

A DISCUSSION OF THE TRANSITION METALS ON THE BASIS OF QUANTUM MECHANICS

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ABSTRACT. The magnetic susceptibilities and electrical conductivities of cobalt, nickel and palladium and of their alloys with copper, silver and gold are discussed on the basis of the quantum theory of metals. It is shown that the number of electrons in the outermost s state must be about 0.6 per atom in the transition metals and one in the noble metals; certain magnetic properties of the alloys are explained on the basis of this fact. A quantum-mechanical explanation of the relatively high resistance of the transition metals is given and is shown to be supported by measurements of the resistance of alloys.

§ 1. INTRODUCTION

WIGNER AND SEITZ⁽¹⁾ have recently shown that the quantum theory is capable of accounting quantitatively for the cohesive forces in a typical metal (sodium); the purpose of this paper is to give a qualitative discussion, based on the same theory, of some properties of the transition metals and in particular of the elements nickel and palladium, which come immediately before copper and silver in the periodic table. After an introductory discussion of the electronic structure of these metals and a comparison between the binding forces of nickel and copper, we shall consider (i) the saturation moments of the ferromagnetic metals and alloys, and the reason why they are not equal to integral numbers of Bohr magnetons per atom (§§ 2 and 3); (ii) the paramagnetism of palladium and of its alloys with copper, silver and gold (§§ 4 and 5); and (iii) the electrical conductivity of the transition elements, and the reason for their low conductivity as compared with that of the noble metals. The resistance of alloys of the transition metals with copper, silver and gold is also discussed (§ 6).

To obtain an approximate solution of the Schrödinger equation for the electrons in a metal we may start from one or other of two models; we may picture the electrons as bound to individual atoms (method of Heitler and London and of Heisenberg) or we may think of them as belonging to the crystal as a whole (method of Bloch). It is to be emphasized that these two models do not correspond to different physical states of the crystal; both lead to wave functions of the whole system which are approximations to the true wave function. Insulators, as well as conductors can be treated, to a certain degree of approximation, by the use of either model. In this paper we shall use that of Bloch not only for the outermost s electrons, which are responsible for the cohesion and for the conductivity, but also

for the d electrons in the incomplete shells, which are responsible for the ferromagnetism of nickel and for the high paramagnetism of palladium. We do not, of course, consider that the Bloch approximation is the better of the two when the overlap between the wave functions of two atoms is as small as it is for, say, the $3d$ states of nickel⁽²⁾; we use it because with this model one may include, in the zero order of approximation, the possibility that an atom may be ionized, or may contain a non-integral number of electrons.* To take these possibilities into account in the Heisenberg model would be much more complicated.

$\psi_{\mathbf{k}}$ In the Bloch approximation, each electron is described by a wave function $\psi_{\mathbf{k}}$, which is a solution of the Schrödinger equation

$$\frac{\hbar^2}{2m} \nabla^2 \psi_{\mathbf{k}} + (E_{\mathbf{k}} - V) \psi_{\mathbf{k}} = 0$$

V where V is the potential of a periodic field extending throughout the crystal. The
 \mathbf{k} subscript \mathbf{k} denotes the state of the electron; owing to the exclusion principle, not
 $E_{\mathbf{k}}$ more than two electrons may be in each state. The allowed energies $E_{\mathbf{k}}$ lie in zones or bands; if the atoms are a long way apart, the zones are extremely narrow, but as the atoms are brought nearer together the zones broaden out and may overlap. Each zone corresponds to a stationary state of a single electron in the field of the isolated atom; † the number of states in any zone is always equal to the statistical weight of the atomic state to which it corresponds, multiplied by the number of atoms N_A in the crystal. For the transition elements we are interested in the bands which correspond to the ns and $(n-1)d$ states of the free atom, n being the principal quantum number of the outermost s electron, i.e. 4 for nickel and 5 for palladium. The ns band contains one state per atom and the $(n-1)d$ band five. Two electrons may be in each state. Since these elements have 10 electrons which must be shared between the two bands, and since the ferromagnetism shows that in nickel at any rate the $3d$ band is not full, it is clear that the two bands must overlap.

N_A
 n

In the elements nickel, palladium and platinum the states with the electron configurations ‡ $\{(n-1)d\}^{10}$ and $\{(n-1)d\}^9 (ns)^1$ have energy differing by an amount considerably less than the binding energies of the crystals (approximately 4 electron-volts per atom). The energies are given in table 1 in electron volts.

Table 1

	Nickel	Palladium	Platinum
Energy required to raise atom from the lowest state with the configuration $\{(n-1)d\}^9 (ns)^1$ to that with $\{(n-1)d\}^{10}$	1.4	-0.81	0.76

* Cf., for example, the work of H. Jones on alloys which obey the Hume-Rothery electronic rule, reference (3).

† The simplified model with which we are working does not include exchange forces, and therefore from our point of view the singlet and triplet states of given quantum number in, for instance, a two-electron system must be regarded as the same state.

‡ The $\{(n-1)d\}^9 (ns)^2$ configuration, which is the lowest for a free nickel atom, is of small importance in the metal, as will appear below.

Thus the work required to take an electron from the s state to the d state is small and, in so far as it is legitimate to refer to the energy of a single electron, we may say that the energy of an electron in the $(n-1)d$ state is nearly the same as in the ns state.

