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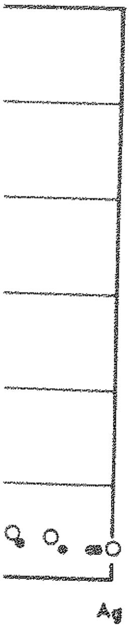

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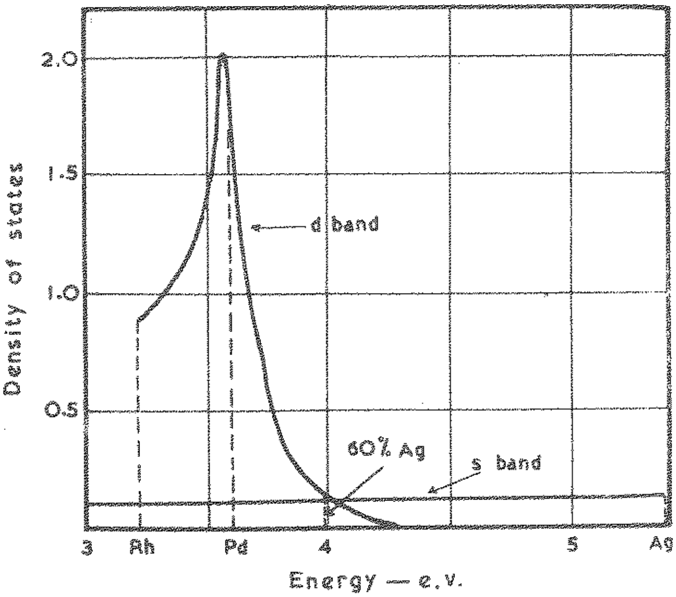
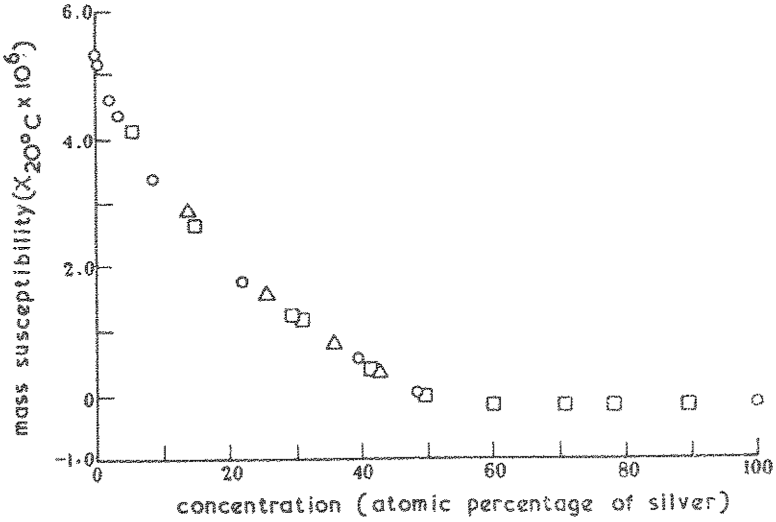


Density of states per atom for the alloy series Rh–Pd–Ag, for one spin direction (Hoare 1963).

Fig. 31

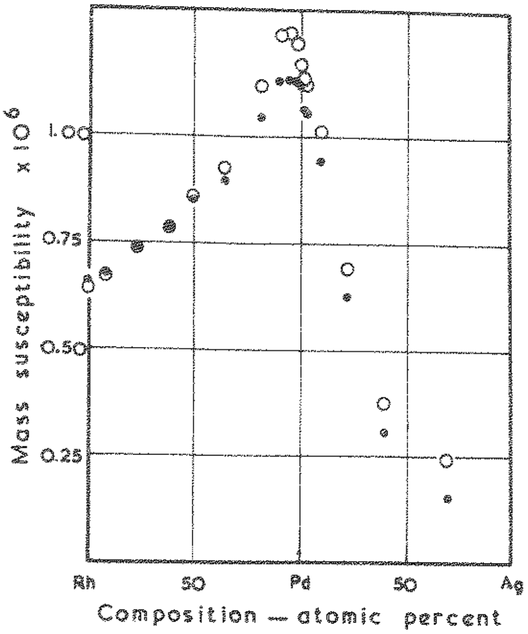


Susceptibility against concentration of Pd–Ag alloys at 20°K. □ Svensson (1932). △ Wucher (1950). ○ Hoare *et al.* (1952, 1953, 1957).

latter to be about 5% of the total, and it will decrease in the alloys as the d band fills up (§ 12).

Shimizu *et al.* (1963 a) have calculated the behaviour of the electronic specific heat at high temperatures using Hoare's $N(E)$ curve, and evaluated the drop below the linear form that must occur since the Fermi level is near a maximum in $N(E)$. Their results are shown in fig. 33. They show that at about 1000°K it should be about a quarter of the extrapolated low-temperature value, and that this agrees roughly with the experimental results, so far as they can be deduced by subtracting the Debye term from the observations. Exactly the same kind of calculation for palladium has been carried out, apparently independently, by Hindley and Rhodes (1963); these authors state that the observed specific heat at high temperatures cannot include so large an electronic term as a linear extrapolation of the low-temperature terms would give.

Fig. 32



Measured susceptibilities of alloys of palladium with rhodium and silver (Hoare 1963). ○ Values at 20°K. ● Values at 290°K.

Mackliet and Schindler (1963) have investigated γ for Ni–Pd alloys, a series for which 0·5 d holes per atom is expected for the whole range of concentration, with a gradual drop in the Curie temperature. The unexplained feature of the results is that γ for an alloy with 20% of nickel lies above that for pure palladium.

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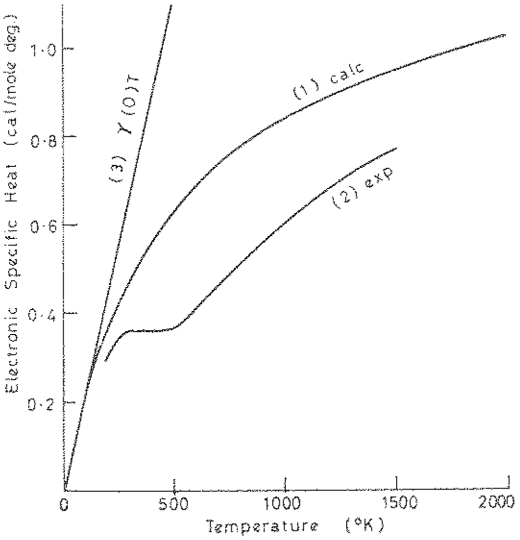
Spin–orbit coupling in palladium and platinum has been investigated by Friedel *et al.* (1964). In platinum, in particular, it is clear that the spin–orbit coupling is *not* broken down in the metal. This was in fact suggested by Mott (1949) on the basis of the observations by Cauchois and Manescu (1940) and by Bearden and Snyder (1941) showing that the intense absorption (white line) at the X-ray absorption edge occurs for the L_{III} edge but not for L_{II}. Bonnelle and Mande (1957) and Mande (1958) find a white line for both L_{II} and L_{III} in palladium.

Fig. 33



Electronic specific heat for palladium at high temperatures (Shimizu *et al.* 1963 a). (1) Calculated from Hoare's values of $N(E)$. (2) Observed values. (3) Extrapolation of linear term.

The increase in the susceptibility of palladium at low temperatures has recently been shown by Manuel and St. Quinton (1963) to be due to ferromagnetic impurities. Palladium is not antiferromagnetic (Abrahams 1962), as was previously suspected.

9.1. *Palladium and Hydrogen*

Of considerable interest are the properties of palladium alloyed with hydrogen; these are reviewed by Mott and Jones (1936), and some recent results and a review of earlier work are given by Tsuchida (1963). One may summarize earlier results by saying that:

(*a*) The susceptibility of palladium decreases linearly as hydrogen is added *as if* the electron went into the d band.

(*b*) The limit of solubility is at about 60% (atomic) of hydrogen.

More recent work has shown that Pd + H separates out into two phases, of which one (according to Cohen and de Bergevin 1958) is nearly pure palladium and the other approximately $PdH_{0\cdot6}$, with hydrogen nuclei occupying octohedral interstitial sites. Two lattice parameters have been observed (Smithells and Ransley 1935) and the linear dependence of magnetic moment on composition suggests the presence of two phases. Theory has thus to account for a minimum in the curve plotting free energy against composition at a composition with 60% of hydrogen, with the hydrogen electron occupying all places in the d band and destroying the paramagnetism.

For Pd + H the two ranges of hydrogen composition for which a single phase is present are rather narrow; they are wider when hydrogen is added to Pd–Ag alloys, for example to palladium with 20% silver, as is shown by Tsuchida's (1963) work. One can then observe a continuous decrease in magnetic susceptibility in a single phase as hydrogen is added. Tsuchida's conclusion from his observations is that the extra electron from hydrogen behaves just like an extra electron that would be contributed by silver.

Burger *et al.* (1957, 1959, 1960) have investigated the effect of hydrogen on alloys of palladium with iron, cobalt and chromium; hydrogen here too has the effect of filling up the d band, though elements such as iron appear to produce localized moments.

We know now from theoretical work reviewed in § 7 that the screening of the charge of a hydrogen nucleus in a metal could occur *either* through the formation of a bound state which is subtracted from the band, *or* by a pile-up of charge in the band. The latter is more likely to occur if the density of states is high. Clearly, since hydrogen diminishes the susceptibility instead of increasing it as a bound state with unbalanced spin would, the latter is what occurs.

Since it is the d band rather than the s band into which the hydrogen's electron goes, and since a negative heat of solution only occurs when there are vacant d places, it seems that screening by d band electrons must give much lower energy than by s band electrons. Although the d wave functions must be 1s-like in the neighbourhood of the hydrogen nuclei, it seems that, as for Ni–Al, etc., this kind of screening as described in § 7 for nickel alloys (fig. 19) is energetically much more favourable.

We may emphasize, then, that though according to the considerations illustrated in fig. 19 the d electrons will provide a charge density round the hydrogen atom which is s-like and not dissimilar to that in the free atom, the spin density will be quite different, there being equal numbers of electrons with the two spin directions.

We have no convincing theoretical explanation to suggest of the occurrence of two phases in Pd + H. The plot of free energy against composition c at the absolute zero must appear somewhat as in fig. 34. A sharp turn-up at round 60% is to be expected because the d band is then full. A concave form of the curve for lower values of c (as long as the d band is not full) would mean that the heat of solution of hydrogen *increases* as more

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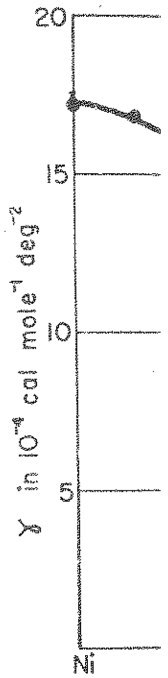

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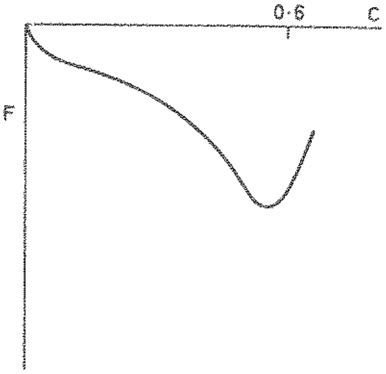
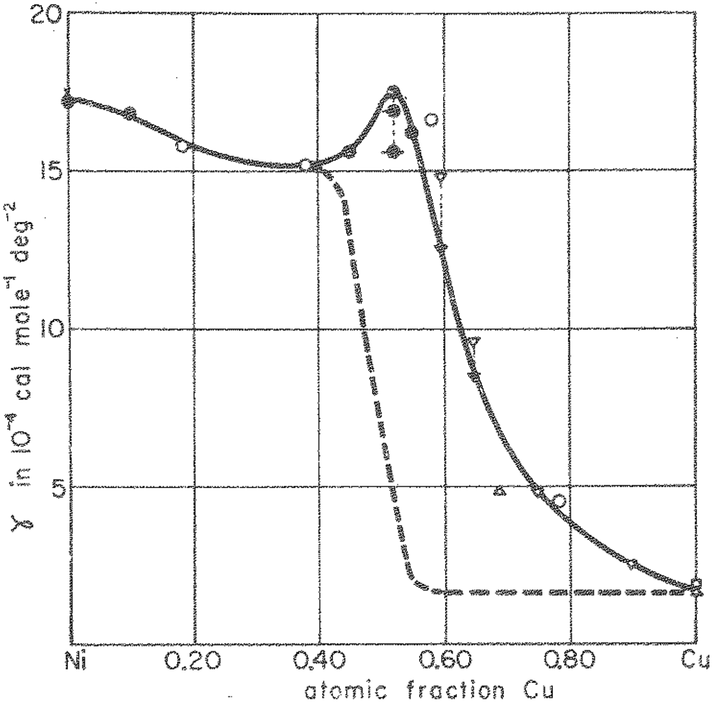


Free energy *F* against concentration *c* of hydrogen for Pd+H (schematic).

Fig. 35



Coefficient γ of low temperature specific heat for nickel–copper alloys (from Gupta *et al.* 1964 a). ● Gupta *et al.* (1964 a). △ Guthrie *et al.* (1959). ○ Keesom and Kurrelmeyer (1940). ▽ Crangle (1963).

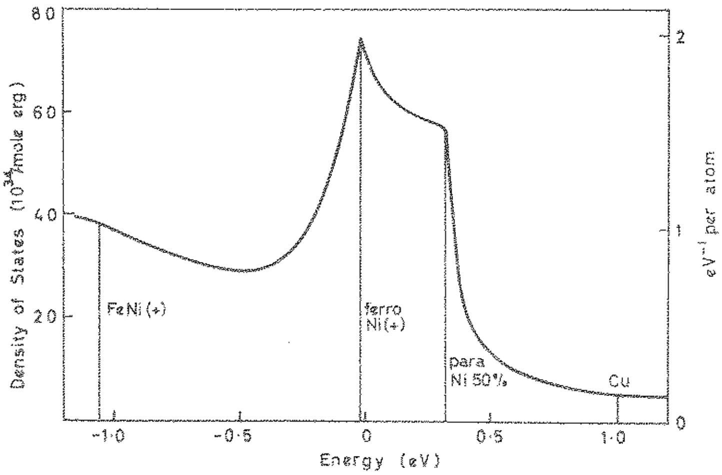
The dotted line shows the coefficient expected on the basis of a simple band model using a density of states similar to that for palladium.

hydrogen is added. This may be due to the lattice expansion of between 2 and 3% which occurs as the hydrogen is added.

