# Possibility of magnetic-field-induced superconductivity in a metal with Kondo impurities

A.N. Podmarkov and I.S. Sandalov

L. V. Kirenskii Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR (Submitted 27 January 1989) Zh. Eksp. Teor. Fiz. **95**, 2235–2247 (June 1989)

An equation is constructed for the boundary of the region in the space of the magnetic-impurity concentration, the temperature, and the external magnetic field in which the superconducting state of a metal exists. There are regions in which superconductivity may be induced by a magnetic field. This effect occurs because the Kondo amplitudes for the scattering of conduction electrons by magnetic impurities decrease in a magnetic field. It may be realized in superconductors with a short coherence length.

### **1.INTRODUCTION**

Meul et al.<sup>1</sup> have experimentally observed a superconducitivity induced by an external magnetic field in  $Sn_{0.25}Eu_{0.75}Mo_6S_{7.2}Se_{0.8}$ . This experimental fact is paradoxical in itself, since a magnetic field ordinarily suppresses superconductivity. First, by perturbing the orbits of the electrons of a Cooper pair a magnetic field tends to disrupt the phase coherence of the motion of these electrons. This mechanism destroys superconductivity at field levels for which the Larmor radius becomes comparable to the coherence length  $\xi_0$  in order of magnitude. Second, the field tends to bring the spins of all of the electrons into parallel alignment and thus destroys superconductivity at a Zeeman energy on the order of the superconducting gap. This second mechanism is ordinarily not seen, since the coherence length for conventional superconductors is  $\xi_0 \sim 10^3 a$  (a is the lattice constant), and the orbital mechanism is predominant. Meul et al.<sup>1</sup> suggest that for the particular compounds which they studied the upper critical field, set by orbital effects, exceeds the "Pauli" limiting field  $H_P$ . Ternary chalcogenides of molybdenum (Chevrel phases) such as the compounds studied in Ref. 1 do indeed have some distinctive features, which we believe allowed Meul et al.<sup>1</sup> to invoke a Zeeman mechanism for a phenomenological explanation of their experiments. It follows from the band calculations of Ref. 2 that the state density near the Fermi surface is dominated by narrow bands of molybdenum 4d electrons ( $Mo_6$  clusters). Because of the low electron velocity  $v_0$  at the Fermi surface,  $H_{c2}$  is high:  $H_{c2} \propto \xi_0^{-2}, \xi_0 \propto v_0$ .

In explaining the induction of superconductivity by an external magnetic field, Meul et al.<sup>1</sup> used Jaccarino and Peter's suggestion<sup>3</sup> of a reduction of the separation of the electron spin subbands,  $\Delta_c$ , by an exchange field. This separation is caused by local impurity magnetic moments:  $\Delta_c$  $= h + A_{sf}c_m \langle S^z \rangle$ , where h is the magnetic field,  $A_{sf}$  is the sf exchange constant,  $c_m$  is the concentration of magnetic impurities, and  $\langle S^z \rangle$  is the expectation value of the magnetic moment of the impurity in the field. A reduction of the separation obviously requires  $A_{sf} < 0$ . In this case, however, the situation is not as simple: When the exchange interaction  $A_{sf}$ has a negative sign, an anomalous enhancement of the scattering of conduction electrons by degenerate magnetic impurity levels, i.e., the Kondo effect proper, occurs as the temperature is lowered in the region  $T \gtrsim T_K$ , where  $T_K$  is the Kondo temperature. In the region  $T < T_K$  an impurity spin is completely screened by electrons of the normal metal. For this reason, the theory of superconductors with magnetic impurities in the case  $A_{sf} < 0$  should incorporate the relationship between the superconducting transition temperature of the material without impurities ( $T_{c0}$ ) and the Kondo temperature. If  $T_K < T_{c0}$ , then there exists a temperature region  $T_K < T < T_{c0}$  in which the scattering processes which lead to the Kondo effect are inconsequential. This region is described by the Abrikosov–Gor'kov theory.<sup>4</sup>

We now lower the temperature of this superconductor. At  $T \sim T_K$ , Kondo anomalies should then appear in the scattering of electrons. This situation was studied theoretically in a series of papers by Müller–Hartmann and Zittartz.<sup>5</sup> They showed that the superconducting state of a system is destroyed by increased Kondo scattering. Analyzing their equations, they also concluded that superconductivity is restored at  $T < T_K$ .

The problem of the behavior of a superconductor of this sort in a magnetic field was not studied. However, one could expect some nontrivial effects in this case, since a magnetic field provides some control over both the separation of the electron subbands and the intensity of the Kondo scattering. The latter capability arises from the circumstance that an external field reduces the importance of Kondo scattering processes by lifting the degeneracy of the impurity magnetic sublevels.<sup>6</sup> A reduction of the electron-spin scattering amplitude, on the other hand, should tend to preserve superconductivity. Accordingly, even if we put aside the Jaccarion-Peter effect we have a region of parameter values,  $T \sim T_K$ ,  $h \sim T_K$ , in which we could expect an extremely unusual behavior of a superconductor with magnetic impurities. Specifically, let us assume that we have prepared a system in a superconducting state with the parameter values which we just listed. The system will then repel an external magnetic field, and the splitting of magnetic levels of the impurity should disappear. In this case, however, a strong Kondo scattering will suppress the superconductivity. The field begins to penetrate into the metal, the degeneracy of magnetic levels is lifted, and the suppression of Kondo scattering thus makes possible the restoration of superconductivity. These ideas suggest that a superconducting state may arise which is capable of existing only in a magnetic field.

Our purpose in the present study is to construct a  $(c_m, T, h)$  phase diagram of a superconductor with a short coherence length and weak coupling which contains normal and magnetic impurities. In our calculations we will incor-

porate all of the mechansisms listed above for the suppression of superconductivity.