For our discussion of the transition metals the essential assumption is that the interaction energy between the d shells of neighbouring atoms is small. As has been pointed out by Slater⁽²⁾ this is probable, because the overlap between the wave functions is small. The d band will therefore be narrow (less than 1 e-V.) and its

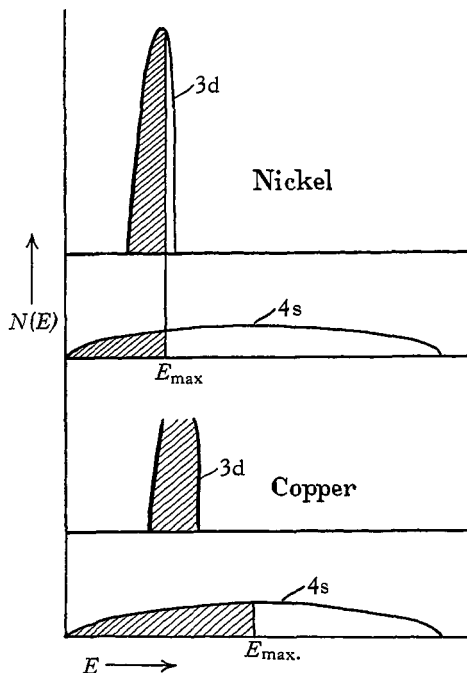


Figure 1. Density of electronic states $N(E)$ as a function of the energy E for a transition metal (nickel) and noble metal (copper). The shaded areas represent occupied states. The total number of states, $N(E) dE$, is $5N_A$ in a d band and N_A in an s band, where N_A is the total number of atoms.

mean energy will not be displaced very much from the position of the d state in the free atom. The s electrons will therefore be responsible for nearly all the cohesion. The number of electrons in the s band will not change with temperature, except by a small quantity of the order of magnitude kT /(binding energy per atom).

We denote by⁽⁴⁾ $N(E) dE$ the number of states in a given band with energy between E and $E + dE$. Figure 1 shows the general form of $N(E)$ plotted against E for two such metals as nickel and copper which, having nearly equal atomic volumes so that they are adjacent in the periodic table, probably have similar internal fields. There are five times as many states in the d band as in the s band. In copper the

N, E

p

$3d$ band is full* with 10 electrons and the $4s$ band half full with one electron per atom. In nickel, with one electron fewer, there will be a certain number p of electrons per atom in the s band and an equal number p of positive holes in the d band.† If one assumes that the energies of the bands in copper and nickel are the same, it is clear from the figure that p is less than unity, i.e. that nickel will have fewer s electrons than copper. If copper is alloyed with nickel we should on the basis of this model expect that the number of s electrons will increase only very slightly with increasing copper content until the d band is full, when the ratio of the number of copper to that of nickel atoms will be $p : (1-p)$. In the next sections, we shall refer to the abundant experimental evidence showing that this is so, and that analogous results hold for palladium alloyed with noble metals.

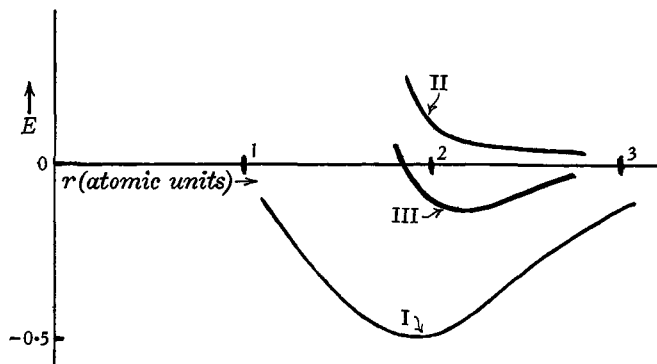


Figure 2. Energy E of the electrons in copper, as a function of the atomic radius r , calculated by the method of Wigner and Seitz. The unit of energy is the ionization potential of hydrogen; (I) the energy of the lowest s state; (II) the energy of the occupied state with maximum energy; (III) the mean energy of the electrons.

The considerations of the next section show that for nickel the number p of electrons in the s band is about 0.6 per atom. In order to gain a better understanding of the energies involved, we have carried out a Wigner-Seitz calculation for the neighbouring element copper, using the atomic field calculated by Hartree. We have only made the calculation to the degree of approximation adopted in Wigner and Seitz's first paper, and have therefore made no allowance for the correlation between the positions of electrons either with parallel or with anti-parallel spin; and we have made no allowance for the effect on the $3d$ electrons of the alteration in charge-density of the $4s$ electron. The Fermi energy was calculated by a method similar to that of Slater⁽⁶⁾ and found to be about 1.4 times greater than the value given by the Sommerfeld formula.

The results of this calculation are shown in figure 2. The curve (I) gives the energy of the electron in the lowest state, (II) that of the electron in the highest

* The considerations set forth in this paper show that if this were not the case copper would have the low conductivity and large magnetic susceptibility characteristic of a transition metal.

† Further evidence of the existence of unoccupied d states with large values of $N(E)$ is afforded by the work of Veldkamp⁽⁵⁾ on the fine structure of L -edges in the X-ray absorption spectra of Ta and W.

state, and (III) the mean energy—i.e. the energy of the lattice. The abscissae r are defined by

$$\frac{4}{3}\pi r^3 = \text{the atomic volume.}$$

The calculation gives $r = 3.15$ atomic units, as against an observed value $r = 2.66$, and a binding energy 0.14 Rydberg units, as against 0.25 observed. The agreement with experiment is not good, but the calculations illustrate our point that the electrons with maximum energy have *greater* energy than in the free atom, so if the $3d$ shell had in it any vacant places of energy about the same as in the free atom (shown by the horizontal line), the electrons would be in a state of lower energy if they occupied those places.

If these ideas are correct, we should expect the binding energies of nickel, palladium and platinum to be greater than those of copper, silver and gold. The values in table 2 are given by Grimm and Wolff⁽⁷⁾.