§ 10. SPECIFIC HEAT OF NICKEL–COPPER ALLOYS

This is discussed here rather than under nickel and its alloys to emphasize the contrast with palladium. The specific heat was first investigated by Keesom and Kurrelmeyer (1940) and more recently by Guthrie *et al.* (1959) and by Gupta *et al.* (1964 a), whose results are shown in fig. 35. For 75, 80 and 90% copper the specific heat was of the usual form $\gamma T + \alpha T^3$, but for higher concentrations of nickel there were deviations which may be due to interaction between regions of abnormally high nickel concentration which are ferromagnetic locally (Schröder 1961).

Fig. 36



Density of states of nickel and nickel–copper alloys obtained from low temperature specific heats (Shimizu *et al.* 1963).

The rise in γ with increasing nickel content is unlike that observed in silver–palladium. Guthrie *et al.* (1959) discuss this effect in terms of clustering, assuming that very small regions are ferromagnetic. But this seems unlikely for low concentrations. Friedel and his co-workers (Friedel 1954, 1956 a, de Faget de Casteljan and Friedel 1956) have given an alternative explanation, of which a summary is given in the review article by Cohen and Heine (1958, p. 430). This is based on the concept of virtual states, and may be explained as follows, following these authors. Let us first neglect hybridization of the s and d bands. The d level in atomic nickel is higher than that in copper. Substituting a nickel atom for a copper atom in the metal is therefore equivalent to introducing a local centre of repulsive potential as far as the d electrons of copper are concerned. This potential, if strong enough, splits off a localized d state from the top of the d band.

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§ 11. ALLOYS

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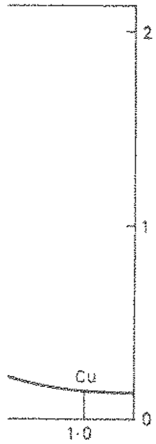

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Bringing the conduction band back into the picture, we see that the localized state must be degenerate with states in the conduction band. Hence, it must be a resonant level, or virtual bound state, rather than a true bound state. Its effect is to increase the density of states in a region of energy given by the lifetime of the resonant level. If the resonant level lies near the Fermi level, it can cause a rapid increase in γ with nickel concentration such as is actually observed. The large residual resistivity and paramagnetism of the copper-rich Cu–Ni alloys can be explained similarly.

Shimizu *et al.* (1963 b) have calculated the density of states for nickel and Cu–Ni alloys from available experimental results on the basis of the rigid band model for the d band. Their curve is shown in fig. 36. They also calculate the specific heat at high temperatures using those values.

Gupta *et al.* (1964 a) have investigated the low-temperature specific heat of nickel-based alloys with Zn, Al, Si and Sb as well as Cu. They believe that for some of these alloys the difference between their behaviour and that of Pd–Ag may be due to a term linear in the temperature due to coupling between localized moments.

§ 11. ALLOYS OF TRANSITION METALS WITH EACH OTHER

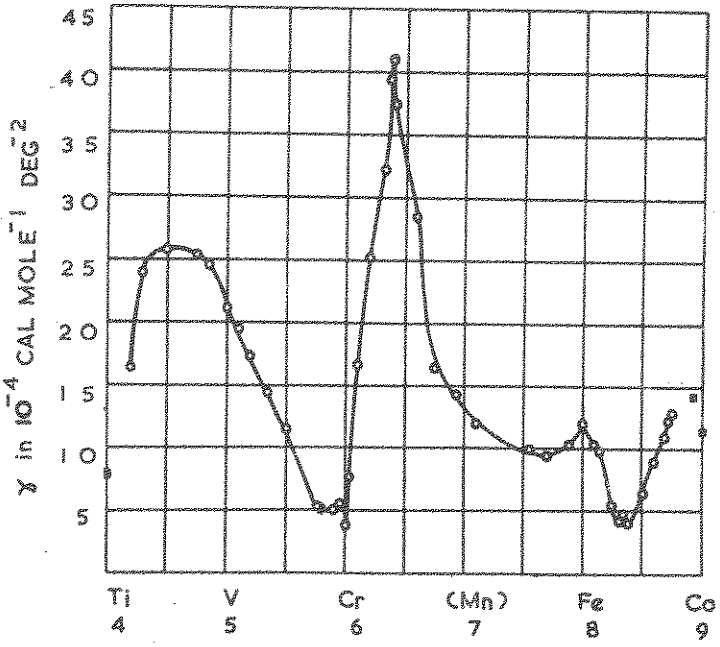
In this section we review the experimental observations of the electronic specific heat of these alloys and the conclusions that may be drawn about the density of states in the d band.

We have already reviewed the evidence that nickel and palladium have about 0·5 electrons per atom in the s band and cobalt about 0·9. In this section we shall show that iron also has 0·9. For alloys of these elements, at any rate, there is thus no question of very much transfer of electrons from s to d bands. We are therefore dealing, particularly in iron–cobalt alloys, with the density of states in a common d band containing a known number of electrons.

In some cases (deviations from the Slater–Pauling curve) it is known that the differences in the fields of the constituent atoms are such that bound states appear above the d band. These cases will be discussed in § 13. In this section we shall assume a common d band, though localized moments may occur. Whether the curves of γ against e/a give the density of states for a pure metal (the rigid band hypothesis) is not yet certain, though some calculations on this assumption, e.g. of high temperature specific heat, are reasonably successful.

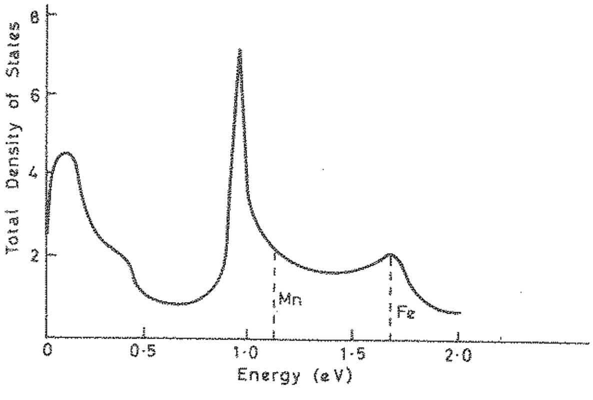
We may distinguish measurements in the first long period, in which moments appear beyond iron, from those in the second, where they do not. In the first long period, fig. 37 shows the measurements of γ by Cheng *et al.* (1960). These have to be interpreted in terms of the model of fig. 14; for the ferromagnetic alloys there are two d-band Fermi levels. We shall interpret all our results by assuming that the spin-down level remains at a fairly constant position at the minimum in $N(E)$ as long as there are holes in the spin-up band; the rise in γ that occurs for Fe–Co for more than 30% of cobalt is explained by Gupta *et al.* (1962) on the assumption that at this

Fig. 37



Specific heat coefficient γ as a function of e/a for b.c.c. alloys Ti–V, V–Cr, Cr–Fe and Fe–Co. Filled square represents close-packed structures (Gupta *et al.* 1962).

Fig. 38



Total density of states of body-centred alloys shown in fig. 37 as a function of energy, deduced from fig. 37 making use of known magnetic intensities (Hoare 1963).

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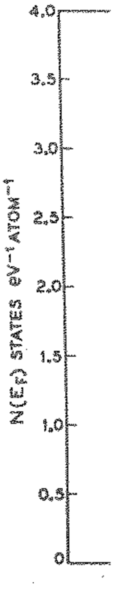

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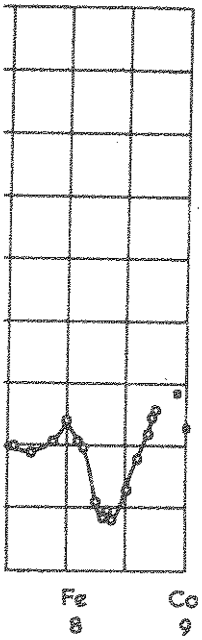

c.c. alloys Ti–V, V–Cr,
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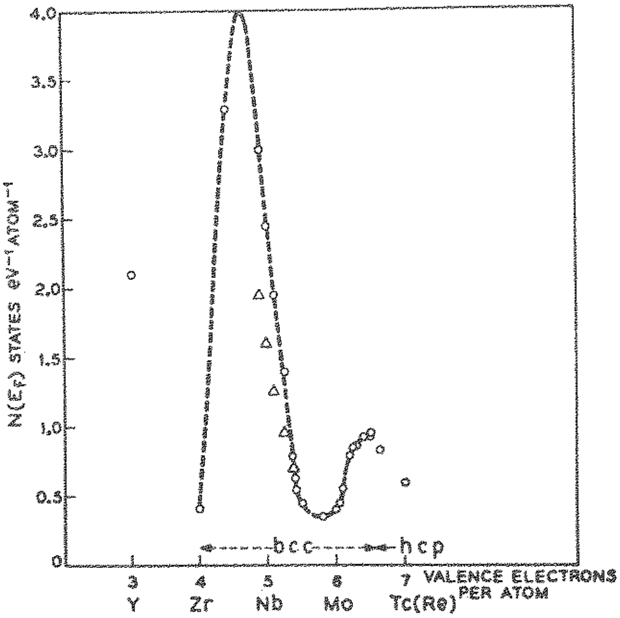
composition the spin-up band is full and so electrons from cobalt must go into the spin-down band. The density of states curve of fig. 38, plotted against E, is deduced by Hoare (1963) on these assumptions†. For the second long period, for which there are no moments, Morin and Maita (1963) have published a curve with a similar sharp minimum and maximum in the plot of γ against e/a for alloys of Zr, Nb, Mo and Tc; this is shown in fig. 39. Van Ostenburg *et al.* (1963) have used these and other results to give a density of states curve for 4d transition metals; this is plotted in fig. 40.

Fig. 39



Density of states deduced from specific heat coefficient of certain alloys in the second long period according to Morin and Maita (1963).

The curves are by no means exactly similar, but the following points stand out. With increasing e/a there is a sharp drop in γ at e/a $\simeq 5{\cdot}7$. We cannot give any particular theoretical significance to this; the two lower d sub-bands together with perhaps 0·9 4s or 5s electrons would contain 4·9 electrons per atom, and so the minimum must be half-way across the broad sub-band described in § 3. Perhaps its presence depends on s–d hybridization. But its existence is shown by other properties of these alloys, notably

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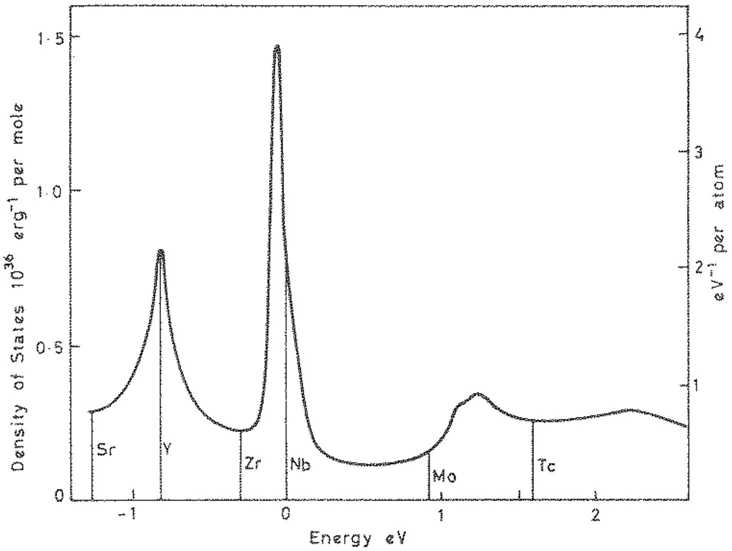
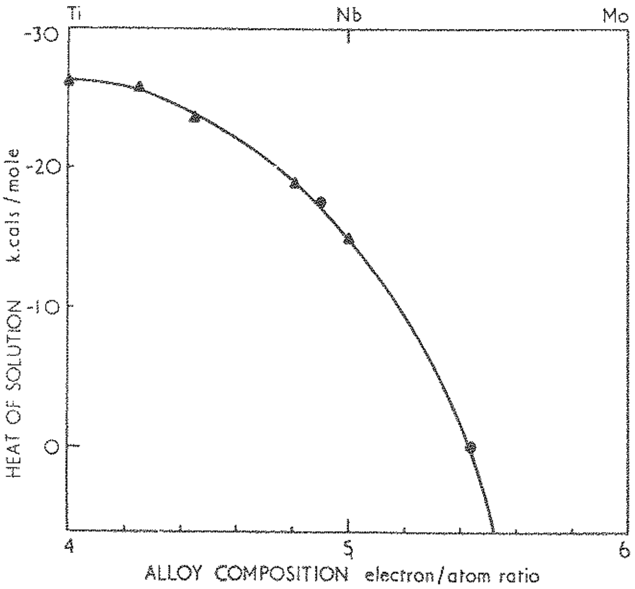
† We have deleted the rising part of the curve for large energies, for the reason given above.

Fig. 40



Density of states of body-centred transition metals in second long period according to Van Ostenburg *et al.* (1963).

Fig. 41



Heat of solution of hydrogen in alloys of titanium, niobium, molybdenum in kcal mol^{-1}, plotted against electron-to-atom ratio (e/a) (Jones *et al.* 1961). ▲ Ti–Nb, ● Ti–Mo.

