

The Theoretical and Experimental Status of the Collective Electron Theory of Ferromagnetism

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This paper is intended to supplement the review articles published by Stoner in 1948 and 1951, firstly by considering in greater detail the quantum-mechanical and statistical-mechanical foundations of the collective electron theory and secondly by considering briefly a wider range of relevant experimental results.

In Sec. 1 previous theoretical work is recalled. In Sec. 2 the difficulties of a rigorous quantum mechanical derivation of the internal energy of a ferromagnetic metal at absolute zero are outlined. In order to determine at least the form of the expressions, a calculation based on the tight binding approximation is described for a crystal containing N singly charged ions, which are fairly widely separated, and N electrons. The forms of the Coulomb and exchange contributions to the energy are discussed in the two instances of maximum and minimum multiplicity. The need for a correlation correction is stressed, and the effects of this correction are discussed with special reference to the state of affairs at infinite ionic separation. The fundamental difficulties involved in calculating the energy as function of magnetization are considered below; it is shown that they are probably less serious for tightly bound than for free electrons, so that the approximation of neglecting them in the first instance is not too unreasonable. The dependence of the exchange energy on the relative magnetization ζ is then of the form $\sum_n A_n \zeta^{2n}/2n$, and the relative orders of magnitude of A_1 and A_2 are considered. A previous calculation by Slater is critically reviewed.

In an application of statistical mechanics the difficulty arises that only if $\zeta=1$ or 0 will the zero-order wave function be in general a single Slater determinant. A calculation by Lidiard on this problem, that of spin degeneracy, is referred to. The relevance of the dependence of the interaction energies on wave vector is stressed. If these energy contributions are constant, then the free energy expression is that derived by Stoner, based on Fermi-Dirac statistics, even if spin degeneracy is taken into account. Several related difficulties are exemplified by a discussion of the properties of the free-electron gas, for which the exchange energy varies rapidly with wave vector $\mathbf{k}_i, \mathbf{k}_j$ when $|\mathbf{k}_i - \mathbf{k}_j| \rightarrow 0$. For tightly bound electrons the dependence on wave vector is much less rapid, and it is suggested that spin degeneracy effects are here less serious. A simple calculation of the low temperature electronic heat of tightly bound electrons, including exchange and correlation, is referred to in exemplification.

In Sec. 3 several experimental results are briefly discussed, including the following: (1) The variation with composition of the Curie temperature and saturation magnetization, and the variation with temperature of the susceptibility of nickel alloys; (2) the variation with temperature of the magnetization, electronic heat, and magnetocaloric effect of cubic cobalt, nickel, and nickel alloys below the Curie point; (3) the high temperature electronic heat of nickel and palladium; (4) the electronic properties of chromium and some other transition metals; (5) the electronic properties of palladium and its alloys.

1. PREVIOUS THEORETICAL WORK

SINCE many aspects of the collective electron treatment of ferromagnetism have recently been reviewed by Stoner,^{1,2} there appears little justification for writing yet another review. Perhaps the main apology for, nevertheless, doing so is that the present paper is intended to supplement the earlier reviews, rather than to present their main substance again, by covering more fully the quantum-mechanical and statistical-mechanical foundations of the treatment and considering a wider range of relevant experimental results.

In this section a brief outline of the historical development of the subject is given. The earliest analysis of the ferromagnetic properties of collective electrons was made by Bloch,³ who considered the effects of introducing exchange terms into the Sommerfeld description of a free-electron gas. Bloch predicted that the lowest energy state at 0°K is the ferromagnetic state if the electron density is small enough. The problem was later taken up by Brillouin.⁴ The introduction and discussion of correlation effects by Wigner^{5,6} left little

doubt, however, that the conditions for ferromagnetism of free electrons are so stringent as to be practically never satisfied. The first attempt at analyzing the properties of a real ferromagnetic metal, nickel, was made by Slater.^{7,8} Basing his discussion on the energy band calculation by Krutter,⁹ Slater recognized the essential features of a satisfactory theory of ferromagnetism and attempted to calculate the exchange energy for the 3d electrons. The main results of this calculation⁷ are: (1) The main contribution to the exchange energy is provided by the atomic exchange integral for electrons within one cell; (2) the contribution arising from nearest neighbor interaction is only about half a percent of the total exchange energy. These conclusions are critically discussed in Sec. 2. Slater also discusses temperature effects:⁸ He calculates the magnetization, temperature curve of nickel below the Curie point, using Fermi-Dirac statistics and representing the exchange energy by a Weiss term, notes that magnetic saturation is not necessarily complete at 0°K, and attains good agreement with the observed low temperature electronic heat coefficient of nickel. In a further paper Slater¹⁰ discusses ferromagnetism by

¹ E. C. Stoner, Phys. Soc. Rept. Progress Phys. **11**, 43 (1948).

² E. C. Stoner, J. phys. et radium **12**, 372 (1951).

³ F. Bloch, Z. Physik **57**, 545 (1929).

⁴ L. Brillouin, J. phys. et radium **3**, 565 (1932).

⁵ E. P. Wigner, Phys. Rev. **46**, 1002 (1934).

⁶ E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

⁷ J. C. Slater, Phys. Rev. **49**, 537 (1936).

⁸ J. C. Slater, Phys. Rev. **49**, 931 (1936).

⁹ H. M. Krutter, Phys. Rev. **48**, 664 (1935).

¹⁰ J. C. Slater, Phys. Rev. **52**, 198 (1937).

interpolating between band theory and spin wave theory. He concludes again that the occurrence of ferromagnetism is determined in the main by the magnitude of the interaction energy for electrons close to one atom and by the band width, but also that the low temperature variation of magnetization follows the $T^{\frac{3}{2}}$ law. In a progress report Slater¹¹ has recently discussed these problems again, and the writer is indebted to him for much fruitful correspondence.

