Electrons in Transition Metals

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CONTENTS

§ 1. The Purpose of the Article

The aim of this article is to summarize our present knowledge of the band structure of the transition metals and of its effect on certain physical properties, in particular on ferromagnetism and electrical conductivity. The article will deal also with the properties of alloys in which the transition metal is a major constituent, but not in any detail with the properties of

dilute solutions of transition metals in other metals. Particular attention will be paid to the contrasting behaviour of nickel and iron, both as regards their magnetic behaviour and their alloys with non-transition metals, about which some new suggestions are made.

§ 2. Concepts used in the Article

In all discussions we shall hope to make clear whether we are discussing different models that can be used, for instance in the one-electron approximation, or different physical states of the metal as represented by an exact many-electron wave function.

As is usual in the electron theory of metals, we shall start with the itinerant electron model, which was first used for transition metals by Slater (1936), Stoner (1936) and the author (1935). In this model Bloch wave functions $\psi_k(xyz)$ are set up, which have the form:

$$\psi_k = u_k(xyz)\exp[i(\mathbf{kr})],$$

the function $u_k(xyz)$ being periodic with the period of the lattice. The functions ψ_k are solutions of a one-electron Schrödinger equation:

$$\nabla^2\psi_k + \frac{2m}{\hbar^2}(E_k - V)\psi_k = 0,$$

where V is a periodic potential. States $\mathbf{k}$ for which E_k lies below a limiting Fermi energy E_F are occupied; the surface in k-space separating occupied and unoccupied states is called the Fermi surface in the one-electron approximation.

To form an approximate many-electron wave function for the whole system, it is necessary to write down in the Hartree–Fock approximation a Slater determinant Ψ', made up from the wave functions ψ_k of occupied states. To determine which states are occupied in the Hartree–Fock approximation, one ought to minimize the energy integral $\int \Psi'^* H \Psi' dq$, where q stands for all the spatial and spin coordinates of the electrons. To so do may lead to a different Fermi surface from that obtained by equating parameters E_k to a constant value, since in the Hartree–Fock equation the energy is not a sum of the parameters E_k.

To obtain a better wave function than the Slater determinant, the effects of interaction between electrons must be introduced, and in particular the correlation between the positions of electrons with opposite spins. It is not the purpose of this report to discuss either the significance of the Fermi surface under these conditions, or the way it is changed by electron interaction or by interaction with phonons†. We shall assume that in terms of

† For phonons it is known that in normal metals a considerable change in effective mass may result (Quinn 1960). We have at present no information about transition metals.

an exact many-electron wave function, a sharp surface in k-space exists, which separates electron-like from hole-like excitations, and that its properties are similar to those obtained on the one-electron approximation usual in band theory calculations.

The Fermi surface will lie in one or more Brillouin zones. Probably it is only for the alkali and noble metals that the Fermi surface lies in a single zone. By definition the transition metals have a Fermi surface lying in at least two zones; in some of them, for instance palladium, it is probably a good approximation to say that, near the Fermi surface, the wave functions of states in one zone must be largely derived from (in this case) 4d atomic functions and in the other from 5s, 5p, 5d, etc. For all transition metals parts of the Fermi surface will lie in zones which, when the lattice parameter is increased indefinitely, tend to atomic states with principal quantum numbers ns and (n − 1)d (n = 4 for the first long period, etc.). Thus copper is not a transition metal because much evidence shows that the 3d zones are full, so that there is no Fermi surface in these zones. There is indirect evidence from the electrical conductivity that some of the alkali metals may become transition metals in this sense under pressure (§ 14.8).

It is only for the transition metals and rare earths, among the metals, that ferromagnetism and antiferromagnetism occur. In ferromagnetic metals below the Curie temperature the numbers of electrons with spins parallel and antiparallel to a fixed direction are not the same, so that there are two differing Fermi surfaces, one for each spin direction.

Turning now to models or approximations, when considering the electron gas in normal metals (Na, Mg, Zn, perhaps Cu), a treatment that has been applied with success in the last few years is as follows. One may consider first the electron gas in the field of a uniform distribution of positive charge (jellium). The interaction between electrons can be considered by perturbation theory only in the case of high densities, so in general the consequent correlation energy must be determined by other methods, on which most work has been done. But however the correlation is treated, it has recently proved very fruitful to treat the periodic potential as a *small* pseudopotential, which can be handled by the methods of perturbation theory, and thus to obtain useful results about band structure, resistivities of solids and liquids and other properties (Johnson and March 1963, Bradley *et al.* (1962). Harrison (1963), too, in his use of the OPW method to determine elastic constants and crystal structure of polyvalent metals, treats matrix elements of the type $\langle \mathbf{k} | V | \mathbf{k}' \rangle$ between OPW functions as small, which comes to the same thing as treating the potential as small. A particularly useful development is that, in distortions in which the volume is unchanged, one can treat the interaction between atoms as the interaction between the oscillating potentials produced in the electron gas by each ion. For applications of this method to liquid metals see the paper by Johnson and March mentioned above, to elastic constants, Harrison (1963) and to alloys, Daniel (1962).

A treatment of this kind is impossible for the d electrons of transition metals. The wave functions must be determined either by the method of tight binding, by cellular methods or by some method which does not treat the atomic potential as a perturbation; also the correlation, which may be as or more important than in a normal electron gas, must be estimated by any suitable method. There is no approach at present available as powerful as the pseudopotential combined with perturbation theory has proved to be for non-transition metals.

It is in the light of these remarks that we must view the contrast sometimes made in the literature between the itinerant electron method and the Van Vleck model (Van Vleck 1953). The latter is, in our view, simply a way of putting correlation into the itinerant description of a d band. A clear-cut example is nickel, discussed by Van Vleck. This metal is believed to have from 0·5 to 0·6 holes per atom in the d bands. Thus, if a many-electron atom is made up of atomic wave functions, the d shells of some of the atoms will be in the state $3d^{10}$, some in $3d^9$ and perhaps† some in $3d^8$, since the ground state of the free atom has the configuration $3d^84s^2$. If we limit ourselves to the first two, we might start with a model in which the $3d^9$ state was localized on fixed atoms, but since the $3d^9$ state can move freely through the lattice, a band of occupied and unoccupied energy levels and a Fermi limit results from this kind of model too. We shall not discuss the Van Vleck model further in this article, though much of our discussion of the origin of ferromagnetism uses the concepts that he had made familiar.

The kind of localization that occurs in the Van Vleck model is not the same as that which can occur when the number of electrons per atomic state is integral. Wigner (1938) was the first to give arguments to suggest that an electron gas of sufficiently low density would 'crystallize' into an array of localized electrons. Mott, in a series of papers (1949, 1958, 1961; see also Anderson 1963 a), has given arguments to show that an array of atoms in its ground state, each atom with an integral number of electrons, would, as the density decreases, go over sharply from a metallic to a non-conducting state with no Fermi surface. Since the latter state is non-conducting it is reasonable to call the state of each electron 'localized'. In Mott's papers it is suggested that these states, if not ferromagnetic, must be antiferromagnetic with the period of the lattice, and in this case, as Slater (1951) has shown, that the state may be described by Bloch-type wave functions different for each spin direction, this being in a one-electron model an alternative description to that using localized functions, but one which leads to the same Slater determinant for the many-electron function. However, in one dimension it is known that theory predicts no antiferromagnetism, and Marshall (1955) has shown that in three dimensions antiferromagnetism occurs probably only if the spin is greater than a Bohr magneton, so it is unlikely that the absence of conductivity is linked to antiferromagnetism. Moreover the absence of conductivity in non-metallic antiferromagnetics

† See § 4.2 for a discussion of this point.

like NiO persists above the Néel temperature. It is difficult therefore to escape from the need to describe non-conducting states by localized wave functions in certain cases. The problem has recently been considered further by Hubbard (1963, 1964 a, b) and by Kohn (1964). Kohn gives a proof, perhaps not quite rigorous because of doubts about the convergence of the perturbation series used, that, for an array of one-electron atoms separated by a sufficiently large distance, the many-electron wave functions $\Psi(\mathbf{r}_1 \ldots \mathbf{r}_N)$ for low-lying states (i.e. those with and without spin waves if the state is magnetic), have the following property; if all the coordinates except one ($\mathbf{r}_n$) are held constant and $\mathbf{r}_n$ is displaced round a circular wire, Ψ falls off exponentially as $\exp(-N\beta)$, where β is a constant of order given by

$$\beta \sim \text{overlap energy integral/excitation energy}$$

and N is the number of atoms traversed. Under these conditions, in the limit of *large* values of N, he shows that there can be no current. There will of course be no Fermi surface either.

Hubbard treats a narrow band, either of s or d character, and asks whether the band of excitations will split into two (or for d states, ten) sub-bands under the influence of the electrostatic repulsion U between two electrons on the same atom. If Δ is the band width, he concludes that if U/Δ is large enough, greater than about 0·8, it will. The conclusions are therefore similar; if the splitting has occurred the wave functions are localized in the sense that the electrons cannot carry a current and there is no Fermi surface. This holds, of course, only if the number of electrons per atom is integral.

It is appropriate to treat the 4f electrons of rare earth metals by many-electron wave functions made up of localized states. In the many-electron wave functions for the whole metal, Kohn's criterion cannot be used since one cannot take a coordinate $\mathbf{r}_n$ and say that it refers to the 4f and not to the conduction electrons; but to ask whether there is a Fermi surface in a Brillouin zone of mainly 4f character is a question with physical meaning. Usually there is not, though ytterbium appears to be an exception, a non-integral number of electrons and a Fermi surface occurring in the 4f band. There are marked effects for instance on the conductivity. These phenomena are reviewed by Rocher (1962) and in § 14.9 of this article.

In the d band of nickel and cobalt the number of electrons is non-integral and there is therefore certainly a Fermi surface. For iron, where the number of magnetic carriers was thought to be integral or nearly so, it was suggested by Mott and Stevens (1957) that the localized model might be appropriate, but the weight of the evidence now appears against it and it seems highly probable that the magnetic electrons are in unfilled bands which contribute to the Fermi surface. The evidence for this statement will be discussed in this article.

Other forms of localization which will be mentioned are the localized states at impurity atoms (§ 7) and localized spins which occur in magnetic

materials even when the existence of unfilled bands and a Fermi surface makes the use of the itinerant electron model appropriate (Friedel *et al.* 1961).

§ 3. The Expected Form of the d Bands

The present author (1935) was the first to propose a band structure for the transition metals of the form shown in fig. 1, with a high density of states in a d band (3d for the first long period), and an s band (4s in this case) with low density of states overlapping it. As was realized at the time (cf. Jones *et al.* 1934), and as more recent calculations have shown very clearly, it is not in principle possible to separate Brillouin zones or curves plotting energy against wave-number into zones or bands derived wholly from s, p or d functions, even in the approximation of tight binding; hybridization is bound to occur. Figure 2 shows schematically the plots of E against k for a 4s band (conduction band) and a 3d band, as they might be obtained by the tight binding or any other method in which the wave functions for the conduction band are expansions of atomic functions of symmetry 4s, 4p, 4d, but orthogonal to 3d. Only along certain special lines of symmetry in k-space can the two curves cross; along any other lines hybridization will occur, as shown by the dashed lines. Thus within any Brillouin zone there may be regions where the wave functions are mainly d-like and the density of states low. This may occur, too, on different regions of the Fermi surface†, which is then likely to have the form shown in fig. 13 of this paper.

If however for all directions in k-space the Fermi surface cuts the same 4s-like branch and the same 3d-like branch, as shown by the dotted lines in fig. 2 (*a*) and (*b*), then the Fermi surface may lie in two (or more) Brillouin zones, one of which is 4s-like and one (or more) 3d-like. This is the case in nickel according to the model of Phillips (1964), and according to the argument of this article for the spin-up electrons in iron. The simple model of fig. 1 is then quite satisfactory.

Some of the most complete and accurate calculations of the band structures of the transition metals in the first long period are those carried out by Professor Slater's school at the Massachusetts Institute of Technology, using the augmented plane wave method‡. In this method hybridization is automatically included. Other authors (Fletcher 1952, Belding 1959, Asdente and Friedel 1961, 1962, Yamashita *et al.* 1963) have used the tight binding method for the 3d electrons, without introducing hybridization with 4s. This approach, treating the 3d electrons separately, remains useful particularly for the consideration of ferromagnetism. The reason is that it may be quite a good approximation in a ferromagnetic metal to treat the unhybridized d bands for the two spin directions as having the same shape, but separated by an electron volt or so along the energy axis; but it would not always be a good approximation to shift the 4s bands by

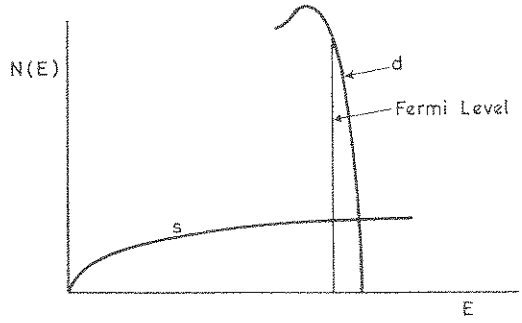
† Compare Lomer's (1962) paper on chromium, and Ehrenreich *et al.* (1963) on nickel.

‡ For references see Mattheiss (1964).

the same amount. Hybridization between 3d and 4s ought to be done separately for the two spin directions.

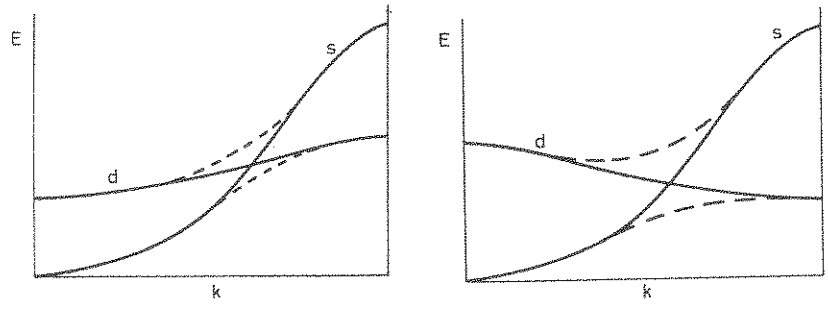
Another application in which it is still convenient to treat the ns and the (n − 1)d bands separately is the theory of alloys, in which the extra electrons added when, for instance, nickel is alloyed with copper are pictured as "going into the d band of nickel". In this review we shall continue to use this expression rather than to say "the electrons go into states which are predominantly s- or d-like".

Fig. 1



Early model of the density of states $N(E)$ in a paramagnetic transition metal, with a d band of high density of states overlapping an s band.

Fig. 2

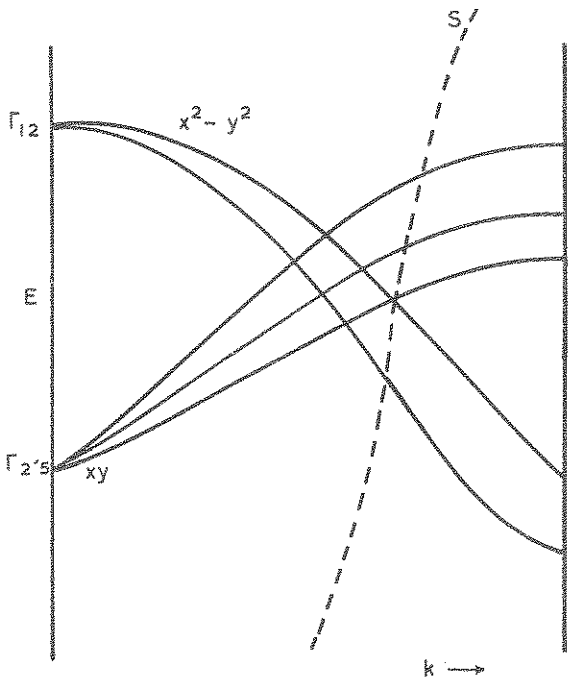


s and d bands in a transition or noble metal, with the energy of a state E plotted against wave number k, and the dotted line showing hybridization. (*a*) and (*b*) show different forms that occur.

We shall next discuss the form of the d band for the two most important structures, face- and body-centred cubic, first of all without s–d hybridization. The first thing to note about many calculations and experimental observations of the density of states $N(E)$ as a function of energy, or as a function of the number of electrons per atom (e/a), is that there is a deep

minimum in the middle of the range. This occurs, according to the experiments of Beck (cf. § 11) at the University of Illinois on body-centred cubic alloys, for values of e/a between 5·7 and 6, and thus just before chromium for the first long period and in an analogous position for the others. It is important to understand in general terms why this should be so.

