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The Electrical Conductivity of the Transition Metals

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The width of the ground state, i.e. 8266 cm.$^{-1}$, is the largest yet recorded. Numerous examples of predissociation are found.

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DESCRIPTION OF PLATE 19

PbF band systems: (*a*) absorption; (*b*) emission; (*c*) system B_1, absorption; (*d*) system E, absorption; (*e*) system B_1, emission.

The electrical conductivity of the transition metals

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INTRODUCTION

1·1. The conductivity of a pure metal depends upon a large number of quantities, and it is difficult to decide the relative importance of the various constants since they often produce compensating effects. It is, however, generally agreed that the low conductivity of the divalent metals, and especially of bismuth, is due to the small effective number of conduction electrons. It has further been suggested by Mott (1935, 1936*a*, 1936*b*) that the low conductivity of the transition elements, which are even worse conductors than the divalent elements, is due to another cause, namely, to the abnormal smallness of the free path. The transition metals possess conduction electrons in an *s*-band and they also have unfilled *d*-bands.

Hence, in addition to the normal *s*-*s* transitions the electrons can also undergo *s*-*d* transitions, and this results in a shortening of the free path.

One of the difficulties in the way of a complete theory is the necessity of separating the normal *s*-*s* transitions from the *s*-*d* transitions, and so far it has not proved possible to do this. In the present paper it is shown that the resistances produced by the two different types of transition have different temperature variations, and therefore that it should be possible to estimate their relative importance by measurements over a sufficiently large range of temperature.

1·2. In order to obtain an insight into what happens we consider a simple model, for which quantitative calculations are carried out in §§2 and 3. Many of the results are, however, qualitatively true for more general models, but at present it is impossible to carry out the calculations completely except under the simplest assumptions. We take the energy zero at the bottom of the *s*-zone, and we assume that for this zone the energy is given by

$$E_s(\mathbf{k}) = \frac{h^2 |\mathbf{k}|^2}{8\pi^2 m_s}, \tag{1}$$

where $\mathbf{k}$ is the wave vector of the state and m_s is the effective mass of an electron in the *s*-zone. The energy in the *d*-zone is assumed to be given by

$$E_d(\mathbf{k}) = A - \frac{h^2 |\mathbf{k}|^2}{8\pi^2 m_d} \quad (A > 0), \tag{2}$$

where m_d is the effective mass of an electron in the *d*-zone and is much greater than m_s. The quantity A and the number of electrons are such that there are some electrons in the *s*-zone and some vacant levels or holes in the *d*-zone. Let ζ be the Fermi energy of the conduction electrons. The value ζ_0 of ζ at $T = 0$ gives the energy of the highest occupied level, and for most purposes the variation of ζ with T is negligible. At $T = 0$ the electrons in the *s*-zone are contained in a sphere in $\mathbf{k}$-space of radius k_s, and the holes in the *d*-zone are contained in a sphere of radius k_d, where

$$\frac{h^2 k_s^2}{8\pi^2 m_s} = \zeta_0 = A - \frac{h^2 k_d^2}{8\pi^2 m_d}. \tag{3}$$

ζ_0 lies between 0 and A, and in general we should expect that $k_d > k_s$, but it is difficult to give any very accurate estimate of these quantities. The energy levels are shown schematically in fig. 1.

When an electron undergoes a transition from a state $\mathbf{k}$ to a state $\mathbf{k}'$ by interacting with a lattice wave whose wave vector is $\mathbf{q}$, energy must be conserved, and hence

$$E(\mathbf{k}') - E(\mathbf{k}) \pm h\nu(\mathbf{q}) = 0, \tag{4}$$

where $h\nu(\mathbf{q})$ is the energy absorbed or emitted by the lattice wave. Since $h\nu(\mathbf{q})$ is very small, we can say that the energy of the electron must be practically unaltered by the collision. Further, on account of the exclusion principle, the final state must be an unoccupied one. Hence, if an electron is to undergo an *s*-*d* transition, its initial state must be one with $|\mathbf{k}|$ nearly equal to k_s, and its final state must have $|\mathbf{k}'|$ nearly equal to k_d. There is, however, one further condition which was omitted by Mott. Owing to the symmetry of the crystal lattice, the transition can only occur if (Wilson 1936, p. 199)

$$\mathbf{k} - \mathbf{k}' \pm \mathbf{q} = 0. \tag{5}$$

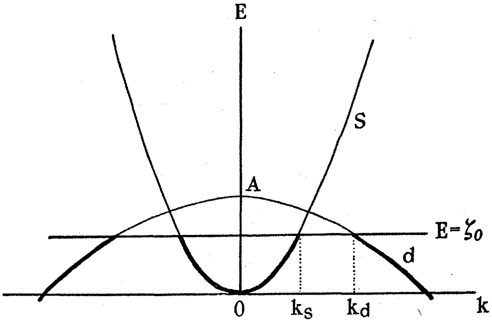

FIG. 1. The *s* and *d* levels in a transition element as functions of *k*. The thick lines represent levels occupied by electrons at the absolute zero.