In the meantime Stoner had published two papers on collective electron ferromagnetism.^{12,13} The main assumptions underlying Stoner's calculations are: (1) the ferromagnetism of a metal results from the holes in the so-called $3d$ band, taken to be parabolic in the neighborhood of the Fermi limit; (2) the exchange energy $J(\zeta)$ is proportional to the square of the relative magnetization ζ , as in the Weiss theory—specifically, $J(\zeta) = \frac{1}{2} N_e k \theta' \zeta^2$, where N_e is the number of holes and θ' a constant parameter; (3) the particles obey Fermi-Dirac statistics. The results of the deductive treatment based on these assumptions were discussed in the earlier reviews.^{1,2} Later Wohlfarth¹⁴⁻¹⁶ was able to make some extensions of the treatment and to apply the results in an analysis of experimental data (see Sec. 3). By extending Stoner's work to rectangular energy bands Wohlfarth¹⁷ showed that band shape is less decisive in determining many of the properties of ferromagnetic substances than the form of $J(\zeta)$ (see Sec. 2). The success of Stoner's treatment in correlating experimental results emphasizes the need for a satisfactory fundamental theoretical treatment to justify the assumptions underlying it and to provide an estimate of the parameters inherent in the treatment, particularly the parameter θ' . A preliminary discussion has already been given.¹⁸ Recently, Lidiard has considered several of the outstanding fundamental problems of the collective electron treatment. He discusses¹⁹ the properties of the free-electron gas, including exchange, and stresses the need for a correlation correction. He also discusses²⁰ the fundamental problem of spin degeneracy (see Sec. 2). This work is valuable in indicating the conditions under which Stoner's equations are valid or approximately valid. Some discussion of relevant problems has also been given by Bell²¹ and Smith.²²

2. QUANTUM-MECHANICAL AND STATISTICAL-MECHANICAL FOUNDATIONS

In this section a quantum-mechanical derivation of the absolute zero internal energy expression, applicable

to a simple model of a ferromagnetic metal, is first outlined. Then the problems of statistical mechanics are briefly discussed.

(a) The Internal Energy of a Ferromagnetic Metal at Absolute Zero

In calculating the internal energy of a ferromagnetic metal many of the hitherto unresolved difficulties in the theory become immediately apparent. It is particularly difficult to treat what is almost an experimental fact, that the electrons outside closed shells may be divided, apparently, into those responsible for a large part of the conduction properties and those responsible for ferromagnetism. The usual description of this state of affairs, first given by Mott,²³ regards the loosely bound electrons, originating largely in the $4s$ shell of the isolated atoms, as principally the conduction electrons and ascribes ferromagnetism to the more tightly bound electrons originating largely in the $3d$ shell. Although Mott's hypothesis finds some confirmation in the band calculation of Krutter⁹ and Slater,⁷ there is little evidence that the conduction electrons are entirely s electrons or the ferromagnetic electrons entirely d electrons. Because of band overlap, there is, doubtless, some very strong mixing between them, and a fully satisfying theory would have to be based on wave functions including this effect.

It is proposed in this paper to consider the collective electrons responsible for ferromagnetism by the tight binding approximation. A first attempt at a quantitative treatment is the energy band calculation of Fletcher and Wohlfarth.^{24,25} In this work the tightly bound electrons in nickel were ascribed pure d character solely so as to keep the computational labor within manageable limits. Even so, an extension to calculate the exchange energy is at present quite impracticable, again owing to computational difficulties. In order to determine at least the form of the energy expression, a calculation is outlined below for a crystal containing N singly charged ions which are widely separated, and $N_e = N$ electrons described by Bloch type wave functions. The Hamiltonian operator for this assembly is

$$\mathbf{H} = -(\hbar^2/8\pi^2\mu) \sum_i \nabla_i^2 + \sum_i \sum_l V_l(\mathbf{r}_i) + \frac{e^2}{2} \sum_i \sum_j r_{ij}^{-1} + \frac{e^2}{2} \sum_l \sum_m R_{lm}^{-1}, \quad (1)$$

where i, j refer to the positions of the electrons, l, m the positions of the ions, and $V_l(\mathbf{r}_i)$ is the potential energy operator for electron i in the field of ion l . For maximum and minimum multiplicity (the relative magnetization $\zeta = 1$ or 0), the zero-order wave function may

¹¹ J. C. Slater, Quart. Progress Rept. M.I.T. No. 2, 4 (1951).

¹² E. C. Stoner, Proc. Roy. Soc. (London) **A165**, 372 (1938).

¹³ E. C. Stoner, Proc. Roy. Soc. (London) **A169**, 339 (1939).

¹⁴ E. P. Wohlfarth, Proc. Roy. Soc. (London) **A195**, 434 (1949).

¹⁵ E. P. Wohlfarth, Phil. Mag. **40**, 1095 (1949).

¹⁶ E. P. Wohlfarth, Proc. Leeds Phil. Soc. **5**, 89 (1949).

¹⁷ E. P. Wohlfarth, Phil. Mag. **42**, 374 (1951).

¹⁸ E. P. Wohlfarth, Phil. Mag. **40**, 703 (1949).

¹⁹ A. B. Lidiard, Proc. Phys. Soc. (London) **A64**, 814 (1951).

²⁰ A. B. Lidiard, Proc. Phys. Soc. (London) **A65**, 885 (1952).

²¹ G. M. Bell, Phil. Mag. **43**, 127 (1952).

²² R. S. Smith, thesis, Case Institute of Technology (1951).

²³ N. F. Mott, Proc. Phys. Soc. (London) **47**, 571 (1935).

²⁴ G. C. Fletcher and E. P. Wohlfarth, Phil. Mag. **42**, 106 (1951).

²⁵ G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).

be written, in general, as a single Slater determinant and as the product of two such determinants, respectively,

$$\Psi(\zeta=1) = (N!)^{-\frac{1}{2}} \Delta^+ |\psi_i(\mathbf{r}_j)|, \quad (2)$$

$$\Psi(\zeta=0) = [(N/2)!]^{-1} \Delta^+ |\psi_i(\mathbf{r}_j)| \cdot \Delta^- |\psi_i(\mathbf{r}_j)|, \quad (3)$$

where Δ^+ contains wave functions for electrons with + spin and Δ^- with - spin. The total energy is

$$E = \int \cdots \int (N) \cdots \int \Psi^* \mathbf{H} \Psi d\tau(\mathbf{r}_1, \cdots, \mathbf{r}_N). \quad (4)$$

The one-electron wave functions in (2), (3) take the form

$$\psi_i(\mathbf{r}_j) = N^{-\frac{1}{2}} \sum_l \exp(i\mathbf{k}_l \cdot \mathbf{R}_i) \phi(\mathbf{r}_j - \mathbf{R}_l), \quad (5)$$

where \mathbf{k}_i is the wave vector of electron i and ϕ the atomic wave function. If the atomic level generating the energy bands is degenerate, e.g. a $3d$ level, then (5) is replaced by a more complicated function.²⁵ The evaluation of (4) is straightforward,²⁶ giving