Fig. 3



Schematic plot of d bands in a metal formed from atomic functions of symmetry xy, x^2–y^2 without hybridization between them. The dotted line shows the s band (Evetts 1962).

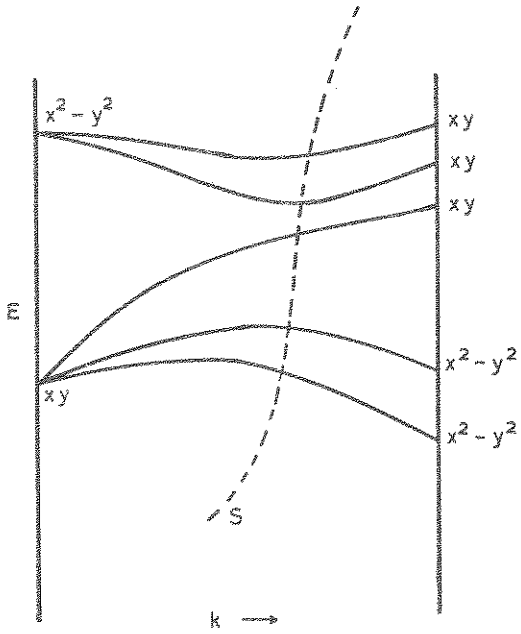
We first emphasize that the calculated 'd band' (unhybridized with s) actually consists of five overlapping bands with degeneracies at certain points. Examination of calculations using the method of tight binding (Fletcher 1952, Asdente and Friedel 1961, 1962) enables one to see that these bands are formed as follows. The five d wave functions of the free atom consist of three with symmetry of the type yx, zx, xy and two with symmetry of the type x^2–y^2, y^2–z^2. One can, formally, set up tight binding wave functions without allowing hybridization between them†. If one

† This was done by Jones and Mott (1937), whose estimates of the form of the d band do not include this hybridization.

does this, then at the centre of the zone for body- or face-centred cubics there are *three* degenerate bonding wave functions (i.e. with no nodes between the atoms) formed from the xy functions, and *two* antibonding functions formed from x^2-y^2, with nodes between the atoms. Thus if one plots E against k in the Brillouin zone, starting at the centre and going in any direction, one expects curves somewhat as sketched in fig. 3 by the full lines. If now one allows hybridization between functions of symmetry xy and x^2-y^2, etc., one finds the following pattern, which is shown in fig. 4.

(*a*) The two lowest bands are made up of bonding functions with xy symmetry at the centres of the zones and of bonding functions with x^2-y^2 symmetry at the boundaries.

Fig. 4



d bands after allowing for hybridization between functions of symmetry xy, x^2-y^2. The s band is shown separately (Evetts 1962).

(*b*) The two highest bands are made up of antibonding x^2-y^2 functions at the centre, antibonding xy functions at the boundaries.

(*c*) The last band is of bonding type with xy symmetry at the centre of the zone and antibonding with xy symmetry at the boundaries, and may thus be broader than the others. A general pattern suggests itself, therefore, of two narrow bonding bands, with room for four electrons, two narrow antibonding bands and a broad band connecting them. One would thus

obtain a density of states curve with a minimum in the middle. It is admitted that all these considerations are qualitative, and depend on the actual parameters, but they do give some indication of the reason for the minimum which is such a marked feature of many experimental results and computations. Whether in any metal a minimum occurs will depend on the separation ΔW in energy of the points Γ_{12} and $\Gamma_{2'5}$ in fig. 3, compared with the width of the bands. We shall give some evidence later that the minimum does not occur for f.c.c. metals.

A further point of interest, particularly for the ferromagnetic metals and their alloys, is the nature of the highest d states. According to Fletcher (1952) and also Phillips (1964), for nickel (f.c.c.) it is at the centre of the (200) faces. The energy is degenerate there, but of the two zones one has much higher density than the other, the density of states being as in fig. 5. The tops of the two zones are separated by spin–orbit interaction: this is discussed by Phillips (1964) who predicts a small separation (0·07 ev) for nickel and in detail by Friedel *et al.* (1964).

Figure 6 shows the separate d bands calculated by the tight binding method for (body-centred) chromium by Asdente† and Friedel (1961, 1962). These curves show very well a broad central band. These bands also show a degeneracy at the highest point, which in this case is at one of the corners of the zone.

When one comes to consider the hybridization of the s and d bands and the resulting form of the sub-bands, there will of course be six sub-bands. The lowest is s-like at the bottom, d-like at the top; the highest is d-like at the bottom and s-like at the top. The intermediate bands will be rather thoroughly mixed up. Figure 7 shows a freehand sketch of the way the combination could occur.

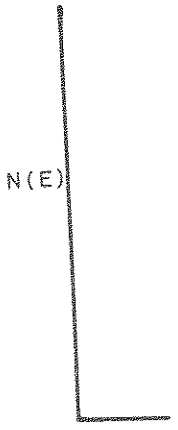
Figure 8 shows schematically the form of the density of states in the six sub-bands; the curves are drawn freehand using the plots of E against k shown in fig. 7.

Figures 9 (*a*) and 9 (*b*) show the total density of states for iron, calculated by Cornwell and Wohlfarth (1962) and by Wohlfarth and Cornwell (1961) from Wood's (1960) calculations of E as a function of k. They differ in the number of points in the Brillouin zone for which calculations of E have been made. The existence or otherwise of these sharp peaks is a matter of considerable interest‡, to which reference will be made in this article.

The minimum in the 3d band, or rather in the 3d band hybridized with 4s, which the calculations show for the body-centred structure, has, as we shall show, a marked effect on the physical properties of body-centred alloys. The observations of specific heat and other properties suggest a more marked minimum than the calculations give (§ 11). On the other hand, for f.c.c. alloys we know of no convincing evidence for the existence

† I am grateful to Miss Asdente for showing me the unpublished results she had obtained on the separate forms of the sub-bands.

‡ The general theory of kinks in the $N(E)$ curve has been discussed by Van Hove (1953) for phonon spectra and by Phillips (1956).



Density of states f
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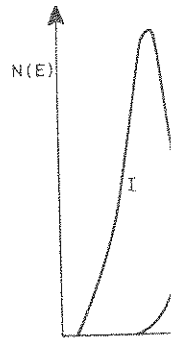
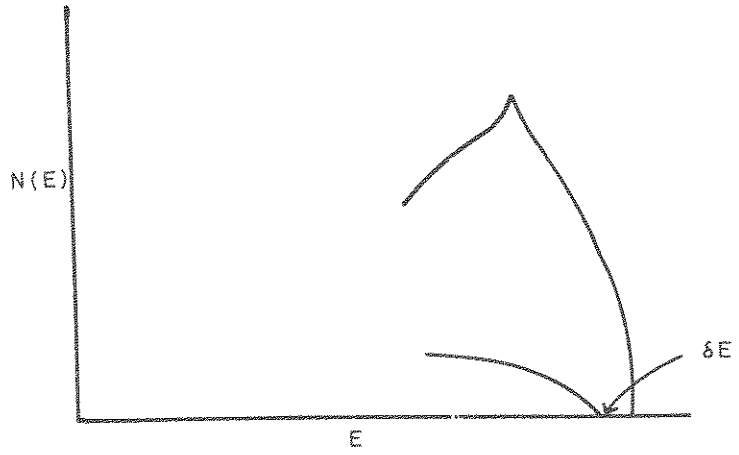


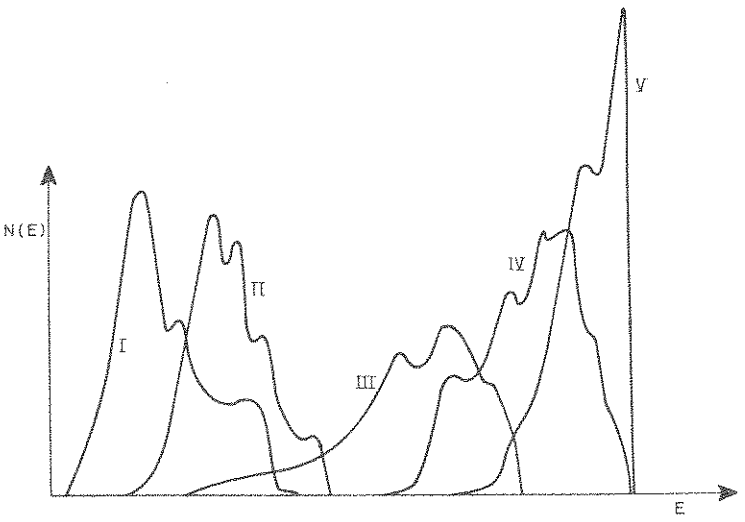
Density of states f

Fig. 5



Density of states for two d sub-bands at the top of the d band for nickel (schematic). A small separation δE is to be expected due to spin–orbit interaction.

Fig. 6

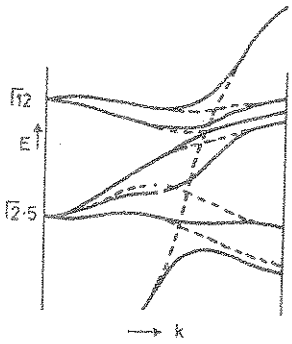


Density of states for the five 3d sub-bands of chromium calculated by Asdente and Friedel (1961, 1962).

of such a minimum, and the most recent calculations for copper do not show one (Burdick 1963). Burdick's $N(E)$ curve † is shown in fig. 10.

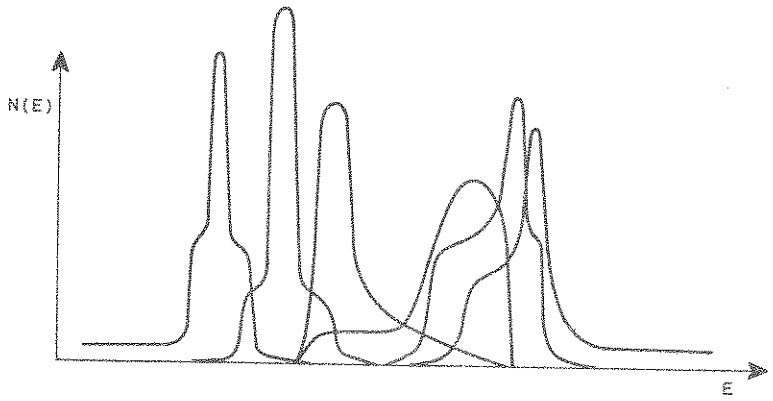
Wood (1960) has emphasized that wave functions of electrons in the lower half of the d band, of bonding type, have a reasonably large amplitude between the atoms; those in the upper half, for which there are usually nodes between the atoms and which are therefore of antibonding type, have wave functions much more like those of free atoms. A sketch is given in fig. 11.

Fig. 7



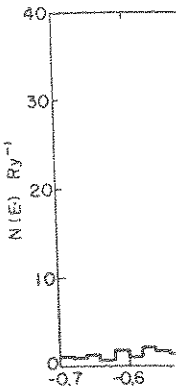
Showing schematically hybridization of s and d bands (Evetts 1962).

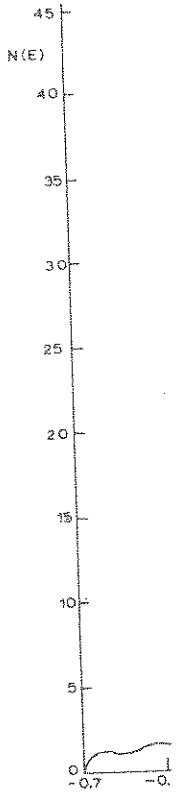
Fig. 8



Showing density of states, of sub-bands deduced from fig. 7.

† Recently Spicer and Berglund (1964) have made observations of photo-emission from copper to determine the form and width of density of states of the d band in this metal, finding a width (3·5 ev) and form very similar to that calculated by Burdick.





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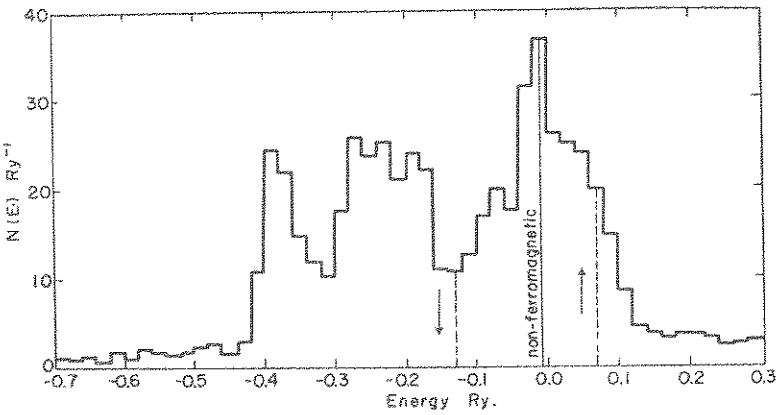

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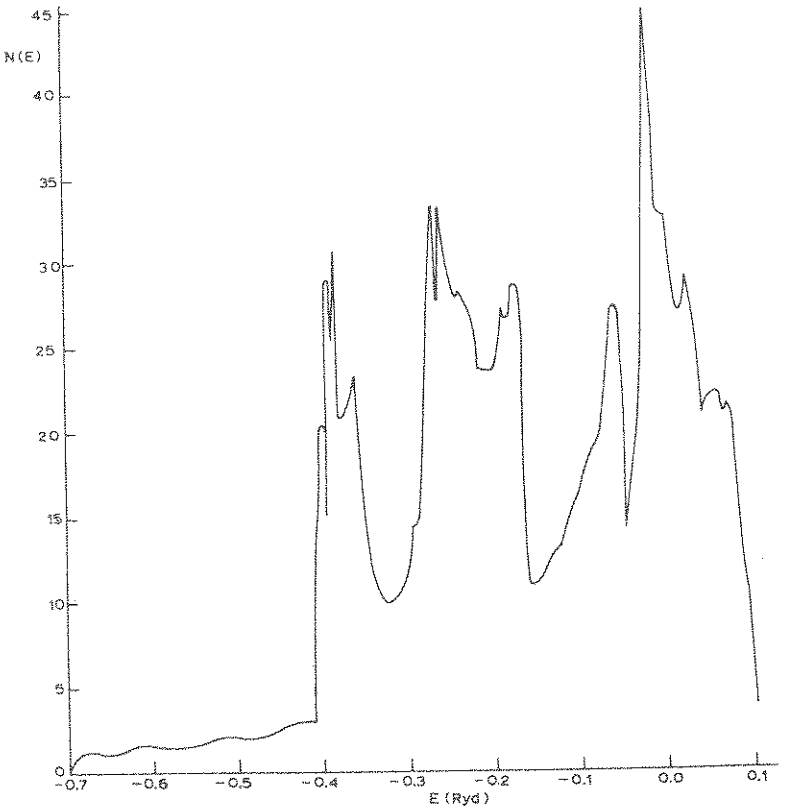


(*b*)

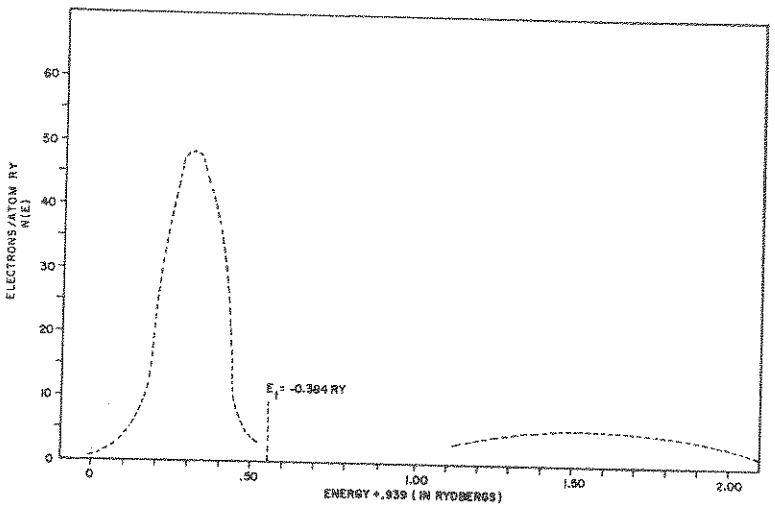
(*a*) Density of states of body-centred iron, calculated by Cornwell and Wohlfarth (1962) from Wood's results, and showing Fermi energies for spin-up, spin-down and for no magnetic moment. (*b*) density of states for iron calculated by Wohlfarth and Cornwell (1961) by another method, showing explicitly the sharp Van Hove peaks.

