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SUMMARY

A method is described for measuring the surface temperature of sliding metals. The temperature reached depends upon the load, speed coefficient of friction, and thermal conductivity of the metals, and is in good agreement with theory. With readily fusible metals the surface temperature reached corresponds to the melting point of the metal. With less fusible metals the local surface temperature may exceed 1000°C .

Even with lubricated surfaces the temperature (under boundary lubrication conditions) is high and may exceed 600°C . This high surface temperature will cause a local volatilization and decomposition of the lubricant, and is a cause of the breakdown of the boundary film.

Collective Electron Specific Heat and Spin Paramagnetism in Metals

By EDMUND C. STONER, Ph.D. (Cambridge); Reader in Physics at the University of Leeds

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1—INTRODUCTION

In two previous papers expressions have been obtained for the susceptibility* and specific heat† of free electrons in forms appropriate for low and high temperatures. With slight interpolation these expressions are adequate to give the temperature variation over the whole temperature range. The results are given in such a form that they are also applicable to electrons not strictly free, as long as the number of states per unit energy range in the unfilled energy band involved is proportional to the square root of the energy, as for free electrons. In this paper more general expressions are obtained which show how the specific heat and the spin paramagnetism, and their temperature variation, depend on the

* Stoner, 'Proc. Roy. Soc.,' A, vol. 152, p. 672 (1935).

† Stoner, 'Phil. Mag.,' vol. 21, p. 145 (1936).

band form. It is only the low temperature range which will be considered, as usually for metals ordinary temperatures fall well within the "low" range.

Although the equivalents of some of the results obtained have been given before, and it has been noticed that there is a relation between the electronic specific heat and the spin paramagnetism,* the general question has not been treated in any detail. Expressions are first obtained for collective electrons neglecting interchange interaction effects, and given in a convenient form for application. The difficult question of the susceptibility arising from the "orbital" motion of collective electrons will not here be discussed. The conditions necessary for a very large orbital effect do not usually hold; and for the more strongly paramagnetic metals, which are discussed here, it will be sufficient to consider the spin effect alone.

Spin susceptibility will depend greatly on those interchange interaction effects with which are associated differences of energy of pairs of electrons with parallel and antiparallel spins. A simple method of determining the general character of their influence is developed. For ferromagnetics interchange interaction effects are of predominant importance. The present discussion indicates that appreciable interchange interaction effects are not limited to the ferromagnetic metals; and that though positive interchange interaction is a necessary condition for ferromagnetism it is by no means sufficient. This has been shown before in connexion with particular models, but the bearing on the question of the magnetic properties of the metals generally does not seem to have been considered.

The electronic specific heat of metals will usually be small, and it is then difficult to estimate its magnitude from experimental results for specific heats with any precision. In ferromagnetic metals, however, there is a comparatively large excess specific heat even above the Curie point. It has previously been suggested† that this "terme inconnu" may be attributed to an electronic specific heat; and the proposed identification receives support from measurements of the specific heat of nickel at very low temperatures. A brief discussion of the excess specific heat of nickel will serve to exemplify the application of the theoretical results.

A central question to be considered is that of the significance of the different types of temperature variation found for paramagnetic metals. This is shown to be connected with the form and the manner of overlapping of the electron energy bands.

In the last section of the paper the magnetic properties and the specific

* Mott, 'Proc. Phys. Soc.,' vol. 47, p. 571 (1935).

† Stoner, 'Phil. Trans.,' A, vol. 235, p. 165 (1936).

heat of a number of particular metals are briefly discussed in the light of the theoretical treatment.

2—ELECTRONIC SPECIFIC HEAT

The basic formulae required in the application of Fermi-Dirac statistics to the specific heat and paramagnetism of electrons have been given in the papers cited above, and may be found in equivalent forms in any of the more detailed treatments, such as those of Nordheim,* Brillouin,† or Sommerfeld and Bethe.‡

Let

ε_0 = maximum electron energy in the completely degenerate state.

ζ = Fermi-Dirac critical energy, at which half the states are occupied. For $T \rightarrow 0$, $\zeta \rightarrow \zeta_0 = \varepsilon_0$.

$\nu(\varepsilon)$ = number of electron states per unit energy range for one direction of spin.

In considering low temperatures ($\varepsilon_0/kT \gg 1$) the various integrals involved may be represented by the usual asymptotic series. To determine the specific heat, an expression is obtained for the total energy. This involves $(\zeta - \zeta_0)$, which can be eliminated by means of the expressions for the total number of electrons.

$$\frac{N}{2} = \int_0^{\varepsilon_0} \nu(\varepsilon) d\varepsilon = \int_0^{\infty} \frac{\nu(\varepsilon) d\varepsilon}{\exp\{(\varepsilon - \zeta)/kT\} + 1} \quad (2.1)$$

$$= \int_0^{\zeta} \nu(\varepsilon) d\varepsilon + \left\{ 2c_2 (kT)^2 \frac{\partial \nu}{\partial \varepsilon} + 2c_4 (kT)^4 \frac{\partial^3 \nu}{\partial \varepsilon^3} \dots \right\}_{\zeta}, \quad (2.2)$$

where

$$c_n = 1 - \frac{1}{2^n} + \frac{1}{3^n} - \frac{1}{4^n} \dots \quad (2.3)$$

In particular

$$c_2 = \pi^2/12 = 0.822 \quad c_4 = 7\pi^4/720 = 0.947 \quad (2.4)$$

$$\int_0^{\zeta} \nu(\varepsilon) d\varepsilon - \int_0^{\varepsilon_0} \nu(\varepsilon) d\varepsilon = (\zeta - \zeta_0) \nu(\zeta_0) + \frac{1}{2} (\zeta - \zeta_0)^2 \left(\frac{\partial \nu}{\partial \varepsilon} \right)_{\zeta} \dots \quad (2.5)$$

$$\left(\frac{\partial \nu}{\partial \varepsilon} \right)_{\zeta} = \left(\frac{\partial \nu}{\partial \varepsilon} \right)_{\zeta_0} + (\zeta - \zeta_0) \left(\frac{\partial^2 \nu}{\partial \varepsilon^2} \right)_{\zeta_0} \dots \quad (2.6)$$

$$\left(\frac{\partial^3 \nu}{\partial \varepsilon^3} \right)_{\zeta} = \left(\frac{\partial^3 \nu}{\partial \varepsilon^3} \right)_{\zeta_0} \dots \quad (2.8)$$

* Müller-Pouillet, 'Lehrbuch der Physik,' vol. 4, iv, p. 271 (Braunschweig, 1934);
'Ann. Physik,' vol. 6, p. 607 (1931).

† "Die Quantenstatistik" (Berlin, 1931).

‡ 'Handbuch der Physik,' vol. 24, ii, p. 473 (Berlin, 1933).

