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COLLECTIVE ELECTRON FERROMAGNETISM IN METALS AND ALLOYS

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Sommaire. — Plusieurs rapports généraux ayant paru récemment sur les diverses méthodes théoriques pour aborder le problème du ferromagnétisme, on s'occupe ici seulement de la méthode des bandes, comme elle a été développée à Leeds. On a pu étendre les travaux antérieurs sur les propriétés magnétiques des métaux (Stoner, depuis 1933), pour embrasser avec précision les variations à toutes les températures, grâce au calcul des intégrales de Fermi-Dirac (Mc Dougall et Stoner, 1938). Une théorie détaillée du ferromagnétisme s'ensuivit, avec une comparaison préliminaire entre les résultats théoriques et expérimentaux (Stoner, 1938-1939). Plus récemment, Wohlfarth (1949-1950) a donné des comparaisons plus étendues, et aussi des développements ultérieurs de la théorie.

Toute théorie du ferromagnétisme se fonde provisoirement sur des prémisses simplifiées, et il faut contrôler sur chaque point les conclusions par des expériences si l'on veut mieux comprendre ces phénomènes complexes. Ceci demande, de la part du théoricien, une appréciation critique des travaux expérimentaux, et souvent une analyse soigneuse et pénible des résultats. Il faut aussi que l'expérimentateur soit au courant des vues théoriques pour pouvoir établir efficacement le plan de ses expériences et présenter convenablement les résultats.

Les prémisses du traitement fondamental du problème sont que les électrons effectifs (ou les trous) sont dans une bande de forme parabolique, que l'énergie d'échange est proportionnelle au carré de l'aimantation et que la distribution des électrons, qui dépend de la température et du champ magnétique, doit être déterminée par application de la statistique Fermi-Dirac. Les paramètres caractéristiques sont le nombre des électrons effectifs dans la bande (qui ne correspond pas, en général, à un nombre entier de spins par atome, à cause du recouvrement des bandes), l'énergie de Fermi, ε_0, et la valeur de $k\theta'$, mesure de l'énergie d'échange. On peut calculer l'aimantation relative, ζ (rapport du nombre des spins parallèles au nombre total), comme fonction de H et de T pour toute valeur de $\frac{k\theta'}{\varepsilon_0}$. Dans la limite $\frac{\varepsilon_0}{k\theta'} \rightarrow 0$, les courbes correspondent à celles qu'on obtient dans la théorie de Weiss. Pour $\frac{k\theta'}{\varepsilon_0} > \frac{2}{3}$ une aimantation spontanée survient au-dessous d'une température θ $\left(\frac{\theta}{\theta'} < 1\right.$, sauf dans la limite classique$\left.\right)$ qui est le point de Curie. La saturation est incomplète même au zéro absolu pour $\frac{k\theta'}{\varepsilon_0} < 0{,}794$. On donne des courbes d'aimantation spontanée au-dessous de θ et de susceptibilité au-dessus de θ pour une série de valeurs de $\frac{k\theta'}{\varepsilon_0}$.

Pour le nickel, avec à peu près 0,6 trous par atome dans la bande d, on obtient une coordination remarquable des résultats expérimentaux pour la variation de la susceptibilité et de l'aimantation spontanée et aussi pour la chaleur spécifique électronique aux basses et à hautes températures. On ne doit pas s'attendre à un accord complet, parce que les valeurs de $k\theta'$ et de ε_0 ne sont pas constantes, mais varient avec la température, à cause de la dilatation thermique. Une anomalie apparente, le renversement de la courbure des courbes $\left(\frac{1}{\chi}, T\right)$ à hautes températures, peut s'expliquer par le transfert calculable d'électrons de la bande d à la bande s. Les écarts de la forme théorique des courbes expérimentales pour la variation de l'aimantation spontanée avec la température peuvent être attribués provisoirement à ce que l'énergie d'échange n'est pas strictement proportionnelle au carré de l'aimantation.

Par un développement naturel de la théorie, on peut traiter, d'une manière semblable, un grand nombre d'alliages du nickel, et l'accord avec les expériences est satisfaisant. Pour de grands domaines de composition de plusieurs alliages, la saturation au zéro absolu est incomplète, ce qui arrive aussi, presque certainement, pour le fer. Pour le fer et le cobalt, pourtant, l'approximation d'une bande parabolique ne peut pas être bonne. On est en train de faire une analyse des effets des diverses formes de bandes.

On donne une brève indication des travaux en cours sur des problèmes plus fondamentaux relatifs aux énergies d'échange et de corrélation, sur l'effet magnétocalorique dans les champs forts et sur les propriétés électriques des métaux ferromagnétiques et autres métaux.

1. **Introduction.**

— Although it has been suggested that participants in this conference should survey generally the present position in the field on which they are reporting, it would serve no useful purpose for me to cover more hurriedly precisely the same ground as do the recent comprehensive and general reviews of the theory of ferromagnetism by Van Vleck [1945, *see* also 1947, 1949] and by myself [Stoner, 1948]. Further, one aspect of the subject will be presented by Van Vleck himself with far more authority than I could claim. There are two main approaches to the theoretical interpretation of the fundamental phenomena of ferromagnetism, one deriving from the Heitler-London treatment of molecules, starting from atomic wave functions, the other deriving from the electron energy band treatment of metals, which has a close analogy with the Hund-Mulliken treatment of molecules, using molecular orbitals. It is the second approach with which I shall deal, and in particular with the theoretical work at Leeds on what I have ventured to call «collective electron ferromagnetism».

The general outlook underlying the Leeds work is outlined in paragraph 2, but it is appropriate to indicate first, very briefly, the historical course of development. In an early paper [Stoner, 1933] it was shown that with the band treatment a satisfying qualitative explanation could at once be given of the occurrence of non-integral magneton values for the saturation moments per atom in the ferromagnetic metals, and of the variation with composition of the mean moment per atom in certain ferromagnetic alloys. The original tentative interpretation could be made more definite only in the light of later work on the energy band structure. A precise calculation of the forms of the energy bands in ferromagnetic metals presents very great difficulties, but it is fairly certain that in nickel a narrow *d* band, approximately parabolic at its upper end, is overlapped by a much wider *s* band (see *fig.* 1 below). This was shown semi-quantitatively by Slater [1936 *a*] on the basis of calculations for copper by Krutter [1935], so confirming an earlier brilliant suggestion by Mott [1935]. Rather loosely, the ferromagnetic properties may be attributed to the " holes " in the *d* band, approximately 0.6 per atom. The theoretical treatment, of a collective electron type, by Slater [1936 *a*, *b*] of the ferromagnetism of nickel, embodied all the essential ideas, but the methods of calculation were such that the results obtained were presented only as very rough approximations.

In the meantime, applications of Fermi-Dirac statistics had been made to free electron susceptibility, both dia-and paramagnetic [Stoner, 1935], free electron specific heat [1936 *a*], and spin paramagnetism [1936 *b*], and to the interrelation in metals between electronic specific heat and spin paramagnetism, both with and without exchange interaction [1936 *c*]. This led naturally to a consideration of ferromagnetism, but it was soon found that rough interpolation between the values given for the relevant Fermi-Dirac integrals by the " high " and " low temperature " series expressions as used in this earlier work, could not give sufficiently precise or reliable values for the intermediate temperature range which is of central physical interest. Comprehensive evaluations of the required Fermi-Dirac functions for the whole temperature range were therefore made [Mc Dougall and Stoner, 1938]; and I should like to state that the preparation of these standard tables would hardly have been undertaken, and would certainly not have been carried out with such completeness, without the collaboration of my colleague Dr J. Mc Dougall. These tables are basic to the quantitative theoretical treatment of the properties of electronic assemblies whether in metals or in stars [e. g. Stoner, 1938 *a*, *b*, 1939 *a*] and in particular are essential to a satisfactory treatment of collective electron ferromagnetism. This subject was treated in two papers [Stoner, 1938 *c*, 1939 *b*] shortly before the War, the first dealing with the temperature variation of intrinsic magnetization below and above the Curie point, the second with the associated energy and specific heat. Except for a short paper on the paramagnetic magneton numbers of the ferromagnetic metals [Stoner, 1938 *d*], however, no detailed comparison with experiment was made.

Work of this kind, like so much of immensely higher value, of necessity stops in the face of the immediate imperatives of total war, and it has not been easy, in the precarious aftermath, to pick up the threads again. But there is now, once more, for how long none can say, a little opportunity and a little time for a university scientist to pursue knowledge and understanding freely and as best he can within his powers; not indifferently to menacing conflicts, not irresponsibly, ready to do all that his opportunities allow towards bringing about a saner world, but conscious that this scientific search, despite its limitations in scope, is yet a thing of value in intself, and not simply a means to a desirable or undesirable material end.

My own active research interests in magnetism have extended to the behaviour of ferromagnetics in low and moderate fields, and problems connected with domain structure and with magneto-thermal effects have occupied much of my available time. I have, however, been fortunate in having as a research student, and later, until very recently, as a research assistant, Dr E. P. Wohlfarth, who, under my initial guidance, has continued the work on collective electron ferromagnetism. Most of what I have to say in this report is based on my own earlier papers [1938 *c*, *d*, 1939 *b*], and on the very recent papers of Wohlfarth [1949-1950]. I do not propose to enter into the technical details of the work, which are readily available to those who wish to study them, but I want rather to indicate the underlying outlook and principles, and then to discuss very briefly the relation between the consequences of the theoretical treatment and the experimental results, so far as this has been examined.

2. **General outlook.** — The status of the collective electron treatment as a " theory " of ferromagnetism is so liable to misunderstanding that I am following the unusual course of describing, in this section, the general outlook underlying the Leeds work.