§ 4. Corrections to the Form of the d Bands

4.1. *Some Effects of* s–d *Hybridization*

The calculations that have been made by the augmented plane wave and other methods of the band forms for copper and for the transition metals show that, while it is usually possible to see which part of the plot of E against k is the original s band, the effect of hybridization is substantial. Figure 12, taken from Segall's (1961) paper for copper, shows the extent of this hybridization. Near the Fermi surface in copper, therefore, the values of E for a given value of k are considerably *raised* by the admixture of 3d. In certain directions however, notably ⟨111⟩, symmetry properties prevent this admixture between 4s and the higher 3d branches, as the figure shows; the two curves cross and therefore in these directions the energies are not raised; of course at the zone boundaries they will not be raised anyhow.

Fig. 10

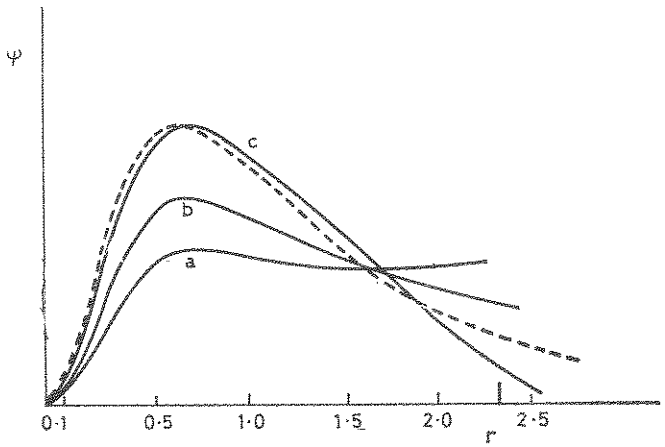


Density of states for copper, calculated by Burdick (1963). Not all the s band is shown, and the s and d bands overlap in the usual way.

The raising of the energies at points other than at the zone boundaries and in the ⟨111⟩ directions certainly contributes to the distortion of the Fermi surface which has as its consequence the touching of the (111) faces of the Brillouin zone by the Fermi surface in copper (Pippard 1957) and the other noble metals (Shoenberg 1960, 1962), since electrons from other regions near the Fermi surface find states of lower energy near the ⟨111⟩ directions. The raising may be even greater in nickel or palladium since the d band is higher, which may lead to the Fermi surface of the conduction band even in nickel (with 0·5 electrons) touching the zone boundary (cf. Phillips 1964 and § 8).

Hybridization between s and d functions is likely in some metals to lead to a situation in which parts of the Fermi surface, in one Brillouin zone, are s-like in some directions and d-like in others. This occurs for instance on the Fermi surface for chromium which Lomer (1962) has calculated using modifications of Wood's wave functions for iron. Figure 13 shows schematically part of the Fermi surface as estimated by Lomer†.

Fig. 11



Plot of radial wave functions ψ for d band electrons in iron (Wood 1960), in atomic units. The curve marked c is for the highest state in the d band, the others (a, b) for decreasing values of the energy parameters. The dotted line is for the free atom. It will be seen that for the states of lower energy there is only a small dip in the values of ψ between atoms; for the state of highest energy, on the other hand, where there is a zero between atoms there is little difference between the wave function in the band and that of the free atom, which is shown by the dotted line.

The s–d hybridization of occupied states will certainly contribute to the cohesion of copper, if as Segall's calculations show some hybridized states are empty. It is possible that this hybridization is sufficient to account for the well-known discrepancy between the observed cohesive energy of the noble metals and the contribution of the s electrons calculated by the Wigner–Seitz method (Kambe 1955; for a review and some other suggestions cf. Mott 1962). It may also account for the cohesive properties of the transition metals.

In spite of the probably rather large effect of s–d hybridization, we shall in this article suppose that it is a useful first approximation to calculate s

† For molybdenum detailed calculations by Altmann (1964) also confirm this form.

and d bands separately; Lomer (1962), Phillips (1964) stress this. One can then shift the d band—or that part of it which contains ferromagnetic electrons—up and down on the energy scale as the magnetic moment varies†.

4.2. *Some Effects of Correlation in the d Band*

At the time of writing, there is considerable uncertainty about the effect of correlation between electrons in the d and s bands, and the question is of major importance for our interpretation of many phenomena, particularly ferromagnetism. The point at issue is the following. There must enter into any theory of the energy of a transition metal in the atomic or metallic state an integral of the type:

$$U = \int \psi_n^*(\mathbf{r}_1)\,\psi_{n'}^*(\mathbf{r}_2)\,(e^2/r_{12})\,\psi_n(\mathbf{r}_1)\,\psi_{n'}(\mathbf{r}_2)\,d\tau_1\,d\tau_2.$$

Here ψ_n, $\psi_{n'}$ are atomic orbitals (or in the metal Wannier orbitals) for two electrons *on the same atom*, either in the same d orbital ($n = n'$) or in different d orbitals ($n \neq n'$). In the first case the integral represents the energy of electrostatic repulsion between two electrons with antiparallel spins on the same atom, in the latter case for electrons in different orbitals with either spin direction.

As emphasized in different connections by Van Vleck (1953), Anderson (1961) and Kanamori (1963), this integral is of order 10 ev, and therefore *large compared to the band width* (*c.* 4 ev). It is sharply to be distinguished from the intra-atomic exchange energy J:

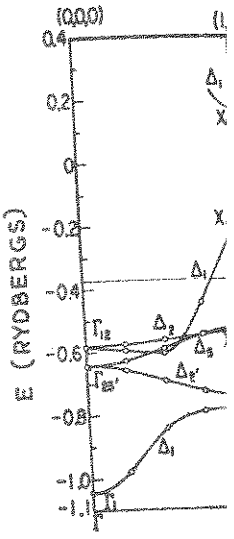
$$J = \int \psi_n^*(\mathbf{r}_1)\,\psi_{n'}^*(\mathbf{r}_2)\,(e^2/r_{12})\,\psi_n(\mathbf{r}_2)\,\psi_{n'}(\mathbf{r}_1)\,d\tau_1\,d\tau_2,$$

which is order 1 ev, and which gives the difference in the energies of two electrons in states ψ_n, $\psi_{n'}$ on the same atom, when they have their spins parallel and antiparallel, the former state lying lower (Hund's rule).

Of the published discussions of the effect of so large a value of U, Hubbard (1963, 1964 a, b) has shown most clearly that the effect of a value larger than the band width would be to split a band containing an integral number of electrons per atom into a number of sub-bands, each containing one electron per atom, and with no Fermi surface and making no contribution to the conductivity. This of course is just what does happen to d bands in most oxides; pure nickel oxide, for instance, is an insulator at low temperatures. Transition metals, on the other hand, have a non-integral number of d electrons, and this is possible because of the presence of the s electrons which can and do take up a non-integral number too. Metallic nickel, for instance, might be made up of ions in the states $3d^8$, $3d^9$ and $3d^{10}$ (Mott and Jones 1936).

Now if the effect of a large integral U is the same as it would be in the absence of the s electrons, the state $3d^8$ must be almost completely absent

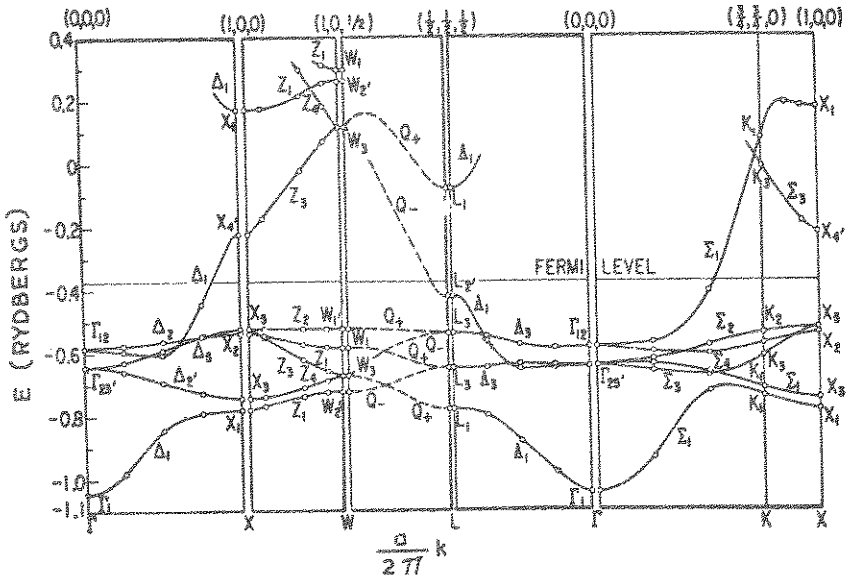
† Phillips and Mattheiss (1963) find that for nickel the shift ΔE_s for the s band is comparable with that for the d band.



The calculated ene
zone (Segall
number k.

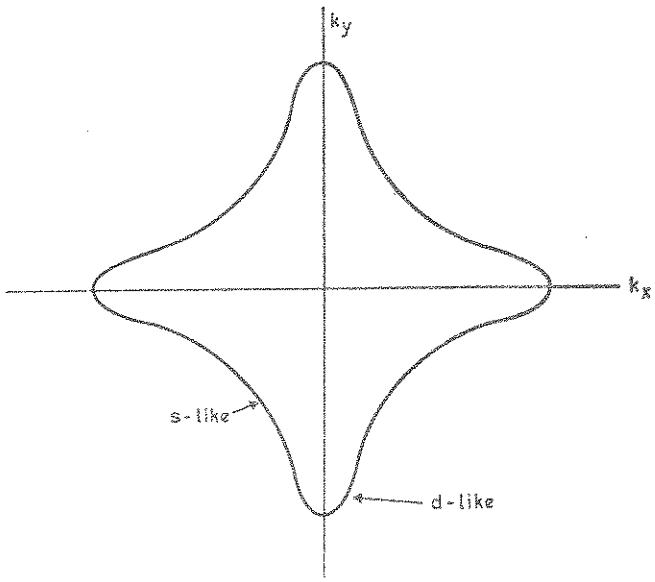
Part of

Fig. 12



The calculated energy bands for copper along various axes in the Brillouin zone (Segall 1961). The curves show energy as a function of wave number k.

Fig. 13



Part of Fermi surface for chromium (schematic ; Lomer 1962).

because of the large repulsion U between the holes. Kanamori (1963) treats nickel on the assumption that this is so, comparing the situation with nuclear matter or liquid helium. Other authors, whose work is reviewed in the next section, ascribe ferromagnetism in nickel to the intra-atomic exchange integral J within ions in the state $3d^8$. Whether U is greater or less than the band width Δ is therefore a matter of considerable importance.

If U is to be brought down to a value of (say) 1 ev, when it can have little effect, this can only happen through the screening action of the s electrons. Kanamori (1963) and in a rather different connection Anderson (1961) (see § 7) state rather categorically that it cannot. Herring (1960; see also footnote on p. 223 to Van Vleck 1953) has taken the opposite point of view. Although the matter cannot be considered as settled and there is no conclusive evidence one way or the other†, we think it probable that the former authors are wrong. Our reasons are as follows.

In nickel we know that ions in the states $3d^{10}$ and $3d^9$ are present, although the energy required to take an electron from a nickel atom in the state $3d^{10}$ to form an ion in the state $3d^9$ is about 6 ev. That the repulsive energy U does not prevent this must be because of s-screening. It is important to remember that in the metal each atom tends to remain neutral, so there will be very few s-electrons on the ions in state $3d^{10}$, but about one per atom (not 0·5) on the ions in the state $3d^9$. The attraction between the ions and these additional s electrons must compensate for a considerable part of the 10 ev or so of repulsive energy represented by U. If an ion is in the state $3d^8$, there will be *two* s electrons screening it, and since in the atom $3d^8\,4s^2$ is the lowest state, it would be surprising if they could not screen out most of the repulsive energy in the metal too.

The belief that s-screening cannot do this has arisen presumably because the radius of the d shell is about 0·4 Å (fig. 11), while the screening radius calculated in the conventional way for about 0·5 free electrons (e.g. Langer and Vosko 1959) gives a larger value, about 0·7 Å, so the piled-up charge round the $3d^8$ ion cannot compensate for the self-energy U. Hubbard in fact using screening by free electrons gets rid of about half the 10 ev. But the use of free electrons in this context cannot be adequate. It is characteristic of the transition metal *atoms* that the penetration of the 4s electrons into the d shell *does* lower the energy sufficiently for the states $3d^8\,4s^2$, $3d^9\,4s^1$, $3d^{10}$ in nickel or $3d^7\,4s^2$, $3d^8\,4s^1$, $3d^9$ in cobalt to lie within 1 to 2 ev of each other. We think this is probably so in the metal. The atomic cell will remain neutral and round an ion in the state $3d^8$ (in nickel) the orbitals of the *two* s electrons with antiparallel spins will both penetrate the d shell in such a way that their interaction with the nuclear charge will compensate for U.

Van Vleck 1953, in a footnote (p. 223) in which he refers to Herring's views, gives essentially this argument. We consider then that if a transition

† Except perhaps that of § 15 of this article.

metal had a single state, e.g. $3d^9\,4s^1$, isolated by a large energy interval from those of other configurations, the d band would behave like NiO with no Fermi surface; if $3d^9\,4s^1$ and $3d^{10}$ alone are close together one should get a non-integral number of d electrons, and thus a Fermi surface, but possibly with strong correlation; but that the proximity of $3d^8\,4s^2$ ensures that the correlation energy is small. But whether it is small enough to prevent U from having the effects predicted by Hubbard and Kanamori remains uncertain.

For the rare earth metals, on the other hand, a value of U even after screening very large compared with the 4f band-width certainly exists and has the expected consequences. Thus most rare earth metals have an integral number of 4f electrons per atom. The evidence that we shall review in § 14.9 suggests that ytterbium is an exception, and that the number can be varied by pressure. However, it does *not* vary smoothly through an integral value and at the integral value the Fermi surface seems to disappear, just as Hubbard's work would predict. In § 15 we shall give evidence to show that here the screened repulsion between holes *is* great enough to prevent two holes from being in the same ion.

§ 5. The Origin of Ferromagnetism

Some recent discussions are due to Herring (1960), Friedel *et al.* (1961), Ruijgrok (1963), Anderson (1963 a, b), Brooks (1963), Mattis (1963) and Kanamori (1963). On these, to a greater or less extent, the following discussion is based.

In any discussions of this problem it is convenient to distinguish between different kinds of material:

(*a*) Non-metals, for example salts and oxides of the rare earths.

(*b*) Metals (e.g. rare earths) in which the magnetic carriers are properly described by electrons in localized states in the sense of § 2, as they are in case (*a*).

(*c*) Ferromagnetism due to dilute solutions of transition metals in other metals (e.g. manganese in copper).

(*d*) Metals such as nickel, cobalt and iron in which the ferromagnetism is due to electrons in a partly filled band of strongly 3d-like character.

In case (*a*), that of non-metals, Anderson's (1963 b) recent discussion is illuminating. He first makes the case that, since these materials are non-conducting and have no Fermi surface, the magnetic carriers *must* be described by localized wave functions in the sense of the ideas put forward by the present author (1949, 1961 and by Hubbard (1963)) and described in § 2. On the other hand, these localized functions should not be the simple wave functions of the free ions, but the functions of ligand field theory which are hybridized with the 2p orbitals of the surrounding oxide ions. These hybridized orbitals extend further from the ion than the wave functions of electrons in a free ion, and thus allow overlap at large

distances. Anderson then discusses the exchange interaction J_{ij} between two localized orbitals ψ_i, ψ_j in a potential $V(r)$, which is given by:

$$J_{ij} = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_i^*\psi_j(\mathbf{r}_1)\psi_j^*\psi_i(\mathbf{r}_2) - 2\int \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)d\mathbf{r}_1 \int \psi_j^*(\mathbf{r}_2)\, V\, \psi_i(\mathbf{r}_2)\, d\mathbf{r}_2. \quad (1)$$

If the orbitals are orthogonal, the second term vanishes and J_{ij} must be positive, giving ferromagnetic interaction, since the integral is the mean value of e^2/r_{12} integrated over the charge distribution $\psi_i^*\psi_i$. If the orbitals are not orthogonal, the second term may lead to antiferromagnetic interaction†.

