

Magnetism of iron. II

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A previously developed theory of the magnetism of iron, based upon the notion of a randomized exchange field, is modified and extended. It is shown that Coulomb fields arise in association with the randomized exchange field; the modification allows one to take into account these fields, which are found to change the details of the previous results without affecting the main conclusions. The theory has been extended to calculate the properties of the model at finite temperatures: the Curie temperature (1840 K), the magnetization curve, the paramagnetic susceptibility (a Curie-Weiss law), and the effective interatomic exchange coupling are calculated for iron. The magnitudes of the atomic spin moments were found to vary little up to 1.5 times the Curie temperature.

I. INTRODUCTION

In a previous paper<sup>1</sup> (which will be referred to as I) we discussed a type of theory<sup>2-9</sup> which unifies the localized and itinerant models of ferromagnetic metals. In particular, we reported results which indicate that such a theory could explain simultaneously both the moment and Curie temperature  $T_C$  of iron. It is the purpose of this paper to describe calculations which give a more complete account of the predictions of the model for iron. In addition, we discuss a modification of the theory to take into account an important physical effect omitted in the work of I.

The physical effect alluded to is the appearance of Coulomb fields in association with the randomized exchange field. The action of the randomized exchange field on the electrons may cause substantial departures from electrical neutrality; these departures then give rise to Coulomb fields tending to restore neutrality. For example, in I we calculated the energy difference between the exchange-field configurations  $V_0$  and  $V_1$  shown schematically in Figs. 1(a) and 1(b);  $V_0$  is the ground-state configuration, but in  $V_1$  the exchange field at one atom (labeled 0) has been changed. Investigation showed that a considerable charge shift might occur in  $V_1$  (relative to  $V_0$ ); when the exchange field at atom 0 is reversed the number of electrons at that site is decreased by about 1.5. Clearly, there must exist in  $V_1$  a strong Coulomb field tending to restore neutrality. In Sec. II and Appendix A we discuss how the theory may be modified to allow for these effects. This modification changes significantly the results of I; these changes provided a strong stimulus to investigate the predictions of the model at elevated temperatures. The finite-temperature calculations (which incorporate the Coulomb-field effects) showed, however, that the general conclusions of I were unchanged.

In I we calculated the energy increase  $\Delta E(\Delta\bar{v})$  on passing from the ground-state configuration  $V_0$  to the configuration  $V_1$  in which the field at atom 0 is changed by  $\Delta\bar{v}$  from its ground-state value. It turns out (see Sec. III) that at finite temperatures, one can define a related quantity  $E(\bar{v})$  which measures the average energy of an atom with exchange field  $\bar{v}$ . The probability of finding an atom with exchange field  $\bar{v}$  is just

$$f(\bar{v}) = N \exp[-\beta E(\bar{v})] \quad (1)$$

where  $N$  is a normalization constant and  $\beta = 1/k_B T$ ,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature. In Appendix B we outline the approximation leading to the definition of  $E(\bar{v})$  and Eq. (1) and show, using the Feynman variation principle,<sup>10</sup> that it is the "best" of a certain class of mean-field-type approximations.

The calculation of  $E(\bar{v})$  involves the estimation of

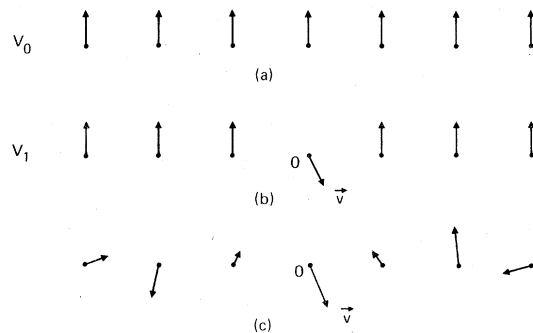


FIG. 1. Some exchange-field configurations (see text).

electronic energies in a random field, for which purpose we employed the coherent-potential approximation (CPA)<sup>11-14</sup>; in Appendix C some details of this application of the CPA are outlined. These calculations may be regarded either as a generalization of the theory of I to finite temperatures, or, alternatively, as a generalization of Hasegawa's calculation<sup>15</sup> to a case with spin-rotational invariance.

The remainder of the paper is devoted to a discussion of the finite-temperature results for iron. The calculations were again based upon Tawil and Callaway's band structure<sup>16</sup> and have no adjustable parameters. It was found that at all temperatures studied (0–3000 K), the energy  $E(\bar{v})$  was well fitted by the formula

$$E(\bar{v}) = E_0(v) + Av_z \quad (2)$$

over the important range of  $\bar{v}$  ( $v < 1.5$  eV), where  $E_0(v)$  is a function of the magnitude  $v = |\bar{v}|$  alone and  $A$  is independent of  $\bar{v}$  (the magnetization is assumed to be in the  $z$  direction).  $E_0$  and  $A$  are both temperature dependent; above 1840 K, which we identify with  $T_C$ , one finds  $A = 0$ . The result given by Eq. (2) is consistent with a cluster expansion of the type suggested by Cyrot,<sup>5</sup> so the failure to obtain it in I must be an artefact due to the omission of Coulomb-field effects.

In Sec. IV the ferromagnetic regime and, in particular, the magnetization curve are discussed. The latter follows closely an  $S = \infty$  Brillouin function, the mean-field result for classical spins; it is in poor agreement with experiment, which is much closer to an  $S = \frac{1}{2}$  Brillouin function. This failure may in part be attributed to the use of a particular approximation which tends to lead to a classical spin description of localized behavior (see Sec. VI). It is possible to deduce an effective interatomic exchange coupling  $J_{\text{ex}}(T)$ , which was found to increase significantly with temperature.

In Sec. V the paramagnetic regime is discussed. The susceptibility was found to obey a Curie-Weiss law throughout the temperature range studied,  $T = T_C - 1.6T_C$ ; the effective moment was somewhat larger than the ground-state moment. We also calculated at a number of temperatures the function giving the distribution of the magnitudes of the atomic spins; while this distribution broadens with increasing temperature, it is still not very broad at  $1.6T_C$ , and the mean value of the spin magnitude changes little with temperature, indicating that the atomic spins tend to rotate rather than alter their lengths. The increase in  $J_{\text{ex}}(T)$  with  $T$  was found to continue into the paramagnetic regime.

Finally, in Sec. VI we discuss these results, draw some tentative conclusions and point out some of the problems to which they lead.

## II. COULOMB-FIELD EFFECTS

In I each exchange-field configuration  $V = \{\bar{v}_1, \bar{v}_2, \dots\}$  was prescribed by giving the exchange field  $\bar{v}_i$  at each site  $i$ ; we now adjoin to this prescription a set of Coulomb potentials  $W = \{w_1, w_2, \dots\}$ , where  $w_i$  is the Coulomb potential at site  $i$ . In the ground-state configuration all the  $w_i$  have the same value, which we may make zero by a suitable choice of origin; the  $w_i$  then represent the deviations of the Coulomb potentials from their ground-state values. How are the fields  $W$  to be related to the configuration  $V$ ? We shall, in fact, choose the  $w_i$  in such a way that the fields  $V$  and  $W$  together just maintain charge neutrality, i.e., the correct number  $n_d$  of  $d$  electrons at each site. This prescription determines the fields  $W$  once the configuration  $V$  is given. It is an approximation which corresponds physically to assuming that the Coulomb-field effects are sufficiently strong to force charge neutrality. This is an overestimate of their effectiveness, but represents, we believe, a much better approximation than the omission of Coulomb effects altogether (as in I). A more complete discussion of the incorporation of Coulomb effects into the functional integral formalism and of the above approximation is given in Appendix A.

