PHYSICAL REVIEW B VOLUME 20, NUMBER 11 1 DECEMBER 1979

Magnetism versus superconductivity—molecular-field theory

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(Received 30 May 1979)

Within the context of molecular-field theory we analyze the thermodynamics of magnetic superconductors over the whole (T,H) plane. The conditions for the coexistence of a long-range magnetic order (including ferromagnetic order) and superconductivity are given. Specific heat and static susceptibility are calculated and anomalies associated with the occurrence of a coexistence phase are observed. Good qualitative agreement with experiments is found and several predictions are made.

I. INTRODUCTION

Experimental as well as theoretical investigations on the interrelationship of magnetism and superconductivity have a long history.[1] Early research was mainly concerned with the effect of paramagnetic impurities on superconductivity. The early microscopic theory of Abrikosov, Gor'kov, and Rusinov[2,3] (AGR) treated a superconductor with uncorrelated paramagnetic impurities. The theory was later extended to include spin-orbit interaction,[4] crystal-field effects,[5] etc. In many instances these theories were capable of explaining the experimental data of systems with relatively low-impurity concentrations. However, a particularly intriguing question on the coexistence of magnetism and superconductivity has been recently reopened by the discovery[6,7] of new rare-earth (R) ternary compounds: RRh_4B_4 and $R_xMo_6(S,Se)_8$. These compounds have been shown to exhibit superconductivity or long-range magnetic order, "reentrant" behavior,[8,9] and, in some cases, even the coexistence of superconductivity and long-range antiferromagnetic order.[10,11] In contrast to the early phenomenological theories,[12] the possiblity of coexistence of magnetic order and superconductivity was predicted in the AGR theory (a similar microscopic model was exactly treated more recently,[13] and similar results were found). However, the aforementioned ternary compounds contain a high concentration of magnetic moments distributed over the regular lattice. Henceforth, applicability of the AGR-type theories is restricted.

Some of the more recent theoretical attempts to understand the interrelationship of magnetism and superconductivity include microscopic theories as well as phenomenological ones.[14–23] However, most of the microscopic theories fall short in treating effects of the external magnetic field. The main difficulty lies in our limited ability to treat microscopically the effects of the external magnetic field, even in pure superconductors. The problem is especially complicated in type-II superconductors where the only sensible approach is a Ginzburg-Landau-type theory as employed, for example, by Abrikosov.[24] A similar approach has been applied recently to the analysis of magnetic superconductors.[21,22] Nevertheless, even in these theories the mathematical complexity is extensive.

Preliminary calculations of Belić and Jarić[23] were made in the context of a phenomenological, molecular-field-type theory. In general there are several advantages of molecular-field theories: (a) mathematical simplicity which allows clear physical interpretations and relatively easy applicability; (b) maximal utilization of the understanding of decoupled subsystems; (c) ability to treat couplings of arbitrary strength; (d) generally good qualitative agreement with experiment, etc. The theory will be extended and completed here in order to describe the thermodynamics of magnetic superconductors in an external magnetic field and at arbitrary temperatures. We will introduce the appropriate thermodynamic Gibbs potential and thus we will be able to avoid a lack of uniqueness in the Maxwell construction encountered previously.[23] The physically intuitive model which we will adapt here considers a magnetic superconductor as consisting of two subsystems: a magnetic one and a superconductor. The chief effect of the magnetic subsystem on the superconductor is to create an effective magnetic field which tends to destroy superconductivity. On the other hand the effect of the superconducting subsystem on the magnetic one is the screening of external as well as local magnetic fields, which have a tendencey to destroy any long-range magnetic order. Hence, if the superconducting subsystem is in the Meissner phase, all fields are completeely screened. Thus ordinary intuition indicates that the Meissner phase and long-range magnetic order cannot coexist in the same volume. This statement should be corrected, however. In the Meissner phase of the superconducting subsystem the effective field acting on the superconductor is completely screened. Therefore, the magnetic induction due to the effective field acting on the superconductor subsystem is zero, whereas the total magnetic induction of the magnetic-superconductor need not be zero. Hence, it will be important to make a distinction between effective fields and magnetic induction.[25]

