Antivortex Paramagnetism in the Magnetic-Field-Induced Superconducting State of $Eu_xSn_{1-x}Mo_6S_8$

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(Received 13 September 1985)

It is shown that the magnetic-field-induced superconducting state recently observed in the system $Eu_xSn_{1-x}Mo_6S_8$ has new and unexpected magnetic properties. In particular, for a certain applied field, the external field will penetrate completely and uniformly into the superconductor. Below this field the superconductor contains antivortices and the magnetic field is enhanced in the superconducting regions. A first observation of the paramagnetic nature of this state is presented.

PACS numbers: 74.30.Ci, 74.70.Rv

Since the discovery of ternary rare-earth superconductors, the interplay of magnetism and superconductivity has attracted considerable interest. Recently a novel phenomenon was discovered in the high-field superconducting materials $Eu_xSn_{1-x}Mo_6S_8$: magnetic-field-induced superconductivity.[1] Around $x=0.75$–0.8 the magnetic field versus temperature phase diagram contains two superconducting regions: one at low fields, and one at high fields and low temperatures. This new and unusual behavior has been shown to result from the Jaccarino-Peter effect.[2] What happens is that at low fields the alignment of the Eu spins produces a strong exchange polarization of the conduction electrons which leads to a destruction of the superconducting state. If the exchange interaction between the Eu spins and the conduction electrons is negative, this exchange polarization can be compensated by an external field leading to the reappearance of superconductivity at high magnetic fields. In this Letter we point out that the field-induced superconducting state has some novel and striking magnetic properties. We find that in the lower part of the high-field superconducting region [see Fig. 1(a)] the currents in the vortex state are reversed giving rise to antivortices—in contrast to all other superconducting materials—and hence a paramagnetism instead of the usual diamagnetism. Note that this is very different from the behavior of other magnetic superconductors where the superconducting state is diamagnetic but the total magnetization is positive because of the magnetic ions. We also present measurements with the first observation of the paramagnetic antivortex state of the superconductor.

With use of the Ginzburg-Landau theory, the free-energy density of a high-field superconductor containing magnetic ions is

$$F_s = F_n + a|\psi(r)|^2 + \tfrac{1}{2}b|\psi(r)|^4 + (1/2m)|(-i\hbar\nabla - 2e\mathbf{A})\psi(r)|^2 + \mu[B + B_J(B,T)]^2|\psi(r)|^2. \quad (1)$$

The last term describes spin-polarization effects. B is in principle the local magnetic field. However, to first order in $|\psi|^2$ we can replace the latter by the external field in the last term. We shall henceforth call the local field $B(r)$ and $B_J(B,T)$ the exchange field given by

$$B_J(B,T) = zJ\langle S_z\rangle/g\mu_B = (J/g^2\mu_B^2 N)M(B,T). \quad (2)$$

Here J is the exchange constant, z the concentration of magnetic ions, $M(B,T)$ their magnetization, and N their total number. Minimizing Eq. (1) over the volume with respect to $|\psi|^2$ and $\mathbf{A}$ leads to the following Ginzburg-

Landau equations:

$$(1/2m)[-i\nabla\hbar - 2eA]^2\psi(r) + a\psi(r) + b|\psi(r)|^2\psi(r) + \mu[B + B_J(B,T)]^2\psi(r) = 0, \tag{3}$$

$$\mathbf{j}(r) = (e/im)[\psi^*(r)\nabla\psi(r) - \psi(r)\nabla\psi^*(r)] - (4e^2/m)|\psi(r)|^2\mathbf{A}(r) - 2\mu\nabla\times[\mathbf{B}+\mathbf{B}_J(B,T)][1+dB_J/dB]|\psi(r)|^2. \tag{4}$$

The last term in Eq. (4) is a paramagnetic current[3] due to spin-polarization effects. By linearizing in $\psi(r)$ and then solving Eq. (3) we get for the critical field

$$B_{c2}(T) = B^*_{c2}(T) - \tfrac{1}{2}\eta[B_{c2}(T) + B_J(B_{c2}(T),T)]^2. \tag{5}$$

Here $B^*_{c2}(T)$ is the orbital critical field obtained for $\mu = 0$, i.e., the critical field obtained by neglect of spin effects. The second term on the right-hand side describes the reduction of this critical field by paramagnetic pair breaking ("magnetic splitting of Cooper pairs") due to the combined effect of the applied and exchange fields. The constant η is given by $\eta = (2\mu/a)B^*_{c2}(0)$. Since the critical field of these materials is very high, we neglect the magnetization $M(B,T)$ of the Eu spins, except in B_J. Equation (5) is equivalent to the equation one obtains from microscopic theory in the limit of strong spin-orbit scattering ($\lambda_{\mathrm{s.o.}} \gg 1$).[4] We identify in mksa units $\eta \cong 0.44\alpha/\lambda_{\mathrm{s.o.}}T_c$, where $\alpha = \sqrt{2}H_{c2}(0)/H_{p0}$, and H_{p0} is the critical field in the Chandrasekhar-Clogston limit. $\lambda_{\mathrm{s.o.}}$ is the spin-orbit scattering parameter, $\lambda_{\mathrm{s.o.}} = 2/3\tau_{\mathrm{s.o.}}k_BT_c$.[5]