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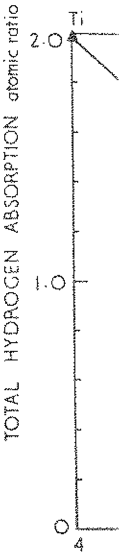

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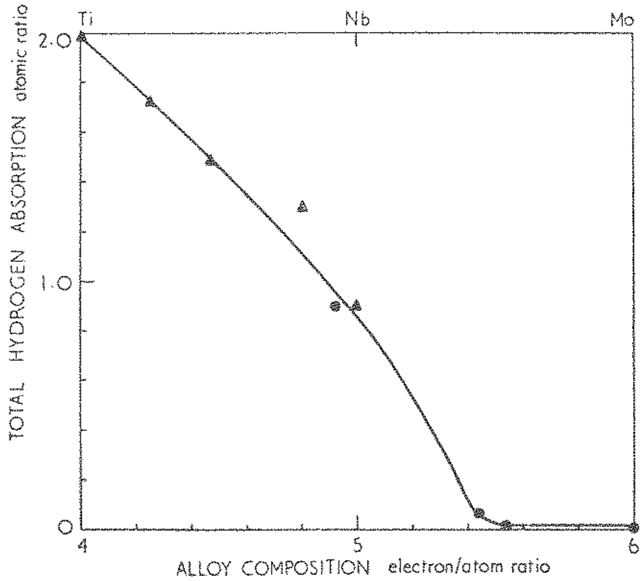
their capacity to absorb hydrogen, as has been pointed out by the author in another review article (Mott 1962). The capacity to absorb hydrogen has been measured by Jones *et al.* (1961), and their results are shown in figs. 41 and 42. Similar results due to Jones (1964) for the second long period are shown in fig. 43. It will be seen that, just as in palladium, a high density of states is necessary for the absorption of hydrogen and that when the parts of the bands with high density are 'full', each hydrogen atom contributing one electron, the heat of solution drops and no more hydrogen will go in.

Fig. 42



Hydrogen absorption in alloys of titanium, niobium and molybdenum (atomic ratio), plotted against e/a (Jones *et al.* 1961). ▲ Ti–Nb, ● Ti–Mo.

The same authors have measured the magnetic susceptibility χ and their results, together with others obtained by Van Ostenburg *et al.* (1963), are shown in fig. 44. It will be seen that χ also drops between the values of 5·6 and 5·7 e/a. The Hall constant also shows a rapid change at this point (for refs. see Mott loc. cit.)†.

We turn now to the peak in the curve of γ against e/a to the right of chromium or molybdenum. For the first long period there has been

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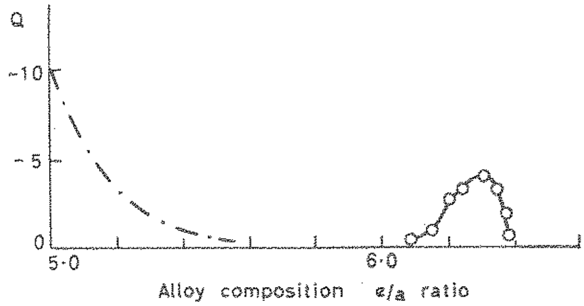
† Dempsey (1963) has given an interesting discussion of bonding in the refractory 'hard metals', such as compounds of the transition metals with boron, carbon and nitrogen, which show metallic conductivity. Dempsey gives evidence to suggest these elements give up their p electrons but not their s electrons to the d band of the transition metal. The work of Lundquist *et al.* (1962) on the paramagnetic properties of the borides of transition metals is also relevant.

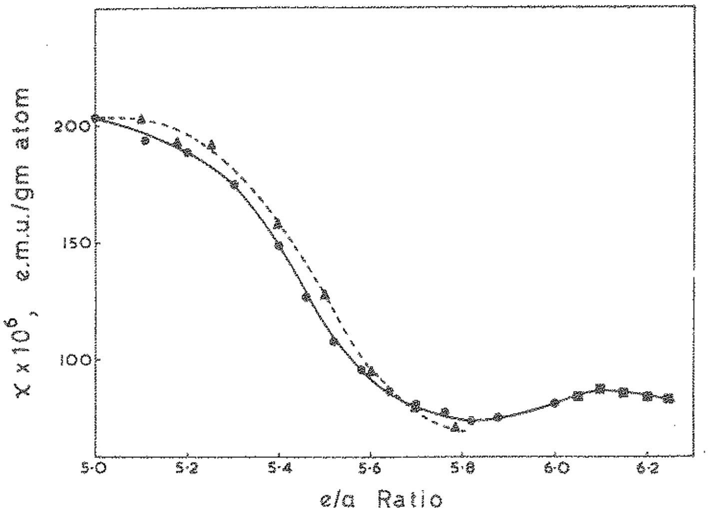
controversy as to whether this is due to the linear term which results from interaction between localized moments (§ 7), but the evidence is strong that it occurs in *all* the long periods (Coles 1963). Schröder (1961) has measured the specific heat at temperatures high enough for any term due to moments to have disappeared, and confirms that the electronic specific heat remains large. Nevertheless it is certainly possible that, for the first long period, *part* of the peak is due to localized moments. Figure 45 (taken from results by Lingelbach 1958) shows the paramagnetic susceptibility of certain alloys of chromium; the very sharp rise for Cr–Fe, Cr–Co certainly suggests

Fig. 43



Heat of solution Q of hydrogen in kcal/mol in alloys in second long period (Jones 1964).

Fig. 44



Atomic susceptibility of alloys of Ti, Nb and Mo (Jones and McQuillan 1962). ● Mo–Nb, ▲Nb–Rh, ■ Mo–Rh.

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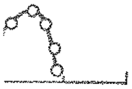

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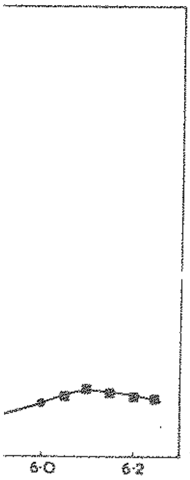

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localized moments. Shimizu (1964) suggests that the form of the peak is best given, assuming the validity of the rigid band model, by the rise in γ for Fe–Co shown at the extreme right of fig. 37, using the explanation given above. He obtains in this way the following values of γ in the peak of the Cr–Fe alloys.

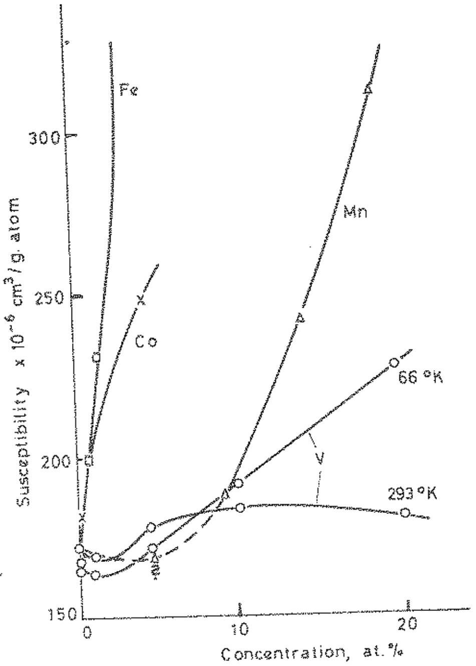
Column I. γ as deduced using values from Fe–Co to give $N(E)$ in the peak for Cr–Fe.

Column II. From Schröder's (1961) measurements at *high* temperatures, at which any linear contribution from localized spins is likely to have disappeared.

Column III. γ as measured (cal/mole. degrees × 10^{-4}).

Fe at. %	I	II	III
15·9	13·4	16·2	32
17·9	14·0	22·9	38
20·1	15·5	29·3	37
21·8	16·5	24·7	33
23·4	17·1	21·9	32

Fig. 45



Atomic susceptibility of Cr alloyed with V, Mn, Fe, Co as a function of composition (from Lingelbach 1958).

The comparison is hardly conclusive, since Schröder's result lies between the two interpretations. Shimizu's $N(E)$ curve, using his interpretation and Fallot's values for the magnetic moments of the ferromagnetic alloys, is shown in fig. 46.

That the sharp peak is in some way associated with a relatively small concentration of Fe (or Mn) in Cr is suggested also by fig. 47, which shows γ as a function of e/a for V–Fe and Cr–Mn, contrasted with the values for Cr–Fe shown in fig. 37. The peak in this case is seen to be less sharp and shifted to lower energies. The peak occurs also for ternary alloys of type TiFe + TiCo and at about the same value of e/a (Starke *et al.* 1962), though a rigid band behaviour (dependence on e/a only) is not observed; neither is it for example for Cr–Fe contrasted with Cr–Co (Vogt and Oehler 1963).

We shall now examine more carefully the behaviour of Fe–Co alloys, making use of the assumption introduced in § 5 and already mentioned in this section that the spin-down Fermi level will remain in the minimum of $N(E)$ as long as there are holes available in the spin-up d band. When however the spin-up d band is full, electrons will go into the spin-down band. This model has the following consequences, (*a*) and (*b*) below, as first pointed out by Gupta *et al.* (1962).

(*a*) As cobalt is added to iron, electrons going into the spin-up d band, the specific heat coefficient γ will drop until that band is full. Electrons then go into the spin-down d band, and as soon as the spin-down Fermi level moves out of the minimum γ should rise again. Figure 37 shows that this is just what happens; the minimum occurs at 30% cobalt, and suggests that there are 0·3 holes in the spin-up d band.

(*b*) The same model predicts that the magnetic moment will increase until the holes in the spin-up d band are full, and then decrease. Figure 48 shows that this does indeed happen in Fe–Co alloys.

These results together suggest that there are about 0·3 holes in the spin-up band of iron, assuming always that any shift of the spin-down limit has a negligible effect on the occupation numbers of the two bands.

The number of unbalanced spins in iron is 2·1, assuming a contribution by the orbital motion of $0{\cdot}12\,\mu_B$ (Meyer and Asch 1961). If the s band polarization is $-0{\cdot}2\,\mu_B$, the number of unbalanced spins in the d band is 2·3; it follows that the number of spin-down holes in the d band is $2{\cdot}3+0{\cdot}3=2{\cdot}6$, and the total number of holes 2·9, which leaves 0·9 electrons per atom in the s band†. This agrees with the estimate made by Hume-Rothery and Coles (1954) from an examination of alloy data.

The spin-down Fermi limit will be, analysing the results in this way, just to the left of chromium (i.e. at e/a $\simeq$ 2·9 for a given spin direction); this suggests that for pure iron the minimum really is here rather than where it appears in fig. 47.

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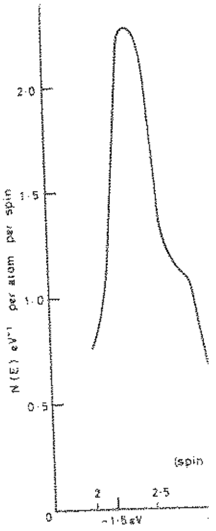
† If the polarization of the s band deduced from the results of Shull is wrong, this would affect this number. Thus a polarization of $+0{\cdot}1\,\mu_B$ would give 0·6 s electrons.



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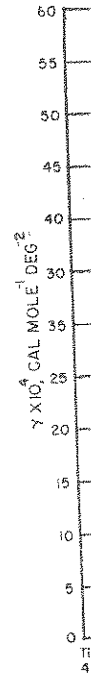

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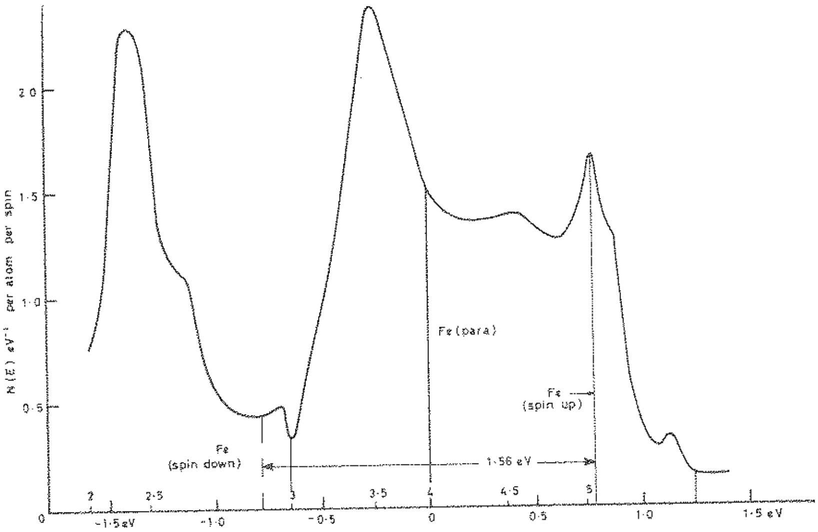
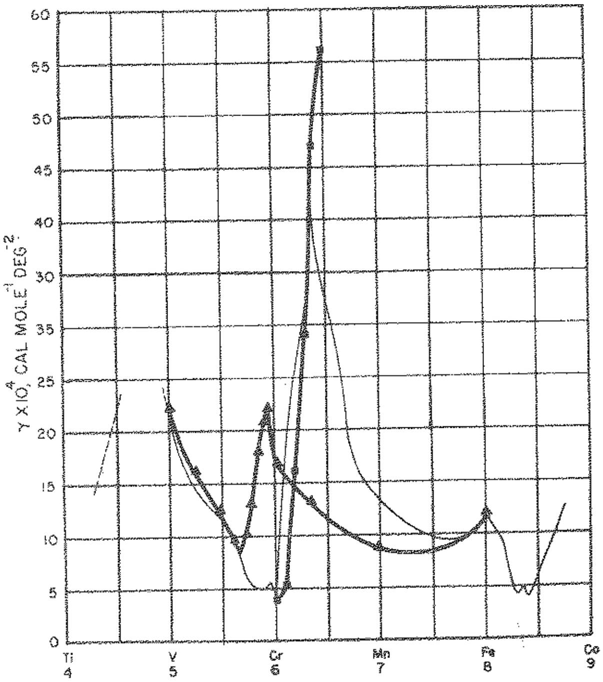


Density of states for first long period b.c.c. alloys deduced by Shimizu (1964) from Beck's results as explained in text.

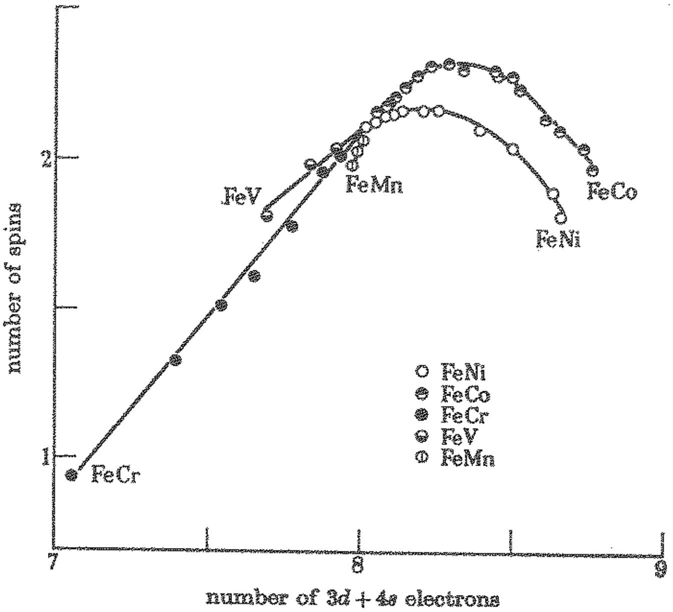
Fig. 47



Specific heat coefficient γ as a function of electron concentration for V–Fe (filled triangles) and Cr–Mn (solid squares), contrasted with the results shown in fig. 37 (thin line).