It is, unfortunately, impossible to determine uniquely a microscopic picture starting from a macroscopic one (i.e., molecular-field theory). However, a microscopic picture, consistent with our intuition, may be one in which there are two electronic bands near the Fermi surface. One band is mainly responsible for superconductivity, while the other one provides most of the indirect coupling between localized magnetic moments. This picture is supported by the electronic structure calculations for some $R\mathrm{Rh_4B_4}$ compounds.[26] These calculations show that superconductivity is due mainly to the Rh $4d$ electrons, while the R $4f$ localized magnetic moments interact strongly with the R $5d$ electrons and weakly with the Rh $4d$ electrons. An implication of this picture is that the exchange coupling, $\vec{\sigma}\cdot\vec{s}$, traditionally employed in microscopic theories of magnetic superconductors, is probably insufficient. One needs to include electromagnetic coupling as well. Another implication is that the Ginzburg-Landau-type theories must include nonlocal, $\vec{m}^2\psi^2$ as well as $\psi\vec{m}\cdot\vec{\nabla}\psi$-type, couplings of the magnetic, $\vec{m}$, and superconducting, ψ, order parameters. Within this picture it also seems that the magnetic subsystem affects the superconductor subsystem chiefly by producing a relative sliding of the up- and down-spin Fermi surfaces. Such conclusion should be true at least at sufficiently low temperatures and/or high external fields where magnetic fluctuations (or the Abrikosov-Gor'kov mechanism) should be suppressed. Some of the aspects of this microscopic picture are treated in Refs. 14, 21, and 22.

In Sec. II we will derive the thermodynamic functions for magnetic superconductors. We will pay special attention to the question of coexistence of long-range magnetic order and superconductivity. At the end of Sec. II we will briefly discuss the applicability of the theory to the more general magnetic structures. In Sec. III we will compare our results with experiments, with special attention focused on $\mathrm{ErRh_4B_4}$. We will also present there the discussion and the analysis of the theory. In the Appendix we will describe numerical calculations performed in order to illustrate some of the consequences of the theory.

II. THERMODYNAMICS

Let us consider decoupled superconducting and magnetic subsytems whose respective magnetizations M_s and M_p, at given temperature T and external fields $H_{es}=H_{ep}=H$, are

$$M_s = h_s(H_{es},T) \ , \quad M_p = h_p(H_{ep},T) \ . \tag{1}$$

The functions h_s and h_p are assumed to be known. For the sake of simplicity we will also assume that the magnetic subsystem is a ferromagnetic one and that all magnetizations and magnetic fields are either parallel or antiparallel to an axis of a long cylindrical sample. We also note that M_s corresponds to the *macroscopic* magnetization of the superconducting subsystem.

The two subsystems are coupled, as described in the Introduction, in a molecular-field fashion.[23] This means that the fields appearing in Eq. (1) are to be taken as effective fields

$$H_{es} = H + \delta M_p \ , \tag{2}$$

$$H_{ep} = H + \delta M_s \ . \tag{3}$$

The parameter δ describes the coupling. If $\delta > 0$ ($\delta < 0$) we will call the coupling of the two subsystems ferromagnetic (antiferromagnetic). If we assume the ferromagnetic and superconducting subsystems known, then δ is the only parameter entering the theory. The introduction of the coupling implies that we should include in Eq. (1) both stable and unstable states, as some of the unstable ones may be stabilized by the interaction. We will assume below that the ferromagnetic subsystem is also described in a molecular-field fashion. Hence, any unstable states of the ferromagnetic subsytem are included explicitly by having the subscript p, in Eq. (1), refer to the uncorrelated paramagnetic moments and by replacing the field H_{ep}, in Eq. (3), by

$$H_{ep} = H + \delta M_s + \lambda M_p \ , \tag{4}$$

where λM_p ($\lambda > 0$) describes the "self-coupling" of the ferromagnetic subsystem.

The equation of the state of the ferromagnetic superconductor (FS), giving the total magnetization M,

$$M(H,T) = M_s + M_p \tag{5}$$

is determined by solving Eqs. (1)–(4). In general several solutions will be found. Unstable ones are eliminated by considering a thermodynamic Gibbs potential G of FS. The solution of Eq. (1) which yields the lowest G is the stable one. The Gibbs potential is given, in accordance with the molecular-field theory, as

$$G(H,T) = G_{es} + \delta M_p M_s + G_{ep} + \tfrac{1}{2}\lambda M_p^2 \ , \tag{6}$$

where G_{es} is the Gibbs potential of the superconducting subsystem in an effective field [Eq. (2)], G_{ep} is the Gibbs potential of the paramagnetic subsystem[27] in an effective field [Eq. (4)], and the term $\delta M_p M_s$ comes from the coupling of the two subsystems.

