$$

The second term corresponds to the s - d transitions, and is large, containing as it does the large factor μ_d (the effective mass of the d electrons).

The quantity (12) vanishes if, for f_s and f_d , we substitute the unperturbed Fermi function f_0 . Therefore, in formula (12) we may substitute g_s for f_s and g_d for f_d . Using (8) for g_s and g_d , we obtain finally for the decrease in the number of electrons in the volume element $d\mathbf{k}$

$$-2 \frac{d\mathbf{k}}{8\pi^3} \frac{df_0}{dE} \frac{eF}{\hbar} \frac{\hbar^2}{\hbar^2} \left[\frac{\mu_s}{k} \frac{\tau_s}{\mu_s} \int (k_x - k'_x) A(\mathbf{k}\mathbf{k}') dS' + \frac{\mu_d}{j} \int \left(\frac{\tau_s}{\mu_s} k_x - \frac{\tau_d}{\mu_d} j_x \right) A(\mathbf{k}\mathbf{j}) dS_j \right]. \quad (13)$$

This must be equated to the increase in the number of electrons due to the applied field, which is, from (7)

$$2 \frac{d\mathbf{k}}{8\pi^3} \left(\frac{df}{dt} \right)_{\text{field}} = -2 \frac{d\mathbf{k}}{8\pi^3} \frac{df_0}{dE} \frac{\hbar^2}{\mu_s} \frac{eF}{\hbar} k_x. \quad (14)$$

Equating (13) and (14) and dividing by common factors we obtain

$$\tau_s \int \left(1 - \frac{k'_x}{k_x} \right) A(\mathbf{k}\mathbf{k}') dS' + \tau_s \frac{\mu_d}{\mu_s} \frac{k}{j} \int A(\mathbf{k}\mathbf{j}) dS_j - \tau_d \frac{k}{j} \int A(\mathbf{k}\mathbf{j}) \frac{j_x}{k_x} dS_j = \frac{k}{\mu_s}.$$

To simplify the integrals, we denote by θ the angle between \mathbf{k} , \mathbf{k}' or \mathbf{k} , \mathbf{j} , by α the angle between \mathbf{k} and the x axis, and by ϕ the angle between the plane $\mathbf{k}\mathbf{k}'$ and the plane containing \mathbf{k} and the x axis. Then,

$$k_x = k \cos \alpha, \quad k'_x = k (\cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \phi) \\ dS = k^2 \sin \theta d\theta d\phi.$$

Carrying out the ϕ integration, we have

$$\int \left(1 - \frac{k'_x}{k_x} \right) A(\mathbf{k}\mathbf{k}') dS' = 2\pi k^2 \int A_{ss}(\theta) (1 - \cos \theta) \sin \theta d\theta \\ = k^2 a_{ss} \quad (\text{say}) \\ \int A(\mathbf{k}\mathbf{j}) dS_j = 2\pi j^2 \int A_{sd}(\theta) \sin \theta d\theta \\ = j^2 a_{sd}^{(1)} \quad (\text{say}) \\ \int A(\mathbf{k}\mathbf{j}) \frac{j_x}{k_x} dS_j = 2\pi \frac{j}{k} j^2 \int A_{sd}(\theta) \cos \theta \sin \theta d\theta \\ = j^2 a_{sd}^{(2)} j/k, \quad (\text{say}).$$

The expressions a_{ss} , a_{sd} , etc., we consider to be all of the same order of magnitude.

Hence finally

$$\tau_s [\mu_s k a_{ss} + \mu_d j a_{sd}^{(1)}] - \tau_d \mu_s a_{sd}^{(2)} j^2 / k = 1. \quad (15)$$

By considering a volume element of j space, *i.e.*, in the d zone, we may obtain similarly

$$\tau_d [\mu_d j a_{dd} + \mu_s k a_{sd}^{(1)}] - \tau_s \mu_d a_{sd}^{(2)} k^2 / j = 1. \quad (16)$$

If now, as we assume, $\mu_d \gg \mu_s$, we obtain approximately from (15) and (16)

$$1/\tau_s = \mu_d j a_{sd}^{(1)} \quad (17)$$

$$1/\tau_d = \mu_d j a_{dd} \left/ \left(1 + \frac{k^2 a_{sd}^{(2)}}{j^2 a_{sd}^{(1)}} \right) \right. \quad (18)$$

τ_s and τ_d are thus of the same order of magnitude, both depending on the effective mass of a d electron.