Anderson argues that in the sense of the Hartree–Fock approximation one must use orthogonal orbitals for electrons with parallel spins, but not for those with antiparallel spins for which the functions $\psi(\mathbf{r})\,\chi(s)$ for spatial and spin coordinates are orthogonal anyhow. Thus if the configuration is antiferromagnetic, we may assume non-orthogonal orbitals and seek to minimize the energy by forming Wannier type functions of form $\psi(\mathbf{r}-\mathbf{r}_1) + \epsilon\psi(\mathbf{r}-\mathbf{r}_2)$ and treating ϵ as an adjustable parameter. The result, a combination of exchange of type (1) and direct interaction, is the 'superexchange' energy. On the other hand, if the interaction is ferromagnetic, direct exchange between orthogonal localized orbitals is all that one has to consider. One has to ask, as for H_2, which arrangement gives the lowest energy. Ferromagnetism is likely to occur, then, if the overlap integral is small for reasons of symmetry, as for instance when a d_z^2 orbital overlaps a d_{xy} orbital, and antiferromagnetism otherwise.

In insulators the magnitude of the interaction must fall off exponentially, though its sign will in general oscillate with distance at large distances (Bloembergen and Rowland 1955).

In cases (*b*) and (*c*) the magnetic electrons are usually treated as localized, while the conduction electrons are not; case (*c*) (dilute alloys) is discussed

† There is an interesting theorem published with acknowledgments to Wigner by Lieb and Mattis (1962) stating that two electrons in their ground state in any field must have zero spin; it follows that H_2 must have zero spin for all interatomic distances. It is well known that the exchange integral between the two (non-orthogonal) atomic functions $\psi(\mathbf{r}-\mathbf{r}_1)$, $\psi(\mathbf{r}-\mathbf{r}_2)$, used in the London–Heitler approximation is negative. On the other hand one could start with two localized orthogonal orbitals of Wannier type

$$\psi(\mathbf{r}-\mathbf{r}_1) - \epsilon\psi(\mathbf{r}-\mathbf{r}_2)$$

and

$$\psi(\mathbf{r}-\mathbf{r}_2) - \epsilon\psi(\mathbf{r}-\mathbf{r}_1),$$

which would give a positive overlap integral and imply ferromagnetism. Since Wigner's theorem shows this to be wrong, the total energy corresponding to this function must clearly be higher and it thus is a less good approximation to the true wave function of the ground state. This simple example illustrates the pitfall which may arise through qualitative discussions of the sign of exchange integrals based on Wannier functions.

further in § 7; in case (*b*) (rare earths) we have given reasons in § 2 (absence of a Fermi surface in a 4f band) for considering it essential to use localized functions. Some interaction may occur through the hybridization of the 4f orbitals with the orbitals of the conduction electrons, in the same way as in salts of the rare earths with the orbitals of the anions. Brooks (1963, p. 14) gives a qualitative discussion of this, but we do not know of any quantitative work.

Undoubtedly, however, a very important part of the interaction is the oscillating term falling off as x^{-3} introduced by Ruderman and Kittel (1954), Yosida (1957), Blandin and Friedel (1959); this occurs via the conduction electrons, depends on the existence of a Fermi surface and is a consequence of exchange or other interaction between the localized magnetic carriers and the conduction electrons. The argument is as follows. Any local perturbation applied to the wave functions of an electron gas, which produces a phase shift in the Bloch functions ψ_k, including those at the Fermi surface, will produce an oscillating variation of charge density which falls off with distance r from the perturbation inversely as some power of r. If the perturbation has a moment, then the charge densities in these oscillations for conduction electrons with the two spin directions will differ from each other. If the moment is due to electrons (not nuclei), the case is that treated by Yosida (1957) and investigated in greater detail by Wolff (1960), in which the phase shift is due to exchange interaction. This gives rise to an interaction energy which falls off with distance R between two elementary magnets as $F(2k_{\mathrm{F}}R)$, where

$$F(x) = (x\cos x - \sin x)/x^3, \tag{2}$$

and where k_{F} is the wave number at the Fermi surface. Since this function oscillates, the interaction between a pair of elementary magnets may be ferromagnetic or antiferromagnetic.

Case (*d*), which includes iron, cobalt and nickel and their alloys, forms the main subject of this article. Here the carriers are electrons in unfilled d bands in which there is a Fermi surface, the saturation moment per atom in units of μ_{B} is normally non-integral and the contribution of orbital momentum is small.

It is in this field that the greatest uncertainty lies. There is first the question of the magnitude of the correlation energy U. This has been discussed in § 4.2. Treatments by Slater (1936), Friedel (1955) and implicitly† Phillips (1964) assume that it is not large enough to prevent two carriers (electrons, holes) from coming onto the same atom, so that the origin of ferromagnetism is the intra-atomic exchange coupling responsible for Hund's rule. Kanamori (1963) and Hubbard (1963, 1964 a, b) and Gutzwiller (1964) take the opposite point of view and find the origin of ferromagnetism in the strong repulsive energy between electrons with antiparallel spins. In their analyses, the tendency to ferromagnetism arises

† Phillips states "we conclude that the order-of-magnitude agreement obtained by Slater is still the best guide".

because electrons with antiparallel spins, since they cannot move onto the same atom, have less volume to move in, so their kinetic energy is increased. Electrons with parallel spins are of course prevented from moving into the same orbital in the same atom by the symmetry of their wave function, but this does not affect their kinetic energy (e.g. $\hbar^2k^2/2m_{\text{eff}}$). Hubbard, assuming a large value of U, finds the quantity ΔE (to be defined below) due to this cause to be about 0·5 ev in nickel, which is the same as we shall obtain from intra-atomic exchange, and so on these grounds one cannot distinguish experimentally between the two mechanisms.

This section is written on the assumption that U is small for nickel, and some of the arguments might be affected if this were not the case. For cobalt, as Hubbard points out, the states $3d^8$ and $3d^9$ must be present in any case if the number of holes in the d band is less than two†, so the intra-atomic exchange interaction in the ions in the state $3d^8$ must contribute to the ferromagnetism whether or not a large repulsive energy U excludes $3d^7$.

The second uncertainty concerns the proper description of moments which can persist above the Curie temperature in the band model; this we shall discuss later in this section.

We turn now to the description of ferromagnetism as due to exchange interaction within the atom. We go back first to the treatment of Slater's early paper (Slater 1936), and introduce an energy W for each pair of electrons‡, which is the difference between their energies when they are parallel and antiparallel, both electrons being in Bloch states normalized to one electron per atom and their wave numbers $\mathbf{k}$ being unchanged. The state with spins parallel will always have the lowest energy (Hund's rule), so there is here a tendency to ferromagnetism, which will occur when it can overcome the increase in the Fermi energy which will result from a magnetic moment. The condition for ferromagnetism is§ (see for example Friedel *et al.* 1961):

$$2W\,N(E_{\text{F}})v > 1, \qquad \ldots\ldots\ldots \quad (3)$$

where v is the atomic volume. If condition (3) is satisfied, either the electrons or holes in the d band will all be lined up, as in nickel, or an

† If the large negative polarization of the s band which we refer to below is confirmed, the number of holes in the d band must be almost exactly two. Since cobalt shows a large value of γ and other properties of an incomplete band, it follows that U is small enough to avoid splitting the band in the sense of Hubbard's work. In other words, the cobalt ions cannot all be in the state $3d^8$, and since the number of holes is integral, there must be a comparable weight of $3d^7$ and $3d^9$. This is perhaps the strongest evidence against any large value of U inhibiting the presence of any of the three states for cobalt.

‡ W will depend on the k-values for the two electrons; in this kind of discussion some kind of average must be understood.

§ This is really the condition that the energy is lowered by a *small* polarization at the Fermi surface. The condition for a large moment will involve the value of $N(E)$ over a considerable range of E: (3) has been generalized for this case by Shimizu and Katsuki (1964) and Shimizu (1964).

equilibrium is reached such that a small change in the moment is exactly balanced by a small change in the Fermi energy, as in iron. Shimizu (1964) gives for (3) for nickel and iron 1·23 and 1·11 respectively.

This model, taken literally, is the pure collective-electron treatment in which no description is given of the localization of the spins in space. Its consequences, particularly as regards the Curie temperature and behaviour of the metal above it, have been worked out in detail by Stoner (1947) and Wohlfarth (1949 a). This work will be reviewed in the next section. It has however been criticized by Friedel *et al.* (1961) who believe that condition (3) is the condition for the existence of *localized* moments which can be coupled antiferromagnetically as well as ferromagnetically; the possibility of either sign of coupling follows also from Mattis' (1963) work. We believe that this interpretation of (3) may be correct, and shall return to it later on.

However, we shall first consider ferromagnetism at the absolute zero of temperature. Condition (3) certainly suggests that ferromagnetism should be confined to transition metals, for which $N(E_F)$ is large, while W may not be correspondingly small because of intra-atomic coupling, as we shall see below. There may in fact be some correlation between a high value of $N(E_F)$ and the occurrence of ferromagnetism; thus Wohlfarth and Cornwell relate the ferromagnetism observed in the Sc–In alloy system (Matthias *et al.* 1961) to the first peak in the caculated $N(E)$ curve reproduced in fig. 9 (*b*), though the argument is not very cogent since these alloys are hexagonal.

Instead of W, it is convenient to introduce the quantity ΔE, which represents on a figure such as fig. 14 the shift along the energy axis of the spin-up band relative to the spin-down band when the magnetic intensity is saturated, or in other words the energy required to reverse the direction of the spin of an electron with wave function ψ_k without changing its wave number. ΔE is the value of this quantity at the absolute zero of temperature, where the magnetic intensity has its maximum value. In terms of the quantity W already defined, if this is the same for all pairs of electrons:

$$\Delta E = nW,$$

where n is the excess number of spins per atom pointing in the direction of magnetization. In terms of the 'molecular field' H of the Weiss phenomenological theory:

$$\Delta E = 2\mu_B H.$$

In Wohlfarth's terminology $\Delta E = 2k\Theta'$, in Mattis' $\Delta E = \Delta$.

Some of the most important papers estimating ΔE are those due to Slater (1936), Van Vleck (1953), Friedel (1955), Phillips (1964) and Ehrenreich *et al.* (1963). As applied to nickel, very varying results ranging from 0·5 ev to 2 ev have been suggested. We think, following Slater,

Friedel and Phillips, that if ΔE is mainly due to intra-atomic coupling and the effect of U is not large, ΔE should be the product of:

(*a*) The energy difference W_A between the states of the free atom for which two spins of electrons in an incomplete d shell are parallel or antiparallel.

(*b*) The chance that an electron with given spin finds itself on the same atom as another electron with a spin which may be parallel or antiparallel to it.

Applying these ideas to nickel, one has to consider the states $3d^8\,4s^2$ of the free atom. Relevant states are ^3F in which the two d holes have parallel spins, ^1D in which they are antiparallel and in different orbits, and ^1G in which they are in the same orbit. Their excitation energies† are:

State	Wave number	Electron volts
^3F	0–2210	0·2
^1D	13 521	1·1
^1G	22 102	1·9

Thus 1·1 ev is the energy W_A required to reverse a spin if the electrons are in different d orbitals. As there are 0·5 d holes per atom, the chance that a given hole finds itself in the same atom as another one—i.e. in an ion with configuration $3d^8$, may be taken to be 0·5 if it is assumed that simple statistical considerations are valid‡. This would give:

$$\Delta E \simeq 0{\cdot}5 \times 1{\cdot}1 = 0{\cdot}55 \text{ ev}.$$

This seems in rough agreement with Phillips' (1964) estimate and with deductions from experiments on alloys based on the rigid band model (§§ 8, 10), but much less than that (2 ev) of Ehrenreich *et al.* (1963).

For iron, with two magnetic electrons per atom, an electron will normally find more than one other electron on the same atom with the same spin, and we should expect ΔE to be greater than the intra-atomic coupling, and thus greater than W_A, i.e. greater than 1·1 if the value of W_A is comparable with that in nickel. Experimental estimates of ΔE range from 1 to 2 ev, as we shall see below§.

† Compare Slater (1936, table 1).

‡ This would be correct if only states $3d^8$, $3d^9$ and $3d^{10}$ were present; the weights of the three states would be $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$. Friedel (1955, formula 15) gives the statistics if it is assumed that a d shell can contain any number of holes. This we consider to be unlikely because only a positive charge equal or less than $2e$ can be screened by penetrating 4s orbitals.

§ In the atomic spectra of iron states with the configuration $3d^6\,4s^2$ and $3d^7\,4s^1$ have energies close together, but the state with configuration $3d^8$ has energy 4 ev higher (Moore 1952). If we are right (§ 11) in ascribing 0·9 s electrons per atom to iron, this means that $3d^8$ must be present in the metal. But owing to its high energy its weight must be small, and so the weight of $3d^6$ must be small too, which would imply a large correlation energy in this metal.

In cobalt $3d^7\,4s^2$ is the ground state, with $3d^8\,4s^1$ very near to it and $3d^9$ with an excitation energy of less than 2 ev.

These crude estimates assume effectively that the electrostatic interaction between carriers, that we have denoted by U in § 4.2, when screened by s electrons is small enough not greatly to affect the weight of the state $3d^8$ in nickel. As we have already stated, Kanamori (1963) and Hubbard (1963) assume just the opposite, as does in a different connection Anderson (1961). We have already given reasons for believing that ions with the configuration $3d^8$ are unlikely to be absent in metallic nickel, as $3d^5\,4s^2$ is the lowest state in the free atom†. The best experimental estimate of ΔE (cf. § 8) is somewhat below 0·55 ev, and this may be due to the effect of U in cutting down the weight of $3d^8$.

The polarization of the s band by the magnetization of the d band is of interest in interpreting the observed magnetization. Two terms affect it, and their signs are opposite:

(*a*) Exchange coupling between d and s electrons, which gives polarization in the direction of the magnetization, in the sense of Hund's rule. Thus in (atomic) nickel with configuration $3d^9\,4s$ it needs about 0·35 ev to reverse the spin of the s electron relative to the magnetization of the 3d shell. An analogous effect must exist in the metal.

(*b*) Due to s–d hybridization, the energy of the Fermi surface is likely to be raised, as already explained in § 3. In ferromagnetic metals, since owing to the exchange interaction ΔE the spin-up d band lies higher on the energy scale than the spin-down band, hybridization will push the spin-up s band to higher energies than the spin-down. Thus electrons will move over into the spin-down band, giving polarization in the *opposite* direction to that of the d electrons.

The total polarization may thus have either sign. Its magnitude is not yet certain. It has of course a large effect on the total effective magnetic field at the nucleus (Marshall 1958) but there are other comparable terms, notably the terms, usually negative (Goodings and Heine 1960) due to the distortion of the inner s shells as a consequence of exchange interaction with the magnetic electrons. As regards its magnitude, in nickel Phillips (1964) following other authors estimates it to be $+0{\cdot}1\,\mu_B$, leaving $0{\cdot}5\,\mu_B$ for the d band. For iron (Shull and Yamada 1962, Shull 1963) and for cobalt (Moon 1963) give evidence from neutron diffraction that the 4s electrons carry a negative moment (i.e. antiparallel to d electrons) of $-0{\cdot}21\,\mu_B$ and $-0{\cdot}28\,\mu_B$ in the two cases. The evidence comes from an analysis of the spin-up electron density towards the boundaries of the atomic cell. This is thought to be due to the s electrons, and Yosida-type oscillations are unlikely to produce any reversal in the interior of the atom. Recent experiments on positron annihilation (Mijnarends and Hambro 1964), confirm this order of negative

† This is not so in palladium where the first state $4d^8\,5s^2$ lies about 2 ev above the ground state $4d^{10}$ and nearly as much above the lowest state with configuration $4d^9\,5s^1$. Professor Vogt has suggested to the author that this may account for the absence of ferromagnetism or antiferromagnetism in this metal.

polarization for iron†. The estimate given by Daniel and Friedel (1963) of $+0{\cdot}12\,\mu_B$ seems therefore incorrect, and for the pure metals the following values seem plausible (in units of μ_B):

	Moment (obs)	Moment (s)	Moment (d)
Ni	0·6	0·1 (?)	0·5
Co	1·7	−0·3	2
Fe	2·2	−0·2	2·4

The next question we have to ask is whether the exchange interaction W is always large enough to ensure that the magnetic carriers (electrons or holes) in the d band all have their spins oriented in the same direction, or in other words whether the spin-up d band is full‡.