Substituting in (2.2)

$$-(\zeta - \zeta_0) \nu(\zeta_0) = 2c_2 (kT)^2 \left(\frac{\partial \nu}{\partial \varepsilon} \right)_{\zeta_0} + 2c_2 (kT)^2 (\zeta - \zeta_0) \left(\frac{\partial^2 \nu}{\partial \varepsilon^2} \right)_{\zeta_0} + 2c_4 (kT)^4 \left(\frac{\partial^3 \nu}{\partial \varepsilon^3} \right)_{\zeta_0} + \frac{1}{2} (\zeta - \zeta_0)^2 \left(\frac{\partial \nu}{\partial \varepsilon} \right)_{\zeta_0}. \quad (2.9)$$

As a first approximation

$$\zeta - \zeta_0 = -2c_2 (kT)^2 \left(\frac{1}{\nu} \frac{\partial \nu}{\partial \varepsilon} \right)_{\zeta_0}. \quad (2.10)$$

Substituting this value in (2.9)

$$\zeta - \zeta_0 = - (kT)^2 \left[2c_2 \left(\frac{1}{\nu} \frac{\partial \nu}{\partial \varepsilon} \right) \right]_{\zeta_0} - (kT)^4 \left[2c_4 \left(\frac{1}{\nu} \frac{\partial^3 \nu}{\partial \varepsilon^3} \right) + 2c_2^2 \left\{ \left(\frac{1}{\nu} \frac{\partial \nu}{\partial \varepsilon} \right)^3 - \frac{2}{\nu^2} \frac{\partial \nu}{\partial \varepsilon} \frac{\partial^2 \nu}{\partial \varepsilon^2} \right\} \right]_{\zeta_0}. \quad (2.11)$$

For free electrons

$$2\nu(\varepsilon) = \frac{3}{2} \frac{N}{\varepsilon_0} \left(\frac{\varepsilon}{\varepsilon_0} \right)^{1/2} = \frac{3}{2} N \zeta_0^{-3/2} \varepsilon^{1/2}. \quad (2.12)$$

Using this value for $\nu(\varepsilon)$ in (2.11)

$$\zeta = \zeta_0 \left[1 - c_2 \left(\frac{kT}{\varepsilon_0} \right)^2 - \frac{3}{4} (c_2^2 + c_4) \left(\frac{kT}{\varepsilon_0} \right)^4 \dots \right], \quad (2.13)$$

in agreement with the expression previously obtained.

For the total energy

$$\frac{E}{2} = \int_0^\infty \frac{\varepsilon \nu(\varepsilon) d\varepsilon}{\exp \{(\varepsilon - \zeta)/kT\} + 1} \quad (2.14)$$

$$= \int_0^\zeta \varepsilon \nu(\varepsilon) d\varepsilon + 2c_2 (kT)^2 \left[\frac{\partial}{\partial \varepsilon} \{ \varepsilon \nu(\varepsilon) \} \right]_{\zeta} + 2c_4 (kT)^4 \left[\frac{\partial^3}{\partial \varepsilon^3} \{ \varepsilon \nu(\varepsilon) \} \right]_{\zeta} \quad (2.15)$$

$$\left. \begin{aligned} \int_0^\zeta \varepsilon \nu(\varepsilon) d\varepsilon &= \int_0^{\zeta_0} \varepsilon \nu(\varepsilon) d\varepsilon + (\zeta - \zeta_0) [\varepsilon \nu(\varepsilon)]_{\zeta_0} \\ &\quad + \frac{1}{2} (\zeta - \zeta_0)^2 \left[\frac{\partial}{\partial \varepsilon} \{ \varepsilon \nu(\varepsilon) \} \right]_{\zeta_0} \end{aligned} \right\} \quad (2.16)$$

$$\int_0^{\zeta_0} \varepsilon \nu(\varepsilon) d\varepsilon = E_0/2$$

The second and third terms in (2.15) may be similarly treated. Values of $(\zeta - \zeta_0)$ are then substituted from (2.11). The final expression obtained is

$$E = E_0 + 4c_2 (kT)^2 \nu(\zeta_0) + 12 (kT)^4 \left[c_4 \frac{\partial^2 \nu}{\partial \varepsilon^2} - c_2^2 \frac{1}{\nu} \left(\frac{\partial \nu}{\partial \varepsilon} \right)^2 \right]_{\zeta_0}. \quad (2.17)$$

For free electrons, using (2.12), this gives

$$E = N\varepsilon_0 \left[\frac{3}{5} + 3c_2 \left(\frac{kT}{\varepsilon_0} \right)^2 - \frac{9}{4} \left(\frac{kT}{\varepsilon_0} \right)^4 (c_4 + c_2^2) \right], \quad (2.18)$$

as obtained previously.

For the specific heat

$$C_V = (\partial E / \partial T)_V = 8c_2 k (kT) \nu(\varepsilon_0) \times \left[1 + 6 (kT)^2 \left\{ \frac{c_4}{c_2} \frac{1}{\nu} \frac{\partial^2 \nu}{\partial \varepsilon^2} - c_2 \left(\frac{1}{\nu} \frac{\partial \nu}{\partial \varepsilon} \right)^2 \right\} \right]_{\varepsilon_0}. \quad (2.19)$$

For free electrons

$$C_V = Nk \left[6c_2 \left(\frac{kT}{\varepsilon_0} \right) - 9 \left(\frac{kT}{\varepsilon_0} \right)^3 (c_2^2 + c_4) \right]. \quad (2.20)$$

It is convenient to use the electron volt (1 electron volt = 1.590×10^{-12} erg) as the unit of energy in dealing with the electron energy distribution, and to obtain an expression for the gram atomic heat in the usual units or as a multiple of R , the gas constant.

Let $\nu(V)$ be the number of electron states per volt per atom for one direction of spin. The first term in the expression for the electronic contribution to the gram atomic specific heat is then

$$\begin{aligned} (C_V)_A &= 8c_2 k N (kT) \nu(V_0) \times \frac{1}{1.590} \times 10^{12} \\ &= 8c_2 R T \nu(V_0) \times \frac{1.371}{1.590} \times 10^{-4}. \end{aligned} \quad (2.21)$$

Expressed in terms of $\nu(V)$, (2.19) becomes

$$\begin{aligned} (C_V)_A / R &= 1.724 \times 10^{-4} \nu(V_0) T \\ &\times \left[4c_2 + 24 (0.8621 \times 10^{-4})^2 T^2 \left\{ c_4 \frac{1}{\nu} \frac{\partial^2 \nu}{\partial V^2} - c_2^2 \left(\frac{1}{\nu} \frac{\partial \nu}{\partial V} \right)^2 \right\} \right]_{V_0}. \end{aligned} \quad (2.22)$$

Inserting numerical values for c_2 and c_4

$$\begin{aligned} (C_V)_A / R &= 5.671 \times 10^{-4} \nu(V_0) T \\ &\times \left[1 + 5.423 \times 10^{-8} T^2 \left\{ 0.947 \left(\frac{1}{\nu} \frac{\partial^2 \nu}{\partial V^2} \right) - 0.676 \left(\frac{1}{\nu} \frac{\partial \nu}{\partial V} \right)^2 \right\} \right]. \end{aligned} \quad (2.23)$$

For free electrons, $2\nu(V) = \frac{3}{2} (q/V_0) (V/V_0)^{1/2}$, where q is the number of free electrons per atom; giving

$$(C_V)_A / R q = 4.253 \times 10^{-4} \left(\frac{T}{V_0} \right) \left[1 - 2.20 \times 10^{-8} \left(\frac{T}{V_0} \right)^2 \right]. \quad (2.24)$$

This is in agreement with the first two terms in the expression previously obtained. It may be noticed that for strictly free electrons, the value of $\nu(V_0)$ in metals would range from about 0.1 to 0.5.