When the Coulomb fields are introduced in the manner described, one must modify the expression for the energy of a configuration,  $E(\bar{v}_1, \bar{v}_2, \dots)$ , used in I; it is replaced by (see Appendix A)

$$E(\bar{v}_1, \bar{v}_2, \dots) = \frac{1}{K} \sum_i \bar{v}_i^2 - n_d \sum_i w_i + F(V, W) \quad (3)$$

(we have changed the notation from I,  $K$  now being written for the parameter denoted there by  $J$ );  $F(V, W)$  is now the thermodynamic potential of electrons moving in the combined fields  $V$  and  $W$ , and the additional term  $-n_d \sum_i w_i$  has appeared. It is understood that the Coulomb potentials  $w_i$  have been chosen to ensure the charge neutrality condition

$$\langle n_i \rangle = n_d \quad (4)$$

where  $n_i$  is the electron number operator for the atom at site  $i$ , given by Eq. (5).

We have repeated the  $\Delta E(\Delta\bar{v})$  calculations of I taking into account the Coulomb-field effects according to the above prescription, i.e., have recalculated the difference in energy of the configuration  $V_1$  and  $V_0$  of Figs. 1(a) and 1(b) as a function of the charge  $\Delta\bar{v}$  in the exchange field at site 0. The model used was the tight-binding model described in Secs. III and IV of Paper I (with the same approximations), to which we refer the reader for details and notation. The one additional quantity required is the electron number operator

$$n_i = \sum_{\sigma} \sum_s c_{is\sigma}^{\dagger} c_{is\sigma} \quad (5)$$

for site  $i$ . The only changes from the calculation of I are that one must now use Eq. (3) for the energy, and the "impurity" potential at site 0 now has the form  $w_0 n_0 + 2\Delta\bar{v} \cdot \bar{S}_0$ , where  $\bar{S}_0$  is the total spin operator at site 0;  $w_0 = w_0(\Delta\bar{v})$  is to be chosen so that  $\langle n_0 \rangle = n_d$  (the  $w_i$  at sites other than  $i=0$  are small and have been neglected).  $\langle n_0 \rangle$  is given in the notation of I by

$$\langle n_0 \rangle = -\frac{1}{\pi} \sum_s \text{Tr} \delta_s(\mu), \quad (6)$$

where  $\mu$  is the Fermi energy. Use of Eq. (3) gives for the energy difference

$$\Delta E(\Delta\bar{v}) = (1/K)[(\bar{u} + \Delta\bar{v})^2 - \bar{u}^2] - n_d w_0(\Delta\bar{v}) + \Delta F(\Delta\bar{v}). \quad (7)$$

The  $\Delta E(\Delta\bar{v})$  calculated with Coulomb corrections is shown for the special case  $\Delta\bar{v} = (0, 0, \Delta v)$  (magnetization in the  $z$ -direction) in Fig. 2. The numerical accuracy of these calculations (which involve differences of large quantities) is much better (error  $\sim 0.003$  eV) than those reported in I. Slightly different parameters from those of I were used, namely,  $K = 0.904$  eV and  $u = 1$  eV (compared to 0.85 and 0.95 eV); they correspond to a moment of 2.21 and  $n_d = 7.32$ .

Comparison of the  $\Delta E$  curve in Fig. 2 with that of Fig. 2 of I (the corresponding calculation without Coulomb corrections) shows that the second minimum, by which we set so much store in I, disappears when the Coulomb effects are included. This evidently calls into question the conclusions of I concerning the magnitude of  $T_C$ , and prompted the investigation of the predictions of the theory at higher temperatures described in the remainder of this paper.

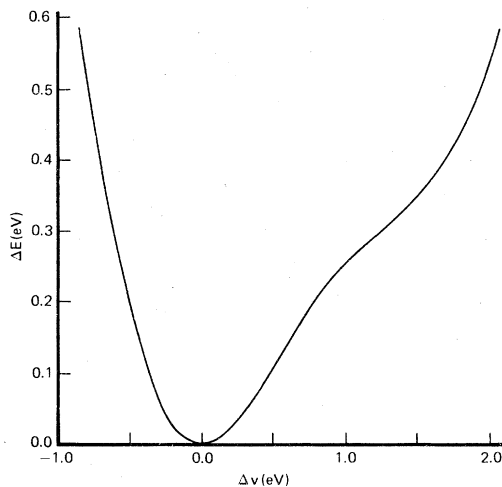


FIG. 2. Excitation energy  $\Delta E(\Delta\bar{v})$  with  $\Delta\bar{v} = (0, 0, \Delta v)$ , as a function of  $\Delta v$ , calculated with Coulomb-field corrections (see Sec. II).

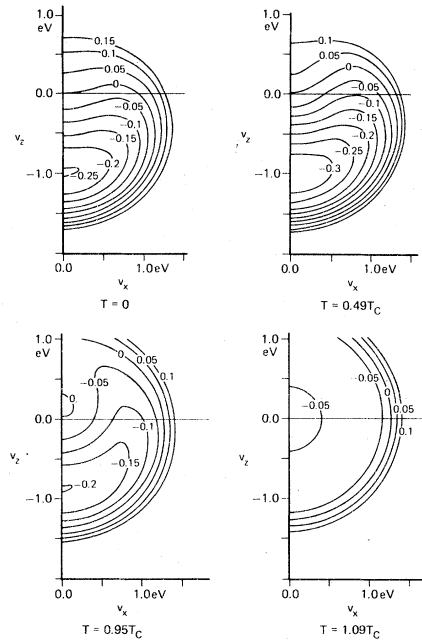


FIG. 3. Contours (labeled in eV) of  $E(\bar{v})$  for  $\bar{v}$  in the  $(v_x, v_z)$  plane at various temperatures  $T$ .

In Fig. 3(a) we show the contours of the function  $E(\bar{v})$  in the  $(v_x, v_z)$  plane at  $T=0$  [ $E(\bar{v})$  is invariant against rotations of  $\bar{v}$  about the magnetization direction]; this  $E(\bar{v})$  is related to  $\Delta E(\Delta\bar{v})$  by  $\Delta E(\Delta\bar{v}) = E(\bar{u} + \Delta\bar{v}) - E(\bar{u})$ . The ring-shaped valley of Fig. 3 of I has disappeared, but the tendency of the field to rotate rather than change its magnitude is still evident. This  $E(\bar{v})$  is quite well fitted for  $v < 1.5$  eV by the formula

$$E(\bar{v}) = E_0(v) + A v_z,$$

with  $A = 0.27$  and the function  $E_0(v)$  shown in Fig. 4 (the  $T=0$  curve).  $E_0(v)$  has the form of a very flat-bottomed well with steep sides; at  $T=0$   $\bar{v}$  is maintained at the value  $\bar{u}$  mainly by the  $A v_z$  term.

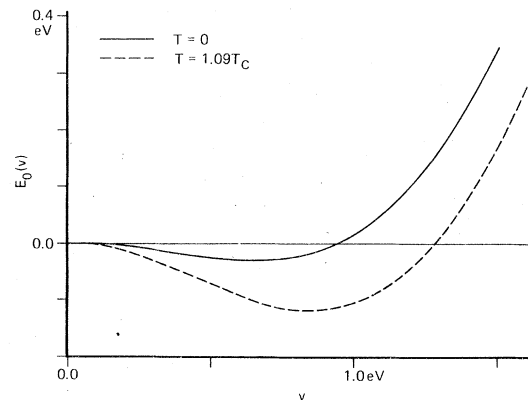


FIG. 4. Function  $E_0(v)$  plotted against  $v$  at two temperatures.