## 2. EQUATIONS FOR THE ORDER PARAMETER AND THE TRANSITION TEMPERATURE

We will analyze a model with the Hamiltonian

$$H = H_{0}' + H_{int}, H_{0}' = H_{0} + H_{sf} + H_{imp},$$

$$H_{0} = \sum_{\alpha} \int d^{3}\mathbf{r} \,\psi_{\alpha}^{+}(\mathbf{r}) \left[ \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right)^{2} - g_{c} \mu_{B} H \sigma_{\alpha \alpha}^{2} \right] \psi_{\alpha}(\mathbf{r}) - \int d^{3}\mathbf{r} \, g_{f} S^{z}(\mathbf{r}) H,$$

$$H_{imp} = \sum_{\alpha} \int d^{3}\mathbf{r} \,\psi_{\alpha}^{+}(\mathbf{r}) \, V(\mathbf{r}) \,\psi_{\alpha}(\mathbf{r}),$$

$$H_{sf} = -\sum_{\alpha,\beta} \int d^{3}\mathbf{r} \left[ A_{\parallel} \sigma_{\alpha\beta}^{z} S^{z}(\mathbf{r}) + \frac{1}{2} A_{\perp} (\sigma_{\alpha\beta}^{+} S^{-}(\mathbf{r}) + \sigma_{\alpha\beta}^{-} S^{+}(\mathbf{r})) \right] \psi_{\alpha}^{+}(\mathbf{r}) \,\psi_{\beta}(\mathbf{r}),$$

$$H_{int} = -|g| \int d^{3}\mathbf{r} \psi_{\dagger}^{+}(\mathbf{r}) \,\psi_{\dagger}(\mathbf{r}) \,\psi_{\dagger}(\mathbf{r}).$$
(1)

Here  $\sigma_{\alpha\beta}^{z,+,-}$  are the spin matrices of a conduction electron, and  $S^{z,+,-}$  are the impurity spins:

$$S(\mathbf{r}) = \sum_{t} \delta(\mathbf{r} - \mathbf{R}_{t}) S_{t},$$

where the sum is over the sites of the magnetic impurites; nonmagnetic impurities are described by the potential  $V(\mathbf{r})$ ; the vector potential **A** is chosen in the gauge (0,xH,0), in which the external magnetic field is assumed to be applied along the z axis, which is directed parallel to the surface of the semi-infinite sample; the s-f interaction is written in anisotropic form, so that in certain cases it is possible to incorporate the splitting of the magnetic impurity levels in the crystal field; and  $H_{sf}$  then describes the interaction of electrons with a resonating pair of levels.<sup>7</sup> The effective attraction between electrons which leads to the superconductivity is described by the Hamiltonian  $H_{int}$ . We will not discuss the nature of this attraction of the possibility of a triplet pairing.

The partition function of the system,

$$Z = \operatorname{Sp}\left\{ e^{-\beta H_0'} T_{\tau} \exp\left(-\int_0^{\beta} H_{int}(\tau) d\tau\right) \right\},\,$$

can be rewritten as follows by the standard procedure<sup>8</sup>:

$$\int D\Delta(\mathbf{r},\tau) D\Delta^{*}(\mathbf{r},\tau) \exp\{-\beta\Omega[\Delta^{*}(\mathbf{r},\tau),\Delta(\mathbf{r},\tau)]\},$$

$$\Omega = \Omega_{0} + \Omega_{1}, \qquad \Omega_{0} = -T \int_{0}^{\beta} d\tau \int d^{3}\mathbf{r} \frac{1}{|g|} |\Delta(\mathbf{r},\tau)|^{2}, \qquad (2)$$

$$\Omega_{1} = -T \ln \langle S_{a}(\beta) \rangle_{0'};$$

$$S_{a}(\beta) = T_{\tau} \exp\{-\int_{0}^{\beta} d\tau \int d^{3}\mathbf{r} (\psi_{1}^{+}(\mathbf{r},\tau)\psi_{1}^{+}(\mathbf{r},\tau)$$

$$\Delta(\mathbf{r},\tau) + H.a.)\}, \qquad (3)$$

For convenience in the calculations below in which averages

1292 Sov. Phys. JETP **68** (6), June 1989

are taken over the impurities, the latter are incorporated in  $H'_0$ . We find an equation for the order parameter in the mean-field approximation by requiring the existence of a path of steepest descent which minimizes the functional  $\Omega[\Delta^*,\Delta]$  and which dominates the partition function (2):

$$\frac{\delta\Omega[\Delta^{\bullet}, \Delta]}{\delta\Delta^{\bullet}(\mathbf{r}, \tau)} = 0 \quad \text{or}$$
$$\Delta(\mathbf{r}, \tau) = |g| \frac{\delta\Omega_{1}[\Delta^{\bullet}(\mathbf{r}, \tau), \Delta(\mathbf{r}, \tau)]}{\delta\Delta^{\bullet}(\mathbf{r}, \tau)}$$

Substituting in the explicit expression for the derivative  $\delta\Omega_1/\delta\Delta^*$ , we find an equation for the order parameter:

$$\Delta(\mathbf{r},\tau) = |g| \frac{\langle T_{\tau}\psi_{\downarrow}(\mathbf{r},\tau)\psi_{\uparrow}(\mathbf{r},\tau)S_{a}(\beta)\rangle_{0'}}{\langle S_{a}(\beta)\rangle_{0'}}.$$
(4)