Table 2. Binding energies (kilocal./gm.-atom)

Nickel	101	Copper	76
Platinum	122	Gold	83

The fact that the work function of all metals is less than the ionization potential of the free atom shows that the top electrons of the Fermi distribution are contributing a negative amount to the cohesion, and will go into the $3d$ shell if there is any room there. From the considerations given above, we should expect the difference between the work function and the ionization potential to be *less* for the transition metals than for the noble metals. The values observed are given in table 3.

Table 3

	Work function (e-V.)	Ionization potentials (e-V.)
Nickel	5.01	7.2*
Copper	4.38	7.68
Palladium	4.96	7.5*
Silver	4.6	7.5
Platinum	6.3	8.9*
Gold	4.8	9.2

§ 2. SATURATION MOMENTS OF THE FERROMAGNETIC ELEMENTS

It is a well known fact that the saturation moments of ferromagnetic elements do not correspond to integral numbers of Bohr magnetons $e\hbar/2mc$ per atom. The saturation moments for the three ferromagnetic elements⁽⁸⁾ are as shown in table 4.

It is generally recognized that the ferromagnetism is due to $3d$ electrons. From the point of view of the Bloch theory there will exist in the solid a band of states†

* The values given are the energies required to ionize an atom in the lowest state having the configuration $\{(n-1)d\}^9 ns^1$.

† Cf. figure 1.

corresponding to the $3d$ states of the atom, and another band corresponding to the $4s$; in nickel the bands must certainly overlap, or the $3d$ shell would be full and the $4s$ band empty, and the metal would be an insulator. There will thus be for each metal a certain number p of electrons per atom in the s band, and $10-p$, $9-p$, $8-p$ in the d band for nickel, cobalt and iron respectively.

Bloch⁽⁹⁾, and more recently Wigner⁽¹⁰⁾ have discussed ferromagnetism starting from the model used here; they have shown that under certain conditions the exchange forces may be such that the state of lowest energy is reached when some of the electrons have their spins uncompensated, i.e. when more spins are parallel to a given direction than are antiparallel.

Table 4

Element	Saturation intensity per atom (units of $e\hbar/2mc$)
Iron	2.2
Cobalt	1.7
Nickel	0.6

Table 5

	Number of electrons per atom in $4s$ band
Nickel	0.6
Cobalt	$1.7 - 1 = 0.7$
Iron	$2.2 - 2 = 0.2^*$

We must now enquire why it is that the state of lowest energy is reached when (in nickel) 0.6 electron per atom have their spins uncompensated. There are two possibilities; either a balance is then reached between the exchange forces and the Fermi force,[†] so that the total energy of the $3d$ electrons is then a minimum with respect to the magnetic moment; or all states in the $3d$ shell with given spin-direction are then full. The former assumption has been made by Stoner;[‡] if, however, it is correct, the work required to reduce the intensity of a saturated magnet by an amount δI is proportional to $(\delta I)^2$, instead of to δI , as in the Weiss theory; the first assumption therefore leads at low temperatures to a very rapid decrease of magnetization with increasing temperature, and is thus incompatible with the observations. We therefore assume the second alternative to be true. The work done in decreasing the magnetization by δI is then proportional to δI , as in the Weiss theory, except in so far as electrons may make transitions from the $4s$ to the $3d$ band; but since the mean kinetic (Fermi) energy E_f of a $4s$ electron is of the order of magnitude of 6 e-V. and increases rapidly with the number of $4s$

E_f

* For iron this conclusion can hardly be accepted, since 0.2 s electron is too few to account for the binding energy. Probably the d band is split by the structure of the crystal, and one of the sub-bands is saturated.

† I.e. the force which keeps the electron spins antiparallel in normal metals.

‡ See reference (8), p. 431.

electrons (see below), the number which can make such a transition is of the order of magnitude kT/E_f , and is therefore negligible.

We thus deduce that the saturation intensity is the maximum possible for the number of positive holes left in the $3d$ band. The number p of electrons in the $4s$ band is therefore as shown in table 5 for the three elements.

We shall see in § 4 that palladium like nickel and cobalt has also about 0.6 electron per atom in the outer s band; the evidence for platinum is less definite.

§ 3. ALLOYS OF NICKEL AND COBALT WITH OTHER METALS

The theory given above accounts at once for the remarkable results of Alder⁽¹¹⁾, who has found that in the copper-nickel alloys, which have a face-centred cubic structure over the whole range, the saturation moment at low temperatures is decreased by one Bohr magneton for each copper atom which replaces a nickel atom in the lattice. This rule has been verified up to 40 per cent of copper; by extrapolation the saturation intensity will reach zero for an alloy containing 60 per cent of copper, and 40 per cent of nickel. Sadron⁽¹²⁾ has found, moreover, that in the alloys of nickel with zinc, aluminium and tin, the replacement of a nickel atom by an atom of one of the three elements mentioned decreases the moment by approximately two, three and four Bohr magnetons respectively.

On the model given above, this is to be explained as follows. In all these alloys the maximum binding energy will be obtained when the number of electrons in the $4s$ band is about 0.6 per atom, as for nickel. The extra electrons will therefore go into the $3d$ band, as long as there is room for them there. But in the $3d$ band, at low temperatures all the states with spin parallel to the direction of magnetization are already occupied (hypothesis of § 2). Therefore the electrons must go into states having the opposite spin. Thus if a nickel atom is replaced by an atom of copper, zinc, aluminium or tin, the saturation intensity of magnetization will be decreased by one, two, three or four Bohr magnetons as the case may be.

