

## Superconductivity and ferromagnetism

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(Received 30 October 1978)

In this paper a theory of superconductivity for metals in which there are localized spins is presented. The spins interact with the conduction electrons via an exchange interaction and with one another via a direct Heisenberg interaction, as well as indirectly via the conduction electrons. The spins are treated as classical vectors in a mean-field approximation. The superconducting pair-breaking mechanism is treated in the approximation of Abrikosov and Gor'kov. Complete interplay of magnetization and pair-breaking processes is taken into account. Phase diagrams are presented. A treatment of alloys of two different magnetic ions is included in a simple approximation. All results are in good qualitative agreement with the experiment.

### I. INTRODUCTION

The considerable interest which has long existed about systems which exhibit superconductivity and magnetism<sup>1</sup> has been intensified recently by the discovery in ternary compounds<sup>2,3</sup> (ErRh<sub>4</sub>B<sub>4</sub> and related alloys) of substances which are superconducting in a given temperature range (8.7 K down to 0.9 K for ErRh<sub>4</sub>B<sub>4</sub>) and which at lower temperatures lose their superconductivity and form a magnetically ordered state. This problem is an extension — or rather a simplification — of the classical question of the behavior of magnetic impurities in superconductors which has been the subject of many experimental<sup>4</sup> and theoretical<sup>5-7</sup> studies. Theories of ferromagnetic superconductor have been formulated in various approximations by Gor'kov and Rusinov<sup>8</sup> (GR) and by Bennemann.<sup>9</sup> The questions to be understood center about the role of the interaction between localized spins and conduction electrons. This interaction has several consequences: (a) it produces on the one hand a Kondo-type scattering of the conduction electrons which tends to destroy the Cooper pairing and the superconductivity<sup>5</sup>; (b) it causes, on the other hand, an indirect interaction between the spins<sup>10</sup> which tends to form a magnetically ordered state; (c) if the system orders ferromagnetically, there is a displacement of spin-up band states with respect to the spin-down band states, and a consequent change<sup>8</sup> of the structure of the superconducting Bardeen-Cooper-Schrieffer (BCS) energy-gap equation<sup>11</sup>; (d) finally, as a consequence of the ordering of the localized spins, the Kondo-type spin-flip scattering becomes frozen out, and the ordinary depression in the superconducting properties<sup>5</sup> is either partially or totally quenched.<sup>9</sup>

The purpose of this paper is to include in a coherent and as-complete-as-possible way all the

effects mentioned above. They have all been discussed by previous authors, although not all in a simultaneous and consistent way. It is our intention to use this complete description to estimate the range of physical parameters (temperature, interaction constant, and density of electronic states) over which the various behaviors in terms of ferromagnetic and superconducting order are to be expected.

In Sec. II we present our model, the details of the calculation, and the method of solution. In Sec. III we include results for  $T=0$  and for finite temperature. Section IV consists of a brief discussion on alloy systems and in Sec. V conclusions are given.

### II. GENERAL FORMULATION

Our system is described by the Hamiltonian,

$$\mathcal{H} = \mathcal{H}_{\text{BCS}} + \mathcal{H}_{eS} + \mathcal{H}_M, \quad (2.1)$$

where  $\mathcal{H}_{\text{BCS}}$  is the usual BCS Hamiltonian

$$H_{\text{BCS}} = \sum_{k\sigma} \epsilon_k C_{k\sigma}^+ C_{k\sigma} - \Delta \sum_k (C_{k\uparrow}^+ C_{-k\downarrow}^+ + C_{-k\downarrow} C_{k\uparrow}) + \frac{\Delta^2}{g}. \quad (2.2)$$

Here  $\Delta$  is the superconducting order parameter

$$\Delta \equiv g \sum_k \langle C_{-k\downarrow} C_{k\uparrow} \rangle, \quad (2.3)$$

$C_{k\sigma}^+$  ( $C_{k\sigma}$ ) is the creation (destruction) operator for an electron with momentum  $k$  and spin  $\sigma$ ,  $g$  is the electron-electron phonon-mediated coupling constant and  $\langle \dots \rangle$  indicates thermodynamic averages. In Eq. (2.1)  $\mathcal{H}_{eS}$  describes the interaction between the elec-

trons and the localized spins of the rare-earth or transition-metal ions as given by a contact interaction of strength  $J$ . We have

$$\mathcal{H}_{eS} = \frac{1}{2} J \sum_{\substack{jk \\ \sigma\sigma'}} e^{i(k-k') \cdot R_j} [\bar{S}_j \cdot (C_{k\sigma}^+ \bar{\sigma}_{\sigma\sigma'} C_{k'\sigma'})], \quad (2.4)$$

where  $\bar{\sigma} \equiv (\sigma^x, \sigma^y, \sigma^z)$  are the three Pauli matrices and  $\bar{S}_j$  described the localized spins at site  $j$ , located at  $R_j$ .

Finally,  $\mathcal{H}_M$  is a magnetic Heisenberg Hamiltonian which couples nearest-neighbor spins. We have

$$\mathcal{H}_M = -J_H \sum_{\langle jj' \rangle} \bar{S}_j \cdot \bar{S}_{j'}, \quad (2.5)$$

the exchange constant  $J_H$  includes all interactions which are not mediated by the conduction electrons, including the dipole-dipole contribution.