### III. EXTENSION OF THE THEORY TO HIGHER TEMPERATURES

We now wish to extend the previous theory to temperatures  $T > 0$ . The strategy will be to try to define at finite  $T$  a function  $E(\bar{v})$  which is a measure of the energy of an atom with exchange field  $\bar{v}$ . It is analogous to the  $\Delta E(\Delta\bar{v})$  discussed earlier apart from a change of origin; it is now natural to choose an origin so that  $E(\bar{v}=0) = 0$  [the relation at  $T=0$  between  $E$  and  $\Delta E$  is  $\Delta E(\Delta\bar{v}) = E(\bar{u} + \Delta\bar{v}) - E(\bar{u})$ ]. We previously defined  $\Delta E(\Delta\bar{v})$  to be, in effect, the energy of the configuration  $V_1$  shown in Fig. 1(b) (apart from the constant energy of the ground-state configuration). For  $T > 0$  we shall have to define  $E(\bar{v})$  to be the energy of a configuration of the type shown in Fig. 1(c), where the exchange field at site 0 is  $\bar{v}$ , but the exchange fields at other sites are variable because of thermal disorder. In these circumstances, the energy of the configuration depends not only upon  $\bar{v}$  but also upon the exchange fields at other sites. Thus, one may only define  $E(\bar{v})$  in an average sense as

$$E(\bar{v}) = \int E(\bar{v}_0 = \bar{v}, \bar{v}_1, \bar{v}_2, \dots) \times f(\bar{v}; \bar{v}_1, \bar{v}_2, \dots) d\bar{v}_1 d\bar{v}_2 \dots, \quad (8)$$

where  $E(\bar{v}_0, \bar{v}_1, \bar{v}_2, \dots)$  is the energy of a configuration, given by Eq. (3), and the average is over all the configurations  $\bar{v}_1, \bar{v}_2, \dots$  of the fields at sites other than 0 with some appropriate distribution function  $f(\bar{v}; \bar{v}_1, \bar{v}_2, \dots)$ , giving the probability of the configuration  $\bar{v}_1, \bar{v}_2, \dots$  at sites other than 0 when  $\bar{v}_0 = \bar{v}$ . It is to be understood that  $E(\bar{v}_0, \bar{v}_1, \bar{v}_2, \dots)$  contains the Coulomb-field effects in the approximation discussed in Sec. II.

The definition (8) is purely formal. To make further progress it is necessary to estimate the distribution function  $f$ . At this stage, approximations of varying degrees of sophistication (and difficulty) could be introduced. In this paper we shall use the simplest of all such approximations, one which, from the point of view of the localized model, corresponds closely to mean-field theory. In fact, we shall write

$$f(\bar{v}; \bar{v}_1, \bar{v}_2, \dots) \simeq f(\bar{v}_1) f(\bar{v}_2) \dots, \quad (9)$$

which neglects detailed correlations between the fields at different atoms, but allows the distribution  $f(\bar{v})$  at each atom to depend upon the angle between  $\bar{v}$  and the magnetization direction. How should one choose  $f(\bar{v})$ ? The most obvious choice is

$$f(\bar{v}) = N \exp[-\beta E(\bar{v})], \quad (10)$$

where  $N$  is a normalization constant such that

$$\int f(\bar{v}) d\bar{v} = 1. \quad (11)$$

It is, in fact, shown in Appendix B that, once the assumption (9) is made, Eqs. (10) and (11) follow and  $E(\bar{v})$  has the form

$$E(\bar{v}) = (1/K)v^2 - n_d w(\bar{v}) + \langle F \rangle_{\bar{v}}, \quad (12)$$

where  $w(\bar{v})$  is chosen so that

$$\langle \langle n_0 \rangle \rangle_{\bar{v}} = n_d. \quad (13)$$

Here,  $\langle X \rangle_{\bar{v}}$  means that  $X$  is to be calculated for the configuration with fields  $\bar{v}_0 = \bar{v}$ ,  $w_0 = w(\bar{v})$  at site 0 and the fields  $\{\bar{v}_i\}$ ,  $\{w(\bar{v}_i)\}$  at other sites, and is then to be averaged over the  $\bar{v}_1, \bar{v}_2, \dots$  at sites other than 0 with the distribution function (9). One now has an involved self-consistent problem; the definitions of  $E(\bar{v})$  and  $w(\bar{v})$  depend upon  $f(\bar{v})$  through the  $\langle \dots \rangle_{\bar{v}}$  averaging process and  $f(\bar{v})$  depends upon  $E(\bar{v})$  through Eq. (10).

There remains an additional problem that has not been solved exactly, namely the calculation of the averages  $\langle \langle n_0 \rangle \rangle_{\bar{v}}$  and  $\langle F \rangle_{\bar{v}}$ . The Hamiltonian for electrons moving in the fields described above is

$$H = \sum_{\bar{k}} \sum_s \sum_{\sigma} c_{\bar{k}s\sigma}^{\dagger} c_{\bar{k}s\sigma} + w(\bar{v}) n_0 + 2\bar{v} \cdot \bar{S}_0 + \sum_{i \neq 0} [w(\bar{v}_i) n_i + 2\bar{v}_i \cdot \bar{S}_i] \quad (14)$$

in the notation of I. This has the character of a Hamiltonian describing the motion of electrons in a random alloy; the  $\langle \dots \rangle_{\bar{v}}$  averages correspond to the configurational averages used in alloy theory except for the restriction on the fields at site 0. In fact, the problem in hand lends itself quite naturally to a treatment by the coherent-potential approximation (CPA) method<sup>11-14</sup> which automatically provides averages of the  $\langle \dots \rangle_{\bar{v}}$  kind (at least in the formulation of Ref. 14).

Since the application of the CPA in this context is nonstandard, we have outlined some of the details in Appendix C; here we quote only the salient results needed. A central quantity in the CPA method is the self-energy  $\Sigma(z)$  which is a function of the complex frequency  $z$ . In the present application it has the form of a  $2 \times 2$  diagonal matrix  $\underline{\Sigma}(z)$  in spin space. It is determined by the self-consistency condition

$$\underline{\Sigma}(z) = \int f(\bar{v}) d\bar{v} \{1 - [V(\bar{v}) - \underline{\Sigma}(z)] \underline{G}(z)\}^{-1} V(\bar{v}), \quad (15)$$

where

$$V(\bar{v}) = w(\bar{v}) \underline{I} + \bar{v} \cdot \underline{\bar{A}}, \quad (16)$$

$\underline{I}$  is the unit matrix and  $\underline{\bar{A}}$  a vector matrix with components equal to the Pauli matrices  $\underline{A}^x, \underline{A}^y, \underline{A}^z$ ;  $\underline{G}(z)$  is the diagonal  $2 \times 2$  matrix

$$\underline{G}(z) = \frac{1}{z} \int [(z - \omega) \underline{I} - \underline{\Sigma}(z)]^{-1} \rho(\omega) d\omega, \quad (17)$$

where  $\rho(\omega)$  is the total density of states for the  $d$  band (for one spin, see Sec. III of Paper I);  $\underline{G}$  is an approximation for the average single-site electron Green's function.

The  $E(\bar{v})$  given by Eq. (12) may be obtained by integrating the equation

$$\nabla_{\bar{v}} E(\bar{v}) = (2/K)\bar{v} - 2\langle\langle\bar{S}_0\rangle\rangle_{\bar{v}} \quad (18)$$

[obtained by differentiating Eq. (12)] and using the condition  $E(\bar{v}=0)=0$ , where  $\langle\langle\bar{S}_0\rangle\rangle_{\bar{v}}$  is the average spin at a site with field  $\bar{v}$ , given by

$$\langle\langle\bar{S}_0\rangle\rangle_{\bar{v}} = 5 \int_C \frac{dz}{2\pi i} \text{tr} \underline{\Lambda} \underline{G}(z) \times \{1 - [\underline{V}(\bar{v}) - \underline{\Sigma}(z)] \underline{G}(z)\}^{-1}, \quad (19)$$

where  $\text{tr}$  means the trace over the  $2 \times 2$  matrix and  $C$  is a contour encircling in an anticlockwise direction that part of the real axis on which the real part of  $z$  is less than the Fermi energy  $\mu$  (we have here assumed that  $k_B T \ll d$ -band width, see Appendix C).