This explanation does not necessarily imply that the $3d$ shells of copper, zinc, etc., are to any extent ionized when alloyed with nickel. In zinc, for instance, the $3d$ levels are much lower than in nickel, and so the $3d$ band will split into two; wave functions corresponding to energies in the lower band will be small except in the neighbourhood of zinc atoms. If the number of zinc atoms is $N_A x$ and of nickel atoms $N_A (1-x)$, the number of states in the lower and upper bands will be $10N_A x$, $10N_A (1-x)$ respectively. The lower band will always be full, so that the mean magnetic moment in the neighbourhood of a zinc atom is zero.

We have seen that cobalt and nickel have about the same number of $4s$ electrons. Experiment* shows that the saturation intensity of cobalt-nickel alloys plotted against atomic composition gives a fairly straight line. This shows that the number of $4s$ electrons remains between 0.6 and 0.7 throughout the range, while the magnetic moment of the $3d$ shells remains as great as the number of positive holes allows.

* Cf. reference (8), p. 532.

Sadron⁽¹²⁾ finds that the replacement of one nickel atom by an atom of manganese *increases* the magnetic moment by three Bohr magnetons, this finding being valid up to about 6 per cent of manganese. This is to be expected, because manganese has three less electrons than nickel, and, assuming always that the firmest binding (lowest energy) occurs with 0.6 electron in the 4s band, the replacement of a nickel atom by one of manganese will decrease the number of electrons in the 3d band by three. If as many electrons in the 3d band as possible have their spins parallel to the field, Sadron's result follows.

On the other hand, it is not easy to see why the addition of manganese to cobalt decreases the moment.

The addition of palladium to nickel leaves the saturation moment unchanged, up to about 50 per cent of palladium. This shows that in these alloys the number of electrons in the s band is also about 0.6, as for nickel. Similarly, the addition of palladium or platinum to cobalt gives a curve for the saturation moment very like that of cobalt-nickel; the cobalt-palladium alloys have a saturation moment of 0.5 Bohr magnetons per atom of *both kinds* even for only 15 per cent of cobalt⁽¹³⁾.

§ 4. PARAMAGNETISM OF PALLADIUM AND PLATINUM

The transition metals palladium and platinum have paramagnetic susceptibilities which vary with temperature much less than a normal paramagnetic substance but are large compared with those of the other metals. This paramagnetism is certainly due to the uncompleted shells: definite evidence to this effect is given below. We consider it extremely improbable that orbital motion is responsible for any significant part of the susceptibility; the gyromagnetic effect shows that in the ferromagnetics, even above the Curie point⁽¹⁴⁾, the magnetism is at any rate mainly due to spin, and thus that the interaction between the spins is sufficient to quench the orbital motion. Now Slater⁽⁶⁾ has pointed out that the overlap for the incomplete d shells is *less* for the ferromagnetic than for the similar non-ferromagnetic elements. We should therefore expect, a fortiori, that the orbital motion would be quenched for the non-ferromagnetic elements.

We shall therefore assume that the paramagnetism is a spin paramagnetism. Pauli⁽¹⁵⁾ has given a theory of the paramagnetism of free electrons, which may be modified* to apply to the case when the electrons move in a periodic field. The formula for the susceptibility χ is

χ

$$\chi = 2\mu^2 N(E_{\max.}) \quad \mu = e\hbar/2mc \quad \dots\dots(1),$$

$N(E_{\max.})$

where $N(E_{\max.})$ is the number of electronic states per unit energy range at the surface of the Fermi distribution—i.e. in the occupied state of highest energy. Since $N(E)$ is very large for a narrow band, one can always obtain agreement with experiment by assuming the breadth of the band to be sufficiently small.†

We shall make an estimate of the breadth of the band for palladium, assuming

* Cf. Sommerfeld and Bethe, reference (4), p. 473.

† Cf., for instance, reference (16).

that the *d* shell is full except for 0.6 electron per atom. At the head of a band $N(E)$ will have the form*

$$N(E) = A(E_0 - E)^{\frac{1}{2}} \quad \dots\dots(2),$$

E_0 being the energy of the highest state in the band.

Now the number n of positive holes per unit volume is

$$2 \int_{E_{\max}}^{E_0} N(E) dE = \frac{4A}{3} (E_0 - E_{\max})^{\frac{3}{2}} \quad \dots\dots(3).$$

Hence, by equation (1)
$$\frac{n}{\chi} = \frac{\frac{4}{3}(E_0 - E_{\max})}{2\mu^2}.$$

With n equal to 0.6 (atomic volume) this gives for the energy interval between the surface of the Fermi distribution and the top of the *d* band

$$E_0 - E_{\max} = 0.05 \text{ e-V.} \quad \dots\dots(4).$$

Since we have at present no a priori knowledge of the breadth of the band, it is not impossible that it should be as narrow as this. On the other hand, the specific heat of the free electrons is given, according to the usual theory, by†

$$c_v = \frac{2\pi^2}{3} N(E_{\max}) k^2 T, \quad T$$

so that, if in palladium and platinum the large paramagnetism were entirely due to a large $N(E)$, there would be a considerable contribution to the specific heat from the *d* electrons. The relation between the specific heat and the susceptibility would be

$$c_v = \frac{\pi^2}{3} \frac{1}{\mu^2} k^2 T \chi \quad \dots\dots(5),$$

which gives for palladium ($\chi = 64 \cdot 10^{-6}$) and platinum ($\chi = 28 \cdot 10^{-6}$) the values 0.009 T and 0.004 T , in calories per gram atom. Such large values are incompatible with the experimental observations, since they give, for palladium at room temperatures, a specific heat greater than R from the electrons.‡

We therefore conclude that, for palladium and platinum, the density of states $N(E)$ for the *d* band, though considerably greater than for free electrons, is not sufficient to give the observed paramagnetism, but that the latter is due to an exchange force of the same type as is responsible for ferromagnetism. We shall therefore assume

$$\chi = 2A\mu^2 N(E_{\max}) \quad \dots\dots(6),$$

where A is in general greater than unity, and depends in some unknown way on the distance apart of the atoms. A

§ 5. PARAMAGNETIC SUSCEPTIBILITY OF ALLOYS OF PALLADIUM WITH COPPER, SILVER AND GOLD AND OF PALLADIUM SATURATED WITH HYDROGEN

Experiments have been carried out by Svensson⁽¹⁷⁾ on the magnetic susceptibility of the copper-palladium and silver-palladium alloys, by Vogt⁽¹⁸⁾ on gold-palladium,

* Cf. Sommerfeld and Bethe, reference (4), p. 473. † Cf. reference (4), p. 430.