$$E = (F' + 2K) + (C' - K) - J, \quad (6)$$

where

$$\left. \begin{aligned} F' &= \sum_i F_i = \sum_i \int \psi_i^*(\mathbf{r}) [-(\hbar^2/8\pi^2\mu)\nabla^2 \\ &\quad + \sum_l V_l(\mathbf{r})] \psi_i(\mathbf{r}) d\tau(\mathbf{r}), \\ C' &= \frac{e^2}{2} \sum_i \sum_j C_{ij} \\ &= \frac{e^2}{2} \sum_i \sum_j \int \int \frac{1}{r_{12}} |\psi_i(\mathbf{r}_1)|^2 |\psi_j(\mathbf{r}_2)|^2 d\tau(\mathbf{r}_1, \mathbf{r}_2), \\ J &= \frac{e^2}{2} \sum_i \sum_j \delta_{ij} J_{ij} = \frac{e^2}{2} \sum_i \sum_j \delta_{ij} \\ &\quad \times \int \int \frac{1}{r_{12}} \psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \psi_j^*(\mathbf{r}_2) \psi_j(\mathbf{r}_1) d\tau(\mathbf{r}_1, \mathbf{r}_2), \\ K &= \frac{e^2}{2} \sum_l \sum_m \frac{1}{R_{lm}} = \frac{Ne^2}{2} \sum_l \frac{1}{R_l}, \end{aligned} \right\} (7)$$

and where $\delta_{ij}=1$ for i, j representing electrons with parallel spins and 0 for antiparallel spins. The energy is written in the particular form (6) since then each of the three terms converges, although F' , C' , K separately diverge for an infinite crystal. Each of the terms in (7)

may be simplified using (5). Thus

$$\left. \begin{aligned} F_i &= E_0 + \sum_l \int |\phi(\mathbf{r})|^2 [V_l(\mathbf{r}) - U(\mathbf{r})] d\tau(\mathbf{r}) \\ &\quad + \sum_l \int \phi^*(\mathbf{r} - \mathbf{R}_l) [V_l(\mathbf{r}) \\ &\quad - U(\mathbf{r})] \phi(\mathbf{r}) d\tau(\mathbf{r}) \exp(i\mathbf{k}_i \cdot \mathbf{R}_l), \end{aligned} \right\} (8)$$

where NE_0 is the energy of the isolated atoms, $U(\mathbf{r})$ the potential energy of an electron in the field of an isolated ion, and the summation means that the potential whose mean value is required is that of the electron in the field of all the ions except the central ion. The second term in (8) thus diverges after summation like $-2K$ (see Eq. 7) so that $F' + 2K$ in (6) converges. The third term in (8) converges since the overlap integral decreases exponentially and is here to be taken negligible beyond nearest neighbors at distance R . The overlap integral is called $A(R)$. This term is the one of interest in energy band calculations and its exact form depends on the lattice structure.²⁵ The dependence of F' on relative magnetization ζ is found by summing F_i over the occupied volume of \mathbf{k} space and this contribution to the total energy, the Fermi energy, is in general least when $\zeta=0$. The second term in (6) is the Coulomb energy, and

$$\begin{aligned} C_{ij} &= N^{-1} \sum_m \sum_n \sum_p \int \int \frac{1}{r_{12}} \phi^*(\mathbf{r}_1) \phi(\mathbf{r}_1 - \mathbf{R}_m) \\ &\quad \times \phi^*(\mathbf{r}_2 - \mathbf{R}_n) \phi(\mathbf{r}_2 - \mathbf{R}_p) d\tau(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad \times \exp\{i[\mathbf{k}_i \cdot \mathbf{R}_m - \mathbf{k}_j \cdot (\mathbf{R}_n - \mathbf{R}_p)]\}. \end{aligned} \quad (9)$$

For simplicity neglect all 3- and 4-center integrals,²⁷ although these as well as nonorthogonality integrals could in principle be included. Also, the exponentially decreasing integrals in (9) are assumed to be negligible for all but nearest neighbors. Then

$$\left. \begin{aligned} C_{ij} &= N^{-1} \{I_0 + \sum_l I_1(\mathbf{R}_l)\} + zN^{-1} \{4I_2(R) \cos\mathbf{k}_i \cdot \mathbf{R} \\ &\quad + 2I_3(R) \cos\mathbf{k}_i \cdot \mathbf{R} \cos\mathbf{k}_j \cdot \mathbf{R}\}, \end{aligned} \right\} (10)$$

where

$$\left. \begin{aligned} I_0 &= \int \int \frac{1}{r_{12}} |\phi(\mathbf{r}_1)|^2 |\phi(\mathbf{r}_2)|^2 d\tau(\mathbf{r}_1, \mathbf{r}_2), \\ I_1(\mathbf{R}_l) &= \int \int \frac{1}{r_{12}} |\phi(\mathbf{r}_1)|^2 |\phi(\mathbf{r}_2 - \mathbf{R}_l)|^2 d\tau(\mathbf{r}_1, \mathbf{r}_2), \\ I_2(R) &= \int \int \frac{1}{r_{12}} |\phi(\mathbf{r}_1)|^2 \phi(\mathbf{r}_2) \phi^*(\mathbf{r}_2 - \mathbf{R}) d\tau(\mathbf{r}_1, \mathbf{r}_2), \\ I_3(R) &= \int \int \frac{1}{r_{12}} \phi^*(\mathbf{r}_1) \phi(\mathbf{r}_1 - \mathbf{R}) \\ &\quad \times \phi^*(\mathbf{r}_2 - \mathbf{R}) \phi(\mathbf{r}_2) d\tau(\mathbf{r}_1, \mathbf{r}_2), \end{aligned} \right\} (11)$$

²⁶ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

²⁷ S. O. Lundqvist and P. O. Löwdin, *Arkiv Fys.* 3, 147 (1951).

where $z(R)$ is the number of nearest neighbors. Relation (10) for C_{ij} contains overlap integrals independent of interatomic distance, I_0 , integrals varying as R^{-1} , I_1 , and integrals decreasing exponentially, I_2 and I_3 . For an infinite crystal the sum involving I_1 diverges after summation over i, j , canceling then exactly with $-K$ in (6), so that $C'-K$ in (6) converges. The final term in (6) is the exchange energy and

$$J_{ij} = N^{-1} \sum_m \sum_n \sum_p \int \int_{r_{12}} \frac{1}{r_{12}} \phi^*(\mathbf{r}_1) \phi^*(\mathbf{r}_2 - \mathbf{R}_m) \times \phi(\mathbf{r}_1 - \mathbf{R}_n) \phi(\mathbf{r}_2 - \mathbf{R}_p) d\tau(\mathbf{r}_1, \mathbf{r}_2) \times \exp i\{\mathbf{k}_i \cdot \mathbf{R}_p - \mathbf{k}_j \cdot (\mathbf{R}_m - \mathbf{R}_n)\}, \quad (12)$$

and with the same simplifications as before

$$J_{ij} = N^{-1} [I_0 + \sum_l I_1(\mathbf{R}_l) \cos \mathbf{k}_i \cdot \mathbf{R}_l \cos \mathbf{k}_j \cdot \mathbf{R}_l] + zN^{-1} [4I_2(R) \cos \mathbf{k}_i \cdot \mathbf{R} + I_3(R)(1 + \cos \mathbf{k}_i \cdot \mathbf{R} \cos \mathbf{k}_j \cdot \mathbf{R})]. \quad (13)$$

Here the sum involving I_1 converges rapidly after summation over i, j , as shown below, and may be replaced by its leading term involving $I_1(R)$, corresponding to nearest neighbor interaction, as for I_2 and I_3 .