Finally, in order to determine  $w(\bar{v})$  from the condition (13), one needs the quantity  $\langle\langle n_0 \rangle\rangle_{\bar{v}, w}$ , which has the same meaning as  $\langle\langle n_0 \rangle\rangle_{\bar{v}}$  except that  $w_0 = w$  is now free [i.e., is not fixed at the value  $w(\bar{v})$ ]; it is given by

$$\langle\langle n_0 \rangle\rangle_{\bar{v}, w} = 5 \int_C \frac{dz}{2\pi i} \text{tr} \underline{G}(z) \times \{1 - [\underline{W}(\bar{v}, w) - \underline{\Sigma}(z)] \underline{G}(z)\}^{-1}, \quad (20)$$

where

$$\underline{W}(\bar{v}, w) = w\underline{I} + \bar{v} \cdot \underline{\Lambda}. \quad (21)$$

Given a  $\underline{\Sigma}(z)$ , the Eqs. (16)–(21) together with Eqs. (13), (10), and (11) enable one to calculate the right-hand side of Eq. (15). If the result of this calculation is denoted by  $\underline{Q}[z; \underline{\Sigma}]$ , then Eq. (15) may be written

$$\underline{\Sigma}(z) = \underline{Q}[z; \underline{\Sigma}]. \quad (22)$$

This equation (or, rather, a slight rearrangement of it to improve convergence) was solved numerically by iteration at selected temperatures, starting from an estimate of  $\underline{\Sigma}(z)$ . It suffices to calculate  $\underline{\Sigma}(z)$  along the contour  $C$ , which was suitably chosen to avoid so far as possible the singularities on the real axis in the  $z$  plane. Beginning at  $T=0$ , where  $\underline{\Sigma}$  is known, we proceeded by steps to higher temperatures in the ferromagnetic regime, obtaining the results reported in Sec. IV. The method of calculation in the paramagnetic region is discussed in Sec. V.

#### IV. FERROMAGNETIC REGIME

The function  $E(\bar{v})$  is symmetric under rotations about the magnetization direction (which we take to be the  $z$  direction). In Fig. 3 we have plotted the contours of  $E(\bar{v})$  in the  $(v_x, v_z)$  plane. As will be seen, as  $T$  increases there gradually develops a ring-shaped valley like that found in Sec. IV of I, until, at  $T=1840$  K, the contours become spherically symmetric. We therefore identify  $T_C=1840$  K for the model (for further comment on the magnitude of  $T_C$ , see Sec. VI).

It was found that at all the temperatures studied (up to  $T=3000$  K  $=1.63 T_C$ )  $E(\bar{v})$  could be well fitted for the important  $\bar{v}$  (those with  $v < 1.5$  eV) by the formula

$$E(\bar{v}) = E_0(v) + Av_z, \quad (23)$$

where  $v = |\bar{v}|$ ,  $A$  is a temperature-dependent coefficient which goes to zero above  $T_C$ , and  $E_0(v)$  is a temperature-dependent function.  $E_0(v)$  changes somewhat with temperature; it is plotted in Fig. 4 at  $T=0$  and in the paramagnetic region. As  $T$  increases towards  $T_C$ ,  $E_0(v)$  develops a more definite minimum around  $v \approx 1$  eV; above  $T_C$  it changes little up to  $1.6 T_C$ . It was found, surprisingly, that the coefficient  $A$  increases initially with temperature, passing through a maximum at  $T \approx 0.3 T_C$  and then decreasing to zero at  $T = T_C$ .

In the course of calculating  $E(\bar{v})$ , we also evaluated the average moment  $\langle\langle\bar{S}\rangle\rangle_{\bar{v}}$  of an atom with field  $\bar{v}$  [see Eq. (19)], from which one may obtain the average moment per atom according to

$$\bar{M} = \int \langle\langle\bar{S}\rangle\rangle_{\bar{v}} f(\bar{v}) d\bar{v}. \quad (24)$$

Alternatively, it may be calculated as

$$\bar{M} = \frac{1}{K} \int \bar{v} f(\bar{v}) d\bar{v} \quad (25)$$

according to the theory of Ref. 3 (which holds good in the present context). Numerical calculation by both methods agreed within one or two parts in a thousand and gave the magnetization curve shown in Fig. 5, where it is compared with the classical spin mean-field theory result and the observed curve for Fe, Co, and Ni (all of which have more or less the same magnetization curve). As will be seen, the fit to experiment is not very good. In fact, our calculated  $M(T)$  follows fairly closely the classical spin result, which is not unexpected in view of certain of the approximations introduced (see Sec. VI).

The coefficient  $A(T)$  in Eq. (23) is evidently a measure of the strength of the effective field tending to align the moment in the magnetization direction. It may be thought of as due to an effective exchange

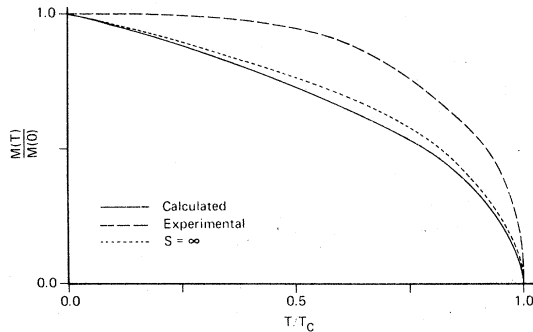


FIG. 5. Calculated magnetization curve  $M(T)$  vs  $T$  (solid curve) together with the corresponding classical spin result (dotted curve) and the experimental curve for iron (dashed).

coupling with neighboring atoms which have, on the average, their moments aligned in this direction to an extent measured by  $M(T)$ . Thus, the ratio  $A(T)/M(T)$  is a measure of the strength of this effective exchange coupling. We may convert this dimensionless measure of the coupling to an exchange energy in a rough and ready way by multiplying it by the energy  $K$ , a choice recommended by the equivalence of the formulas (24) and (25). If one supposes the coupling is to the eight nearest neighbors only (this assumption is a convenience, there is nothing in our results which necessarily leads to such a conclusion), then one obtains an effective exchange coupling between nearest neighbors given by

$$J_{\text{ex}}(T) = KA(T)/8M(T) \quad (26)$$

This quantity is plotted in Fig. 6; the calculations were extended into the paramagnetic region by consideration of cases in which a moment is induced by the application of a small magnetic field (see Sec. V).  $J_{\text{ex}}(T)$  was found to increase significantly with tem-

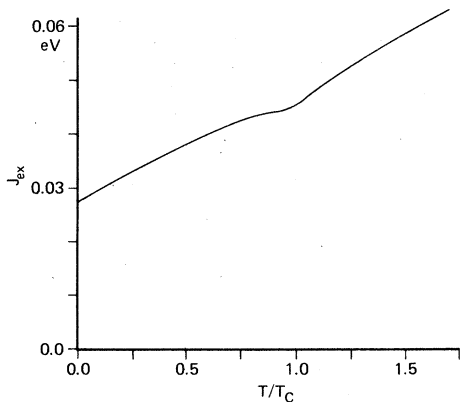


FIG. 6. Effective interatomic exchange coupling (represented as a nearest-neighbor exchange interaction, see Sec. IV) vs the temperature  $T$ .

perature, almost doubling over the range  $T=0$  to  $T=1.5T_C$ . It is this increase which leads to the maximum in  $A(T)$  in spite of the falling  $M(T)$ . We have no simple physical explanation of this effect.