‡ Note added in proof. Keesom and Clark⁽³²⁾ have recently found for nickel below 4° K. a value for the specific heat of 0.0019 T , which suggests that $E_0 - E_{\max}$ is about 0.2 e-V. for this element.

and by Aharoni and Simon⁽¹⁹⁾ and by Svensson⁽²⁰⁾ on palladium saturated with hydrogen. If our interpretation of the paramagnetism is correct, the effect on the susceptibility of substituting an atom of a noble metal is twofold; by altering the interatomic distance the exchange forces, and hence A in equation (6), may be changed; and by filling up the d band $N(E_{\max.})$ will be decreased. Since we are not in a position to calculate A , we shall discuss the change in $N(E_{\max.})$.

For any nearly full band of a pure metal, $N(E_{\max.})$ is equal to the cube root* of the number of unoccupied "holes" in the band considered ($4d$ for palladium). If we assume the same to be true for the alloy, this would give us, for an alloy consisting of Nx atoms of copper, silver or gold and $N(1-x)$ of palladium,

$$N(E_{\max.}) = \text{const.} \times (p-x)^{\frac{1}{3}} \quad \dots\dots(7),$$

where p is the number of positive holes per atom in pure palladium. On the other hand, as explained in § 3, if the d levels have different energies in the two atoms

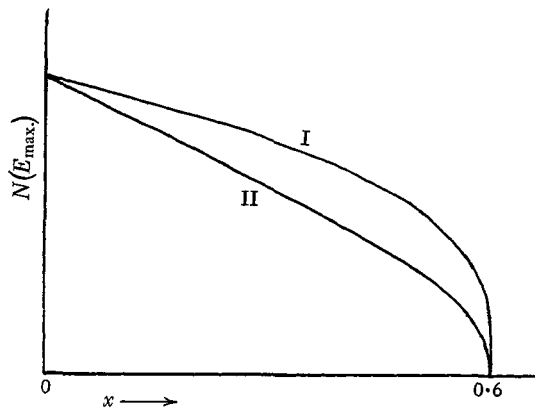


Figure 3. The density of states at the surface of the Fermi distribution (I) from equation (7); (II) from equation (8).

concerned, the d band will split into two, and only the upper band, corresponding to the $4d$ states of palladium, will have positive holes. In this case, the number of positive holes per palladium atom is

$$\frac{p-x}{1-x},$$

and hence for $N(E_{\max.})$ we should write

$$N(E_{\max.}) = \text{const.} \times (1-x) \left(\frac{p-x}{1-x} \right)^{\frac{1}{3}} \quad \dots\dots(8),$$

$N(E_{\max.})$ according to equations (7), (8) is illustrated in figure 3 with p equal to 0.6.

This formula, moreover, is only accurate if the palladium atoms are arranged in a regular way in the crystal—i.e. if they form a superlattice, which is not in general the case. For a random distribution of the palladium atoms, we should

* This is easily seen from equations (2) and (3).

expect the upper limit of the band to be less sharp. In consequence, $N(E_{\max.})$ will not disappear so suddenly with increasing x as equations (7) and (8) suggest.*

In the case of hydrogen dissolved in palladium, it is probable that the hydrogen atoms give all their electrons to the $4d$ levels of palladium, since the proton does not replace a palladium ion in the lattice. Thus for Ny hydrogen atoms dissolved in N atoms of palladium, we shall have

$$N(E_{\max.}) = \text{const.} (p - y)^{\frac{1}{2}} \quad \dots\dots(9).$$

Figure 4 shows the observed susceptibility of palladium-silver plotted against x (where $100x$ is the number of silver atoms per 100 atoms of both kinds), and of palladium-hydrogen against y (where $100y$ is the number of hydrogen atoms per 100 palladium atoms). As the equations (8) and (9) lead us to expect, the susceptibility

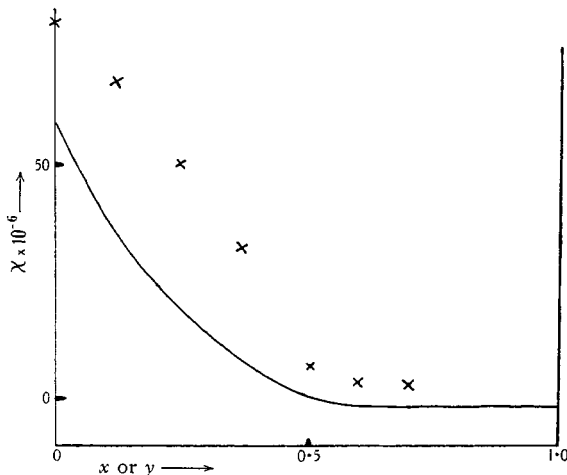


Figure 4. The full lines shows the susceptibility of palladium-silver, and the crosses the susceptibility of palladium + hydrogen. x denotes the ratio of silver to atoms of both kinds ; y denotes ratio of hydrogens to palladium atoms.

for palladium-hydrogen falls to zero more sharply. Neither curve follows at all exactly the theoretical curve; this may be ascribed to the variation of the exchange force, and to lack of sharpness of the edge of a band mentioned above.