Writing out in full the expression for $a_{sd}^{(1)}$ we obtain

$$a_{sd}^{(1)} = 2\pi \int_0^\pi A_{sd}(\theta) \sin \theta d\theta$$

$$A_{sd}(\theta) = \frac{2\pi}{h^3} \left| \int \psi_j^* \frac{\partial V}{\partial x} \psi_d d\tau \right|^2 \frac{\hbar^2}{k} \frac{T}{M\Theta^2},$$

where θ is the angle between the vectors \mathbf{k} of the initial s state and \mathbf{j} of the final d state.

With the assumptions made in this section, the density of states in the d zone is (*cf.* (3))

$$N_d(E) = 2\mu_d j / h^2;$$

we see, therefore, that

$$1/\tau_s \propto N_d(E)_{E=\zeta}, \quad (19)$$

which is the required result.

The current due to the s electrons is

$$i = e \int g_s(\mathbf{k}) v_x \frac{2 d\mathbf{k}}{8\pi^3},$$

where $v_x = \hbar k_x / \mu_s$ is the velocity of an s electron. If $n_s =$ number of s electrons $= \frac{8\pi}{3} (k_{\max}/2\pi)^3$, this easily reduces to

$$i = - \frac{n_s e^2}{\mu_s} F \int \tau_s \frac{df_0}{dE} dE. \quad (20)$$

Since df_0/dE is a function which vanishes except in a range kT in the

neighbourhood of $E = \zeta$, *i.e.*, at the surface of the Fermi distribution, and since further $\int (df_0/dE) dE = -1$, this reduces to

$$i = n_s e^2 F \tau_s / \mu_s,$$

so long as τ_s can be considered constant in the range kT .

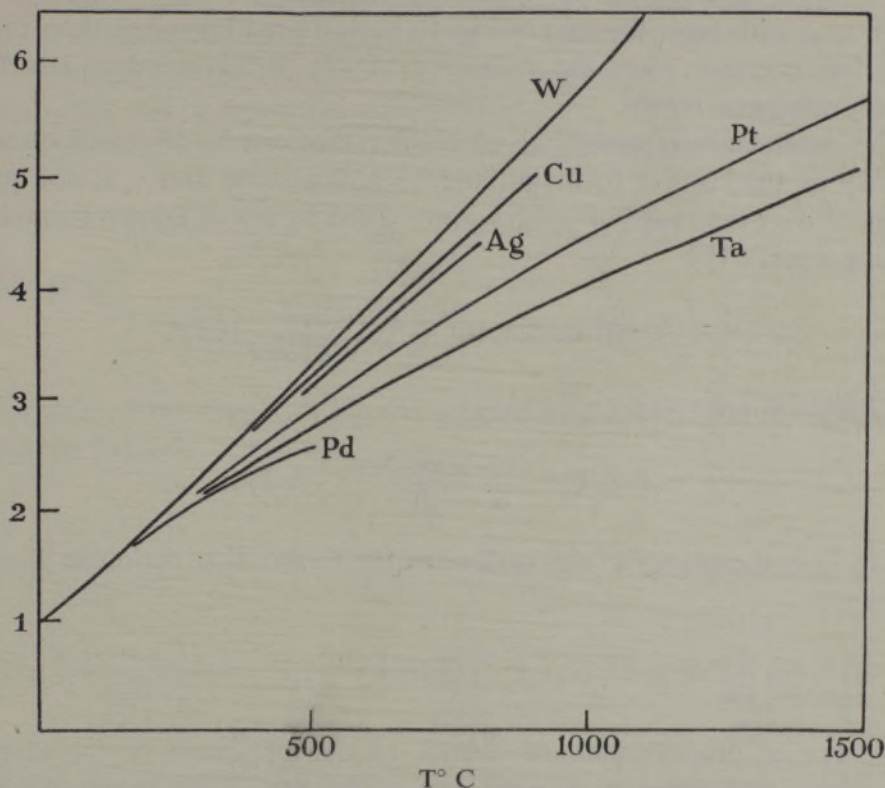


FIG. 2—Experimental values of R/R_0 for various metals; from Grüneisen, 'Handb. d. Phys.,' vol. 10, p. 16 (1928).

5—RESISTANCE OF PALLADIUM AND PLATINUM AT HIGH TEMPERATURES

At high temperatures the resistance of Cu, Ag, Au, and also of W increases rather more rapidly with the temperature than a linear law implies*; for the paramagnetic elements Pd, Pt, and Ta, on the other hand, the increase is considerably less rapid† (*cf.* fig. 2). This behaviour may easily be explained in terms of the theory of the preceding section.