In our theory we take the spins  $\bar{S}_j$  to be classical vectors, and we assume the magnetization to be along the  $z$  direction

$$M \equiv \langle S^z \rangle. \quad (2.6)$$

It is convenient to add to  $\mathcal{H}_{BCS}$  a term of the form

$$\mathcal{H}_0 = \frac{1}{2} J M \sum_{\substack{jk \\ \sigma\sigma'}} e^{i(k-k') \cdot R_j} (C_{k\sigma}^+ \sigma_{\sigma\sigma'}^z C_{k'\sigma'}), \quad (2.7)$$

which in turn is subtracted from  $\mathcal{H}_{eS}$ . This is equivalent to changing, in Eq. (2.2),

$$\epsilon_k \rightarrow \epsilon_{k\sigma} = \epsilon_k \pm \frac{1}{2} J M \quad (2.8)$$

and at the same time replacing in Eq. (2.4),

$$\bar{S}_j \rightarrow \bar{S}_j - \langle \bar{S}_j \rangle. \quad (2.9)$$

In this way we have separated the effects of the electron-spin coupling into two parts: a diagonal term, which influences the spin dependent part of the one-electron energies, and an off-diagonal part which described the fluctuations and contributes to the scattering of the electrons.

The electronic state of the system is described by the usual Green's function matrices,<sup>9</sup>

$$\begin{aligned} G_{\sigma\sigma'}(k) &\equiv \langle \langle C_{k\sigma} C_{k\sigma'}^+ \rangle \rangle, \\ F_{\sigma\sigma'}(k) &\equiv \langle \langle C_{k\sigma} C_{k\sigma'} \rangle \rangle, \end{aligned} \quad (2.10)$$

and their Hermitian conjugates  $G^+$  and  $F^+$ , with elements  $\langle \langle C_{k\sigma}^+ C_{k\sigma'} \rangle \rangle$  and  $\langle \langle C_{k\sigma}^+ C_{k\sigma'}^+ \rangle \rangle$ , respectively. We evaluate these by writing down their equations of motion<sup>12</sup> keeping terms up to second order in  $J$ , and decoupling them by replacing the spin variables by their thermodynamic averages. In particular we have

$$\langle \langle (S_j^z - M) (S_{j'}^z - M) \rangle \rangle = [ \langle \langle (S^z)^2 \rangle \rangle - M^2 ] \delta_{jj'}, \quad (2.11)$$

$$\langle \langle (S_j^x S_{j'}^x) \rangle \rangle = \langle \langle S_j^y S_{j'}^y \rangle \rangle = \langle \langle (S^x)^2 \rangle \rangle \delta_{jj'}, \quad (2.12)$$

$$\langle \langle S_j^x S_{j'}^y \rangle \rangle = 0. \quad (2.13)$$

This procedure yields a system of coupled equations in the components of  $G, G^+, F$ , and  $F^+$  which, replaced in Eq. (2.3), yield gap equations<sup>5</sup> similar to that of AG, with the difference that up and down spins do not have now the same equation. Details are given in the Appendix.

The thermodynamic average of the (classical) spins is given by a Langevin equation

$$M = S \left( \coth \theta - \frac{1}{\theta} \right), \quad (2.14)$$

where  $S$  is the magnitude of the spin,

$$\theta \equiv \left( -\frac{1}{2} J S M_e + z J_H S M \right) / k_B T \quad (2.15)$$

here  $z$  is the coordination number and

$$M_e \equiv \sum_k \left( \langle \langle C_{k\uparrow}^+ C_{k\uparrow} \rangle \rangle - \langle \langle C_{k\downarrow}^+ C_{k\downarrow} \rangle \rangle \right). \quad (2.16)$$

The parameter  $M_e$  is the conduction electron magnetization, and is directly related to the Green's function  $G^+$ . In the absence of superconductivity, a Curie temperature is determined by the highest-temperature  $T_\theta$  for which a nonvanishing solution for  $M$  exists. This yields

$$k_B T_\theta = \frac{1}{3} [z J_H S^2 + 2 \rho_0 (J S)^2], \quad (2.17)$$

where  $\rho_0$  is the density of states of conduction electrons per spin at the Fermi level.

In general two order parameters exist in the system:  $\Delta$ , which governs the existence of superconductivity, and  $M$ , which describes the magnetization.

Thus we have

$\Delta = M = 0$  describes a paramagnetic state  $P$ ,  
 $\Delta \neq 0, M = 0$  describes a superconducting state  $S$ ,  
 $\Delta = 0, M \neq 0$  describes a ferromagnetic state  $F$ ,  
 $\Delta \neq 0, M \neq 0$  describes a state  $D$  in which superconductivity and ferromagnetism coexist.

### III. PHASE DIAGRAM

In order to construct a phase diagram we take as independent parameters the quantities  $I_0 = \frac{1}{2} J S$ , proportional to the electron-spin coupling,  $J_H$ , the spin-spin direct coupling,  $\rho_0$ , the density of conduction states at the Fermi level, and  $k_B T$ , the temperature. The quantity  $I_0$ , as seen in Eq. (2.8) gives the maximum relative displacement that the up-spin band can have with respect to the down-spin band; it is a measure of the "ferromagnetic driving force." On the other hand,  $\rho_0$  is the density of conduction states per spin and the quantity

$$(1/\tau) \equiv 2\pi \rho_0 I_0^2 \quad (3.1)$$

gives the strength of the spin-flip scattering and

therefore the strength of the pair-breaking mechanism of the AG theory.