With C_{ij} and J_{ij} given by (10) and (13) the last two terms in the total energy expression (6) may be calculated by summation over $\mathbf{k}_i, \mathbf{k}_j$. It is convenient to discuss separately the two cases $\zeta=1$ and 0.

(i) $\zeta=1$. Here the electron spins are all parallel and every state in the Brillouin zone is singly occupied. In summing over the zone it may be noted that, if \mathbf{R}_l is a lattice vector,

$$\sum_{\text{zone}} \cos(\mathbf{k} \cdot \mathbf{R}_l) = \begin{cases} 0 & \text{when } \mathbf{R}_l \neq 0, \\ N_e & \text{when } \mathbf{R}_l = 0, \end{cases} \quad (14)$$

where N_e is the number of electrons. Hence the total energy is easily seen to be identical with that calculable with the Heitler-London approximation, a well known theorem²⁶ relating to full zones which has applicability in discussing nonconducting solids like diamond.²⁸ It may be specially noted that the term $\sum_i \sum_j I_0$ in C' is here canceled exactly by the term $\sum_i \sum_j I_0 \delta_{ij}$ in J .

(ii) $\zeta=0$. Here (14) no longer holds and the total energy differs from that calculable with the Heitler-London treatment. Consider first the terms in (6) which do not vanish as $R \rightarrow \infty$. In this limit

$$E - NE_0 = \frac{e^2 I_0}{2N} \sum_i \sum_j (1 - \delta_{ij}) = \frac{e^2 N_e^2}{4N} I_0 = \frac{Ne^2 I_0}{4}, \quad (15)$$

when $N_e = N$. Hence as $R \rightarrow \infty$ the total energy is larger for $\zeta=0$, by an amount given by (15), than for $\zeta=1$,

so that the crystal is apparently ferromagnetic at infinite separation of the atoms. This "catastrophe" was noted by Seitz.²⁶ Now as $R \rightarrow \infty$ $E - NE_0$ must vanish whether $\zeta=1$ or 0, and this result is given correctly by the Heitler-London treatment. The form of the integral I_0 in (11) shows that the anomalous molecular field arises from the interaction of electrons close to one atom. Hence the anomaly results from the overemphasis in the Bloch approximation of ionized states. In this limit the anomalous term is in fact canceled exactly by the correlation correction, equal to $-Ne^2 I_0/4$ when $\zeta=0$ and zero when $\zeta=1$, when $E - NE_0 = 0$ on both approximations [see (i) above].

For finite values of R the total energy of the demagnetized crystal includes all the terms given in (10) and (13). The problem of calculating the correlation energy in this general case is perhaps the most difficult one in the electron theory of metals. A similar problem, that of calculating configurational interactions, arises in the quantum theory of molecules.²⁹ For H_2 , Coulson and Fischer³⁰ have given a very clear exposition of the nature of the problem and have gone a long way towards its solution. A similar calculation for the present case is, however, quite impracticable. Since, as already noted, the correlation energy in the limit $R \rightarrow \infty$ is known, and in the absence of a rigorous treatment, it will be assumed that for *finite, though still large* values of R , the correlation energy remains equal to the value $-Ne^2 I_0/4$ for infinite separation, thus canceling exactly the anomalous terms in the Coulomb and exchange energy involving I_0 . Although it is clear that the R dependent terms must also be modified, it is probable, though impossible to prove, that these modifications are slight, since the bulk of the correlation correction must be included in the large term required to cancel the anomalous terms in C' and J . On the basis of this approximation the parameter θ' varies with R via overlap integrals of the type $I(R)$ given in (11). At the same time the degeneracy temperature, which depends on the band width, varies with R via overlap integrals of the type $A(R)$ given in (8). Hence θ' and the degeneracy temperature are expected to be both very much of the same order of magnitude and, as pointed out below, this result is also indicated by the experimental results for real ferromagnetic metals.

In order to calculate the Coulomb and exchange energies arising from the R dependent terms in C_{ij} and J_{ij} for the demagnetized crystal, it is strictly necessary to calculate first the shape of the occupied part of the Brillouin zone. For simplicity this may be assumed to be spherical with radius k_0 . Now

$$\sum_{\text{sphere}} \cos(\mathbf{k} \cdot \mathbf{R}) = \frac{V}{8\pi^3} \int \cos(\mathbf{k} \cdot \mathbf{R}) d\tau(\mathbf{k}) = \frac{N_e}{2} f(k_0 R), \quad (16)$$

²⁹ Coulson, Craig, and Jacobs, Proc. Roy. Soc. (London) A206, 297 (1951).

³⁰ C. A. Coulson and I. Fischer, Phil. Mag. 40, 386 (1949).

²⁸ K. Ganzhorn, Naturwiss. 39, 62 (1952).

where

$$f(x) = 3(\sin x - x \cos x)/x^3 = 3(\pi/2)^{1/2} x^{-3/2} J_{3/2}(x), \quad (17)$$

V is the volume and N_e the number of electrons. The function $f(x)$ tends to 1 as $x \rightarrow 0$ and converges rapidly as x increases. Hence the R dependent terms in C' and J have the general form

$$n e^2 N_e^2 I(R) f^p(k_0 R)/N, \quad (18)$$

where n is a numerical factor of order unity, $I(R)$ one of the overlap integrals in (11), and $p=0, 1$, or 2 depending on whether the term which has been integrated is constant, depends on either \mathbf{k}_i or \mathbf{k}_j only or on both. In particular, $p=2$ for the term in J_{ij} in (13) which involves I_1 . Hence this contribution to the exchange energy converges very rapidly beyond nearest neighbors through the convergence of $f^2(k_0 R)$ and will at most be of the same order of magnitude as the other contributions to J involving I_2 and I_3 , for some of which $p=0$. For these latter terms the convergence occurs only through the exponential dependence on R of the integrals which may not be as rapid as the dependence on R of $f(k_0 R)$. In an early calculation by Brillouin³¹ integrals of the form I_2, I_3 were not considered, the exchange energy being taken to be proportional to $I_1(R)$ only. The above discussion shows that Brillouin's calculation may be at fault (see also below). In the same paper³¹ Brillouin also considers the Coulomb contribution to the total energy. The present discussion shows that, whereas terms in C_{ij} which are independent of $\mathbf{k}_i, \mathbf{k}_j$ reduce after summation to the same value whether $\zeta=1$ or 0 , those terms which depend on \mathbf{k} give differing contributions depending on ζ . Hence the Coulomb as well as the exchange energy contributes towards the molecular field energy. It is only for free electrons, where C_{ij} is constant, that C' is strictly independent of magnetization.