As we have seen, in order to calculate the resistance, we only need to know the scattering probabilities for electrons in a narrow range of

* Probably because Θ_D decreases as the solid expands.

† The atomic susceptibilities are ($\chi \times 10^6$). Cu, -5.6 ; Ag, -20 ; W, $+41$; Pd, $+550$; Pt, $+160$; Ta, $+150$.

energies kT , in which $-\partial f_0/\partial E$ is finite, at the surface of the Fermi distribution. Now it is quite certain that the velocities, etc., of electrons in the broad s -band may be taken as constant throughout this range, but at high temperatures it is possible that $N_d(E)$, the density of states in the d band, to which the s electrons make transitions, will vary appreciably. Since $N_d(E)$ decreases with increasing energy,* we should expect the s electrons with most thermal energy to be scattered less often than those with less energy. Thus the resistance of the metal increases less fast than it otherwise would.

The dependence of resistance on temperature can be discussed quantitatively on the basis of formula (20); we now assume that τ_s is not quite constant over the range of integration. Then by a well-known formula,† writing $\tau_s = \tau_s(E)$

$$-\int \tau_s(E) \frac{df_0}{dE} dE \simeq \tau_s(\zeta) + \frac{\pi^2}{6} \left(\frac{d^2 \tau_s}{dE^2} \right)_{E=\zeta} (kT)^2,$$

ζ is itself a function of T ; we have†

$$\zeta = \zeta_0 - \frac{\pi^2}{6} \left(\frac{d \log N}{dE} \right)_{E=\zeta_0} (kT)^2,$$

where ζ_0 is the energy at the surface of the Fermi distribution at $T = 0$.

Hence

$$-\int \tau_s(E) \frac{df_0}{dE} dE = \tau_s(\zeta_0) + \frac{\pi^2}{6} (kT)^2 \left[\tau''(\zeta_0) - \frac{\tau'(\zeta_0) N'(\zeta_0)}{N(\zeta_0)} \right]. \quad (21)$$

Now $1/\tau_s$ is proportional, of course, to the amplitude of the atomic vibrations, and hence to T , and also, as we have seen, to $N_d(E)$, the density of states in the d -zone. Further, $N(E)$ is approximately equal to $N_d(E)$, so that the factors in (20) and hence in the expression for the conductivity which contain T are

$$\frac{1}{T} \left[1 + \frac{\pi^2}{6} (kT)^2 \left\{ \frac{\tau''}{\tau} + \frac{\tau'^2}{\tau^2} \right\} \right].$$

Writing‡ $N_d(E) = C \sqrt{E_0 - E}$, $\tau \propto 1/N_d$, this becomes

$$\frac{1}{T} \left[1 + \frac{\pi^2}{6} \left(\frac{T}{T_0} \right)^2 \right],$$

* Because the band is nearly full, *cf.* paper A, p. 573.

† *Cf.* Sommerfeld and Bethe, *loc. cit.*, pp. 346 and 429.

‡ The first of these assumptions should not lead to serious error for Pd and Pt, where the d band is nearly full, but may be quite incorrect for Ta.

where $kT_0 = E_0 - \zeta_0$; or for the resistance

$$R = \text{const. } T \left[1 - \frac{\pi^2}{6} \left(\frac{T}{T_0} \right)^2 \right]. \tag{22}$$

This formula is, of course, only valid if T is small compared with T_0 . We may call T_0 the "degeneracy temperature" for the d shell.

In deriving this formula, we have neglected the factors which in copper, for instance, make the resistance increase more rapidly than T , and which, presumably, will be operative also in Pd and Pt. To compare our theory with experiment, we shall therefore express the theoretical result in the form:—

$$\left(\frac{R}{R_0} \right)_{\text{Pt}} = \left(\frac{R}{R_0} \right)_{\text{Cu}} \left[1 - \frac{\pi^2}{6} \left(\frac{T}{T_0} \right)^2 \right], \tag{23}$$

which gives

$$\left(\frac{R}{R_0} \right)_{\text{Cu}} - \left(\frac{R}{R_0} \right)_{\text{Pt}} \simeq \text{const. } T^3. \tag{24}$$

A formula of the type (24) fits the experimental results for Pt well, as is shown in Table I.