For certain values of the parameters Eq. (5) has multiple solutions for B_{c2}, corresponding to the field-induced state. Two examples of $B_{c2}(T)$ curves are shown in Fig. 1, where we used the result of the microscopic theory for $B_{c2}(T)$.[6] The magnetic properties can be deduced to first order in $|\psi|^2$ from Eqs. (2) and (3). Following Abrikosov[7] the internal field $B(r)$ is calculated as

$$B(r) = B - (\phi_0/4\pi\lambda^2)(4/n_s)\{1 + \eta[B + B_J(B,T)][1 + dB_J(B,T)/dB]\}|\psi(r)|^2, \tag{6}$$

where ϕ_0 is the flux quantum, λ the London penetration depth, and n_s the superconducting electron density. When $B_J = 0$, one recovers the Abrikosov flux-line lattice with a lowering of the field in the superconducting region [with $\psi(r) \neq 0$]. When $B_J \neq 0$ we may have, in contrast to ordinary superconductors, a complete flux penetration, i.e., $B(r) = B$. The condition for this is

$$1 + \eta[B + B_J(B,T)][1 + dB_J(B,T)/dB] = 0. \tag{7}$$

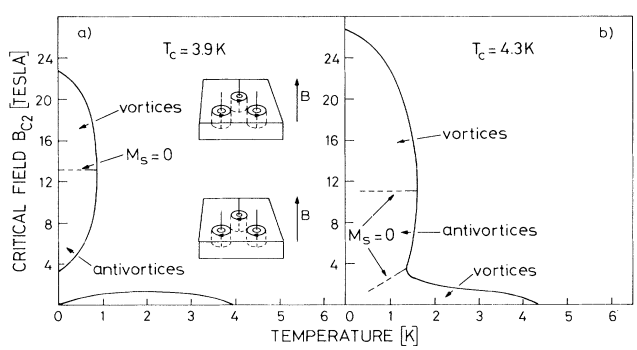

FIG. 1. Critical field vs temperature as obtained from Eq. (5). The parameters were chosen close to the values for the $Eu_{1-x}Sn_xMo_6S_8$ system ($x \sim 0.75$), where $H_J \sim -30$ T. The vortex and antivortex structures are illustrated schematically.

This surprising result follows from the fact that in general a vortex carries magnetic flux due to a paramagnetic current (i.e., spin polarization) as well as a diamagnetic current. While the flux due to the diamagnetic current behaves as in an ordinary superconductor, the flux due to spin polarization has the opposite sign in the present circumstances. When Eq. (7) is satisfied these two components exactly cancel each other. This corresponds to the points at the phase boundary where $dB_{c2}/dT = \infty$. This can be seen by differentiating Eq. (5) with respect to T and substituting Eq. (7) into this expression. In the high-field superconducting region of Fig. 1(a) we have $B_J(B,T) = B_{J0} = \mathrm{const}$ (~ -30 T) and condition (7) gives $B = B_{J0} - 1/\eta$. Thus the high-field region is divided into two parts by the horizontal line given by Eq. (7). Above this line the superconductor behaves normally in that the flux is expelled from the superconducting region. However, below this line we have $B(r) > B$ when $|\psi(r)|^2 > 0$, and thus the field is *enhanced* in the superconducting region. The current in the vortices will be opposite to the normal case leading to "antivortices."

The free energy can be calculated following the procedure for ordinary type-II superconductors.[8] When the Ginzburg-Landau parameter $\kappa \gg 1$ and $\eta(B + B_J) \lesssim 1$, corresponding to the experimental conditions considered here, the free-energy difference

$F_s - F_n$ will just be

$$F_s - F_n \cong -(1/2\kappa^2\beta_A)\{B_{c2}^* - B - \tfrac{1}{2}\eta[B + B_J(B,T)]^2\}^2, \tag{8}$$

where $\beta_A = \langle\psi^4\rangle/\langle\psi^2\rangle^2$. The magnetization of the superconducting state, $M_s(r)$ (without the magnetization of the Eu spins), is

$$M_s(r) \cong -\frac{1}{2\kappa^2\beta_A}\{B_{c2}^* - B - \tfrac{1}{2}\eta[B + B_J(B,T)]^2\}\left[1 + \eta[B + B_J(B,T)]\left(1 + \frac{dB_J}{dB}(B,T)\right)\right]. \tag{9}$$

The free energy and the magnetization are depicted in Fig. 2 with use of parameters corresponding to Fig. 1(a). $M_s(r)$ assumes positive values because the superconducting free energy is lowered as the field increases through the combined action of the exchange and external fields on the conduction-electron spins. Note that the solution for $\psi(r)$ will in all cases be the standard one, corresponding to a minimum β_A.