This of course is not necessarily the case; polarization may be partial. Some of the most direct evidence comes from the study of alloys, to be reviewed in § 11. In nickel however polarization of the d band is complete; Phillips (1964), following Thompson *et al.* (1964), gives evidence that the top of the full d band for spins parallel to the field is 0·1 ev below the Fermi surface (the experimental results suggesting a term $\exp(-\Delta W/kT)$ with $\Delta W = 0{\cdot}1$ ev in the curve plotting saturated magnetic intensity against T). In iron, on the other hand, it has been suggested by many authors§ that the magnetization of the d band is *not* saturated, and the evidence now seems conclusive, as will be shown subsequently in this article. The evidence to be reviewed in § 11 shows that the density of states in body-centred iron is roughly as in fig. 14 with the Fermi level for electrons with spin-up and with spin-down as shown by the vertical lines. The 'molecular field' is strong enough or in other words W is large enough to push the spin-down Fermi level to a point in the minimum in the d band, but no farther. To push it through the minimum would take a large value of W, because to do so would raise the Fermi energy more rapidly than in a region of high density of states. The condition for an equilibrium of this sort to exist is the following. Let E_1, E_2 be the energies of the spin-up and spin-down Fermi surface in fig. 14. Thus the energy required to take an electron from one to the other, with change of spin, must vanish, so that:

$$\Delta E = nW = E_1 - E_2.$$

† Shirane *et al.* (1963), in a Mössbauer study of iron–rhodium alloys, conclude that in these alloys the s electrons may have positive polarization. The reason is that according to neutron diffraction data, in alloys with about the same concentration of both metals, the iron carries a moment of $3{\cdot}2\,\mu_B$ contrasted with a maximum value of $2{\cdot}8\,\mu_B$ in the comparable alloys of Fe–Co or Fe–Ni. If our model is correct, the d electrons cannot contribute more than about $3\,\mu_B$, so the s electrons must be making a positive contribution.

‡ Obviously the question may only have meaning in the approximation to which s and d bands are separated.

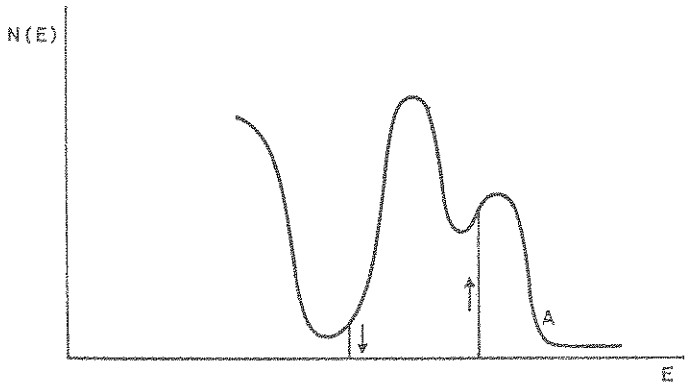
§ Stoner (1947, p. 90 of his review article), Wohlfarth (1949 a), Friedel (1954), Coles and Bitler (1956) (the explanation given there of the properties of Fe–Al, etc. is not in accord with that given in this article), Mott (1962).

This may be written:

$$W=(E_1-E_2)/v\int_{E_1}^{E_2}N(E)\,dE,$$

where v is the atomic volume. If $N(E)$ is small over a range of E, the numerator will increase proportionately more rapidly than the denominator as E_2 enters this region, so the right-hand side will increase and may become equal to W, even though the inequality (3) is satisfied at the Fermi surface.

Fig. 14



Schematic density of states $N(E)$ for body-centred transition metals, with spin-up and spin-down Fermi levels marked for iron. The point A marks the upper limit of the d band.

To show with a simple model how this might work out, we take for $N(E)$ for each spin:

$$v\,N(E)=A, \quad E>E_0$$
$$=B, \quad E<E_0,$$

where $A\gg B$. Suppose that in the paramagnetic state there is one electron per atom with $E_k>E_0$. Suppose that in the ferromagnetic state the spin-down Fermi limit is at ν electrons per atom to the low energy side of E_0, the spin-up $2+\nu$ to the high energy side, so that the moment is $(2\mp 2\nu)\mu_B$. A simple calculation shows the condition for equilibrium to be:

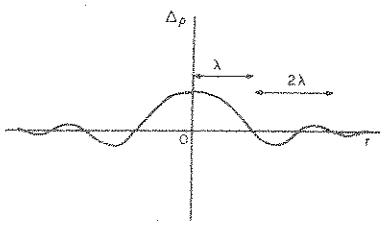
$$\nu\left[\frac{1}{B}+\frac{1}{A}-2W\right]=2W-\frac{2}{A}.$$

The right hand is positive, this being the condition (3) for ferromagnetism. There will be an equilibrium if the quantity in the square brackets is positive, and thus if B is small enough. Moreover, if W and $1/A$ are comparable, ν is of order B/A and thus small; the spin-down Fermi limit is held at a small distance from E_0 in the region of small $N(E)$.

In the f.c.c. alloys there is no experimental evidence that any sharp minimum exists, or that the metal or most of its alloys are normally other than saturated, though a departure from saturation certainly occurs in face-centred Ni–Fe alloys for a proportion of iron above 75% atomic as we shall see below.

We turn now to the question whether condition (3) is in fact the condition for ferromagnetism, or whether it is the condition for the formation of localized spins on each lattice site, which may be coupled ferro- or antiferromagnetically, as first suggested by Friedel *et al.* (1961), see also Gautier (1963). Their argument is as follows. They consider the effect of intra-atomic exchange coupling W within one *ion* on the electrons described by Bloch wave functions ψ_k in the partially occupied d band. If the condition (3) is satisfied, their conclusion is that W will produce a *local* polarization; that is to say that locally ψ_k near the Fermi level will have different values for spins up and down. They suggest that the excess spin density should oscillate in the way already described as following from Yosida's work, though quantitatively different because we have to do with a d band.

Fig. 15



Change in excess electron density $\Delta\rho$ for a given spin direction as a function of distance from the moment (Friedel *et al.* 1961). λ denotes $1/k_F$.

The type of oscillation is shown in fig. 15; the wavelength should depend on $2k_F$, where k_F is the (averaged) wave number at the Fermi surface. We refer to the integrated moment as the moment on the ion. Between these moments there will be an oscillating interaction of Yosida type transmitted by the d electrons themselves as well as the s electrons, and which, though not given quantitatively by eqn. (2), may have either sign†.

The consequences of the model are:

(1) The interaction may be either ferromagnetic or antiferromagnetic, the former being favoured by a small value of k_F. This conclusion is also obtained by Mattis (1963).

(2) The coupling between the moments *may* be small compared with the intra-atomic exchange coupling W, in which case we would expect coupled

† Giovannini *et al.* (1964) point out that the amplitude and phase of oscillations round a localized magnetic moment will depend on the exchange energy between the Bloch orbitals ψ_k; no such effect is included in this analysis.

spins to survive at high temperatures; they probably do in iron, and not in chromium where the entropy change on going through the Néel point is small (cf. § 11.2). The persistence of moments will be discussed later in this article.

If these considerations are correct, the position of the minimum in the $N(E)$ curve, or the bottom of the d band in the absence of a minimum, should determine the size of the individual moment, whether the material is ferromagnetic or antiferromagnetic.

The case of face-centred iron and its alloys is relevant to these considerations. Face-centred iron has been discussed by Kaufman *et al.* (1963) and by Weiss (1963, 1964), according to whom there are two possible electronic states, a ferromagnetic one with a moment of about $2{\cdot}9\,\mu_B$ per atom, stable at high temperatures, and at low temperatures an antiferromagnetic state with moment about $0{\cdot}5\,\mu_B$. Both can be stabilized by suitable alloying. According to Weiss (1964) the atomic volume of the antiferromagnetic form is 6% smaller than the ferromagnetic. The smaller moment of about $0{\cdot}5\,\mu_B$ has also been observed by neutron scattering in several austenitic (f.c.c.) steels by Nathaus and Pickart (1964). In terms of the above model the large moment ($2{\cdot}8\,\mu_B$, which taking account of orbital moment and the g-factor means 2·7 carriers) suggests that the minimum in $N(E)$ near chromium which Beck's results (§ 11) show so clearly for the b.c.c. alloys may be absent or less marked for the f.c.c. structure and unable to prevent *all* the holes in the d band from lining up. We shall find later there are 2·9 holes per atom in iron and if the s band polarization is $-0{\cdot}2\,\mu_B$ as in α-iron, this just fits. The small moment ($0{\cdot}5\,\mu_B$) suggests that there must be a minimum in $N(E)$ a small way below the paramagnetic Fermi surface in f.c.c. iron to stabilize it. We implicitly assume that the relative number of s and d electrons is little changed by the change of structure, which can produce changes only in the form of the d band which have a small effect on the energy (see Mott 1962).

Face-centred iron is discussed further in the next section.

§ 6. The Effect of Temperature on the Intensity of Magnetization

In ferromagnetic insulators, which can be treated by a Heisenberg spin hamiltonian, the first excitations of the system are spin waves, and in general the magnetism behaves at low temperatures like†:

$$I = I_0(1 - \alpha T^{3/2} \ldots).$$

Magnetic anisotropy however can produce an energy gap w in the spin-wave spectrum, so that $I - I_0$ behaves like $T^{3/2}\exp(-w/kT)$ and in certain circumstances as T^2 (Niira 1960, Mackintosh 1963). These authors discuss the behaviour of ferromagnetic rare earth metals in this respect.

† cf. Mott and Jones (1936), van Kranendonk and van Vleck (1958). Also the work of Dyson (1956) on the interaction of spin waves giving the next term in the series is well known, together with other derivations by Oguchi (1960) and Keffer and Loudon (1961).

On the existence of spin waves in metals, the first phenomenological approach was due to Lifshitz (1945) and Herring and Kittel (1951). More recently Edwards (1962) and Mattis (1963) have given a description which shows clearly that low-lying spin waves do exist and that the above formula is valid too for metals. There is also direct experimental proof due to Lowde (1956) and Sinclair and Brockhouse (1960) of the existence of spin waves in ferromagnetic metals from inelastic neutron scattering, and from spin-wave resonance work (Tannenwald 1961).

The disappearance of ferromagnetism as the temperature is raised is not only due to spin waves, however; there is bound to be at low temperatures an additional term in $I_0 - I$ of the form $B\exp(-\Delta W/kT)$, where ΔW is the energy required to excite electrons from the full (spin-up) band to the Fermi level of the partially empty spin-down band; for nickel according to Phillips (1964) ΔW is 0·1 ev. In iron ΔW will be zero and this term in $I_0 - I$ cannot be present in this form, since in metals such as iron there are, as already stated, holes in d-like bands with both spin directions. For such metals Thompson *et al.* (1964) found that the term $\exp(-\Delta W/kT)$ in $I_0 - I$ is replaced by one in T^2. They consider that experimental work by Argyle *et al.* (1963) is consistent with this.

In the collective electron treatment the quantity ΔE defined in the last section is related directly to the Curie temperature Θ. In the calculations of Stoner (1947) and Wohlfarth (1949a, 1951), if we write in Wohlfarth's notation:

$$k\Theta' = \tfrac{1}{2}\Delta E,$$

then Θ' is the Curie temperature Θ if the band-width is zero. For the case of nickel and nickel–copper alloys Wohlfarth (1949a) finds that, for the actual band width, $\Theta \sim \frac{1}{2}\Theta'$, and to give agreement with experiment for the Curie temperature, ΔE should be about 0·2 ev. A convenient formula connecting Θ and Θ' is that deduced by Wohlfarth (1951) for a rectangular band form with a density of states $N/2\epsilon_0$ up to some limiting value, where it vanishes; this is:

$$k\Theta = -\epsilon_0/\ln(1-\epsilon_0/k\Theta'),$$

which tends to $\Theta = \Theta'$ as ϵ_0 tends to zero, but otherwise gives $\Theta < \Theta'$.

There are several arguments however against the collective-electron treatment as a description of what happens as the material approaches the Curie temperature; these apply with particular force to iron. They are as follows:

(*a*) ΔE deduced from various experimental evidence for iron appears between two and three times too great to account correctly for the Curie temperature according to the formulae above. For nickel with the smallest estimates of ΔE the disagreement is not serious.

(*b*) The analysis made by Hofman *et al.* (1956) of the entropy associated with the transition through the Curie temperature gives $0{\cdot}6\,Nk\ln 2$ for nickel and $Nk\ln 3$ for iron. These are the values to be expected from a Heisenberg model, and bear no particular relationship to those expected

from the collective model, which as we have seen involves both ΔE and the band width. Though the value for nickel is probably unreliable, that for iron is less so and may be significant.

(*c*) If the main contribution to ΔE is *intra-atomic*, it seems physically plausible to suppose that one can destroy the ferromagnetism without destroying the intra-atomic coupling. This argument applies with particular strength to iron, but if ΔE for nickel depends on the weight of $3d^8\,4s^2$ in the many-electron wave function, there is no reason why this weight should be greatly changed on going through the Curie temperature.

(*d*) Neutron scattering in iron above the Curie temperature shows the existence of moments (Shull *et al.* 1951, Lowde 1956, Elliott 1956, Ericson and Jacrot 1960, de Gennes and Villain 1960). This means that there are regions having a moment extending over a volume larger than the lattice parameter.

(*e*) The investigations of Wachtel and Urbain (1962) show no observable change of susceptibility at the melting points of nickel and cobalt. Though the susceptibility in the usual band theory should follow the Curie–Weiss law at high enough temperatures (Rhodes and Wohlfarth 1963), one would probably expect on the band theory *some* effect of melting†.

We believe therefore that, while the collective-electron calculations of the Curie temperature may be an approximation to the truth for nickel, they require serious revision for iron. We do not have a proper theory, as yet, as to how this should be done. The qualitative work of Friedel, Leman and Olszewski (1961) suggests that the localized moments they describe might interact through a Yosida-type interaction and be treated by a Heisenberg hamiltonian and persist at high temperatures, but what happens will depend on the ratio between intra-atomic coupling and coupling between neighbouring atoms, as appears also from Mattis' (1963) work. If the intra-atomic coupling W is large compared with the Yosida-type coupling between the oscillations of fig. 15, moments greater than μ_B will persist, and this will be true in iron; if not, they will not persist.

The following model is designed to show how the existence of a Fermi surface is consistent with a Heisenberg model and (for iron) an entropy increase of $Nk\ln 3$ on going through the Curie point. Suppose that we take an idealized model of iron, in which there are two magnetic electrons per atom, and that we describe them by Bloch wave functions ψ_k in which the k-values all lie in two of the sub-bands of the d band. We suppose that the overlap between atomic orbitals is small, so that the method of tight binding is appropriate. Then the band width will be determined by integrals of the type:

$$\int \psi_a^*(\mathbf{r})\, V\, \psi_b(\mathbf{r})\, d\mathbf{r},$$

where ψ_a, ψ_b are atomic wave functions on adjacent atoms. We take as an

† The more complicated behaviour of iron observed by Wachtel *et al.* may depend on the existence of two moments in gamma-iron as suggested by Weiss (1964).

empirical fact that this integral is of the same order as ΔE due to intra-atomic coupling. With this model the spin waves and Curie temperature are appropriately treated by the Heisenberg model. This is because the Slater determinant formed from the functions ψ_k is *identical* with that formed from (orthogonalized) localized functions of Wannier type. And the Heisenberg exchange integral, of type :

$$\int \psi_a^*(\mathbf{r}_1)\,\psi_b^*(\mathbf{r}_2)\,(e^2/r_{12})\,\psi_a(\mathbf{r}_2)\,\psi_b(\mathbf{r}_1)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

is an *order of magnitude smaller* than ΔE when the overlap is small.

Of course some of the occupied states ψ_k are not in the two top sub-bands, but it may be a good conceptual picture to start with the Heisenberg model as above, and introduce some holes into these two sub-bands and electrons in another d sub-band. The ferromagnetic coupling could then be of Yosida type between the coupled magnetic electrons via these electrons and holes as described by Friedel *et al.* (1961), possibly via the s electrons too, and partly due to the direct interatomic Heisenberg coupling, though this is unlikely to be large enough to be the main cause of ferromagnetism†.

A model of this kind may give a qualitative description of the properties of iron. It allows the magnetic electrons to be in a zone in which there is a Fermi surface; but the entropy on going through the Curie point will be approximately $Nk \ln 3$ with some smaller additional term due to the change in the Fermi surface, and the intra-atomic coupling is not broken down at the Curie temperature.

The question of the persistence of localized moments is particularly interesting in connection with face-centred iron. We have already mentioned the work of Weiss (1964) and earlier papers which propose that face-centred iron can exist with two electronic arrangements, antiferromagnetic with a small moment ($0{\cdot}5\,\mu_B$) and ferromagnetic with a large moment ($2{\cdot}8\,\mu_B$). The former is the one stable at low temperatures and has the lower atomic volume (by about 6%), but by alloying with sufficient nickel or palladium the order can be reversed. As the temperature is raised, Weiss considers each atom as having its own moment, with one value or the other, and the number of atoms having the moment with the higher energy as being given by a Boltzmann factor. Weiss (1963) gives a description of the thermal expansion of invar in terms of this model.