We first consider the  $J_H = 0$ ,  $T = 0$  case. In this case Eq. (2.14) yields two solutions,  $M = S$  and  $M = 0$ . In either case all other equations of Sec. II take very simple forms.

For  $M = S$ , we obtain

$$\langle (S^x)^2 \rangle = \langle (S^z)^2 - M \rangle = 0.$$

The problem is now reduced to a simple BCS system but with two displaced bands, as seen in Eq. (A13). The displacement of these bands is the maximum allowed value  $I_0$ . The resulting equation has been

$$E_S - E_P = \begin{cases} -\frac{1}{2}\rho_0\Delta^2 \left[ 1 - \frac{1}{2}\pi \left( \frac{1}{\tau\Delta} \right) + \frac{2}{3} \left( \frac{1}{\tau\Delta} \right)^2 \right], & \text{for } \left( \frac{1}{\tau\Delta} \right) \leq 1, \\ -\frac{1}{2}\rho_0\Delta^2 \left[ 1 - \left( \frac{1}{\tau\Delta} \right) \sin^{-1}(\tau\Delta) + \left( \frac{1}{\tau\Delta} \right)^2 \left[ 1 - [1 - (\tau\Delta)^2]^{1/2} \right] - \frac{1}{3} \left( \frac{1}{\tau\Delta} \right)^2 \left[ 1 - [1 - (\tau\Delta)^2]^{3/2} \right] \right], & \text{for } \left( \frac{1}{\tau\Delta} \right) > 1. \end{cases} \quad (3.3)$$

For ordinary values of  $\rho_0$  (say 1 state/eV atom) Eqs. (3.2) and (3.3) are such that, plotted as functions of  $I_0$ , in the range of meaningful variation of Eq. (3.2),  $(E_S - E_P)$  remains essentially a constant

$$E_S - E_P \approx \frac{1}{2}\rho_0\Delta_{00}^2 = \frac{1}{2}\rho_0(k_B T_{co}/0.57)^2, \quad (3.4)$$

where  $\Delta_{00}$  is the superconducting order parameter for  $J = 0$ ,  $T = 0$ , and  $T_{co}$  is the superconducting critical temperature for  $J = 0$ . Equations (3.2) and (3.4) now yield a critical value of  $I_0$ ,

$$I_{0c} = \frac{1}{2}\Delta_{00} = \frac{1}{1.14}k_B T_{co} \quad (3.5)$$

or, equivalently

$$(1/\tau_c) = 4.83\rho_0(k_B T_{co})^2. \quad (3.6)$$

For  $I_0 < I_{0c}$  the stable state at  $T = 0$  is  $S$ ; for  $I_0 > I_{0c}$  the stable state is  $F$ .

For the sake of comparison, the AG theory predicts a complete destruction of superconductivity at  $T = 0$  due to the pair-breaking mechanism for a value of  $(1/\tau)$  given by

$$(1/\tau_{AG}) = \frac{1}{2}\Delta_{00} = \frac{1}{1.14}k_B T_{co}, \quad (3.7)$$

which for typical values of  $T_{co}$  ( $\sim 10$  K) and  $\rho_0$  yields a ratio

$$(\tau_{AG}/\tau_c) \sim 5 \times 10^{-3}.$$

In other words, at  $T = 0$  the  $S$  state becomes meta-stable against the formation of an  $F$  state at values of the coupling constant  $J$  which are between one and

shown<sup>1</sup> to yield only the solution  $\Delta = 0$ , i.e., an  $F$  state.

The  $M = 0$  case reduces in our approach exactly to the AG theory<sup>5</sup> and a pure  $S$  state. In order to determine which of the three states,  $F, S$ , or  $P$ , is the most stable one, it is necessary to calculate the total energy of the system as a function of the parameter  $I_0$ . We obtain

$$E_F - E_P = -2\rho_0 I_0^2. \quad (3.2)$$

Since the right-hand side of this equation is negative definite, the  $P$  state is never stable at  $T = 0$ .

The energy of the  $S$  state, calculated from the complete BCS theory, is given by<sup>13</sup>

two orders of magnitude smaller than the value required to destroy the superconductivity via a pair-breaking mechanism.

At  $T \neq 0$ , the analysis of the phase stability should be carried out by examining the behavior of the free energy function  $\mathfrak{F}(\Delta M; I_0, J_H, \rho_0, k_B T)$  and by determining its absolute minimum with respect to  $\Delta$  and  $M$ . We consider again the  $J_H = 0$  case. This analysis is much more complicated than the previous one for  $T = 0$ , and it can only be accomplished by numerical and approximate methods. We define the following temperatures:  $T_{SF}$  is the temperature where  $\mathfrak{F}_S = \mathfrak{F}_F$ ;  $T_\theta$  is the (Curie) temperature where  $\mathfrak{F}_P$  develops a negative curvature with respect to a small variation in  $M$ ;  $T_c$  is the (superconducting critical) temperature where  $\mathfrak{F}_P$  develops a negative curvature with respect to a small variation in  $\Delta$ ;  $T_{S\theta}$  is the temperature ( $T_{S\theta} < T_c$ ) at which the superconducting minimum in  $\mathfrak{F}$  develops a negative curvature with respect to a small variation in  $M$ ;  $T_{FC}$  is the temperature ( $T_{FC} < T_\theta$ ) at which the ferromagnetic minimum in  $\mathfrak{F}$  develops a negative curvature with respect to a small variation in  $\Delta$ .