It is sufficient to retain the terms linear in  $\Delta(\mathbf{r},\tau)$  on the right side of (4) in constructing a phase-transition curve, since we are assuming that a second-order transition occurs. Expanding the right side of (4) in powers of  $\Delta$ , we find

$$\Delta(\mathbf{r},\tau) = \int_{0}^{\tau} d\tau_{i} \int d^{3}\mathbf{r}_{i} K_{i}(\mathbf{r},\tau;\mathbf{r}_{i},\tau_{i}) \Delta(\mathbf{r}_{i},\tau_{i}), \qquad (5)$$

where

$$K_1(\mathbf{r}, \tau; \mathbf{r}_1, \tau_1)$$

$$= -\langle T_{\tau}\psi_{\downarrow}(\mathbf{r},\tau)\psi_{\uparrow}(\mathbf{r},\tau)\psi_{\uparrow}^{+}(\mathbf{r}_{i},\tau_{i})\psi_{\downarrow}^{+}(\mathbf{r}_{i},\tau_{i})\rangle_{0'}^{\mathrm{coup}}.$$
 (6)

The correlation function (6) no longer contains  $\Delta(\mathbf{r},\tau)$ . We will calculate it by the standard diagram techniques,<sup>9,10</sup> collecting in the *S*-matrix the interaction with all impurites  $(H_{imp} + H_{sf})$ . We restrict the analysis to the following region of the parameters of the system. The magnetic impurity concentration is assumed to be small, and the magnetic field is assumed to be weak enough that we can treat the distance between Landau levels as small in comparison with the temperature and with the impurity width:

$$eH/cm < \pi T + \tau^{-1}.$$
 (7)

We assume that the coherence length of the superconductor, like the electron mean free path, is short in comparison with the Larmor radius.

We are interested in Eq. (5) averaged over the impurity positions. Following Ref. 4, we discard the term  $(\hat{K}_1 - \hat{K})(\Delta - \overline{\Delta})$  from the right side of (5). (This term may prove important in a study of mesoscopic effects, but for bulk samples it is sufficient to solve the equation  $\Delta = \hat{K}_1 \overline{\Delta}$ .) To find the average two-particle Green's function  $K_1$  we must first find the average one-particle function. In the absence of magnetic impurites, it is<sup>8</sup>

$$G_{0}^{\sigma}(i\omega,\mathbf{r},\mathbf{r}') = G_{00}^{\sigma}(i\omega,\mathbf{r}-\mathbf{r}') \exp\left\{i\frac{e}{c}\int_{\mathbf{r}}^{\mathbf{r}'}\mathbf{A}(\mathbf{s})d\mathbf{s}\right\},\qquad(8)$$

where the integral is carried out along the line which connects points  $\mathbf{r}$  and  $\mathbf{r}'$ , and

$$G_{00}^{\sigma}(i\omega,\mathbf{r}) = -\frac{m}{2\pi r} \exp\left\{\left[i(p_0v_0 - \mu_B g_c \sigma^z H) \operatorname{sgn} \omega - |\omega| - \frac{1}{2\tau}\right] \frac{\mathbf{r}}{v_0}\right\}.$$
(9)

Here  $p_0$  and  $v_0$  are the electron momentum and velocity on the Fermi surface, and  $\tau$  is the ordinary relaxation time for the relaxation of electrons among nonmagnetic impurities.<sup>9</sup> Physically, the Green's function (8) has a simple structure: for  $|\mathbf{r} - \mathbf{r}'| > l(l = v_0 \tau)$ , the function (9) is itself small, while for  $|\mathbf{r} - \mathbf{r}'| < l$  an electron, not "sensing" an impurity at this distance, "lives" only in a external magnetic field. This effect is described by the phase factor  $\int \mathbf{A} \cdot d\mathbf{s}$ . Since the Bohr quantum orbit corresponding to the twisting of the path of an electron in a magnetic field does not fit into a mean free path, the magnetic field in (9) acts only on the electron spin.

We turn now to magnetic impurities. We know<sup>6</sup> that the existence of a small transition energy  $(-\mu_B H)$  between impurity sublevels makes it possible to distinguish a parquet sequence of diagrams which contribute to the self-energy part of the conduction electrons,

and to the vertex function for s - f electron-spin scattering,

The dashed lines here represent the electron Green's functions ( $\Delta$  corresponds to  $\sigma = \downarrow$ , and  $\rightarrow$  corresponds to  $\sigma = \uparrow$ ); the solid lines correspond to the spin Green's functions.<sup>10,7</sup> The ovals looped by the spin lines have been omitted for brevity. The mass operator describing the multiple scattering of an electron by an impurity is a local operator, so the phase factor with  $\int \mathbf{A} \cdot d\mathbf{s}$  does not appear in it. In calculating the total Green's function, however, we need to sum expressions of the type

$$\xrightarrow{\mathbf{r}}_{\mathbf{r}_{1}} \xrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{1}} \xrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{2}} \xrightarrow{\mathbf{r}_{2}} \xrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{2}} \xrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{2}} \xrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{2}} \xrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{2}} \overrightarrow{\mathbf{r}_{$$

or, in analytic form,

$$\delta G(\mathbf{r},\mathbf{r}') \propto \int G_0(\mathbf{r},\mathbf{r}_1) \Sigma(r_1) G_0(\mathbf{r}_1,\mathbf{r}_2) \Sigma(\mathbf{r}_2) G_0(\mathbf{r}_2,\mathbf{r}') d^3 \mathbf{r}_1 d^3 \mathbf{r}_2.$$

We seek a solution in the form (8), so we write

$$\delta G = \delta \tilde{G} \exp \left\{ i \frac{e}{c} \int_{r}^{r'} \mathbf{A}(\mathbf{s}) d\mathbf{s} \right\}.$$

Moving the phase factor over to the right side, we find an additional phase due to the magnetic field, which is determined by an integral over a closed contour:

$$\int_{r}^{r_{1}} \mathbf{A} \, d\mathbf{s} + \int_{r_{1}}^{r_{2}} \mathbf{A} \, d\mathbf{s} + \int_{r_{2}}^{r'} \mathbf{A} \, d\mathbf{s} - \int_{r}^{r'} \mathbf{A} \, d\mathbf{s}.$$
(12)

Since the function (9) "forbids" the separation of the points r and  $r_1$ ,  $r_1$  and  $r_2$ , etc., by distances greater than the mean free path l, the integral (12) gives us an area  $\leq l^2/R_c^2$ , where  $R_c$  is the magnetic length. By virtue of (7) we cannot ignore these corrections. In this sense the situation is no different

from that which prevails for nonmagnetic impurities, and we reach the conclusion that even when we do take magnetic impurities into account the Green's functions retain their form in (8), but now the role of  $G_{00}$  should be played by a function which incorporates exchange scattering by magnetic impurities.