TABLE I

I T (° K)	II $\left(\frac{R}{R_0} \right)_{\text{Cu}} - \left(\frac{R}{R_0} \right)_{\text{Pt}}$	III $T^3/\text{column II}$
571	0.17	1.1
771	0.4	1.2
1071	0.8	1.5
1271	1.4	1.5

From the observed resistances and formula (23) we may deduce T_0 ; we obtain

	Pd	Pt	Ta
T_0	2100°	3100°	(2800°)

We may compare the value of T_0 for nickel deduced from the atomic heat at liquid helium temperatures, namely* 1950°.

The specific heat due to the d -electrons depends on T_0 , and is, assuming $N_d(E) \propto \sqrt{(E_0 - E)}$

$$n_d F (T/T_0),$$

where n_d is the number of positive holes in the d -shell, and

$$\begin{aligned} F &= \frac{1}{2} \pi^2 k T/T_0 && T \ll T_0 \\ &= \frac{3}{2} k [1 - 0.0667 \dots (T_0/T)^3] && T \gg T_0 \end{aligned}$$

* Discussion on Superconductivity, *loc. cit.*

For immediate values F can be calculated numerically.‡ Assuming n_d to be 0.6 per atom,§ the contribution of the d -electrons to the atomic heat, with the above values of T_0 , is in cal/gm atom

T °C	Pd	Pt
500	1.2	1.1
1000	1.55	1.4
1500	1.65	1.55

The observed values of C_v (the observed atomic heat corrected for dilation) do in fact rise considerably above the value 5.98 for Pd and Pt, as Table II shows, though not quite so much as the theory requires.

TABLE II—OBSERVED ATOMIC HEATS (C_v)

T °C	Pd*	Pt*	Cu†	Ag†	Au†
500	6.594	6.38	6.2	6.0	6.0
900	7.072			6.13	
1000	7.146	6.65	6.5		6.12
1300	7.251				
1500	7.232				
1600		6.8			

* Jaeger and Rosenblum, 'Proc. Acad. Sci. Amst.,' vol. 33, p. 457 (1930).

† The mean of several determinations, *cf.* Euken, 'Handb. exp. Physik,' vol. 8, p. 211 (1928).

The excess specific heat of platinum has been attributed by Born and Brody|| to anharmonic terms in the potential energy of the lattice waves; such terms may make either a positive or a negative contribution to the specific heat. It is not at present possible to state how large this contribution is.

6—RESISTANCE OF FERROMAGNETICS

The resistance of nickel as a function of temperature and external magnetic field has been extensively investigated by Gerlach¶ and his co-workers and also by Potter.**

Fig. 3 shows the resistance of nickel as a function of temperature. The sharp change in the temperature coefficient near the Curie point should

‡ Mott, 'Proc. Camb. Phil. Soc.' (*in the press*).

§ *Cf.* paper A.

|| 'Z. Physik,' vol. 6, p. 132 (1921); 'Handb. Physik,' vol. 24, p. 675 (1933).

¶ *Cf.* Englert, 'Ann. Physik,' vol. 14, p. 589 (1932), where other references are given.

** 'Proc. Roy. Soc.,' A, vol. 132, p. 559 (1931).

be noted. It is found, moreover, that in the neighbourhood of the Curie temperature, the resistance *decreases* in a magnetic field, the change in the resistance being given by

$$\frac{\Delta R}{R} = - \frac{b \Delta (\sigma^2)}{\sigma_\infty^2}, \quad (25)$$

where $\Delta\sigma$ is the increase in the magnetization due to the field.

A qualitative explanation may be given in terms of the above theory. We have seen that the resistance of nickel is mainly due to conduction

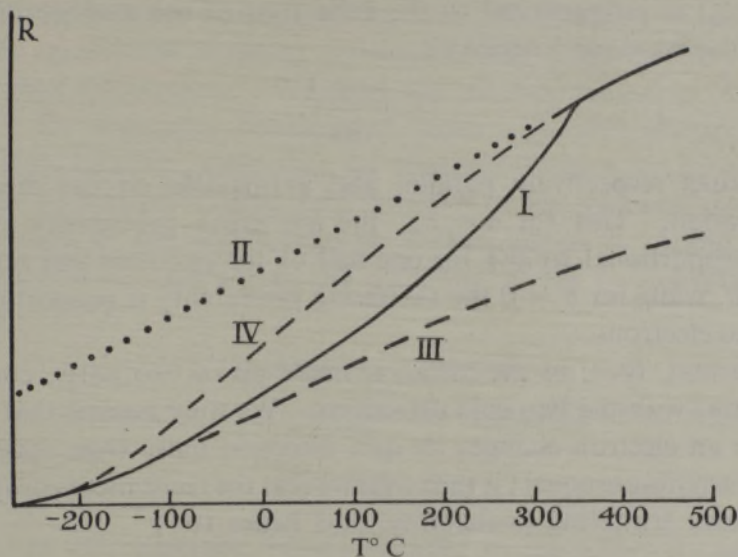


FIG. 3—Resistance of nickel, in arbitrary units. Curve I, experimental values, from Gerlach, 'Leipziger Vortraeger,' p. 21 (1933); Curve II, extrapolation of resistance curve observed above the Curie point; Curves III and IV, types of theoretical curve to be expected for $\sigma = \sigma_\infty$ and $\sigma = 0$ respectively.