With this model of iron–cobalt, it is important to ask where the excess moments are likely to reside in, say, an alloy of 30% Co in Fe. We assume that the atoms remain neutral and that the pile-up of charge has the consequence that $\int|\psi_d|^2\,d\tau$ over an atomic cell and integrated over all d states is likely to be unchanged in the alloy in either type of atom. Thus cobalt atoms cannot have more than two Bohr magnetons per atom on them. The iron atoms have 2·9 holes, but in the pure metal their spins are not all lined up; as the number of holes is decreased by the addition of cobalt, one can obtain about 2·5 lined up, as we have seen. Thus we should expect the extra moment to be on the iron atoms. The Mössbauer investigations of Wertheim *et al.* (1964) and on neutron scattering by Collins and Forsyth (1963) indicate that this is so.

Fig. 48



Number of uncompensated spins in b.c.c. iron alloys (Crangle and Hallam 1963).

From the curves of this section, one can make estimates for iron of the shift ΔE of the spin-up d band relative to the spin-down. From fig. 38 it appears to be about 1 ev. If on the other hand the peak in $N(E)$ is partly due to localized moments, as proposed by Shimizu (1964), ΔE is increased; Shimizu, from the data of fig. 46, deduces $\Delta E = 1{\cdot}56$ ev. These values, as already stated, are less than that deduced from the band form of Wood (1960), which is about 2 ev, but as we pointed out in § 3, following Cornwell and Wohlfarth (1962), these values give too low a value of γ, so the estimated band width and hence ΔE may be too large.

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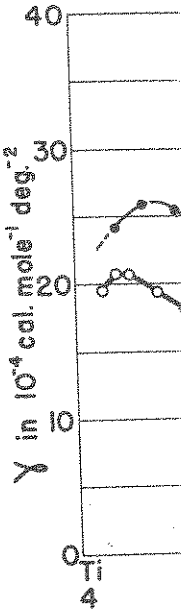

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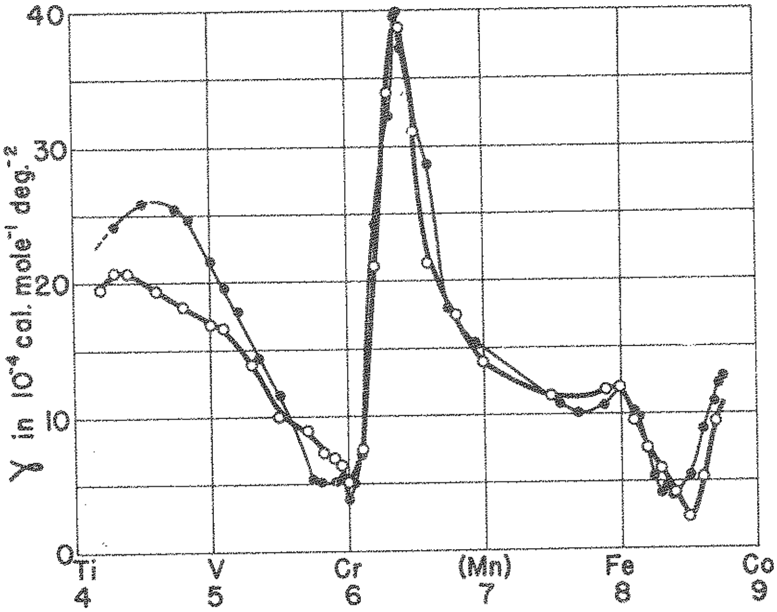
All these considerations are based on the assumption that the spin-down Fermi level is unchanged in position in the Fe–Co alloys. In the Fe–V and Fe–Cr alloys, in which the moment drops as the last-named element is added, the drop (in Bohr magnetons) is greater than the values of 3 and 2 that this hypothesis would suggest; Nevitt and Aldred (1963) find $-3{\cdot}286$ and $-2{\cdot}36$ per atom added. This would suggest that the spin-down Fermi level moves gradually to the right as vanadium or chromium is added, as a consequence presumably of a drop in the ferromagnetic coupling.

The resistivity of iron–cobalt alloys is discussed in § 14.7.

Fig. 49



Specific heat of certain alloys with (○) and without (●) 10% of aluminium.

11.1 *Effect of Adding Aluminium*

Pessall *et al.* (1964) have measured γ for the body-centred alloys Cr–Fe and Fe–Co with the addition of 10% of aluminium. The results are shown in fig. 49. The fact that the peaks are not displaced is evidence that the extra electrons from the aluminium remain in the s band and do not go into the d band, so that these alloys behave like iron in this respect, if our model of § 8 is accepted.

Also, as Professor Beck has pointed out to the author, *if* part of the peak at $e/a \simeq 6{\cdot}5$ is due to localized moments, it is surprising that this is not affected by the presence of aluminium.

11.2. *Properties of Chromium and Chromium-rich Alloys*

The particular position of chromium, with the Fermi level adjacent to a sharp rise in the $N(E)$ curve, would make it likely that the electronic specific heat coefficient γ would rise sharply with increasing temperature. An analysis of this effect has been given by Shimizu *et al.* (1962), who, using the data of fig. 37, predict a rise by about 4 as the temperature rises to 500°K, and whose analysis of the experimental results shows that the observed effect is even greater. This suggests that the peak in fig. 37 *is* characteristic of a pure metal, and not a result of alloying. Calculations are now in train to determine whether Beck's peak (fig. 37) or Shimizu's revised peak (fig. 46) gives the best agreement.

Similar calculations for V, Ti and V–Cr and V–Ti alloys have been made by these authors (1963 c). They also give a discussion of the Knight shift (see below). Van Ostenburg *et al.* (1963) have done the same for a number of alloys of Nb–Tc and Nb–No.

Other facts about chromium may be noted here. Lomer's (1962) calculation of the Fermi surface has already been mentioned. Fawcett and Griffiths (1962) have obtained from the anomalous skin effect estimates of the Fermi surface areas of Cr, Mo, W. On a two-band model with spherical surfaces these would give 0·11 carriers for chromium and 0·08 for molybdenum and tungsten. Lomer's surfaces are far from spherical and Fawcett and Griffiths think their results are not inconsistent with his.

Recently Brandt and Rayne (1963) have made low-field de Haas–van Alphen studies of the chromium group transition elements; only for molybdenum do they find agreement with Lomer's model. For chromium the disagreement is marked, presumably due to the antiferromagnetic ordering, known to exist in chromium as well as alpha-manganese and gamma-iron (Corliss *et al.* 1959, Shull and Wilkinson 1953, Kasper and Roberts 1956, Abrahams *et al.* 1962, Bykov *et al.* 1959, Bacon 1961).

Overhauser (1962, 1963) has stressed that there is much evidence that the antiferromagnetism of chromium is *not* due to localized moments. The moment per atom is about $\frac{1}{2}\mu_B$ per atom, but the entropy yield on going through the Néel point is (Beaument *et al.* 1960) 0·44 cal/deg, much less than $\frac{1}{2}R\ln 2$ (~ 600). There is no paramagnetic neutron scattering above the Néel temperature. Overhauser therefore proposes a model in which above the Néel point the metal retains no localized moments, just as in the Stoner–Wohlfarth model of a ferromagnetic metal. Overhauser's model is similar to that of Slater (1951; see also Slater and Koster 1954) and Lidiard (1953) in which one uses different Bloch wave functions ψ_k for the two-spin directions, except that in his description the wavelength of the spin modulation is *not* the lattice parameter. He refers to these oscillations as spin density waves. Lomer (1962) has given reasons for believing that the kind of Fermi surface shown in fig. 13 makes such spin density waves particularly likely to occur.

The resistivity of chromium is discussed in § 14.7.

§ 12. PARAMAG

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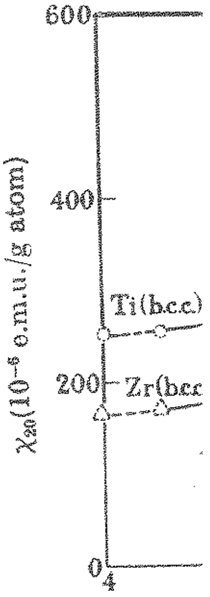

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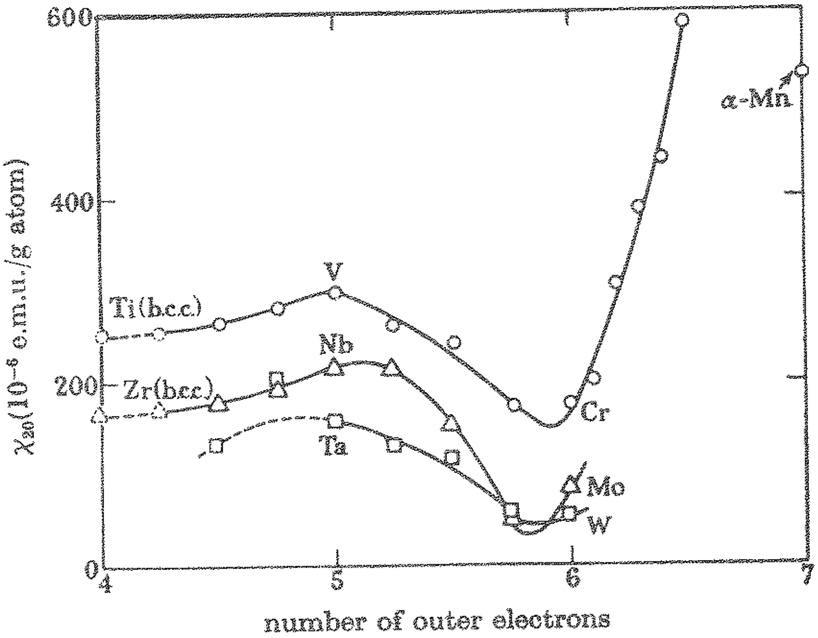
§ 12. PARAMAGNETIC SUSCEPTIBILITY OF BODY-CENTRED ALLOYS OF TRANSITION METALS

In general the main contributions to the susceptibility of a paramagnetic transition metal alloy are:

(*a*) The Pauli spin paramagnetism. This depends on the density of states at the Fermi surface, and will fall off with temperature, behaving at high temperatures according to a Curie–Weiss law ($\chi \propto N\mu^2/k(T+\Theta)$), where Θ will be of the order of the band width but will be greatly modified as outlined in § 9 by the exchange interaction (molecular field). If the Fermi level is near a peak in $N(E)$, or if $N(E)$ is increased at the Fermi level by virtual states, the fall off with temperature will be even more rapid.

Fig. 50

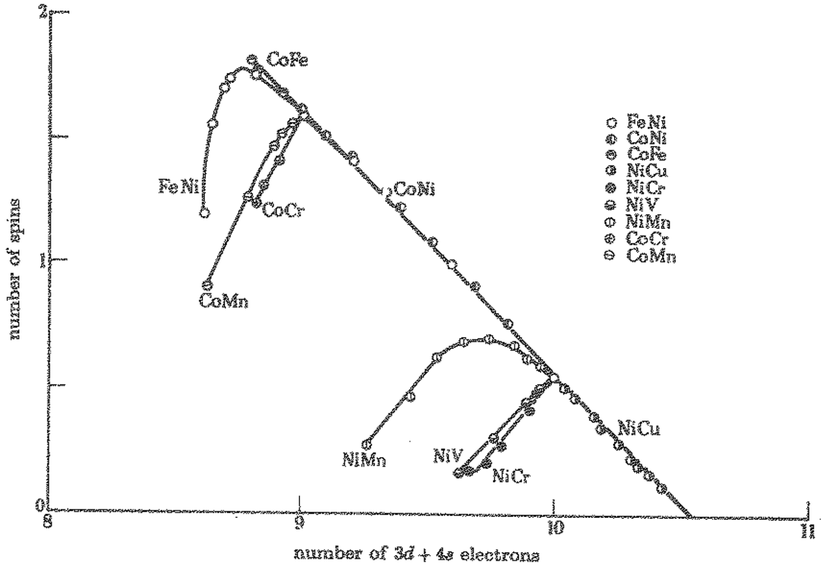


Room temperature susceptibility of b.c.c. alloys, showing the minimum that occurs for all three periods.

(*b*) The temperature-independent orbital paramagnetism. Of the theory of this a recent account as applied to transition metals has been given by Denbigh and Lomer (1963). It is *not* a property of the Fermi surface but depends on interband transitions from the whole occupied d band, and is large when such transitions have low energy as is likely to be the case in transition metals. As stressed particularly by Marshall and Johnson (1962), it may have a large effect both on paramagnetism and yperfine field in alloys particularly if $N(E_F)$ is not particularly large, for instance for chromium. Its magnitude is roughly proportional to the product of the number of d electrons and d holes.

Both because of the molecular field and the orbital paramagnetism, we do not expect any close parallelism between the susceptibility and the specific heat as plotted against e/a. The magnetic susceptibility of some paramagnetic alloys has been plotted by Taniguchi *et al.* (1962). Their results are shown in fig. 50. The same minimum occurs as for the specific heats, but the curves are dissimilar, probably on account of the influence mentioned above of the molecular field and the orbital paramagnetism.

Fig. 51



The number of magnetic electron spins per atom plotted against number of 3d + 4s electrons per atom for f.c.c. binary alloys of iron and nickel (Slater–Pauling curve; Crangle 1963).

Van Ostenburg *et al.* (1963) have given a discussion both of the susceptibility of some of these alloys and of the Knight shift. Relevant factors determining magnetic properties are, as we have seen:

(*a*) The density of states.

(*b*) The molecular field, which together with the density of states determines the spin paramagnetism.

(*c*) The temperature-independent orbital paramagnetism.