This involves a considerable restriction on the possible transitions, since $k_s \neq k_d$, and hence a large value of $|\mathbf{q}|$ is required. We therefore deduce that lattice waves with small wave numbers are ineffective in producing *s*-*d* transitions. This is a general result and does not depend on the simplifications introduced by our model. A more complicated model would not change the result essentially, but it might change considerably the limiting wave number which produces transitions.

At high temperatures all the lattice vibrations are excited and the *s*-*d* transitions must be frequent. At low temperatures, however, only the low-frequency vibrations, with small values of $|\mathbf{q}|$, occur with appreciable intensity, and hence the *s*-*d* transitions must decrease exponentially with temperature. Thus, although the resistance may be dominated by the *s*-*d* transitions at high temperatures, the resistance at sufficiently low temperatures should be entirely due to the normal *s*-*s* and *d*-*d* transitions. It should, therefore, be possible to separate the two effects.

The resistance of platinum does not show an abnormal decrease at low temperatures which can be ascribed to the falling off of the *s*-*d* transitions. The significance of this, and of the behaviour of the thermoelectric power, is discussed in §§ 2·3 and 3·2.

The quantitative theory is exceedingly complicated, even for the simplified model which is discussed here. Although approximations have finally to be made, the calculations have been given in detail so that the various assumptions can be clearly seen. This is particularly desirable, since the expressions obtained for the second-order quantities differ from those given by Mott.

THE EQUATIONS FOR THE DISTRIBUTION FUNCTION

2·1. Let f denote the velocity distribution function of the electrons, and let $\mathscr{W}(\mathbf{k},\mathbf{k}')$ be the probability that in unit time an electron makes a transition from the state $\mathbf{k}$ to the state $\mathbf{k}'$. Also let $[\partial f/\partial t]$ denote the net rate of increase in f due to the collisions. Then (Wilson 1936, p. 158)

$$\left[\frac{\partial f}{\partial t}\right] = \iiint [\mathscr{W}(\mathbf{k}',\mathbf{k}) f(\mathbf{k}')\{1-f(\mathbf{k})\} - \mathscr{W}(\mathbf{k},\mathbf{k}') f(\mathbf{k})\{1-f(\mathbf{k}')\}]\, dk_1' dk_2' dk_3'. \tag{6}$$

If we put $f = f_0 + f_1$, where f_0 is the Fermi function, and make various plausible assumptions, we can show that the net rate of change in f for the electrons in the s-band, due to transitions to and from the d-band, is

$$\begin{aligned}\left[\frac{\partial f_s}{\partial t}\right]_{sd} = \frac{\varpi_d C_{sd}^2 \Delta}{8\pi^3 M h} \iiint \frac{|\mathbf{q}|^2}{\nu(\mathbf{q})} \Big[&\{f_{1d}(\mathbf{k}+\mathbf{q})\,[N(\mathbf{q})+1-f_{0s}(\mathbf{k})] \\ &- f_{1s}(\mathbf{k})\,[N(\mathbf{q})+f_{0d}(\mathbf{k}+\mathbf{q})]\}\, \Omega\{E_s(\mathbf{k}) - E_d(\mathbf{k}+\mathbf{q}) + h\nu(\mathbf{q})\} \\ &+ \{f_{1d}(\mathbf{k}+\mathbf{q})\,[N(\mathbf{q})+f_{0s}(\mathbf{k})] - f_{1s}(\mathbf{k})\,[N(\mathbf{q})+1-f_{0d}(\mathbf{k}+\mathbf{q})]\} \\ &\times \Omega\{E_s(\mathbf{k}) - E_d(\mathbf{k}+\mathbf{q}) - h\nu(\mathbf{q})\}\Big]\, dq_1 dq_2 dq_3. \end{aligned} \tag{7}$$

This only differs from the expression for one band (Wilson 1936, p. 204), because the initial and final states belong to different bands and must be distinguished by suffixes s or d. C_{sd} is an interaction energy which measures the effectiveness of the s-d transitions, Δ and M are the volume and mass of a unit cell of the crystal, $N(\mathbf{q})$ is the energy distribution function of the lattice, and Ω is a time factor whose effect is considered below. ϖ_d is the weight of the

d-states (apart from the weight factor 2 due to the spin); the weight of the s-states is taken as unity.