3—SPIN PARAMAGNETISM

The magnetic moment M is given by

$$M = -(\partial F / \partial H)_{T, \nu} = -(\partial \Omega / \partial H)_{\xi, T, \nu}, \quad (3.1)$$

where

$$\Omega = -kT \sum_s \log [1 + \exp \{(\xi - \epsilon_s) / kT\}]. \quad (3.2)$$

Corresponding to the two directions of spin, the energies ϵ_H in a field associated with a state of energy ϵ in the absence of a field are

$$\epsilon_H = \epsilon \pm \mu H. \quad (3.3)$$

The first terms in the appropriate series expansion for Ω are readily obtained, and may be put in a convenient form by using (2.10). The following expression derived for M is equivalent to that of Sommerfeld and Bethe.*

$$M = 2\mu^2 H \nu(\epsilon_0) \left[1 + 2c_2 (kT)^2 \left\{ \frac{1}{\nu} \frac{\partial^2 \nu}{\partial \epsilon^2} - \left(\frac{1}{\nu} \frac{\partial \nu}{\partial \epsilon} \right)^2 \right\}_{\epsilon_0} \right]. \quad (3.4)$$

This gives for free electrons, using for $\nu(\epsilon)$ the value given by (2.12),

$$M = \frac{3}{2} \frac{N\mu^2 H}{\epsilon_0} \left[1 - c_2 \left(\frac{kT}{\epsilon_0} \right)^2 \right], \quad (3.5)$$

as previously obtained.

With $\nu(V)$ as the number of states for one direction of spin per atom per volt, the electronic contribution to the gram atomic susceptibility is given by

$$(\chi_A)_e \times 10^6 = 64 \cdot 21 \nu(V_0) \left[1 + 1 \cdot 222 \times 10^{-8} T^2 \left\{ \frac{1}{\nu} \frac{\partial^2 \nu}{\partial V^2} - \left(\frac{1}{\nu} \frac{\partial \nu}{\partial V} \right)^2 \right\}_{V_0} \right]. \quad (3.6)$$

This is in agreement with the expression previously given for free electrons

$$(\chi_A)_e \times 10^6 = 48 \cdot 15 (q/V_0) [1 - 6 \cdot 11 \times 10^{-9} (T/V_0)^2], \quad (3.7)$$

where q is the number of free electrons per atom.

* 'Handbuch der Physik,' vol. 24, ii, p. 476 (1933).

4—RANGE OF VALIDITY OF FORMULAE

RELATION BETWEEN SPECIFIC HEAT AND PARAMAGNETISM

Range of Validity of Formulae

In the expressions derived, the specific heat and paramagnetism are represented by asymptotic series. For free electrons, the series with a few terms are appropriate for

$$kT/\varepsilon_0 \ll 1. \quad (4.1)$$

In practice the series with two terms give satisfactory approximations for

$$kT/\varepsilon_0 < 0.4. \quad (4.2)$$

It is hardly possible to give any strict criterion in the general case. The successive terms involve higher powers of T , and higher derivatives of ν with respect to ε . A rough criterion corresponding to that for free electrons is

$$kT \frac{1}{\nu} \frac{\partial \nu}{\partial \varepsilon} \ll 1,$$

or

$$kT \ll \nu \frac{\partial \varepsilon}{\partial \nu}. \quad (4.3)$$

By analogy with the results for free electrons, it may be assumed that the two terms series give a fair approximation as long as the second term is numerically appreciably less than half the first term.

Relation between Specific Heat and Paramagnetism

In the low temperature limit the relation between the specific heat and the spin paramagnetism is readily obtained* from (2.19) and (3.4). With the specific heat in ergs per degree per gram

$$\begin{aligned} C_V/\chi &= (8c_2 k^2 T)/(2\mu^2) \\ &= \frac{\pi^2}{3} \left(\frac{k}{\mu}\right)^2 T. \end{aligned} \quad (4.4)$$

Let $(C_V)_A$ be the gram atomic specific heat, χ_A the gram atomic susceptibility. From (2.23) and (3.6)

$$\frac{(C_V)_A}{\chi_A RT} = \frac{5.671 \times 10^{-4}}{6.421 \times 10^{-5}} = 8.833. \quad (4.5)$$

* Cf. Mott, 'Proc. Phys. Soc.,' vol. 47, p. 571 (1935).

As an indication of orders of magnitude, this gives for $T = 300^\circ \text{K}$

$$(C_V)_A = 2.65 \times 10^3 R\chi_A = 0.00526 (\chi_A \times 10^6). \quad (4.6)$$

The relation (4.4) holds only in the low temperature range. From the previous results, it may be shown that for free electrons, in the high temperature limit

$$\left. \begin{aligned} C_V/\chi &= \frac{3}{2} \left(\frac{k}{\mu} \right)^2 T \\ \frac{(C_V)_A}{\chi_A RT} &= 4.03 \end{aligned} \right\}. \quad (4.7)$$

For paramagnetic susceptibilities of the order found for the transition metals (χ_A of the order 10^{-4}) these relations would indicate large electronic contributions to the specific heat at ordinary temperatures, the values being, in fact, too high to be compatible, in general, with the experimental results. So far, however, the effect of interchange interaction has been neglected. A positive interaction will result in an increase in susceptibility without a corresponding increase in the specific heat. The modification in the formulae resulting from the inclusion of interaction effects will therefore be considered.

5—INTERACTION EFFECTS

The following treatment gives a simple method of determining the general character of the modification introduced into the expressions for the susceptibility when account is taken of interaction effects. The equation for the energy per unit volume, E , neglecting interaction effects, may be written

$$E = E_1 = IH, \quad (5.1)$$

The magnetic moment may be determined from the condition that E is a minimum for constant H .

$$\frac{\partial E}{\partial I} = 0 \quad \frac{\partial E_1}{\partial I} = H. \quad (5.2)$$

The value of I is given by

$$I = \kappa_0 H,$$

where κ_0 is the susceptibility calculated with neglect of interchange interaction, as in § 3.

