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Coupling between Anderson-Type Localized Moments in Relation to the Theory of Transition-Metal Ferromagnetism*

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When the wave functions of two identical Anderson-type localized moments overlap, the moments tend to align in either parallel or antiparallel configuration. The relative stability of the two configurations is studied in the limit of very small overlap using the Hartree-Fock approximation. It is found that in the highly localized limit, i.e., extremely small d-level width, the antiferromagnetic alignment is energetically favored. A necessary condition for ferromagnetic alignment is to have partially occupied d states. Similar consideration can be applied to the N-spin problem. If one expands the total energy of the system in terms of the ratio of overlap energy versus intra-atomic Coulomb energy, the lowest-order spin-dependent term has the form of a Heisenberg Hamiltonian. On the other hand, for a ferromagnetically ordered system, the Fermi level is found to fall in the region where the s and d bands hybridize. This indicates that the Fermi surface has strong d character. It will be shown that this model gives a qualitative and roughly quantitative fit to all the important magnetic and electronic properties of iron and nickel.

I. INTRODUCTION

THE historical development of the theory of ferromagnetism in metals has followed two parallel paths, the localized-spin theory and the itinerant-electron theory. In the former theory, the electrons carrying the permanent magnetic moment are assumed to be confined to the ion core. Rare-earth metals are the best examples of this kind of material. In the latter theory, the magnetization is regarded as arising from the polarization of the conduction electrons. The moment-carrying electrons are more or less uniformly distributed throughout the metal. The antiferromagnetism in chromium seems to fit this description very well. In order to determine which model is applicable to materials like iron and nickel, various experiments have been conducted. The situation up to around 1964 is very well summed up in the monumental review of Herring.[1] He concluded that neither model in its simplest form explains all the experiments, and that refinements of each model can duplicate many of the features of the other, so that almost all experiments can be crudely understood. Since then new evidence has been accumulated and it tends to sharpen the conflict. We review this evidence briefly here.

It is well known that the initial susceptibility χ_0 of a ferromagnet diverges at the Curie temperature. Kovel and Fisher[2] analyzed the susceptibility data of Weiss and Forrer[3] for nickel and found that

$$\chi_0^{-1} \propto (T-T_c)^\gamma$$

just above the Curie temperature. The value of γ is 1.35±0.02. This is in good agreement with the value $\gamma \cong \frac{4}{3}$ for the Heisenberg model.[4a] One may think that it is possible to understand the critical fluctuation of the magnetic metal by including the correlation effect as done by Kubo *et al.*[4b] However, the Kubo theory relies crucially on the Landau assumption that all quantities can be expanded in powers of $(T-T_c)$ just above the Curie point. This type of theory can only give $\gamma=1$. Whether the Kubo theory can be improved to give a different value for γ is not clear at the present time. For this reason the critical fluctuation properties are often discussed in terms of the localized model even for transition-metal ferromagnets.

Neutron-diffraction experiments[5] showed that the spin density distribution in metallic ferromagnetic iron, cobalt, and nickel can be accurately described by a positive free-atom $3d$ contribution and a negative constant. This indicates that the moment-carrying electrons have wave functions which are not severely disturbed by the metallic bonding and ferromagnetic coupling. The assumption that the magnetic moment is uniformly distributed in the metal is invalid.

The Fermi surfaces in iron and nickel have been mostly mapped out.[6] The results show that the d bands are split and the spin-up and spin-down Fermi surfaces are quite different. The difference in their volumes

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[1] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV, Chap. 6, pp. 118–145.

[2] J. S. Kouvel and M. E. Fisher, Phys. Rev. **136**, A1626 (1964).

[3] P. Weiss and R. Forrer, Ann. Phys. (Paris) **5**, 153 (1926).

[4] (a) C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962); J. Gammel, W. Marshall, and L. Morgan, Proc. Roy. Soc. (London) **A275**, 257 (1963); (b) T. Izuyama, D. J. Kim, and R. Kubo, J. Phys. Soc. Japan **18**, 1025 (1963).

[5] C. G. Shull, *Electronic Structure and Alloy Chemistry of the Transition Elements* (Interscience Publishers, Inc., New York, 1963), p. 69; R. M. Moon, Phys. Rev. **136**, A195 (1964); H. A. Mook and C. G. Shull, J. Appl. Phys. **37**, 1034 (1966).

[6] J. R. Anderson and A. V. Gold, Phys. Rev. Letters **10**, 277 (1963); E. Fawcett and W. A. Reed, *ibid.* **9**, 336 (1962); A. S. Joseph and A. C. Thorsen, *ibid.* **11**, 554 (1963); D. C. Tsui and R. W. Stark, *ibid.* **17**, 871 (1966); A. V. Gold, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (Institute of Physics and the Physical Society, London, 1965), p. 124; D. R. Stone, thesis, Iowa State University, 1967 (unpublished).

accounts for the magnetization per atom. As was pointed out by Herring, this is a definite proof that the electrons are itinerant.

We would like to show in this paper that one can understand both the localized property and the itinerant property of the magnetic electrons if we regard nickel and iron as a lattice of overlapping Anderson-type localized moments. This type of model was first put forward by Friedel *et al.*,[7] but many details of the model were not worked out in the original article. The basic idea is the following: The *d* states in transition metals act like scattering resonances of the conduction electrons. They are occupied only part of the time by an electron, so that over a long period of time one finds partially occupied *d* states. The spin-up and spin-down electrons in a particular *d* orbital repel each other by the intra-atomic Coulomb force. Depending on the position and the width of the *d* states and the size of the Coulomb energy, the spin-up and spin-down states may have the same or different occupation numbers. In the latter case, one speaks of a localized magnetic moment. A quantitative theory of the one-spin problem was first worked out by Anderson.[8] Hence, it has become customary to refer to this model of localized state as the Anderson model. In practice, the model has proven very helpful in understanding the magnetic properties of dilute alloys of transition metals.

In a pure ferromagnetic metal we expect the *d* orbitals of near-neighbor ions to overlap, so that *d* bands of finite widths appear. This makes it possible for the neighboring ions to exchange their partially trapped electrons and so a kind of exchange interaction takes place. This interaction has been considered as a two-spin problem by Alexander and Anderson[9] and by Moriya.[10] In general they found that the interaction may be either ferromagnetic or antiferromagnetic, and its size agrees with what is needed to explain the observed Curie temperature.

The idea of treating the *d* band as a lattice of scattering resonances has also been applied to nonmagnetic transition metals. In a recent paper, Heine[11] showed that the structure of the *d* band in copper can be quantitatively understood from this point of view. The width of the *d* band is determined mainly by intra-atomic interactions rather than interatomic overlap integrals.

The present paper is a natural outgrowth of the two-spin problem. In Sec. II we summarize the important results of the one-spin problem. In Sec. III the two-spin problem is formulated and the conditions for ferromagnetic or antiferromagnetic coupling are discussed. We also show that, in the limit of small overlap integral, the effective-spin Hamiltonian of the two-spin system is of the Heisenberg form. The same consideration is extended to the N-spin problem in Sec. IV. It is found that, as far as the dynamics of the spins is concerned, the Heisenberg Hamiltonian is valid. In this respect the present model has the property of the localized-spin model. From the band point of view the spin-up and spin-down *d* bands are split by the Coulomb interaction, and they hybridize with the *sp* bands. For ferromagnetic metals the Fermi level is found to lie in the region of *s*-*d* hybridization. Hence, the Fermi surface shows *d* characters, as in the itinerant model. It is therefore possible to understand both the critical properties and the Fermi surface of nickel and iron. Section V summarizes the results of a more physical but rather complex model involving many degenerate levels. Quantitative calculations are carried out for the properties of nickel and iron, and the results are shown to compare well with experiments and band calculations.