The reduction of the triple integral to a single integral proceeds in the usual manner. We take polar co-ordinates q, ϑ, ϖ in the $\mathbf{q}$ space, the polar axis being in the direction of $\mathbf{k}$. Then

$$\begin{aligned} &E_s(\mathbf{k}) - E_d(\mathbf{k}+\mathbf{q}) \pm h\nu(\mathbf{q}) \\ &\quad = \frac{h^2|\mathbf{k}|^2}{8\pi^2 m_s} - A + \frac{h^2}{8\pi^2 m_d}(|\mathbf{k}|^2 + 2\mathbf{k}.\mathbf{q} + |\mathbf{q}|^2) \pm h\nu(\mathbf{q}) \\ &\quad = \left(\frac{1}{m_s}+\frac{1}{m_d}\right)\frac{h^2k^2}{8\pi^2} + \frac{h^2}{8\pi^2 m_d}(2kq\cos\vartheta + q^2) - A \pm h\nu(\mathbf{q}). \end{aligned} \tag{8}$$

Now (Wilson 1936, p. 197)

$$\Omega(x) = \frac{\sin 2\pi x t/h}{2\pi x/h}.$$

Hence, putting

$$y = 2\pi t\{E_s(\mathbf{k}) - E_d(\mathbf{k}+\mathbf{q}) \pm h\nu(\mathbf{q})\}/h,$$

we have

$$\int_0^\pi \Omega\{E_s(\mathbf{k}) - E_d(\mathbf{k}+\mathbf{q}) \pm h\nu(\mathbf{q})\}\sin\vartheta\, d\vartheta = \frac{2\pi m_d}{hkq}\int_{\vartheta=\pi}^{\vartheta=0}\frac{\sin y}{y}\,dy. \tag{9}$$

For large t, the integral on the right of (9) is π if the limits of integration are of opposite sign, and it is zero otherwise. It is not possible to express the limits simply, but if we neglect the small term $h\nu(\mathbf{q})$ we obtain much simpler expressions, which are adequate for our purpose. The condition for the top limit to be positive is that

$$q > \sqrt{\left(\frac{8\pi^2 m_s A}{h^2} - \frac{m_d}{m_s}k\right)} - k.$$

Since only the electrons near the top of the Fermi distribution contribute to the conductivity, we may put $k = k_s$. Then, by (3), the above condition becomes

$$q > k_d - k_s.$$

Similarly the bottom limit is negative provided that

$$q > k_s - k_d.$$

One or other of these conditions is always satisfied, and hence the condition for an s-d transition to be possible is

$$q > |k_d - k_s|. \tag{10}$$

This condition is obvious from the arrangement of the energy surfaces. For, the smallest value of q is required when an electron jumps from a point on the s-sphere in $\mathbf{k}$ space to the nearest point on the d-sphere. In this case $\mathbf{k}$ and $\mathbf{k}'$ have the same direction and hence $q = |k_d - k_s|$.

We may remark here that if the energy surfaces are not spheres it is possible for the s- and d-surfaces to cut. The minimum value of q is then 0. This applies, however, only to those electrons whose energy levels lie along the intersections. For the vast majority of the electrons a non-zero value of q is required to produce a transition, and the argument is not essentially altered by the presence of a negligible number of electrons which can be scattered from one band to the other by long lattice waves.

We now restrict ourselves to problems in which the current is along the x-axis, and we put

$$f_1 = -k_1 c(E) \frac{\partial f_0}{\partial E}. \tag{11}$$

We can replace any slowly varying functions of $\sin\vartheta$ by their values when $y = 0$, since practically the whole of the integral (9) comes from small values of y. The integration over ϖ can then be carried out. If θ and θ_1 are the angles between the x-axis and $\mathbf{k}$ and $\mathbf{q}$, we have

$$q_1 = q\cos\theta_1 = q(\cos\theta\cos\vartheta + \sin\theta\sin\vartheta\cos\varpi)$$

and

$$\int_0^{2\pi} q_1\,d\varpi = 2\pi q\frac{k_1}{k}\cos\vartheta_0$$

$$= 2\pi k_1\left[\frac{m_d}{2m_s E}(A \mp h\nu) - \frac{m_s + m_d}{2m_s} - \frac{h^2q^2}{16\pi^2 m_s E}\right] \tag{12}$$