Theoretical. — The theoretical problem of ferromagnetism might perhaps be stated somewhat as follows, with reference to nickel purely for definiteness in exemplification : on the basis of the wide theoretical scheme of quantum mechanics, whose validity, over the relevant range, must be accepted as established, and given a fairly complete and precise knowledge of the structure and properties of free nickel atoms, it is to be shown that the lowest energy state of an aggregate of such atoms is one in which they form a crystal, of a certain type (face-centred cubic) and lattice dimensions, and whose properties vary with temperature in a specific way; in particular, that these crystals are spontaneously magnetized at absolute zero to a degree corresponding to approximately (but not exactly) 0.6 Bohr magnetons per atom; that the spontaneous magnetization decreases in a definite way with temperature to zero at the Curie point; that above the Curie point, the aggregate is paramagnetic, the susceptibility varying in a particular way with temperature; and that there are thermal and other characteristics intimately connected with the magnetic characteristics. It would no doubt be possible, with an adequate supply of dots, to set up equations whose solutions, it might be stated, would give everything that was sought. Such a procedure would, however, be completely unrevealing and indeed useless; it is only necessary to consider the immense difficulty of obtaining a rigorous solution of the hydrogen molecule problem to realise that the problem of ferromagnetism, attacked in this way, would be completely intractable.

The problem must be enormously delimited. It may be taken as given that nickel atoms form a crystal of known lattice spacing and that it is a metal, so that what is known generally about the electronic structure of metals may be taken as a basis. No exact calculation of the electronic band structure in nickel has been made, even if it could be made, and the simplest assumption consistent with available knowledge may be adopted. The interaction energy with which ferromagnetism is associated is only a small part of the total, and is unlikely to be of importance in determining the band structure itself. The " ferromagnetic interaction " may, moreover, be represented by a " molecular field ". The manner in which this originates as a result of exchange interaction is known in a general way, but rigorous calculations of the dependence on magnetization present formidable difficulties. It is reasonable to make the tentative assumption that the associated energy is proportional to the square of the magnetization, and to examine the consequences to which this leads. Further, it must be assumed that the distribution of electrons among available states, dependent on temperature, molecular field, and applied field, is determined by Fermi-Dirac statistics. Finally, it may be assumed, in accordance with the experimental evidence on the gyromagnetic effect, that orbital moment plays a minor part in connection with the primary effects, the important part it may play in various secondary effects (e. g. magnetocrystalline anisotropy) being left for subsequent, or at least separate, consideration.

The collective electron treatment of ferromagnetism, when a parabolic form is assumed for the relevant electron band, as in the basic calculations, may be regarded formally as a replacement, in the simplest molecular field treatment adapted to electron spins as carriers of the magnetic moment, of Maxwell-Boltzmann by Fermi-Dirac statistics. This greatly complicates the calculations, and, indeed, it has been suggested that the elaboration on the statistical side is disproportionate, in view of the over-simplification of the physical situation in other premises of the treatment. This, however, is completely to misunderstand the position. It is just because the consequences of a rigorous treatment of the " distributional " side of the problem are in detail so complex and often unexpected (although only one additional parameter, the band width, is introduced) that it is essential to keep all other premises as simple as possible, so that the logical interconnection between premises and consequences shall be clear.

It turns out that the theoretical scheme, in its simplest form, gives a wide coordination of both the magnetic and the associated thermal properties of metallic ferromagnetics. Exact agreement with experiment (that is for both these sets of properties over the entire temperature range) is, indeed, not attained; nor should it be, for it is known thet the premises are an oversimplification. The character of the agreement or disagreement may, however, give a valuable guide as to the direction in which theoretical effort may be concentrated in the search for fuller elucidation. Without such guidance, in view of the complexity of the total problem, the most intensive theoretical efforts and computational labour may well be largely in vain.

Experimental. — The aim of theoretical physics is to coordinate experimental results, and in so doing, to " predict " others which might be obtained under prescribable conditions. On the experimental side, in the field of immediate interest, although there are many important gaps, there is a wealth of reliable experimental information, provided, in a large degree, by the brilliant series of investigations carried out between the wars at Strasbourg, under the inspiration of Pierre Weiss, whose name will be honoured as long as there are men who are interested in magnetism.

Comparison of the results of a " theory " with experiment is by no means so trivial or routine a task as is sometimes supposed. In connection with collective electron ferromagnetism, it would be desirable to have measurements of the susceptibility over a wide temperature range above the Curie point, of the magnetization at a series of high fields at suitably spaced temperatures between the Curie point and absolute zero, and of the specific heat over the entire temperature range for pure ferromagnetic metals and for many alloys. Where extensive results are available, they are often due to a number of different investigators who have made measurements over different temperature ranges using the diverse techniques which are appropriate. Nominally similar materials may differ significantly in purity, and with alloys the composition, and, hardly less important, the degree of homogeneity, may be uncertain. Unsuspected secondary effects may invalidate the results, and there are always the inevitable " experimental errors " of many kinds. Again, experimental results may be presented, often unavoidably, in a form far from convenient for comparison with theory. Essential information may be unrecorded, observations may be presented for only a few arbitrarily chosen and badly spaced temperatures, or the results may be " economically " presented in terms of one or two values derived on the basis of some imperfect theory. If, for example, interest is centred on the non-linearity of the relation between $\frac{1}{\chi}$ and T above the Curie point, it is baffling to be given only a Bohr magneton value, p_B, corresponding to the slope of the " best " straight line that can be drawn through unrecorded experimental points over an arbitrarily chosen temperature range.

The intercomparison of experimental results, their critical assessment and their reduction to a convenient form calls for care and patience and an ability to appreciate both experiment and theory of a kind which tends to become atrophied when physicists confine themselves too narrowly to imaginarily closed domains proper to the experimentalist and to the theorist. Experimental results must not always be taken at their face value, but where there is unambiguous disagreement between experiment and theory, it is experiment which is right, for it is the experimental results which are to be explained by the theory. The theory, however, is not necessarily wrong. The disagreement may be due to the sometimes enforced oversimplification of the premises of a manageable deductive argument. It is suggested that this is the position with respect to the collective electron treatment of ferromagnetism. Once the general applicability is established, as it has been, genuine disagreement between theory and experiment becomes much more interesting and exciting than agreement, for it is just this which is the challenge to the discovery of, and the invention of a method of treating, important factors which may have been insufficiently appreciated or entirely overlooked.

3. **Statement of premises.** — In this section the premises of the basic treatment [Stoner, 1938 *c*] are stated as simply as possible, with a few brief comments.

(i) The system under consideration is a set of N electrons in a partially filled electronic energy band in which the energy density of states is given by

$$\frac{d\nu}{d\varepsilon} = \frac{3}{4}\left(\frac{N}{\varepsilon_0^{\frac{3}{2}}}\right)\varepsilon^{\frac{1}{2}}, \qquad (3.1)$$

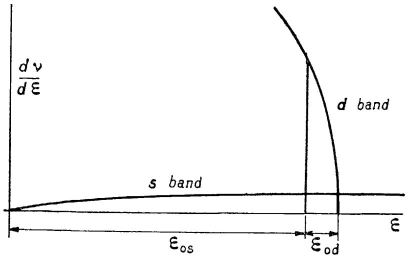

Fig. 1. — Diagrammatic representation of band structure of nickel near the Fermi limit.

where ε_0 is the maximum electron energy when the electrons are in balanced pairs in the lowest energy states. Alternatively, N may be the number of " holes " in a band [*cf.* Stoner, 1936 *c*], the energy then being measured from the top of the band. The number N corresponds to q electrons (or holes) per atom, and q is not necessarily integral. This can arise from band overlap. In nickel the value of q is approximately 0.6, this corresponding to the number of holes in the d band, as illustrated in figure 1.

The electrons are not to be thought of as " free "; the wave functions may be very complicated, incorporating, for example, some " d-like " characteristics. That the band is parabolic, as for free electrons, is a simplifying assumption (which, for nickel at least, in the relevant region, has some justification); but the value of ε_0 (or, correspondingly, of the effective mass of the electrons, or holes) may be widely different from that for free electrons.

(ii) Exchange interaction gives rise to a term in the energy expression proportional to the square of the magnetization, so that the energy of an electron with spin antiparallel and parallel to the magnetization may be written

$$\varepsilon_1 = \pm k\theta'\zeta, \tag{3.2}$$

where ζ is the relative magnetization $\left(\text{i. e. } \frac{M}{N\mu_B}\right.$ where M is the magnetic moment of the aggregate of N electrons$\left.\right)$, and θ' is a parameter with the dimensions of temperature, and which with the simple " classical " treatment would correspond to the Curie temperature. The equation (3.2) is equivalent to the first approximation given by most treatments of the exchange interaction problem. Reference is made later (§ 5) to the deficiencies of this approximation.

(iii) The distribution of electrons in the band as dependent on the temperature, molecular field, and applied field, H, is to be determined by application of Fermi-Dirac statistics.

This completes the statement of the premises. It follows from (iii) that the expression for the energy distribution of electrons in the band may be put in the form

$$\frac{\mathrm{d}N}{\mathrm{d}\varepsilon} = \frac{\dfrac{\mathrm{d}\nu}{\mathrm{d}\varepsilon}}{\exp\left\{\dfrac{\varepsilon+\varepsilon'}{kT} - \eta\right\} + \mathrm{I}}, \tag{3.3}$$

where ε is taken to include the whole of the electronic energy except that dependent on the magnetization [as given by eq. (3.2)] and on the external field. The corresponding terms make up ε'. An implicit equation for the statistical parameter, η, related to the Gibbs free energy per particle, is

$$N = \frac{3}{4}N\left(\frac{kT}{\varepsilon_0}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\eta+\beta+\beta') + F_{\frac{1}{2}}(\eta-\beta-\beta')\right\}, \tag{3.4}$$

in which the two terms give the numbers of electrons with spins parallel and antiparallel to the resultant field; and the corresponding total magnetic moment, M, and relative magnetization, ζ, are given by

$$M = N\mu_B\zeta = \frac{3}{4}N\mu_B\left(\frac{kT}{\varepsilon_0}\right)^{\frac{3}{2}} \times \left\{F_{\frac{1}{2}}(\eta+\beta+\beta') - F_{\frac{1}{2}}(\eta-\beta-\beta')\right\}, \tag{3.5}$$

where

$$\beta = \frac{k\theta'\zeta}{kT}, \qquad \beta' = \frac{\mu H}{kT},$$

and

$$F_k(\eta) = \int_0^\infty \frac{x^k\,\mathrm{d}x}{e^{x-\eta}+\mathrm{I}}.$$

The Stoner-Mc Dougall tables of the Fermi-Dirac functions (1938) give $F_{\frac{3}{2}}(\eta)$, $F_{\frac{1}{2}}(\eta)$, and derivatives of $F_{\frac{1}{2}}(\eta)$ for the range -4 to $+20$ (corresponding, in the simple case, to a range of $\frac{kT}{\varepsilon_0}$ from approximately 0.05 to 12); outside the range of the tables the functions are readily evaluated from series.