## V. PARAMAGNETIC REGIME

In the paramagnetic regime  $E(\bar{\nu})$  depends only upon  $\nu = |\bar{\nu}|$  and the coefficient  $A$  vanishes. In this region we were mainly interested in calculating the paramagnetic susceptibility. For this purpose it is necessary to extend the theory of Sec. III and Appendices B and C to allow for the presence of an applied magnetic field, i.e., an additional term

$$-\bar{h} \cdot \sum_i \bar{S}_i \quad (27)$$

in the Hamiltonian. The extension is straightforward and we give no details. In the limit  $\bar{h} \rightarrow 0$  the Eq. (22) for  $\underline{\Sigma}(z)$  is replaced by

$$\underline{\Sigma}_h(z) = \underline{Q}[z; \underline{\Sigma}_h] + h\underline{F}(z) \quad (28)$$

where  $\underline{\Sigma}_h(z)$  is the self-energy in the presence of a magnetic field of magnitude  $h$  in the  $z$  direction, and  $\underline{F}(z)$  is given by

$$\underline{F}(z) = \frac{2\beta}{K} \int [1 - [\underline{V}(\bar{\nu}) - \underline{\Sigma}(z)]\underline{G}(z)]^{-1} \times \underline{V}(\bar{\nu})_{z,z} f(\bar{\nu}) d\bar{\nu} \quad (29)$$

calculated using the  $\underline{\Sigma}$  and  $\underline{G}$  appropriate in the absence of the magnetic field [ $\underline{V}$  and  $\underline{G}$  are given by Eqs. (16) and (17)].

$\underline{F}(z)$  was calculated via Eq. (29) from the solutions in zero field, a small value of  $h$  taken and Eq. (28) was solved numerically by iteration to obtain  $\underline{\Sigma}_h$  and  $E(\bar{\nu})$ , from which  $M$  was calculated using Eq. (24) or (25) and the susceptibility  $\chi$  obtained. These calculations also supplied the data used to extend the calculation of  $J_{\text{ex}}$  into the paramagnetic region.

The susceptibility thus calculated followed very closely a Curie-Weiss law

$$\chi = \frac{1}{3} m_{\text{eff}}^2 / (T - T_C) \quad (30)$$

over the range  $T = T_C$  to  $T = 1.6T_C$  studied. The value of the effective moment was  $m_{\text{eff}} \approx 2.7\mu_B$  (where  $\mu_B$  is the Bohr magneton), somewhat greater than the ground-state moment but not as great as is observed, namely  $m_{\text{eff}} = 3.12\mu_B$ .<sup>17</sup>

The fact that a Curie-Weiss law was obtained with so large an  $m_{\text{eff}}$  leads one to enquire the magnitudes of the atomic moments predicted by the theory. Since one has the distribution  $f(\bar{\nu})$  of the fields, and for each field the corresponding average moment  $\langle\langle \bar{S} \rangle\rangle_{\bar{\nu}}$  [see Eq. (19)], it was possible to evaluate at each temperature the distribution function  $f_s(S)$  giv-

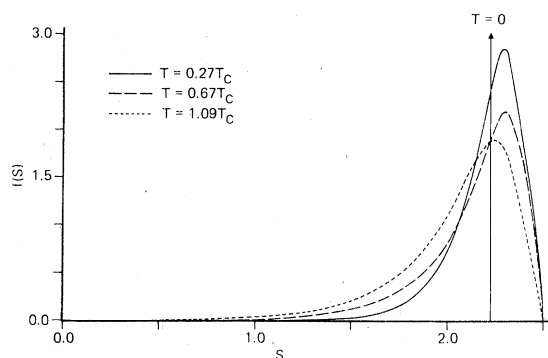


FIG. 7. Distribution function  $f_s(S)$ , giving the probability of finding an atom with atomic moment  $S$ , plotted at various temperatures  $T$ .

ing the probability that an atom has a moment of magnitude  $S$ . These distributions are plotted at several temperatures in Fig. 7. Even at the highest temperatures studied, the distributions are not very wide, and the mean value changes little with temperature, indicating that over this temperature range the principal change is a disordering of the atomic spin directions rather than a change in their magnitudes.

## VI. CONCLUSIONS AND COMMENTS

The results discussed in Sec. II show that there is a strong coupling between the exchange and Coulomb fields, at least in the ferromagnetic regime, so the latter must be taken into account. In fact, the results of I are to some degree invalidated by the neglect of these effects. Nevertheless, the finite-temperature calculations show the general conclusions of I, namely that this kind of theory can simultaneously explain both the moment and the Curie temperature of iron, still stands. One interesting effect of the introduction of the Coulomb-field effects is to restore the cluster-expansion type of result represented by Eq. (2).

The finite-temperature calculations gave the estimate  $T_C = 1840$  K, about 75% greater than the observed value, but of the right order of magnitude. Various approximations have been made, most of which will lead to an overestimate of  $T_C$ . The treatment of the Coulomb effects overestimates their effectiveness (by requiring complete neutrality) which, in turn, leads to an overestimate of  $T_C$ . The approximation introduced in I, and used here, of assuming that the density of states in each  $d$  subband is one fifth of the total  $d$ -band density of states  $\rho$  causes one to overestimate  $T_C$ . A more proper treatment would introduce the densities of states  $\rho_e$  and  $\rho_t$  for the band states with  $e_g$  and  $t_{2g}$  symmetry; each of these densities of states is somewhat more compact than  $\rho$ ,

reducing the effective interatomic exchange coupling and hence  $T_C$ . Another important effect tending to reduce  $T_C$  is associated with renormalizations brought about by Coulomb correlations. These correlations are neglected in the treatment given here (when, in the discussion of Appendix A, the time fluctuating part of the Coulomb field was dropped); our calculations were based upon Tawil and Callaway's<sup>16</sup> Hartree-Fock band structure. We expect that when these renormalizations are taken into account, the essence of the theory described above will remain, but that all energy parameters, including  $T_C$ , will be scaled down. This scaling effect on the bandwidth is recognizable, perhaps, in the photoemission results of Eastman *et al.*<sup>18</sup> on nickel, which show a bandwidth reduced by 40% compared to Hartree-Fock predictions. In our treatment such a reduction would entail a corresponding reduction in  $K$  and  $T_C$ .

The magnetization curve obtained was not in very good accord with experiment. It is, in fact, very close to the classical spin result. This is not unexpected since we have made use of an approximation (the replacement of the functional integral over time-dependent fields by the ordinary integral over static fields in Appendix A) which prevents one from seeing the proper quantum statistics for the "spins" of the localized aspects of the model. It is not clear whether a more correct treatment of this point would explain the near "universal" character of the observed magnetization curves (in spite of the wide variation in moment between nickel and iron).

The paramagnetic susceptibility obtained obeys closely a Curie-Weiss law, a result in good accord with experiment; in fact, the value of  $m_{\text{eff}}$  found is quite good considering the many approximations.

Finally we may note that, in spite of the fact that the formulation of the theory allowed ample opportunity for one to find a wide distribution of the magnitudes of the atomic moments, the calculations actually showed rather little spread, a result we take to indicate behavior markedly similar to that of a Heisenberg model (in iron, at least).

A number of obvious problems remain. First, how large are the Coulomb renormalization effects? Second, how does one formulate and calculate with the theory in order to obtain proper quantum statistics (or whatever is appropriate)? Third, how does one explain the "universal" character of the magnetization curve?