Other thermodynamic functions can be obtained from the Gibbs potential. The entropy S is found to be

$$S(H,T)=S_{es}+S_{ep} \ , \tag{7}$$

where S_{es} is the entropy of the superconducting subsystem in an effective field [Eq. (2)] and S_{ep} is the entropy of the paramagnetic subsystem in an effective field [Eq.(4)]. The static susceptibility χ is given by

$$\chi(H,T)=\chi_{es}+(1+\delta\chi_{es})^2\overline{\chi}_{ef} \ , \tag{8}$$

where χ_{es} is the static susceptibility of the superconducting subsytem in an effective field [Eq. (2)] and $\overline{\chi}_{ef}$ is the static susceptibility of an effective ferromagnetic system with "self-coupling" $\overline{\lambda}$

$$\overline{\lambda}(H,T)=\lambda+\chi_{es}\delta^2 \ , \tag{9}$$

in an effective field

$$H+\delta M_s-\delta^2\chi_{es}M_p \ . \tag{10}$$

Similarly, the specific heat C is given by

$$C(H,T)=C_{es}+\overline{C}_{ef}\gamma \ , \tag{11}$$

where

$$\gamma\equiv 1+\frac{\alpha_{ep}^2\overline{\lambda}}{2\alpha_{es}\alpha_{ep}\delta+\alpha_{es}^2\chi_{ep}\delta^2} \tag{12}$$

and a notation analogous to the one employed in Eq. (8) is adopted. The α's are the usual response functions, equal to the temperature derivative of the magnetizations.

In what follows we will assume that the superconducting subsystem is a type-II superconductor. General magnetic and thermodynamic properties of type-II superconductors are well known.[24,28] Three phases may be distinguished in a type-II superconductor. These three phases divide the (T,H) plane into three regions which define the upper critical field $h_2(T)$ and the lower critical field $h_1(T)$. The strength of the external field H_{es} determines the phases and the corresponding macroscopic magnetization M_s. (i) The phase where $|H_{es}|<h_1(T)$ is called a Meissner phase and we will denote it by I; in this phase $M_s=-H_{es}$.[29] (ii) The phase where $h_1(T)\leq|H_{es}|<h_2(T)$ is called a mixed phase and we will denote it by II; in this phase $-H_{es}\leq M_s<0$. (iii) The phase where $|H_{es}|\geq h_2(T)$ is called a normal phase and we will denote it by n; in this phase $M_s=0$.[30] Phase transitions in type-II superconductors are of second order.

Similarly, the ferromagnetically ordered state of the ferromagnetic subsystem is defined by a nonzero spontaneous magnetization, $M_p\neq 0$. This phase we will denote by f. Therefore, in the simplest case,[31] we may define six different phases of an FS in zero external field. We denote them by I, II, n, If, IIf, and f. Which of these phases may be reached in an actual FS will be mainly determined by the interplay of the spontaneous magnetization curve of the ferromagnetic subsystem and the lower and upper critical field curves of the superconducting subsystem. Thus, six typical cases, may be distinguished

$$|\delta m_0|>h_1^0 \ , \quad h_1^0\leq|\delta m_0|<h_2^0 \ , \quad |\delta m_0|\geq h_2^0 \ , \tag{13}$$

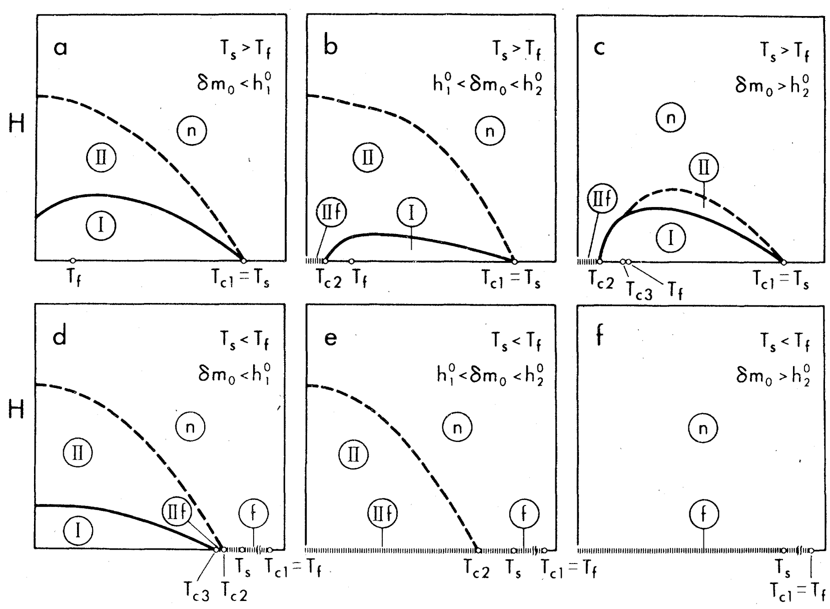

FIG. 1. Typical phase diagrams for a FS. A dashed line corresponds to a second-order phase transition whereas a full line corresponds to a first-order phase transition (Ref. 32).