Let E_2 be the interaction energy

$$E = E_1 + E_2 - IH. \quad (5.3)$$

The moment will now be determined from

$$\frac{\partial E_1}{\partial I} = H - \frac{\partial E_2}{\partial I}, \quad (5.4)$$

and the value of I will be given by

$$I = \kappa_0 \left\{ H - \frac{\partial E_2}{\partial I} \right\}. \quad (5.5)$$

The appropriate forms for the terms in the expressions for the energy resulting from the interchange interaction effects are not discussed. The interchange term can in general be expanded as a series with even powers of the magnetization (I per unit volume). Considering only the first terms in this series, let

$$E_2 = (E_2)_0 - \frac{1}{2}\alpha I^2, \quad (5.6)$$

where $(E_2)_0$ is independent of I . In the Heisenberg treatment, based on the Heitler-London approximation, α is proportional (to a first approximation) to the interchange interaction integral, J_0 , for electrons in neighbouring atoms; that is, α is positive if J_0 is positive. With the treatment starting from that for free electrons (that is, using free electron wave functions) Bloch* has shown, effectively, that α is positive; though calculations by Wigner† indicate that the Bloch value is an overestimate. The quantitative treatment of interchange interaction effects‡ from the collective electron standpoint in more general cases would be a matter of great complexity, and no attempt is made here to obtain theoretical estimates of the values of α . It is simply the dependence of the magnetic effects on the magnitude of α which is considered.

From (5.6)

$$\partial E_2 / \partial I = -\alpha I. \quad (5.7)$$

Substituting in (5.5)

$$\left. \begin{aligned} I &= \kappa_0 (H + \alpha I) \\ \kappa &= I/H = \kappa_0 / (1 - \alpha \kappa_0) \\ \frac{1}{\kappa} &= \frac{1}{\kappa_0} - \alpha \end{aligned} \right\}. \quad (5.8)$$

The α in the above equations is formally equivalent to the Weiss molecular field coefficient N . Similar expressions are obtained for the mass

* 'Z. Physik,' vol. 57, p. 545 (1929).

† 'Phys. Rev.,' vol. 46, p. 1002 (1934).

‡ For a fuller discussion, see Sommerfeld and Bethe, 'Handbuch der Physik,' vol. 24, ii, pp. 483-6, 585-613 (1933).

and gram atomic susceptibilities (χ and χ_A), α being replaced by $\alpha\rho$ and $\alpha\rho/A$ respectively.

Thus

$$\frac{1}{\chi_A} = \frac{1}{(\chi_A)_0} - \alpha \left(\frac{\rho}{A} \right) = \frac{1}{(\chi_A)_0} - \alpha_A. \quad (5.9)$$

As long as the interaction effect is independent of temperature, and can be sufficiently closely represented by (5.6), the very simple result is thus obtained that the value of $1/\kappa_0$ calculated with neglect of interaction is decreased (positive interaction) or increased (negative) by a constant amount. The Curie law, $\chi = C/T$, for example, is transformed into the Weiss law, $\chi = C/(T - \alpha\rho C)$; while the temperature independent collective electron susceptibility obtained above (for low temperatures) is simply increased or decreased by an amount which can at once be calculated if the interchange interaction term, E_2 , is known.

Conditions for Ferromagnetism

If classical statistics were applicable, positive interaction would give rise to ferromagnetism provided that the temperature were below a certain critical value. With Fermi-Dirac statistics, however, positive interaction does not necessarily result in ferromagnetism even at the lowest temperatures. The essential points are most clearly brought out by consideration of the special case in which the temperature variation of susceptibility, in the absence of interaction, can be determined over the whole temperature range; that is, for collective electrons in which the number of states per unit energy range in the band varies as the square root of the energy. For simplicity it will be supposed that there is 1 quasi-free electron per atom. The gram atomic susceptibility due to the collective electrons calculated neglecting the interaction will be denoted by $(\chi_A)_0$.

In the low temperature limit, by (3.5)

$$(\chi_A)_0 = \frac{3}{2} N \mu^2 / \varepsilon_0, \quad (5.10)$$

where N is Avogadro's number.

In the high temperature limit

$$(\chi_A)_0 = N \mu^2 / kT. \quad (5.11)$$

With α_A defined as above, at high temperatures, using (5.9) and (5.11)

$$\begin{aligned} \chi_A &= (N \mu^2 / kT) / \left(1 - \alpha_A \frac{N \mu^2}{kT} \right) \\ &= \frac{N \mu^2 / k}{T - \theta'}, \end{aligned} \quad (5.12)$$

with

$$\theta' = \alpha_A N \mu^2 / k.$$

Ferromagnetism would occur for $T < \theta'$, the usual condition, if the relation (5.11) were valid over this range. This criterion corresponds to

$$\alpha_A > kT / N \mu^2. \quad (5.13)$$

The value of $(\chi_A)_0$, however, falls below that given by (5.11) as the temperature is decreased in the manner previously discussed. The general condition for ferromagnetism is

$$\alpha_A (\chi_A)_0 > 1,$$

or

$$\alpha_A > 1 / (\chi_A)_0. \quad (5.14)$$

The maximum value of $(\chi_A)_0$ occurs for $T \rightarrow 0$, when the value is given by (5.10). For ferromagnetism to occur at any temperature, a necessary condition therefore is

$$\alpha_A > \frac{2}{3} \frac{\varepsilon_0}{N \mu^2}. \quad (5.15)$$

With the first approximation derived from Heisenberg's treatment, α_A would be equal to $\frac{1}{2} z J_0 / N \mu^2$, where z is the number of nearest neighbours of each atom, and J_0 the interchange interaction integral for neighbouring atoms. The conditions (5.13) and (5.15) would then correspond to $\frac{1}{2} z J_0 > kT$ and $\frac{1}{2} z J_0 > \frac{2}{3} \varepsilon_0$. This will make clear the kind of relation expressed by the equations, though the appropriate interchange integrals with the Heisenberg treatment will differ from those with the collective electron treatment.

The close relation between (5.13) and (5.15) is at once apparent, for (kT) is two-thirds of the mean thermal energy at the high temperatures, while ε_0 is the average energy of the electrons which contribute to the paramagnetism at the low temperatures. If the condition (5.15) is satisfied, ferromagnetism will occur for $T < \theta$, where $0 < \theta < \theta'$.

The nature of the $(1/\chi_A)$, T relations indicated by these considerations is shown in fig. 1,* which is drawn for $\theta' = 2000^\circ \text{K}$, $q = 1$, $V_0 = 0.2$.