II. THE ONE-SPIN PROBLEM

We review here some important properties of the Anderson model. The model consists of a *d* orbital imbedded in a sea of *s*-like band. The Hamiltonian may be written as

$$H=\sum_{\mathbf{k}\sigma}\epsilon_k n_{\mathbf{k}\sigma}+E(n_+ + n_-)+Un_+n_- + \sum_{\mathbf{k}\sigma}\left[V_{sd}c_{\mathbf{k}\sigma}{}^{\dagger}c_\sigma + V_{sd}{}^{*}c_\sigma{}^{\dagger}c_{\mathbf{k}\sigma}\right], \tag{2.1}$$

where the first term on the right-hand side is the total energy of the conduction band, the second term the energy of the *d* orbital, the third term the Coulomb repulsion between the spin-up and spin-down electrons in the *d* orbital, and the last term the configuration mixing between the plane-wave *s* electron states and the *d* orbital. The operators labeled by $\mathbf{k}\sigma$ refer to the *s* electrons and those labeled only by σ refer to the *d* electrons. In the Hartree–Fock (HF) approximation the energy of the *d* electron in spin state σ is given by

$$E_\sigma = E + U\langle n_{-\sigma}\rangle, \tag{2.2}$$

and these quasiparticle states are broadened by the *s*-*d* admixing by the amount

$$2\Delta = 2\pi\hbar^{-1}\sum_{\mathbf{k}} |V_{sd}|^2\delta(E-\epsilon_k). \tag{2.3}$$

Hence the density of the *d* state with spin σ is given by

$$\rho_\sigma(\epsilon) = (1/\pi)\Delta/[(\epsilon-E_\sigma)^2+\Delta^2]. \tag{2.4}$$

The total number of electrons in this state is

$$\langle n_\sigma\rangle = \int_{-\infty}^{\epsilon_F}\rho_\sigma(\epsilon)\,d\epsilon = (1/\pi)\cot^{-1}\{(1/\Delta)(E_\sigma-\epsilon_F)\}. \tag{2.5}$$

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[7] J. Friedel, G. Leman, and S. Olszewski, J. Appl. Phys. **32**, 325S (1961).

[8] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[9] S. Alexander and P. W. Anderson, Phys. Rev. **133**, A1594 (1964).

[10] T. Moriya, Progr. Theoret. Phys. (Kyoto) **33**, 157 (1965).

[11] V. Heine, Phys. Rev. **153**, 673 (1967).

Combining Eqs. (2.5) and (2.2) we find the self-consistent equations for the d-state occupation numbers;

$$\langle n_\sigma\rangle = (1/\pi)\cot^{-1}\{(1/\Delta)(E-\epsilon_F+U\langle n_{-\sigma}\rangle)\}. \quad (2.6)$$

This set of equations may have one solution,

$$\langle n_+\rangle = \langle n_-\rangle,$$

or three sets of solutions,

$$(1) \quad \langle n_+\rangle = n_1, \quad \langle n_-\rangle = n_2,$$

$$(2) \quad \langle n_+\rangle = \langle n_-\rangle,$$

$$(3) \quad \langle n_+\rangle = n_2, \quad \langle n_-\rangle = n_1, \quad n_1 \neq n_2,$$

depending on the sizes of E, U, and Δ. In the first case the net spin of the d states is zero, so that it corresponds to no localized moment. In the second case the solution $\langle n_+\rangle = \langle n_-\rangle$ is unstable. The other two solutions correspond to the spin-up and spin-down configurations of a localized spin with net moment

$$m = \tfrac{1}{2}\hbar n_s,$$

$$n_s = |n_1 - n_2|. \quad (2.7)$$

In a material where there is a set of uncoupled localized states, the spin-up and spin-down configurations are equally likely to occur, so that the material is paramagnetic.

The condition for the localization of a spin is given by, according to Schrieffer and Mattis,[12a]

$$U\rho(\epsilon_F) \geq 1, \quad (2.8)$$

where $\rho(\epsilon_F)$ is the density of the unsplit d states at the Fermi level. This is similar to the condition for the existence of ferromagnetism in the simple band theory.[12b] Schrieffer and Mattis also showed that when the correlation effect is included, the Anderson model will never have a localized moment in the case of low densities $\langle n_\sigma\rangle < 0.3$, or $1-\langle n_\sigma\rangle < 0.3$. However, by including the oribtal degeneracy of the d states as well as the Hund's rule interaction, the localized moment again may occur. It seems that although the Anderson model is not adequate from a rigorous point of view, it does give a simple physical description of a localized spin. Hopefully, after taking into consideration the correlation effect and the degeneracy, the theory in the next few sections will remain valid at least qualitatively.

In the following we present a not so well known property of the one-spin system, namely, the Zeeman splitting. It will be shown that the number of Bohr magnetons as determined from the Zeeman splitting is quite different from that determined from the localized moment n_s. To see this we apply a small steady magnetic field B in the z direction. The additional term to the Hamiltonian is

$$H_f = -\mu_B B(n_+ - n_-), \quad (2.9)$$

where μ_B is the Bohr magneton. The energies of the d states become

$$E_\sigma = E + U\langle n_{-\sigma}\rangle - \mu_B B\sigma, \quad (2.10)$$

where $\sigma = \pm 1$ for the two spin states. Consider the case where the moment is localized: The spin-up and spin-down configurations will no longer have the same energy in the magnetic field. The problem is easily solvable when B is very small. Define a small parameter

$$h = \mu_B B/U; \quad (2.11)$$

then for the spin-up state, the population of the two d states are modified in the presence of the field to

$$\langle n_+\rangle = n_1 + h\xi_1,$$

$$\langle n_-\rangle = n_2 + h\xi_2, \quad (2.12)$$

with $n_1 > n_2$. Putting Eq. (2.12) into Eqs. (2.10) and (2.6) and expanding all quantities in powers of h, we find that the zeroth-order terms cancel from both sides and the first-order terms give the following equations for ξ_1 and ξ_2:

$$\xi_1 + \lambda_1\xi_2 = \lambda_1,$$

$$\xi_2 + \lambda_2\xi_1 = -\lambda_2,$$

where

$$\lambda_1 = \pi^{-1}\frac{U\Delta}{(E_+ - \epsilon_F)^2 + \Delta^2} = U\rho_+(\epsilon_F), \quad (2.13)$$

and $\lambda_2 = U\rho_-(\epsilon_F)$. The solutions are

$$\xi_1 = \lambda_1(1+\lambda_2)/(1-\lambda_1\lambda_2),$$

$$\xi_2 = -\lambda_2(1+\lambda_1)/(1-\lambda_1\lambda_2). \quad (2.14)$$

The Gibbs free energy of the spin-up configuration is

$$G_+ = (E-\epsilon_F)(\langle n_+\rangle + \langle n_-\rangle) + U\langle n_+\rangle\langle n_-\rangle$$
$$= G_0 - \mu_B B n_B + O(h^2).$$

Here

$$n_B = n_1 - n_2 - U^{-1}[(E_+^{(0)} - \epsilon_F)\xi_1 + (E_-^{(0)} - \epsilon_F)\xi_2]. \quad (2.15)$$

G_0 is the free energy of the free spin, and E_1, E_2 are defined by

$$E_1^{(0)} = E + Un_2,$$

$$E_2^{(0)} = E + Un_1.$$

The same thing can be done for the spin-down configuration. The Gibbs free energy for this case is

$$G_- = G_0 + \mu_B B n_B + O(h^2).$$

Hence, the total Zeeman splitting is

$$\Delta G = 2\mu_B B n_B, \quad (2.16)$$

and the quantity n_B is the equivalent number of Bohr

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[12] (a) J. R. Schrieffer and D. C. Mattis, Phys. Rev. **140**, 1412 (1965); (b) See Ref. 1 and the review article of N. F. Mott, Advan. Phys. **13**, 325 (1964).

magnetons. The reason that we compare the Gibbs free energies instead of the internal energies is that the number of particles in the d states change with the field. Since the total number of electrons in the metal is fixed, a change δn_d in the d states brings about a change $-\delta n_d$ in the number of conduction electrons, so that the energy of the conduction electron system changes by $-\epsilon_F \delta n_d$. The change in energy of the entire metal is $\delta E_d - \epsilon_F \delta n_d$, which is just the change in Gibbs free energy of the d states.

At a finite temperature T, the magnetic moment of a collection of N noninteracting localized moments is given by

$$M = \mu_B N n_s \tanh(\mu_B B n_B / kT). \tag{2.17}$$

For $kT \gg \mu_B B n_B$, we can define a paramagnetic susceptibility

$$\chi = N \mu_B^2 n_s n_B / kT. \tag{2.18}$$

Let n_χ be the number of Bohr magnetons determined by the susceptibility measurement; we find the relation

$$n_\chi^2 = n_s n_B. \tag{2.19}$$

It is true, in general, that

$$n_B \geq n_s, \tag{2.20}$$

so that

$$n_\chi \geq n_s. \tag{2.21}$$

The Bohr-magneton numbers of many materials are listed by Rhodes and Wohlfarth.[13] From their data and the assumption that the localized spins of nickel are best represented by $S = \frac{1}{2}$, one can deduce that $n_s = 0.61$ and $n_\chi = 0.93$. Hence, the above-mentioned inequalities are verified.