The discussion so far has been limited to the two extreme cases $\zeta=1$ or 0 , since only then can the total wave function be represented by a single Slater determinant. As shown below, however, the approximation of using the above expressions in calculating the total energy as a function of magnetization $E(\zeta)$ is probably less serious for tightly bound than for perfectly free electrons. Then, considering the expression (13) giving J_{ij} , a term, involving the integral $I_3(R)$, is independent of $\mathbf{k}_i, \mathbf{k}_j$. The corresponding contribution to the exchange energy $J(\zeta)$ is $(ze^2/2N)I_3(R) \times (N_1^2 + N_2^2)$, where $N_1, N_2 = \frac{1}{2}N_e(1 \pm \zeta)$. Hence the contribution to $E(\zeta)$ is $-(ze^2/4N)N_e^2 I_3(R)\zeta^2$, equivalent to a constant value of the parameter θ' , given by $k\theta' = \frac{1}{2}zqe^2 I_3(R)$, where $q = N_e/N$ is the number of electrons per atom. Again (13) contains a term, involving $I_2(R)$, which depends on \mathbf{k}_i but not on \mathbf{k}_j . This contributes to $E(\zeta)$ a term equal to

$$-(ze^2/2N)I_2(R)\{N_1^2 f(k_{01}R) + N_2^2 f(k_{02}R)\}, \quad (19)$$

where $k_{01}^3 = (6\pi^2 N_1/V)$, $k_{02}^3 = (6\pi^2 N_2/V)$. Now $f(x)$ may be expanded in the form $f(x) = 1 - x^2/10 + 0(x^4)$. Hence (19) becomes

$$\left. \begin{aligned} & -\frac{1}{2}N_e k\theta' \zeta^2 (1 + \frac{1}{2}A\zeta^2 + 0(\zeta^4)), \\ & \text{where} \\ & k\theta' = \frac{1}{2}zqe^2 I_2(R), \quad A \doteq (2/243)(3\pi^2 qNR^3/V)^{3/2}, \end{aligned} \right\} (20)$$

corresponding to an effective θ' which increases with magnetization. For nickel, $q=0.6$, $A \doteq 0.07$. Finally, (13) contains terms, involving $I_1(R)$ and $I_3(R)$, which depend on both \mathbf{k}_i and \mathbf{k}_j . These again give a contribution to $E(\zeta)$ of the form (20) but with A twice as large as before. In general, with the approximation that $E(\zeta)$ is calculable from the above formulas, the dependence of energy on magnetization has the form $\sum_n A_n \zeta^{2n}/2n$; the rough calculation just outlined shows that $A = A_2/A_1$ may be of order 0.1 (see Sec. 3).

This subsection will be concluded by a critical discussion of Slater's paper.⁷ It seems to the writer (1) that in taking the main contribution to the exchange energy to be the atomic integral he calls J , Slater has taken no account of correlation, thus obtaining anomalous ferromagnetism at large interatomic separation as discussed above. Slater has recently reconsidered this problem¹¹ and also concludes that the result of the earlier paper is due to the neglect of correlation. His method of overcoming the difficulty, however, is to postulate that beyond some large value of R ionized states must be completely excluded from the treatment and the Heitler-London treatment used in describing the metallic state. This view is also held by Mott.³² The work of Coulson and Fischer³⁰ suggests to the writer, however, that the Bloch approximation, duly corrected for correlation as suggested above, is applicable over the whole range of R . In both cases the correct energy is obtained as $R \rightarrow \infty$. (2) With the atomic integral J virtually cancelled by the correlation correction Slater's expression (3) is reduced to the R dependent second term. The reason why this gives only half a percent of the total calculated exchange energy (which, incidentally, leads to roughly the correct value of the Curie temperature) seems to be the following. Slater, like Brillouin,³¹ reduces this term to

$$(ze^2/2N)I_1(R) \sum_i \sum_j \cos \mathbf{k}_i \cdot \mathbf{R} \cos \mathbf{k}_j \cdot \mathbf{R} \quad (21)$$

(see Eq. 13), and states that "the quantities \mathbf{k}_i and \mathbf{k}_j should be allowed to range over a polyhedral cell in \mathbf{k} space." Now (14) shows that then the above contribution vanishes identically. A small nonvanishing contribution was in fact obtained only because Slater replaced the zone by a sphere of equal volume and radius k_0 , which, understandably, makes the value of $(k_0 R)$ lie close to a zero of $f(k_0 R)$ (see Eq. 17). The above discussion suggests that the exchange energy is given by summing the *full* expression for $J_{ij}(R)$ given by (13) over the *occupied* part of the zone, while Brillouin and

³¹ L. Brillouin, J. phys. et radium 4, 333 (1933).

³² N. F. Mott, Proc. Phys. Soc. (London) A62, 416 (1949).

Slater consider only the term (21) involving I_1 . Further, the occupied volume in \mathbf{k} space only corresponds to a full zone, and summation only reduces the contribution to zero, when $\zeta=1$. For the unmagnetized state the zone is half-full and the contribution does not vanish.

Although the formulas derived above are applicable to a very simple model of a ferromagnetic, it seems clear empirically that many features of a satisfactory theory of ferromagnetism, applicable to real metals, are given by considering the magnetic carriers (holes in the d band) much in the same way as were the tightly bound electrons to which these formulas apply. In summing expressions like (13) over effectively the unoccupied part of the d band, the volume of integration for holes with $+$ and $-$ spin depends on ζ and does not in general correspond to a full zone. Consequently, the nearest neighbor contribution to the exchange energy, here suggested to be the most important contribution, does not vanish after summation.