with either $T_s > T_f$ or $T_s < T_f$; where m_0 is the saturation magnetization of the ferromagnetic subsystem T_f is its transition temperature, T_s is the transition temperature of the superconductor subsystem, and $h_{1,2}^0 \equiv h_{1,2}(0)$. Typical phase diagrams are sketched in Fig. 1.[23,32] It is seen that the behavior of FS may range from superconductinglike, $T_f << T_s$ and $|\delta m_0| << h_1^0$, Fig. 1(a), to ferromagneticlike, $T_f >> T_s$, $|\delta m_0| >> h_2^0$, Fig. 1(f). It can also be seen that although originally the transition from II to I was of second order, the interaction with the ferromagnetic subsystem changes the transition to first order. This is essentially due to the infinite susceptibility of the superconducting subsystem at the lower critical field. In the case of the superconductinglike behavior the transition is weakly first order. In Fig. 1(c) we note a transition at T_{c3} to type-I superconducting behavior. A similar tendency towards type-I superconducting behavior was also predicted in Ref. 19. We also note that Fig. 1(d) corresponds to the transition from a magnetically ordered state to a superconducting one. Such transition has, as yet, never been observed experimentally. Although there is some interest in further studying all six possible cases we wish to focus our attention here on the question of coexistence of superconductivity and ferromagnetism.

We define the coexistence phase, If, in zero external field as characterized by a spontaneous magnetization of the ferromagnetic subsystem, $M_p \neq 0$, and by zero magnetic induction of the superconductor subsystem, $B_s = H_{es} + M_s = 0$ [i.e.,$|H_{es}| < h_1(T)$]. Note that nonzero total magnetic induction, $B = H + M$, in the coexistence phase,[33] does not contradict $B_s = 0$. The simplest way to analyze the coexistence phase is by presenting Eqs. (1)–(4) graphically[34] in the (M_p, M_s) plane, as shown in Fig. 2. A solution is given by the intersection of the two curves associated with Eq. (1). The two curves are closely related to properties of the superconducting and ferromagnetic subsystems, respectively. The coexistence is associated with a solution which satisfies $M_s = -\delta M_p$ and $M_p \neq 0$, i.e., corresponds to the complete Meissner effect of the superconducting subsystem. It is seen that the occurrence of the coexistence solutions is determined by the slopes of the two curves at the origin. Thus a necessary condition for coexistence, which appears at a temperature $T < T_2$, is to have a solution for T_2 of

$$[\chi_p(0,T_2)]^{-1} = \lambda - \delta^2 \ . \tag{14}$$

For a typical case with no crystal-field effects, $\chi_p(0,T) \sim T^{-1}$, which reduces Eq. (14) to

$$T_2 = T_f(1 - \delta^2/\lambda) \ , \tag{15}$$

if $T_2 < T_s$; otherwise $T_2 = T_s$. The trivial solution, $M_p = M_s = 0$, is always present. However it can be

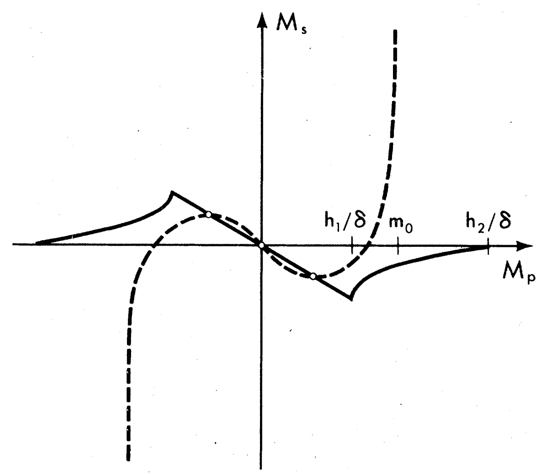

FIG. 2. Equation (1) presented graphically. The full line is associated with the superconductor subsystem described in the first line of Eq. (1). The dashed line is associated with the ferromagnetic subsytem described in the second line of Eq. (1). The intersections correspond to the solutions. The inversion symmetry is due to $H = 0$.

shown that the coexistence solution is a more stable one. The reason is that these two solutions are equivalent to the two solutions of a pure ferromagnetic system with an effective "self-coupling" $\bar{\lambda} = \lambda - \delta^2$ [cf. Eq. (9)]. Thus, the coexistence solution will be a truly stable one if no other solutions, except the trivial one, exist (e.g., $\delta m_0 << h_1^0$ or $T \approx T_2 \approx T_f << T_s$). However, if $\delta m_0 > h_1^0$ then the coexistence phase will be destroyed at a sufficiently low temperature T_1. Transition to the IIf phase will occur. It is also noteworthy that the coexistence solution, even when stable, is associated with unstable states of the ferromagnetic subsystem, as anticipated in the Introduction.