III. THE TWO-SPIN PROBLEM

When there are two spins with their wave functions overlapping, the Hamiltonian may be written as, with a proper choice of phase,

$$\begin{aligned} H = {} & \sum_{\mathrm{k}\sigma} \epsilon_k n_{\mathrm{k}\sigma} + E \sum_\sigma (n_{1\sigma} + n_{2\sigma}) + U(n_{1+} n_{1-} \\ & + n_{2+} n_{2-}) + \sum_\sigma V[c_{1\sigma}{}^\dagger c_{2\sigma} + c_{2\sigma}{}^\dagger c_{1\sigma}] \\ & + \sum_{\mathrm{k}\sigma} \{ V_{sd} [c_{\mathrm{k}\sigma}{}^\dagger c_{1\sigma} \exp(-i_{\mathrm{k}} \cdot \mathbf{R}_1) \\ & + c_{\mathrm{k}\sigma}{}^\dagger c_{2\sigma} \exp(-i_{\mathrm{k}} \cdot \mathbf{R}_2)] + \mathrm{H.c.} \}. \end{aligned} \tag{3.1}$$

The quantity V is the overlap integral between the two orbitals. We define the Green's functions as in the work of Alexander and Anderson.[9] If the indirect exchange effect is ignored,[14] the one-particle Green's functions for the d states satisfy the equations

$$\begin{aligned} &(\epsilon - E_{i\sigma} + i\Delta) G_{ii}{}^\sigma(\epsilon) - V G_{ji}{}^\sigma(\epsilon) = 1, \\ &(\epsilon - E_{j\sigma} + i\Delta) G_{ji}{}^\sigma(\epsilon) - V G_{ii}{}^\sigma(\epsilon) = 0, \qquad i,j = 1,2. \end{aligned} \tag{3.2}$$

The solution is

$$\begin{aligned} G_{ii}{}^\sigma(\epsilon) &= \frac{\epsilon - E_{j\sigma} + i\Delta}{(\epsilon - E_{i\sigma} + i\Delta)(\epsilon - E_{j\sigma} + i\Delta) - V^2}, \\ G_{ji}{}^\sigma(\epsilon) &= \frac{V}{(\epsilon - E_{i\sigma} + i\Delta)(\epsilon - E_{j\sigma} + i\Delta) - V^2}, \end{aligned} \tag{3.3}$$

where $E_{i\sigma} = E + U\langle n_{i,-\sigma} \rangle$. The self-consistent conditions are

$$\begin{aligned} \langle n_{i\sigma} \rangle &= \int_{-\infty}^{\epsilon_F} \rho_{i\sigma}(\epsilon)\, d\epsilon, \\ \rho_{i\sigma}(\epsilon) &= -(1/\pi) \operatorname{Im} G_{ii}{}^\sigma(\epsilon). \end{aligned} \tag{3.4}$$

The off-diagonal Green's functions are related to the expectation values

$$\langle c_{i\sigma}{}^\dagger c_{j\sigma} \rangle = -\pi^{-1} \int_{-\infty}^{\epsilon_F} \operatorname{Im} G_{ji}{}^\sigma(\epsilon)\, d\epsilon. \tag{3.5}$$

We shall discuss the coupling energy in the limit of very small V. The Green's functions may be approximated by

$$\begin{aligned} G_{ii}{}^\sigma(\epsilon) &\cong (\epsilon - E_{i\sigma} + i\Delta)^{-1} + \frac{V^2}{(\epsilon - E_{i\sigma} + i\Delta)^2 (\epsilon - E_{j\sigma} + i\Delta)}, \\ G_{ji}{}^\sigma(\epsilon) &\cong V / (\epsilon - E_{i\sigma} + i\Delta)(\epsilon - E_{j\sigma} + i\Delta). \end{aligned} \tag{3.6}$$

Consider first the spin-parallel configuration. By symmetry, we must have

$$\begin{aligned} \langle n_{1+} \rangle &= \langle n_{2+} \rangle = n_1 + \eta_1 V^2, \\ \langle n_{1-} \rangle &= \langle n_{2-} \rangle = n_2 + \eta_2 V^2. \end{aligned} \tag{3.7}$$

Substituting into Eq. (3.6) and expanding again in powers of V^2, we obtain

$$\begin{aligned} G_{ii}{}^\sigma(\epsilon) &\cong (\epsilon - E_\sigma{}^{(0)} + i\Delta)^{-1} + \frac{\eta_1 V^2 U}{(\epsilon - E_\sigma{}^{(0)} + i\Delta)^2} \\ &\qquad + V^2 / (\epsilon - E_\sigma{}^{(0)} + i\Delta)^3, \\ G_{ji}{}^\sigma(\epsilon) &= V / (\epsilon - E_\sigma{}^{(0)} + i\Delta)^2, \end{aligned} \tag{3.8}$$

where

$$\begin{aligned} E_+{}^{(0)} &= E + U n_2, \\ E_-{}^{(0)} &= E + U n_1. \end{aligned} \tag{3.9}$$

The self-consistent condition, Eq. (3.4), gives the following equations for η_1 and η_2:

$$\begin{aligned} \eta_1 + \lambda_1 \eta_2 &= \mu_1, \\ \eta_2 + \lambda_2 \eta_1 &= \mu_2, \end{aligned} \tag{3.10}$$

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[13] P. Rhodes and E. P. Wohlfarth, Proc. Roy. Soc. (London) A273, 247 (1963).

[14] The indirect-exchange effect in the Anderson model has been discussed by D. Kim and Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **30**, 743 (1963); and recently by B. Caroli, J. Phys. Chem. Solids **28**, 1427 (1964).

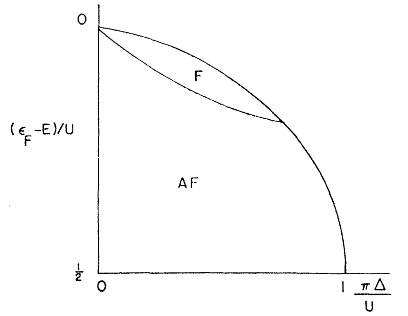

FIG. 1. The figure shows one-half of the region on the $(\epsilon_F-E)/U$ and Δ/U plane in which a localized spin is stable according to the Anderson one-orbital model. This region is subdivided so that in the area marked by F the coupling between two identical localized spins is ferromagnetic and in the area marked AF the coupling is antiferromagnetic.

where λ_1, λ_2 are defined in Eq. (2.13) and

$$\mu_1=\frac{\Delta(E_+^{(0)}-\epsilon_F)}{\pi[(E_+^{(0)}-\epsilon_F)^2+\Delta^2]^2},$$

$$\mu_2=\frac{\Delta(E_-^{(0)}-\epsilon_F)}{\pi[(E_-^{(0)}-\epsilon_F)^2+\Delta^2]^2}. \qquad (3.11)$$

Hence,

$$\eta_1=(\mu_1-\lambda_1\mu_2)/(1-\lambda_1\lambda_2),$$

$$\eta_2=(\mu_2-\lambda_2\mu_1)/(1-\lambda_1\lambda_2). \qquad (3.12)$$

Similarly, Eq. (3.5) gives

$$\langle c_{i+}{}^\dagger c_{j+}\rangle=-(V/U)\lambda_1,$$

$$\langle c_{i-}{}^\dagger c_{j-}\rangle=-(V/U)\lambda_2. \qquad (3.13)$$

The Gibbs free energy of the two spins can be easily found to be

$$\begin{aligned}G_p=(E-\epsilon_F)&\sum_{i\sigma}\langle n_{i\sigma}\rangle+U\sum_i\langle n_{i+}\rangle\langle n_{i-}\rangle\\&+V\sum_\sigma[\langle c_{i\sigma}{}^\dagger c_{2\sigma}\rangle+\langle c_{2\sigma}{}^\dagger c_{1\sigma}\rangle]\\=2G_0+2V^2[(E_+^{(0)}-\epsilon_F)\eta_1&+(E_-^{(0)}-\epsilon_F)\eta_2\\&-(1/U)(\lambda_1+\lambda_2)],\end{aligned} \qquad (3.14)$$

where $2G_0$ is the free energy of the two noninteracting spins.

For the antiparallel spin case, we put in

$$\langle n_{1+}\rangle=\langle n_{2-}\rangle=n_1+\zeta_1V^2,$$

$$\langle n_{1-}\rangle=\langle n_{2+}\rangle=n_2+\zeta_2V^2. \qquad (3.15)$$

A similar treatment gives

$$\zeta_1=(\nu_1-\lambda_1\nu_2)/(1-\lambda_1\lambda_2),$$

$$\zeta_2=(\nu_2-\lambda_2\nu_1)/(1-\lambda_1\lambda_2), \qquad (3.16)$$

where

$$\nu_1=(\lambda_1-1)/U^2(n_1-n_2),$$

$$\nu_2=(\lambda_2-1)/U^2(n_2-n_1). \qquad (3.17)$$

Also, Eq. (3.5) gives

$$\langle c_{1\sigma}{}^\dagger c_{2\sigma}\rangle=\langle c_{2\sigma}{}^\dagger c_{1\sigma}\rangle=-V/U.$$

The Gibbs free energy is found to be

$$\begin{aligned}G_a&=2G_0+2V^2[(E_+^{(0)}-\epsilon_F)\zeta_1+(E_-^{(0)}-\epsilon_F)\zeta_2-2/U]\\&=2G_0-2V^2/U.\end{aligned} \qquad (3.18)$$

We can define the exchange energy J as

$$J=G_a-G_p, \qquad (3.19)$$

so that the sign of J will determine the relative stability of the two-spin configurations.