The equations (3.4) and (3.5) are the basic equations of the treatment. Their " solution ", which in general can only be effected numerically, involves, formally, the elimination of the statistical parameter η. The solutions must finally be expressed in a form convenient for comparison with experiment, that is, essentially, in tables or curves giving the variation of the magnetization with T and H for a sufficient series of values of the interaction and band width energy parameters $k\theta'$ and ε_0. For an account of the manipulation of the equations, reference must be made to the original papers. It must suffice to say that the numerical work, even for the most unfavourable ranges, is reasonably straightforward, and that for some problems (e. g. the variation of susceptibility above the Curie point) the equations reduce to much simpler forms which are dealt with readily. It may be noted that in the limit $\left(\frac{\varepsilon_0}{k\theta'}\right) \to 0$ the equations reduce to those of the simple classical treatment.

It may be useful to include here the expression, corresponding to (3.4) and (3.5), for the total energy, E, which is basic to the treatment of the energetic characteristics,

$$\frac{E}{N\varepsilon_0} = \left(\frac{kT}{\varepsilon_0}\right)\left\{\frac{F_{\frac{3}{2}}(\eta+\beta+\beta') + F_{\frac{3}{2}}(\eta-\beta-\beta')}{F_{\frac{1}{2}}(\eta+\beta+\beta') + F_{\frac{1}{2}}(\eta-\beta-\beta')} - \beta'\zeta - \frac{\mathrm{I}}{2}\left(\frac{\theta'}{T}\right)\zeta^2\right\}, \tag{3.6}$$

and, for completeness, that for the free energy, F,

$$\frac{F}{N\varepsilon_0} = \left(\frac{kT}{\varepsilon_0}\right)\eta - \frac{\mathrm{I}}{2}\left(\frac{kT}{\varepsilon_0}\right)^{\frac{3}{2}}\left\{F_{\frac{3}{2}}(\eta+\beta+\beta') + F_{\frac{3}{2}}(\eta-\beta-\beta')\right\} + \frac{\mathrm{I}}{2}\left(\frac{k\theta'}{\varepsilon_0}\right)\zeta^2. \tag{3.7}$$

In the absence of exchange interaction and of an external field, these expressions reduce to the much simpler " standard " forms for the thermodynamic functions with Fermi-Dirac statistics, which have been treated in detail [Stoner, 1939 *a*].

4. **General character of the results of the theoretical treatment.** — Reasonably complete

numerical results have been obtained for the variation with temperature of the magnetic properties of the " idealized ferromagnetic ", as described above, for a series of values of the specifying parameters $k\theta'$ and ε_0; results for the variation of the electronic energy and specific heat are less detailed, but sufficiently representative. It is to be understood that the basic calculations apply to N electrons or holes (q per atom) in a single band of standard (parabolic) form. No account is taken of the possibility of a temperature variation of $k\theta'$ and ε_0. This almost certainly occurs in actual ferromagnetics, with effects which are by no means negligible, as a concomitant of thermal expansion. Another important effect, the " transfer " effect, has been taken into account in more refined calculations in special cases, as mentioned below.

The results have been presented in the various papers in the form of numerical tables, with a degree of accuracy more than adequate as a basis for a comparison of theory with experiment, but which is essential if various interesting points are to be brought out clearly. It will be sufficient here to indicate the general character of the results by diagrams, with a few short comments. It should be noted that it is usually appropriate to plot suitably reduced quantities, so that each curve is a " corresponding state " curve (analagous to the curve obtained in the Debye theory of specific heat, by plotting against $\frac{T}{\theta_d}$ rather than against T).

Magnetic characteristics. — A basic relation is that between $\frac{1}{\chi}$ and T for electron spin paramagnetism with zero exchange interaction. This is shown, in reduced form, in figure 2, curve 1, the corresponding " classical curve " being the straight-line 1′. The Fermi-Dirac curve approaches the classical straight line asymptotically. Writing $\varepsilon_0 = k\theta_F$, the value of θ_F would be of the order of 10^4 for strictly free electrons; for the holes in a d band it may be of the order 10^3. The limit $\varepsilon_0 \rightarrow 0$ corresponds to classical statistics.

The effect of positive exchange interaction is to lower the reduced inverse susceptibility curve by $\frac{k\theta'}{\varepsilon_0}$. If the lowered curve cuts the T axis, the point of intersection corresponds to the Curie temperature, θ. The continuation of the susceptibility curves below θ has no physical significance, as spontaneous magnetization sets in at this temperature and increases as the temperature decreases. The Curie temperature θ is always less than θ' (except in the classical limit), and a positive exchange interaction does not necessarily give rise to ferromagnetism. A necessary condition for ferromagnetism (i. e. the occurrence of spontaneous magnetization) is

$$\frac{k\theta'}{\varepsilon_0} > \frac{2}{3} = 0.6667. \tag{4.1}$$

It may also be shown that a condition for complete parallelism of the spins in the spontaneously magnetized state at absolute zero is

$$\frac{k\theta'}{\varepsilon_0} \geq 2^{-\frac{1}{3}} = 0.7937. \tag{4.2}$$

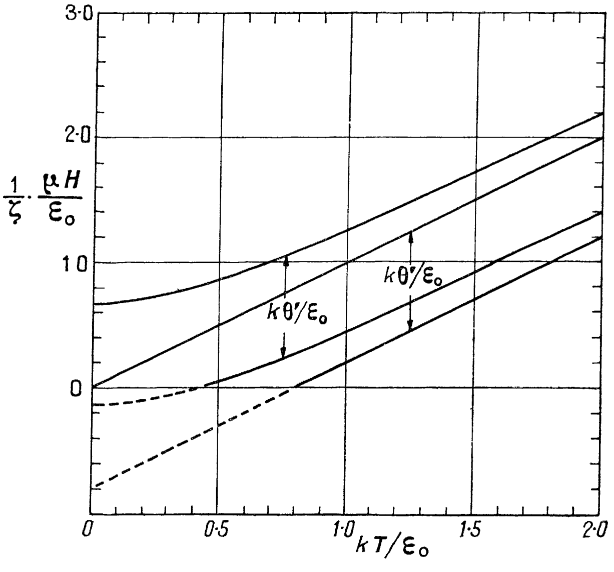

Fig. 2. — Relation between reduced inverse susceptibility and reduced temperature.

1, 1′, Fermi-Dirac and classical curves for electron spin paramagnetism, without exchange interaction; 2, 2′, corresponding curves with positive exchange interaction, drawn for $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}}$.

In the intermediate range the relative spontaneous magnetization at 0° K is less than unity. Symbolically

$$0 < \zeta_0 < 1 \qquad \text{for} \quad \frac{2}{3} < \frac{k\theta'}{\varepsilon_0} < 2^{-\frac{1}{3}}. \tag{4.3}$$

(*see* also *fig.* 5). The numerical values in (4.1) and (4.2) depend, of course, on the particular form of band assumed, but the possibility of incomplete saturation at absolute zero for a certain range of values of the exchange interaction energy is not peculiar to this form.

The variation of spontaneous magnetization below, and of the inverse susceptibility above the Curie point, θ, is shown in figure 3. The relation between $\frac{k\theta'}{\varepsilon_0}$ and $\frac{k\theta}{\varepsilon_0}$, it may be noted, is precisely the same as that given by curve 1 in figure 2 (the vertical and horizontal scales are to be re-labelled $\frac{k\theta'}{\varepsilon_0}$ and $\frac{k\theta}{\varepsilon_0}$ respectively).

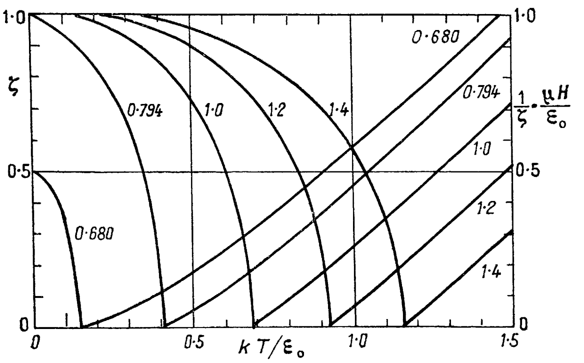

Fig. 3. — Spontaneous magnetization below (falling curves, scale on left) and inverse of susceptibility above (rising curves, scale on right) the Curie point as functions of $\frac{kT}{\varepsilon_0}$. (Stoner, 1938 *c.*)

The reduced curves of figure 3 (and the numerical results from which they are drawn) are those most directly obtainable from the computations, but they do not bring out clearly the essential differences in form for different values of $\frac{k\theta'}{\varepsilon_0}$, nor are they convenient for comparison with experiment. A more illuminating representation is that shown in figure 4,