The density of states can be obtained from the specific heats already reproduced in this article as fig. 40. Thus for each alloy one has two unknowns, the molecular field and the temperature-independent spin paramagnetism, and the known susceptibility and its temperature-dependence, together with the density of states, from which to determine these. This is

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§ 13. An

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what these authors do. They find that the orbital paramagnetism varies by a factor less than two in the alloy series Nb–Mo, and near molybdenum where the spin paramagnetism is small contributes more than half the total. Most of the internal field which determines the Knight shift is due to this term.

§ 13. ANOMALIES IN THE SLATER–PAULING CURVE

Figure 51 shows the Slater–Pauling plots corrected by Crangle (1963) to give electrons per atom for b.c.c. and f.c.c. metals; certain parts of the curve have been discussed earlier, and we discuss in this section the anomalies.

The well-known anomalous behaviour of chromium, manganese and vanadium in nickel is discussed by Friedel (1958, 1962) in terms of bound states. Friedel's explanation is as follows. Suppose chromium is added to nickel; if chromium behaved like cobalt one would expect every substitution of a chromium for a nickel atom to increase the number of holes in the d band by 4 and hence the moment by $4\mu_B$. But if the four extra holes were uniformly distributed, this would leave a large excess negative charge $-4e$ on the chromium atom. Naturally this would be screened by the four holes. But even so, so strong a repulsive field may form bound states above the d band and so above the Fermi surface. These states will be empty, and, by forming them, states are subtracted from the d band for each spin direction. Thus ten states are removed from the d band at the same time as four holes are added (i.e. four electrons subtracted). For atoms other than chromium, one must take instead of four the difference between the atomic number and that for nickel. The magnetic moment is thus reduced by the following amounts (in Bohr magnetons).

	Per atom substituted	Per electron (d + s) subtracted
Cr in Ni	$10-4=6$	1·5
V in Ni	$10-5=5$	1·0
Ti in Ni	$10-6=4$	0·67
Cr in Co	$10-3=7$	2·3
Mn in Co	$10-2=8$	4·0

The agreement with the slopes in fig. 47 is fair except for Co–Mn; the assumption that the bound state has room for ten electrons is of course open to doubt, as Friedel points out, so these slopes are likely to be too great. Chromium is anomalous, and Friedel suggests that the level is partially occupied, in other words forms a virtual bound state; he points out that this element gives an anomalously large residual resistance in nickel.

The model as it stands does not discuss the screening of the charge left on the vanadium atom (for instance), which in nickel with the crude model is $+5e$. This must be understood in terms of the model of fig. 19; the surrounding nickel atoms have their d shells full and the ten orbitals must penetrate into the atomic cell of the vanadium atom, with both d and s forms there, and in such a way as to produce five charges there. Since by our assumption 10 states are pushed above the d band, this large penetration must not introduce any extra states into the d band. Whether this can actually occur may require further theoretical investigation.

Alternatively one can describe the whole phenomenon, as we have done for iron and nickel with aluminium (§ 7), in terms of orbitals of ligand field type. Let ϕ_V, ϕ_{Ni} be d orbitals for vanadium and a neighbouring nickel atom. We set up bonding and antibonding orbitals of the type:

$$\left.\begin{array}{l}\phi_{Ni}+\alpha\phi_V\\ \phi_V\ +\beta\phi_{Ni}\end{array}\right\}\alpha,\beta<1,$$

which are orthogonal and, since ϕ_V has the higher energy, the first is bonding. Since screening has to be provided by the first orbital:

$$\sum|\alpha|^2=5,$$

the summation being over the 12 nickel atoms that are nearest neighbours and over the 9·5 occupied d orbitals. The antibonding orbital is empty, so no new states are introduced by the penetration.

Similar observations to those described above have been made by Chen (1962) on Fe–Co alloys with admixture of Mn, Ni, Ca, Ti, V and Cr. He finds that manganese adds $3\,\mu_B$ to the magnetism of these alloys. Professor Vogt (private communication) has pointed out to the author that manganese in cobalt produces a change in the moment of $-2{\cdot}9\,\mu_B$, Friedel's model failing here, and that $3\,\mu_B$ is the magneton number for a free atom of manganese without s electrons. It looks as if manganese is producing bound states with localized moments on the manganese atom, rather than getting rid of its electrons as in Friedel's model. The neutron results mentioned below confirm this.

The bound state model implies that the distribution of magnetic moment will be widely diffused round the impurity in the case of the anomalous impurities chromium or vanadium in nickel or cobalt; the moment should be mostly on the 12 surrounding atoms of the matrix. This seems in accord with the observations† of Low and Collins (1963) and Collins and Low (1963) on the neutron atom form factor in **Ni**–Cr and **Ni**–V; in **Ni**–Mn on the other hand the *additional* spin due to manganese is located on the manganese atom. Collins and Wheeler (1963) show that for cobalt in nickel the extra spin moment is on the cobalt atom, which can be reconciled with the band model which is so successful for these alloys by using wave functions ψ_k which have different amplitudes within the chromium atom and in the surrounding matrix.

Gerstenberg (1958) found an effect very similar to the ferromagnetic behaviour of **Ni**V when investigating the paramagnetism of palladium alloyed with vanadium and titanium; fig. 52 shows his results. The fact that vanadium and titanium rapidly destroy the paramagnetism by

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† Apart from the moment on the neighbours there is also one on the vanadium of $-1{\cdot}2\mu_B$.

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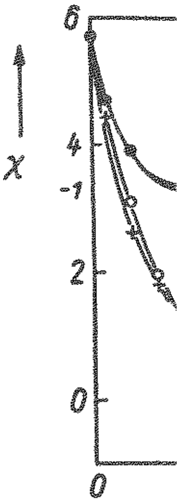

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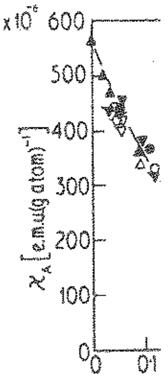

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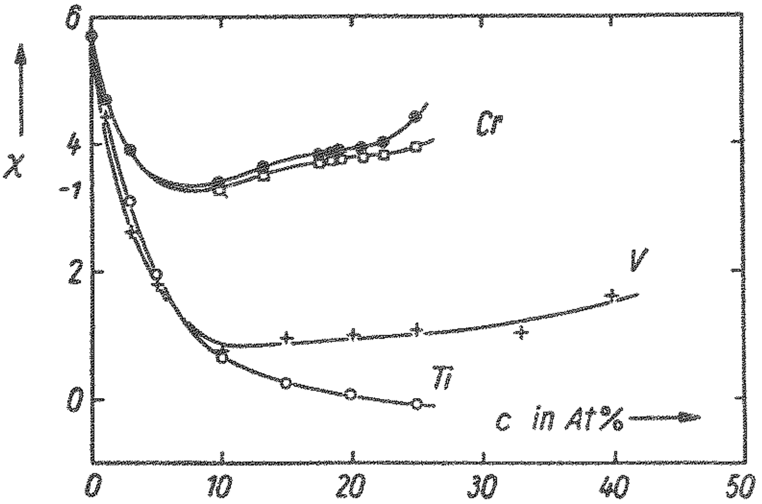
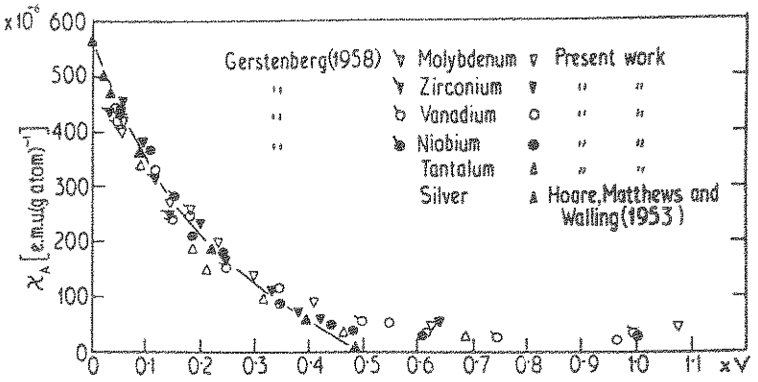
Fig. 52



Susceptibility χ of Pd–V, Pd–Ti and Pd–Cr as a function of concentration c of the second element (Gerstenberg 1958).

Fig. 53



Gramme-atomic susceptibility χ_A at room temperature of certain alloys of palladium according to Kudielka-Arter and Argent (1962). V is the difference between the number of electrons in the solute and that in palladium, x the concentration.

number of electrons outside a closed shell. In palladium, as the table shows, V is also the number of states subtracted from the d band when a transition metal is added; and if V is taken as unity for silver, V is here the number of electrons added. It is thus satisfactory that χ plotted against xV lies on the same curve for silver as for the other elements.

The resistivity of some of these alloys is discussed in § 14.2.

§ 14. CONDUCTIVITY OF THE TRANSITION METALS

14.1. *Introduction*

Unless a transition metal shows ferromagnetism or antiferromagnetism, its properties as a conductor are not different in principle from those of other metals. However, as we have seen, it is a property of many transition metals that part of the Fermi surface is mainly s-like, and thus is in a region of k-space having a low density of states, and part is mainly d-like and thus with a high density of states. These parts may or may not be in different Brillouin zones; if they are, we call them an s band and a d band. A model first given by the author (1936 a, b, Mott and Jones 1936) in which the current is assumed to be carried mainly by electrons in an s band, but resistance mainly due to transitions from the s to the d band (or, from an s to a d part of the Fermi surface), is still useful† whether the s and d-like parts of the Fermi surface are in the same zone or not. Recently a good deal of experimental evidence has been obtained showing the usefulness of the model, and this will be reviewed in this article.

The resistance of a metal is due to the following:

(*a*) Scattering of electrons by phonons.

(*b*) Scattering of electrons by impurities or defects.

(*c*) Scattering of electrons by other electrons.

The last term (*c*) may be of particular importance in transition metals, and the effect can take place through two processes which are physically different. These are:

(i) The direct scattering of one electron near the Fermi surface by another. For a spherical Fermi surface this makes no contribution to the electrical conductivity, though it does to the thermal conductivity (Ziman 1960, p. 416). For a non-spherical Fermi surface, a term in the resistance proportional to T^2 arises, as was first shown by Baber (1937) and this is particularly large for transition metals.

(ii) In ferromagnetic materials there is a term in the resistance due at low temperatures to the scattering of conduction electrons by spin waves (also proportional to T^2) and at high temperatures to spin disorder.

These terms will be discussed later in this section.

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† Wilson (1938) criticizes quantitative aspects of the model, but states in his book (second edition, 1953, p. 271) that he believes it to be qualitatively correct.

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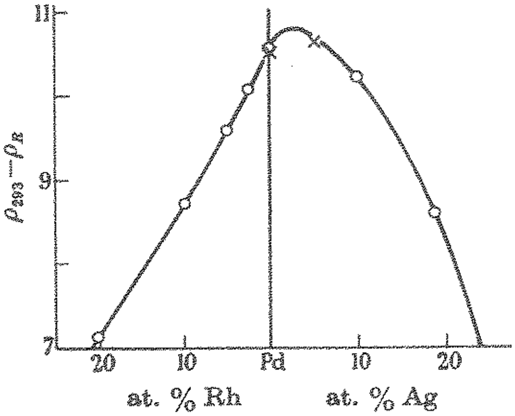
14.2. *Scattering from an s to a d Band*

In this section we shall treat non-ferromagnetic metals, of which palladium is typical. The assumption made by the present author (1936a, b; see also Mott and Jones 1936) is that the current is largely carried by the s electrons of effective mass comparable with that of copper, of which there are about 0·5 per atom in palladium for example, but that the main term in the resistance is due to transitions which these electrons make to the Fermi surface of the d band. These transitions are due to phonons, in some measure also to electron–electron collisions, and in alloys also to impurity scattering. They have higher probability than s–s transitions because the density of states at the Fermi surface of the d band is high. This accounts in principle for the low conductivity σ of these metals compared with the noble metals ($\sigma/M\Theta_D^2$ is 12·4 for silver, 1·3 for palladium).

Fig. 54



Experimental values of $\rho_{293}-\rho_R$ ($\mu\Omega$ cm) for palladium-rich Pd–Rh and Pd–Ag (Coles and Taylor 1962). ρ_R is the residual resistivity, ρ_{295} that at room temperature.

Most of the early evidence for the correctness of this model comes from the study of the electrical resistance and thermoelectric power of Pd–Ag alloys and is summarized by Mott and Jones (1936); briefly the phenomena peculiar to palladium disappear as the d band is filled up. A recent thorough investigation of the electrical resistance of these alloys and also of Pd–Rh has been made by Coles and Taylor (1962), which fully confirms the model, though particularly for palladium-rich alloys they find evidence of a contribution to the current from the d holes. Figure 54, taken from their paper, shows the *temperature-dependent* part of the resistance of these alloys, with a maximum near palladium, though not quite at the same position as the maximum in the electronic specific heat; the difference, according to these authors, is due to the mobility of the d holes†. Figure 55 shows the same quantity for the whole range of Pd–Ag alloys, which drops as the d band is filled up; the maximum at about 50% silver occurs because only for quite high concentrations of silver can silver cause s–d transitions‡ (Mott and Jones 1936).

Wilson (1938) remarks that the s–d transitions normally involve a finite change in **k** and will thus in pure metals disappear at low temperatures§. One might expect, therefore, that the resistivity ρ in the T^5 region would be abnormally low compared with that in the region where ρ is proportional to T. No such effect seems to be observed, but it may be masked by the Baber term (see below), which does lead to large changes of **k** at low temperatures.

It is disappointing that nothing can at present be deduced from the Hall effect about the number of s electrons in these transition metal alloys. Unfortunately, in the simplest alloy system, Ag–Au, where the number of s electrons and the atomic volume remain almost constant, the Hall constant certainly does not. Thus $n^*(n^* = 1/NecR$, $R =$ Hall const, $N =$ number of atoms per unit volume) is plotted for those alloys in fig. 56 (from Coles 1956). Similar results from the same paper are shown in fig. 57 for silver alloys with divalent metals and palladium, showing the cusp for the pure metal. It is clear from these results that the Hall constant depends markedly on the mechanism of scattering, and on whether this is due to phonons or impurities‖. Thus the elegant explanation of the measurements of Hall effect in Cu–Ni alloys offered by Schindler and Pugh (1953) in terms of the author's s–d scattering process in ferromagnetics reviewed in § 14.6 cannot be accepted, as realized by Schindler (1956) when the results were repeated in Ag–Pd. The original idea was that n should be 0·3 per atom

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† The current carried by the holes may be from 25 to 30% of the total (Coles, private communication).