The stability analysis is done numerically and the results are plotted in Figs. 1 and 2. Figure 1 shows one-half of the region in $(\epsilon_F-E)/U$ and the Δ/U plane where the spin is localized. The region is subdivided so that in the area marked by F the exchange energy J is positive and in the area AF the quantity J is negative. Figure 2 shows the same region mapped on the n_1, n_2 plane. There is a localized moment everywhere in the square except along the diagonal $n_1=n_2$. The various curves in the drawing are the contours of constant J with the values of J marked beside them. The unit of J is V^2/U. It can be seen that in the strictly localized case $n_1=1$, $n_2=0$ or vice versa, the coupling is always antiferromagnetic. This is consistent with the electron-spin alignment in a hydrogen molecule. The ferromagnetic coupling becomes possible when both n_1 and n_2 are less than unity, i.e., when the moments are partially localized. The solid curve on the bottom part of the diagram is the boundary under which the quantity $n_B<1$. Experimentally we find that n_s and n_χ are not too much different. This implies that n_B is nearly unity for one localized electron. It is clear from the diagram that the region around $n_B\cong1$ is mostly ferromagnetic. For an order-of-magnitude estimate of J,

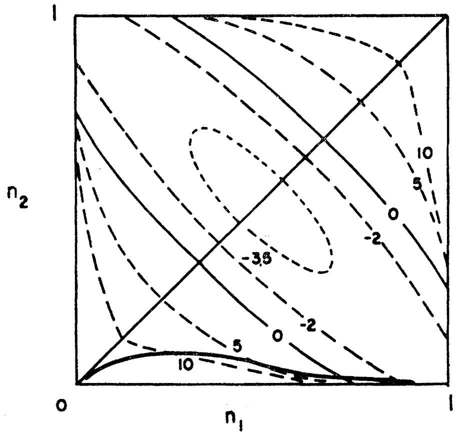

FIG. 2. The contour lines of constant exchange energy on the n_1, n_2 diagram as derived from the one-orbital model. The thick curve on the bottom of the diagram is the contour line for $n_B=1$.

we take

$$J \cong V^2/U.$$

For nickel, we estimate that $V \cong 0.2$ eV from the width of the d band, and we take $U \cong 5$ eV. These give $J \cong 0.01$ eV, and a Curie temperature of about 600°K for a face-centered cubic (fcc) lattice. The model predicts the correct order of magnitude of the Curie temperature for nickel.

The criterion for the relative stability of the ferromagnetic versus antiferromagnetic coupling was discussed from the physical point of view by Alexander and Anderson. In the well localized case, the energy can be gained by virtual transfer of an electron in the filled spin-down level on one ion to the empty spin-down level on another ion. This is just the superexchange mechanism,[15] and it favors antiferromagnetism. On the other hand, in the partially localized case, energy can be gained by real transitions of electrons of one spin back and forth between the two ions. This interaction favors ferromagnetism and is most strong when one level has a high density of states at the Fermi level.

It will be shown in the following that if the two spins are quantized along different axes making an angle θ, the exchange energy between them is modified by the factor $\cos\theta$. The implication is that the effective Hamiltonian between the spins is the Heisenberg Hamiltonian

$$H_s = -2J\mathbf{S}_1 \cdot \mathbf{S}_2, \tag{3.20}$$

where $\mathbf{S}_1$, $\mathbf{S}_2$ are spin-$\frac{1}{2}$ operators. For this problem the overlap term in the Hamiltonian of Eq. (3.1) is of the form

$$V[c_{1+}{}^{\dagger}c_{2+}\cos\tfrac{1}{2}\theta + c_{1+}{}^{\dagger}c_{2-}\sin\tfrac{1}{2}\theta - c_{1-}{}^{\dagger}c_{2+}\sin\tfrac{1}{2}\theta + c_{1-}{}^{\dagger}c_{2-}\cos\tfrac{1}{2}\theta + \text{H.c.}]. \tag{3.21}$$

The equation for the Green's functions are

$$\begin{aligned}
(\epsilon - E_{1\sigma} + i\Delta)G_{11}{}^{\sigma\sigma}(\epsilon) - V\cos\tfrac{1}{2}\theta G_{21}{}^{\sigma\sigma}(\epsilon) \\
- V\sin\tfrac{1}{2}\theta G_{21}{}^{-\sigma\sigma}(\epsilon) &= 1, \\
(\epsilon - E_{1,-\sigma} + i\Delta)G_{11}{}^{-\sigma\sigma}(\epsilon) + V\sin\tfrac{1}{2}\theta G_{21}{}^{\sigma\sigma}(\epsilon) \\
- V\cos\tfrac{1}{2}\theta G_{21}{}^{-\sigma\sigma}(\epsilon) &= 0, \\
(\epsilon - E_{2\sigma} + i\Delta)G_{21}{}^{\sigma\sigma}(\epsilon) + V\sin\tfrac{1}{2}\theta G_{11}{}^{-\sigma\sigma}(\epsilon) \\
- V\cos\tfrac{1}{2}\theta G_{11}{}^{\sigma\sigma}(\epsilon) &= 0, \\
(\epsilon - E_{2,-\sigma} + i\Delta)G_{21}{}^{-\sigma\sigma}(\epsilon) - V\cos\tfrac{1}{2}\theta G_{11}{}^{-\sigma\sigma}(\epsilon) \\
- V\sin\tfrac{1}{2}\theta G_{11}{}^{\sigma\sigma}(\epsilon) &= 0,
\end{aligned} \tag{3.22}$$

and other four similar equations with indices 1, 2 exchanged. Solving for $G_{11}{}^{\sigma\sigma}(\epsilon)$, $G_{12}{}^{\sigma\sigma}(\epsilon)$, and $G_{12}{}^{-\sigma\sigma}(\epsilon)$ to the lowest order in V, we obtain

$$\begin{aligned}
G_{11}{}^{\sigma\sigma}(\epsilon) &\cong (\epsilon - E_{1\sigma} + i\Delta)^{-1} + \frac{V^2\cos^2\frac{1}{2}\theta}{(\epsilon - E_{1\sigma} + i\Delta)^2(\epsilon - E_{2\sigma} + i\Delta)} \\
&\quad + \frac{V^2\sin^2\frac{1}{2}\theta}{(\epsilon - E_{1\sigma} + i\Delta)^2(\epsilon - E_{2,-\sigma} + i\Delta)}, \\
G_{21}{}^{\sigma\sigma}(\epsilon) &\cong \frac{V\cos\frac{1}{2}\theta}{(\epsilon - E_{1\sigma} + i\Delta)(\epsilon - E_{2\sigma} + i\Delta)}, \\
G_{21}{}^{-\sigma\sigma}(\epsilon) &\cong \frac{V\sin\frac{1}{2}\theta}{(\epsilon - E_{1\sigma} + i\Delta)(\epsilon - E_{2,-\sigma} + i\Delta)}.
\end{aligned} \tag{3.23}$$

The Green's functions $G_{22}{}^{\sigma\sigma}$, $G_{12}{}^{\sigma\sigma}$, and $G_{21}{}^{-\sigma\sigma}$ are given by similar expressions. Again from the basic symmetry of the problem, we assume

$$\begin{aligned}
\langle n_{1+}\rangle &= \langle n_{2+}\rangle = n_1 + \eta_1 V^2, \\
\langle n_{1-}\rangle &= \langle n_{2-}\rangle = n_2 + \eta_2 V^2, \\
E_{1+} &= E_{2+} = E_{+}{}^{(0)} + U\eta_1 V^2, \\
E_{1-} &= E_{2-} = E_{-}{}^{(0)} + U\eta_2 V^2.
\end{aligned} \tag{3.24}$$

Using the same procedure as the derivation of Eq. (3.10), we obtain

$$\begin{aligned}
\eta_1 + \lambda_1\eta_2 &= \mu_1\cos^2\tfrac{1}{2}\theta + \nu_1\sin^2\tfrac{1}{2}\theta, \\
\eta_2 + \lambda_2\eta_1 &= \mu_2\cos^2\tfrac{1}{2}\theta + \nu_2\sin^2\tfrac{1}{2}\theta.
\end{aligned} \tag{3.25}$$