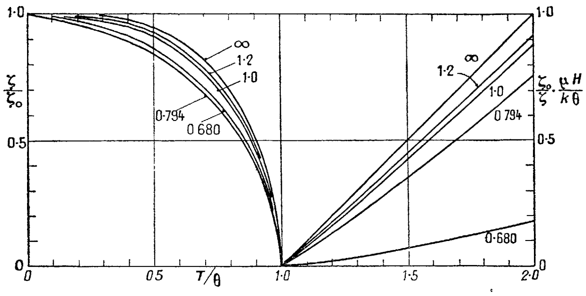

Fig. 4. — Reduced magnetization below, and reduced inverse susceptibility above the Curie point as functions of $\frac{T}{\theta}$. The numbers on the curves give the values of $\frac{k\theta'}{\varepsilon_0}$. The limiting curves labelled ∞ correspond to the use of classical statistics. (Stoner, 1938 *c.*)

in which the reduced quantities plotted are related to the experimentally observable specific magnetization, σ (with the value σ_0 at absolute zero), and the mass susceptibility, χ, by

$$\frac{\zeta}{\zeta_0}=\frac{\sigma}{\sigma_0},\qquad \frac{\zeta_0}{\zeta}\frac{\mu_B H}{k\theta}=\frac{\mu_B\sigma_0}{k\theta}\frac{1}{\chi}. \tag{4.4}$$

The spontaneous magnetization curves (on the left in figure 4) plotted against $\frac{T}{\theta}$, are always lower with Fermi-Dirac statistics than the limiting curve (labelled ∞) with Maxwell-Boltzmann statistics. The variation with $\frac{k\theta'}{\varepsilon_0}$ is regular, but not monotonic. The lowest curve is that for the value of $\frac{k\theta'}{\varepsilon_0}$ for which complete parallelism of the electron spins is just attained at absolute zero. The inverse susceptibility curves are also lower (i. e. the corresponding susceptibilities are higher) than the limiting classical curve. The differences between these curves is not very great for the higher values of $\frac{k\theta'}{\varepsilon_0}$, but becomes much more marked in the range of $\frac{k\theta'}{\varepsilon_0}$ values [*see* (4.1) to (4.3)] for which the relative magnetization at absolute zero, ζ_0, is less than unity. The variation of ζ_0 with $\frac{k\theta'}{\varepsilon_0}$ is shown in

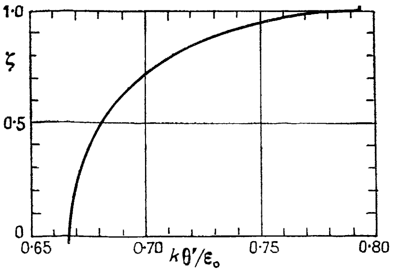

Fig. 5. — ζ_0 as a function of $\frac{k\theta'}{\varepsilon_0}$. (Stoner, 1938 *c.*)

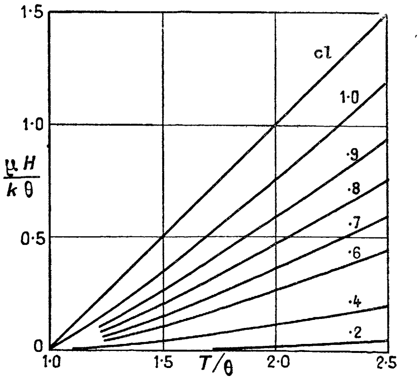

Fig. 6. — Reduced inverse susceptibility curves for a single band. Values of ζ_0 are given on the curves. The curve for $\zeta_0 = 1$ is that for $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}}$. For values of $\frac{k\theta'}{\varepsilon_0}$ greater than this, the curves lie between the $\zeta_0 = 1$ curve, and the limiting curve, cl, corresponding to classical statistics. (After Wohlfarth, 1949 *a.*)

figure 5, and the reduced inverse susceptibility curves for $\frac{k\theta'}{\varepsilon_0}$ corresponding to suitably spaced values of ζ_0 in figure 6. These curves (or the more complete set of numerical values corresponding to them) are of great value in the analysis of experimental results.

Associated thermal characteristics. — The variation of electronic energy and specific heat for electrons in a band of standard form when spontaneous magnetization does not occur (i. e. for a non-ferromagnetic metal) is shown in figure 7.

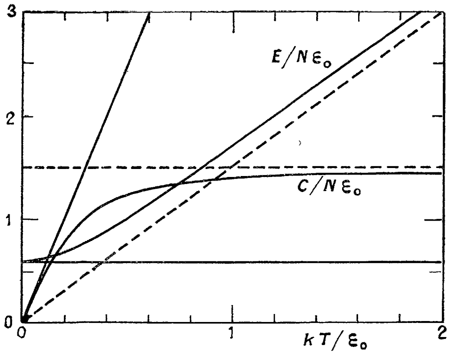

Fig. 7. — Variation with temperature of electronic energy and specific heat.

E, *C*, energy and specific heat for *N* electrons. ε_0, maximum electron energy (band width) at absolute zero. *k*, Boltzmann constant. The full straight lines are tangents at $\frac{kT}{\varepsilon_0} = 0$, and the broken lines the asymptotes to the curves. (Stoner, 1938 *b*.)

The limiting value of the electronic specific heat for $\frac{kT}{\varepsilon_0} \to 0$ is given by

$$\frac{C}{Nk} = \frac{\pi^2}{2}\frac{kT}{\varepsilon_0} = 4\;934\,\frac{kT}{\varepsilon_0}. \tag{4.5}$$

From measurements in the liquid helium range, where the electronic contribution to the total specific heat can be unambiguously separated from the lattice contribution, it is found that the electronic contribution is in fact proportional to the temperature. For some metals (e. g. Cu, Ag) the proportionality factor is in good agreement with that given by (4.5) if ε_0 is calculated on the assumption that the electrons are free; for other metals (e. g. Fe, Ni, Pd, Pt, Ta, Nb) the experimental factor is much higher, indicating that the energy density of states at the top of the Fermi distribution is much greater, or, if the band is of standard form, that the width of the occupied region (or unoccupied region, if holes at the top of a band are involved) is much narrower.

For a ferromagnetic below the Curie temperature, θ, the numbers of spins pointing in opposite directions are unequal; the distributional energy differs from that for a non-ferromagnetic (for the same N and ε_0), and in addition there is the exchange energy proportional to ζ^2 [*cf.* (3.6)]. Above θ, the results illustrated by figure 7, are applicable. The calculation of the variation of electronic energy and specific heat over the temperature range up to θ is troublesome and has been carried through in detail only for $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}}$ (the value for which parallelism of spins is just attained at absolute zero). The results for the specific heat are shown in figure 8.

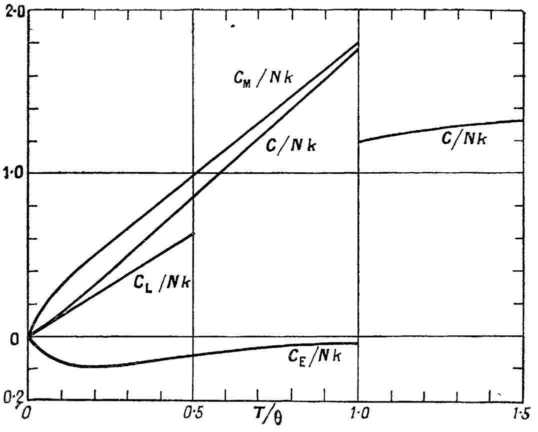

Fig. 8. — Electronic specific heat as a function of $\frac{T}{\theta}$ for $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}} = 0.7937 \left(\frac{k\theta}{\varepsilon_0} = 0.4065\right)$. (Stoner, 1939 *b*.)

The electronic specific heat, *C*, may be regarded as made up of a quasi-magnetic part, C_M, associated with the temperature variation of $Nk\theta'\zeta^2$, and a part, C_E, associated with the variation in the energy distribution. The part C_E may in turn be considered as a sum of two parts, C_1 and C_2, the first corresponding to change of temperature with ζ constant, the second to change of ζ with temperature. A rather unexpected general result (*see* Stoner, 1939 *b*, p. 353) is that for all values of $\frac{k\theta}{\varepsilon_0}$, in the low temperature limit $\frac{T}{\theta} \to 0$, the quasi-magnetic contribution, C_M is numerically equal to, but of opposite sign to C_2. Thus the limiting low temperature specific heat is calculable directly from the distribution at absolute zero, and is not dependent on the manner of variation of ζ with temperature. The general result is :

For $\frac{kT}{\varepsilon_0} \to 0$,

$$\frac{C}{Nk} \to \frac{\pi^2}{4}\left\{(1+\zeta_0)^{\frac{1}{3}} + (1-\zeta_0)^{\frac{1}{3}}\right\}\frac{kT}{\varepsilon_0}. \tag{4.6}$$

For $\zeta_0 = 0$, this reduces to (4.5).
For $\zeta_0 = 1$,

$$\frac{C}{Nk} = \frac{2^{\frac{1}{3}}\pi^2}{4}\,\frac{kT}{\varepsilon_0} = 3.109\left(\frac{kT}{\varepsilon_0}\right). \qquad (4.6\,a)$$

Apart from the complete results for $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}}$, and the limiting low temperature specific heat, given by (4.6), values have been obtained, effectively for the whole range of values of $\frac{k\theta'}{\varepsilon_0}$ $\left(\text{or of } \frac{k\theta}{\varepsilon_0}\right)$, of the change of energy between absolute zero and the Curie point and of the specific heat immediately below θ (and of the component contributions), and of the specific heat immediately above θ, and so of the Curie point discontinuity. The curves showing the variation of these quantities with $\frac{k\theta}{\varepsilon_0}$ have many interesting features, but they will not be discussed here, more particularly because adequate consideration has not yet been given to the analysis of the available experimental results in the light of them. It must suffice to state that although the " classical " values are approached for $\frac{k\theta'}{\varepsilon_0}$ considerably greater than unity, for $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}}$ or less (the relevant range for most actual ferromagnetics), the theoretical values may be widely different from those given by the " classical " treatment, and to a degree offering promise of far more satisfactory agreement with experimental results. As is well known, a strict application of Maxwell-Boltzmann statistics gives results which are completely incompatible with experiment.