Finally, putting $x = h\nu/kT$ and $\eta = (E-\zeta)/kT$ (k here is Boltzmann's constant), we obtain

$$\begin{aligned}\left[\frac{\partial f_s}{\partial t}\right]_{sd} = &-\frac{k_1}{E^{\frac{3}{2}}}\frac{\partial f_0}{\partial E}\varpi_d m_d P_{sd}\left(\frac{T}{\Theta}\right)^3\int_{\Theta_E/T}^{\Theta/T}\frac{z^2\,dz}{e^z - 1}\\ &\times\left[\left\{c_d(\eta+z)\left(E + \frac{m_d A}{2m_s} - \frac{m_s+m_d}{2m_s}E + \frac{m_d kTz}{2m_s} - D\frac{T^2}{\Theta^2}z^2\right) - Ec_s(\eta)\right\}\frac{e^\eta+1}{e^\eta+e^{-z}}\right.\\ &\left.+\left\{c_d(\eta-z)\left(E + \frac{m_d A}{2m_s} - \frac{m_s+m_d}{2m_s}E - \frac{m_d kTz}{2m_s} - D\frac{T^2}{\Theta^2}z^2\right) - Ec_s(\eta)\right\}\frac{e^\eta+1}{e^{\eta-z}+1}\right]\\ = &-\frac{k_1}{E^{\frac{3}{2}}}\frac{\partial f_0}{\partial E}\varpi_d m_d P_{sd}\left(\frac{T}{\Theta}\right)^3\left[\int_{-\Theta/T}^{-\Theta_E/T} + \int_{\Theta_E/T}^{\Theta/T}\right]\frac{e^\eta+1}{e^{\eta+z}+1}\frac{z^2\,dz}{|1-e^{-z}|}\\ &\times\left[c_d(\eta+z)\left\{A\frac{m_d}{2m_s} - E\frac{m_d-m_s}{2m_s} + \frac{m_d kTz}{2m_s} - D\frac{T^2}{\Theta^2}z^2\right\} - Ec_s(\eta)\right],\end{aligned} \tag{13}$$

where

$$D = \frac{(6\pi^2)^{\frac{2}{3}}h^2}{16\pi^2 m_s a^2}, \quad P_{sd} = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}}\frac{3\pi^2 C_{sd}^2}{\sqrt{2}m_s^{\frac{1}{2}}Mak\Theta}.$$

Θ is, as usual, the Debye temperature, and $k\Theta_E = h\nu_E$, where ν_E is the frequency corresponding to the minimum value of q necessary to excite the s-d transitions. When $E = \zeta_0$ the value of q is $|k_d - k_s|$. It is to be noted that Θ_E is a function of E, and that (13) is to be taken as zero if $\Theta_E > \Theta$.

2·2. The formula we have just derived is so complicated that we must make some approximations before going any further. Since A, E and D are all of the same order of magnitude, the coefficient of c_d is probably considerably smaller than the coefficient of c_s, and we therefore neglect c_d. As a reasonable estimate we might take $A - E = \frac{1}{10}E$ and $E = D$. The approximation is then justified unless m_d/m_s is very large. Very large values of m_d/m_s of the order 10 to 20 have sometimes been proposed to account for the properties of the transition metals (e.g. Baber 1937). I cannot believe that such large values ever occur. Measurements of the specific heat or magnetic susceptibility give $\varpi_d m_d$ and not m_d. Now in an atom the d-states have a fivefold degeneracy. In a cubic crystal this degeneracy is partly removed (Bethe 1929), and the states split up into two sets, one of which is doubly and the other triply degenerate. It is not possible to say whether these states overlap or not. But, if we put $\varpi_d = 3$, then values of m_d/m_s of the order of 3 to 5 are sufficient to explain all the results. These values are small enough to justify our approximation.

It should be noted that the probability of scattering is proportional to $\varpi_d m_d$, but not to the density $\mathfrak{n}_d(E)$ of states in the d-band as stated by Mott. Thus the scattering probability is of the same order as that predicted by Mott but it has a different form, and this has important consequences in connexion with the second-order effects. The reason why he arrived at the wrong result is that he did not take account of the conditions (5) and assumed instead that every $\mathbf{k}'$ state is attainable from every $\mathbf{k}$ state.