This gives

$$\eta_1 = \cos^2\tfrac{1}{2}\theta\,\frac{\mu_1 - \lambda_1\mu_2}{1 - \lambda_1\lambda_2} + \sin^2\tfrac{1}{2}\theta\,\frac{\nu_1 - \lambda_1\nu_2}{1 - \lambda_1\lambda_2}, \tag{3.26}$$

and a similar expression for η_2. Similar to the derivation of Eq. (3.13), one finds

$$\begin{aligned}
\langle c_{1+}{}^{\dagger}c_{2+}\rangle &= -V\lambda_1\cos\tfrac{1}{2}\theta/U, \\
\langle c_{1-}{}^{\dagger}c_{2-}\rangle &= -V\lambda_2\cos\tfrac{1}{2}\theta/U, \\
\langle c_{1-}{}^{\dagger}c_{2+}\rangle &= \langle c_{1+}{}^{\dagger}c_{2-}\rangle = -V\sin\tfrac{1}{2}\theta/U.
\end{aligned} \tag{3.27}$$

The free energy of this state, G_θ, is found to be

$$\begin{aligned}
G_\theta &= G_p\cos^2\tfrac{1}{2}\theta + G_a\sin^2\tfrac{1}{2}\theta \\
&= \tfrac{1}{2}(G_p + G_a) - \tfrac{1}{2}J\cos\theta.
\end{aligned} \tag{3.28}$$

This shows that the equivalent spin Hamiltonian is that given by Eq. (3.20).

Although the derivation of the spin Hamiltonian given here is semiclassical, it seems that a fully quantum-mechanical treatment is possible if the Green's functions are solved in a rotationally invariant way rather than the HF decoupling scheme. This remains to be worked out.

Alexander and Anderson showed that the overlap between two orbitals also influences the stability of the localized moments. In fact, the region of stable moment in Fig. 1 is significantly reduced even with a rather small amount of overlap. Thus, the model developed

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[15] P. W. Anderson, Solid State Phys. 14, 99 (1963).

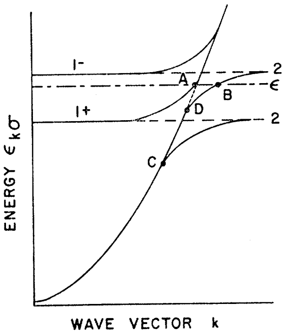

FIG. 3. The schematic band structure of a ferromagnetic metal based on the one-orbital model. See text for the meaning of the symbols.

here for ferromagnetism is only stable when the *d* bands are narrow. This may be the reason that ferromagnetism is only observed in 3*d* transition metals but not in 4*d* and 5*d* elements.

IV. THE *N*-SPIN PROBLEM

Now we consider a pure metal in which there is a whole lattice of localized moments. The Hamiltonian for such a system may be written as

$$H=\sum_{\mathbf{k}\sigma}\epsilon_k n_{\mathbf{k}\sigma}+E\sum_{i\sigma}n_{i\sigma}+U\sum_i n_{i+}n_{i-}+\sum_{i<j,\sigma}V[c_{i\sigma}{}^\dagger c_{j\sigma}+c_{j\sigma}{}^\dagger c_{i\sigma}]+\sum_{\mathbf{k},i,\sigma}[V_{sd}c_{\mathbf{k}\sigma}{}^\dagger c_{i\sigma}\exp(-i\mathbf{k}\cdot\mathbf{R}_i)+\text{H.c.}],\quad(4.1)$$

where the overlap term is summed over nearest neighbors only. The various properties of the system will be discussed in the following subsections.

A. Equivalent Spin Hamiltonian

We first establish the result that when the energy is expanded in powers of V/U, the lowest-order term which depends on spin orientations consists of sums of energies for pairs of spins. Assume that all the localized moments are quantized along the same direction and the particular spin configuration to be studied has a number of up spins and a number of down spins in a definite spatial distribution. In the same approximation as in Sec. III, the Green's functions are found to satisfy the coupled equations

$$(\epsilon-E_{i\sigma}+i\Delta)G_{ii}{}^\sigma(\epsilon)-V\sum_j G_{ji}{}^\sigma(\epsilon)=1,\quad(4.2)$$

$$(\epsilon-E_{j\sigma}+i\Delta)G_{ji}{}^\sigma(\epsilon)-V\sum_l G_{li}{}^\sigma(\epsilon)=0,\quad(4.3)$$

where i, j, and l label the lattice sites, the sum on j is over the nearest neighbors of i, and the sum on l is over the nearest neighbors of j. From past experience we know that $G_{ij}{}^\sigma$ is of the order $(V/U)G_{ii}{}^\sigma$ if i and j are nearest neighbors. From Eq. (4.3) we can readily see that $G_{ij}{}^\sigma$ is of the order $(V/U)^2G_{ii}{}^\sigma$ if i and j are next neighbors, and in general $(V/U)^nG_{ii}{}^\sigma$ if the shortest route between i and j connects $(n-1)$ other lattice sites. Hence, to the lowest order in V/U we may ignore all $G_{ij}{}^\sigma$ except the nearest-neighbor ones. When i and j are nearest neighbors, the sum on l in the second term of Eq. (4.3) consists of next-neighbor Green's functions except the one with $l=i$. Following the above argument we keep only this term. Then the above equations form a closed set and the Green's functions are found to be

$$G_{ii}{}^\sigma(\epsilon)\cong\left[\epsilon-E_{i\sigma}+i\Delta-\sum_j\frac{V^2}{\epsilon-E_{j\sigma}+i\Delta}\right]^{-1}\cong\frac{1}{(\epsilon-E_{i\sigma}+i\Delta)^{-1}}+\sum_j\frac{V^2}{(\epsilon-E_{i\sigma}+i\Delta)^2(\epsilon-E_{j\sigma}+i\Delta)},\quad(4.4)$$

$$G_{ji}{}^\sigma(\epsilon)\cong(V/\epsilon-E_{j\sigma}+i\Delta)G_{ii}{}^\sigma(\epsilon)\cong V/(\epsilon-E_{j\sigma}+i\Delta)(\epsilon-E_{i\sigma}+i\Delta).\quad(4.5)$$

The sum appearing in Eq. (4.4) is over nearest neighbors only.

The rest of the discussion follows the same path as the two-spin problem. Assume that the central spin i is in the up state, and among its z nearest neighbors y of them are in the spin-up state and $(z-y)$ in the spin-down state. For the occupation numbers, we assume

$$\langle n_{i+}\rangle=n_1+\eta_1V^2,\qquad\langle n_{i-}\rangle=n_2+\eta_2V^2.\quad(4.6)$$

Then together with the self-consistent condition, Eq. (3.4), we find

$$\eta_1+\lambda_1\eta_2=y\mu_1+(z-y)\nu_1,\qquad\eta_2+\lambda_2\eta_1=y\mu_2+(z-y)\nu_2.\quad(4.7)$$

Thus,

$$\eta_1=y\left(\frac{\mu_1-\lambda_1\mu_2}{1-\lambda_1\lambda_2}\right)+(z-y)\left(\frac{\nu_1-\lambda_1\nu_2}{1-\lambda_1\lambda_2}\right),\quad(4.8)$$

and a similar expression for η_2. For the off-diagonal correlation functions, we find

$$\langle c_{i+}{}^\dagger c_{j+}\rangle=-V\lambda_1/U\quad(4.9)$$

for parallel spin pairs, and

$$\langle c_{i+}{}^\dagger c_{j+}\rangle=-V/U\quad(4.10)$$

for antiparallel spin pairs. The spin-down correlation functions have similar expressions. When we calculate the free energy of the central spin, it is rather straightforward to obtain

$$G_i=G_0+V^2[(E_+{}^{(0)}-\epsilon_F)\eta_1+(E_-{}^{(0)}-\epsilon_F)\eta_2]-(2V^2/U)[y(\lambda_1+\lambda_2)+(z-y)]=G_0+y(G_p-G_0)+(z-y)(G_a-G_0).\quad(4.11)$$

If we carry out this calculation for all spins and add up the result, keeping in mind that the mutual interaction term is to be divided by 2, we obtain

$$G=NG_0+\sum_{p1}(G_p-G_0)+\sum_{p2}(G_a-G_0), \quad (4.12)$$

where $\sum_{p1}$ is over all parallel spin pairs and $\sum_{p2}$ over all antiparallel spin pairs. The expression for G may be rewritten in a more illuminating manner:

$$G=NG_0+\tfrac{1}{2}Nz(G_p+G_a-2G_0)+\tfrac{1}{2}\sum_{p1}(-J)+\tfrac{1}{2}\sum_{p2}(J).$$

This in turn suggests the spin Hamiltonian

$$H_s=-2J\sum_{i<j}\mathbf{S}_i\cdot\mathbf{S}_j \quad (4.13)$$

summed over pairs of nearest neighbors. One can justify the Heisenberg form of the Hamiltonian in detail by assuming arbitrary axes of quantization for all the spins. But this is hardly necessary because to the order of V/U that we have expanded the energy, the contributions from various pairs simply add. The Heisenberg Hamiltonian must therefore follow on the basis of the two-spin calculation of Sec. III.