## APPENDIX A: THE INTRODUCTION OF COULOMB FIELDS

The material of this appendix represents an extension of that of Appendix A of I, to which the reader is referred for some details and notation. It was remarked there that in the case of the narrow energy

band model<sup>19</sup> a useful factorization of the interaction is

$$Un_{i\uparrow}n_{i\downarrow} = \frac{1}{4}Un_i^2 - U(\bar{\epsilon}_i \cdot \bar{S}_i)^2, \quad (\text{A1})$$

where  $n_i = n_{i\uparrow} + n_{i\downarrow}$  is the total electron operator and  $\bar{S}_i$  the total spin operator of atom  $i$ ;  $\bar{\epsilon}_i$  is an arbitrary unit vector. Using this factorization one may obtain by the functional integral method<sup>1,20-21</sup> and the procedure of averaging the  $\bar{\epsilon}_i$  over all directions, discussed in I, the expression

$$Z \propto \int \prod_i [D\bar{v}_i(t) D\phi_i(t)] \exp \left[ -\frac{1}{U} \sum_i \int_0^\beta [v_i^2(t) + \phi_i^2(t)] dt \right] \\ \times \text{Tr} \exp \left[ -\int_0^\beta H_0(t) dt - \sum_i \int_0^\beta [\iota\phi_i(t)n_i(t) + 2\bar{v}_i(t) \cdot \bar{S}_i(t)] dt \right], \quad (\text{A2})$$

for the partition function  $Z$ , where  $i$  labels sites,  $\bar{v}_i(t)$  and  $\phi_i(t)$  are exchange and Coulomb "fields",  $D\bar{v}_i(t)$  and  $D\phi_i(t)$  indicate functional integration over the  $\bar{v}_i(t)$  and  $\phi_i(t)$  on the range  $t = (0, \beta)$ , Tr means the quantum-mechanical trace,  $\exp_+$  the time-ordered exponential, and  $H_0 = h - \mu N_e$  where  $H$  is the Hamiltonian describing the band motion of noninteracting electrons,  $\mu$  is the Fermi energy, and  $N_e$  is the total electron number operator.

Simplifying Eq. (A2) by neglecting the time fluctuating parts of the  $\bar{v}_i$  and  $\phi_i$  fields, one obtains the approximation

$$Z \approx \int \prod_i (d\bar{v}_i d\phi_i) \exp \left[ -\frac{\beta}{U} \sum_i (v_i^2 + \phi_i^2) - \beta F(V, \Phi) \right], \quad (\text{A3})$$

where

$$V \equiv \{\bar{v}_1, \bar{v}_2, \dots\}, \quad \Phi \equiv \{\phi_1, \phi_2, \dots\}$$

and

$$F(V, \Phi) = -\frac{1}{\beta} \ln \text{Tr} \exp \left[ -\beta H_0 - \beta \sum_i (\iota\phi_i n_i + 2\bar{v}_i \cdot \bar{S}_i) \right]. \quad (\text{A4})$$

It is this approximation which leads to the classical spin description of the localized aspects of the model and to the loss of renormalization effects associated with Coulomb correlations.

In Appendix A of I we now proceeded by (a) neglecting altogether the Coulomb fields  $\phi_i$  in Eqs. (A3) and (A4), and (b) passing from the narrow energy band model to the degenerate  $d$ -band case by interpreting  $\bar{S}_i$  as the total spin of the atom and replacing  $U$  by some appropriate parameter  $K$  (called  $J$  in I) measuring the strength of the intra-atomic exchange interaction. Here, we shall abandon the approximation (a) and pass to the degenerate band case by interpreting  $n_i$  and  $\bar{S}_i$  as the total electron number operator and spin operator of the atom at  $i$ , rewriting Eq. (A3) as

$$Z \approx \int \prod_i (d\bar{v}_i d\phi_i) \exp \left[ -\frac{\beta}{2C} \sum_i \phi_i^2 - \frac{\beta}{K} \sum_i v_i^2 - \beta F(V, \Phi) \right], \quad (\text{A5})$$

where  $C$  and  $K$  now measure the strength of the intra-atomic Coulomb and exchange interactions.

The theory of I could be recovered from Eq. (A5) by simply dropping the Coulomb fields  $\phi$ . Here, our treatment will be just one degree less cavalier: we shall evaluate the  $\phi_i$  integrals in Eq. (A5) by steepest descents for each configuration  $V$ , deflecting the contours of the  $\phi_i$  integration through the values  $\phi_i = \phi'_i(V)$  which maximize the exponent in Eq. (A5); these  $\phi'_i(V)$  are, in fact, pure imaginary. Setting to zero the derivatives of the exponent with respect to the  $\phi_i$ , one obtains for the  $\phi'_i(V)$  the

equations

$$\phi'_i = -\iota C \langle n_i \rangle_{V, \Phi'}, \quad (\text{A6})$$

where  $\langle n_i \rangle_{V, \Phi'}$  is the expectation of  $n_i$  calculated in the fields  $V, \Phi' \equiv \{\phi'_1, \phi'_2, \dots\}$ . These equations determine the  $\phi'_i(V)$  for each  $V$ ; the expectation of  $n_i$  appears because from Eq. (A4)

$$\partial F(V, \Phi) / \partial \phi_i = -\iota \beta \langle n_i \rangle_{V, \Phi}. \quad (\text{A7})$$

In the case of the ground-state configuration  $V_0$ , translational symmetry dictates that the  $\phi'_i(V_0)$  have



the same value  $\phi_0$  for all  $i$ . Equation (A6) then gives

$$\phi_0 = -\iota C n_d, \quad (\text{A8})$$

where  $n_d$  is the number of  $d$  electrons per site. It is convenient to introduce in place of the pure imaginary  $\phi_i'(V)$  the real fields  $w_i$  defined by

$$w_i = -\iota[\phi_i'(V) - \phi_0]. \quad (\text{A9})$$

Then Eq. (A6) may be written

$$\langle n_i \rangle_{V,W} - (1/C) w_i = n_d, \quad (\text{A10})$$

where  $\langle n_i \rangle_{V,W}$  is the expectation of  $n_i$  calculated in the fields  $V, W \equiv \{w_1, w_2, \dots\}$ , i.e., with the electron Hamiltonian

$$H(V, W) = H_0 + \sum_i (w_i n_i + 2\bar{v}_i \cdot \bar{S}_i) \quad (\text{A11})$$

derived by using Eq. (A9) in Eq. (A4).

The Eqs. (A10) now determine the  $w_i$ , and hence, through Eq. (A9), the  $\Phi'$  to be used in evaluating Eq. (A5) by steepest descents. When this evaluation is carried out one obtains, using Eqs. (A8) and (A9),

$$Z \propto \int \prod_i d\bar{v}_i \exp \left[ -\frac{\beta}{K} \sum_i v_i^2 + \beta n_d \sum_i w_i - \frac{\beta}{2C} \sum_i w_i^2 - \beta F(V, W) \right], \quad (\text{A12})$$

where  $F(V, W)$  is the thermodynamic potential of electrons moving in the fields  $V, W$  according to Eq. (A11).

Our final approximation is to assume that the intra-atomic Coulomb interaction is much stronger than the exchange interaction; this is equivalent to taking the limit  $C \rightarrow \infty$  in the above theory. When this is done, the Eqs. (A10) determining the  $w_i$  as functions of  $V$  reduce to Eq. (4) of the main text, representing the maintenance of charge neutrality, and Eq. (A12) assumes the form

$$Z \approx \int \prod_i d\bar{v}_i \exp[-\beta E(V)], \quad (\text{A13})$$

with  $E(V)$  given by Eq. (3) of the main text.

#### APPENDIX B: DERIVATION OF THE FINITE-TEMPERATURE THEORY

In this appendix we explain how the "mean-field"-type approximation represented by Eqs. (8)–(13) of Sec. III may be derived as an approximation in the functional-integral formalism.