The probability of scattering due to s-s transitions is (Wilson 1936, p. 207)

$$\left[\frac{\partial f_s}{\partial t}\right]_{ss} = -\frac{k_1}{E^{\frac{3}{2}}}\frac{\partial f_0}{\partial E} m_s P_{ss}\left(\frac{T}{\Theta}\right)^3$$
$$\times \int_{-\Theta/T}^{\Theta/T} \left[c_s(\eta+z)\left\{E + \tfrac{1}{2}kTz - D\frac{T^2}{\Theta^2}z^2\right\} - Ec_s(\eta)\right]\frac{e^\eta+1}{e^{\eta+z}+1}\frac{z^2\,dz}{|1-e^{-z}|}. \tag{14}$$

This has to be added to (13) in order to obtain the complete expression for $[\partial f_s/\partial t]$. The corresponding expressions for $[\partial f_d/\partial t]$ can be readily obtained, but we do not need them. The conductivity due to one band is (Wilson 1936, pp. 161 or 208),

$$\sigma = \frac{n\epsilon^2}{m}\tau(\zeta).$$

Hence, even if the time of relaxation is of the same order for both s- and d-bands, the conductivity due to the d-band can be neglected, since $m_d \gg m_s$ and since our theory is at best only an indifferent approximation. (Note that the weight ϖ_d does not come into the conductivity of the d-band if we assume, as is reasonable, that an electron in one of the d-bands can be scattered into any of the degenerate d-bands. There is then a factor $1/\varpi_d$ in the conductivity due to the ϖ_d possibilities of scattering, but there is also another factor ϖ_d due to there being ϖ_d bands to carry the current, and hence ϖ_d does not come into the expression for the conductivity except through the time of relaxation.) If we take into account the contributions of the d-electrons to the current, the conductivity is increased and the thermo-electric power is decreased.

2·3. After all the approximations have been made we have

$$\left[\frac{\partial f_s}{\partial t}\right] = -\frac{k_1}{E^{\frac{3}{2}}}\frac{\partial f_0}{\partial E} m_s P_{ss}\left(\frac{T}{\Theta}\right)^3$$

$$\times \int_{-\Theta/T}^{\Theta/T} \left[c_s(\eta+z)\left\{E+\tfrac{1}{2}kTz - D\frac{T^2}{\Theta^2}z^2\right\} - Ec_s(\eta)\right]\frac{e^{\eta}+1}{e^{\eta+z}+1}\frac{z^2\,dz}{|1-e^{-z}|}$$

$$+\frac{k_1}{E^{\frac{3}{2}}}\frac{\partial f_0}{\partial E}\varpi_d m_d P_{sd}\left(\frac{T}{\Theta}\right)^3\left\{\int_{-\Theta/T}^{-\Theta_E/T} + \int_{\Theta_E/T}^{\Theta/T} Ec_s(\eta)\frac{e^{\eta}+1}{e^{\eta+z}+1}\frac{z^2\,dz}{|1-e^{-z}|}\right\}. \quad (15)$$

To solve this equation for small values of Θ/T we adopt the usual method of expanding the integrands in terms of z and retaining only the leading terms. We obtain

$$\left[\frac{\partial f_s}{\partial t}\right] = k_1 c_s(\eta)\frac{\partial f_0}{\partial E}\frac{T}{\Theta}\frac{1}{E^{\frac{3}{2}}}\left\{\tfrac{1}{2}m_s P_{ss} D + \varpi_d m_d P_{sd} E\left(1-\frac{\Theta_E^2}{\Theta^2}\right)\right\}. \quad (16)$$

Since the time of relaxation τ_s, when it exists, is defined by

$$\left[\frac{\partial f_s}{\partial t}\right] = -\frac{f_s - f_{s0}}{\tau_s},$$

we have
$$\frac{1}{\tau_s} = \frac{T}{\Theta}\frac{1}{E^{\frac{3}{2}}}\left\{\tfrac{1}{2}m_s P_{ss} D + \varpi_d m_d P_{sd} E\left(1-\frac{\Theta_E^2}{\Theta^2}\right)\right\}. \quad (17)$$

2·4. Although it is not possible to define a time of relaxation at low temperatures it is easy to obtain a solution for $c(\eta)$ when the only external influence is an electric field. This calculation follows exactly the same lines as Bloch's calculation of the conductivity of monovalent metals (see, for example, Wilson 1936, p. 212); it gives

$$\frac{1}{\sigma} = \frac{2m_s}{n\epsilon^2\zeta^{\frac{3}{2}}}\left[m_s P_{ss} D\left(\frac{T}{\Theta}\right)^5\int_0^{\Theta/T}\frac{z^5\,dz}{(e^z-1)(1-e^{-z})}\right.$$
$$\left.+\varpi_d m_d P_{sd}\zeta\left(\frac{T}{\Theta}\right)^3\int_{\Theta_E/T}^{\Theta/T}\frac{z^3\,dz}{(e^z-1)(1-e^{-z})}\right]. \qquad (18)$$

This is the general expression for the specific resistance and can be used for all temperatures except very high ones. When τ_s exists it can be obtained from the relation $\sigma = n\epsilon^2\tau_s/m_s$.