In summary, the treatment of ferromagnetism on a collective electron basis, using Fermi-Dirac statistics, leads to a consistent scheme covering all the related electronic properties, thermal as well as magnetic. As compared with the classical treatment an additional parameter is required, the band width, ε_0, but this is not introduced arbitrarily, but is necessitated by the physical situation. The results of the theoretical and computational treatment are broadly consistent with experimental findings, but owing to the simplifications made in the premises, the scheme should not be expected to give complete and exact agreement with experiment. Rather, the scheme provides logically consistent sets of results for a complete family of " idealized " ferromagnetics, by comparison with which the interpretation of the significance of experimental results for actual ferromagnetics may be enormously facilitated.

5. Applications to metals and alloys. — 5 (i) *General.* — In the two papers summarized in §§ 3 and 4 (Stoner, 1938 *c*, 1939 *b*) very brief general discussions were given of the then available experimental results on the ferromagnetic elements in relation to the theoretical scheme; and these were supplemented by a somewhat fuller consideration of the susceptibility above the Curie point (1938 *d*). Some of the later experimental results are included in a subsequent review article on ferromagnetism (Stoner, 1948). More detailed consideration was given to nickel and nickel-copper alloys [*see* § 5 (ii)] by Wohlfarth [1949 *a*]. who has also discussed (1949 *b*) nickel-cobalt and related alloys [*see* § 5 (iii)] and made a preliminary attack [1949 *c*, *d*, 1950], on some of the underlying quantum mechanical problems [*see* § 5 (iv)].

Until the advent of the collective electron treatment, experimental results had usually been considered with reference to the simple form of the molecular field treatment, as adapted to electron spins as carriers of the magnetic moment. This modified Weiss-Heisenberg treatment, as it may be called, is essentially characterized, on the statistical side, by the use of Maxwell-Boltzmann statistics. It gives, in a simple way, theoretical curves for the variation of spontaneous magnetization below, and of susceptibility above the Curie point, which, as far as their general form is concerned, appear at first to be reasonably consistent with the experimental results. Even leaving aside such matters as the departures from linearity of the relation between $\frac{1}{\chi}$ and T above θ, there are, however, serious quantitative discrepancies. For example, the number of effective spins per atom, q_f, deduced from the ferromagnetic saturation magnetization for $T \rightarrow 0$, differs greatly from the value, q_p, deduced from the paramagnetic susceptibility. For Fe, Co and Ni the q_f values are 2.22, 1.71 and 0.60_5 respectively; the q_p values are 3.37, 3.27 and 0.86. While it is not suggested that the q_f and q_p values " should " be identical, no " natural " explanation (i. e. no explanation consistent with the general wider theoretical scheme) was ever given of the very great differences on the basis of the Weiss-Heisenberg treatment. Further, although this treatment could account in an unforced way for the order of magnitude of the " excess " specific heat below, and the sudden decrease in the neighbourhood of the Curie point, it could not account in any way either for the observed excess above the Curie point, or for the electronic specific heat at very low temperatures. It may be added that the quantitative characteristics of the magneto-caloric effect (which imply a decrease of the molecular field coefficient over the range from the Curie point to room temperature by a factor of 10 or more) are in complete disaccord with either an assumed constancy of the molecular field coefficient, N_W, or with the modest degree of variation which might be consistent with the quantum mechanical origin of the molecular field [*see* Stoner, 1936 *d*].

The experimental results which are most immediately appropriate for comparison with the collective electron treatment are those for the susceptibility above the Curie point. Very careful measurements have been made on iron, cobalt and nickel by Sucksmith and Pearce (1938) and by Fallot (1944) [*see* also Stoner, 1948]. The results are in good agreement with each other. The $\frac{T}{\theta}$ range covered is from just over 1 to about 1.7 for Fe ($\theta = 1043^\circ$ K), 1.2 for Co ($\theta = 1393$) and 2.4 for Ni ($\theta = 631$). (For iron, values are obtained for the β and δ ranges, or by extrapolation from alloys in which they γ range is suppressed.) For Fe and Co, and for Ni up to about $\frac{T}{\theta} = 1.8$, the reduced curves are similar in form to those shown in figure 6, and fall between the curves for $\zeta_0 = 0.9$ and $\zeta_0 = 1.0$ (i. e. well below the classical limiting curve). The results indicate that the values of $\frac{k\theta'}{\varepsilon_0}$ appropriate to this temperature range are such as correspond to an exchange interaction effect just sufficient to produce complete parallelism of the spins at absolute zero for Ni $\left(\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}} = 0.7937,\ \frac{k\theta}{\varepsilon_0} = 0.4065\right)$, and somewhat smaller for Fe and Co (corresponding to ζ_0 values less than 1, but probably not less than 0.9, *see* figure 5). A preliminary coordination of the susceptibility results is thus obtained without the need to invoke any change in the effective number of carriers between the lower and higher temperatures, and one of the major discrepancies between theory and experiment mentioned above (the apparent difference between the q_f and q_p values) is removed. At temperatures above about $\frac{T}{\theta} = 1.8$, however, the $\frac{1}{\chi}$, T curve for nickel becomes concave to the T axis (i. e. the decrease of χ with T is less than that corresponding to the curves of figure 6). This is discussed below [§ 5 (ii)].

In the liquid helium range the electronic specific heat is proportional to the temperature, the proportionality factor usually being denoted by γ. Measurements on iron (Keesom and Kurrelmeyer, 1939), cobalt (Duyckaerts, 1939) and nickel (Keesom and Clark, 1935) give for $\gamma \times 10^4$, 12.0, 12.0 and 17.4 respectively (the specific heat being expressed in cal.deg.$^{-1}$ mole^{-1}). According to the usual theoretical treatment, the value of γ is proportional to the density of states at the top of the Fermi distribution; this can be calculated from a known or assumed energy distribution of states. Using the values of ε_0 derived from the high temperature susceptibility, and assuming a strictly parabolic form for the relevant part of the energy bands (see *fig.* 1), the calculated values of $\gamma \times 10^4$ for Fe, Co and Ni are about 50, 30 and 24 respectively. Since a change in the effective value of ε_0 by perhaps 20 per cent with a temperature change of the order of 1000° is to be expected (*see* § 4) the discrepancy for nickel (of about 40 per cent) is not serious, and may be taken as an indication of only a comparatively slight departure from a parabolic band form. For cobalt, the comparison is not significant owing to the change in lattice structure from hexagonal at the lower to cubic at the higher temperatures. For iron, the difference, by a factor of 4, between the observed value of γ and that " calculated " from the paramagnetic characteristics, suggests that the band deviates widely from a parabolic form. This is consistent with the detailed calculations by Manning [1943] on the energy bands in iron, the curve given having a minimum near the top of the occupied region. The value of γ calculated by Manning is, however, about 3 times smaller than that obtained from experiment.

The fact that a comparison of the band width parameter derived from the high temperature susceptibility and the low temperature specific heat shows fair agreement for nickel and a wide discrepancy for iron supports rather than invalidates the general ideas underlying the theoretical treatment; for it is consistent with other evidence indicating that the simple parabolic band form assumed in the detailed numerical work is a fair approximation for nickel, and a very poor approximation for iron. In view of the wide difference in the band forms, it is remarkable that both the reduced spontaneous magnetization and the susceptibility curves for the two metals should be so similar. The position is perhaps analogous to that in the Debye theory of specific heat, where a simple assumption as to the energy distribution of vibrational states, which is known to be wrong in detail, none the less leads to a reduced specific heat, temperature curve in good general agreement with the experimental results for nearly all metals.

The experimental spontaneous magnetization, temperature curves for iron, cobalt and nickel all lie well above the theoretical curves for any reasonable value of $\frac{k\theta'}{\varepsilon_0}$ (e. g. the curve labelled 0.794 in figure 4), and in fact agree for better (though in detail not well) with the classical curve (labelled ∞ in figure 4). This undoubted discrepancy cannot be attributed primarily to energy band form peculiarities, as the curves for the three metals (though not for alloys) are so similar. It is thought at present, as discussed further below, that the disagreement here is primarily due to the oversimplification in the assumption made [§ 3, premise (ii)] as to the dependence of exchange energy on magnetization.

The more detailed comparative studies which have so far been carried out have been concerned mainly, for obvious reasons, with nickel and its alloys. It is impossible to present this work convincingly in a short space, and reference must be made to the original papers for details; mention can be made here of only a few salient points.

5 (ii) *Nickel and nickel-copper alloys : the transfer effect.* — In his analysis and discussion of the experimental results for nickel and nickel-copper alloys, Wohlfarth (1949 *a*) introduces a refinement into the collective electron treatment by taking account of what may be called the " transfer " effect. In the original treatment (*cf.* § 3), a single band was considered, and the available electron spins were regarded as fixed in number. Now in nickel, the total number of electrons is just sufficient to fill the *d* band (see *fig.* 1), but, owing to overlap with the *s* band, there is a number of " holes ", N_d, in the *d* band which must be equal to the number of electrons N_s in the *s* band. At absolute zero, the number per atom, sufficiently closely, is 0.6. With increase in temperature, the electrons move to higher energy states, and since the number of available states is limited in the *d* band, and effectively unlimited in the *s* band, the number of electrons in the *s* band increases, and, correspondingly, the number of holes in the *d* band; symbolically, the ratio $\frac{N_d}{N_{od}}$ increases with temperature. The increase is greater the smaller the ratio $\frac{\varepsilon_{os}}{\varepsilon_{od}}$ (see *fig.* 1), denoted by *r*. The results for a single band correspond to $r \to \infty$. Detailed calculations have been made for $r = 10$. (In all this part of the numerical work, the value taken for $\frac{\varepsilon_{od}}{k}$ was 2×10^3 °K, corresponding to $\varepsilon_{od} = 0.17$ eV. The value $r = 10$, which was chosen partly for convenience in the computations, and partly to bring out clearly the effects of transfer, corresponds to a value of $\frac{\varepsilon_{os}}{k}$ (2×10^4 °K) which is of the same order as, but somewhat smaller than, that estimated from the energy band calculations.)

