Phase separation in rare-earth superconducting metal compounds

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On the basis of the fluctuation theory of phase transitions, we constructed a phase diagram of rare-earth superconducting metal compounds $Er_{1-x}Ho_{0x}Rh_4B_4$ using the temperature-anisotropy variables $(T,|\alpha_{\parallel}(x)|)$. The existence of a high-temperature superconducting phase is predicted in rare-earth metal alloys with aluminum TbAl–NdAl. It is shown that this phase, which may be metastable, can occur at $T \approx 40$ K in a narrow temperature range.

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Recently, it was established experimentally[1,2] that in rare-earth metal compounds such as $Er_{1-x}Ho_{0x}Rh_4B_4$, $Er_xMo_6Se_8$, $Tb_{1,2}Mo_6S_8$, $Dy_{1,2}Mo_6S_8$, and MRh_4B_4 (where M = Th, Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm) the system changes from one steady state to another as a result of phase transitions from the paramagnetic phase to the ordered state. It was found that at a specific concentration x and temperature T one of these phases is superconducting and the others are purely magnetic.

It was shown recently[3,4] by the authors that a separation of phases with different magnetic order occurs as a result of phase transitions in materials with a complex magnetic structure (rare-earth metals and their alloys).

In this communication we show that on the basis of the theory developed in Refs. 3 and 4 we can obtain a phase diagram which was constructed experimentally by Fertig *et al.*[1]

Let us examine the compound $Er_{1-x}Ho_{0x}Rh_4B_4$. The magnetic structure of this compound (see, for example, Ref. 3) can be represented in the form of a superposition of two spin-density waves: a longitudinal wave modulated along the preferred axis of the crystal and a helical wave with a wave vector **q** directed along the same axis. These waves correspond to two complex spin-density vectors,

$$S_{\parallel} = s_{\parallel}^{+} + i s_{\parallel}^{-} , \qquad S_{\perp} = s_{\perp}^{+} + i s_{\perp}^{-} . \tag{1}$$

The degree of freedom connected with the superconductivity can be taken into account by introducing into the thermodynamic potential the following invariants[3]:

$$\Delta\Delta^*, \ (\Delta\Delta^*)^2, \quad \Delta\Delta^*(S_{\parallel} S_{\parallel}^*), \qquad \Delta\Delta^*(S_{\perp} S_{\perp}^*) \tag{2}$$

where Δ is the gap in the conduction-electron spectrum. Thus, the free energy of the system has the form:

$$F = \frac{1}{2}\tau_{\parallel}(s_{\parallel}^{+2} + s_{\parallel}^{-2}) + \frac{1}{2}\tau_{\perp}(s_{\perp}^{+2} + s_{\perp}^{-2}) + \frac{1}{2}\tau_{\delta}|\Delta|^2 + \frac{1}{8}\Gamma_{1\delta}|\Delta|^4$$

$$+ \frac{1}{8}\Gamma_{1\parallel}(s_{\parallel}^{+2} + s_{\parallel}^{-2})^2 + \frac{1}{8}\Gamma_{1\perp}(s_{\perp}^{+4} + s_{\perp}^{-4}) + \frac{1}{4}\Gamma_{2\perp}s_{\perp}^{+2}s_{\perp}^{-2}$$

$$+ \frac{1}{4}\Gamma_4(s_{\parallel}^{+2} + s_{\parallel}^{-2})(s_{\perp}^{+2} + s_{\perp}^{-2}) + \frac{1}{4}\Gamma_5|\Delta|^2(s_{\parallel}^{+2} + s_{\parallel}^{-2})$$

$$+ \frac{1}{4}\Gamma_6|\Delta|^2(s_{\perp}^{+2} + s_{\perp}^{-2}), \tag{3}$$

where

$$\Gamma_{1\perp}^{\circ} = \Gamma_{1\parallel}^{\circ} = \Gamma_{10}, \quad \Gamma_{2\perp}^{\circ} = \Gamma_{1\perp}^{\circ} - 2\Gamma_{30}, \quad \Gamma_4^{\circ} = \Gamma_5^{\circ} = \Gamma_6^{\circ} = \Gamma_{20},$$

$$\Gamma_{10} - \Gamma_{30} < \Gamma_{1\delta}^{\circ} < \Gamma_{10} < \Gamma_{20},$$

and the seeding temperatures $\tau_{\parallel}^0$, $\tau_{\perp}^0$, and τ_{δ}^0 are functions of the concentration x,

$$\tau_{\parallel}^{\circ} = \tau - |a_{\parallel}(x)|, \quad \tau_{\perp}^{\circ} = \tau - |a_{\perp}(x)|,$$

$$\tau_{\delta}^{\circ} = \tau - \phi(|a_{\parallel}(x)|, \ |a_{\perp}(x)|). \tag{4}$$

Let us examine the behavior of the system depending on the relation between the values $\tau_{\parallel}^0$, $\tau_{\perp}^0$, and τ_{δ}^0.