The above treatment is probably too oversimplified to apply immediately to actual metals; but if the general treatment is correct, a qualitative interpretation is provided of the curvature of the $1/\chi$, T graphs for ferromagnetics above the Curie point (sometimes considered as the problem of the two Curie points). It should be noted that the Curie point θ may differ widely from θ' , so that $k\theta$ does not give an immediate indication

* Cf. Stoner, 'Proc. Roy. Soc.,' A, vol. 152, p. 672, fig. 1 (1935).

of the magnitude of the quasi-magnetic interchange interaction; θ depends both on this and on the energy distribution of states in the unfilled electron band. The value of θ' , moreover, will not in general be obtainable with certainty by extrapolation from the results for practically attainable high temperatures; for the $1/\chi$, T curve may become almost linear well before the range of validity of the classical formula. It may finally be noted that the interaction (proportional to θ') may be large (comparable with that in ferromagnetics) without ferromagnetism occurring.

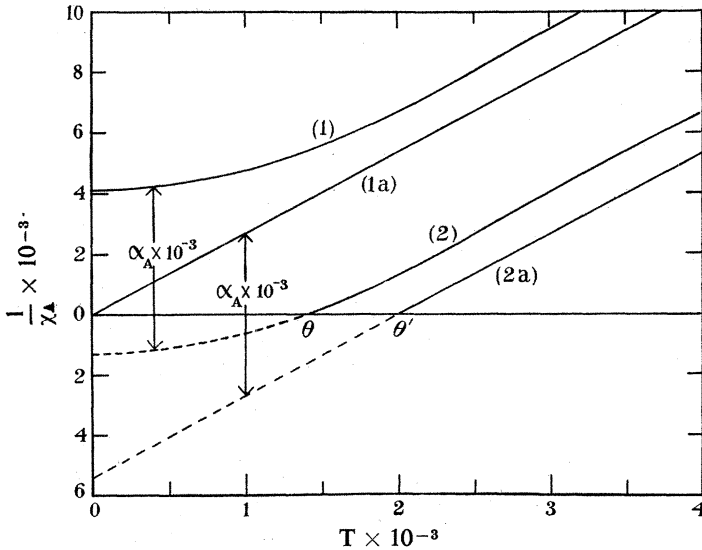


FIG. 1—Relation between $1/\chi_A$ and T . (1) Neglecting interaction; (2) with positive interaction. The curves are drawn for $V_0 = 0.2$ volts, $q = 1$, $\theta' = 2000^\circ \text{ K}$. The straight lines (1a) and (2a) correspond to the expressions appropriate at the high temperature limit.

Modified Relation between Specific Heat and Paramagnetism

If the interaction term in the energy expression is independent of temperature, as it usually will be to a first approximation, the expression for the specific heat will be unaltered. (The specific heat is that at constant magnetization—in the ordinary specific heat of paramagnetics; for ferromagnetics the specific heat at constant field will include another term associated with the change in the intrinsic magnetization). Using (4.4) and (5.8) the relation between C_V and χ therefore becomes

$$\begin{aligned} C_V/\chi &= \frac{\pi^2}{3} \left(\frac{k}{\mu} \right)^2 T (1 - \alpha' \chi_0) \\ &= \frac{\pi^2}{3} \left(\frac{k}{\mu} \right)^2 T \times \frac{1}{1 + \alpha' \chi}, \end{aligned} \quad (5.16)$$

where α' is the appropriate coefficient for the mass considered. For the gram atomic specific heat and susceptibility, using (4.5)

$$\frac{(C_v)_A}{\chi_A RT} = \frac{8.833}{1 + \alpha_A \chi_A},$$

or

$$\frac{(C_v)_A}{\chi_A RT} = 8.833 - \frac{(C_v)_A \alpha_A}{RT}. \quad (5.17)$$

These relations hold only in the range of applicability of the limiting low temperature expressions for C_v and χ . They will ordinarily give an upper limit for the ratio.

Effect of Spin Coupling in Atoms

In the treatment so far given it has been tacitly assumed that, except for electrons which form inner closed groups in the free atoms, the interchange interaction between electrons associated with different atoms (when these are separated) is of the same order of magnitude (in the metallic aggregate of atoms) as the interaction between electrons in the same atom. Some such assumption is essential for the collective electron treatment to remain manageable, and in some cases there is experimental evidence that it is appropriate as a first approximation. The assumption, however, is probably never strictly justified; and it is therefore of interest to consider a simple limiting case in which the interchange interaction between the electrons in one atom is much greater than that between electrons in different atoms. Such an interaction may be said to couple the spins in the atom. Suppose that there are $2j$ electrons in an incomplete group in the atom coupled together to give a resultant spin moment j . There are $2j + 1$ orientational states, corresponding to the "resolved" values $j, j - 1, j - 2 \dots -j$. It may then easily be shown that the first term in the expression for the specific heat corresponding to (2.20), becomes

$$C_v = 4c_2 (2j + 1) k (kT) \nu(\epsilon_0), \quad (5.18)$$

where $\nu(\epsilon_0)$ is the number of states per unit energy range for one particular resolved value of j . (In the case previously considered, $j = \frac{1}{2}$.) The first term in the expression for the susceptibility, corresponding to (3.4), becomes

$$\chi = \frac{4}{3} j(j + 1) (2j + 1) \mu^2 \nu(\epsilon_0). \quad (5.19)$$

The total number of states per unit energy range at ϵ_0 will be $(2j + 1) \nu(\epsilon_0)$ for quasi-independent electrons, $2\nu(\epsilon_0)$. Thus for the same total number

in the two cases, the specific heat is unchanged, the susceptibility increased in the ratio $\frac{4}{3}j(j+1)$; and the ratio of the susceptibility to the electronic specific heat, as given by (4.4), is increased by this factor;

$$\chi/C_v = \frac{4}{3}j(j+1) \times \frac{3}{\pi^2} \left(\frac{\mu}{k}\right)^2 \frac{1}{T}. \quad (5.20)$$

The following are the values of the ratio for values of j which may occur:—

j	1/2	1	3/2	2	5/2	3	7/2
$\frac{4}{3}j(j+1)$	1	8/3	5	8	35/3	16	21

This interchange interaction is a specialized type of that considered above, leading to (5.16); both, when positive, result in a decreased ratio of specific heat to susceptibility.

In the high temperature limit the susceptibility of N atoms, each containing $2j$ quasi-independent spins, is

$$\chi = \frac{N\mu^2}{kT} \times 2j. \quad (5.21)$$

For $2j$ coupled spins, giving a resultant spin moment j per atom

$$\chi = \frac{N\mu^2}{kT} \times \frac{4j(j+1)}{3}. \quad (5.22)$$

The points discussed above link up with these well-known results.

It may be noted that a particular example, of a different kind, of systems with strongly coupled spins, is provided by the “domains” in ferromagnetics.