Furthermore, as we go through the procedure of averaging over the positions of the magnetic impurities we also find interference corrections of the type

$$= \frac{D}{T} \frac{1}{\tau \epsilon_F}; \qquad \qquad \sim cA^2 g_0 \ln \frac{D}{T} \frac{1}{\tau} \tau,$$

where a dotted line connects crosses which refer to the same atom.<sup>9</sup> Comparisons of diagrams a and b shows that the former is small in comparison with the latter by a factor on the order of the customary small parameter<sup>9</sup>  $(p_0l)^{-1} \ll 1$ . In the very dirty limit, with  $p_0l \sim 1$ , the very procedure of calculating independent averages over the magnetic and nonmagnetic impurities is dubious, and our analysis breaks down.

We thus conclude that the influence of the magnetic field on the orbital part of the motion of an electron is described completely by the phase factor

$$G(\mathbf{r},\mathbf{r}') = \widetilde{G}(\mathbf{r},\mathbf{r}') \exp\left\{i\frac{e}{c}\int_{\mathbf{r}}^{\mathbf{r}} \mathbf{A}(\mathbf{s}) d\mathbf{s}\right\}$$

and that Kondo scattering, which determines the form of  $\tilde{G}(\mathbf{r},\mathbf{r}')$ , can be studied by taking are Green's functions in the form (9).

The mass operator (which, we recall, is a local operator and does not contain  $\int \mathbf{A} \cdot d\mathbf{s}$ ) is expressed in terms of the amplitudes for the scattering of conduction electrons by a magnetic impurity:

$$\Sigma_{\uparrow} = - \star \bigcirc - - \bigcirc \star - + - \star \bigcirc - - \bigcirc \star - - ,$$

where the Kondo-scattering amplitudes

$$- \star \bigoplus \Gamma_{\parallel}(\omega) , \quad - \star \bigoplus (1) + \star \bigoplus \Gamma_{\perp}(\omega)$$

are given by a parquet sequence of diagrams of the form (11).

In analytic form, we have the following in the case h/T < 1:

$$\operatorname{Im} \Sigma_{\sigma} = -\frac{\pi c}{2g_{0}} \operatorname{sgn} \omega \left[ \Gamma_{\parallel}^{2}(\omega) \left( S(S+1) - SB_{s}\left(\frac{h}{T}\right) \operatorname{cth} \frac{h}{2T} \right) \right. \\ \left. + \Gamma_{\perp}^{2}(\omega) SB_{s}\left(\frac{h}{T}\right) \left( \operatorname{cth} \frac{h}{2T} - \eta(\sigma) \right) \right], \\ \left. h = g_{I} \mu_{B} H, \quad \eta(\sigma) = \begin{cases} 1, \ \sigma = \uparrow, \\ -1, \ \sigma = \downarrow. \end{cases}$$

Here  $B_S(x)$  is the Brillouin function.

The calculations are precisely the same as those of Ref. 7; they lead to the following expressions:

 $\Gamma_{\parallel} = A_{\perp} g_{0} \gamma_{1} \operatorname{ctg} \{ \operatorname{arcsin} \gamma_{1} + A_{\perp} \gamma_{1} g_{0} x \},$   $\Gamma_{\perp} = A_{\perp} g_{0} \gamma_{1} / \operatorname{sin} \{ \operatorname{arcsin} \gamma_{1} + A_{\perp} \gamma_{1} g_{0} x \}, \qquad (11A)$  $x = \ln[D/\max\{|\omega|, h, \tau^{-1}\}], \quad \gamma_{1} = [1 - (A_{\parallel}/A_{\perp})^{2}]^{\gamma_{0}},$ 

where D is a cutoff parameter.

The one-particle Green's function is thus

$$G^{\sigma}(i\omega, \mathbf{r}, \mathbf{r}') = -\frac{m}{2\pi r} \exp\left\{\left[i\left(p_{0}v_{0} - \eta\left(\sigma\right)\frac{\Delta_{c}}{2}\right)\right] \times \operatorname{sgn}\omega - |\omega| - \frac{1}{2\tau_{\sigma}}\right] \frac{|\mathbf{r} - \mathbf{r}'|}{v_{0}} + \frac{ie}{c} \int_{\mathbf{r}}^{\mathbf{r}'} \mathbf{A} \, d\mathbf{s}\right\}, \quad (13)$$

where

$$\Delta_{c} = \mu_{B}g_{c}H + cA_{\parallel}\langle S^{z}\rangle,$$
  
$$\tau_{\sigma}^{-1} = \tau^{-1} + (\tau_{\sigma}^{sf})^{-1}, \quad (\tau_{\sigma}^{sf})^{-1} = 2\mathrm{Im}\Sigma_{\sigma}.$$

The kernel  $K_1(\mathbf{r},\tau;\mathbf{r}',\tau')$  in Eq. (5) can be evaluated by expanding (6) in a perturbation-theory series and using the same procedure to average each term over the positions of the impurities. All of the diagrams which give rise to independent averaging of the two one-particle Green's functions in (6) (in the present approximation) are taken into account in (13). We are left with examing the contributions which link these functions:



The function K appears in (6) with joined ends, but for convenience in the analysis below we will not carry out the summation over external frequencies at this point. Studies of superconductors with impurities usually consider diagrams of types O,a, and d (Ref. 4). In the case at hand for  $T \gtrsim T_{\kappa}$ , the Kondo corrections are not small. As a result, the amplitude for scattering by fluctuations of the z component of the spin, a, is "dressed" by diagrams of types b and c, while that for the scattering of electrons with spin flip, d is dressed by diagrams of types e and f. Diagrams of type g, which contain more than a single spin line referring to a single atom and connecting electron Green's functions, contain a power of the logarithm  $(\ln D/T)$  which is lower than that of the parquet corrections, which dress each vertex independently. In the leading-log approximation, they should therefore be discarded.