These temperatures, if the absolute minimum falls in the correct region of parameter space, correspond to the following phase transitions:  $T_{SF}$ , first-order transition  $F \rightarrow S$ ;  $T_\theta$ , second-order transition  $F \rightarrow P$ ;  $T_c$ , second-order transition  $S \rightarrow P$ ;  $T_{S\theta}$ , second-order transition  $S \rightarrow D$ ; and  $T_{FC}$ , second-order transition  $F \rightarrow D$ . These do not cover all possibilities, since other first-order transitions are possible, e.g.,  $S \rightarrow D$ ,  $F \rightarrow D$ , and  $D_1 \rightarrow D_2$ .

The temperatures defined above can be calculated

by different methods. In particular  $T_c$  is calculated following the AG theory<sup>5</sup> and  $T_\theta$  is given by Eq. (2.17),  $T_{S\theta}$  can be obtained from linearization of Eqs. (2.14)–(2.16), keeping in mind that  $M_e$  is a function of  $\Delta$  in this case. This yields

$$T_{S\theta} = T_\theta [\chi_S(T_{S\theta})/\chi_P(T_\theta)], \quad (3.8)$$

where  $\chi_S(T)$  and  $\chi_P(T)$  are the conduction-electron

$$\ln \frac{T_{FC}}{T_{co}} = \left[ \frac{\omega_- + (i/\tau) (\langle S_z^2 \rangle - M^2)/S^2}{\omega_+ - \omega_-} \psi \left( \frac{1}{2} + i \frac{\omega_-}{2\pi k_B T} \right) - \frac{\omega_+ + (i/\tau) (\langle S_z^2 \rangle - M^2)/S^2}{\omega_+ - \omega_-} \psi \left( \frac{1}{2} + i \frac{\omega_+}{2\pi k_B T} \right) + \psi \left( \frac{1}{2} \right) \right], \quad (3.9)$$

where we have

$$\omega_\pm = -\frac{1}{2} \frac{i}{\tau} \left[ 1 - \frac{2M^2}{S^2} + \frac{\langle S_z^2 \rangle}{S^2} \right] \pm \left[ \frac{I_0^2 M^2}{S^2} - \frac{1}{4} \left( \frac{1}{\tau} \right)^2 \left[ 1 - \frac{\langle S_z^2 \rangle}{S^2} \right]^2 \right]^{1/2} \quad (3.10)$$

and  $\psi(z)$  indicates the digamma function.<sup>5</sup> Finally  $T_{SF}$  is calculated numerically.

For the specific value of  $I_0$  such that  $T_c = T_\theta$ , all five temperatures defined above are equal. This point is indicated by a star in Fig. 1, and the corresponding values of the quantities are denoted  $T^*$ ,  $I_0^*$ ,  $(1/\tau^*)$ , etc. For  $I_0 > I_0^*$ ,  $\mathcal{F}_S$  is never an absolute minimum; its value is always larger than either  $\mathcal{F}_F$  or  $\mathcal{F}_P$ . In addition there is no solution for  $T_{FC}$ . These two facts together strongly suggest that for  $I_0 > I_0^*$  there is no superconductivity of any kind, either in the pure form  $S$  or in coexistence with ferromagnetism  $D$ ; the stable solution is always  $\Delta = 0$ .

For  $1/\tau_c < 1/\tau < 1/\tau^*$ , where  $\tau_c$  is given by Eq. (3.6), we find, as shown in Fig. 1(b),

$$T_{S\theta} < T_{SF} < T_{FC},$$

which indicates a first-order transition  $F \rightarrow S$  as the temperature increases; no coexistence  $D$  state appears since the second-order instabilities never take place in the region of the absolute minimum.

For  $1/\tau < 1/\tau_c$  the  $F$  state is not stable at any temperature. As shown in the insert of Fig. 1(b),  $T_{S\theta}$  takes extremely small values, smaller than  $4 \times 10^{-5}$  K for the example under consideration. For  $T > T_{S\theta}$  the  $S$  state is stable; a coexistence  $D$  state exists for  $0 < T < T_{SD}$  and as  $T \rightarrow 0$  the stable state is  $S$  once again.

We can estimate now the effect of the direct interaction between the localized spins  $J_H \neq 0$ . It is evident from the formulation that if  $J = 0$  and  $J_H \neq 0$ , the two order parameters  $\Delta$  and  $M$  are independent of each other, and at low enough tempera-

susceptibilities for the  $S$  and  $P$  states, respectively, at temperature  $T$ . These susceptibilities were first calculated<sup>8</sup> in GR with a different approximation which however yields identical results to ours up to terms linear in  $M$ .