The derivation is based upon the Feynman variation principle.<sup>10</sup> We will first explain the manner of its application in rather general terms. Let the sym-

bol  $\int$  indicate an integration over some space the points of which we label  $x$ . The Feynman variation principle is based upon the inequality

$$\ln \int e^{D(x)} \geq \ln \left[ \int e^{D'(x)} \right] + \langle D - D' \rangle, \quad (\text{B1})$$

where  $D(x), D'(x)$  are real functions defined on the space and the averages  $\langle X \rangle$  are defined relative to the distribution function

$$f'(x) = \exp\{D'(x)\} / \int \exp(D'),$$

$$\langle X \rangle = \int X(x) \exp(D') / \int \exp(D'). \quad (\text{B2})$$

Suppose now one wishes to approximate the distribution  $f(x) = \exp\{D(x)\} / \int \exp(D)$  by the "best" of the distribution functions

$f'(x) = \exp\{D'(x)\} / \int \exp(D')$ , where the  $D'$  are restricted to a certain class  $R$  of functions. Then Eq. (B1) shows that the best choice is  $D' = D_0$ , where  $D_0$  is the function of the class  $R$  which maximizes the right-hand side of Eq. (B1); furthermore,  $\int \exp(D_0)$  is the best approximation to  $\int \exp(D)$  available restricting the  $D'$  to  $R$ .

The case at hand is one in which  $x$  stands for a set of vectors  $x_1, x_2, \dots$  [in our application each  $x_i$  will be a vector with the four components  $x_i \equiv (\phi_i, \bar{v}_i)$  in the notation of Appendix A]; then,  $D(x) \equiv D(x_1, x_2, \dots)$  and likewise for  $D', D_0$ . Suppose now one takes for the class  $R$  all the functions  $D'$  of the form

$$D'(x_1, x_2, \dots) = \sum_i d_i(x_i), \quad (\text{B3})$$

where  $d_i(x_i)$  is an arbitrary function of the single variable  $x_i$ . Then, maximization of the right-hand side of Eq. (B1) with respect to the  $d_i$  with  $D'$  given by Eq. (B3) yields the equations

$$d_i(x) = \int D(x) |_{x_i=x} \prod_{j \neq i} f_j(x_j) \prod_{j \neq i} dx_j \quad (\text{B4})$$

for the best choice of the  $d_i$ , where

$$f_i(x) = \exp[d_i(x)] / \int \exp[d_i(x')] dx' \quad (\text{B5})$$

is an effective distribution function for  $x_i$ . Equation (B4) asserts that  $d_i(x)$  is just  $D(x)$  with  $x_i$  fixed at the value  $x$  and averaged over all the other  $x_j$ , each with the appropriate distribution function  $f_j$ . Further, the corresponding approximation to the distribution function  $f$  is

$$f \approx f'(x_1, x_2, \dots) = \prod_i f_i(x_i). \quad (\text{B6})$$

To obtain the results described in Sec. III, we will now apply the above theory to the case in which  $e^D$  is the integral in Eq. (A3). It is convenient, however, to first rewrite this integral in terms of the new variables

$$y_i = -\iota(\phi_i - \phi_0), \quad (\text{B7})$$

which will replace the  $\phi_i$ ;  $\phi_0$  is defined at Eq. (A8) [cf. Eq. (A9)]. In terms of these variables, the integral in Eq. (A3) can be written  $\int \exp(D)$  (apart from an unimportant factor), with  $\int$  interpreted as  $\int \prod_i (d\bar{v}_i d\phi_i)$ , and  $D = -\beta E_T'(V, Y)$ , where

$$E_T'(V, Y) = \frac{1}{K} \sum_i v_i^2 - n_d \sum_i y_i + \frac{1}{2C} \sum_i y_i^2 + F'(V, Y), \quad (\text{B8})$$

$Y$  standing for  $Y = \{y_1, y_2, \dots\}$  and

$$F'(V, Y) = -\frac{1}{\beta} \ln \text{Tr} \exp \left[ -\beta H_0 - \beta \sum_i (y_i n_i + 2\bar{v} \cdot \bar{S}_i) \right]. \quad (\text{B9})$$

A type of mean-field theory can now be obtained employing the Feynman variation principle in the manner described above, taking for the class  $R$  of functions  $D'$  all those functions of the form

$$D'(V, Y) = -\beta \sum_i E'(\bar{v}_i, y_i). \quad (\text{B10})$$

[The translational symmetry of our problem enables one to infer that the  $d_i$  of Eq. (B3) are all the same function  $E'(\bar{v}, y)$ .] Then Eq. (B4) becomes in our application

$$E'(\bar{v}, y) = \int E_T'(V, Y) |_{y_0=y, \bar{v}_0=\bar{v}} \times \prod_{i \neq 0} f'(\bar{v}_i, y_i) \prod_{i \neq 0} d\bar{v}_i dy_i, \quad (\text{B11})$$

where

$$f'(\bar{v}, y) = \exp[-\beta E'(\bar{v}, y)] / \int \exp[-\beta E'(\bar{v}', y')] \times d\bar{v}' dy'. \quad (\text{B12})$$

The corresponding approximation for the distribution function  $\exp[-\beta E_T'(V, Y)] / \int \exp(-\beta E_T')$  is

$$f'(V, Y) = \prod_i f'(\bar{v}_i, y_i). \quad (\text{B13})$$

Finally, we graft onto this theory the approximate treatment of the Coulomb fields described in Appendix A. To do this we use what is again essentially the method of steepest descents. We assume that  $f'(\bar{v}, y)$  is, for each  $\bar{v}$ , so sharply a peaked function of  $y$  that we may write

$$f'(\bar{v}, y) \simeq \delta(y - w(\bar{v})) f'(\bar{v}, w(\bar{v})) \equiv \delta(y - w(\bar{v})) f(\bar{v}), \quad (\text{B14})$$

where  $w(\bar{v})$  is the value of  $y$  which minimizes  $E'(\bar{v}, y)$ . Defining  $E(\bar{v}) = E'(\bar{v}, w(\bar{v}))$ , one has

$$f(\bar{v}) = \exp[-\beta E(\bar{v})] / \int \exp[-\beta E(\bar{v}')] d\bar{v}'. \quad (\text{B15})$$

Then, using Eq. (B14) in Eq. (B11), one finds that  $E(\bar{v})$  satisfies

$$E(\bar{v}) = \int E_T(V) |_{\bar{v}_0=\bar{v}} \prod_{i \neq 0} f(\bar{v}_i) \prod_{i \neq 0} d\bar{v}_i, \quad (\text{B16})$$

where

$$E_T(V) = \frac{1}{K} \sum_i v_i^2 - n_d \sum_i w(\bar{v}_i) + \frac{1}{2C} \sum_i w^2(\bar{v}_i) + F(V), \quad (\text{B17})$$

and

$$F(V) = -\frac{1}{\beta} \ln \text{Tr} \exp \left[ -\beta H_0 - \beta \sum_i [n_i w(\bar{v}_i) + 2\bar{v}_i \cdot \bar{S}_i] \right]. \quad (\text{B18})$$

To find  $w(\bar{v})$ , one must use  $0 = [\partial E'(\bar{v}, y) / \partial y]_{y=w(\bar{v})}$ . Carrying out the variation with respect to  $y$  in Eq. (B11) with the aid of the definition (B8) of  $E_T'$ , and using the approximation (B14) for  $f'$ , one obtains for  $w(\bar{v})$  the equation

$$\langle \langle n_0 \rangle \rangle_{\bar{v}} - (1/C) w(\bar{v}) = n_d, \quad (\text{B19})$$

where  $\langle \langle \dots \rangle \rangle_{\bar{v}}$  is defined after Eq. (13) of Sec. III. If one now lets  $C \rightarrow \infty$ , as discussed in Appendix A, Eq. (B19) becomes Eq. (13) of Sec. III, and Eq. (B16) becomes Eq. (12) of Sec. III when use is made of Eq. (B17).