‡ This is because we do *not* expect a high value of $|\psi_{\mathrm{d}}|^2 N_{\mathrm{d}}(E_{\mathrm{F}})$ at the Fermi surface within the silver atoms. That this is compatible with our screening model is explained in § 7. Therefore the deviation from periodicity due to a small concentration of silver does not make a proportional contribution to s–d scattering. For large concentrations, however, both silver and palladium atoms act as deviations from the mean periodic field.

Chen (1962, 1963) and Chessin *et al.* (1964) find very large contributions to the resistivity of nickel and of certain ferromagnetic alloys (e.g. Fe Co) due to 1% of Cr, V, Ti, Nb and Ta. These are just the elements which, according to Friedel (cf. § 13), form a bound state above the d band of the matrix of nickel and empty their electrons into it. Chen ascribes these results to the formation of a virtual bound overlapping the Fermi surface; this is probably right for chromium, which gives the biggest effect. Other contributing factors may be that the scattering obstacle is *large*, and s–d transitions *are* possible in the atoms which are modified by the obstacle. On the other hand, for nickel and FeCo (with equal concentration of both elements) we believe the spin-up d band is full, so that only half the electrons can make s–d transitions. Thus probably the virtual state contributes the main effect.

§ In an intermediate range he predicts a variation as T^3.

‖ cf. Ziman 1961.

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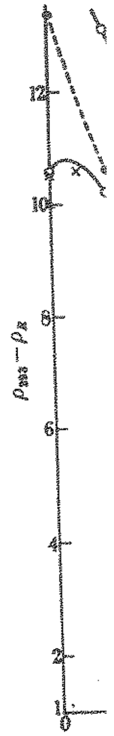

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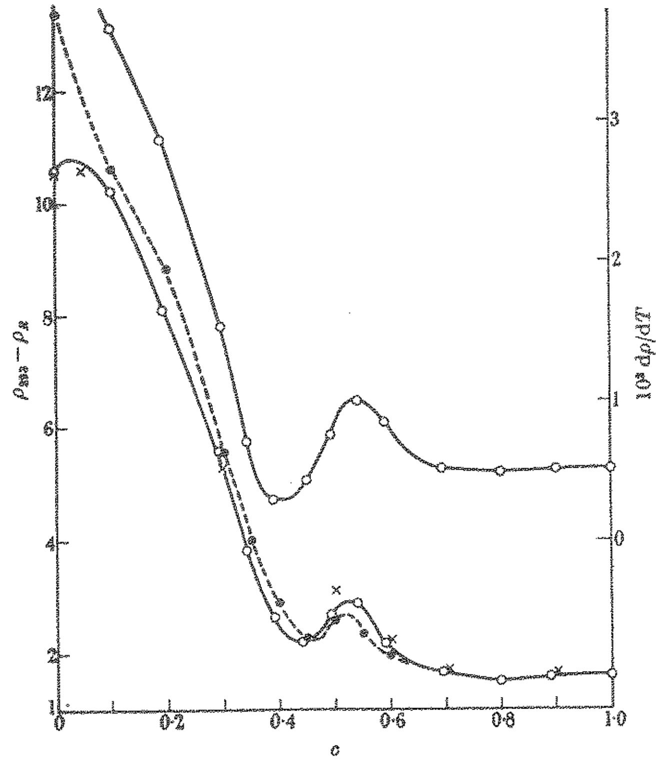
for ferromagnetic alloys at low temperatures because only half the s electrons could make s–d transitions, so that the other half only would have high conductivity and make a significant contribution to the Hall constant. On the other hand, Pugh and his colleagues, in a series of papers (for references see Ehrlich *et al.* 1964), have shown that this model works well

Fig. 55



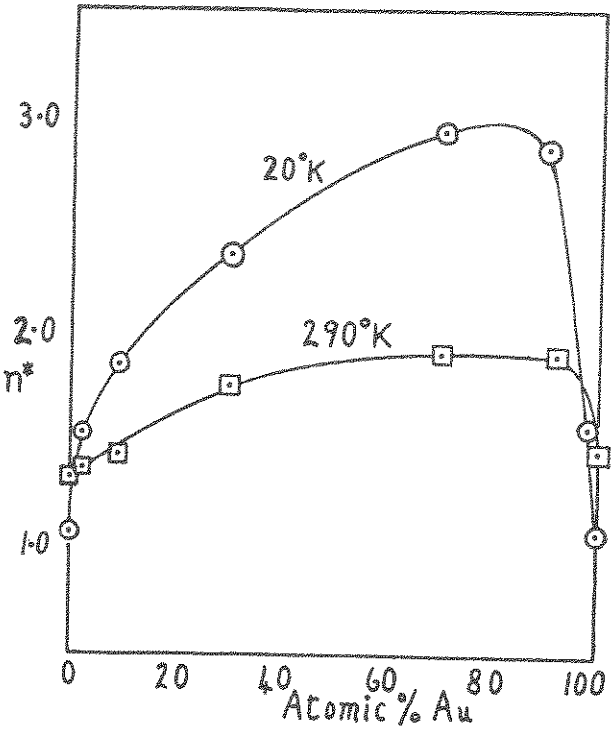
Temperature-dependence of resistivity of palladium–silver alloys as a function of concentration c of silver (Coles and Taylor 1962). The upper curve is $d\rho/dT$ at 273° ($\mu\Omega$ cm per degree). The lower full curve shows the resistivity as measured (ρ_{293}) minus the residual resistivity ρ_R. The dotted line shows calculated values of the same quantity.

for Cu–Ni and Cu–Fe–Ni provided the concentration of nickel in the alloy is less than 75%; the effective number of electrons deduced from the Hall constant rises from about 0·25 to 0·5 as the temperature approaches the Curie temperature, as predicted. The reason why the model works only for these alloys, and not for those of higher nickel concentration or Ag–Pd, is not known.

14.3. *Resistance at High Temperatures*

The present author has discussed the resistance of the transition metals at high temperatures (Mott 1936 a, b, Mott and Jones 1936, p. 269). Whatever the scattering is due to, if transitions from an s to a d band are primarily responsible for $1/\tau$ (where τ is the time of relaxation), then $1/\tau$ should be proportional to the average value of $N_d(E)$ over the range kT at the surface of the Fermi distribution. The assumptions are that the values of N, N' and N'' for the d band are big compared with those in the s band.

Fig. 56



Values of n^* from Hall coefficient from silver–gold alloys (Coles 1956).

Then the conductivity due to the s electrons is proportional to :

$$-\int \tau_s(E)\frac{df}{dE}\,dE,$$

where τ_s is the time of relaxation for the s electrons and $f(E)$ the Fermi distribution function. A simple calculation, taking into account the change of the free energy ζ with temperature, gives

$$\tau(\zeta_0)+\frac{\pi^2}{6}(kT)^2\{-\tau_s''-\tau' N'/N\}.$$

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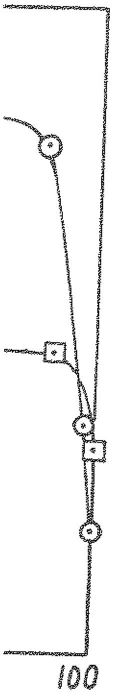

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Taking $\tau \sim 1/N$, which should be valid if s–d transitions are predominant this gives a term proportional to

$$1+\frac{\pi^2}{6}(kT)^2\{N''+2N'^2/N\}.$$

If N has a parabolic form near the top of the d band, so that

$$N=\text{const.}\ \sqrt{(E_0-E)},$$

this gives :

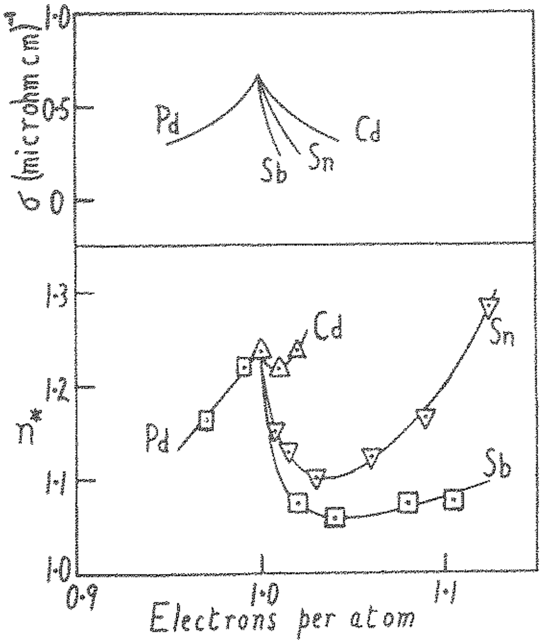
$$1-(\pi^2/6)(T/T_0)^2,$$

where $kT_0=E_0-E_F$. If the resistivity is due to phonon scattering and the mean squared amplitude of the lattice vibrations is proportional to T, a resistivity proportional to

$$T(1-AT^2)$$

is to be expected.

Fig. 57

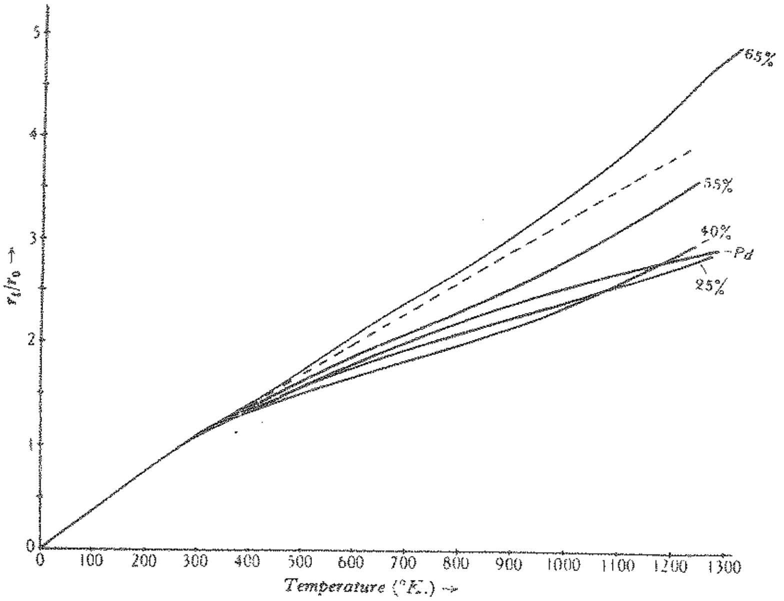


Values of conductivity σ and n^* at room temperature for dilute alloys of palladium, cadmium, tin, antimony in silver (Coles 1956).

Wilson (1938) criticizes this result on the grounds that the assumption that all s–d transitions are equally probable, made in the author's original paper, is a rough approximation. His introduction of the idea that the d electrons are in three equal zones is probably not correct. His remarks on p. 277 of his book (Wilson 1953)—that T_0 ought to be the degeneracy temperature of the s band—seems to be based on a misunderstanding.

The evidence for the general correctness of these ideas, however, comes primarily from the behaviour of alloys. Coles and Taylor's (1962) work on palladium alloys has already been mentioned; the results fit well to a formula $\rho_d(1-AT^2)$, where ρ_d is due to s–d scattering calculated using the $N(E)$ curve deduced from the specific heat. The term in AT^2 is very prominent in the alloys, modifying as it does the large impurity scattering. Figure 58 shows the results of Conybeare (1937) for the temperature-dependent part of the resistivity of several alloys of palladium and gold over a wide range of T. It will be seen that the abnormal behaviour of the metal represented by the T^2 term disappears as the d band is filled up.

Fig. 58



Temperature-dependent part of the resistivity of Pd–Au alloys (Conybeare 1937). The figures show the concentration of gold.

Kimura and Shimizu (1964) have given a recent discussion of the thermoelectric power of these alloys (Pd–Ag and Pd–Rh) in terms of the two-band model.

Many complicated effects have been discussed in terms of interband scattering. We may mention the work of Friedel (1956 b) on uranium, of Blatt (1961) on uranium–molybdenum alloys and of Hake *et al.* (1961) on titanium–molybdenum.

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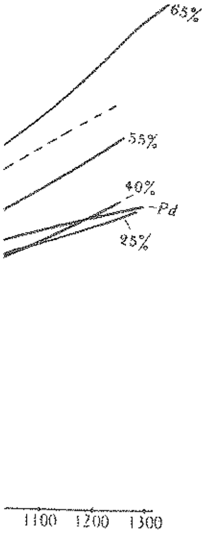

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14.4 *Electron–Electron Collisions: Baber Scattering*

This has already been mentioned in the introduction; the evidence for its existence is perhaps not yet quite certain†. The term in the resistance proportional to T^2 can be derived qualitatively as follows. Consider an s electron which is to be scattered through a large angle by a d electron. The only d electrons capable of doing this are a proportion kT/ζ_d of the whole number; the others would have to give more energy to the s electron than, by the exclusion principle, the s electron can accept. Moreover, of all the collisions possible for two isolated electrons, only those in which there is very little interchange of energy can actually take place, and this introduces another factor kT/ζ_s.

In the case of a parabolic band form implicity assumed here, with two degeneracy temperatures ζ_s, ζ_d, Appel (1963) finds that the time of relaxation τ for such collisions is given by:

$$\frac{1}{\tau} = v\,\frac{(kT)^2}{nQ\,\zeta_s\,\zeta_d},$$

where v is the average relative velocity for electron–hole pairs, ζ_s, ζ_d are the degeneracy temperatures of the s and d bands and Q a collision cross section of the order of the square of the screening radius. The small value of ζ for the d band means that this term will be more important for transition metals than for other metals.

No one seems to have discussed collisions in which the s electron makes transitions to the d-like part of the Fermi surface on hitting a d hole, a process which ought to give an even bigger value of $1/\tau$, or order $(kT)^2/\zeta_d^2$ instead of $(kT)^2/\zeta_s\,\zeta_d$.

An approximate T^2 dependence of the electrical resistance has been measured below 10°K by de Haas and de Boer (1933) in platinum, by Justi (1960) in molybdenum, and by White and Woods (1959) in a systematic investigation on several transition metals, particularly those with a large electronic specific heat. According to Appel the measured coefficients have the right order of magnitude assuming a total scattering cross section $Q_{sd} = 10^{-15}\,\text{cm}^2$. Kondorsky *et al.* (1958) have found a term in T^2 in the resistance of ferromagnetic metals, but a term due to spin waves probably accounts for at least part of this (see § 14.5).