The temperature  $T_{FC}$  is obtained by linearizing the gap Eq. (A13) in  $\Delta$ , keeping in mind that  $M \neq 0$ . This yields

tures,  $T < T_c$  and  $T < T_\theta$ , a coexistence  $D$  state will be stable.

If  $J \neq 0$ ,  $J_H \neq 0$  the five temperatures defined above,  $T_{SF}$ ,  $T_\theta$ ,  $T_c$ ,  $T_{S\theta}$ , and  $T_{FC}$  have different expressions:  $T_c$  is still given by the AG theory<sup>5</sup> and  $T_\theta$  by Eq. (2.17). The new expression for  $T_{S\theta}$  is

$$T_{S\theta} = \frac{1}{3} z J_H S^2 + \frac{2}{3} \rho_0 (J_S)^2 [\chi_S(T_{S\theta})/\chi_P(T_\theta)]; \quad (3.11)$$

$T_{FC}$  is still given by Eq. (3.9) and (3.10) but  $\langle S_z^2 \rangle$  and  $M$  should now be calculated taking the direct exchange  $J_H$  into account;  $T_{SF}$  is once again calculated numerically by comparing  $\mathcal{F}_S$  with  $\mathcal{F}_F$ .

In Fig. 2 we show results for an example with  $J_H$  such that  $z J_H S^2 / 3 k_B = 1$  K,  $T_{co} = 10$  K, and  $\rho_0 = 5 \times 10^{-4}$  states/K · atom. Using the same definition of  $1/\tau$  given by Eq. (3.1) we find five regions: (i) For  $1/\tau > 1/\tau^*$  there is no superconductivity, and as  $T$  increases there is a second-order transition  $F \rightarrow P$  at  $T_\theta$ . (ii) For  $1/\tau_3 < 1/\tau < 1/\tau^*$  the results are similar to our previous case  $J_H = 0$ . As  $T$  increases we have a first-order transition  $F \rightarrow S$  at  $T_{SF}$  and a second-order transition  $S \rightarrow P$  at  $T_c$ . The value of  $(1/\tau_3)$  corresponds to the point where  $T_{FC} = T_{SF}$ . (iii) For  $1/\tau_2 < 1/\tau < 1/\tau_3$ , the ground state is  $F$ . There is a second-order transition  $F \rightarrow D$  at  $T_{FC}$ , a first-order transition  $D \rightarrow S$  at an intermediate temperature and another second-order transition  $S \rightarrow P$  at  $T_c$ . The value  $(1/\tau_2)$  is that for which the temperature of the first-order  $D \rightarrow S$  equals  $T_{S\theta}$ . (iv) In the region  $1/\tau < 1/\tau_1$  the ground state of the system is a  $D$  state. The value  $1/\tau_1$  corresponds to  $T_{FC} = 0$ . (v) In the region  $1/\tau < 1/\tau_1$  as well as in  $1/\tau < 1/\tau_2$  there may be several  $D$  phases with possible first-order transitions between them, as well as either first- or second-order transitions between  $D$  and  $S$  and second-order transitions  $F \rightarrow D$ .

The richness of the structure in the small  $I_0$  low  $T$  regime in this case depends very sensitively on the numerical details of the calculation. We have not carried out this calculation to its conclusion.