1. $\tau_{\perp}^0 < \min(\tau_{\parallel}^0, \tau_{\delta}^0)$.

In this case, after the transition from the paramagnetic phase the fluctuation of the vector field $\mathbf{S}_{\perp}$ will be stronger than the natural fluctuations of the fields $\mathbf{S}_{\parallel}$ and Δ.

It follows from the solution of the equations for the renormalization group[3] (RG) that when $0 < \gamma_{2\perp} = (\Gamma_{2\perp}/\Gamma_{1\perp}) < 3$ the system undergoes a first-order phase transition to the superconducting state. The temperature of the helical subsystem changes after the phase transition to the state with $\Delta \neq 0$.[4] However, since the temperature of the longitudinal magnetic subsystem also changes, the inequality of the values $\tau_{\perp}^0 < \tau_{\parallel}^0$ remains. As a result of further decrease of the temperature, the fluctuations of the transverse magnetic subsystem again increase and the subsystem approaches a stable, stationary point $\gamma_{2\perp} = 1$. The longitudinal magnetic subsystem is unstable because of transfer to it of the fluctuation energy of the transverse subsystem. A first-order phase transition to the c-sin state occurs in the system.[3,4] The magnetic order destroys the superconducting state of the system and the order parameter approaches zero ($\Delta \to 0$) as a result of further decrease of the temperature. The system then goes over to the state of tapered spiral via the second-order phase transition.

2. $\tau_{\parallel}^0 < \min(\tau_{\perp}^0, \tau_{\delta}^0)$.

This condition indicates that after the transition from the paramagnetic region the vector field $\mathbf{S}_{\parallel}$ will have the strongest fluctuation. In this case, however, we have a first-order phase transition to the magnetically ordered state of the flat spiral (*NS*). Therefore, although functional (3) allows a first-order phase transition to the superconducting state, the destructive effect of magnetic order of superconductivity must be taken into account. Thus, a transition to the given state probably does not occur. As a result of further decrease of the temperature, a second-order phase transition to the state of the tapered spiral (*TS*) will occur in the system.

On the basis of the examined cases, we constructed a phase diagram of the system using the variables $(T, |\alpha_{\parallel}(x)|)$ (see Fig. 1). The shaded areas in the diagram represent

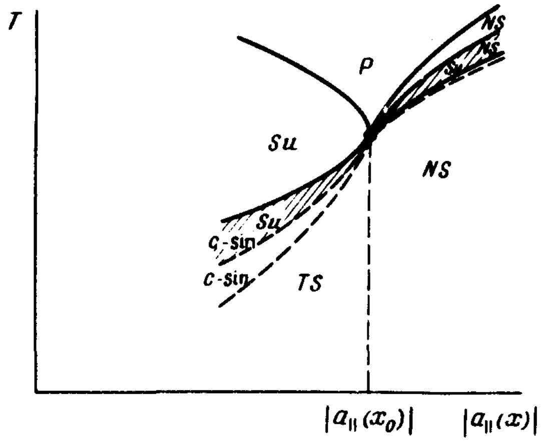

FIG. 1. Phase diagram of $(Er_{1-x}Ho_x)Rh_4B_4$ compounds.

regions of possible coexistence of superconductivity and magnetism. If, however, this state does exist, then it will be confined to a narrow temperature range and may be metastable. It can be seen in the phase diagram that it has a singular point at which the lines of the first- and second-order phase transitions cross. The behavior of the system in the neighborhood of this point can be described by the set of equations (RG) for the case $\tau_{\parallel}^0 \to \tau_{\perp}^0 \to \tau_{\delta}^0$. An analysis of the equations shows that this point is unstable, in agreement with the results of Sakurai.[5]

The second part of this paper is devoted to the study of a possible development of the high-temperature superconducting phase in the rare-earth metal alloys with aluminum. On the basis of experiments on neutron scattering in TbAl-NdAl alloys,[6] it was established that the magnetic structure of these materials has a complex antiferromagnetic order with strong anisotropy in the basal plane (x,y) (see Fig. 2). The Néel temperatures of TbAl and NdAl are equal to 72 K and 29 K, respectively.

The magnetic structure of TbAl-NdAl (space group $P_{2a}b'cm'$, orthorhombic symmetry) can be represented by four vectors:

$$\mathbf{m} = \frac{1}{2}(S_1 + S_2 + S_3 + S_4) \to 0,$$

$$\mathbf{l}_1 = \frac{1}{2}(S_1 - S_2 + S_3 - S_4) \to 0,$$

$$\mathbf{l}_2 = \frac{1}{2}(S_1 + S_2 - S_3 - S_4),$$

$$\mathbf{l}_3 = \frac{1}{2}(S_1 - S_2 - S_3 + S_4). \quad (5)$$

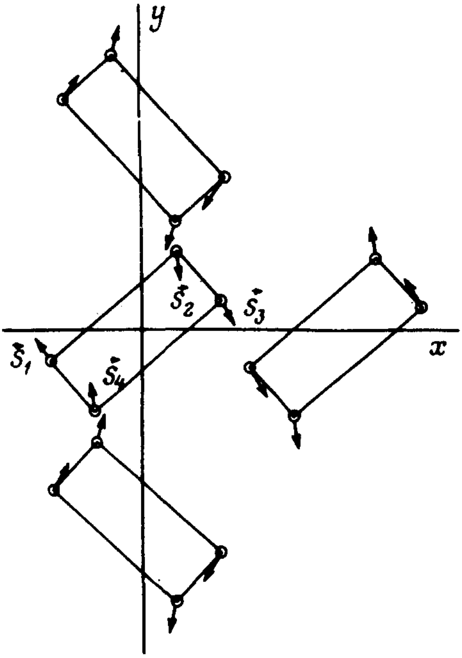

FIG. 2. Magnetic structure of TbAl-NdAl alloys, space group $P_{2a}b'cm'$.

Since the antiferromagnetism vectors l_2 and l_3 oscillate in the x,y plane, we have

$$l_2(x, y) = l_{2x} e^{i\pi x} + l_{2y} e^{i\pi(x+y)},$$

$$l_3(x, y) = l_{3x} e^{i\pi(x+y)} + l_{3y} e^{i\pi x}. \qquad (6)$$

Experimental studies of the temperature dependence of the magnetic susceptibility[6] $\chi(T)$ of TbAl showed that it decreases sharply at $T \approx 40$ K after the phase transition to the ordered state at $T = T_N = 72$ K and then increases sharply and peaks at $T \approx 20$ K (see Fig. 3). The measurements of the dependence of magnetization on the external

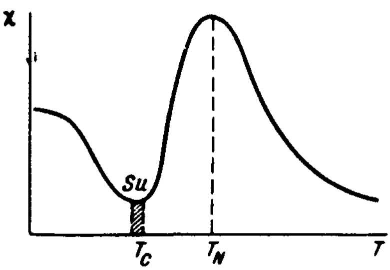

FIG. 3. Temperature dependence of the magnetic susceptibility of TbAl alloy.

magnetic field applied along the z axis perpendicularly to the basal plane indicate that strong magnetic anisotropy is present in the TbAl alloy. Therefore, the magnetic phase transition in the given material must be accompanied by structural changes (lattice hardening). Thus, on the basis of the experimental data, we expect a superconducting phase to occur in the temperature range corresponding to minimum magnetic susceptibility. The symmetry of the system allows the existence of the following invariants:

$$\Delta\Delta^*(l_{2x}^2 + l_{3y}^2), \quad \Delta\Delta^*(l_{2y}^2 + l_{3x}^2), \tag{7}$$

Hence, the free energy of the Landau system in the paramagnetic region for large anisotropy has the form:

$$F = \frac{1}{2} r_1 (l_{2x}^2 + l_{3y}^2) + \frac{1}{2} r_2 (l_{2y}^2 + l_{3x}^2) + \frac{1}{2} r_\delta |\Delta|^2$$

$$+ \frac{1}{8}\Gamma_1 (l_{2x}^4 + l_{3y}^4) + \frac{1}{4}\Gamma_2 l_{2x}^2 l_{3y}^2 + \frac{1}{8}\Gamma_3 (l_{2y}^4 + l_{3x}^4)$$

$$+ \frac{1}{4}\Gamma_4 l_{2y}^2 l_{3x}^2 + \frac{1}{8}\Gamma_\delta |\Delta|^4 + \frac{1}{4}\Gamma_5 (l_{2x}^2 + l_{3y}^2)(l_{2y}^2 + l_{3x}^2)$$

$$+ \frac{1}{4}\Gamma_6 |\Delta|^2 (l_{2x}^2 + l_{3y}^2) + \frac{1}{4}\Gamma_7 |\Delta|^2 (l_{2y}^2 + l_{3x}^2),$$

$$\frac{1}{2}(\Gamma_{30} + \Gamma_{40}) < \Gamma_{\delta 0} < \Gamma_{50}, \Gamma_{60}, \Gamma_{70}, \quad \Gamma_{50} = \Gamma_{60} = \Gamma_{70}, \tag{8}$$

when $\tau_{10} < \min(\tau_{20}, \tau_{\delta 0})$, it follows from the RG equations that, as the paramagnetic phase approaches the ordered state at $0 < (\Gamma_{20}/\Gamma_{10}) < 3$, the first-order phase transition to the state with the order parameter $s_{10}^2 = l_{2y_0}^2 + l_{3x_0}^2$ will occur first. If the temperature continues to decrease, then the first-order phase transition to the state with nonzero parameter Δ will occur again, i.e., a superconducting phase may occur in the system. However, since magnetic order already exists in the system, it will destroy the superconductivity; hence the given phase, which is probably metastable, and will occur in a narrow temperature range.

If the temperature continues to decrease, then a second-order phase transition to the ground state will occur in the system. The phase diagram in Fig. 1 illustrates the case corresponding to one isolated trajectory at $|\alpha_{\parallel}(x_0)| < |\alpha_{\parallel}(x)|$.

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