B. Energy Bands and Fermi Surface

We consider the energy bands at 0°K when all spins are in the up state. In the HF approximation the Hamiltonian for the system, Eq. (4.1), may be approximated by

$$\begin{aligned}H=&\sum_{\mathbf{k}\sigma}\epsilon_k n_{\mathbf{k}\sigma}+\sum_i(E_+^{(0)}n_{i+}+E_-^{(0)}n_{i-})\\&-U\sum_i\langle n_{i+}\rangle\langle n_{i-}\rangle+\sum_{\sigma,i<j}V(c_{i\sigma}^\dagger c_{j\sigma}+c_{j\sigma}^\dagger c_{i\sigma})\\&+\sum_{\mathbf{k}\sigma i}[V_{sd}c_{\mathbf{k}\sigma}^\dagger c_{i\sigma}\exp(i\mathbf{k}\cdot\mathbf{R}_i)+\text{H.c.}]. \quad (4.14)\end{aligned}$$

The first term gives the plane wave like s (or p) band. For the second and third term we make a transformation to the Bloch states

$$b_{\mathbf{k}\sigma}=1/(N)^{\frac{1}{2}}\sum_i c_{i\sigma}\exp(i\mathbf{k}\cdot\mathbf{R}_i). \quad (4.15)$$

Then these terms give the split d bands in the tight-binding approximation

$$\sum_{\mathbf{k}\sigma}E_{\mathbf{k}\sigma}n_{\mathbf{k}\sigma}', \quad (4.16)$$

where

$$\begin{aligned}n_{\mathbf{k}\sigma}'&=b_{\mathbf{k}\sigma}^\dagger b_{\mathbf{k}\sigma},\\E_{\mathbf{k}\sigma}&=E_\sigma^{(0)}+zV\gamma(\mathbf{k}),\\\gamma(\mathbf{k})&=\frac{1}{z}\sum_{\delta}\exp(i\mathbf{k}\cdot\boldsymbol{\delta}). \quad (4.17)\end{aligned}$$

The last sum is over all nearest neighbors of an arbitrary lattice point. The band splitting is

$$\Delta E=E_{\mathbf{k}-}-E_{\mathbf{k}+}=U(n_1-n_2), \quad (4.18)$$

which is proportional to the total saturation moment. Finally, the s-d admixing term causes the s and d bands to hybridize near their crossing point. The hybridized bands are given by

$$\epsilon_{\mathbf{k}\sigma}^{1,2}=\tfrac{1}{2}\{\epsilon_k+E_{\mathbf{k}\sigma}\pm[(\epsilon_k-E_{\mathbf{k}\sigma})^2+4N\,|\,V_{sd}\,|^2]^{1/2}\}, \quad (4.19)$$

where the superscript 1 refers to the positive value of the square root and 2 refers to the negative value. A schematic diagram of the bands is shown in Fig. 3. The various bands are identified by the superscript defined above and the spin state. The finite width of the d band is ignored because, as observed by Heine,[11] the structure of the d band is largely determined by the s-d hybridization. We choose to represent nickel by a point on Fig. 2, where the spin-up state is almost completely filled and the spin-down state about half-filled. This gives rise to a Fermi level at the position shown in Fig. 3. Since the width of the localized d states corresponds to the region where the s-d hybridization takes place, the Fermi level must go through this region for both bands. The Fermi surfaces are represented by the points A and B on the band scheme. For the majority spin band, the Fermi surface at A is largely of s character. This piece has been observed experimentally to resemble very much the Fermi surface of copper.[6] For the minority spin band the Fermi surface B shows strong d character.

There is some indirect experimental confirmation to our prediction that the Fermi surface for the minority spin band in nickel is in the s-d hybridization region. In the band calculations of Phillips and Hodges *et al.*[16,17] the ordering of the d bands is chosen to resemble that in copper, i.e., they put L_2' above L_3. This band scheme explains the Kerr effect in nickel, as shown by Cooper.[18] According to this scheme, there should be a small hole pocket centered at the point L on the reciprocal lattice. Experimentally, this piece was not observed.[19] Krinchik[20] pointed out that one can understand the Kerr effect equally well if the d bands are in an inverted order, so that L_{32} lies above L_2. The band structure he suggested shows that the copper-like neck in the majority spin band is given by the L_{32} level and the hole pocket at L no longer exists. Recently, Hodges[21] repeated the interpolation calculation using the inverted band order and confirmed the postulated bands of Krinchik. In this new band scheme the Fermi level for the minority band passes through the middle of the hybridization

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[16] J. C. Phillips and L. F. Mattheiss, Phys. Rev. Letters **11**, 556 (1963); J. C. Phillips, Phys. Rev. **133**, A1020 (1964).

[17] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).

[18] B. R. Cooper, Phys. Rev. **139**, A1504 (1965); B. R. Cooper and H. Ehrenreich, Solid State Commun. **2**, 171 (1964); B. R. Cooper, H. Ehrenreich, and L. Hodges, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (Institute of Physics and the Physical Society, London, 1965), p. 110.

[19] D. C. Tsui and R. W. Stark, Ref. 6. D. R. Stone, Ref. 6.

[20] G. S. Krinchik and E. A. Canshina, Phys. Letters **23**, 294 (1966).

[21] L. Hodges (private communication).

band gap at L as a dramatic verification of our prediction.

If we roughly divide the electrons as localized and free according to whether they have any appreciable d character, we find that in the majority spin band the free electrons fill up the k space to the point C in Fig. 3; and in the minority spin band they fill up to the point D. It is evident from Fig. 3 that there are more free electrons in the spin-down state than in the spin-up state. This negative polarization of the conduction electrons was first derived by Anderson[8] using the localized-spin picture. Schrieffer and Wolff[22] showed that the s-d admixing leads to a spin-dependent s-d interaction which is antiferromagnetic. One may regard the negative polarization of the free electrons as the result of this effective exchange force.[23]

At finite temperatures two things happen to the d bands. If we denote the reduced magnetization by m,

$$m=M(T)/M(0), \tag{4.20}$$

then the average occupation number of the spin-up and spin-down states will be

$$\begin{aligned}\langle n_+\rangle &= \tfrac{1}{2}(1+m)n_1+\tfrac{1}{2}(1-m)n_2,\\ \langle n_-\rangle &= \tfrac{1}{2}(1-m)n_1+\tfrac{1}{2}(1+m)n_2.\end{aligned} \tag{4.21}$$

Hence, the d-band splitting becomes

$$\Delta E=U(\langle n_+\rangle-\langle n_-\rangle)=Um(n_1-n_2). \tag{4.22}$$

Eventually, when the temperature is above the Curie point, the d bands become degenerate in spin. On the other hand, the fluctuation in occupation numbers of the localized states gives rise to a finite width of the Bloch states. The disruption of the perfect periodic lattice produces the temperature-dependent spin disorder resistivity and other related transport properties.

As in the previous section, if we take $U\cong 5$ eV, $n_1-n_2\cong 0.5$, we obtain the d-band splitting for nickel,

$$\Delta E\cong 2.5 \text{ eV},$$

which is much too large compared with the band-calculation result $\Delta E\cong 0.5$ eV.[19,17] It will be shown in Sec. V that better agreement may be achieved by including the orbital degeneracy of the d states in the analysis.

C. Elementary Excitations

We have derived a localized spin Hamiltonian H_s and demonstrated a band structure. It is important to determine which type of description one should use to discuss the various types of excitations. The key to the answer lies in the lifetime of the localized d states $\tau_d=\hbar/\Delta$. Since $\Delta\cong 1$ eV, we estimate $\tau_d\cong 10^{-15}$ sec. We first examine the spin waves. The typical spin-wave energy is of the order $kT_c\cong 0.05$ eV, so that over one period of the spin-wave oscillation, the d states are filled and emptied a large number of times. As a result, only the average occupation numbers of the localized d states play a role in the spin-wave excitations, and it is correct to treat the spin waves by using the Heisenberg Hamiltonian, Eq. (4.13). (The indirect-exchange effect, which has been ignored in the present discussion, may significantly modify the spin-wave spectrum.) The same criterion applies to the critical-fluctuation problem. Hence, it is understandable why the critical parameter γ is close to the value $\frac{4}{3}$ for a Heisenberg model.