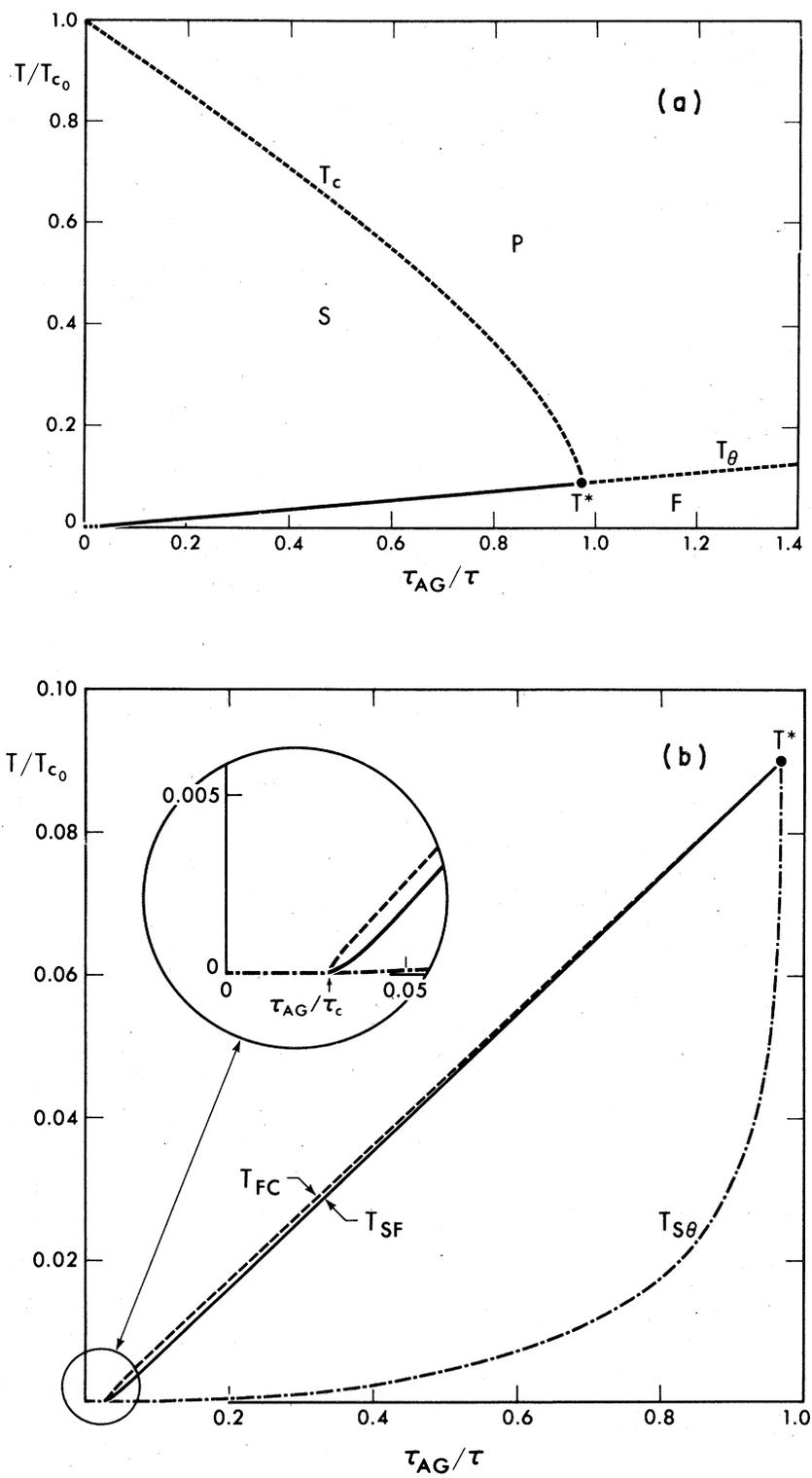


FIG. 1. (a) Phase diagram for  $J_H=0$ ,  $T_{c0}=10$  K, and  $\rho_0=5 \times 10^{-4}$  states/ K atom. The temperatures are given as a function of  $(1/\tau)$ , defined by Eq. (3.1), and normalized to the AG value given by Eq. (3.7). Full lines are first-order transitions; dotted lines are second-order transitions. (b) Details of the diagram in the low-temperature regions.

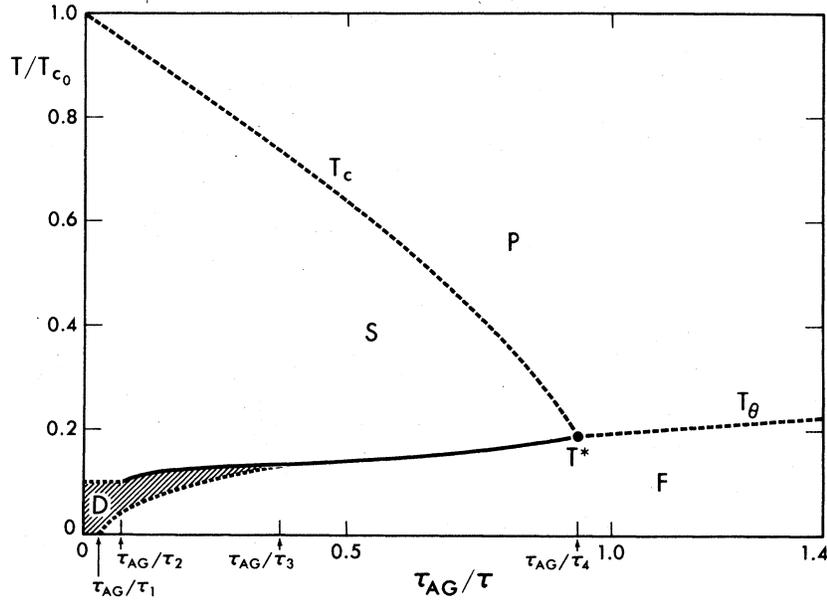


FIG. 2. Phase diagram for  $J_H S^2 / 3k_B = 1$  K,  $T_{c0} = 10$  K, and  $\rho_0 = 5 \times 10^{-4}$  states/K atom.

#### IV. ALLOYS

The experiments<sup>3</sup> performed on  $\text{Er}_x\text{Ho}_{1-x}\text{Rh}_4\text{B}_4$  have been our motivation to extend our model calculations of the last sections to alloys. The problem is considerably more complex now, since it involves all the complications inherent in alloy theory.<sup>14</sup> Only a simple qualitative discussion is presented here.

The presence of two elements  $A$  and  $B$  with concentrations  $x$  and  $(1-x)$  and spins  $S_A$  and  $S_B$  brings several new interaction constants to our model: two spin-conduction electron coupling constants  $J_A$  and  $J_B$ , and three direct exchange constants  $J_{HAA}$ ,  $J_{HAB}$ , and  $J_{HBB}$ .