Next we will analyze in more detail the case when coexistence occurs. We assume $T_f < T_s$ and $h_1^0 < \delta m_0 < h_2^0$.

The typical evolution of the solutions, as the temperature changes, is shown in Fig. 3. We also show the total Gibbs potential (as a function of M_p) so that the stable solutions may be identified. As could be seen from Fig. 3, the transition at T_2 from phase I to the coexistence phase If is of *second order* whereas the transition at T_1 from phase If to phase IIf is of the *first order*. The main reason for the first-order transition is the infinite susceptibility of the superconducting subsystem at the lower critical field. A lower bound for the coexistence, T_1', is given by (cf. Fig. 3)

$$h_1(T_1') = \delta h_p \left[\frac{\bar{\lambda}}{\delta} h_1(T_1'), T_1' \right] \ . \tag{16}$$

The actual temperature T_1 at which the coexistence is

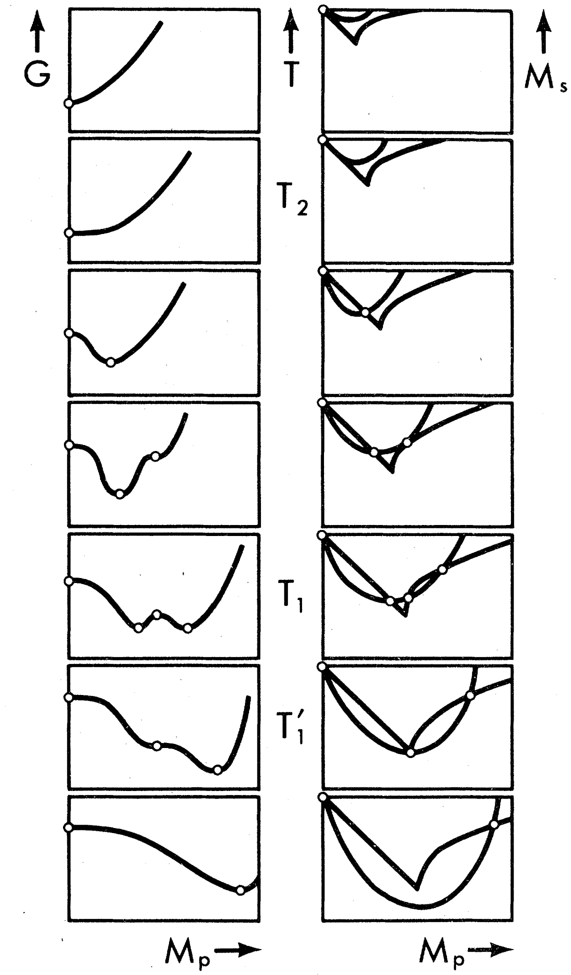

FIG. 3. Schematic evolution of solutions of Eq. (1) with the change of temperature for the case of coexistence. Only the lower right-hand quadrant of the (M_p, M_s) plane is shown. Temperature decreases from the top to the bottom of the figure, starting with the temperature $T < T_f < T_s$. The total Gibbs potential is shown in the left-hand side of the figure.

destroyed by the long-range ferromagnetic order is greater than T_1'. However, the equations which give T_1 are much too cumbersome to be of any practical use.

In Fig. 3 we assumed $T_f < T_s$ (or more generally $T_2 < T_s$). However, if $T_2 = T_s$ and/or there is more than one transition temperature T_1, an interesting, albeit unlikely situation may occur. In such a case we may find several alternating temperature regions of coexistence If and IIf phases.