One expects that, as the holes in a d band become non-degenerate, the contribution from hole scattering should flatten out, as in fig. 59. The exact form has not been calculated with any model, even for parabolic bands.

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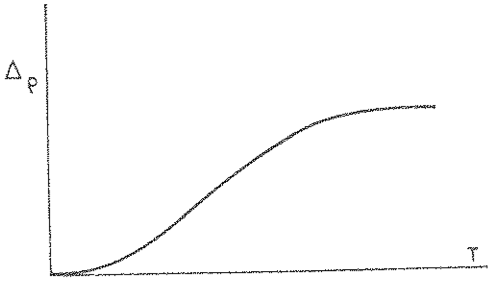
† Wilson (1953) remarks that Baber's explanation of a T^2 term is " not very convincing ". Ziman (1960, p. 415) gives a discussion of the T^2 term and some comparison with experiment. Abrahams (1954) shows that it is unimportant for alkali metals. Peierls (1956) deduces the term (p. 133) and considers that it may play a role in limiting phonon drift. Appel (1963) in a recent note gives what he claims to be an exact formula for a simple two-band model, though I do not agree with his statement that the T^2 term becomes small at high temperatures.

Whether the existence of this term as illustrated in fig. 59 is compatible with observations on the electrical resistivity of palladium, which does not show any marked anomaly, is uncertain. As mentioned previously, it may compensate for the disappearance of phonon-induced s–d scattering at low temperatures. Owing to the peaked nature of the $N(E)$ curve for palladium one might expect a drop in $\Delta\rho$ below the T^2 form at more moderate temperatures, say 500°K.

14.5. *Scattering by Spin Waves*

In ferro- or antiferromagnetic metals there is an additional term due to scattering of conduction electrons by spin waves or spin disorder. Vonsovski (1948) was the first to discuss this kind of scattering. At low temperatures Turov (1955) first showed that in ferromagnetism the resistivity due to this cause should vary as T^2 at low temperatures. More recent treatments are by Kasuya (1956, 1959), by Mannari (1959) and by Goodings (1963) who discusses also s–d transitions caused by spin waves.

Fig. 59



Contribution $\Delta\rho$ to the resistance from electron–electron scattering (schematic).

Above the Curie or Néel temperatures theoretical work has been done by de Gennes (1958), de Gennes and Friedel (1958) and by Russian workers (cf. Abelsky and Turov 1960 and the summary in English by Vonsovski 1961). A review of experimental material has been given by Coles (1958).

In ferromagnetic transition metals, where a fairly large term in T^2 due to the Baber mechanism of electron–hole collisions is to be expected, there is no way known to the author of separating the two terms experimentally or of finding out which is the most important. They are physically quite distinct, the Baber term being due to scattering through large angles and the spin waves term at low temperatures through small angles only.

The rather complicated analysis which leads, at any rate approximately, to a resistivity proportional to T^2 can best be understood by comparing spin waves with phonons. For phonons the resistivity is given as regards its

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variation with temperature by an integral of the type (Mott and Jones 1936, p. 262, Peierls 1956, p. 119),

$$\int I(\theta)\,(1-\cos\theta)\,2\pi\sin\theta\,d\theta, \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where $I(\theta)$ is the chance per unit volume that the electron is scattered through an angle θ. At low temperatures $I(\theta)$ is proportional to T for all angles less than $\theta_{\max}$, where $\theta_{\max}=q_{\max}/k_F$, and where $q_{\max}$ is the maximum phonon wave number q strongly excited at the temperature T. Since the energy of a phonon is proportional to q, $q_{\max}$ is proportional to T. It follows that, when $\theta_{\max}$ is small, (4) is proportional to T^5.

Scattering by spin waves differs in two ways. The first is that the energy of a spin wave is a quadratic function Jq^2 of its wave number q, so that

$$\theta_{\max}=q_{\max}/k_F\sim(kT/J)^{1/2}/k_F\,;$$

the variation is with the square root of T, not T. The second is that the term $(1-\cos\theta)$ does not occur. This is because we are considering collisions in which a spin wave is created or destroyed, and in these the spin of the conduction electron must change sign. Since in a ferromagnetic its chance of creating a spin wave is not the same as destroying one it follows that the times of relaxation of spin-up and spin-down conduction electrons are not the same. The consequent solution of the Boltzmann equation shows that small-angle transitions from $\mathbf{k}$ to $\mathbf{k}'$ are *not* nearly balanced by transitions from $\mathbf{k}'$ to $\mathbf{k}$, as they are for phonons, and so the term $(1-\cos\theta)$ which takes account of this is absent.

It follows then that the resistivity due to spin waves is of the form:

$$\int^{\theta_{\max}} I(\theta)\sin\theta\,d\theta,$$

and with $I(\theta)$ proportional to T and $\theta_{\max}$ to $T^{1/2}$; this is proportional to T^2.

If the Fermi surface of the conduction band is polarized, there is a *minimum* value of Δk by which the wave number of a conduction electron can change when the spin changes direction; this is of order pk_F, where $p\mu_B$ is the polarization of the conduction band. As a very rough approximation, below a temperature $T_0\sim p^2\Theta_c$, there should be no spin wave scattering of this kind. For nickel, if $p\sim 0{\cdot}1$, this should be about 6°K. This effect is treated in detail in the Russian work quoted above.

In the transitions discussed above, in which the spin of the conduction electron changes direction, the wave vectors before and after the collision are connected by the equation:

$$\mathbf{k}-\mathbf{k}'+\mathbf{q}=0,$$

where $\mathbf{q}$ is the wave vector of the spin wave created or destroyed. Transitions must also be possible in which there is no change of spin, and in which the spin wave changes its wave number so that:

$$\mathbf{k}-\mathbf{k}'+\mathbf{q}-\mathbf{q}'=0.$$

As we shall show, at the Curie temperature transitions without change of spin are half as likely as those with change of spin. At low temperatures no theoretical treatment has been given, but the resistivity should vary with T as a higher power than T^2, because the factor $(1-\cos\theta)$ will occur in the integral (4) as it does for phonons. It should thus be negligible in comparison at low temperatures, except at very low temperatures where change of spin of the conduction electron cannot occur.

If, as discussed by Niira (1960) and Mackintosh (1963) an energy gap w is introduced in the spin wave spectrum by magnetic anisotropy, a factor $\exp(-w/kT)$ must be introduced into the magnetic resistivity at low temperatures.

The interpretation of the observed resistivity of rare earth metals remains obscure. Thus Colvin and Arajs (1964) find that between 4°K and 20°K the resistivity of gadolinium behaves like AT^n with $n=3{\cdot}73\pm0{\cdot}03$. $I-I_0$ in this metal follows the Bloch law $T^{3/2}$, but the authors quoted above show that under certain conditions the relation between the energy of a spin wave and q may be linear, in which case they conclude that $n=4$ would follow. They consider this to be the case in gadolinium.

At high temperatures above the Curie or Néel points, treatments appropriate to the rare earths where the spins are localized have been given by Kasuya (1956) and by de Gennes and Friedel (1958). De Gennes derives formulae from a Heisenberg hamiltonian describing the interaction between a conduction electron and a system with spins in a localized state, and this method is of course valid whatever the value of the moments. We shall give an alternative treatment in terms of scattering cross sections, which shows rather simply that collisions in which the conduction electron changes its spin, and those in which it does not, make comparable contributions.

In the theory of the elastic scattering of an electron by a hydrogen atom (Mott and Massey 1949), one introduces the amplitude of $f(\theta)$ of the scattered wave and that $g(\theta)$ of the wave that occurs when the two electrons change places. Using antisymmetrical wave functions, one finds the following collision cross sections:

$$|f-g|^2$$

if the spins are parallel, and

$$|f|^2+|g|^2$$

if the spins are antiparallel. The term $|f|^2$ then corresponds to scattering without change of spin direction, the term $|g|^2$ to scattering with change of spin direction.

In a ferromagnetic material above the Curie temperature, *half* the sites will be occupied by electrons with spin opposite to that of a given conduction electron. One might thus expect a term in the resistance proportional to $\frac{1}{2}|g|^2$, corresponding to processes in which the spin changes. For those processes in which it does not, we can use exactly the same procedures as in a disordered alloy. Half the atoms scatter a wave proportional to $f-g$, the other half a wave proportional to f. The mean is $f-\frac{1}{2}g$, with waves of amplitude $\pm\frac{1}{2}g$ scattered from atoms of the two types. The term in the

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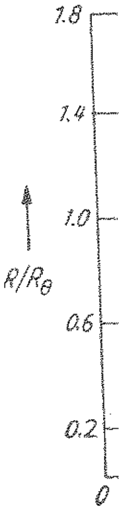

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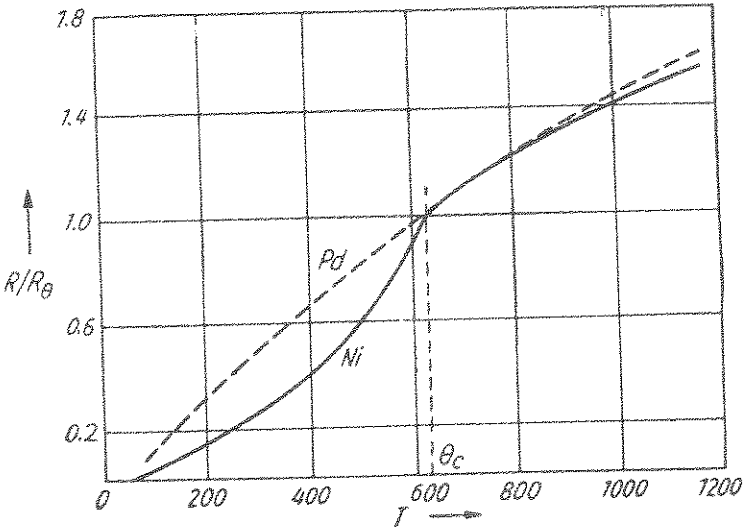
resistance should thus be proportional to $\frac{1}{4}|g|^2$ or *half* that due to collisions in which the spin changes.

Goodings (1963) has considered the effect of s–d transitions due to scattering by spin waves, which he shows may be considerable at moderate temperatures, though it must disappear at low temperatures since a minimum change of **k** is required, just as it is for phonons.

14.6. *Resistance of Nickel and Iron*

The effects described in the last sub-section, namely scattering of conduction electrons by spin waves, will certainly exist in iron and nickel, complicated probably at high temperatures by strong Baber scattering; indeed it is not clear whether *at high temperatures* the two are really separate phenomena. Some authors (e.g. Weiss and Marotta 1959) ascribe the whole of the resistance anomaly (figs. 60, 61) in ferromagnetics to this cause. On the other hand, Mott (1936 b) and Mott and Jones (1936) ascribed it in nickel to the change in the Fermi surface on approaching the Curie temperature. The argument is as follows. At low temperatures conduction electrons with spins parallel to the direction of magnetization cannot make transitions to the d band, since the spin-up d band is full. Thus these electrons would have much longer mean free path than those with opposite spin. But, as the temperature is raised, s–d transitions can occur for electrons with either spin direction. According to this model, nickel above

Fig. 60



Electrical resistance of nickel and palladium (Coles 1958).

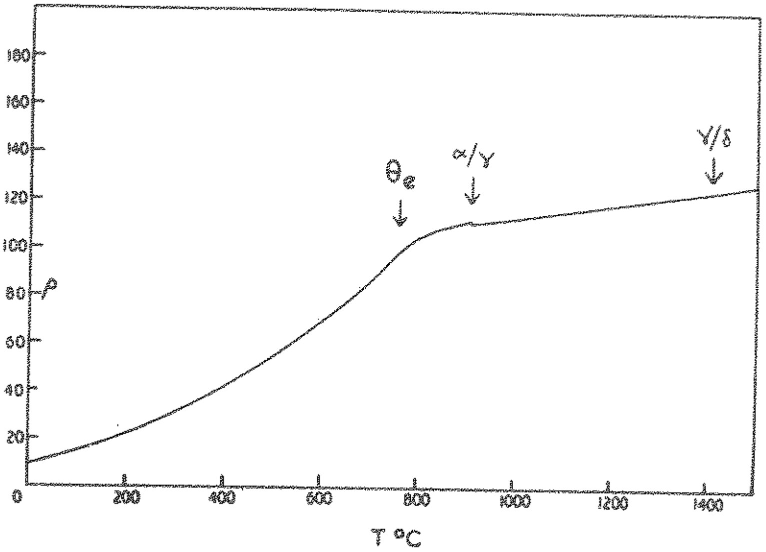
the Curie temperature should behave like palladium. In fact, fig. 60 shows that it does. This tends to suggest that the scattering by spin disorder, though doubtless present, is not the main effect. For iron, on the other hand, we expect scattering by spin disorder to be more important than the change in the Fermi surface above the Curie point. The reasons are:

(*a*) If our analysis in § 11 is correct, ferromagnetic α-iron has a Fermi surface both for the spin-up and spin-down sub-bands. Thus the effect predicted by Mott (1936 b) should be smaller.

(*b*) It is much more likely than for nickel that coupled spins persist above the Curie point (§ 6).

(*c*) The spin on each atom is large ($2\mu_B$), so that scattering by spins should be larger than in nickel.

Fig. 61



Electrical resistance of iron, showing Curie, α/γ and γ/δ transition points (Coles 1958).

The electrical resistivity is shown in fig. 61. It will be seen that the resistance–temperature curve above the Curie temperature is relatively flat, suggesting a large spin-disorder term.

A method of distinguishing between the two types of resistivity has been suggested by Mott and Stevens (1957; see also Coles 1958). The increased resistance above the Curie temperature due to the greater effect of s–d scattering should show both for scattering due to phonons and for that due to impurities. Suppose then one introduced 1% of Ru in Fe, 1% of Pd in

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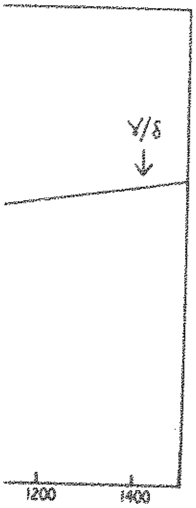

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Ni, the alloying elements being chosen so as to affect the band structure as little as possible. One would expect the increase in resistance $\Delta\rho$ to be relatively little affected by temperature in iron, but to increase greatly on going through the Curie temperature in nickel. According to Coles (1958), this does in fact occur.