In the simplest approximation, the virtual crystal approximation, our equations of Sec. II and III remain unchanged if we write

$$J_H S^2 \equiv x^2 J_{HAA} S_A^2 + 2x(1-x) J_{HAB} S_A S_B + (1-x)^2 J_{HBB} S_B^2, \quad (4.1)$$

$$I_0 \equiv \frac{1}{2} [x J_A S_A + (1-x) J_B S_B], \quad (4.2)$$

$$(1/\tau) \equiv \frac{1}{2} \pi \rho_0(x) [x (J_A S_A)^2 + (1-x) (J_B S_B)^2]. \quad (4.3)$$

In Eq. (4.3),  $\rho_0(x)$  is the density of conduction electron states at the Fermi level for the alloy of concentration  $x$ . It should be noted that our approximation is a reasonable one, since we are dealing with very wide conduction bands where better alloy models, like the coherent potential approximation,<sup>14</sup> yield results very similar to the virtual crystal approximation.

The interesting behavior in the alloys appears when  $J_A$  and  $J_B$  have opposite signs, i.e., when the coupling of the spins to the conduction electrons is ferromagnetic for one element and antiferromagnetic for the other. In this case there is a concentration  $x_0$  such that  $I_0(x_0) = 0$  and for that alloy, in the virtual crystal approximation, the equation for the magnetization (2.14) is independent of the conduction electrons. As a consequence, for concentrations close to  $x_0$  the  $D$  state of coexistence of superconductivity and ferromagnetism is more favorable.

For the alloys in our model there are two possible behaviors. If  $\text{sgn } J_A = \text{sgn } J_B$ , as shown schematically in Fig. 3(a), there is a monotonic change in transition temperatures as a function of  $x$ . If  $\text{sgn } J_A = -\text{sgn } J_B$ , as displayed in Fig. 3(b), the line of  $F \rightarrow S$  transitions has a dip in the neighborhood of  $x_0$ , with a region of coexistence bound to occur in that region.

If we take a better model for the alloy, Eq. (4.2) will not be valid and consequently there will be no concentration for which  $I_0 = 0$ . The transition temperature does not drop to zero at  $x_0$  in that case. However the qualitative features of the diagram must remain valid, with a dip in the phase diagram and a region of coexistence.

#### V. DISCUSSION

Our theory, as presented in the last sections, treats ferromagnetic superconductors and ferromagnetic superconducting alloys in a generalized mean-field approximation, with the spin being considered classical

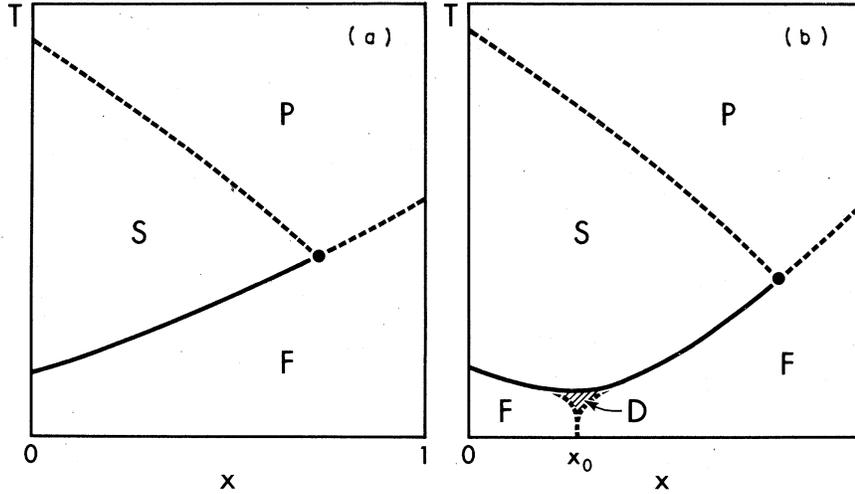


FIG. 3. Schematic phase diagrams (temperature vs concentration) for alloys. (a)  $J_A$  and  $J_B$  are of the same sign; (b)  $J_A$  and  $J_B$  are of opposite signs.

vectors, the pair-breaking mechanisms being treated in AG fashion,<sup>5</sup> with the magnetization being fully taken into account in the pair-breaking process, and with the alloy properties treated in the virtual crystal approximation. Our study differs from that<sup>8</sup> of GR in the fact that GR assume constant pair-breaking scattering time, independent of the magnetization. This tends to favor coexistence states. Our model on the other hand is very similar to that of Bennemann,<sup>9</sup> with the difference that he treated the spins as quantum vectors, but as a consequence of the numerical complexity, he stopped short of a full analysis of the phase diagram, focusing his attention mostly on the problem of dilute ferromagnetic impurities in a bulk nonmagnetic superconductor.

The results of our theory are best described by the three figures. In summary, we have: (i) In the absence of a direct spin-spin interaction,  $J_H = 0$ , there is no coexistence of superconductivity and ferromagnetism at  $T = 0$ . (ii) For  $T \neq 0$  and  $J_H = 0$  the phase diagram shows once again almost exclusively pure states,  $F, S$ , or  $P$ , with a possible region of weak coexistence  $D$  at unphysically low temperatures. (iii) When there is direct coupling between the spins,  $J_H \neq 0$ , the diagrams become rich in structure, with many structures,  $F, S, D$ , and  $P$ , and a variety of first- and second-order phase transitions which depend on the detailed values of the parameters. (iv) Our simple treatment of the alloys, as shown in Fig. 3, reproduces some of the characteristics of the experimental data; the important features arise from the interplay between the two spin-conduction electron-coupling constants which, under some conditions, may interfere destructively and thus favor the existence of  $D$  states at lower temperatures.