The first-order transition at T_1 is marked by discontinuities in total entropy and magnetizations (the discontinuities may be small for the weakly first-order transitions, e.g., $\delta m_0 \approx h_1^0 << h_2^0$). Hence, the transitions at T_1 and T_2 will have their signatures in the specific heat C and the static susceptibility χ. Notably there will be a δ-function jump in both C (latent heat) and χ (magnetization discontinuity) at T_1, characteristic of first-order transitions. Other features of C and χ can be analytically expressed for temperatures above T_1. From Eqs. (8) and (11), we obtain

$$\chi(0,T) = \begin{cases} \chi_f(0,T) \ , & T > T_s \ , \\ -1 + (1-\delta)^2 \bar{\chi}_f(0,T) \ , & T_1 < T < T_s \ , \end{cases} \tag{17}$$

and

$$C(0,T) = \begin{cases} C_f(0,T) \ , & T > T_s \ , \\ C_s(0,T) + \bar{C}_f(0,T) \ , & T_1 < T < T_s \ . \end{cases} \tag{18}$$

We see that above T_s the FS behaves like an ordinary ferromagnetic system. At $T = T_s$ there is a discontinuity in χ and C, very much like in a pure superconducting system, with an additional contribution from the ferromagnetic subsytem. In the region between T_s and T_1 the superconducting subsytem is in the Meissner phase. In the same region FS behaves as if it were completely decoupled, except that the ferromagnetic subsystem is replaced by the effective one [with $\bar{\lambda}$ replacing λ, cf. Eq. (9)]. Therefore there is a second-order transition into the coexistence phase at T_2. The transition is marked by a divergence in the susceptibility and a discontinuity in the specific heat (mean-field behavior), typical of ferromagnetic systems. Below T_2 both χ and C decrease. At T_1, superimposed on a finite discontinuity, there is a δ-function singularity associated with the first-order transition. The finite discontinuity, which is caused mainly by the superconducting sub-

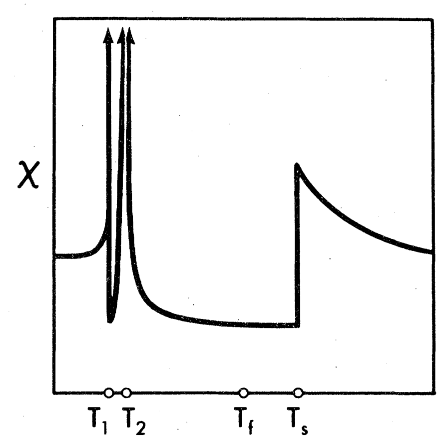

FIG. 4. Static susceptibility χ for FS which exhibits coexistence of ferromagnetism and superconductivity, as calculated in the model described here (see the text and the Appendix).

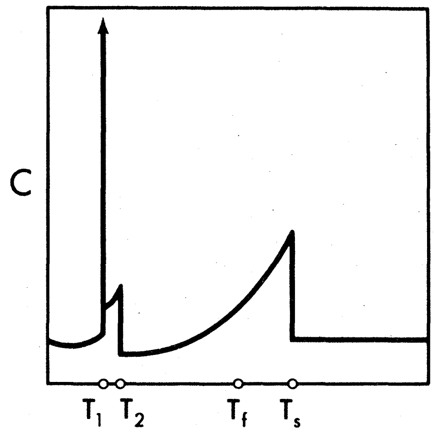

FIG. 5. Specific heat C for FS which exhibits coexistence of ferromagnetism and superconductivity, as calculated in the model described here (see the text and the Appendix).

system, may be particularly large due to the singularities in C_s and χ_s at the lower critical field. Typical curves for χ and C, given by our model, are displayed in Figs. 4 and 5. A more detailed discussion of corresponding model calculations is given in the Appendix. We note that the discontinuities at T_2 are smoothed out by an external field in very much the same way that they would be smoothed out in a pure ferromagnetic system.

Several more features, related to the coexistence state, are worth mentioning. First we note that the total magnetization at zero temperature must depend on an applied external field

$$M(H,0)=m_0+h_s(H+\delta m_0,0) \quad . \tag{19}$$

In a more general case, when the crystal-field effects are present, m_0 in Eq. (19) should be replaced by its field dependent form. Equation (19) merely restates the fact that the superconductor screens localized magnetic moments. Only at sufficiently high fields this screening disappears. Another interesting feature may appear in the magnetization: a maximum in the magnetization at some temperature below T_1. A physical reason is easily understood if we consider a magnetization of the effective ferromagnetic subsystem (i.e., $\lambda \rightarrow \bar{\lambda}$). An effective field acting on the superconducting subsystem will have a maximum, relative to either the upper or lower critical field, due to the sharp rise of the magnetization of the ferromagnetic subsystem below T_1. Therefore a maximum in M_s ($M_s<0$) is obtained. Hence the screening of the ferromagnetic subsystem is minimized, thus obtaining a maximum both of M_p and of the total magnetization M. In conclusion we display in Fig. 6 a typical phase diagram appropriate for FS which exhibits a coexistence. Hysteresis regions associated with the discontinuous transitions are not displayed.