The holes in the *d* band are probably entirely responsible for the strictly ferromagnetic characteristics, and the relative contributions of the *s* band electrons to the paramagnetic susceptibility is small, but not negligible. The effect of transfer is to make the susceptibility increasingly greater, with increasing temperature, than that given by the single band treatment, mainly owing to the increase in the number of holes in the *d* band. This is shown in figure 9, where the calculated reduced inverse susceptibility curves are shown for $r = 10$ and $r \to \infty$. For $r = 10$ the curve becomes concave, rather than slightly convex to the *T* axis, at the higher temperatures, and the excellent agreement with the experimental values can leave little doubt that the main remaining " anomaly " in the experimental results on the temperature variation of the paramagnetic susceptibility can be largely accounted for in terms of the transfer effect.

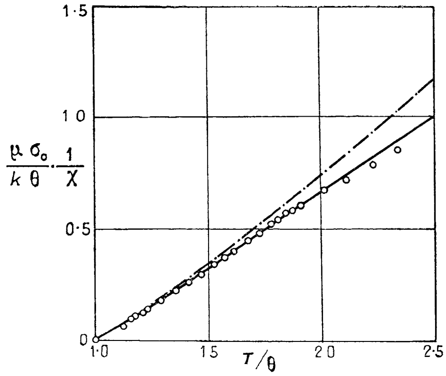

Fig. 9. — Paramagnetic susceptibility of nickel. Experimental points due to Sucksmith and Pearce (1938). Broken curve, calculated by single band treatment ($r \to \infty$). Full curve calculated for overlapping bands (see *fig.* 1) allowing for transfer effect ($r = 10$). (After Wohlfarth, 1949 *a*.)

The experimental results for the Ni-Cu alloys show that both the Curie temperature and the spontaneous magnetization at absolute zero decrease practically linearly with copper concentration to zero at a fractional concentration of 0.6. It is reasonable to make the provisional assumption that the *s* electrons of copper fill up the *d* and *s* bands to a common Fermi limit higher than that in nickel. It is then a simple matter, given the ratio $\frac{\varepsilon_{os}}{\varepsilon_{od}}$ for nickel, to determine the value of $(\varepsilon_{od})_c$ [and of $(\varepsilon_{os})_c$] as a function of the copper concentration *c*. [For example, for $r = 10$, (ε_{od}) becomes zero, i. e. the 0.6 holes in the *d* band are filled, for $c = 0.6922$.] Further, knowing θ, $\frac{k\theta}{\varepsilon_0}$ and hence $\frac{k\theta'}{\varepsilon_0}$ may be determined. The corresponding value of ζ_0 (*fig.* 5), equal to unity for nickel, decreases with increasing *c* at first slowly, and then more rapidly to zero at $c = 0.6$. The values so obtained for ζ_0 may be compared with those derivable from the reduced inverse susceptibility curves for the alloys, as described above for nickel. These curves are similar to those for nickel (*fig.* 9), but of decreasing slope with increasing copper content (*fig.* 10), indicating decreasing values of $\frac{k\theta'}{\varepsilon_0}$ and of ζ_0 (*fig.* 6). The agreement is surprisingly good. For an alloy with $c = 0.352$, for example, the estimated value of ζ_0 by the first method is 0.86, and by the second method approximately 0.87. Although such close numerical agreement is probably fortuitous, the general run of the experimental results is entirely consistent with the theoretical scheme.

Measurements of the specific heat of nickel-copper alloys in the liquid helium range are of great interest, for it would be expected that the coefficient γ in the electronic term would decrease proportionately to the density of states at the top of the occupied part of the energy band; in particular that the value of $\gamma \times 10^4$ would decrease with the concentration c, of copper from 17.4 for pure nickel [*see* § 5 (i)] to a value comparable with that for copper (1.78) for c equal to, or slightly greater than 0.6. The experimental results of Keesom and Kurrelmeyer (1940) [*see* also Stoner, 1948, p. 93] on four alloys show a somewhat irregular variation of γ with c, but there is no indication of any considerable decrease over the c range from 0 to 0.6. This is quite inexplicable on the simple theoretical treatment. When change in ζ_0 and transfer are taken into account, however, the calculated relative change in γ nowhere exceeds 10 per 100 over the c range from 0 to 0.5, and even for $c = 0.6$, the calculated value is only about 20 per 100 below that for nickel (Wohlfarth, 1949 *a*). Thus a simple refinement of the original theoretical treatment accounts broadly for the most baffling general feature of the experimental results, namely the smallness of the change in γ over the c range from 0 to 0.6, though it does not explain the irregularities in the variation indicated by the values obtained for the four alloys examined.

5 (iii). *Other metals and alloys.* – The available experimental results on the fundamental magnetic properties, both below and above the Curie point, of binary alloys of the ferromagnetic elements are now very extensive. In comparatively recent years much of the earlier work on the ferromagnetic metals and interferromagnetic alloys has been repeated, with improved methods, and a wealth of new knowledge has been gained through the systematic studies of alloys with non-ferromagnetic elements by Sadron, Manders, Marian, Fallot and others [for detailed references, *see* Stoner, 1948].

Many of the results have now been " analysed " in the light of the collective electron treatment; that is to say, the results, usually from diverse sources for the low temperature saturation magnetization, the Curie temperature, and the variation with temperature of the spontaneous magnetization below, and of the susceptibility above the Curie temperature have been brought together, critically examined, and reduced to the form (whether in numerical tables or in graphs) appropriate for comparison with the results of the theoretical treatment for the idealized ferromagnetic. Representative examples of this analysis are given in the papers already mentioned [Stoner, 1939 *d*, Wohlfarth, 1949 *a*] and in a later paper by Wohlfarth [1949 *b*]. The brief statements which can be made here on this work must be in very general terms, and it must be understood that there is no suggestion that the coordination so far obtained for any sets of experimental results is as yet quantitatively complete; each alloy system presents, in detail, its own complex of problems, whose gradual elucidation can be achieved only by much further experimental and theoretical work.

It has been known for some time [*cf.* Stoner, 1933, 1948] that the saturation magnetization of many nickel alloys is consistent with a decrease of mean moment per atom, expressed in Bohr magnetons, with atomic concentration of the solute metal, $\frac{dq_f}{dc}$, closely equal to the number of loosely bound electrons (or the effective valency) of the added atoms. This holds, for example, in the alloys with Cu, Au $\left(\frac{dq_f}{dc} \simeq -1\right)$, Zn (— 2), Al (— 3), Sn (— 4). With the older theoretical treatment, however, no satisfactory interpretation could be given of the experimental $\frac{1}{\chi}$, T curves for these alloys above the Curie point [*cf.* Néel, 1940, p. 128, 133]. When the reduced susceptibility curves are plotted as described above, they are all very similar to those for the Ni-Cu alloys, shown diagrammatically in figure 10.

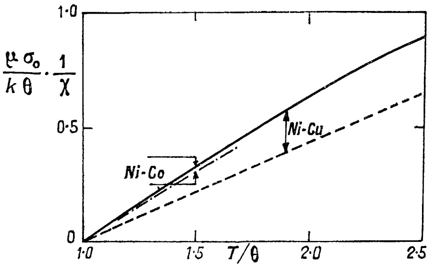

Fig. 10. — Reduced inverse susceptibility curves for Ni-Cu and Ni-Co alloys. With increasing concentration, c, of Cu, the curves change from the full curve (for Ni, i. e. $c = 0$) to the broken curve ($c = 0.476$). The curves for Ni, Co and all the Ni-Co alloys fall in the narrow range shown.

For the elements mentioned the results indicate that the value of $\frac{k\theta'}{\varepsilon_0}$ decreases with increase of concentration, and correspondingly that ζ_0 decreases. To the same extent as for the Ni-Cu alloys, the collective electron treatment provides a satisfactory coordination of the high and low temperature magnetic characteristics. While a similarity in behaviour might be expected for alloys of nickel with the simpler elements (i. e. those in which the atoms have incomplete outer groups of s or p electrons), it is remarkable that it extends also to alloys with some of the transitions elements (in which the atoms have incomplete d groups), including Ti, V and Cr.

For the nickel-cobalt alloys the behaviour is entirely different, in that, for all the alloys, the reduced susceptibility curves almost coincide (see *fig.* 10). In so far as the idealized scheme is applicable, this would indicate that parallelism of the spins associated with the holes in the unfilled *d* band is complete ($\zeta_0 = 1$) or nearly complete ($\zeta_0 > 0.95$) at absolute zero over the whole composition range. For the nickel iron alloys, values of ζ_0 well below 1 are indicated (e. g. $\zeta_0 = 0.82$ for the 57.7 per cent alloy), but the change with composition is irregular, and any suggestions as to the detailed interpretation of the results would at present be purely speculative. This last remark applies even more forcibly to the curves for the Ni-Mn alloys.

The available data for the variation of the spontaneous magnetization of alloys are far less complete and reliable than those for the susceptibility, but interesting and certainly significant differences are shown in the reduced curves for the nickel-cobalt alloys on the one hand and the nickel-copper alloys on the other. The experimental results are due to Bloch (1911, 1912) and Alder (1916) respectively.

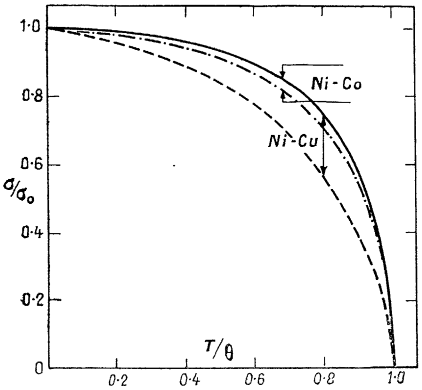

Fig. 11. — Reduced spontaneous magnetization curves for Ni-Cu and Ni-Co alloys. With increasing concentration, *c*, of Cu, the curves change from the full curve (for N i. e. $c = 0$) to the broken curve ($c = 0.281$). The curves for Ni, Co and all the Ni-Co alloys fall in the narrow range shown.