The equation which we have been seeking for the function K can thus be represented as follows:

$$\begin{array}{c} - \stackrel{}{\rightarrow} \\ - \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \\ - \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \\ - \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel{}{\rightarrow} \stackrel$$

The function  $K_1$  in (5) depends only on the time difference  $\tau - \tau_1$ . We take Fourier transforms in  $\tau$  and  $\tau_1$  in (5), and we

consider only the equation which corresponds to a zero frequency  $\Omega$ , since the instability arises first for specifically  $\Omega = 0$ . Following the standard procedure,<sup>4</sup> we write an equation for the order parameter in terms of  $T_{c0}$  (the superconducting transition temperature in the absence of impurities):

$$\Delta(\mathbf{r})\ln\frac{T_{c0}}{T_{c}} = \sum_{n} \int d^{3}\mathbf{r}' \left\{ \frac{\delta(\mathbf{r}-\mathbf{r}')}{|2n+1|} - K_{\omega}(\mathbf{r},\mathbf{r}') \right\} \Delta(\mathbf{r}'). \quad (15)$$

According to (14), the equation for  $K_{\omega}$  is

$$K_{\omega}(\mathbf{r},\mathbf{r}') = K_{\omega}^{0}(\mathbf{r},\mathbf{r}') + (\tau_{1}^{-1} - \tau_{\parallel}^{-1}(\omega))$$

$$\times \int d^{3}\mathbf{r}'' K_{\omega}^{0}(\mathbf{r},\mathbf{r}'') K_{\omega}(\mathbf{r}'',\mathbf{r}')$$

$$+ \tau_{3}^{-1}(\omega) \int K_{\omega}^{0}(\mathbf{r},\mathbf{r}'') T \sum_{\omega'} P_{\omega'-\omega} K_{\omega'}(\mathbf{r}'',\mathbf{r}') d^{3}\mathbf{r}''.$$
(14A)

Here we have made use of the circumstance that the function  $\tau_{\parallel,3}$  vary slowly in comparison with K and P. Here

 $K_{\omega}^{0}(\mathbf{r}, \mathbf{r}') = Tg_{0}^{-1}G^{\dagger}(i\omega, \mathbf{r}, \mathbf{r}')G^{\downarrow}(-i\omega, \mathbf{r}, \mathbf{r}'),$ 

and  $K = Tg_0^{-1}K_1$ . The relaxation times in (14A) are written in dimensionless form:

$$\begin{aligned} \tau_{1}^{-1} &= (\pi T_{c0}\tau)^{-1}, \ \tau_{\parallel}^{-1}(\omega) = \pi c_{m}\Gamma_{\parallel}^{2}(\omega) \langle S_{z}^{2} \rangle / (\pi g_{0}T_{c0}), \\ \tau_{3}^{-1}(\omega) = \pi c_{m}\Gamma_{\perp}^{2}(\omega) \langle S_{z} \rangle / (\pi g_{0}T_{c0}), \\ P_{-\omega-\omega'} = (-i\omega - i\omega' - h)^{-1}. \end{aligned}$$

Equation (14A) is an integral equation both in terms of coordinates and in terms of frequencies. In deriving it, however, we made use of the small value of the parameter h/T. For this reason, the sum over  $\omega'$  in (14A) is difficult to evaluate. To within terms  $\sim (h/T)^2$  we find

$$K_{\omega}(\mathbf{r},\mathbf{r}') = K_{\omega}^{0}(\mathbf{r},\mathbf{r}') + \int d^{3}\mathbf{r}'' K_{\omega}^{0}(\mathbf{r},\mathbf{r}'')$$

$$\times [(\tau^{-1} - \tau_{\parallel}^{-1}(\omega)) K_{\omega}(\mathbf{r}'',\mathbf{r}')$$

$$+ \tau_{\perp}^{-1}(\omega) K_{-\omega}(\mathbf{r}'',\mathbf{r}')]. \qquad (16)$$

Here

$$\tau_{\perp}^{-1}(\omega) = \tau_{3}^{-1}(\omega) \operatorname{cth}(h/2T).$$

The summation over frequencies has thus led to a system of two integral equation for  $K_{\omega}$  and  $K_{-\omega}$ . To solve it we use the standard procedure: We introduce the eigenfunctions of the operator  $K_{\omega}^{0}(\mathbf{r},\mathbf{r}')$ , which turn out to be independent of  $\omega$  (Ref. 11):

$$\int K_{\omega}^{0}(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}')d^{3}\mathbf{r}'=s_{\omega}\varphi(\mathbf{r}).$$
(17)

We also note that all of the  $\tau_i^{-1}$  are even functions of the frequency. Making use of this circumstance and Eq. (17), we can easily derive

$$\int K_{\omega}(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}')d^{3}\mathbf{r}' = K(\omega)\varphi(\mathbf{r}), \qquad (18)$$

where

$$K(\omega) = \frac{s_{\omega} [1 - (\tau_{1}^{-1} - \tau_{\parallel}^{-1} - \tau_{\perp}^{-1}) s_{-\omega}]}{[1 - (\tau_{1}^{-1} - \tau_{\parallel}^{-1}) s_{\omega}] [1 - (\tau_{1}^{-1} - \tau_{\parallel}^{-1}) s_{-\omega}] - \tau_{\perp}^{-2} s_{\omega} s_{-\omega}}$$
(19)