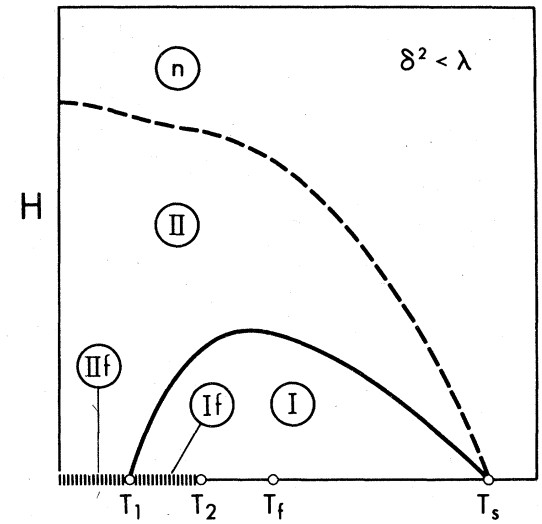

FIG. 6. Typical phase diagram for FS which exhibits a coexistence. Dashed line corresponds to a second-order phase transition whereas full line corresponds to a first-order transition.

III. DISCUSSION

An important feature of our model is its ability to treat quite general magnetic structures of the magnetic subsystem. When the magnetic subsystem is treated in a molecular-field fashion one only needs to introduce the appropriate vector and tensor quantities by considering a subscript p in Eqs. (1)–(4) as an index referring to the sublattices of the magnetic subsystem. In the simplest case, when the magnetic subsystem can exhibit an antiferromagnetic state, the coexistence is trivial. In a more general case, however, some other, originally unstable structure, (e.g., ferrimagnetic) may be stabilized by the interaction with the superconducting subsystem. The anomalies in specific heat in the superconducting phase of some ternary compounds, recently reported,[35] may be related to such phenomena.

As already mentioned, the coexistence of antiferromagnetism and superconductivity is trivially predicted by our model. Such coexistence has already been observed experimentally.[10] The behavior of the upper critical field experimentally observed,[9] is also in good qualitative agreement with our theory. However, the more intriguing question is the one of coexistence of ferromagnetism and superconductivity. There has been some speculation that such coexistence is actually present in a narrow temperature region[8,36] in $ErRh_4B_4$ and $Ho_{0.5}Lu_{0.5}Rh_4B_4$. Various interesting features have been observed in $ErRh_4B_4$. (a) A Schottky anomaly has been observed,[37] which suggests crystal-field splittings (a similar anomaly has been also observed[36] in $Ho_{0.5}Lu_{0.5}Rh_4B_4$). (b) A magnetic field dependence of the zero temperature magnetization, which seems not to be entirely consistent with the crystal-field effects, has been observed.[38] [Similar dependence has been observed[39] in some $R\mathrm{Mo_6(S,Se)_8}$.] (c) The observed magnetoresistance,[8] at low temperatures, is inconsistent with the ferromagnetic order.[8] (d) Hysteresis at the lower transition temperature has been observed.[8,40] (e) A fine shoulderlike anomaly has been observed in the specific heat[41,42] just above the lower transition temperature at which a spikelike feature is seen. (A similar anomaly has also been observed[36] in $\mathrm{Ho_{0.5}Lu_{0.5}Rh_4B_4}$.)

The crystal-field splitting makes quantitative analysis of the experiments difficult at present.[43] Therefore we limit ourselves to a qualitative analysis of $\mathrm{ErRh_4B_4}$ experiments. From the size of the jump in the specific heat at the lower transition temperature one finds 2×2 degeneracy of the crystal-field ground state (degeneracy 4 being forbidden by the symmetry). On the other hand, data from Refs. 38 and 8 indicate that the increase in effective magnetic moment deviates from H^2 behavior, expected from the crystal-field theory. Our theory is capable of predicting such deviation, if the screening effect is important [if $\delta m_0 < h_2^0$ and cf. Eq. (19)]. A strange field dependence of the resistance may be, therefore, partially attributed to the same effect.

Both features, the hysteresis and spikelike jump in specific heat, at the lower transition temperature suggest that the transition is of the first order. This is consistent with the prediction of our theory that a "reentrant" transition must be first order. However, the steplike feature in the specific heat near and above the lower transition temperature is puzzling. Our theory predicts a similar steplike feature, associated with the second-order transition into a coexistence phase (cf. Fig. 5). There, superconductivity should coexist with long-range ferromagnetic ($M_p \neq 0$) order. However, in order to prove coexistence conclusively, one should also be able to detect an anomaly in the static susceptibility (cf. Fig. 4).