2·5. The resistance of platinum does not show any abnormal decrease at low temperatures of the kind predicted. The resistance does indeed behave abnormally, but the variation is in the wrong direction. At very low temperatures the resistance is proportional to T^2, instead of to T^5 as for a normal metal. This variation with T^2 has been ascribed by Baber (1937) to the collisions between the *s*- and *d*-electrons.

The resistances of the other transition elements are not known accurately at low temperatures. If they behave like platinum we must conclude either that the *s*-*d* transitions are not important or that $k_s = k_d$ for all the metals. If this latter condition were found to be satisfied, it could only be so for some very general reason, connected presumably with the stability of the metallic state.

The second-order effects

3·1. The effects, such as the thermoelectric power, which depend on the derivatives of τ, present considerable difficulties. Mott (1936*b*) has given a theory of the thermoelectric properties of the transition elements based on the assumption that the probability of *s*-*d* transitions is proportional to the density of *d*-states. We have seen in § 2·2 that this is not correct. The incorrectness of the assumption does not have much effect on σ, but it completely changes the theory of the second-order quantities. However, Mott and Jones (1936, p. 313) give some numerical values for $A-\zeta$ which seem to confirm Mott's theory. I believe that this confirmation is not as convincing as it seems.

Mott cites the large thermoelectric powers of the transition elements as evidence of the *s*-*d* transitions. The thermoelectric power of platinum at high temperatures is about $-1{\cdot}8\times10^{-2}T\,\mu$V/degree and that of palladium is about $-3{\cdot}4\times10^{-2}T\,\mu$V/degree. These are very much smaller than the thermoelectric powers of the alkalis and could be explained without much difficulty by the elementary theory based upon the assumption that the s-electrons are perfectly free. The thermoelectric power is $-\mathfrak{S}/\epsilon$, where (Wilson 1936, p. 177)

$$\mathfrak{S} = \tfrac{1}{3}\pi^2k^2T\left(\frac{1}{E}+\frac{1}{l}\frac{\partial l}{\partial E}\right)_{E=\zeta}, \tag{19}$$

l being the free path. For perfectly free electrons l is proportional to E^2, and hence

$$\mathfrak{S} = \frac{\pi^2k^2T}{\zeta}. \tag{20}$$

If we take the number of s-electrons per atom to be 0·6 and assume that $m_s = m$, the mass of a free electron, we find for platinum that the thermoelectric power is $-2{\cdot}15\times10^{-2}T\,\mu$V/degree. To explain the considerably higher thermoelectric power of palladium we should have to assume that m_s is larger than m, but this is quite a reasonable assumption and the value of m_s required is about $1{\cdot}5\,m$. On these grounds alone we are therefore not obliged to adopt Mott's hypothesis.

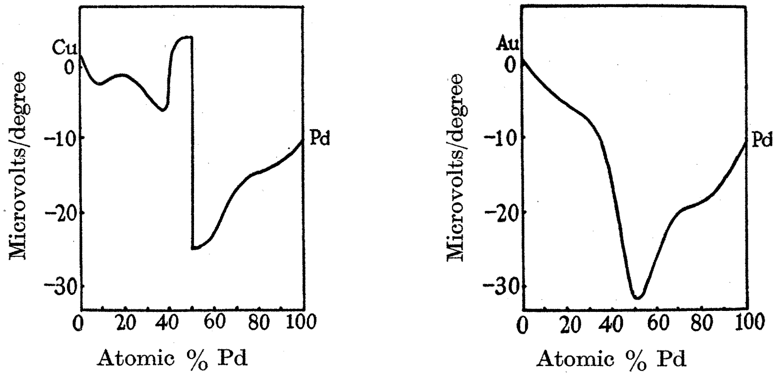

FIG. 2. Absolute thermoelectric powers of Pd alloys at 0° C.