#### ACKNOWLEDGMENT

This work was supported in part by the NSF through Grant No. DMR 78-03408.

#### APPENDIX

The procedure described in Sec. II yields a system of coupled equations which can be written

$$\begin{vmatrix} (\omega - \epsilon_k - \sigma^z I - \hat{\Sigma}^0) - (\hat{\Delta} + \hat{\Sigma}^1) & G \\ (\hat{\Delta} + \hat{\Sigma}^1) (\omega + \epsilon_k + \sigma^z I - \hat{\Sigma}^0) & F^+ G^+ \end{vmatrix} = \frac{1}{2\pi}, \quad (\text{A1})$$

where

$$I = \frac{1}{2} J M, \quad (\text{A2})$$

$$\hat{\Delta} = \begin{vmatrix} 0 & -\Delta \\ \Delta & 0 \end{vmatrix}, \quad (\text{A3})$$

and

$$\begin{aligned} \hat{\Sigma}^0 &= \frac{1}{2} \pi J^2 [ \langle (S^z)^2 \rangle - M^2 ] \sum_{k'} G^0(k') \\ &\quad - \pi J^2 \langle (S^x)^2 \rangle \sum_{k'} [ \sigma^y G^0(k') \sigma^y ], \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} \hat{\Sigma}^1 &= \frac{1}{2} \pi J^2 [ \langle (S^z)^2 \rangle - M^2 ] \sum_{k'} G^{+0}(k') \\ &\quad - \pi J^2 \langle (S^x)^2 \rangle \sum_{k'} [ \sigma^y G^{+0}(k') \sigma^y ], \end{aligned} \quad (\text{A5})$$

$$\begin{aligned} \hat{\Sigma}^1 &= \frac{1}{2} \pi J^2 [ \langle (S^z)^2 \rangle - M^2 ] \sum_{k'} F^0(k') \\ &\quad + \pi J^2 \langle (S^x)^2 \rangle \sum_{k'} [ \sigma^y F^0(k') \sigma^y ], \end{aligned} \quad (\text{A6})$$

$$\hat{\Sigma}_1 = \frac{1}{2} \pi J^2 [\langle (S^x)^2 \rangle - M^2] \sum_{k'} F^{+0}(k') - \pi J^2 \langle (S^x)^2 \rangle \sum_k [\sigma^y F^{+0}(k) \sigma^y]. \quad (\text{A7})$$

The functions  $G^0$ ,  $G^{+0}$ ,  $F^0$  and  $F^{+0}$  are the Green's functions evaluated to zero order in  $J$ . In the usual way,<sup>7</sup> they are replaced by  $G$ ,  $G^+$ ,  $F$ , and  $F^+$ , respectively.

This procedure is equivalent to evaluating the self-energy in a self-consistent way<sup>6</sup> and for  $M=0$  the AG solution is obtained.

It can be shown<sup>8</sup> that the following relations are satisfied:

$$\hat{\Sigma}^0 = \hat{\Sigma}_0 \text{ and } \hat{\Sigma}^1 = \hat{\Sigma}_1.$$

It is convenient to define a new set of variables<sup>5,7,8</sup>

$$\omega_{\pm} = \omega \mp I_0 \frac{M}{S} - \frac{1}{\tau} \frac{[\langle (S^x)^2 \rangle - M^2]}{S^2} \frac{U_{\pm}}{(1 - U_{\pm}^2)^{1/2}} - \frac{1}{\tau} \frac{\langle (S^x)^2 \rangle}{S} \frac{U_{\mp}}{(1 - U_{\pm}^2)^{1/2}} \quad (\text{A8})$$

and

$$\tilde{\Delta}_{\pm} = \Delta - \frac{1}{\tau} [\langle (S^x)^2 \rangle - M^2] (1 - U_{\pm}^2)^{-1/2} - \frac{1}{\tau} (1 - U_{\pm}^2)^{-1/2}, \quad (\text{A9})$$

where

$$U_{\pm} = \tilde{\omega}_{\pm} / \tilde{\Delta}_{\pm}, \quad (\text{A10})$$

$$I_0 = (\frac{1}{2} J S), \quad (\text{A11})$$

and

$$1/\tau = 2\rho_0 (\frac{1}{2} J S)^2. \quad (\text{A12})$$

In terms of these variables the gap equation (2.3) can be written

$$\Delta = \frac{g}{2\pi} \int_{-\infty}^{\infty} f(\omega) \sum_k' \text{Im} \left( \frac{\tilde{\Delta}_+}{\tilde{\omega}_+^2 - \tilde{\Delta}_+^2 - \epsilon_k^2} + \frac{\tilde{\Delta}_-}{\tilde{\omega}_-^2 - \tilde{\Delta}_-^2 - \epsilon_k^2} \right), \quad (\text{A13})$$

where  $f(\omega)$  is the Fermi function.

\*On a fellowship from the CNICT, Argentina, on leave from Centro Atomico Bariloche, Argentina.

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