As regards the reason for the existence of two alternative moments, the model of Friedel *et al.* (1961) would lead one to suppose that the lower moment would occur if there were a minimum in $N(E)$ situated at a value of e/a of about 7·0; this would stabilize the moment at about $0{\cdot}5\,\mu_B$. We have no independent evidence to show whether this minimum exists.

The model is useful in explaining the results on the magnetic moment and Curie temperature of the Fe–Ni alloy system shown later in figs. 22 and 23.

† Stuart and Marshall (1960) have calculated the exchange integral and find it too small by a factor 70 to explain ferromagnetism in metals, though it has the right sign.

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§ 7. Alloys :

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Figure 22 suggests that iron atoms remain in the ferromagnetic state with moment $2{\cdot}6\,\mu_B$ until the concentration exceeds about 60% of iron, when probably small moments and antiferromagnetic coupling set in. This may produce non-saturation, or some antiferromagnetically aligned moments (Gupta *et al.* 1964). Figure 23 shows that the Curie temperature begins to drop for a lower concentration of iron; this is in Weiss's view because as the temperature is raised some of the iron atoms switch to the lower moment with antiferromagnetic coupling.

Hatherly *et al.* (1964) have measured the energies of spin waves of long wavelength in a range of iron–nickel alloys, using a neutron small angle scattering technique. They interpret their results in terms of a Heisenberg hamiltonian with constant moments and exchange integrals between iron–iron, nickel–nickel and iron–nickel. They find the former to be negative (antiferromagnetic) in the f.c.c. structure. This is *not* in accordance with Weiss's interpretation sketched here, in which the large moment in f.c.c. iron is coupled ferromagnetically.

There is some evidence about the range of the coupling between moments, which comes from measurements of internal magnetic fields in alloys, for instance by the Mössbauer effect. Friedman and Nicholson (1963) have measured this for a series of iron–aluminium alloys, and have detected several different fields at iron atoms corresponding to sites surrounded by different numbers of aluminium atoms. Wertheim *et al.* (1964) have investigated the range of interaction in iron alloys of type Fe–X, where X is Ti, V, Cr, Mn, Co, Ru, Al, Ga or Sn. Measuring the internal magnetic field at the iron nucleus by nuclear magnetic resonance, they find that this depends on the nature and number of nearest neighbours and next-nearest neighbours only, thus suggesting a rather short-range interaction.

§ 7. Alloys: the Rigid Band and other Approximations

The rigid band approximation assumes that, in an alloy system such as Cu–Zn or Cu–Ni, the form of the density of states curve, $N(E)$ as a function of E, does not change over a wide range of composition though of course $N(E_F)$ changes due to the change in the electron-to-atom ratio (e/a). The approximation is known to break down in many cases. For our consideration of transition metals, we have to ask:

(*a*) Does $N(E)$ change for an s band?

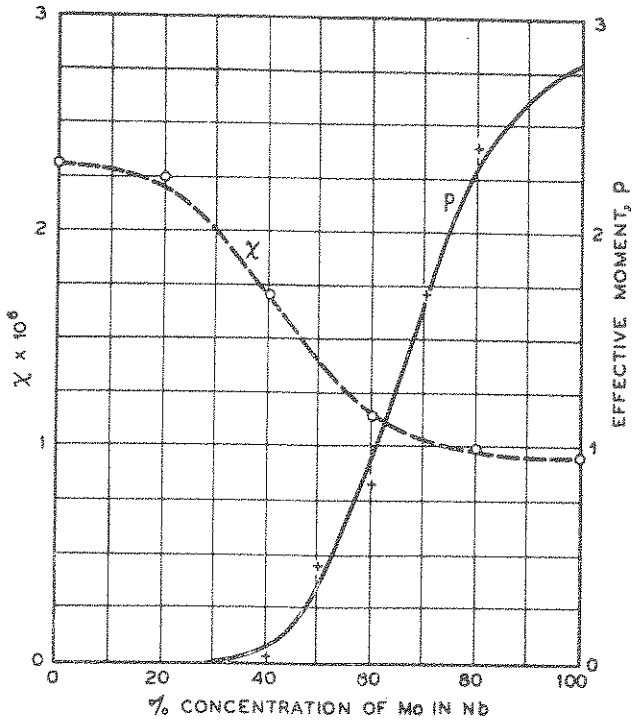
(*b*) Does $N(E)$ change for a d band?

(*c*) Do the relative energies of the s and d bands change?

Cases in which divergencies from the rigid band approximation may occur, not particularly relevant to transition metals, have been discussed by Cohen and Heine (1958) and by Raimes (1962). More relevant to this paper are certain concepts relating to dilute alloys. There is first of all the question of whether, at the impurity, there is an unbalanced spin moment. This can occur when a transition metal is dissolved in a non-transition metal or for one transition metal dissolved in another. In terms

of a model, one can describe such a situation in terms of Bloch wave functions ψ_k which extend through the lattice but which, in the neighbourhood of the impurity and for a certain range δE of E_k, have different amplitudes for spin up and spin down. This treatment was put forward by Friedel (1958) and developed by Wolff (1961); obviously it leads in general to a non-integral value of the moment. Alternatively one can describe the electrons

Fig. 16



Plot of moment of iron atom, denoted on the diagram by p, in Nb–Mo containing 1% of iron (Matthias *et al.* 1963). The broken line gives the susceptibility at 300°K in the absence of iron.

at the impurity by a localized wave function (Anderson 1961), which itself will have an integral moment (in terms of $\frac{1}{2}\hbar$) but by polarizing the electrons in the neighbourhood near the Fermi surface it too will produce a non-integral moment. There is no sharp physical distinction between the two representations.

For a matrix which is not a transition metal, manganese in copper is a case where the impurity has a spin, nickel in copper a case where it does not.

Isolated moments also appear in dilute solutions of iron in certain transition metal alloys. There is some indication that a high density of states $N(E_F)$ in the d band of the matrix inhibits these moments. Thus fig. 16 shows the results of Matthias *et al.* (1963) on the moment of 1% of iron in Nb–Mo alloys; the susceptibility is also shown, and it appears that the moment appears as the susceptibility (and hence $N(E_F)$) drops. We know from other evidence put forward in § 11 that γ drops at about e/a $\simeq$ 5·6. Clogston *et al.* (1962) have followed up this work; their fig. 2 (not reproduced here) shows that there are no moments in the alloy series Nb–Mo–Re–Ru between e/a = 7 and e/a = 8·2, which is just where this series absorbs hydrogen (see fig. 43), indicating high † $N(E)$.

Apart from a value of $N(E)$ not too high, the condition for the appearance of moments is probably complicated and has been discussed by the authors quoted above and by Suhl and Fredkin (1963) and White and Clogston (1963). Friedel, who assumes that the wave functions ψ_k of the matrix are large in the impurity over an energy range δE, considers that if W is the exchange energy gained when the electrons are lined up with spins parallel, the condition for a moment is that $\delta E < W$. This fits with the observed fact that the existence of moments is prevented by large $N(E_F)$, at any rate if δE is near the Fermi surface, since a high density of states in the matrix will increase δE. Wolff emphasizes that moments are formed more easily if δE is near the Fermi surface.

Anderson's treatment, using localized wave functions, shows that the energy of the localized state can be split into two states on account of the repulsion U (§ 4.2) between electrons with antiparallel spins within the impurity (e.g. iron) atom. An unbalanced moment with this model occurs only if one state is above and the other below the Fermi surface. The resonance energy V with the 'conduction' electrons, in this case probably those in the d band of the matrix, is of the same type that leads to s–d hybridization in the one-electron model; by introducing this quantity he obtains a width of the level:

$$\Delta = \pi \langle V^2 \rangle_{\mathrm{av}} N(E),$$

and a condition for a moment that $U/\pi\Delta$ should be somewhat greater than unity, depending on where the two states are situated relatively to the Fermi energy. High density of states in the matrix thus inhibits moments in this model too.

A controversial point in Anderson's work, and one in which as he emphasizes it differs from Friedel's, is that the splitting is due to the electrostatic repulsion U, not the exchange energy. This must be correct if

† See also the work of Childs *et al.* (1963) who show that manganese, iron, nickel and cobalt do not in general give localized moments, but decrease the susceptibility, in vanadium-based solid solutions. With iron, moments appear at high concentrations, and in V–Fe, Lam *et al.* (1963) find moments above about 23% of iron.

U, screening by s electrons notwithstanding, is large compared with the intra-atomic exchange energy. We have given reasons in §§ 4.2 and 5 for doubting whether this is so in general, though iron may be a special case. The agreement that Anderson gets with experiment depends on taking V about 2 ev, which may be too large for states near the top of the d band.

Another interesting point that we shall not discuss here is the occurrence of very large moments, of up to $12\,\mu_B$, in dilute solution of iron in alloys containing palladium (Gerstenberg 1958, Crangle 1960, Cable *et al.* 1963).

Turning now to less controversial matters, the interaction between moments via the conduction electrons has already been mentioned; an interesting and important point is that, due to the random values of the distance between moments, it can give rise to a term in the specific heat linear in the temperature at low temperatures, but disappearing at high temperatures (Marshall 1960, Kim and Nagaoka 1963, Alexander and Anderson 1964).

A quite different possibility in terms of a one-electron model is that an impurity may cause a bound state to appear below the Fermi distribution, a possibility that was first discussed by Friedel (see Friedel 1954). A repulsive field also may cause states to appear above the d band, and this concept is used in § 13 for an explanation of divergences from the Slater–Pauling curve. These bound states exist in the one-electron approximation, and their description is analogous to that of Wolff (1961) mentioned above; in terms of a many-electron wave function, the question whether a bound state exists does not admit of a precise answer. A bound state may contain one electron with an unbalanced spin, or an even number of electrons with no resultant spin moment, or no electrons if the state is above a d band as in the discussion of § 13. Conversely, an unbalanced moment does not imply a bound state below the band.

Finally there is the important concept of 'virtual bound states' introduced by Friedel (for a recent review see Friedel 1962). Here the Bloch functions ψ_k of electrons with energies in the conduction band, or in a relatively broad d band, are thought to resonate with a narrow d or f level of an impurity, i.e. to become d- or f-like in the impurity. The mathematical formulation is similar to that of Wolff (1961) for unbalanced spin moments, but in some of the cases discussed by Friedel there is no such moment. This resonance will lead to an enhancement of $N(E)$ over a narrow band of energies δE, of order 1 or 2 ev for a d state and 0·02 ev for an f state, and a considerable phase shift for the wave functions ψ_k in this range. If δE overlaps the Fermi energy of the metal, one expects, in the absence of a moment:

(*a*) An increase in the specific heat coefficient γ (cf. the discussion in § 10 of Ni–Cu), together with an increase in the Pauli spin paramagnetism.

(*b*) A considerable residual electrical resistance due to the phase shifts of the functions ψ_k.

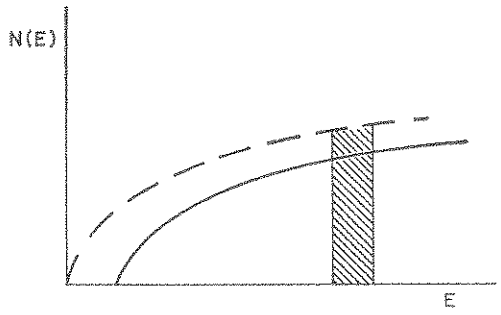
(*c*) A large thermoelectric power because the phase shift is sensitive to energy.

Friedel has discussed particularly aluminium-based alloys of the transition metals in these terms. There is here no moment, because of the high density of occupied states near the Fermi surface in this trivalent metal†.

We turn now to cases in which the form of $N(E)$ for an s band may not be altered much by alloying, but may be shifted on the energy scale. Consider first the case of α-brass, Cu–Zn. The wave functions ψ_k must have larger amplitudes round a zinc atom than elsewhere, to ensure that the charge on the zinc atom is screened. At first sight it would be surprising if this did not drastically alter the band form; but this has been discussed by Friedel (1954), who concludes that to a first approximation, i.e. one that treats the screened field as a perturbation, it does not. Friedel however shows that the band would be shifted to lower energies by the screened field round the zinc atoms, and has proved the remarkable theorem that, using certain approximations, the extra electrons added will keep the energy *of the Fermi surface* unchanged. The situation is illustrated in fig. 17. This theorem will be used in this article is discussing alloys of nickel and iron with non-transition metals‡.

We turn now to alloys of one transition metal with another. The evidence reviewed in § 11 suggests that many transition metals have about 0·5

Fig. 17



Density of states in copper and Cu–Zn, or iron and Fe–Al, according to Friedel's theorem. The dotted line applies to the alloy, and the shaded area shows the volume on the diagram occupied by the electrons added.

† Friedel's article (1962) shows clearly the relationship between the existence of a moment and the density of states at the Fermi level in the matrix. Thus in Pd+H, with the d band full and only 0·5 s electrons per atom, one obtains moments on a wider range of transition metals than in any other metal.

‡ There is some experimental evidence of the correctness of Friedel's theorem. It would imply that in Cu–Zn the addition of zinc would not change the position of the optical absorption edge which corresponds to a transition from the d levels of copper to the Fermi surface. That this is so has been shown in recent measurements of the optical constants by Lettington (1964), who finds also that for transitions to the top of the s bands the frequency does vary with composition as expected.

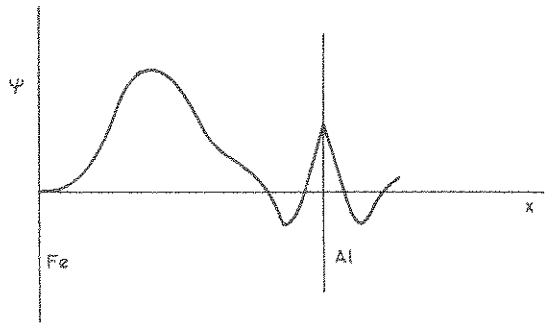
to 0·9 electrons in the s band, not differing too much, so that in the alloys there should be a common s band, and the d band will retain a position on the energy scale such that on alloying there is little overflow of electrons from s to d or vice versa. What happens to the d band, or whether it is 'rigid', is by no means obvious. Sometimes, when unbalanced spin moments occur or deviations from the Slater–Pauling curve (to be explained in § 13) due to bound states, it certainly does not remain rigid. If the atoms are close together in the periodic table (e.g. Cr–Fe, Fe–Co), it is often assumed to be a reasonable approximation to treat the band as rigid. In recent theoretical investigations Beeby (1964) and Stern (1964) have examined this problem, and it seems probable that under these conditions it is legitimate to treat a plot of γ against composition, as in § 11, as giving correctly the density of states. We shall refer again to this problem in later sections (cf. § 9).

Finally we come to alloys between transition metals and non-transition metals (e.g. Ni–Cu, Pd–Ag, Ni–Zn, Fe–Al, Ni–Si or Fe–Si). Here the number of electrons in the s band is different in the two constituents, 0·5 to 0·9 for the transition metal, 1, 2 or 3 or 4 for the other metal. It is a well-known fact that nickel and palladium on the one hand and iron on the other behave very differently. Nickel and palladium behave as if the relative position of the d and s bands remain unchanged, so that the extra electrons (0·5 for copper, 2·5 for aluminium) go into the d band, thus reducing the number of holes there and reducing the moment on surrounding atoms. The simple rigid band model of this phenomenon was first given by Mott (1935). This behaviour is to be expected if the relative position on the energy scale of the 3d and 4s (or 4d and 5s) bands are unchanged by alloying. For iron alloyed with aluminium or silicon, on the other hand, as emphasized by Stoner (1947) and by Hume-Rothery and Coles (1954), the iron atom seems to keep its moment, so that the non-transition metal acts as a diluent. The experimental evidence is reviewed later in this article. Coles and Bitler (1956) tried to explain this in terms of the non-saturation of the moment in iron, suggesting that the extra electrons might go into the d band without producing any additional moment; Mott and Stevens (1957) suggested that the electrons carrying the moments in iron were in localized states as in the rare earths, and so were unaffected by alloying. Neither explanation now appears correct. In fact, in view of Friedel's considerations which fig. 17 illustrates, the behaviour of iron now seems easier to explain that that of nickel. The argument is as follows:

Let us set up a model of an iron–aluminium alloy in which the extra two (or 2·1) s electrons contributed by aluminium, over and above the 0·9 or so in the iron s band, go into the s band and serve to screen the charge on the aluminium atom. Then, according to Friedel's theorem illustrated in fig. 17, there is no change in the energy of the Fermi surface. There will therefore be no transfer of electrons to the d band *if the mean energy of the d band is unchanged by alloying*. But this is just what one would expect, if the electrons in the d band of iron do not penetrate much into the aluminium

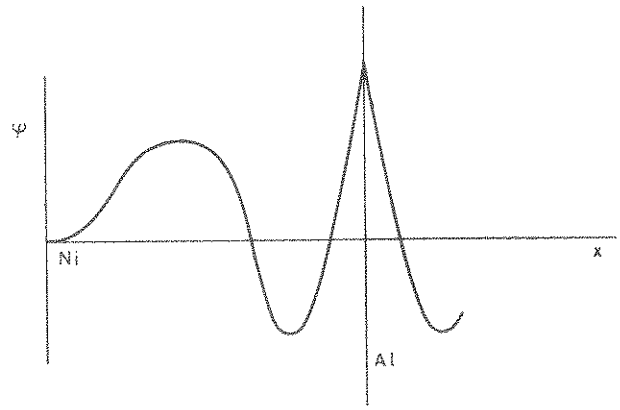
atom. A wave function for an electron in the d band of iron, in the neighbourhood of an aluminium atom, will look as in fig. 18; within the aluminium atom it will be 3s- or 3p-like, but the amplitude will normally be small. Thus, as regards the energy of the d electrons, the strong screened attractive field of aluminium will have little effect.