Our understanding of the anomalous behavior of the maximum of H_{c2} in the $\mathrm{Gd_xEr_{1-x}Rh_4B_4}$ alloy[44] is the competition of two processes: depression of T_s by essentially the Abrikosov-Gor'kov mechanism (which is expected to be larger for Gd) and the "molecular-field mechanism" (i.e., electromagnetic coupling, which is expected to be smaller for Gd). Nevertheless we will not make an attempt here to understand general properties of the $R_x'R_{1-x}''\mathrm{Rh_4B_4}$ alloys.

The most significant drawback of any mean-field-type theory is its failure to account for fluctuations. The introduction of fluctuations in M_p, for example, should correspond in our theory to the Abrikosov-Gor'kov mechanism. The Abrikosov-Gor'kov mechanism is undoubtedly important near and above the magnetic transition temperature. It is particularly important to find whether fluctuations are capable of destroying the ferromagnetic coexistence state which we find.

Our phenomenological theory treats single domain, macroscopic magnetizations. However, it is important to study both the domain structure as well as the spatial variation of the magnetization. The obvious choice for such a task is a Ginzburg-Landau-type theory. A full renormalization-group treatment of such a theory could also give a proper account of the fluctuations. Our theory suggests that the magnetic and superconducting subsystems in a Ginzburg-Landau theory may be coupled in an "effective-field" fashion.

Finally, although our theory is a phenomenological one, it would be interesting to give a microscopic interpretation of the coupling δ. Unfortunately this would call for a complete microscopic treatment of FS's. Therefore, a microscopic calculation of δ seems unlikely at present.

ACKNOWLEDGMENTS

I would like to thank Professor L. M. Falicov for reading of the manuscript and Dr. P. Thalmeier, Professor L. M. Falicov, and Dr. C. Balseiro for several useful discussions. I also acknowledge a fellowship from the Miller Institute for Basic Research in Sciences, and partial support from NSF Grant No. DMR78-03408.

APPENDIX

Figures 4 and 5 represent the results of a model calculation, the aim of which was to illustrate some qualitative predictions of our theory. For the paramagnetic subsystem we have chosen the spin-$\frac{1}{2}$ system

$$h_p(H,T) \equiv m_0 \tanh\left(\frac{C}{T}H\right) , \tag{A1}$$

where $C = T_f/\lambda m_0$. We have taken $m_0 = 1.0$, $t_f = 0.8$, and $\lambda = 0.8$.[45] For the superconducting subsystem we only wanted to mimic typical features

$$h_s(H,T) = \begin{cases} -H , & |H| < h_1(T) , \\ -H + h_2(T)\,\mathrm{sgn}(H)\, h^{3/4} , & h_1(T) \le |H| < h_2(T) , \\ 0 , & |H| \ge h_2(T) , \end{cases} \tag{A2}$$

where $h \equiv [|H| - h_1(T)]/[h_2(T) - h_1(T)]$ and the lower and upper critical fields are assumed to be of the form

$$h_{1,2}(T) = \begin{cases} h_{1,2}^0[1-(T/T_s)^2] , & T \le T_s , \\ 0 , & T > T_s . \end{cases} \tag{A3}$$

The fractional power law for the interval

$h_1(T) \leq |H| < h_2(T)$ is permitted for our choice $h_2^0 = 3h_1^0 = 1.8$. Better dependence could have been chosen for that interval,[24,28,46] but it is unnecessary in our case. For the transition temperature T_s we choose $T_s = 1.1$ so that $T_s > T_f$. We assume ferromagnetic ($\delta > 0$) coupling of the superconductor and ferromagnetic subsystems, and we take $\delta = 0.7$. This choice guarantees that $\delta^2 < \lambda$ and $h_1^0 < \delta m_0 < h_2^0$ so that we are able to find coexistence. The calculation was performed numerically. We have expressed M_s and the total Gibbs potential G in terms of M_p. Then we solved Eq. (1), numerically for M_p. The stable solution is picked as one with smallest G. Once a stable M_p was found we were able to determine G and therefore all other thermodynamic properties.

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[29]Our definition of the magnetizations includes a factor 4π.

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[32]Phase diagrams shown here are an improvement over the ones of Ref. 23 where we have encountered nonuniqueness in the Maxwell contruction. We do not show hysteresis regions here.

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