electrons being scattered by a vibrating atom into the d band. The conduction electrons may be considered to have their spins either parallel or antiparallel to an external magnetic field, and the probability that the direction of the spin is changed during the scattering process is negligible. Now at low temperatures, when the spontaneous magnetization of nickel attains its maximum value, all the unoccupied states ("positive holes") in the d shell are those with spin direction antiparallel to the direction of magnetization.* Therefore it is only possible for *half* of the conduction electrons to make transitions to the d band, namely those with spin antiparallel to the direction of magnetization. On the other hand, above the Curie temperature, positive holes with both spin directions will be present,

* Mott, paper A.

and *all* the conduction electrons can make transitions to the d band. We suggest, then, that this is the reason why the destruction of the spontaneous magnetization increases the resistance.

We shall first discuss the dependence of the resistance on σ and hence on H at low temperatures (above the Debye characteristic temperature but well below the Curie point). The probability of scattering is proportional to the density of states $N_d(E)$ in the d band at the surface of the Fermi distribution ($E = \zeta_0$). Making the reasonable assumption that $N_d = C\sqrt{E_0 - E}$ (*cf.* § 5) near the head of the d band, it follows that $N_d(\zeta_0)$ is proportional to the cube root of the number of positive holes in the band, and hence to

$$\left(1 \mp \frac{\sigma}{\sigma_\infty}\right)^{\frac{1}{3}},$$

for electrons respectively parallel and antiparallel to the direction of magnetization. This for $\sigma = \sigma_\infty$, the scattering probability into the d band is proportional to $2^{\frac{1}{3}}T$ for one half of the electrons and zero for the other half, while for $\sigma = 0$ the scattering probability is proportional to T for all the electrons.

The current, then, in the metal, is made up of two parts, contributed by electrons with the two spin directions. We may assume that during a free path an electron changes its spin direction more than once, so that the two currents are equal; it then follows that the resistance is proportional to the mean scattering probability, and hence to

$$R = \text{const. } T \left[\left(1 - \frac{\sigma}{\sigma_\infty}\right)^{\frac{1}{3}} + \left(1 + \frac{\sigma}{\sigma_\infty}\right)^{\frac{1}{3}} \right]. \quad (26)$$

For σ/σ_∞ small, this gives

$$R = \text{const. } T \left[1 - \frac{1}{9} \left(\frac{\sigma}{\sigma_\infty}\right)^2 \dots \right]. \quad (27)$$

The change of resistance in a magnetic field will thus be for small σ/σ_∞

$$\frac{\Delta R}{R_T} = -\frac{1}{9} \frac{\Delta(\sigma^2)}{\sigma_\infty^2}.$$

Thus we expect that near the Curie point the constant b will have the value 0.11.

Actually b is not found to be constant near the Curie point*; Stoner, however, has pointed† out that below the Curie point $\Delta(\sigma^2)$ does not

* Englert, 'Z. Physik,' vol. 74, p. 748 (1932).

† *In the press.*

correspond to the true magnetization; the work of Potter (*loc. cit.*) shows that $\Delta R/R_T$ is in fact proportional to the change in the internal energy determined from the magneto-caloric effect. Estimating from the latter effect the "true" change in $\Delta(\sigma^2)$, we find

$$b \simeq 0.5 \quad (\text{experimental}).$$

The agreement is perhaps as good as we can expect with so simple a model of a ferromagnetic near the Curie point.

The derivation of formulae (25) and (26) is actually valid only for low temperatures, because it neglects the fact discussed in § 4, that $N_d(E)$ cannot be considered constant throughout the range kT at the surface of the Fermi distribution. We shall not attempt to give a quantitative theory of the resistance temperature curve near and above the Curie point. It is, however, clear that the theoretical curve for constant σ will be similar to that for Pt and thus concave to the temperature axis. In fig. 3 we show by the dotted lines the sort of curves we should expect to obtain for $\sigma = \sigma_\infty$ and $\sigma = 0$, the ordinates of the two curves being in the ratio $1 : 2^{2/3}$.