The spin waves have also been discussed by many authors[24] on the fully itinerant model. A spin wave is pictured as a collective motion of an electron in the spin-down state and a hole in the spin-up state. However, from the d-state lifetime criterion, one can see that such an electron-hole pair must undergo many changes of identity between s and d characteristics during one spin-wave period. Any discussion of spin waves on a single, unhybridized band model is incompatible with the present model.

We now turn to the single-electron excitations. Since the energy of this type of modes is of the order of $\epsilon_F=5$ eV, so that the concept of average occupation numbers of d states has no meaning. Instead, the d electrons must be treated as a part of the band. In band calculations the d-band splitting is determined by the occupation numbers of the Bloch states. However, since

$$\sum_{\mathbf{k}} n_{\mathbf{k}\sigma}'=N^{-1}\sum_{\mathbf{k}}\sum_{ij} c_{i\sigma}{}^{\dagger}c_{j\sigma}\exp(-i\mathbf{k}\cdot\mathbf{R}_{ij})=\sum_i n_{i\sigma},$$

the present calculation of d-band splitting in terms of the occupation numbers of the localized d states is entirely equivalent to the usual procedure.

The specific heat of the material is determined by the spectra of the elementary excitations. The electronic contribution depends on the density of states at the Fermi level, so that the d character of the Fermi surface will give rise to a larger density of states and a larger specific heat than s-band metals. The spin-wave contribution can be calculated in the familiar way from the effective spin Hamiltonian.

D. Neutron Scattering Form Factor

The velocity of thermal neutrons is estimated to be of the order 10^5 cm/sec. Taking the diameter of the magnetic ion to be 1 Å, we find the neutron scattering reaction time to be 10^{-13} sec, which is two orders of magnitude longer than the d-state lifetime. Therefore, the neutron detects only the average occupation of the d states. If the orbital wave function of the d state at the ith ion is $\psi(\mathbf{r}-\mathbf{R}_i)$, then the form factor for the

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[22] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).

[23] For a discussion of other mechanisms of conduction electron polarization, see Ref. 1, pp. 259–267.

[24] A comprehensive list of references on the spin waves of itinerant electrons is given in the review article of C. Herring, Ref. 1, p. 367, Table X.

d electron with spin σ is given by

$$f_\sigma(\mathbf{q})=\langle n_\sigma\rangle\int\exp(i\mathbf{q}\cdot\mathbf{r})\,|\psi(\mathbf{r})|^2d^3r. \tag{4.23}$$

The total form factor is

$$f(\mathbf{q})=f_+(\mathbf{q})-f_-(\mathbf{q})=(n_1-n_2)\int\exp(i\mathbf{q}\cdot\mathbf{r})\,|\psi(\mathbf{r})|^2d^3r. \tag{4.24}$$

In the tight-binding case, $\psi(\mathbf{r})$ is the same as the atomic orbital wave function, so that the neutron form factor in the metal is identical to that in the free atom except for a numerical factor. The observed negative background is perhaps due to the negative polarization of the s-like electrons as discussed earlier in this section. There is no essential difference between our discussion of the form factor and those of Kubo *et al.*[4a] and Hodges *et al.*[17]

V. PROBLEM OF MANY DEGENERATE LEVELS

Since the d states are degenerate even in the presence of crystalline fields, a more realistic model of the localized moments should include the orbital degeneracy and the Hund's rule interaction between the degenerate levels. In the original work of Anderson,[8] he solved the one-spin problem in the HF approximation using the following Hamiltonian:

$$\begin{aligned}H=\sum_{\mathbf{k}\sigma}\epsilon_k n_{\mathbf{k}\sigma}+E\sum_{m\sigma}n_{m\sigma}+U\sum_{mm',m\leq m'}n_{m+}n_{m'-}\\+(U-J')\sum_{mm'\sigma,m<m'}n_{m\sigma}n_{m'\sigma}\\+\sum_{\mathbf{k}m\sigma}(V_{sd}c_{m\sigma}{}^\dagger c_{\mathbf{k}\sigma}+\text{H.c.}),\end{aligned} \tag{5.1}$$

where J' is the exchange energy between the degenerate orbitals, assumed to have the same value for all different pairs of orbitals. The sums on m and m' are over all the $\mathfrak{N}$ degenerate levels. It was found that the condition for the existence of a localized moment is

$$[U+(\mathfrak{N}-1)J']\rho(\epsilon_F)\geq 1. \tag{5.2}$$

Schrieffer and Mattis[12] showed that it is possible to find a localized moment in this model even when the correlation effect is considered. However, the present discussion is limited to the HF approximation. All the calculations in Secs. II, III, and IV can be carried out for the present model although the algebra is more tedious. We shall only outline the highlights of the results.

If we study the case when the orbital angular momentum is completely quenched, all orbitals must have the same occupation number in the same spin state. The occupation numbers are given by

$$\langle n_\sigma\rangle=\pi^{-1}\cot^{-1}[(E_\sigma-\epsilon_F)/\Delta], \tag{5.3}$$

where

$$E_\sigma=E+\mathfrak{N}U\langle n_{-\sigma}\rangle+(\mathfrak{N}-1)(U-J')\langle n_\sigma\rangle. \tag{5.4}$$

Let the solutions of Eq. (5.3) be n_1 and n_2, then the moment of a localized spin is

$$\begin{aligned}m&=\tfrac{1}{2}\hbar n_s,\\n_s&=\mathfrak{N}\,|n_1-n_2|.\end{aligned} \tag{5.5}$$

The number of Bohr magnetons for Zeeman splitting can be found from the energy separation between the spin-up and spin-down states. As before, if we define

$$\lambda_1=\pi^{-1}U\Delta/[(E_+-\epsilon_F)^2+\Delta^2] \tag{5.6}$$

and a similar expression for λ_2, we can calculate the fractional change of the occupation numbers ξ_1 and ξ_2 which are given by identical expressions as Eq. (2.14). Then the number of Bohr magnetons is found to be

$$n_B=\mathfrak{N}\{n_1-n_2-U^{-1}[(E_+-\epsilon_F)\xi_1+(E_--\epsilon_F)\xi_2]\}. \tag{5.7}$$

The energy $2\mu_Bn_BB$ is the separation between the highest and the lowest Zeeman levels. We cannot calculate the number of intermediate levels in general. In the one-orbital problem there are only two Zeeman levels. In the strictly localized case when the occupation numbers are integral, Hund's rule may be applied to determine the total spin. When the occupation numbers are fractional, as in a partially localized spin of many orbitals, there seems to be no simple way to extend Hund's rule. Perhaps the rapid fluctuation in electron numbers gives rise to a corresponding fluctuation in total spin and in the number of Zeeman levels. This situation must await further theoretical and experimental clarification.

For two spins with overlapping orbitals, the overlap term may be written as

$$V\sum_{mm'\sigma,m\leq m'}[c_{im\sigma}{}^\dagger c_{jm'\sigma}+\text{H.c.}]. \tag{5.8}$$

Using the same method of calculation as in Sec. III, we find the expression for the exchange energy to be

$$\begin{aligned}2JS^2=-\mathfrak{N}^2V^2[(E_+-\epsilon_F)\eta_1+(E_--\epsilon_F)\eta_2]\\+\mathfrak{N}^2V^2(\lambda_1+\lambda_2)/U+\mathfrak{N}^2V^2/[U+(\mathfrak{N}-1)J'],\end{aligned} \tag{5.9}$$

where λ_1 and λ_2 are defined in Eq. (5.6) and

$$\begin{aligned}\eta_1&=\{\mu_1[1+\lambda_2(\mathfrak{N}-1)(1-j)]-\mathfrak{N}\lambda_1\mu_2\}/D,\\\eta_2&=\{\mu_2[1+\lambda_1(\mathfrak{N}-1)(1-j)]-\mathfrak{N}\lambda_2\mu_1\}/D,\end{aligned} \tag{5.10}$$

with μ_1 and μ_2 given by identical expressions as Eq. (3.11),

$$D=[1+(\mathfrak{N}-1)(1-j)\lambda_1][1+(\mathfrak{N}-1)(1-j)\lambda_2]-\mathfrak{N}^2\lambda_1\lambda_2, \tag{5.11}$$

$$j=J'/U, \tag{5.12}$$

and S is some equivalent spin number. If we quantize the two sets of spins along two different directions in space, we find again that the interaction energy depends on the cosine of the angle between the two spin axes.

An equivalent Heisenberg Hamiltonian may be found for the N-spin problem as was done in the previous section. It is difficult to write down the Hamiltonian, however, because the equivalent spin number S is not known in general. This difficulty does not arise in either the localized model or the band model because Hund's rule may be applied in the former case, while in the latter case the electrons are entirely in the band and there is no need to worry about the internal structure of the ions. In the present model the knowledge about S is important because it determines the entropy of the spin system.