(b) Statistical Mechanics—Spin Degeneracy

For an arbitrary value of the relative magnetization ζ , a Slater determinant including spin functions may be constructed to give the total wave function for the metal. The spin functions may, however, be permuted in a large number of ways, so that the energy state is very highly degenerate. The correct zero-order wave function is thus a linear combination of a large number of Slater determinants. If this problem could be correctly formulated,³⁸ the final energy expression would be accurate even in as far as it would include some correlation terms. In analyzing this problem, that of spin degeneracy, Lidiard²⁰ shows that the more accurate free energy expression is identical with that derived by Stoner, if the sum of the Coulomb and exchange energies, $C_{ij}+J_{ij}$, is independent of $\mathbf{k}_i, \mathbf{k}_j$. Now, as shown above (see also Lidiard¹⁹), if C_{ij} were constant summation over i, j gives C' independent of ζ , and if J_{ij} were constant $J(\zeta) \propto \zeta^2$, corresponding to a constant molecular field coefficient. For this simple case, it is permissible to consider the electrons (or holes) with $+$ spin to be distributed in a sub-band whose lowest state is displaced relative to that of the sub-band for electrons with $-$ spin by an amount proportional to ζ and to the (constant) value of J_{ij} . On the other hand, if J_{ij} is not constant, this familiar description of the ferromagnetic state, on which Stoner's equations are based, is no longer applicable. This situation arises in its most serious form in discussing the free-electron gas. Here C_{ij} is constant but J_{ij} is not, being given by

$$J_{ij} = (4\pi/V) |\mathbf{k}_i - \mathbf{k}_j|^{-2}. \quad (22)$$

It is thus easy to understand why use of (22) in calculating many of the properties of the free-electron gas leads to absurd results: (1) The low temperature elec-

tronic heat varies anomalously with temperature;³⁴⁻³⁶ (2) the magnetization, temperature curve drops suddenly at a critical temperature;¹⁹ (3) the low energy tail of the soft x-ray emission curve has infinite width.³⁷ It was suggested^{35,37} that results in better agreement with observation could be obtained if allowance were made for correlation by the use of a screened Coulomb potential in the Hamiltonian operator [Eq. (1)], giving a less rapid variation of J_{ij} . The fundamental validity of this procedure is, however, very doubtful (Wohlfarth³⁵ pointed out that the total energy could not now be calculated correctly); the problem has been reconsidered by Macke,³⁸ and Bohm and Pines.³⁹

Relation (13) for tightly bound electrons shows that here the variation of J_{ij} is much less rapid than the variation (22) for free electrons. It is, therefore, suggested that here spin degeneracy effects are much less serious and that Stoner's equations, based on Fermi-Dirac statistics, give a very good approximation to the accurate statistical equations which would be obtained by inclusion of spin degeneracy effects. Apart from the general consistency of the above argument, two further supporting arguments for the general viewpoint may be given: (1) As already noted, constant J_{ij} implies a constant value of the parameter θ' . For tightly bound electrons it was shown earlier that the effective θ' varies with ζ , the molecular field energy being given by $-\frac{1}{2}N_e k\theta' \zeta^2 (1 + \frac{1}{2}A\zeta^2 + \dots)$. Both theory and experiment (see Sec. 3) show, however, that the variation is very gradual, since A is only about 0.1. (2) A calculation has been carried out⁴⁰ of the temperature variation of the electronic heat C_e of tightly bound electrons including that contribution to J_{ij} which depends most strongly on \mathbf{k} , *viz.* the term in (13) involving I_1 . The method of calculation used was that suggested by Koppe,³⁴ giving $C_e = \gamma T$, where γ is related to the corresponding coefficient neglecting exchange, γ_0 , by

$$\gamma_0/\gamma = 1 + \frac{z}{24} e^2 f^2 (k_0 R) I_1(R) / A(R). \quad (23)$$

Here R is the interatomic distance, z the number of nearest neighbors, f is given by (17), and $A(R)$ is the overlap integral determining band width, given in (8). In deriving (23) the electrons are taken to be distributed in a sphere with radius k_0 in \mathbf{k} space. The other contributions to J_{ij} have similar but less pronounced effects. It appears, therefore, that, contrary to the behavior of the free-electron gas,³⁵ the electronic heat of tightly bound electrons is strictly proportional to T , with γ only slightly less than the value derivable by

³⁴ H. Koppe, Z. Naturforsch. 2A, 429 (1947).

³⁵ E. P. Wohlfarth, Phil. Mag. 41, 534 (1950).

³⁶ A. B. Lidiard, Phil. Mag. 42, 1325 (1951).

³⁷ P. T. Landsberg, Proc. Phys. Soc. (London) A62, 806 (1949).

³⁸ W. Macke, Z. Naturforsch. 5A, 192 (1950).

³⁹ D. Bohm and D. Pines, Phys. Rev. 80, 903 (1950); 82, 625 (1951); 85, 338 (1952).

⁴⁰ E. P. Wohlfarth (unpublished).

³⁸ S. F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950).

neglecting exchange. It may be recalled, however, that unless a correction is made for correlation, the assembly exhibits anomalous ferromagnetism at large R and hence an anomalous magnetic specific heat. As for free electrons,³⁵ reasonable results are only obtained after allowing for correlation.

(c) Summary

The results obtained in this section may be conveniently summarized by relating them directly to the premises underlying Stoner's treatment,^{12,13} recalled in Sec. 1. (1) "The ferromagnetism of a metal results from the holes in the so-called $3d$ band." It is suggested that the magnetic carriers are best described by tight binding wave functions. These allow in principle the calculation of band shape and width, determined by overlap integrals of the form $A(R)$ given in (8). (2) "The exchange energy $J(\zeta)$ is proportional to the square of the relative magnetization—specifically $J(\zeta) = \frac{1}{2}N_e k\theta'\zeta^2$." It is shown that this assumption is not strictly true, $J(\zeta)$ being more generally given by relations of the form (20), involving overlap integrals $I(R)$ of the type given in (11). The fundamental requirement of correcting for correlation has been discussed. It is shown how, in the absence of a rigorous treatment, this requirement may be approximately satisfied. The condition for ferromagnetism in Stoner's treatment, that the ratio of the parameter θ' to the degeneracy temperature be larger than a critical value, may be formulated in principle in the form that the ratio of certain overlap integrals be large enough. The appearance of ferromagnetism is thus closely related to the structure of the metal and to the magnitude of the interatomic distance. (3) "The particles obey Fermi-Dirac statistics." The fundamental problem of spin degeneracy is outlined and the relevance of the dependence of J_{ij} on $\mathbf{k}_i, \mathbf{k}_j$ pointed out. It is suggested that for particles described by tight binding wave functions the variation is slow enough for Stoner's statistical equations to be good approximations to the exact equations.

3. SOME EXPERIMENTAL RESULTS

In this section certain experimental results are briefly discussed, including some having a bearing on the theoretical results obtained in Sec. 2 and others having some topicality in view of recent developments in the theory of the properties of transition metals.