Fig. 18



Suggested form of the wave function in the d band of iron near an aluminium atom in Fe–Al.

Fig. 19



Suggested form of the d band wave function near an aluminium atom in Ni–Al.

If this is the correct explanation for iron, the question arises of how to explain the properties of nickel or palladium. Friedel (1954) has emphasized that in Ni–Al, Ni–Zn, etc. the excess charge on the non-transition atom is 'screened by d electrons'; since the excess electrons are observed to fill up holes in the d band, it must mean that screening by electrons in the d band leads to lower energy than screening by electrons in the s band. But this cannot mean that electrons providing the screening charge either stay outside the non-transition atom (e.g. aluminium), or that there are d-like

electrons within it. The wave functions within the aluminium atom must appear as in fig. 19; in contrast to fig. 18, the amplitude within the aluminium atom is now comparatively large, but with s-like symmetry.

What we are saying, then, is that in the neighbourhood of an aluminium atom the 3d state is a *localized* state *above* the top of the d band of the surrounding matrix; or if the diluent is copper or zinc, the d state is a fully occupied one *below* the d band of the matrix. In neither case does the diluent add to the number of states in the surrounding nickel matrix. But we are suggesting that none the less penetration by d band wave functions of the type illustrated in figs. 18 and 19 can be—and in nickel and palladium is—sufficient to screen the excess charge on the non-transition atom.

If this model is correct for nickel and palladium, we have to ask why iron behaves in one way and palladium in another. If the d electrons penetrate the foreign (non-transition) atom, the presence of this atom will affect the position of the d band Fermi limit as well as that of the s band, and in an unknown way. It may be more logical to ask, therefore, whether s-screening or d-screening, as we have described them, give screening with lower energy. One possibility is that the 4 to 5 electrons in antibonding states, with high values of $N(E)$, that one has in nickel and palladium may be effective in setting up d-screening without great distortion of the wave functions that would cost much energy, while the absence of so many of these electrons in iron favours s-screening. It would be interesting to investigate in detail such series as Fe–Co†, Fe–Ni to see where the change from one behaviour to the other occurs.

An alternative model has been suggested to the author by Dr. Marshall, which has the advantage of showing why both nickel-like and iron-like behaviour can occur. In this model, instead of treating the s-screening round aluminium as a pile-up of charge in the 4s band, one treats the 3p electrons of aluminium as fitting onto the 4s electrons of iron, and the 3s state as being to a first approximation a sharp localized level, with wave function $f(r)$. We also take the twelve surrounding nickel or iron atoms as having localized d levels with wave functions $g_n(r)$, $n = 1 \ldots 12$. Then any pair of functions g and f will combine together to form two orthogonal functions:

$$f + \alpha g, \quad g + \beta f,$$

as in ligand field theory. If there is an energy difference between the two states, α, β will normally be small. In the metal, probably, the criterion

† Certain Fe–Co alloys with up to 10% aluminium were investigated by Coles and Bitler (1956); the transition appears to occur between 20 and 35% cobalt. This supports their model, according to which the electrons go into the d band but with balanced spins. We reject this model because it is difficult to see why cobalt should behave differently from iron, and on account of the γ-values discussed in this article (§ 11).

Chen (1962) finds that the addition of copper to FeCo has an effect near to dilution on the moment, but this is to be expected if iron, cobalt and copper have almost the same number of electrons in the s band.

which has most effect on the energy will be that the aluminium atom has to be neutral, or in other words that there should be two 3s electrons in aluminium. The constants α, β will take up values so that this is so, consistent with orthogonality. But this can happen in two ways. If the energy of the 3s in aluminium lies *below* the 3d states in the surrounding matrix, which we assume to be the case in iron, the lowest state is $f+\alpha g$, with α small; this is doubly occupied, while the antibonding state $g+\beta f$ is probably empty. We thus get screening by the double occupation of the 3s state, and no extra electrons go into the d band. If on the other hand (as we assume to be the case in nickel) the 3d states lie below the 3s state of aluminium, then the lowest state is a bonding one of type $g+\beta f$, where β is small, and to ensure screening

$$12\times 10\beta^2=2,$$

so that the s-like overlap of the d function (as in fig. 18), though small for each d orbital, is sufficient because of the 12 neighbours to provide the two electronic charges on the aluminium. The antibonding state $f+\alpha g$ will now be empty. So what has happened is that *without* increasing the number of states in the d band, we have added two electrons to it and can call on them to provide the screening.

The two possible behaviours are sharply separated in this model, though of course in the metal all states would be broadened and the situation would be less clear cut.

If the kind of screening envisaged here for nickel occurs, and if a considerable number of the 9·5 electrons per atom in the d band take part in it, we should *not* expect in alloys like Ni–Cu or Pd–Ag that at the Fermi surface $N(E_F)|\psi_k|^2$ would be large at the noble metal atom. This is important in connection with s–d scattering in alloys (§ 14.2).

§ 8. Magnetic Moments of Alloys of Nickel and Iron with Non-transition Elements

8.1. *Alloys of Nickel*

We shall first summarize what is known about metallic nickel. At the top of the d band there should be two sub-bands, degenerate at their highest points; spin–orbit interaction will remove this degeneracy, but the separation will be small (0·07 ev) compared with the band width (Friedel *et al.* 1964). As we have seen, there are 0·5 holes per atom in the d band and probably a polarization of the s band of about 0·1 μ_B, and at the absolute zero the top of the *full* d band (spin-up band) is 0·1 ev below the Fermi level. If the shape of the d band for each spin direction is the same as for that obtained for palladium from the specific heats of Pd–Ag assuming a rigid band model, then one can obtain ΔE, the shift of the spin-up d band relative to the spin-down band, by comparing the experimental values of γ for the two metals. These are (Parkinson 1958) 7·5 for nickel, 13·0 for palladium in joules $\times 10^3$ mol^{-1} deg^{-2}; thus for palladium the value for each half band of given spin will be 6·5, compared with 7·5 for nickel. If

palladium had 0·5 holes in the half d band instead of the actual value of 0·25, this would bring the value of γ, according to fig. 30, down to about 5. This suggests that the nickel band is narrower than that for palladium in the ratio 7·5 to 5 (3 to 2).

If then we put a Fermi limit with 0·5 holes in a d band for one spin direction into fig. 29, it will be at about 3·3 ev, or 0·7 ev from the top of the d band which we take at 4 ev. If we cut 0·7 ev down in the ratio 3 : 2, we obtain 0·46. If we add 0·1 ev on to this, which is the estimate given by Thompson *et al.* (1964) of the distance of the Fermi level from the top of the full band, we obtain for ΔE, in fair agreement with our theoretical estimates,

$$\Delta E \simeq 0{\cdot}56 \text{ ev},$$

The density of states curve deduced by Shimizu *et al.* (1963 b) from γ values for copper–nickel alloys and reproduced in this article as fig. 36 gives about $\Delta E = 0{\cdot}35$ ev from the Fermi surface to the top of the spin-up d bands, somewhat smaller than the estimate above.

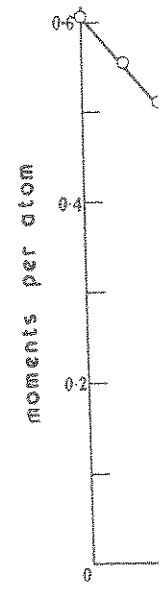
Fawcett and Reed (1962) investigated the anisotropy of the magnetoresistance of nickel. They concluded that the electronic band structure of nickel comprises a multiply connected surface of high mobility electrons (the s band), and an equal number of low mobility electrons (the holes). Phillips (1964) and Phillips and Mattheiss (1963) and Fawcett and Reed (1963) have discussed whether it is in the s band or the d band that the multiply-connected surface exists, i.e. whether the Fermi surface in the s band touches the (111) zone boundaries as in copper and silver. Phillips (1964) considers that it probably does. That this should occur for only 0·5 electrons per atom in the 4s zone is surprising, and would imply that the energies of states in directions other than ⟨111⟩ were strongly raised by hybridization with 3d, which is quite possible (§ 4).

Turning now to the alloys, the classic evidence that the energies of the 4s and 3d bands remain 'rigid' relative to each other comes from plots of saturation moment against composition for such alloy systems as Ni–Cu, Ni–Zn, Ni–Al (Mott 1935, Mott and Jones 1936). If the extra electrons due to the added element all go into the d band, as they would if there were no shift of one band relative to the other on the energy scale, the moment per atom due to a concentration c of the non-transition metal of valency z would be:

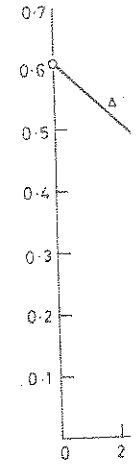
$$\mu_B (n_0 - cz),$$

where n_0 is the number of holes in nickel (0·5) and z is 1 for copper, 2 for zinc, etc.

Figure 20 shows the moment for Ni–Cu alloys due to Ahern *et al.* (1958). A careful analysis of the number of holes in the d band for a number of alloys has been made on the basis of these and other results by Crangle (1963), taking account of the g value and the orbital motion. This is shown in fig. 47. Figure 21 shows results similar to fig. 20 for Ni–Si, which are typical of alloys of nickel with polyvalent metals. A straight line drawn through the experimental points cuts the axis at $c = 15\%$, which would suggest 0·6 holes in the d band, though this result should not be



Magnetic saturation



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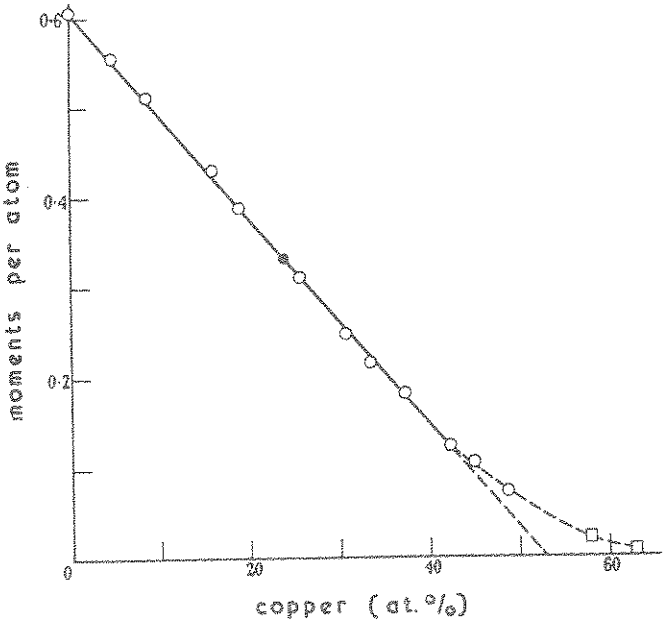
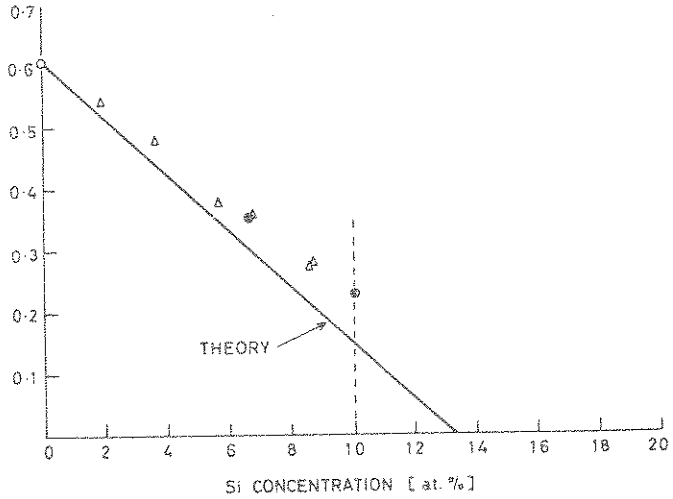


Magnetic saturation moment per atom in Bohr magnetons of Ni–Cu alloys (Ahern *et al.* 1958).

Fig. 21



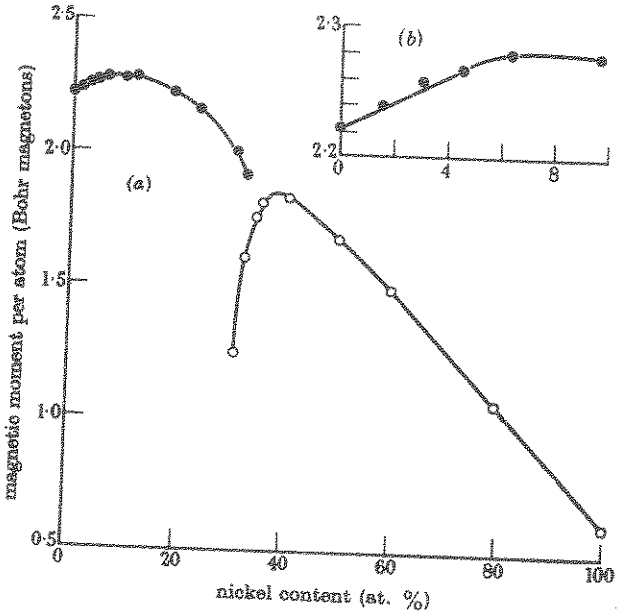
Magnetic moment per atom in Bohr magnetons of alloys of nickel with silicon. The diagram is modified from an unpublished report by Arajs. △ Marian (1937), ○ Ahern *et al.* (1958), ● Crangle and Martin (1959).

taken too seriously since some electrons from silicon may well go into the s band.

It seems likely that in most face-centred nickel-rich alloys the magnetic moment contributed by the d band is saturated. However, Ni–Fe alloys, as the concentration of iron is increased, show a contrary behaviour; fig. 22 shows† the moment of these alloys (Crangle and Hallam 1963) and fig. 23 the Curie temperature. The sudden drop in both, for increasing concentration of iron, may be due to a drop in the molecular field (i.e. in ΔE), with consequent lack of saturation. Gupta *et al.* (1964 b), however, give evidence that it may be due to the onset of antiferromagnetism superimposed on the ferromagnetism. This explanation is consistent with work on the Mössbauer effect for these alloys by Johnson *et al.* (1963). Some discussion of these alloys has already been given in § 6.

Evidence for non-saturation has been deduced by Wohlfarth from the dependence of magnetization on temperature and other evidence for a number of alloys; for Cu–Ni see Wohlfarth (1949 b, 1962), for Pd–Ni Wohlfarth (1956) and for the dilute alloys of nickel, etc. in palladium Rhodes and Wohlfarth (1963).