We deduce that in palladium the number of $5s$ electrons per atom is about 0.5 .† That the number (0.5) of s electrons in palladium is less than for nickel (0.6) is to be expected, because in atomic palladium the $(4d)^{10}$ state is the lowest, whereas in nickel the $(3d)^{10}$ state is 1.4 e-V. higher than the lowest state with the configuration $(3d)^9 (4s)^1$. Therefore in palladium more electrons will go into the d band.

If the view given here of the absorption of hydrogen by palladium is correct,

* Svensson (17) has found that for the copper-palladium alloys, where the susceptibility disappears at about 50 per cent of copper, the disappearance is sharper for annealed alloys in which the atomic arrangement is ordered than for quenched alloys, where the arrangement, as the electrical conductivity shows, is disordered.

† The relation between the disappearance of paramagnetism of palladium for 50 per cent noble metal or hydrogen, and the disappearance of the ferromagnetism of nickel for about the same amount of copper, was first pointed out in an interesting paper by Dorfmann (21).

the fact that palladium becomes saturated at the composition Pd_2H is not to be attributed to the formation of a compound, as suggested by Linde and Borelius⁽²²⁾ and others. It must be interpreted as meaning that a hydrogen atom can only enter the lattice if its electron goes into the d shells of the surrounding palladium atoms, so that when these d shells are full, no more hydrogen can be absorbed. The saturation at a composition near Pd_2H follows from the fact that palladium has about 0.5 positive holes in the d shell.

§ 6. ELECTRICAL CONDUCTIVITY

All the transition metals are comparatively poor conductors; the conductivities of nickel, palladium and platinum are compared below with the conductivities of the elements that follow them in the periodic table, namely copper, silver and gold.

Table 6. Conductivity σ ($\text{cm}^{-1} \Omega^{-1} \times 10^{-4}$) at 0°C .

Nickel	16.1	Palladium	10.3	Platinum	10.2
Copper	64.5	Silver	66.7	Gold	49.0

According to modern theories, a perfect lattice has infinite conductivity; but when the atoms are displaced from their mean positions owing to thermal motion, the electrons may be scattered and the metal has a finite resistance.

In a recent paper⁽²³⁾ the author has compared the conductivities of the elements for equal mean displacement of the atoms from their positions of equilibrium; the results ($\sigma/M\Theta^2$) are shown in table 7, Θ being the characteristic temperature.

Table 7. $\sigma/M\Theta^2$ (arbitrary units)

Nickel	0.2	Palladium	0.24	Platinum	0.105
Copper	1.05	Silver	1.32	Gold	0.82

In the paper quoted it was suggested that the scattering power of two ions, for given atomic displacement, would only differ by a few per cent for atoms near together in the periodic table, and having nearly equal atomic volume, such as for instance nickel and copper. It was therefore suggested that the difference between the conductivities of two neighbouring metals was due to the different effective* numbers of free electrons. Experimental results on the resistance of dilute solid solutions were quoted to show that this is the case for such metals as silver, cadmium, magnesium, etc., which have no incomplete shells. For nickel and palladium, however, we have found the actual number of electrons in the s band to be 0.6 and 0.5, and so the effective number of free electrons should not be less than half that for copper, silver and gold. The reason for the big difference in $\sigma/M\Theta^2$ must therefore be sought elsewhere.

The positive holes in the d band make a certain contribution to the conductivity—i.e. they are free to move through the lattice. But since the atomic d wave functions

* Cf. Sommerfeld and Bethe, reference (4), p. 378; or Mott⁽²³⁾.

do not overlap much, the positive holes will take a much longer time to move from one atom to the next than would be taken by an s electron, and so the contribution to the effective number of free electrons is small. The positive holes, however, will increase the *resistance* in the following way. The resistance of a metal is proportional, among other things, to the number of times per second an electron is scattered—i.e. to the number of times per second that it makes a transition from a state specified by a wave vector \mathbf{k} to any other state \mathbf{k}' . Now the probability for such a transition is proportional† to $N(E_{\text{max}})$, the density of states; for if $N(E_{\text{max}})$ is big, there are more states into which the electron can jump. In the transition metals, $N(E)$ is big in the d band; and therefore electrons will jump more frequently from the s to the d band than from one s state to another. The time of relaxation for such metals is therefore shorter, and the conductivity smaller than for the noble metals, in which only s — s transitions can take place.

\mathbf{k}, \mathbf{k}'

In order to convince ourselves of the truth of this hypothesis, we must show that the transition-probability from a given state in the s band to one in the d band is comparable with that between two states in the d band. The transition-probability between two states with wave functions $\psi_{\mathbf{k}}, \psi_{\mathbf{k}'}$ is proportional to the square of a matrix element of the type‡

$$\int \psi_{\mathbf{k}'}^* (r) \text{grad } V \psi_{\mathbf{k}} (r) d\tau,$$

where V is the potential energy of an electron in the lattice. For $\psi_{\mathbf{k}'}$, the wave function of the final state of the electron, we may take, to a sufficient approximation, the wave function ψ_d^{n-1} in an unperturbed atom in the $(n-1)$ d state. The perturbing energy, $\text{grad } V$, is the change in the potential due to moving an atom through unit distance from its position of equilibrium; the perturbing energy in the neighbourhood of any one atom will therefore be of the form