As shown diagrammatically in figure 11, the curves for the whole range of Ni-Co alloys are almost coincident with the curves for the pure metals, which, as already stated [§ 5 (i)], agree roughly with the " classical " theoretical curve. For the Ni-Cu alloys, the curves become less convex with increasing copper content; the curves for alloys with 19.2, 24.1 and 28.1 per 100 copper agree quite closely with the lowest theoretical curve of figure 4 (the curve albelled 0.794).

The change in form of the curves for the Ni-Cu alloys cannot be attributed simply to the decrease in the values of ζ_0; for the theoretical curves for all values of $\frac{k\theta'}{\varepsilon_0}$ corresponding to the range $0 < \zeta_0 < 1$ are nearly coincident, and it is only for impossibly high values of $\frac{k\theta'}{\varepsilon_0}$ that the higher " classical " curve is approached. A possible explanation of the different types of curve for the different alloys is suggested below [§ 5 (iv)].

In the binary alloys of iron, the effect of the solute atoms on the saturation magnetization is very different from that in nickel. With many elements, including Al, Si, V, Cr, Mn, Sn, Au, the initial value of $\frac{dq_f}{dc}$ is approximately -2.2, the effect being equivalent to that which would be produced by the replacement of iron atoms (of moment $2.2\ \mu_B$) by atoms of zero moment. For the nickel alloys a satisfactory general interpretation of the facts is obtained by supposing that the loosely bound electrons of the added atoms fill up the holes in the *d* band, and consistency demands that a basically similar process should occur in the iron alloys. In nickel, however, all the states in the *d* band for one direction of spin are fully occupied ($\zeta_0 = 1$), and added electrons can enter the band only with the opposite direction of spin. In iron, the evidence indicates that the states in the *d* band are not fully occupied for either direction of spin (i. e. $\zeta_0 < 1$), and added electrons can enter the band in balanced pairs. This tentative explanation of the difference between the nickel and iron alloys [Stoner, 1948, p. 90] seems to be broadly consistent with the experimental results, but it has not yet been developed in detail.

It is appropriate to conclude this section by brief reference to some of the non-ferromagnetic metals: It is an immediate conclusion from the collective electron treatment that a positive exchange interaction does not necessarily give rise to ferromagnetism (see *fig.* 2); with $\frac{k\theta'}{\varepsilon_0}$ positive and below the critical value required to give spontaneous magnetization, i. e. for the range $0 < \frac{k\theta'}{\varepsilon_0} < \frac{2}{3}$, the paramagnetic susceptibility may still be enhanced to a value much greater than can reasonably be accounted for merely in terms of a high density of states at the top of the Fermi distribution. It has been suggested that the magnitude and temperature variation of the susceptibility of many of the transition elements can be qualitatively accounted for in this way [Stoner, 1936 *c*]. More recently a detailed quantitative analysis has been made, from this point of view, of the experimental results for platinum and palladium [Wohlfarth, 1949 *e*]. For palladium, the various experimental results (susceptibility, electronic specific heat, magnetic properties of alloys) are remarkably consistent with those derived theoretically for a band structure similar to that of nickel, with 0.6 holes per atom in the *d* band, and a $\frac{k\theta'}{\varepsilon_0}$ value of about 0.65. For platinum, the correlation is less complete, but the results correspond qualitatively to a smaller number of holes (0.2 to 0.3) and a smaller, but still positive value of $\frac{k\theta'}{\varepsilon_0}$ (0.4 to 0.6).

5 (iv). *Temperature variation of spontaneous magnetization.* — The discussion of the general theory of exchange effects is outside the scope of this report, but it is proper that brief mention should be made of some recent contributions of Wohlfarth in this field which bear directly on the significance of the analysis of experimental results in the light of the simple form of the collective electron treatment.

In a particular development of the Heisenberg treatment of ferromagnetism, Bloch (1930) obtained a relation for the variation of spontaneous magnetization at low temperatures which may be expressed in the form

$$\frac{\sigma}{\sigma_0} = 1 - \left(\frac{T}{T_0}\right)^{\frac{3}{2}}, \qquad (5.1)$$

where T_0 is expressible in terms of the exchange interaction integral. This relation has been widely accepted as an inescapable consequence of a rigorous theoretical treatment which is fully confirmed by experiment. In a discussion of the limitations of Bloch's spin-wave treatment, Wohlfarth [1949 *d*] points out that an essential premise of the treatment is that there is complete parallelism of all the spins at absolute zero (i. e. $\zeta_0 = 1$). Even a small departure from parallelism would make the theoretical method inapplicable, and the indications of the analyses summarized above are that in most actual ferromagnetics the parallelism is incomplete. Even if the premise of complete parallelism were valid, Wohlfarth shows that the relation (5.1) would be a quantitatively satisfactory approximation only for a very restricted temperature range, probably less than 1°. It is true that Fallot's results for iron and nickel are not inconsistent with a $T^{\frac{3}{2}}$ law extending over a fairly wide range, but the value of the Curie temperature which can then be estimated from the experimental T_0 does not agree well with that observed, and the experimental points fit a T^2 law almost as well as a $T^{\frac{3}{2}}$ law. The Bloch relation (5.1) is, in short, a consequence of very special premises, and even then holds only over a very restricted temperature range; it is quite unjustifiable to regard it as generally applicable, or to use it as a basis for estimating values of the exchange integral from experimental results for the temperature variation of the spontaneous magnetization.

It may be noted that with the collective electron treatment, the variation of $1 - \left(\frac{\sigma}{\sigma_0}\right)$ with T at low temperatures depends on the value of $\frac{k\theta'}{\varepsilon_0}$. In the range for which ζ_0 is less than 1, a T^2 law is closely followed; at the critical value for $\zeta_0 = 1$, namely $\frac{k\theta'}{\varepsilon_0} = 2^{-\frac{1}{3}}$, approximately a $T^{\frac{3}{2}}$ law; for higher values, an exponential term, of the form $\exp\left(-\frac{a}{T}\right)$, becomes dominant.

A related, but more general problem arises in connection with the theory of electronic specific heat at low temperatures. The usual treatment gives, for $T \to 0$,

$$C_e \to \gamma T, \qquad (5.2)$$

and the coefficient γ is proportional to the density of states at the top of the Fermi distribution. In the derivation of this expression, no account is taken of exchange, or correlation, effects, and it was stated by Bardeen (1936) and Wigner (1938) that their inclusion would lead to very different relations; this has been confirmed by the quantitative treatment of Koppe (1947). The expression derived gives a non-linear variation with T, and at the lower temperatures a value of C_e differing from that given by (5.2) by a large factor. In both respects the " improved " theoretical expression is completely incompatible with experiment, but it is, none the less, very disturbing, for it is clearly quite unjustifiable to ignore these correlation effects. It is suggested by Wohlfarth [1950] that the manner in which they are treated is oversimplified; and he shows that if the Coulomb potential in the relevant exchange integrals is modified by the inclusion of an exponentially decreasing factor to allow for screening, the final expression for the specific heat may be very little different from that given by (5.2). This provides some justification for treating low temperature electronic specific heat on a simple " density of states " basis as a manageable approximation, but at the same time it underlines the need for caution in attaching undue weight to detailed numerical agreement or disagreement between experiment and a simplified theory.

Finally, reference must be made to a preliminary attack on the fundamental theoretical problem of exchange interaction [Wohlfarth, 1949 *c*]. In the collective electron treatment, as quantitatively developed, it is assumed that exchange interaction gives rise to a term in the energy expression proportional to the square of the magnetization [§ 3, premise (ii)]. It is virtually impossible to develop a satisfactory general quantitative treatment of correlation effects, and even for free electrons only rough estimates can be made of the variation with magnetization of terms of the Bloch type corresponding to parallel spins, and of the Wigner type corresponding to anti-parallel spins. From his detailed discussion, however, Wohlfarth concludes that in general the variation of the resultant energy with ζ^2 will be effectively linear for small values of ζ, but that there will be increasing departure from linearity as ζ approaches unity. As long as ζ is small, therefore, the numerical results of the collective electron treatment should be applicable; in particular they should apply to the paramagnetism above the Curie point. Below the Curie point, in contrast, ζ varies over the wide range from o to ζ, or, perhaps more significantly, the intensity, I, of the spontaneous magnetization, corresponding to the density of parallel spins, varies from o to I_0. Now for the Ni-Cu alloys with the higher copper concentrations, I_0 (and also in this case ζ_0) is small, and the temperature variation of spontaneous magnetization agrees with the theoretical curves calculated on the assumption that the exchange energy is proportional to ζ^2 (see *fig.* 11). For the ferromagnetic metals, and for the Ni-Co alloys, the range of I is large, and the deviation of the experimental curves from the theoretical ones (see *fig.* 11) can reasonably be attributed to the effect of the higher order terms in the expression for the exchange energy. Alternatively expressed, if the exchange energy should be represented by a series of the form $a\zeta^2 + b\zeta^4 \ldots$, and is forcibly represented by an expression proportional to $k\theta'\zeta^2$ the effective value of $k\theta'$ would decrease with decreasing ζ, i. e. with increasing temperature. The rate of decrease of magnetization with temperature, as shown by the $\frac{\zeta}{\zeta_0}$, $\frac{T}{\theta}$ curves (or the experimental σ, T curves) would thus be initially slower and finally more rapid than that corresponding to the theoretical curves for the idealized ferromagnetic. These considerations seem to provide a reasonable tentative interpretation of the observed forms of the spontaneous magnetization curves, though it must be freely admitted that a fully quantitative explanation, on an atomic theory basis, is very unlikely to be readily attained.