### APPENDIX C: THE APPLICATION OF THE CPA

In this appendix we outline the derivation of Eqs. (15)–(21) of Sec. III. The method is a straightforward adaptation of the derivation of the CPA given by Brouers *et al.*<sup>14</sup> [This paper will be referred to as Ref. A; use is made only to Eqs. (1)–(8) of this reference, not of the further developments described there.]

The basic problem is to calculate averages like the  $\langle \langle \bar{S}_0 \rangle \rangle_{\bar{v}}$  over all configurations in which the exchange potential at site 0 is fixed at  $\bar{v}$ . The Hamiltonian describing the electronic motion in a particular field configuration has the form shown in Eq. (14). It will be convenient to first consider the case of a nondegenerate band and to rearrange the Hamiltonian in the form

$$H = \sum_{ij} \sum_{\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_i \sum_{\sigma\sigma'} (V_i)_{\sigma\sigma'} c_{i\sigma}^{\dagger} c_{i\sigma'}, \quad (\text{C1})$$

where  $V_i$  is a  $2 \times 2$  matrix of the form  $V_i = w_i I + \bar{v}_i \cdot \bar{\Delta}$  representing the field at site  $i$ , and

the  $t_{ij}$  are the transfer integrals giving rise to the band motion. Because of the variable direction in spin space of the exchange potentials it is necessary to consider all four spin components of the electron Green's functions  $g_{ij}^{\sigma\sigma'}$  ( $z$  is a complex frequency); it is therefore convenient to introduce the  $2 \times 2$  matrix Green's functions  $\underline{g}_{ij}(z)$  with components  $(\underline{g}_{ij})_{\sigma\sigma'} = g_{ij}^{\sigma\sigma'}$ . Following Ref. A, we note that these Green's functions will satisfy the equations

$$\underline{g}_{ij}(z) = \underline{g}_{ii}^0(z) \delta_{ij} + \sum_k \underline{g}_{ii}^0(z) t_{ik} \underline{g}_{kj}(z), \quad (C2)$$

where

$$\underline{g}_{ii}^0(z) = (z - \underline{V}_i)^{-1}. \quad (C3)$$

Iteration of Eq. (C2) yields (see Ref. A)

$$\underline{g}_{ii}(z) = [z - \underline{V}_i - \underline{\Delta}_i(z)]^{-1},$$

where

$$\begin{aligned} \underline{\Delta}_i(z) = & \sum_{j \neq i} t_{ij}^2 \underline{g}_{jj}^0(z) \\ & + \sum_{\substack{j,k \\ j \neq i, k \neq i}} t_{ij} \underline{g}_{jj}^0(z) t_{jk} \underline{g}_{kk}(z) t_{ki} + \dots \end{aligned} \quad (C4)$$

The method of Ref. A develops the CPA by the approximation of replacing the  $\underline{g}_{kk}^0(z)$  appearing in Eq. (C4) by the quantity  $[z - \underline{\Sigma}(z)]^{-1}$ ,  $\underline{\Sigma}(z)$  representing some average effect of the variable potentials  $\underline{V}_k$ . Then, the series in Eq. (C4) may be summed to give

$$\underline{\Delta}_i(z) \approx z - \underline{\Sigma}(z) - [\underline{G}(z)]^{-1}, \quad (C5)$$

where

$$\underline{G}(z) = \int [(z - \omega) \underline{I} - \underline{\Sigma}(z)]^{-1} \rho(\omega) d\omega, \quad (C6)$$

in which  $\rho(\omega)$  is the density of states corresponding to the band structure determined by the  $t_{ij}$ ;  $\underline{G}$  is an approximation to  $\langle \underline{g}_{ii} \rangle$ , where the average is over all field configurations.

Substituting the approximation (C5) into Eq. (C3) gives the approximation

$$\langle \underline{g}_{ii}(z) \rangle_{\bar{v}, -\bar{v}} \approx [\underline{G}^{-1} + \underline{\Sigma} - \underline{V}(\bar{v})]^{-1}, \quad (C7)$$

where  $\underline{V}(\bar{v})$  is defined at Eq. (16) and  $\langle \underline{g}_{ii} \rangle_{\bar{v}, -\bar{v}}$  is the average over all configurations in which  $\bar{v}_i$  is held at the value  $\bar{v}$ . Following Ref. A, we now obtain the CPA by choosing  $\underline{\Sigma}(z)$  so that the  $\underline{G}(z)$  given by Eq. (C6) agrees with the average of

$\langle \underline{g}_{ii} \rangle_{\bar{v}, -\bar{v}}$  [given by Eq. (C7)] over all  $\bar{v}$  with the appropriate weight  $f(\bar{v})$ . This leads, using Eq. (C7), to the equation

$$\underline{G}(z) = \int [\underline{G}^{-1} + \underline{\Sigma} - \underline{V}(\bar{v})]^{-1} f(\bar{v}) d\bar{v}. \quad (C8)$$

This equation may be rearranged into the form of Eq. (15) of Sec. III, while Eq. (C6) is the same as Eq. (17) when allowance is made for the  $d$ -band degeneracy [the factor 5 in Eq. (17), derived using the approximation of identical densities of states for all  $d$  subbands, as in I].

Next, we consider the derivation of Eq. (19). For any configuration of the field, one has

$$\langle \bar{S}_0 \rangle = \frac{t}{\beta} \sum_{\nu} \text{tr} \bar{\Lambda} \underline{g}_{00}(\omega_{\nu}), \quad (C9)$$

where the sum is over all  $\omega_{\nu}$  of the form

$\omega_{\nu} = i\pi\nu/\beta + \mu$ ,  $\nu = \pm 1, \pm 3, \pm 5, \dots$ , and  $\mu$  is the Fermi energy. One may in the usual way convert this to a contour integral

$$\langle \bar{S}_0 \rangle = \int_{C'} \frac{dz}{2\pi i} f_{\text{FD}}(z) \text{tr} \bar{\Lambda} \underline{g}_{00}(z), \quad (C10)$$

where  $C'$  is a contour encircling the real axis in an anticlockwise direction and  $f_{\text{FD}}(z) = [\exp[\beta(z - \mu)] + 1]^{-1}$  is the Fermi-Dirac distribution function. At the temperatures we consider  $k_B T$  is much less than the  $d$ -band width, so one may approximate  $f_{\text{FD}}(\omega)$  on the real axis by  $f_{\text{FD}}(\omega) = 1$  if  $\omega < \mu$ , = 0 otherwise. Correspondingly, one may approximate Eq. (C10) in this case by

$$\langle \bar{S}_0 \rangle = \int_C \frac{dz}{2\pi i} \text{tr} \bar{\Lambda} \underline{g}_{00}(z), \quad (C11)$$

where  $C$  is a contour encircling in an anticlockwise direction that part of the real axis on which  $\omega < \mu$ , i.e., is the contour used in Eq. (19). If we now carry out the  $\langle \dots \rangle_{\bar{v}}$  average in Eq. (C11), we obtain

$$\begin{aligned} \langle \langle \bar{S}_0 \rangle \rangle_{\bar{v}} &= \int_C \frac{dz}{2\pi i} \text{tr} \bar{\Lambda} \langle \underline{g}_{00}(z) \rangle_{\bar{v}_0 = \bar{v}} \\ &= \int_C \frac{dz}{2\pi i} \text{tr} \bar{\Lambda} \underline{G} [1 + [\underline{\Sigma} - \underline{V}(\bar{v})] \underline{G}]^{-1} \end{aligned} \quad (C12)$$

using Eq. (C7), reproducing Eq. (19) of Sec. III when allowance is made for the  $d$ -band degeneracy. Equation (20) of Sec. III is similarly derived.

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