6—DEPENDENCE OF TEMPERATURE VARIATION ON BAND FORM

The spin susceptibility will increase or decrease with temperature in the low temperature range as the sign of the quantity in curly brackets in (3.4) is positive or negative. Denoting this quantity by γ

$$\gamma(\epsilon_0) = \left\{ \frac{1}{v} \frac{\partial^2 v}{\partial \epsilon^2} - \left(\frac{1}{v} \frac{\partial v}{\partial \epsilon} \right)^2 \right\}_{\epsilon_0}. \quad (6.1)$$

In the standard case of free electrons, or of electrons in bands such that $v(\epsilon) \propto \epsilon^{1/2}$ over the relevant range, γ is negative; and it is easily seen that γ will be negative in the more general case in which

$$v(\epsilon) = A\epsilon^n, \quad (6.2)$$

where A and n are positive.

For bands which are nearly full, it is convenient to consider the number of "holes" in the band, and to measure the energy from the top of the band. Let the energy difference from the top of the band, of width a , be denoted by ϵ' . The distribution of states near the top of the band may be represented by

$$\nu(\epsilon) = f(a - \epsilon) = f(\epsilon'). \quad (6.3)$$

The susceptibility arising from a deficit of x electrons in such a band will be the same as that due to the presence of the same number x of electrons in a band in which the distribution is given by

$$\nu(\epsilon) = f(\epsilon). \quad (6.4)$$

For, under these conditions ϵ'_0 in (6.3) will be equal to ϵ_0 in (6.4); the first term in the expression (3.8) for the susceptibility, will be the same in the two cases, and also the term giving the dependence on temperature, as is readily seen by carrying out the differentiations in (6.1). Thus the susceptibility arising from a symmetrical band which can accommodate N electrons will be the same when it contains x and $N - x$ electrons. In general bands will not be completely symmetrical (as is apparent from a consideration* of the simplest cubic type of Brillouin zone, the form of which is roughly represented in fig. 2); the susceptibility (and also specific heat) relations will, however, be the same for a band containing $N - x$ electrons, and in "inverted" band containing x electrons. Otherwise stated, relations involving the number of electrons in a band, with the energy measured from the bottom of the band, may be alternatively expressed in terms of the number of holes in the band, with energies measured from the top of the band. In some cases this principle may greatly simplify discussions of magnetic properties in relation to band structure.

The conditions necessary for a positive temperature coefficient will now be considered. The second term in (6.1) is negative (or zero), and a positive temperature coefficient therefore requires that the first term should be positive. Near the bottom of a band, the form (6.2) will be appropriate, and this leads to a negative value for γ . This also holds near the top of a band (replacing ϵ by ϵ'). In the region where $\nu(\epsilon)$ is a maximum, the second term in (6.1) is zero, but the first term is necessarily negative. It may therefore be said that, in general, unless the distribution of states in a band has a very unusual character the temperature coefficient of the susceptibility due to electrons in an isolated band will be negative. When there is an overlapping of bands, however, as

* Stoner, 'Proc. Leeds Phil. Soc.,' vol. 3, p. 120 (1936).

in fig. 2, there may be a minimum in $\nu(\epsilon)$ as a function of ϵ . In the neighbourhood of the minimum, the distribution may be represented by

$$\nu(\epsilon) = A + B(\epsilon - b)^2, \quad (6.5)$$

where A is the value of $\nu(\epsilon)$ for $\epsilon = b$. Substituting (6.5) in (6.1), the condition for γ positive is

$$(\epsilon - b)^2 < A/B. \quad (6.6)$$

If the top of the Fermi distribution falls near b , the temperature coefficient will therefore be positive. The range of values of ϵ_0 for which a positive temperature coefficient will occur will be greater the greater the ratio A/B ; the maximum value of the coefficient, however, is proportional to B/A . (The coefficient here considered is $(1/\chi)(\partial\chi/\partial T)$. The maximum

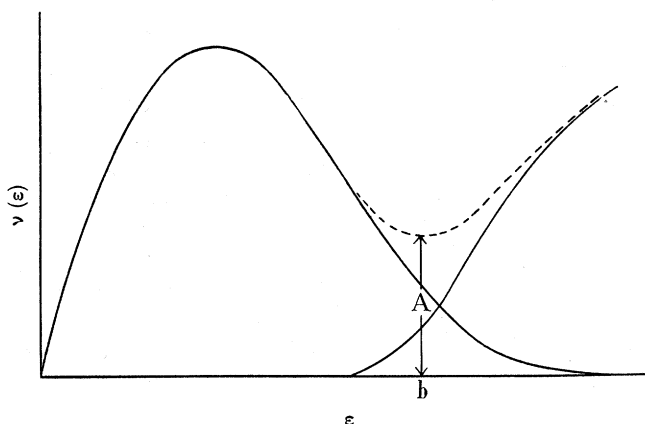


FIG. 2—Overlapping bands. For ϵ_0 in the neighbourhood of b , the temperature coefficient of the spin susceptibility will be negative.

value of $\partial\chi/\partial T$ will be proportional to B .) The possibility of a positive temperature coefficient may be said to arise from the possibility of transfer of electrons between the two bands, so that the number of holes in the lower band and the number of electrons in the upper band are both increased. This effect may more than compensate the normal temperature decrease of susceptibility for the two bands considered separately.

7—APPLICATIONS

The present treatment is not sufficient to enable a theoretical calculation to be made of the susceptibilities of particular metals; it does, however, provide a basis for a general discussion of the observed magnetic properties of at least the more strongly paramagnetic metals. A few illustrative

points will serve to amplify the discussion of the metals given in "Magnetism and Matter".*

Non-transition Metals—For the metal of Group I (alkali metals, Cu, Ag, Au) allowance for the diamagnetism of the closed electron groups shows that the collective electron contribution to the susceptibility is always paramagnetic. It varies very little with temperature, but it is from 1.5 to 3 times as great as that calculated for free electrons. In view of the similarity of the energy, momentum relations which have been calculated for the *ns* electrons in Li, Na, and Cu to those for free electrons, the discrepancy is probably to be attributed to positive interchange interaction effects. The Bloch interaction term over-estimates the effect, but, as has been mentioned, Wigner has shown that the Bloch term is too large.

The elements of group II are of particular interest, since here the metallic character shows conclusively that there is an overlapping of what are usually loosely described as the *s* and *p* bands. The magnitude of the spin susceptibility is proportional to $\nu(\epsilon_0)$ and this will be greater the greater the degree of overlap. (If there were no overlap, the *s* band would be full, giving a zero susceptibility.) Zn, Cd, and Hg are diamagnetic, but allowance for the closed group diamagnetism shows that the collective electron contribution is paramagnetic, though rather less than the value for free electrons except for mercury. This is precisely what would be expected for a moderate overlap of the electron bands. As an example the value calculated from (3.6) for Cd is $\nu(V_0) = 0.13$. For the *a* sub-group elements, some of the experimental values for the susceptibility are doubtful owing to the presence of iron; but Mg, Ca, and Ba are certainly much more strongly paramagnetic than elements of the *b* sub-group. For Ba, Lane's value at room temperature is $\chi_A = 20 \times 10^{-6}$; this corresponds to a $\nu(V_0)$ value of not less than 0.3. A much greater overlapping of the bands is indicated. This may be linked up with the fact that the separations between the 1S_0 and the next higher state for the free atoms are 1.9, 1.8, and 1.6 volts for Ca, Sr, and Ba, while for Zn, Cd, and Hg they are 4.0, 3.8, and 4.9 volts. Now it has been shown (see equation (6.6)) that when the top of the Fermi distribution falls in a region of band overlap, the spin susceptibility may increase with increasing temperature. This appears to provide an interpretation of the remarkable increase found by Lane† for Ba from $\chi_A = 20$ (10^{-6} units) at 20° C to 57 at 400° C. This effect may also

* Stoner, "Magnetism and Matter," chap. XIV (Methuen, 1934).