6. **Concluding remarks.** — The collective electron treatment of ferromagnetism provides a consistent set of quantitative relations, derived from simple premises with a clear physical significance, for the electronic properties, thermal as well as magnetic, of a complete family of idealized metallic ferromagnetics and paramagnetics. The general calculations must be made for a particular energy band form, and with a particular form of expression for the dependence of exchange energy on magnetization. Bearing in mind that this necessarily precludes exact numerical agreement between the theoretical results and the experimental results for actual metals and alloys, the degree of quantitative coordination of these experimental results which is attained is very remarkable. Much that was previously obscure may now be said, in a general way, to be understood. Moreover, analysis of the experimental results in the light of the theoretical treatment often provides valuable guidance for further theoretical and experimental investigations. It is my hope that the scheme will be much more widely used in this way, for the survey given here will at least have indicated how many questions there are which still remain to be answered.

The collective electron treatment, as presented here, is not in any sense complete as a theory of even the basic properties of metallic ferromagnetics. A full theory of ferromagnetism is necessarily an integration of the results of diverse theoretical investigations carried out by many individuals in different centres. Even bare reference to the very relevant recent work, or work in progress, on such problems as the electronic band structure of particular metals and alloys, would unduly extend this report. It may be appropriate to conclude this report by reference to two of the directions along which theoretical investigations are at present proceeding at Leeds. The first is a development, straightforward in principle, of the collective electron treatment to cover what may most simply be described as the magneto-caloric effect in ferromagnetics in high fields. It has already been mentioned [5 (i)] that the experimental results cannot be satisfactorily accounted for on the basis of the older theoretical treatment; such tentative suggestions as were put forward earlier to account for the large variation with temperature of the apparent value of the Weiss molecular field coefficient in terms of domain effects are now realised to be untenable. Preliminary calculations by K. L. Hunt have now shown that such a variation is entirely consistent with the new treatment, arising essentially from the fact that change of magnetization in general involves a change of " distributional " energy as well as in molecular field energy, and that these changes may be of opposite sign. It is hoped that a more detailed quantitative study may lead to the derivation from the experimental results of fuller information about the magnitude of the exchange effects in actual ferromagnetics.

Some characteristics of the " electronic structure " of metals and alloys are manifested in the magnetic properties, others by the associated thermal properties. Ample illustration has been given of the way in which combined theoretical studies of the two types of property may lead to the gaining of information about that electronic structure. It is believed that much further information could be obtained through a study of electrical and associated properties, for which very extensive experimental results are available. Work is in progress by P. Rhodes with this long-term aim in mind. The theoretical problem of electrical properties is much more complicated than that of magnetic properties, because the electron-lattice interaction is an essential factor determining the observable properties. It was soon found that no quantitatively satisfactory theoretical treatment had been given of even the temperature variation of resistance except for " very high " and " very low " temperatures. Numerically precise solutions of the relevant equations have now been obtained for the intermediate temperature range (Rhodes, 1950), which in some ways is of major physical imporrance in connection with the theoretical analysis of the experimental results. This work may seem far removed from collective electron ferromagnetism, but it is a necessary step in the theoretical treatment of electrical properties, and may help towards the exploration of a third approach to the problem of the electronic structure of metals and alloys.

Acknowledgement. — It is a pleasure to acknowledge the assistance I have had from Dr P. Rhodes in the preparation of this report.

Remarque de M. Van Vleck. — Ce que je vais dire ne concerne pas directement le modèle des « électrons collectifs » de Stoner, mais je crois que, dans ce modèle, se posent aussi des questions de convergence du même genre qu'avec celui de Heitler-London. En 1937 et 1939, Opechowski, utilisant le modèle de Heisenberg, a développé les calculs en poussant plus loin le développement en fonction des puissances du rapport de l'intégrale d'échange à kT. Je désire signaler une erreur découverte par Zehler, étudiant de Döring, dans le calcul d'Opechowski. Celui-ci avait obtenu

$$\frac{1}{\chi T} = 1 - \frac{6}{T} + \frac{6}{T^2} + \frac{6}{T^3} + \frac{83}{4T^4} + \ldots, \qquad (1)$$

où T est, à un facteur près, le rapport de la température à l'intégrale d'échange. La température de Curie, T_c, dans une unité convenable, est la température à laquelle s'annule l'expression (1). Les valeurs de T_c obtenues en tenant compte de 2, 3, ..., 5 termes dans l'expression (1) sont :

	Nombre de termes.			
	2.	3.	4.	5.
T_c....	6	4,7	4,27	imaginaire

L'approximation conventionnelle de Heisenberg consiste à retenir seulement 2 termes. Le fait qu'en retenant 5 termes on obtienne un résultat absurde semblait indiquer que le développement n'était pas convergent (les calculs avec 6 et 7 termes sont beaucoup trop difficiles à faire). Aujourd'hui, en 1950, Opechowski a repris ses calculs après la découverte de Zehler et a trouvé que le dernier coefficient dans l'expression (1) était de $\frac{3}{4}$ au lieu de $\frac{83}{4}$. La valeur obtenue en tenant compte de 5 termes devient alors égale à 4,25 très voisine de la valeur obtenue (4,27) avec 4 termes. Le développement (1) est donc bien convergent.

Demande de M. Néel. — Comment se pose la question du fer et de ses alliages dans le modèle des « électrons collectifs » ?

Réponse de M. Stoner. — Les variations de moment se présentent de manières très différentes dans les alliages de fer et dans les alliages de nickel; comme on le sait, l'explication est très satisfaisante pour le nickel. Les spins des électrons effectifs (c'est-à-dire les trous dans la bande *d*) sont parallèles dans le nickel et les électrons ajoutés peuvent seulement abaisser le moment. Dans le fer, la saturation n'est pas complète (dans le symbolisme de mon rapport, $\zeta_0 < 1$) et les électrons peuvent entrer deux à deux dans la bande avec des spins antiparallèles. En principe, cela ne pourra se produire que jusqu'à des limites fixes et il me semble que cette idée est compatible avec les expériences : les détails n'ont pas encore été étudiés (*voir* mon rapport). Quant aux alliages inter-ferromagnétiques, on peut donner une explication satisfaisante dans chaque cas individuel, en donnant aux bandes une forme convenable. Il faut cependant être prudent dans le développement de la théorie.

Demande de M. O. Berg. — I should like to ask Prof. Stoner a question pertaining to figure 9. The value of $\frac{1}{\chi}$ of Sucksmith and Pearce quoted are lower than the computed values at the highest temperature. This admittedly very small discrepancy is accentuated when the comparison is made to the data of Fallot. I wonder if Prof. Stoner attaches any significance to this discrepancy and if it can be accounted for by the theory.

Réponse de M. Stoner. — Dans les grandes lignes, l'accord avec la théorie est très satisfaisant sans être parfait. Mais on a, de propos délibéré, négligé dans la théorie des effets, comme celui de la dilatation, qui peuvent être importants. Il n'y a donc pas à s'étonner que l'accord ne soit pas parfait puisqu'on a négligé ces effets secondaires.

Demande de M. C. J. Gorter. — Dans le modèle des « électrons collectifs », l'entropie est-elle nulle au zéro absolu, en accord avec la loi de Nernst ?

Réponse de M. Stoner. — Nous n'avons pas fait une étude directe de l'entropie des ferromagnétiques à 0° K, ni de sa variation avec la température. Sans l'avoir fait, je suis bien sûr qu'il n'y a pas de contradictions avec les demandes de la thermodynamique.

Demande de M. Néel. — La théorie des « électrons collectifs » permet-elle d'expliquer les courbures accentuées de la courbe $\left(\frac{1}{\chi}, T\right)$ au voisinage du point de Curie ?

Réponse de M. Stoner. — Les courbures obtenues avec la théorie donnant la variation de $\frac{1}{\chi}$ avec T au-dessus de θ, quoique importantes, sont très lentes. Je pense que peut-être les courbures plus grandes, observables au voisinage immédiat du point de Curie, sont en principe explicables par les « fluctuations » de M. Néel.

Remarque de M. Shockley. — The distribution of electrons betwen two bands can be visualized with the aid of a mechanical model. In the model (*fig.* 12) the bands are represented by bottles in which the height corresponds to the energy in the band and the area to the number of quantum states per unit energy. The potential energy of the water in the bottle then corresponds to the total " kinetic energy " or Fermi energy of the electrons in a energy band. The reduction of energy of one band in respect to the other due to exchange is represented in the model by the displacement of one bottle in respect to the other due to unbalance when water in transfered from one to the other. If the restoring force is linear in the displacement of the bottles, the model is mathematically equivalent to Prof. Stoner's theory of collective electron ferromagnetism applied to bands of arbitrary form at 0° K.

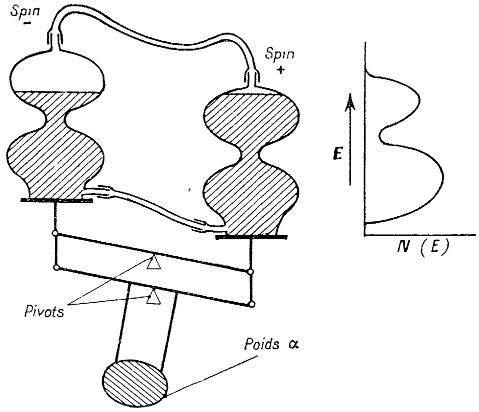

Fig. 12.

If the bands are separated into two major parts by an energy interval of low density, then behaviour of figure 1 of Prof. Smoluchowski's report may be reproduced if the exchange constant has an appropriate magnitude. When one band is emptied to the constriction, then a gradual transition will occur until further removal of electrons will come entirely from the other band.

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Note. — The papers listed below are restricted to those with which this report is most directly concerned. References to related theoretical and experimental work are given in these papers, most fully in the review article on ferromagnetism, Stoner, 1948.

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