7—ALLOYS OF NICKEL

From the theoretical point of view, the resistance of an alloy is made up of two parts:—

$$R = R_0 + R_T,$$

where R_0 is the resistance due to disorder in the alloy, R_T and to the thermal vibration of the atoms. In general R_0 is independent of temperature, while R_T increases linearly with T as for a pure metal. In paper A, however, it was shown from experimental evidence that in certain Pd-Ag alloys, at least part of R_0 (and hence of the resistance at 0°K) is due to transitions from the s to the d band. This is probably the case for other paramagnetic or ferromagnetic alloys. It follows that R_0 will also be a function of the temperature, that part of R_0 which is due to s - d transitions being proportional to

$$\left(1 - \frac{\sigma}{\sigma_\infty}\right)^{\frac{1}{2}} + \left(1 + \frac{\sigma}{\sigma_\infty}\right)^{\frac{1}{2}}, \quad (28)$$

and hence increasing by a factor $2^{\frac{1}{2}} = 1.59$ between 0°K and the Curie temperature.

Fig. 4 shows measurements of the resistance of a series of Cu-Ni alloys due to Chevenard.* The sharp rise with T in the resistance of the alloy

* 'C.R. Acad. Sci. Paris,' vol. 181, p. 29 (1925). Cf. also similar results by Krupkowski and de Haas, 'Comm. Phys. Lab. Leiden,' No. 194a (1928).

containing 20% copper below the Curie point, compared with the gradual rise above, suggests that R_0 as well as R_T depends on T below the Curie point, as suggested by formula (28).

For paramagnetic and ferromagnetic alloys above the Curie point, that part of R_0 which is due to s - d transitions will be given by (*cf.* equation (23))

$$\text{const.} \left[1 - \frac{\pi^2}{6} \left(\frac{T}{T_0} \right)^2 \right] \quad T \ll T_0. \quad (29)$$

Thus if R_T is not too large, the resistance will *decrease* with temperature.

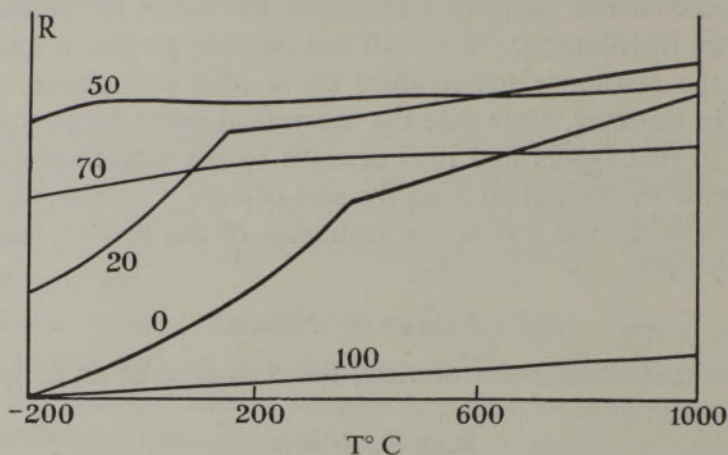


FIG. 4—Resistance of copper-nickel alloys. The figures give the proportion of copper in atomic per cent.

We may thus understand why alloys with about the composition CuNi (constantan) have a maximum in the resistance near room temperature. In these alloys the d shell is nearly full up, so that T_0 will have a value considerably less than 1000° – 2000° , the values estimated for pure nickel. On the other hand, probably only a small part of R_0 is due to s - d transitions and thus dependent on temperature. The parts of the resistance, therefore, which depend on temperature will be a term of the type (29) with T_0 , say, 300° , and a term due to thermal vibrations of the same order of magnitude as the resistance of pure copper. Two such terms will account for the observed maximum.

SUMMARY

The quantum theory of electrical conductivity developed by Bloch and others is extended to metals where the conduction electrons occupy more than one Brillouin zone, as is the case for all real metals except the

alkalis and noble metals. The theory is applied to the transition metals; certain anomalies in the resistance temperature curves of the paramagnetic metals Pd, Pt, Ta are explained. A theory is given to account for the fact that the resistance of nickel decreases in a magnetic field, and an expression for the decrease obtained, which is of the same order of magnitude as that observed. Finally, a qualitative discussion is given of the resistance temperature curves of copper-nickel alloys such as constantan.