As a result we find from (17)–(19) an equation for  $T_c$ :

$$\ln \frac{T_{c0}}{T_{c}} = \sum_{n} \left[ \frac{1}{|2n+1|} - K(\omega_{n}) \right].$$
 (20)

It follows from (19) and (20) that we are interested in the lower eigenvalue of Eq. (17). The derivation of  $s_{\omega}$  is completely analogous to the derivation in Ref. 11, so we will omit it. The result if

$$s_{\omega} = h_0^{-\nu_b} t J(\alpha_{\omega}), \quad J(\alpha) = 2 \int_0^{\infty} dx \ e^{-x^2} \frac{1}{2i} \ln \frac{1+i\alpha x}{1-i\alpha x}. \quad (21)$$

Here  $h_0 = 2eH\xi_0^2/c$ ,  $\xi_0 = v_0/(2\pi T_{c0})$ ,  $t = T/T_{c0}$  and

$$\alpha_{\omega} = \frac{h_{0}^{'b}t^{-1}}{\tau_{1}^{-1} + \tau_{\parallel}^{-1}(\omega) + \tau_{\perp}^{-1}(\omega) + |2n+1| + i\Delta \operatorname{sgn} \omega}$$
(22)

and  $\Delta = \Delta_c (\pi T_c)^{-1}$ . Equations (19)–(22) completely define a surface in the parameter space at which a phase transition occurs. We wish to emphasize that these equations contain all of the mechanisms for the suppression of superconductivity which we have been discussing: The scattering by magnetic impurities is described by the relaxation parameters  $\tau_{\parallel}$  and  $\tau_1$ ; the parameter  $\Delta$  describes the spin mechanism; and  $h_0$  describes the orbital mechanism. If, for example, we set  $\tau_{\parallel} = \tau_1 = \Delta_c = 0$  in (22), we find the ordinary equations for  $H_{c2}$  on the basis of the purely orbital mechanism.<sup>11</sup> In the limit  $H \rightarrow 0$  we find suppression of the first Born approximation, we find the Abrikosov–Gor' kov result.<sup>4</sup> To save space, we will not reproduce those known results here.

#### **3. PHASE DIAGRAMS**

Let us examine the situation with  $T_K < T_{c0}$ . The effects in which we are interested here, which stem from the magnetic field, are significant in the Kondo amplitudes (11) and (11A) if the Zeeman splitting of the impurity levels by the external field is comparable to the Kondo temperature. The latter can vary over a fairly wide range, even for an impurity of a given element, in different metallic matrices. In ternary chalcogenides of molybdenum we would have  $T_{c0} \sim 10$  K, so  $T_K$  in our case must be taken in the interval 0.1-1 K. The magnetic field must thus be  $\gtrsim 0.1-1$  T (recall that we have  $H_{c2} \sim T_{c0}$  in these materials). The relative importance of the various mechanisms tending to suppress superconductivity depends strongly on the coherence length  $\xi_0$ . In particular, as  $\xi_0$  decreases the superconductivity "survives" if there are a large number of magnetic impurities, while in a magnetic field the orbital suppression mechanism becomes less important. As we mentioned earlier, the Fermi electron velocity and thus  $\xi_0$  are small in Chevrel phases. Accordingly, the Pauli mechanism here may be comparable in importance to the orbital mechanism, in contrast with the situation in ordinary superconductors. To demonstrate the point, we calculate from Eqs. (19)-(21) the small shift of the transition temperature caused by a magnetic field when we ignore impurities. For this purpose, we assume that  $\alpha$  is small in (22) (all of the  $\tau$  values are infinite), and we expand the integral  $J(\alpha)$  in (21) to third order inclusively:  $J(\alpha) = \alpha - \alpha^3/3$ . This approach makes it possible to incorporate orbital effects. We find

$$\frac{T_{c0}-T_{c}}{T_{c0}} = -\delta t = \delta t_{P} + \delta t^{\text{orb}} = 2,4 \frac{2h}{\pi T_{c0}} \left(\frac{2h}{\pi T_{c0}} + \frac{1}{3} \frac{T_{c0}}{\varepsilon_{F}} \left(\frac{\xi_{0}}{a}\right)^{2}\right).$$

Substituting  $T_{c0} \sim 10$  K and  $\varepsilon_F \sim 10^5$  K, we see that in fields  $h \sim 0.1-1$  K with  $\xi_0 \sim (10-100)a$  the contribution of the Pauli mechanism is comparable to that of the orbital mechanism. The condition  $\alpha_n < 1$  may hold for n = 1 and, especially, for n > 1. This point can also be verified for T = 0, by comparing  $H_{c2}^{orb}$  and  $H_{c2}^P$  in a pure superconductor. From Eqs. (19)–(22) we find the standard results for T = 0:

$$H_{c2}^{\text{orb}} = \frac{e^2}{4\gamma} \frac{\hbar^2}{4m\xi_{\theta}^2}, \quad H_{c2}^{P} = \frac{\pi}{4\gamma} T_{c0}.$$

We see that the critical fields become comparable in magnitude at  $\xi_0 \sim 10^2 a$ . Finally, we recall that introducing nonmagnetic impurities results in an increase in  $H_{c2}^{\text{orb}}$ ; this increase may also strengthen the role of the Pauli mechanism in suppressing the superconductivity.