Fig. 22



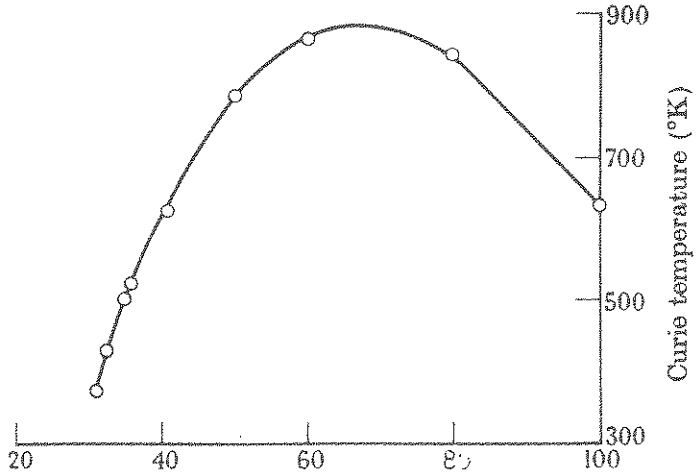
The variation of magnetic moment of b.c.c. alloys (solid points) and f.c.c. alloys (open points) with composition for Fe–Ni alloys (Crangle and Hallam 1963). The inset shows alloys of low nickel content on a magnified scale.

† Very recent work by Bando (1964) extends this curve to lower iron concentrations.

8.2. *Alloys of Iron with Non-transition Metals*

We summarize first the situation for iron. As we have already stated, the moment of the d band is not saturated (fig. 14). The displacement ΔE of energies of spin-up electrons relative to spin-down, if one takes the curve deduced by Cornwell and Wohlfarth (1962) from Wood's calculation (fig. 9 *a*), is 0·2 Ry or 2·6 ev. These authors, however, point out that the calculated value of γ (the specific heat coefficient) is much too low ($6{\cdot}3 \times 10^{-4}$ cal mol^{-1} deg^{-2} compared with the experimental value of $12{\cdot}0 \times 10^{-4}$), and if the whole band were contracted to give the right result, ΔE would be about 1·4 ev. The measurements of the specific heat (§ 11) of iron alloys by Beck and his colleagues (§ 11) give an $N(E)$ curve from which,

Fig. 23

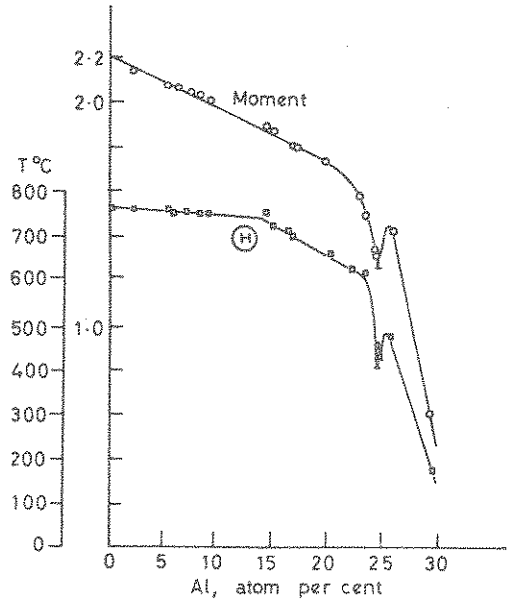


The dependence of the Curie temperature of iron–nickel alloys on composition (Crangle and Hallam 1963).

on certain assumptions, one can deduce $\Delta E \sim 1{\cdot}5$ ev, but this is probably too small if the peak in γ at e/a = 6·5 is a property of the alloys rather than the pure metal. Shimizu (1964) making this assumption also finds about this value (see § 11). Our earlier discussion suggests that ΔE may be due mainly to intra-atomic coupling within the iron d shells; this coupling should *not* be broken down above the Curie temperature. Our discussion in § 11 suggests that there are about 0·9 electrons in the s band, 0·3 holes in the spin-up d band and 2·6 holes in the spin-down d band, and a small negative polarization $-0{\cdot}2\,\mu_B$ of the s band.

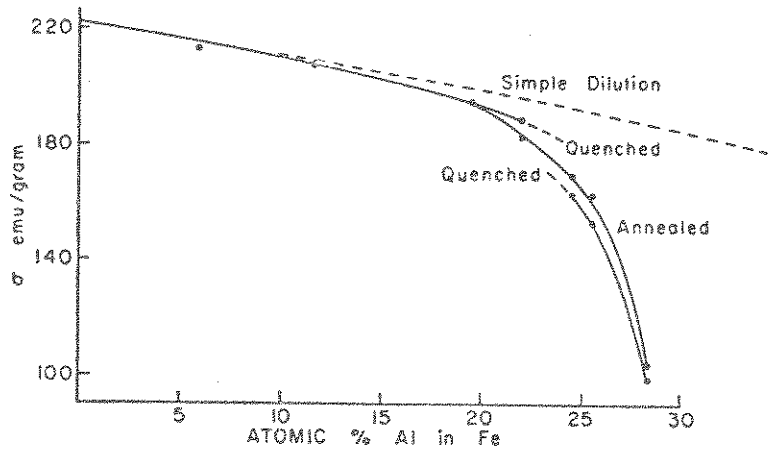
Turning now to the alloys of iron with non-transition metals, the first evidence that iron behaves differently from nickel comes from the work of Fallot (1936) on Fe–Al and Fe–Si. Figure 24 shows his results for the magnetic and Curie temperature of Fe–Al. Figure 25 shows similar data for the magnetic moment from Arrott and Sato (1959). Figure 26 shows

Fig. 24



Magnetic moment in Bohr magnetons and Curie temperature Θ of iron–aluminium (Fallot 1936).

Fig. 25



Magnetic moment σ in e.m.u./gram of Fe–Al alloys (Arrott and Sato 1959).

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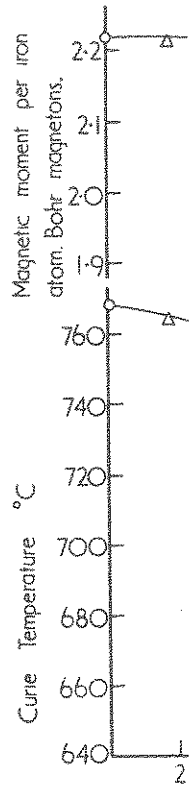

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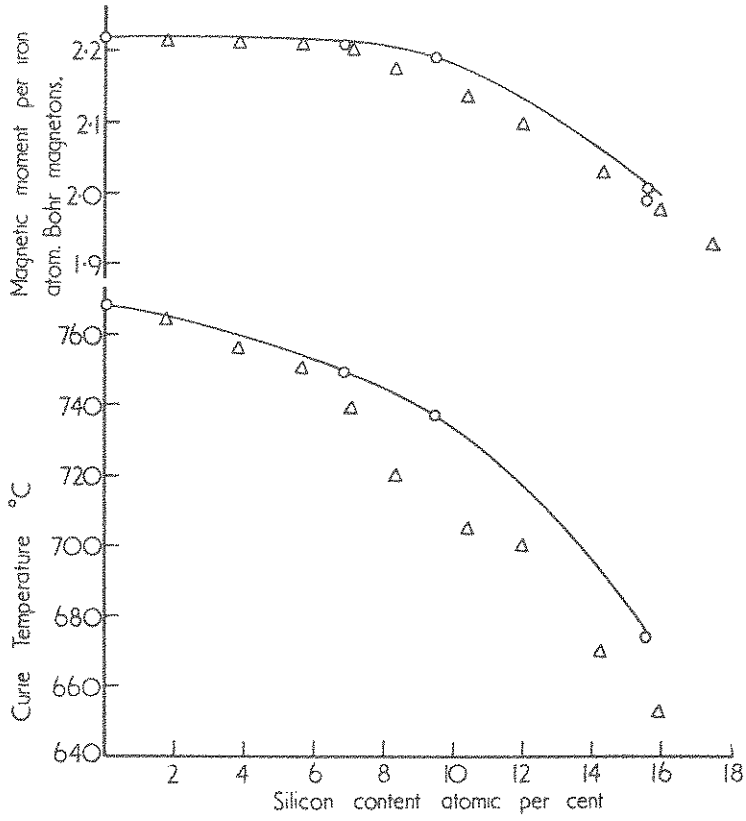
results due to Parsons *et al.* (1958). All these show that for these alloys the extra electrons from aluminium and silicon behave as if they went into the s band, as explained previously. One would not expect the experimental behaviour to correspond *exactly* to dilution, since this would imply that the spin-down Fermi surface is anchored rigidly at the minimum of the $N(E)$ curve, and it would be surprising if this were so. A decrease in the magnetic moment approximately given by the dilution concept is all the model can be said to predict.

Fig. 26



Magnetic moment and Curie temperature of Fe–Si alloys (Parsons *et al.* 1958), the former being plotted as moment per iron atom.

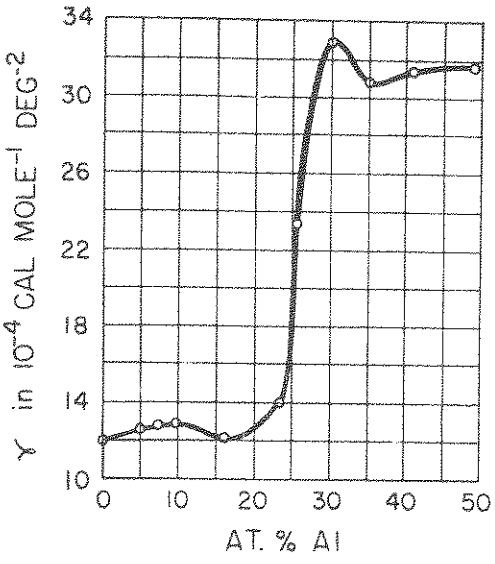
Further evidence that the extra electrons for aluminium go into the s band, and that there is no large shift of the spin-down Fermi level to the right, is provided by recent measurements of the specific heat coefficient γ for Fe–Al by Cheng *et al.* (1964). These are shown in fig. 27. Gupta *et al.* (1964 a) have made measurements also for Fe–Si, Fe–Ge, Fe–Sn and Fe–Sb; for none of these is there a particularly rapid rise in γ (fig. 28). A sharp rise

would occur if the added electrons went into the spin-down sub-band. The rise in γ for high concentrations in Fe–Al may be due to localized magnetic states, as the authors suggest, or to electrons going into the spin-down band as the molecular field (ΔE) drops. Here the moment and Curie temperature drop rapidly (fig. 24). Theoretical work of Sato and Arrott (1959) suggests that the coupling between iron atoms may change sign as the aluminium content increases.

§ 9. Palladium and its Alloys

The discussion we have given about the alloys of nickel and iron refer to the relative positions of the s and d bands in alloys. Palladium, as is well known, behaves like nickel rather than iron. In addition, however, specific heats of such alloys as palladium–silver are often used to obtain the form of the d band. How good an assumption this is, is not known†.

Fig. 27

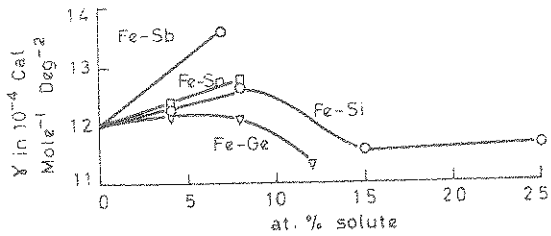


Electronic specific heat coefficient γ for Fe–Al (Cheng *et al.* 1964).

† Very recent work by Stern (1964) in the author's laboratory and by Beeby (1964) suggests that it does at any rate give the right band width for Pd–Ag and Ni–Co. The argument is that the d wave functions of the transition metal do not penetrate the noble metal much, so that alloying decreases the number of effective nearest neighbours and in the spirit of the tight binding approximation narrows the d band; but since there are fewer states in the band, the density of states $N(E_F)$ for a given value of e/a is the same as it would be if the band were rigid.

It is at any rate fairly certain that there are no d holes in the silver 4d shell in the alloys. This follows most directly from the discussions of the resistivity of these alloys given by Mott (1936 a, Mott and Jones 1936, Coles and Taylor 1962); no s–d scattering is caused by the deviation from periodicity caused by a silver atom in a palladium matrix. This is not inconsistent with the model of fig. 19, because the amplitude of the wave function illustrated there in the foreign atom at the Fermi surface is not expected to be large. It suggests too that in Pd–Ag or Ni–Cu the transition and noble metal do not form a common d band, but that the d shell of the noble metal is more likely to form a bound state below the d band of Pd or Ni.

Fig. 28



Electronic specific heat coefficient γ for Fe–Si, Fe–Sn, Fe–Ge, Fe–Sb (Gupta *et al.* 1964 c).

A recent review of the experimental material has been given by Hoare (1963), including both the electronic specific heat and the magnetic properties of the metal and of its alloys with silver and rhodium. The electronic specific heat is shown in fig. 29; it will be seen that it drops to a value comparable with silver at about 55 at. % of silver. If, as for nickel, the s and d bands are not displaced from each other on the energy scale by alloying, this would mean that palladium has about 0·55 holes per atom in the d band.

Figure 30 shows the density of states curve deduced by Hoare from these measurements, using a rigid band model†.

Figure 31 shows the magnetic susceptibility of palladium–silver alloys, the experimental data being taken from Svensson (1932), Wucher (1950) and Hoare *et al.* (1952, 1953, 1957). Again it will be seen that the susceptibility drops to zero at about 50% of silver.

Figure 32 shows the susceptibility of alloys of palladium with silver and rhodium at two different temperatures, from measurements by Budworth *et al.* (1960). The position of the peak clearly corresponds to the peak in the

† As pointed out by Vogt and Oehler (1963) on the basis of measurements of susceptibility, breakdowns of the model occur in the binary and tertiary alloys of these metals. Thus additions of equal amounts of Pd and Rh to palladium do have an effect on the susceptibility. This is perhaps not surprising, as even if $N(E)$ were unaffected the intra-atomic coupling would be.

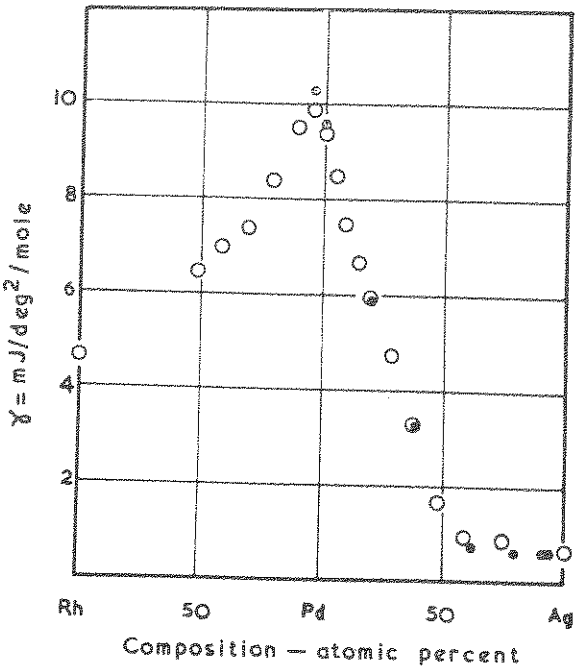
density of states, but the dependence on temperature is interpreted by these authors in terms of the following formula:

$$1/\chi_m = 1/\chi_0 - C.$$

Here χ_m is the measured susceptibility and χ_0 the susceptibility without exchange interaction, which should be given by:

$$\chi_0 = 2\mu_B^2 N(E_F)\left[1 + \frac{\pi^2}{6}(kT)^2\left\{\frac{N''}{N} - \left(\frac{N'}{N}\right)^2\right\}\right].$$

Fig. 29



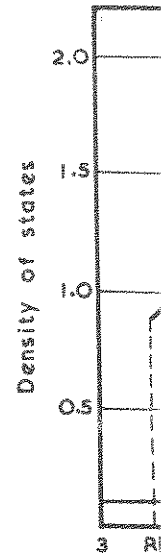
Electronic specific heat coefficient γ for Pd–Ag and Pd–Rh alloys.
○ Hoare and Yates (1957).
● Montgomery (unpublished); quoted by Hoare (1963).

Both C, which depends on the molecular field, and the constant multiplying the T^2 factor will be different for each alloy, but making reasonable assumptions about C, Hoare is able to show that the variation of χ_m is compatible with the values of $N(E)$ deduced from the specific heat.

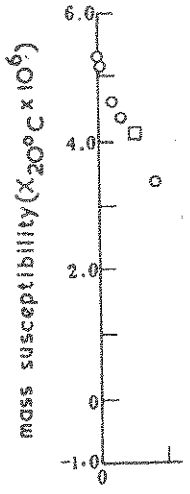
Shimizu (1961) has given an analysis of the paramagnetic susceptibility of palladium at high temperatures, which he takes to be of the form:

$$\chi = B/(T + \Theta) + \chi_c,$$

where χ_c is independent of temperature and mainly due to temperature-independent orbital paramagnetism of the d electrons. He estimates the



Density of states per



Susceptibility agair
(1932). Δ