Another piece of evidence which has been advanced is the dependence upon composition of the thermoelectric power of the palladium alloys. If copper, silver or gold is added to a transition metal, the holes in the d-band are filled up and at the same time $\mathfrak{S}$ becomes larger. When all the holes are full, further addition of the monovalent metal causes $\mathfrak{S}$ to decrease. The interpretation of this phenomenon is not, however, as unambiguous as might appear at first sight. In fig. 2 are shown the absolute thermoelectric powers of the two alloys PdCu and PdAu (Borelius 1935, pp. 404–5). The anomalies in the PdCu curve at 75 and 50 % Cu are due to the formation of superlattices. Since the formation of the superlattice CuPd is associated with a change in the crystal structure from face-centred to body-centred cubic, we consider only the superlattice Cu_3Pd. Even for this superlattice there is a slight change in structure, the ordered state being very slightly tetragonal. However, if our present ideas about superlattices are correct, there ought to be no essential difference in the electronic energy levels of the ordered and disordered Cu_3Pd lattices. On the other hand, the thermoelectric power of the ordered state is considerably smaller than that of the disordered state. This suggests that some of the change in the thermoelectric power of the alloys is due to the random distribution of the atoms. (Since condition (5) does not apply to electronic transitions caused by the random distribution of atoms, the *s*-*d* transitions might be more frequent in the disordered than in the ordered metal. It is difficult to say what effect this would have.) It is impossible to estimate what the thermoelectric power of an alloy would be if it were ordered at all compositions, and it may be that the effect would not be large. It is, however, obvious that the behaviour of these alloys indicates that the simple theory is inadequate, which assumes that the arrangement of the energy levels is independent of the composition and that all the effects can be ascribed to the change in the number of valency electrons.

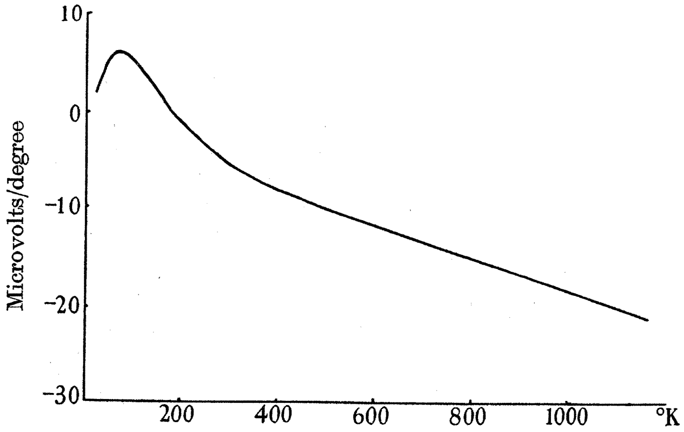

Fig. 3. Absolute thermoelectric power of Pt.

3·2. The thermoelectric power of platinum as a function of the temperature is shown in fig. 3 (Borelius 1935, p. 400). The thermoelectric power is negative at high temperatures and positive at low. The obvious interpretation is that the current is carried by electrons at high temperatures and by positive holes at low temperatures, but it is extremely difficult to see how such a state of affairs could possibly happen. Another possible explanation is that $\partial l/\partial E$ is positive at high temperatures and negative at low temperatures. It is perhaps worth pointing out that such a behaviour is possible with the model we are considering.

If we take τ from equation (18) we have

$$\begin{aligned}\frac{\partial}{\partial E}\log l &= \frac{\partial}{\partial E}\log(\tau E^{\frac{1}{2}})\\ &= \frac{2}{E}-\frac{\partial}{\partial E}\log\left[m_s P_{ss}\left(\frac{T}{\Theta}\right)^5\int_0^{\Theta/T}\frac{z^5\,dz}{(e^z-1)(1-e^{-z})}\right.\\ &\qquad\left.+\varpi_d m_d P_{sd}\,E\left(\frac{T}{\Theta}\right)^3\int_{\Theta_E/T}^{\Theta/T}\frac{z^3\,dz}{(e^z-1)(1-e^{-z})}\right].\end{aligned} \tag{21}$$

This expression cannot be used at very low temperatures since τ does not then exist. The correct expression can be obtained by a method which I have given recently (Wilson 1937), but the results are exceedingly complicated and (21) is sufficiently accurate for the present discussion. If the second term on the right of (21) is zero, that is, if the *s*-*d* transitions are unimportant, we regain (20). In order to obtain the desired behaviour of l, the second term must be small at high and large at low temperatures. The only factor which can possibly vary in such a manner is

$$\frac{\partial}{\partial E}\int_{\Theta_E/T}^{\Theta/T}\frac{z^3\,dz}{(e^z-1)(1-e^{-z})}. \tag{22}$$