Unfortunately, when all the mechanisms—orbital, Pauli, magnetic impurities, and nonmagnetic impurities are taken into account, we cannot find solutions of Eqs. (19)–(22) in analytic form. We accordingly report the results of a numerical solution below. As follows from the discussion above, we are interested in superconductors with small values of  $\xi_0$ .

As an example, we give the results calculated for the following values of the parameters of the model:  $A_{sf}$ /  $T_{c0} = 400$ ,  $T_{c0}g_0 = 2 \cdot 10^{-4}$ . At these values we find  $T_K/$  $T_{c0} = 0.02$ . The choice of such a large *s*-*f* exchange parameter reflects our wish to see a manifestation of the Jaccarion-Peter effect,<sup>3</sup> which is regarded as the primary mechanism for explaining experiments on Chevrel phases.<sup>1</sup> The Kondo temperature was found above as the temperature at which the amplitude (11A) diverges in the absence of an external field and in the absence of impurities. If there are many more nonmagnetic impurities than magnetic impurities, the relaxation time which arises from the scattering by the nonmagnetic impurities cuts off the Kondo logarithms<sup>7</sup> (over the transit time between two magnetic impurities, an electron has time to collide with nonmagnetic impurities many times). We should emphasize, however, that the nonmagnetic relaxation times in the logarithm in (11A),  $\tau_{0K}$ , and in Green's function (9),  $\tau_0$ , are generally not the same: Magnetic impurities usually have a valence and dimensions different from those of the ions of the matrix. The electron momentum thus undergoes relaxation in the course of scattering by impurities of both types, so the sum of the reciprocal time scales for nonmagnetic scattering appears in Green's function (9). On the other hand, as Abrikosov has shown,<sup>6</sup> the potential part of the scattering by magnetic impurities does not appear in the Kondo logarithms. For the numerical calculations we chose these times to be  $T_{c0} \tau_{0K} = 10$ ,  $\tau_0 T_{c0} = 1$ . Since we have  $\tau_{0K} > T_K$ , the Kondo infinities are cut off before a unitary level is reached, and amplitudes (11A) can be used over the entire temperature range.

The solid lines in Fig. 1 show the transition temperature versus the magnetic-impurity concentration for s = 1/2 and  $\xi_0 = 50$ . In the absence of a magnetic field we find the customary behavior of a superconductor with magnetic impurities, with a reentrant superconductivity in terms of the temperature.<sup>5</sup> We now turn on the magnetic field. The curve



FIG. 1. Superconducting transition temperature as a function of the concentration of magnetic impurities at various values of the external magnetic field ( $\xi_0/a = 50$ ).

corresponding to  $h = 0.2T_{c0}$  is shown by the dashed line in Fig. 1. We see that the maximum transition temperature at  $c_m = 0$  decreases, as it should, but the concentration range in which superconductivity exists expands! The effect can be seen even more vividly at  $h/T_{c0} = 0.4$  (the dot-dashed line in Fig. 1).

What role does Kondo scattering play? To answer this question, we discard the logarithmic contributions to the scattering amplitude. We find the following result: The limiting concentration of magnetic impurities at which superconductivity still occurs increases substantially, but the region of reentrant superconductivity and thus all of the nontrivial effects in a magnetic field disappear.

We turn now to a study of the (T,H) diagrams of a superconductor for various  $c_m$ . Figure 2 shows the dynamics of the changes in the phase diagrams with increasing  $c_m$ . For  $c_m < c_{m1}^*$  the superconductivity exists over the entire region below the  $T_c(H)$  curve. As magnetic impurity concentration increases, superconductivity is suppressed in weak fields and at low temperatures, where Kondo scattering is strongest. With a further increase in  $c_m$ , this region expands, and when a certain concentration is reached the region in



FIG. 3. The same as in Fig. 1, but for  $\xi_0/a = 100$ .

which superconductivity exists breaks up into two unconnected regions. In each of these regions, a reentrant superconductivity exists in terms of both the field and the temperature. However, the concentration  $c_m$  is still lower than that  $(c_{m2}^*)$  at which the concentration disappears at h = 0. Finally, at  $c_m > c_{m2}^*$  a superconductivity can appear only if induced by an external magnetic field. Since the region adjacent to the H = 0 plane disappears in the case  $c_m > c_{m2}^*$ , a reentrant superconductivity in terms of the temperature is no longer possible; it is possible only in terms of the field. These calculations also apply to the case  $\xi_0/a = 50$ .

What happens if we let  $\xi_0/a$  increase? We consider the case  $\xi_0/a = 100$ . The corresponding  $(T-c_m)$  diagram is shown in Fig. 3. Now the dashed line corresponds to a field  $h = 0.1T_{c0}$ , and the dot-dashed line to  $h = 0.2T_{c0}$ . An increase in  $\xi_0$  leads to an increase in the importance of the orbital mechanism for the suppression of superconductivity by an external field and to a weakening of effects stemming from the Kondo scattering of electrons. On the (T-H) diagrams (Fig. 4) for the various values of  $c_m$ , there are again regions of superconductivity induced by the external field, but now these regions are smaller. Their appearance is possible in a certain interval of the concentration of magnetic



FIG. 2. (*T*-*H*) diagrams of the superconductor for various values of the concentration of magnetic impurities  $(\xi_0/a = 50)$ .



FIG. 4. The same as in Fig. 2, but for  $\xi_0/a = 100$ .

impurities:  $c_{m1}^* < c_m < c_{m2}^*$ . In this case, therefore, there are no regions along the scale of the magnetic-impurity concentration in which a superconductivity would not occur at h = 0 and would appear in a nonzero field.