$V, \psi_{\mathbf{k}}$

$$f(r) \cos \theta.$$

Therefore if $\psi_{\mathbf{k}}$ were an s function (i.e. spherically symmetrical) the transition-probability would be zero. For a wave function at the surface of the Fermi distribution, however, $\psi_{\mathbf{k}}$ will be of the form⁽²³⁾ given by

$$\psi_{\mathbf{k}} = A \psi_s^n + B \psi_p^n + C \psi_d^n + \dots \quad \dots\dots(10),$$

where ψ_s, ψ_p, ψ_d are supposed normalized and have the symmetry of s, p, d wave functions with principal quantum number n and $A \gg B \gg C$. The transition-probability between two states in the s band will be of the order of

$$|AB \int \psi_s^n \text{grad } V \psi_p^n d\tau|^2,$$

and between two states, one in the s band and the other in the d band,

$$|B \int \psi_d^{n-1} \text{grad } V \psi_p^n d\tau|^2.$$

These two expressions contain the same power of the small coefficient B , and may be taken to be of the same order of magnitude.

Evidence of the truth of the hypothesis that the high resistance of the transition metals is due to the large density of states, $N(E)$, in the d band can be derived from

† Cf. reference (4), p. 519.

‡ Cf. reference (4), p. 512.

the electric resistance of the gold-palladium and silver-palladium series of alloys. Both have the face-centred cubic structure throughout the range of composition, and do not form a superlattice.

R_0
 R_t The resistance of any disordered alloy is made up of two parts; the resistance R_0 due to disorder, and the resistance R_t due to thermal motion of the atoms. The latter may be taken to be given by

$$R_t = T \frac{dR}{dT}.$$

In figure 5 we have multiplied the right-hand side by a constant differing slightly from unity, to obtain the correct resistance of the pure metal.

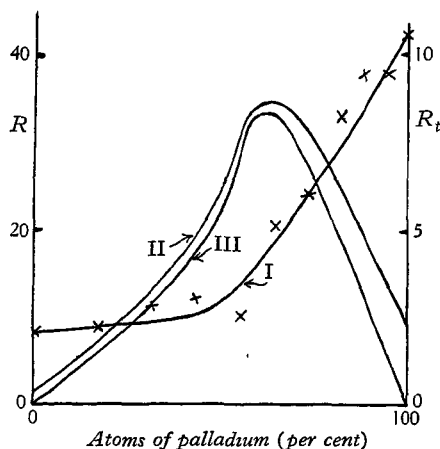


Figure 5. Resistance of palladium-gold and palladium-silver alloys. The crosses denote the experimental values of R_t for palladium-gold; curve (I) is drawn through these points. Curves (II) and (III) show the total resistance of palladium-silver at 20°C . and -273°C . respectively.

Since R_t may be as little as one-tenth of the total resistance, its accurate estimation is difficult. Figure 5 shows the values deduced from measurements of the resistance and temperature coefficient due to Giebel⁽²⁵⁾, for palladium-gold. The behaviour of palladium-silver is similar.*

According to our hypothesis, if palladium is added to gold, the number p of s electrons will decrease to a limiting value of about 0.55 at 45 per cent of palladium. This should increase the resistance, but since the palladium ion has probably less scattering-power than that of the heavier gold, we may expect the thermal part R_t of the resistance to remain roughly constant up to this composition. For less than 55 per cent of gold, however, the d band has vacant places in it, and we should expect R_t to increase, and the increase in the resistance to be proportional to $N(E_{\text{max.}})$. As figure 5 shows, the variation of $N(E_{\text{max.}})$ that one deduces from this curve is very similar to that given by the paramagnetic susceptibility of palladium-

* Since the total resistance $R_0 + R_t$ is greater for this alloy, the experimental values of R_t are probably less certain.

silver, figure 4. Again, the disappearance of $N(E_{\max.})$ at about 50 per cent of silver is not so sharp as the theoretical equation (8) suggests.

In figure 5 we show also the total resistance at room temperature of the silver-palladium alloys, and further the resistance at the absolute zero of temperature, obtained by subtracting the observed values of TdR/dT . The curves for gold-palladium and copper-palladium are similar, but the maximum occurs nearer to the 50 per cent composition. For the copper-nickel alloys⁽²⁶⁾ the dependence on temperature is complicated by the fact that the alloys are ferromagnetic, and the change in the temperature coefficient in the neighbourhood of the Curie point, which for about 50 per cent of copper is in the neighbourhood of room temperature. At low temperatures, however, the measurements of de Haas and Krupkowski⁽²⁷⁾ show a curve very similar to that of figure 5 with the maximum at 45 per cent of copper. The sharp maximum of the resistance curves is in sharp contrast to the resistance of, say, silver-gold or palladium-platinum at low temperatures, which follow a curve of the type

$$R \propto x(1-x) \quad \dots\dots(11),$$

with a much flatter maximum; cf. figure 6.

We give in table 8 the increase ΔR in the resistance of the noble metals due to admixture of 1 per cent of a transition metal and *vice versa*.*

Table 8. ΔR ($\mu\Omega./\text{cm}^3$)

Gold in palladium	1.0	Palladium in gold	0.407
Silver in palladium	1.28	Palladium in silver	0.436
Copper in palladium	1.27	Palladium in copper	0.82
Copper in nickel	1.1	Nickel in copper	1.25

As the author has pointed out in a previous paper⁽²³⁾, the scattering-power due to 1 per cent of a metal A in solid solution in B is the same as that due to 1 per cent of B in solid solution in A , and for pairs of metals of similar valency and structure (silver-gold or palladium-platinum), the increase of resistance ΔR is the same. If however atoms of a foreign metal can cause transitions from a state in the s band to the d band, we should expect ΔR to be much greater for, say, copper in nickel than for nickel in copper. This is not the case, and, even for the silver and gold alloys with palladium, the difference is only such as may well be accounted for by the fact that silver and gold have *one* s electron per atom in the s band and palladium only about 0.5. It is known from other evidence that the s electron of copper is rather less free than for silver and gold,† so that the effective number of free electrons per atom is rather less than unity. We deduce that the transition probabilities from s to d states in the metal are small, probably smaller than the $s-s$ transition-probabilities. This is to be expected for the following reason: the possibility that in a transition metal an electron will make a transition from the s

* The values are due to Svensson⁽¹⁷⁾ and Linde⁽²⁸⁾, except for copper-nickel, where they are taken from (29).