Just above the Curie temperature of ferromagnetic metals a consideration of short-distance order has led Duk-Joo Kim (1964) to predict a drop in the resistivity. This is sometimes observed, see for instance the work on gadolinium of Nigh *et al.* (1963).

We may comment here on the curious fact that there is only a very small change in the resistivity for both iron and iron–chromium alloys at the α–γ transition point (Powell *et al.* 1961), of order from 1 to 3% according to the concentration of chromium. We have seen (§ 6) that f.c.c. iron at high temperatures has according to Kaufmann *et al.* (1963) a moment not very different from b.c.c. iron, and the same number of s electrons, so the spin scattering should be similar in the two phases. On the other hand, s–d transitions should be important, whatever the mechanism of scattering, and this result suggests that the densities of states at the Fermi surface in the non-magnetic state cannot be very different in α and γ iron.

14.7. *Resistance of Chromium and of Iron–Cobalt Alloys*

Chromium has

(*a*) A low density of states at the Fermi surface (fig. 37).

(*b*) A low conductivity; the values of $\sigma/M\Theta_D^2$ at room temperature for chromium and for neighbouring transition metals are as follows (Gerritsen 1956):

	Ti	V	Cr	Fe	Co	Cu
$\sigma/M\Theta_D^2$	0·65	0·13	0·79	0·94	1·65	9·0

If then the main part of the Fermi surface of chromium is† as in fig. 13, the s-like part must have a very small area; one cannot explain the low conductivity by a high probability of s–d transitions.

These considerations may well be relevant to iron. The spin-down Fermi surface in iron may be similar to chromium, the spin-up to nickel, with separate s and d bands. If so, the iron–cobalt alloys are of particular interest. At about 30% of cobalt the spin-up d band is full (§ 11). Thus the spin-up s electrons should have high conductivity because they cannot make s–d transitions. That this is so is shown by the measurements of resistivity of these alloys made by Beitel and Pugh (1958) and illustrated in fig. 62. The actual figures for the difference defined by:

$$\Delta\rho = \rho_{289} - \rho_{77},$$

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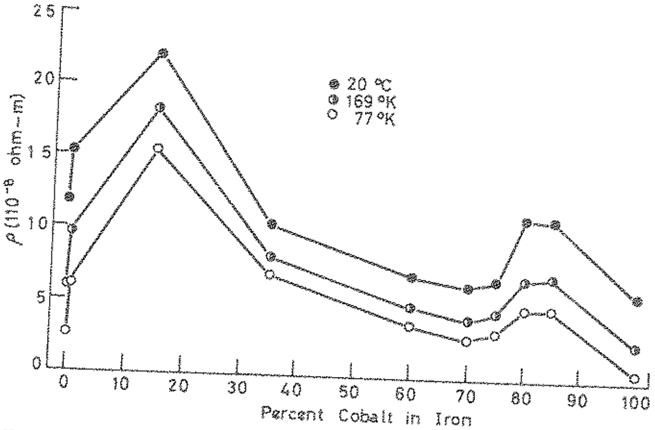
† Recent calculations by Altmann (1964) have confirmed that molybdenum has a Fermi surface of this form.

which is a measure of the resistance due to scattering by phonons, are as follows:

Percentage cobalt	15	35	60	70
$\Delta\rho$ (relative)	6·52	3·57	3·46	3·81

Neither the total resistance nor $\Delta\rho$ rises appreciably as the cobalt concentration increases beyond 30%. We interpret this as meaning that, since the extra electrons from cobalt are added to the spin-down band, by increasing the density of d-like states at the Fermi surface they can only decrease the conductivity of the spin-down electrons, which is small (as in chromium) and, we assume, small compared with the contribution from the spin-up electrons.

Fig. 62



Resistivities of iron–cobalt alloys (Beitel and Pugh 1958).

The total resistivity will be affected by the superlattice formed at 50% Co, but according to Sato (1943) the effect on the resistivity is not large.

In chromium itself the resistivity is doubtless influenced by the antiferromagnetism which may affect the Fermi surface by introducing superlattice zone boundaries. In fact, the resistivity above the Néel point at 310°K is about 20% less than the extrapolation of the values below (Arajs *et al.* 1962).

14.8. *Resistance at High Pressures*

The very great increase at pressures of the order 500 kbar of the resistance of potassium and rubidium (not sodium), by factors of the order of 50 at room temperature, observed by Stager and Drickhamer (1963) suggests that in these metals at high pressures some overlap into the d band may occur, though the increase does not set in suddenly and is in any case much bigger than the usual difference between transition and non-transition metals.

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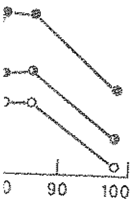

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14.9. *Electrical Resistance of the Rare Earths*

We do not wish to give any detailed review of the electrical resistance of the rare earth metals, particularly in view of the recent article in this journal by Rocher (1962). In most rare earths there is a considerable contribution to the resistance from scattering by 4f spins (see § 14.5); moreover, antiferromagnetic arrangements of spins can have a considerable effect on the resistance by splitting the Brillouin zone for the conduction electrons (Elliott and Wedgwood 1963). The spin-wave resistivity at low temperatures has been mentioned in § 14.2.

We do however wish to discuss the resistivity of ytterbium, because of the contrast with that of transition metals. This metal is unique among the rare earths in that the number of electrons in the f band is non-integral. According to measurements of the magnetic properties by Lock (1957), most of the 4f shells are full, with 14 electrons, though there are a few with 13 giving a moment and this is confirmed by measurements of Stewardson (private communication) on x-ray absorption (see below). The contribution to the resistivity by spin scattering is thus small. As Rocher points out, however (see his fig. 3), the experimental results of Trombe (1956) show that under pressure the resistance rises by a factor 15 but at 60 000 atmospheres drops rapidly to a normal value. Rocher concludes, correctly in our view, that under pressure the occupation number of the f band gradually changes from 14 to 13 per atom, but does not go any further. He interprets the resistivity as due to resonance of conduction electrons at the Fermi surface with virtual 4f states. This is not, in his view, the same as transitions from the conduction band to the 4f band, which must also occur, but a consequence of spin disorder. He considers that strong resonance, accompanied by large phase shift, will occur for one spin direction rather than the other, or differently for the two spin directions, so that the metal behaves like a totally disordered alloy.

The main interest of this phenomenon from the point of view of this review, however, is that in the pressure range 0–60 000 atmospheres there must be a Fermi surface in the f band, but on reaching 13 electrons per atom further increase of pressure does *not* cause a drop below 13. Hubbard's criterion (§ 4.2) for splitting ($\Delta/U < 1$) is clearly satisfied here, as we should expect, because the 4f band-width Δ is probably a few hundredths of an electron volt. Our assumption throughout this article is that it is not for the transition metals. The matter is discussed further in the next section.

§ 15. X-RAY ABSORPTION

It has long been known that the L_{III} x-ray absorption of many transition metals shows a strong maximum (a 'white line' in the transmission) at the absorption edge, due to transition from the initial 2p level to the vacant states in the 3d band. Some early references are given in Mott and Jones

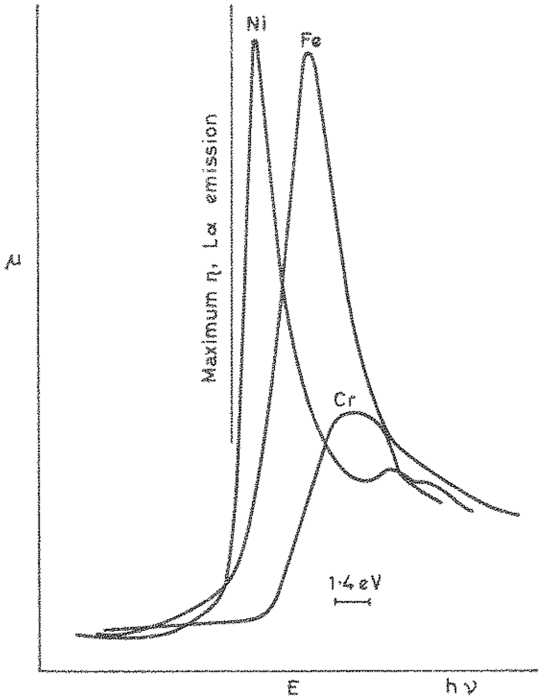
(1936). Figure 63 shows some recent results due to Bonnelle† on the L_{III} edge of nickel, iron and cobalt.

We shall in this article discuss two points about these results; these are:

(*a*) The fact that the line appears sharper for nickel than for iron, and much sharper than for chromium (fig. 63).

(*b*) The line appears *at* the edge and not below it, as it would if an exciton state were formed.

Fig. 63



X-ray absorption coefficient μ of chromium, iron and nickel, plotted on an energy scale such that the maximum of the emission line is the same for all three metals.

The theory of x-ray absorption in solids has been discussed particularly by Mott (1949) and Friedel (1954). The point to emphasize is that after ejection the electron moves in the field of the lattice and in that of the (screened) positive charge left behind in the inner shell. This can have two effects.

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† I am indebted to Mme C. Bonnelle of Professor Cauchois' laboratory for making this curve available.

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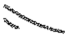

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(*a*) It *may* produce bound states below the bottom of the conduction band ; in non-metals it certainly will, and the absorption spectrum then consists of a series of lines leading to a series limit; but in metals the screening by the conduction electrons is normally so great that this does not occur (Mott 1949). However there is no reason why this should be so in all cases.

(*b*) It will certainly affect the transition probabilities, because the wave function ψ_k of the final state will be changed by the screened positive charge on the inner shell.

In the light of these considerations we can understand, in a purely qualitative way, the difference between nickel, iron and chromium shown in fig. 63. For a *sharp* maximum in the absorption, it is necessary that the positive charge should be very effectively screened and provide little perturbation of the final wave function ψ_k. Only then will ψ_k within the absorbing atom be d-like in the small range of energies occupied by the vacant d states of the matrix (say 0·4 ev in nickel, 1·5 ev in iron perhaps rather more in chromium). Now we have seen that when impurities of different valency are introduced into nickel, d-screening results, while s-screening is the rule in iron, and d-screening may well be closer than s-screening. In chromium with its low density of states, the screening radius should be considerably greater than in nickel or iron. We think it probable that the difference in the absorption line is due rather to this, rather than to any difference in the range of energies occupied by the vacancy d states, which are probably not as big as those observed in fig. 63.

We turn now to the fact that the line is *at* the edge. In the rare earths this is not so, even in ytterbium where as we have seen there is a mixture of ions in the states $4f^{13}$ (about 1%) and $4f^{14}$. Stewardson has found in this metal a weak absorption line corresponding to the transition $3d \rightarrow 4f$ (i.e. M_V) at an energy of 15 ± 1 ev below the absorption edge†. This result seems to us very relevant to the question discussed in §§ 4.2 and 5, namely whether the correlation energy U is large or small compared with the band width Δ. In this case U will be the repulsive energy of two holes in the 4f shell. In the rare earths we can hardly doubt that $U/\Delta \gg 1$; in the transition metals, if U is screened by s electrons it is not yet certain.

The fact that in ytterbium one has a mixture of *two* states $4f^{13}$ and $4f^{14}$ does not of course mean that $U/\Delta \gtrsim 1$; it means that, taking into account screening by the conduction electrons, the energy difference between ions in the states $4f^{13}$ and $4f^{14}$ is comparable with the binding energy of the

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† I am grateful to Professor Stewardson for informing me of these results prior to publication ; they are expected to appear in the *Proceedings of the Physical Society*. The line is at the same frequency as in the oxide, and might conceivably be due to contamination. Professor Stewardson does not believe this to be so, but even if it were, the true line which must be there should be at approximately the same frequency as for an ion in the state $4f^{13}$ in the oxide. The important point is that the energy of the transition is 15 ev below the edge.

metal, so that the number of conduction electrons (5d and 6s) can take the value, normally non-integral, for which the total energy of the metal is a minimum. But it would be very surprising, in view of the very narrow 4f band, if *two* f holes could come into one ion, i.e. if $4f^{12}$ existed in the metal. This will not occur if $U/\Delta \gg 1$.

If this is so, let us consider the absorption process. An electron jumps from the 3d level in an ion into the state $4f^{13}$, leaving that ion in the state $3d^9\,4f^{14}$. The energy interval between the absorption line and the absorption edge represents that required to take this electron away from the hole, leaving an ion in the state $3d^9\,4f^{13}$. The screening of this must be similar to that for an ion in the state $3d^{10}\,4f^{12}$, and the fact that the absorption line *is* displaced by about 15 ev from the edge shows that it does cost this amount of energy to form this ion, and that U is of this order of magnitude.

Now let us contrast the situation in nickel. The absorption process, taking place say in an ion in the initial state $2p^6\,3d^9$, leaves an ion in the state $2p^5\,3d^{10}$. Since the process produces a line *at* the absorption edge, the process costs the same energy as to take an electron to the Fermi surface, leaving a screened ion in the state $2p^5\,3d^9$. The energy released by the s electrons in screening this ion must be about the same as that for an ion in the state $2p^6\,3d^8$. In other words, it follows that the energy U required to form an ion in nickel by bringing two holes into one ion *is* comparable with or less than the band width. If it were, say, 10 ev, there should be an exciton line 10 ev below the edge.

We believe, therefore, that the existence of these absorption maxima which occur at the edge in nickel and in other transition metals does give evidence in favour of a small value of U/Δ for such states as $3d^8$ in nickel.

On the other hand in insulators containing the nickel $3d^8$ ion one would in all cases expect a strong absorption line below the series limit. The L_{II} and L_{III} absorption of nickel oxide has recently been observed by[†] Bonnelle and Jørgensen and both show a splitting of the line, which these authors, correctly in our view, attribute to an effect of this kind.

ACKNOWLEDGMENTS

The author would like to express his indebtedness to many colleagues with whom he has discussed the subject matter of this article, particularly P. A. Beck, B. R. Coles, J. Friedel, V. Heine, J. Hubbard, W. M. Lomer, W. Marshall, M. Shimizu, E. P. Wohlfarth.

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[†] C. Bonnelle and K. Jørgensen, " Influence de l'operateur bielectronique sur les transitions 2p–3d dans l'oxyde de nickel ". I am grateful to these thors for showing me their results prior to publication.

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