We do not have room here to reproduce the phase diagrams for  $\tau_0 T_{c0} < 1$ . Roughly speaking, an increase in  $\tau_0^{-1}$ leads to an expansion of the region of magnetic fields in which an induced superconductivity exists. Futhermore, since there is a nonmagnetic mechanism for the scattering of electrons by magnetic impurities,  $\tau_0$  also depends on the concentration of magnetic impurities. We ignore this dependence. Taking it into account will also tend to expand the region in which a field-induced superconducting phase exists. We also note that it follows from a phase analysis of the diagrams of materials with lower values of  $T_K/T_{c0}$  that the region in which a field-induced superconductivity exists shifts down the temperature scale. This shift indicates that the effect is "tied" to the Kondo effect.

### 4. DISCUSSION OF RESULTS

This analysis of the phase boundaries of superconductivity in materials containing magnetic impurities suggest that an external magnetic field is sometimes capable of reactivating superconductivity which has been suppressed by impurities. Although we have not studied the lower phase, the arguments which we presented in the Introduction indicate that a superconductor of this sort might have some extremely unusual properties. Recall that Meul *et al.*<sup>1</sup> observed a paramagnetic response in the superconducting phase of the compound  $\operatorname{Eu}_x \operatorname{Sn}_{1-x} \operatorname{Mo}_6 \operatorname{S}_{7.2} \operatorname{Se}_{0.8}$ . In the present study we have attempted to describe that phenomenon by means of the Jaccarino–Peter effect. Although the *s*–*f* exchange interaction constant is negative, the influence of the Kondo effect was not discussed in Ref. 1.

We have also attempted to find the induction of a superconductivity by the Jaccarino–Peter effect alone. Within the framework of our equations, this attempt has failed, at least for  $\xi_0 \ge 30a$ . For parameter values chosen especially to cause  $\Delta_c$  to cross zero  $[(g_0T_{c0})^{-1} = 8 \cdot 10^3, c_m = 2 \cdot 10^{-4}, S = 3)]$ , the influence of the Jaccarino–Peter effect again turns out to be negligible. In the phase diagrams in Figs. 2 and 4, the last region along the magnetic-impurity scale in which superconductivity still exists disappears before the Jaccarino–Peter effect becomes significant. For the regions of the parameter values which we have studied here, the Kondo effect is thus responsible for the superconductivity which is induced by a field and which is reentrant in terms of the field.

Meul *et al.*<sup>1</sup> suggested that the magnetic scattering in the compounds  $\operatorname{Eu}_x \operatorname{Sn}_{1-x} \operatorname{Mo}_6 \operatorname{S}_8$  is negligible. This situation is possible only if there is no exchange interaction between conduction electrons and impurity spins, because of the structural features of these compounds. We wish to stress that if this were the case then the Jaccarino-Peter effect would also be absent: Both these effects arise only with  $A_{sf} \neq 0$  and require  $A_{sf} < 0$ . It may be that some of the europium impurities nevertheless reach positions in the lattice at which the wave function of the conducting electrons is not zero.

It follows from this study that a magnetic-impurity concentration of  $10^{-4}$ – $10^{-3}$  is sufficient for the onset of an induced superconductivity (see the parameters in Figs. 2 and 4). If a europium impurity manages to "settle" not only at a tin site but also at other sites, the presence or absence of the effect will depend strongly on the method by which the samples were synthesized. Lacking an analysis of the distribution of impurities among the various positions in the experiments which have been carried out to date, we find it difficult to conclude that Kondo scattering is totally responsible for the induction of superconductivity. Other situations are quite possible. For example, if all of the europium impurities were involved in an exchange interaction, the impurity-impurity interaction at such high concentrations might suppress the Kondo effect, and the impurities might become ordered in some way or other. In such a case, the Jaccarino– Peter effect would increase in importance.

The mechanism which we have studied in the present paper and that which we just mentioned above share the following feature: The intensity of the spin-dependent interactions which are involved in the formation of the superconductivity is changed by an external magnetic field. It follows from our analysis that this feature can be manifested only if the orbital mechanism is not predominant. The latter case assumes small values of  $\xi_0$  or—what amounts to the same thing for conventional superconductors-small velocities at the Fermi surface. In addition to Chevrel phases, examples of such compounds are heavy-fermion systems. Indeed, experiments<sup>12</sup> on CePb<sub>3</sub> have revealed that superconductivity can be induced by a magnetic field. In a theoretical paper<sup>13</sup> on a spin-fluctuation model of a heavy-fermion system it was pointed out that nontrivial  $H_{c2}(T)$  dependences can arise. The reason is a change in a spin-dependent amplitude for the scattering of electrons by a magnetic field. The contribution of orbital effect was not discussed in that paper.

As we know, the new superconductors also have short coherence lengths. Taking  $T_{c0} \sim 90$  K, we should restrict ourselves to  $h \sim T_K \sim 0.1$  and  $T_{c0} \sim 10$  T in our theory. We would then require  $\xi_0 \leq (30-50)a$ . According to existing estimates, we have  $\xi_0 \approx 30-50$  Å in these superconductors; these figures fall in the necessary range. However, an experimental realization of the predicted effects in yttrium superconductors would run into the following difficulties: Rare earth impurities occupy yttrium positions, where the wave function of the conducting holes of the  $CuO_2$  planes is zero, so the s-f exchange is also zero. Iron-group impurities settle primarily in Cu-O chains,<sup>1)</sup> "killing" the superconductivity not by the mechanisms discussed above but (apparently) through a change in the doping of  $CuO_2$  planes with holes. Accordingly, in order to resolve whether it is possible to realize the effects discussed here in yttrium metal oxides it will be necessary to find a way to put a controllable number of transition metal impurities (Fe, Co, Ni, Mn) in specifically CuO<sub>2</sub> planes, so the suppression of superconductivity by *s*-*f* exchange scattering will become the predominant effect. Lanthanum superconductors are more promising from this standpoint.

<sup>&</sup>lt;sup>1)</sup>We wish to thank I. F. Shchegolve and O. G. Novikov for pointing out this circumstance.

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