† 'Phys. Rev.,' vol. 44, p. 43 (1933).

account for the numerical increase in the diamagnetic susceptibility of Zn and Cd with decreasing temperature found by de Haas and van Alphen. (For Cd, $\chi = -0.183$ at 289°K , -0.326 at 14.2°K .)

Most of the remaining non-transition elements cannot be usefully discussed without a more detailed consideration of the collective electron diamagnetic effect. The extreme example is provided by bismuth, but consideration of the magnitudes of the susceptibilities and of the changes at the melting point suggest that there are similar effects for Ga, In, Tl, Sn (grey), Pb, and Sb, these effects being associated according to the treatment of Jones,* with the occurrence of nearly full zones.

The highest of the more reliable values of the gram atomic susceptibilities of the non-transition elements at room temperature is $\chi_A = 20 \times 10^{-6}$ for Ba. Using (4.6), this gives a value of 0.1 for $(C_V)_A$. It is clear that very precise estimates of the various contributions to the specific heats of these metals would be necessary to enable definite conclusions to be drawn as to the electronic contributions.

TABLE I—GRAM ATOMIC SUSCEPTIBILITIES OF TRANSITION METALS
AT ROOM TEMPERATURE

Unit for $\chi_A = 10^{-6}$. $\Delta\chi_A$ = change of χ_A for increase of
temperature of 100°

	χ_A	$\Delta\chi_A$		χ_A	$\Delta\chi_A$		χ_A	$\Delta\chi_A$
Ti	57	~ 0	Zr ..	91	~ 0	Hf ..		
V	76	~ 0	Nb ..	120	~ 0	Ta ..	145	-3
Cr ..	150	~ 0	Mo ..	91	—	W....	52	~ 0
Mn ..	648	-42	Ma ..			Re ..		
Fe ..			Ru ..	44	+1	Os ..	10	+1.6
Co ..			Rh ..	104	+4	Ir	25	+1.9
Ni			Pd ..	555	-100	Pt ..	190	-13.6

Transition Metals—The transition metals which have been investigated are all paramagnetic. Some of the more reliable results are summarized in Table I. The values given for the palladium and platinum triads are due to Guthrie and Bourland,† those for niobium, molybdenum, and tungsten to de Haas and van Alphen,‡ that for manganese (amorphous) to Bates and Pantulu,§ the remainder to Honda|| and Owen.¶

* 'Proc. Roy. Soc.,' A, vol. 147, p. 396 (1934).

† 'Phys. Rev.,' vol. 37, p. 303 (1931).

‡ 'Proc. Acad. Sci. Amst.,' vol. 36, p. 263 (1933).

§ 'Proc. Phys. Soc.,' vol. 47, p. 197 (1935).

|| 'Ann. Physik,' vol. 32, p. 1027 (1910).

¶ *Ibid.*, vol. 37, p. 657 (1912).

The indications of the change with temperature given in the table are necessarily rather rough. At higher temperatures Ti, V, and Cr all show a slight increase with temperature; while Ti shows an increase with decreasing temperature below -80°C .

The collective electron susceptibility will be somewhat greater than the values given for χ_A , since no allowance has been made for the diamagnetism of inner atomic closed groups. The correction would range from about 10 to 40 units, being greater for the series of higher atomic number. The susceptibilities are usually much higher than the values for free electrons. Using (3.6) (that is assuming there are no interaction effects) the values calculated from the observed χ_A for $\nu(V_0)$ for Ti, V, Cr, and Mn, for example, are 1.1, 1.5, 2.8, and 12; the values of $\nu(V_0)$ for free electrons, assuming 4, 5, 6, and 7 electrons per atom, respectively, are 0.22, 0.21, 0.20, and 0.21. The high values of the susceptibility will in part be due to the narrowing of the energy bands as compared with the bands for nearly free electrons; but there must be, in addition, at least for the more strongly paramagnetic elements, a positive interchange interaction effect. This is shown most clearly by a consideration of the specific heat. If there were no interchange interaction effects, the relations (4.5) and (4.6) would hold; indicating, for $\chi_A = 100$, an electronic contribution to the specific heat of 0.526 (calories per degree per gram atom) even at room temperature. Contributions of this order are quite incompatible with the specific heat results. It follows that for most of these metals the values calculated for $\nu(V_0)$ by (3.10) are too high and that there are strong positive interchange interaction effects; but it is not generally possible to determine, without more extensive data, whether this is primarily of the coupling type between electrons in the same atom, or to more general interchange effects.

The effective electrons in these metals are those in bands associated with the *s* and *d* states in the free atoms. There will in all cases be a considerable overlapping of the bands. Since the temperature coefficient of the susceptibility may be positive when the top of the Fermi distribution falls near a minimum in the $\nu(\epsilon)$, ϵ curve, it seems significant that the values of χ_A are usually smaller for those elements whose susceptibility increases with temperature.

The largest temperature changes are those for Mn, Pd, and Pt. The susceptibility variation of these elements has usually been represented by a Weiss expression, $\chi = C/(T - \theta)$. Although such an expression may cover the observations over certain ranges of temperature, the representation appears to be purely formal. Large negative values of θ are required (such as would be obtained by considering a portion of the

upper curve of fig. 1), and at least in the case of Pt, larger numerical values of θ are required the lower the range of temperature considered. As an example, for a specimen of Pt studied by Collet and Foëx,* values of θ given as appropriate in a field of 6990 gauss were -3420 (-180° C to -110°), -2180 (-110° to -30°) and -1130 (-30° to $+100^\circ$). The variation with temperature is of a type approaching that for the "standard" distribution of states, as shown in fig. 1; it is not precisely of this standard form (that is, the variation cannot be closely represented by $\chi = \chi_0 - cT^2$), but it would hardly be expected that the distribution with overlapping bands would be similar to that for quasi-free electrons. From the present point of view, the possibility of representing the observed susceptibility over any considerable temperature range by a Weiss law must be regarded as largely fortuitous; and the values of θ in such a representation give no indication of the magnitude or sign of the quasi-magnetic interchange interaction effects.