The quantity $\partial\Theta_E/\partial E$ can be either positive or negative and is of the order* $\pm\Theta_E/E$. For, $\Theta_E = \text{constant}\;|k_d-k_s|$, and hence

$$\begin{aligned}\frac{\partial\Theta_E}{\partial E} &= \frac{\partial\Theta_E}{\partial k_s}\bigg/\frac{\partial E}{\partial k_s}\\ &= \pm\,\frac{\text{constant}}{2E}\left(k_s+\frac{m_d k_s^2}{m_s k_d}\right)\end{aligned}$$

by (3). The plus sign is to be taken if $k_d<k_s$ and the minus sign if $k_d>k_s$. (This is obvious from fig. 1.) The expression (22) is therefore of the order

$$\mp\frac{1}{E}\frac{(\Theta_E/T)^4}{(e^{\Theta_E/T}-1)(1-e^{-\Theta_E/T})}, \tag{23}$$

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* It is probably larger than this by a factor of the order m_d/m_s, but this does not affect the argument.

the numerical value of which is small for both large and small values of Θ_E/T but which is large for intermediate values of Θ_E/T. In order that $\partial l/\partial E$ may be negative for some range of temperature it is necessary that (22) should be positive, that is, that $k_d > k_s$.

Whether $\partial l/\partial E$ ever becomes negative is an extremely difficult question to answer, since the expression (23) occurs multiplied by a complicated factor, including powers of T. It seems probable, however, that this could be arranged by a proper choice of the constants. If the explanation put forward here is correct, then at low temperatures where (23) is small the thermoelectric power ought to become negative once more. This would be a decisive test of the theory, but unfortunately the measurements do not extend to sufficiently low temperatures. Changes in the sign of the thermoelectric power occur for some substances at liquid helium temperatures, but the thermoelectric power of platinum has not been measured in this region. Finally, although the present theory does give rise to the possibility of $\partial l/\partial E$ changing sign, yet the explanation advanced seems too artificial to be the correct one.

3·3. The resistance of platinum at very high temperatures increases less rapidly than T. This is a second-order effect which depends on the second derivative of τ and therefore involves even greater refinements than does the theory of the thermoelectric power. We must now use a more accurate formula for σ than we have hitherto done. We have (Wilson 1936, p. 162)

$$\sigma = -\frac{\epsilon^2}{3\pi h^2}\iiint \tau \,|\,\mathrm{grad}_{\mathbf{k}} E\,|\,\frac{\partial f_0}{\partial E}\,dk_1\,dk_2\,dk_3$$

$$= -\frac{16\sqrt{2}\pi^2 m^{\frac{1}{2}}\epsilon^2}{3h^3}\int \tau E^{\frac{3}{2}}\frac{\partial f_0}{\partial E}\,dE.$$

This can be evaluated by the approximate formula

$$-\int \phi(E)\frac{\partial f_0}{\partial E}\,dE = \phi(\zeta)+\frac{\pi^2}{6}k^2T^2\left(\frac{\partial^2\phi}{\partial E^2}\right)_{E=\zeta}.$$

Now τ is given by (17). If we neglect the s-d transitions, we obtain (compare Wilson 1937, equation (14))

$$\sigma = \frac{\text{constant}}{T}\left[1+\left(\frac{\pi kT}{\zeta}\right)^2\right].$$

In order that this formula should fit the experimental results, the value of ζ must be small and therefore the effective mass of the s-electrons must be large, of the order $4m$. This is too large to be reasonable.

If we use the expression (17) for τ_s, which includes the effect of the *s-d* transitions, we obtain an even worse result if Θ_E is treated as constant. In fact, if we assume in addition that the *s-d* transitions are much more important than the *s-s* transitions, we find

$$\sigma = \frac{\text{constant}}{T}\left[1+\frac{1}{3}\left(\frac{\pi kT}{\zeta}\right)^2\right].$$

In order to obtain a larger effect with the present model it is necessary to invoke the variation of Θ_E with E. It seems impossible, however, to obtain any numerical estimate of how much difference this would make, and the theory is very speculative.

SUMMARY

By using a model in which the energy surfaces are spheres, a complete theory is worked out of the *s-d* transitions in a metal containing incomplete *d*-bands. The results are of the same order of magnitude as those given by Mott's qualitative theory, but differ considerably in detail and in interpretation. It is shown that the *s-d* transitions should fall off exponentially as the temperature is lowered. A suggestion is put forward to explain the change in sign of the thermoelectric power of platinum at low temperatures.

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