† From the measurements of the optical constants⁽²⁷⁾, and also from the fact that $\sigma/M\Theta^2$ is less for copper than for silver, in spite of the smaller ion of copper and the larger number of electrons per unit volume.

band to a d state under the influence of an atom of copper, silver or gold in solid solution is proportional to

$$|\int \psi_{d^{n-1}}(r) \Delta V \psi_k(r) d\tau|^2 \quad \dots\dots(12),$$

where $\psi_{d^{n-1}}$ and ψ_k are defined above and ΔV is the change in the potential in the lattice due to the addition of an atom of copper, silver or gold. But this integral will only have a finite magnitude if the wave function $\psi_{d^{n-1}}$ of the final d state of the electron is finite in the region where ΔV is different from zero; i.e. in the immediate neighbourhood of the foreign atom. This will only be so if the d shell of the foreign atom is actually ionized, and we have seen in § 3 that this is probably not the case. Thus, so far as the resistance due to impurities is concerned, nickel and palladium behave like copper or silver or gold.

On the other hand, this argument cannot apply to alloys containing comparable amounts of the two metals, because here ΔV must be taken to be the difference between the potential in the real lattice and the periodic potential which approaches most nearly to it⁽³¹⁾, and so will be finite in the nickel or palladium atoms as well as those of the noble metal. Hence scattering of the electrons from s to d states will occur, so that the resistance rises more steeply than it otherwise would for increasing concentration of the noble metal.

This is the probable reason for the surprising sharpness of the maximum of the curve (III) of figure 5 as compared with that for silver-gold, palladium-platinum, etc.

A quantitative theory may be given as follows. If $V_A(r)$ is the potential energy of an electron in a palladium atom, and $V_B(r)$ in an atom of copper, silver or gold, and if x is the concentration of the noble metal, then, according to Nordheim, the periodic potential which approaches most nearly to the true potential is

$$V = (1-x) V_A + x V_B.$$

The difference between this and the potential in a palladium atom is

$$V - V_A = x \Delta V, \quad \Delta V = V_B - V_A,$$

and since there are $1-x$ of them, the probability of being scattered by a palladium atom is proportional to

$$(1-x) x^2 |\int \psi_k \Delta V \psi_k d\tau|^2.$$

Similarly, the probability of being scattered by a silver atom is proportional to

$$x (1-x)^2 |\int \psi_k \Delta V \psi_k d\tau|^2.$$

If now the d shells are full, we have simply to add these two terms, whence we see that the resistance is

$$\beta \{(1-x) x^2 + x (1-x)^2\} = \beta x (1-x) \quad \dots\dots(13),$$

where β is a constant, which is Nordheim's result.

If, on the other hand, the palladium atoms have incomplete d shells, the probability of scattering by a palladium atom is greater than by a silver atom. Assuming

in rough agreement with the experimental results shown in figures 4 and 5, that for the d band $N(E_{\text{max.}})$ is proportional to

$$(p-x)^2 \quad x < p,$$

and zero otherwise, we see that the resistance due to transitions of the electrons into the d shells is

$$\alpha (p-x)^2 x^2 (1-x) \quad \dots\dots(14),$$

where α is another constant.

In figure 6 we show the two terms which contribute to the resistance; curve (II) is calculated from equation (14); curve (I) has the general form of equation (13), but we have shifted the maximum slightly to the right to take account of the fact that palladium has fewer electrons than silver. It is seen that with suitable choice of the ratio $\alpha : \beta$, the general form of the experimental curve of figure 5 can be reproduced, curve (III).

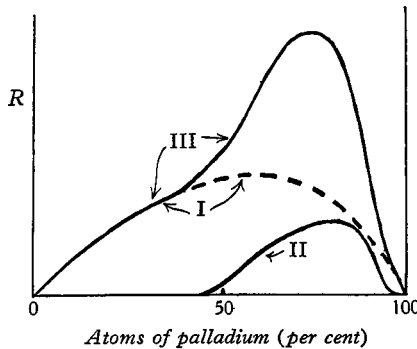


Figure 6. Theoretical curve for the resistance, at 0° K. of silver-palladium alloys: (I) due to $s-s$ transitions; (II) due to $s-d$ transitions; (III) total; (I) plus an arbitrary multiple of (II).

The constants α and β cannot be calculated without a detailed knowledge of the wave functions.

The experimental resistance curves show, however, that the effect of the d shells cannot increase the resistance by a factor of more than about two, as against a factor of five to ten for thermal agitation; this may be explained by the fact that ΔV is spherically symmetrical in the neighbourhood of any atom, and so formula (12) may be written in the following form, which should be compared with equation (10):

$$| C \int \psi_a^{n-1} \Delta V \psi_a^n d\tau |^2 \quad \dots\dots(15),$$

whereas the transition probability from one s state to another is

$$| A^2 \int \psi_s^n \Delta V \psi_s^n d\tau |^2 \quad \dots\dots(16).$$

Since $C \ll A$ we may assume the quantity (15) to be small compared with (16).

§ 7. ACKNOWLEDGMENTS

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