The d bands before s-d hybridization are given by an $\mathfrak{N}\times\mathfrak{N}$ determinant of the form

$$\det[(E_\sigma - E)\delta_{mm'} + V_{mm'}] = 0,$$

with

$$V_{mm'} = zV\gamma(\mathbf{k}). \tag{5.13}$$

This description of the d bands is similar to but more simplified than that of Heine.[11] The splitting between the corresponding spin up and spin-down bands is again given by

$$\begin{aligned}\Delta E &= E_- - E_+ \\ &= [U + (\mathfrak{N}-1)J'](n_1 - n_2).\end{aligned} \tag{5.14}$$

In terms of n_s defined in Eq. (5.5)

$$\Delta E = U_{\text{eff}} n_s, \tag{5.15}$$

where

$$U_{\text{eff}} = [U + (\mathfrak{N}-1)J']/\mathfrak{N}. \tag{5.16}$$

If we compare this with the one-orbital result in Eq. (4.18), we find that there is a smaller band splitting in the many-orbital model. The reason for this is that the electrons are dispersed among the many degenerate orbitals. Therefore, the Coulomb repulsion, which depends on the product of particle occupation numbers, is also reduced. This effect was discussed on the itinerant-electron model by Kanamori.[25] His result for U_{eff} reduces to Eq. (5.16) in the HF approximation.

It is interesting to note that in Schrieffer and Mattis's discussion of correlation effect in the Anderson model, they found the localized moment to be stable when

$$U_{\text{eff}}\rho(\epsilon_F) \geq 1, \tag{5.17}$$

where their U_{eff} has exactly the same expression as that of Kanamori. This further demonstrates the close resemblance between the present model and the itinerant model for ferromagnetism.

Just like the one orbital problem, the s-d hybridization plays an important part in determining the band structure. The Hamiltonian for the entire bands has the same structure as that proposed by Hodges *et al.*[17] For ferromagnetic coupling the Fermi level must cut through the region of s-d hybridization for both spin bands. As a result, the Fermi surface of at least one spin band should have a strong d character.

In the following we would like to make some numerical estimates for Ni and Fe. The parameters U and J' are estimated by Herring to be $U \cong 5$ eV, $J' \cong 1$ eV. We choose $\mathfrak{N}=5$ for $3d$ levels. For these values of the parameters the exchange energy, Eq. (5.9), as a function of the occupation numbers n_1 and n_2 is depicted in the contour diagram Fig. 4. Compared with the one-orbital case, Fig. 2, the dependence of the exchange energy on the occupation numbers is more gradual in the present case. This indicates greater stability of the coupling between the spins.

For Ni the number of localized spin per ion is $n_s = 0.6$. Using Eq. (5.15) we find the d-band splitting to be

$$\Delta E = 1.1 \text{ eV}.$$

This value exceeds the band-calculation result by almost a factor of 2. The inclusion of correlation tends to reduce U_{eff} and to bring the agreement somewhat closer. There is no unique way to determine separately the values of n_1 and n_2. We choose for convenience

$$\begin{aligned} n_1 &= 0.92, \\ n_2 &= 0.80, \end{aligned} \tag{5.18}$$

which give a total number of electrons in the d state

$$5(n_1 + n_2) = 8.6.$$

This should be compared with the value 8.85 estimated by Hodges *et al.* on the basis of their band calculation. In order that Eq. (5.3) should have the above set of solutions we must have

$$\Delta/U = 0.086.$$

This requires $\Delta = 0.43$ eV, or a band gap due to hybridization $2\Delta = 0.86$ eV. The band gaps are calculated to be about 1 eV near the Fermi energy and 2 eV at lower energies.

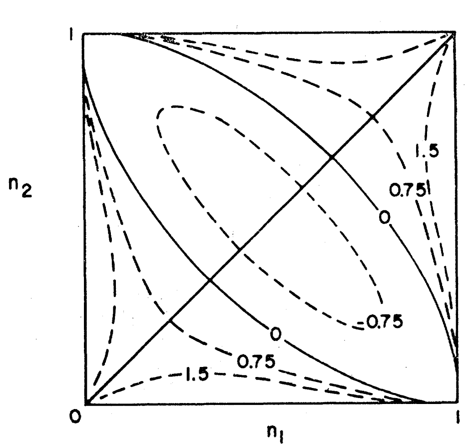

FIG. 4. The contour lines of constant exchange energy on the n_1, n_2 diagram as derived from the five-degenerate-orbital model.

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[25] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **30**, 275 (1963); C. Herring, Ref. 1, Chap. 4, pp. 223–227.

The number of Bohr magnetons n_B is found to be 1.3. If we assume that the localized spin for Ni is well represented by $S=\frac{1}{2}$, the relationship Eq. (2.19) should hold. Then we find

$$n_x=0.88,$$

which is in close accord with the value 0.93 estimated from the data of Rhodes and Wohlfarth.[13]

The exchange energy is found to be

$$2JS^2=1.4\mathfrak{N}^2V^2/U.$$

We may estimate the value of V from the width of the d band. In the tight-binding approximation, the total d bandwidth is $2zV\mathfrak{N}$, where z is the number of nearest neighbors. For Ni with fcc lattice, we have $z=12$. The total bandwidth is taken to be 4 eV. Hence, for $S=\frac{1}{2}$, we find

$$J=0.016 \text{ eV}.$$

The Curie temperature as estimated from the molecular-field theory is

$$T_c=1100\text{°K},$$

compared with the experimental value 631°K.

The total density of the d states at the Fermi level is given by

$$N_d(\epsilon_F)=\mathfrak{N}(\lambda_1+\lambda_2)/U=20.4 \text{ Ry}^{-1}$$

for the chosen set of n's in Eq. (5.18). The total number of s electrons is

$$N_s=10-5(n_1+n_2)=1.4.$$

Assuming a parabolic s band with $\epsilon_F\cong 0.6$ Ry, we find the density of s states to be

$$N_s(\epsilon_F)=3N_s/2\epsilon_F=3.5 \text{ Ry}^{-1}.$$

The total density of states calculated in this way is 23.9 $(\text{Ry})^{-1}$, compared with 27.1 $(\text{Ry})^{-1}$ calculated by Hodges *et al.* The specific-heat coefficient γ may be found from

$$\gamma=\pi^2k^2N(\epsilon_F)/3=0.99\times10^{-3} \text{ cal/mole deg}^2.$$

This is about 70% lower than the experimental value.[26] The discrepancy is likely to be due to phonon and magnon enhancement effects.

Since much less is known about the various energy parameters for Fe, it is difficult to achieve more than an order-of-magnitude estimate. We choose

$$n_1=0.93,$$

$$n_2=0.49.$$

The following numerical results are then obtained. The effective number of Bohr magnetons from Zeeman splitting is

$$n_B=2.89.$$

The size of the hybridization band gap is

$$2\Delta=1.8 \text{ eV}.$$

The d-band splitting is

$$\Delta E=4.0 \text{ eV}.$$

The Curie temperature is

$$T_c=1500\text{°K}.$$

The specific-heat coefficient is

$$\gamma=1.32\times10^{-3} \text{ cal/mole deg}^2.$$

Except for the band splitting, which seems to be much too large, the other quantities are in reasonable agreement with our present knowledge. The band splitting may be substantially reduced by including the correlation effect.

VI. CRITERION FOR FERROMAGNETISM

We conclude our discussion by reiterating qualitatively the criterion for ferromagnetism according to the present model. The necessary conditions are that the moment carrying electrons must be localized in the Anderson sense, and that the localized states must have a high enough density of states at the Fermi level. These conditions imply the following requirements:

(1) The magnetic electrons are tightly bound to the ions, so that there is small but finite overlap between nearest-neighbor wave functions. The bands of these electrons are narrow.

(2) There are many degenerate orbitals for the localized state and sizable Coulomb and Hund's rule interaction between them.

(3) There must be significant admixing between the localized state wave function and the conduction electrons, so that the localized levels are broadened.

(4) The Fermi level is at the region of s-d hybridization at least for one spin band.

Based on these conditions, one can see that s- and p-band metals cannot be ferromagnetic. Ferromagnetism is not found in $4d$ and $5d$ metals perhaps because of the wide bands. Direct exchange interaction discussed here plays no role in the ferromagnetism of $4f$ elements.

Note added in proof. The angular dependence of the interaction between two spins was discussed previously by Alexander [S. Alexander, Phys. Letters **13,** 6 (1964)].

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[26] J. A. Rayne and W. R. G. Kemp, Phil. Mag. **1,** 918 (1956).