(a) The Variation with Composition of the Curie Temperature and Saturation Magnetization, and the Variation with Temperature of the Susceptibility of the Alloys Ni-Cu, Ni-Co, and Ni-Pd

(i) Ni-Cu.¹⁴ Analysis of the susceptibility results leads to an estimated variation with concentration c of $k\theta'/\epsilon_0$ and ζ_0 , where ϵ_0/k is the degeneracy temperature and ζ_0 the relative magnetization at 0°K. The

observed variation with c of the Curie temperature θ may be used to estimate the variation of ζ_0 , in good agreement with the values derived from the susceptibility results, and of θ' (reference 14, Fig. 4). Now the working formula for θ' derived in Sec. 2 is $k\theta' = \frac{1}{2}zqe^2I(R)$. For Ni-Cu the overlap integrals $I(R)$ probably do not vary appreciably with c , since the atomic functions ϕ of Ni and Cu are probably not very different, and the interatomic distance R is almost constant. The practically linear variation of θ' with c derived from the θ values is thus in qualitative agreement with this formula, since $q \approx 0.6 - c$. Using the estimated values of ζ_0 the variation with c of σ_0 , the saturation magnetization, may be obtained (reference 14, Fig. 5), in good agreement with the observed linear variation. Values of $k\theta'/\epsilon_0$ estimated from the data are of order 1, confirming that the molecular field arises from overlap forces of the same origin and order of magnitude as those causing band spread (see Sec. 2).

(ii) Ni-Co.¹⁵ Analysis of the susceptibility results indicates that $k\theta'/\epsilon_0$ and ζ_0 are practically independent of c . Since for this alloy system both q and $I(R)$ must vary appreciably with c , the analysis is less conclusive. Using the experimental values of σ_0 the variation with c of the Curie temperature θ may be estimated, in fair agreement with experiment (reference 15, Fig. 5).

(iii) Ni-Pd.¹⁶ Analysis shows that θ' varies only slowly with c (with particular approximations $\theta' = 1.23 \times 10^3$ °K for Ni, 1.02×10^3 °K for Pd). For Ni-Pd, q is probably constant (remaining equal to about 0.6), and the above formula for θ' shows that the slight variation of θ' results from small changes of $I(R)$ with Pd concentration c . The observed values of σ_0 may be used to estimate the variation of θ with c , in excellent agreement with experiment (reference 16, Fig. 2).

(b) The Variation with Temperature of the Magnetization, Specific Heat, and Magnetocaloric Effect of Co, Ni, and Ni Alloys below the Curie Point

The curve for Ni relating the reduced magnetization σ/σ_0 with the reduced temperature T/θ differs considerably from the theoretical curve deduced from Stoner's calculations.¹² It was suggested^{17,18} that better agreement should be obtained by using the more general expression for the exchange energy (20) in carrying out the calculation. A full analysis by Hunt,⁴¹ based on this suggestion, indicates that excellent agreement may be obtained for Ni and Co⁴² with the parameter A in (20) equal to about 0.1. Hunt also considers the data for Ni-Cu alloys¹⁴ and finds that A decreases with increasing Cu concentration, in qualitative agreement with the expression (20). A similar modification of Stoner's equations is necessary in analyzing the specific heat data. For Ni, for example, the calculated reduced spe-

⁴¹ K. L. Hunt, Proc. Roy. Soc. (London) A (to be published).

⁴² H. P. Myers and W. Sucksmith, Proc. Roy. Soc. (London) A207, 427 (1951).

cific heat discontinuity at the Curie point, $\Delta C/N_e k$, is about 0.6,^{18,17} the observed value being 1.5. Hunt shows that the excellent agreement over the whole temperature range may again be attained with $A \doteq 0.1$; a value of this order is also required in interpreting the magnetocaloric data for Ni, but here difficulties arise from domain effects.⁴⁸

Went⁴⁴ has recently found that the σ/σ_0 , T/θ curves for many Ni alloys are all, to a varying extent, less concave to the T/θ axis than the curve for pure Ni. He interprets this finding by postulating the presence of small isolated nickel-rich particles in the alloys, giving rise to rapid density fluctuations.⁴⁵ It seems to the writer that this interpretation is strictly inadmissible for the more dilute alloys, where the deviations are probably mainly the result of the above mentioned effect, a variation of the parameter A with composition. For the less dilute alloys the deviations may be the result of density fluctuations, the alloy consisting of regions of differing compositions and Curie temperatures, giving rise to pronounced tailing of the curves in

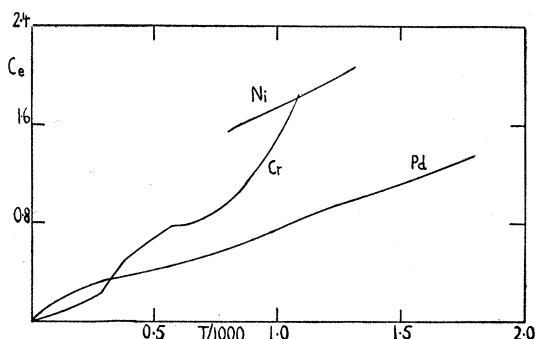


Fig. 1. The electronic heat of Ni above the Curie point, Pd and Cr. C_e , electronic heat, cal mole⁻¹ deg⁻¹; T , absolute temperature.

the "Curie point" region: Went's curve for Ni-Si for example is suggested to be "all tail." This situation has been very fully investigated by Marian.⁴⁶ Both the above effects are the more pronounced the higher the valency of the solute metal, in qualitative agreement with Went's results.⁴⁴

(c) The High Temperature Specific Heat of Ni and Pd

(i) Ni. Very reliable data were obtained by Persoz⁴⁷ (800°–1300°K). The variation of the derived electronic heat C_e ($C_p - C_v$, Stoner;⁴⁸ $\theta_D = 400^\circ\text{K}$) is shown in Fig. 1. Contrary to earlier theoretical treatments¹⁸ C_e does not approach a constant value at high temperatures. The observed variation is, in fact, that given by Wohlfarth,¹⁴ who showed that an approximately linear

variation, as observed, is calculable by inclusion of the "transfer effect" (reference 14, Fig. 14). With the overlap parameter r_0 ¹⁴ equal to 10 and $q=0.6$, the theoretical and experimental curves may be brought into coincidence taking the degeneracy temperature to equal $2.3 \times 10^8^\circ\text{K}$, in agreement with independent estimates. (ii) Pd. Experimental data are available covering the temperature range 0°–1800°K.^{49–51} The variation of C_e ($C_p - C_v$, Jaeger and Rosenbohm;⁵² $\theta_D = 275^\circ\text{K}$) is shown in Fig. 1. The low and medium temperature values of C_e are anomalously low; at higher temperatures C_e is approximately proportional to T as for Ni, but the Pd values are consistently smaller. The deviations are difficult to explain on the assumption¹⁶ that the band structures of the two metals are closely similar [see (e) below].