Rare Earth Metals—The Honda-Owen values for χ_A for the rare earths Ce, Pr, and Nd at room temperature are 2100, 3520, and 5200, the values of $\Delta\chi_A$ being about -210 , -860 , and -1120 . These elements behave more nearly as "normal" paramagnetics, the variation with temperature approaching that given by a Curie law. The magnetic moments per atom deduced by applying the usual relations are about 2, 3, and 4 Bohr magnetons—of the same order as for the ions in salts. The experimental results are hardly sufficiently precise for more definite conclusions to be drawn; but it is apparent that for these elements the state is approached in which the "high temperature" expressions are appropriate as approximations rather than the low. The results suggest a high density of states (presumably corresponding to the f electrons) at the top of the Fermi distribution, with a coupling of the spins of the atoms.

It has recently been found by Urbain, Weiss, and Trombe† that metallic gadolinium is ferromagnetic, with a Curie temperature at about 16° C, and a saturation moment estimated at 35.4 Weiss magnetons per atom (corresponding to 7.1 Bohr magnetons). According to Trombe's observations,‡ the $1/\chi$, T graph above the Curie temperature shows a definite curvature up to 90° C, but from 90° C to 360° C is practically linear. The linear portion gives a Weiss magneton value, p_W of 39.3 (corresponding to a Bohr magneton value, p_B of 7.94). It is of interest that this corresponds exactly with the value for seven coupled spins, as

* 'J. Phys. Rad.,' vol. 2, p. 290 (1931).

† 'C.R. Acad. Sci. Paris,' vol. 200, p. 2132 (1935).

‡ 'C.R. Acad. Sci. Paris,' vol. 201, p. 652 (1935).

in the gadolinium ion. This coupling is a possibility which has been discussed in § 5. In addition, to account for the ferromagnetism, there is the positive interchange interaction between electrons not in the same atom. Owing to the strong coupling between the f electrons in the atom, the atomic moment relations are much simpler than for Fe, Co, and Ni.

Specific Heat—For nickel, the electronic specific heat can be estimated with fair precision. The various terms contributing to the specific heat have been considered in detail by Lapp*; a consideration largely in the light of her discussion of the “normal terms” of her experimental results together with those of Grew,† Klinkhardt,‡ and Rodebush and Michalek,§ indicates that the “terme inconnu” which is here identified with the electronic specific heat, has the value

$$(C_V)_A = 0.18 (\pm 0.01) \times 10^{-2} \text{ T.} \quad (7.1)$$

This value is based mainly on the observations above the Curie point, supplemented by a consideration of its compatibility with the results below the Curie point. Recently Keesom and Clark|| have measured the specific heat at very low temperatures, and find that over the range $1.1\text{--}9^\circ \text{ K}$ the electronic specific heat can be represented by

$$(C_V)_A = 0.174 \times 10^{-2} \text{ T} \quad (7.2)$$

in close agreement with the value which had been deduced prior to their measurements.¶

Using (2.23), the above values give for nickel

$$\nu(V_0) \doteq 1.6. \quad (7.3)$$

This value is considerably larger than for free electrons, but the corresponding value for the susceptibility without interchange interaction at low temperatures, from (3.10), is only $\chi_A \doteq 102$. The susceptibility of nickel above the Curie point corresponds to a downward shift of a $1/\chi$, T curve approaching the standard type, as indicated in fig. 1. It must be pointed out, however, that the assumption that the distribution of states

* ‘Ann. Physique,’ vol. 12, p. 442 (1929).

† ‘Proc. Roy. Soc.,’ A, vol. 145, p. 509 (1934).

‡ ‘Ann. Physik,’ vol. 84, p. 167 (1927).

§ ‘J. Amer. Chem. Soc.,’ vol. 47, p. 2117 (1925).

|| ‘Physica,’ vol. 2, p. 513 (1935).

¶ The treatment here summarized was developed independently of that of Mott, ‘Proc. Roy. Soc.,’ A, vol. 152, p. 42 (1935). Similar conclusions are reached, but Mott has discussed certain aspects of the problem more fully.

is of the form $\nu(\epsilon) \propto \epsilon^{1/2}$ (corresponding to the use of (2.24) and (3.7)) is not adequate to give a good approximation to the experimental results; as indeed would be expected from the complex character of the band structure.

For platinum the results of Magnus* indicate a temperature proportional term in the specific heat given approximately by

$$(C_V)_A = 5.0 \times 10^{-4} T. \quad (7.4)$$

This has usually been attributed to the Born-Brody anharmonicity effect, but the magnitude of this is very problematical. Assuming that the whole of the temperature proportional effect may be attributed to the electronic specific heat, from (2.23)

$$\nu(V_0) \doteq 0.44. \quad (7.5)$$

This value corresponds to a value of $(\chi_A)_0$, without interaction, of about 28.2; this is much smaller than the value observed (Table I), and again gives an indication of positive interchange interaction effects.

It is only for comparatively few metals that estimates of C_V (as distinct from C_P) have been made with any precision; but there are indications that these values often exceed the theoretical value of 5.95. Such an excess may undoubtedly be attributed in part to an electronic specific heat. The electronic specific heat can, however, be determined much more accurately from measurements at very low temperatures. The interest of such determinations has been sufficiently indicated by the examples considered here and by the general discussion.

SUMMARY

Expressions are obtained, neglecting interchange interaction, for the spin paramagnetism and electronic specific heat, and their temperature variation, as dependent on the number of states per unit energy range, $\nu(\epsilon)$, at the top of the Fermi distribution in collective electron energy bands, and the variation of this number with energy, ϵ . The results apply for the "low" temperature range, and extend previous results for free electrons (or for electrons in bands such that $\nu(\epsilon)$ varies as $\epsilon^{1/2}$) for the whole temperature range. The expressions for the spin susceptibility and electronic specific heat, and for the relation between them, are given in a convenient form for application.

* 'Z. Physik,' vol. 7, p. 141 (1921).

A simple method of determining the general character of the effect of interchange interaction is developed. Positive interchange interaction is shown to reduce the value of $1/\chi$, calculated with neglect of interaction, by an amount which is approximately independent of temperature. The discussion leads to a general condition for ferromagnetism, which shows that positive interchange interaction does not necessarily result in ferromagnetism even at the lowest temperatures. The specific type of interchange interaction corresponding to coupling of spins in an atom is also considered. This results in an enhancement of the paramagnetism relatively to the specific heat.

For isolated bands the temperature coefficient of the spin susceptibility will generally be negative. For overlapping bands it may be positive when the top of the Fermi distribution falls near a minimum of the $\nu(\epsilon)$, ϵ curve.

The magnetic properties of the elements of the first two columns of the periodic table, and of the transition elements and rare earths are briefly considered in the light of the theoretical treatment, and also the specific heat of nickel and platinum.