(d) Magnetic and Thermal Properties of Cr

Recent investigations give the following results: (i) The linear low temperature electronic heat coefficient γ is equal⁵³ to only 3.74×10^{-4} cal mol⁻¹ deg⁻², (ii) the high temperature variation of electronic heat C_e is anomalous, the observed values⁵⁴ being many times larger than γT (see Fig. 1, curve drawn from published data), (iii) the paramagnetic susceptibility increases quite markedly at high temperatures.⁵⁵ In metallic Cr the overlap of d as well as s wave functions must be much stronger than in nickel, and the electrons outside closed shells will then behave much more nearly as if they were free.¹⁵ The supposition that the d - s band in Cr is relatively wide has recently been supported by the results of soft x-ray measurements.^{55a} If the Fermi limit of the electron distribution lies close to a minimum in the density of states curve, the γ value would be lower than for neighboring metals in the periodic table,⁵⁸ the susceptibility would increase with temperature^{56,14} and, as for Ni, owing to the transfer effect, C_e would be anomalously large at high temperatures, as observed. Measurements on some other transition metals^{57–59} indicate that an increase of susceptibility with temperature is at least as common as a decrease. The interpretation put forward above to account for the properties

⁴⁹ G. L. Pickard and F. E. Simon, Proc. Phys. Soc. (London) **61**, 1 (1948).

⁵⁰ K. Clusius and L. Schachinger, Z. Naturforsch. **2A**, 90 (1947).

⁵¹ F. M. Jaeger and W. A. Veenstra, Proc. Koninkl. Nederland. Akad. Wetenschap. **37**, 280 (1934).

⁵² F. M. Jaeger and E. Rosenbohm, Rec. trav. chim. **51**, 13 (1932).

⁵³ Friedberg, Estermann, and Goldman, Phys. Rev. **85**, 375 (1952).

⁵⁴ L. D. Armstrong and H. Grayson-Smith, Can. J. Research **A28**, 51 (1950).

⁵⁵ T. R. McGuire and C. J. Kriessman, Phys. Rev. **85**, 452 (1952).

^{55a} E. M. Gyorgy and G. G. Harvey, Phys. Rev. **87**, 861 (1952).

⁵⁶ E. C. Stoner, Proc. Roy. Soc. (London) **A154**, 656 (1936).

⁵⁷ C. J. Kriessman, Bull. Am. Phys. Soc. **27**(3), 33 (1952).

⁵⁸ F. E. Hoare and J. C. Matthews, Proc. Roy. Soc. (London) **A212**, 137 (1952).

⁵⁹ C. F. Squire and A. R. Kaufmann, J. Chem. Phys. **9**, 673 (1941).

⁴³ E. C. Stoner, Trans. Roy. Soc. (London) **A235**, 165 (1936).

⁴⁴ J. J. Went, Physica **17**, 98, 596 (1951).

⁴⁵ A. D. Fokker, Physica **8**, 109, 159 (1941).

⁴⁶ V. Marian, Ann. phys. **7**, 459 (1937).

⁴⁷ B. Persoz, Ann. phys. **14**, 237 (1940).

⁴⁸ E. C. Stoner, Phil. Mag. **22**, 81 (1936).

of Cr may have wider applicability, although for some of the other transition metals the γ values are large, an extreme case being W.⁶⁰

(e) Magnetic Properties of Pd and its Alloys

The electronic properties of Pd had been discussed earlier.¹⁶ Recent very careful low temperature measurements⁵⁸ show that the paramagnetic susceptibility χ varies anomalously with temperature at about 80°K, where the curve passes through a slight maximum. No immediate interpretation of this behavior can be given, but, as stated,⁵⁸ it cannot result from the metal being antiferromagnetic since there is no corresponding anomaly in the specific heat curve at this temperature.⁶⁰ Also, recently, magnetic measurements have been reported by Wucher⁶¹ on alloys of Pd with diamagnetic metals and on Pd-H. Although the susceptibility measurements were not extended to low temperatures, some attempt may be made to extrapolate the $1/\chi$, T curves to 0°K. Figure 2 shows the variation of χ_0 , the extrapolated paramagnetic susceptibility, with the *electronic* concentration (H/Pd for the Pd-H system). The points for the alloys lie approximately on a single curve *A*, showing that, as for the variation of σ_0 in nickel alloys, the decrease must be primarily an electronic effect. The points on *B* for Pd-H are higher than those for the alloys; the difference may result from the more complicated phase diagram of this system. Both curves *A* and *B* tend to zero at a value of c close to 0.6. Figure 2 also contains a "theoretical curve" *C*, calculated on the assumption of parabolic band shape and taking the parameter θ' to be proportional to q , the number of holes

⁶⁰ A. A. Silvidi and J. G. Daunt, Phys. Rev. 77, 125 (1950).

⁶¹ J. Wucher, Ann. phys. 7, 317 (1952).

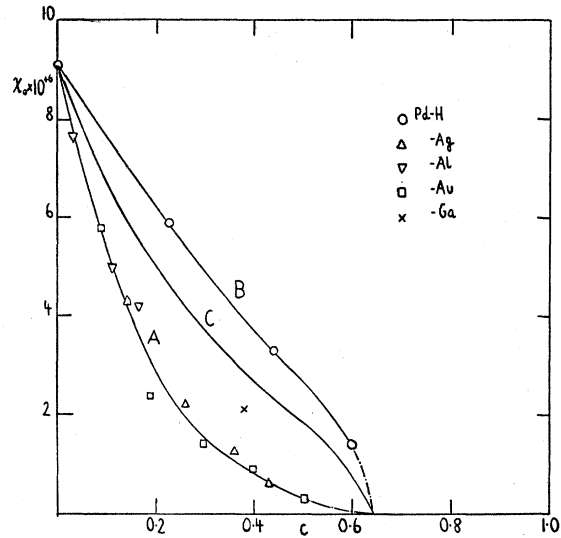


FIG. 2. Paramagnetic susceptibility of Pd alloys and Pd-H. χ_0 , mass susceptibility at 0°K (see reference 61) (Pd-Au, 90°K (E. Vogt, Ann. Physik 14, 1 (1932))); c , electronic concentration or H/Pd. *A*, Pd alloys; *B*, Pd-H; *C*, theoretical (see text).

per atom (see Sec. 2). The difference between *A* and *C* may result from a variation of θ' which c more complicated than that assumed, since, owing to an appreciable variation of interatomic separation with concentration, the overlap integrals $I(R)$ discussed above may also vary appreciably on alloying.

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