In Fig. 1(b) we have only one superconducting region in the B-T phase diagram. The behavior at high fields is similar to Fig. 1(a), i.e., there will be a line where $M_s(r) = 0$. However, here there is also a second line where $M_s(r) = 0$. The solution of Eq. (7) is temperature dependent. At very low fields where

$$B_J(B,T) = (B_{J_0}/M_0)\chi(T)B, \tag{10}$$

where M_0 is the saturation value of the magnetization of the Eu spins, the local field becomes

$$B(r) = B - (\phi_0/4\pi\lambda^2)(4/n_s)\{1 + \eta[1 + (B_{J_0}/M_0)\chi(T)]^2B\}|\psi(r)|^2, \tag{11}$$

and the system behaves as a normal diamagnetic superconductor. Thus the superconducting domain will be divided up into three regions by the lines $M(r) = 0$. In the intermediate region the superconductor is a paramagnet and contains antivortices.

In this situation of a new magnetic structure, a particularly interesting area of investigation should be the flux-flow behavior and pinning properties. For example, what happens at the points where the field penetrates uniformly through the superconductor, and how does the transition from the antivortex to the vortex state take place in the presence of pinning? Although a thorough investigation is impossible here, we would like to point out a few preliminary results. By solving the time-dependent linearized Ginzburg-Landau equation for $\psi(r)$ in the presence of an electric field E in the x direction and substituting this result into Eq. (4), we get the following expression for the average current in the direction of the electric field: $J_x \sim (E/BD)\langle|\psi(r)|^2\rangle$ (D is the diffusion constant). Thus the flux-line lattice moves in the transverse direction with velocity E/B giving rise to the flux-flow resistivity, even in the case when there is no current or field associated with the modulation of the order parameter $[M_s(r) = 0]$. The electric field couples only with the diamagnetic component of the flux. Note that the usual flux quantization within a region bounded by lines $\nabla\psi(r) = 0$ still holds even when $M_s(r) = 0$. In the usual case where flux pinning is present in the

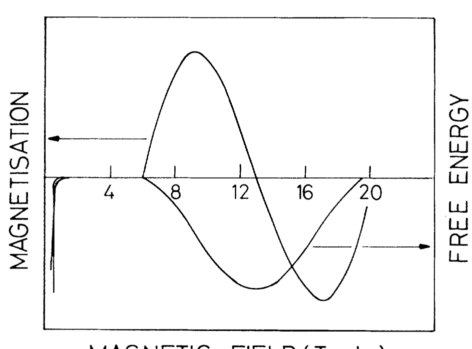

FIG. 2. Free-energy difference $(F_s - F_n)$ and magnetization M_s of the superconducting state as a function of field. [Parameters correspond to Fig. 1(a) and $T = 0.6$ K.]

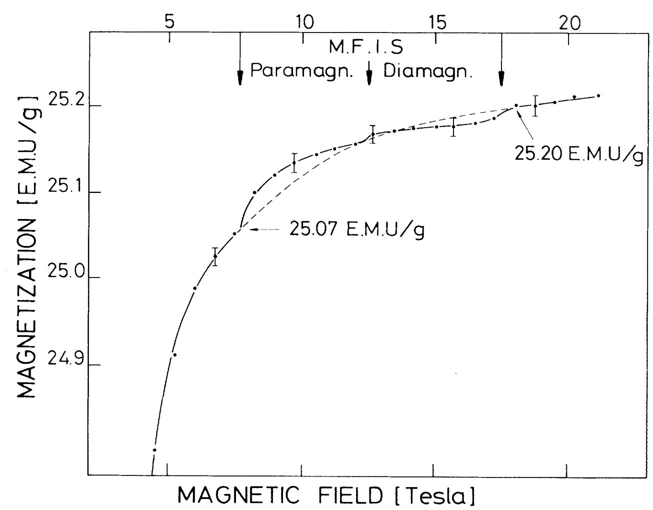

FIG. 3. Magnetization vs field for $Eu_{0.75}Sn_{0.25}Mo_6S_{7.73}$-$Se_{0.27}$ at $T \sim 1.2$ K. Error bars are shown for some of the points. The measurements were taken in an increasing field.

material, a sweep in field will lead to domains of frozen-in flux partly in the form of antivortices. One may expect vortex-antivortex annihilation leading to noise when one measures the flux-flow resistance. An unusual noise which could have this origin was indeed observed in the resistive transition when the high-field domain was entered in the $Eu_xSn_{1-x}Mo_6S_8$-type samples.[9]

We have carried out magnetization measurements on a sample with the composition $Eu_{0.75}Sn_{0.25}Mo_6$-$S_{7.73}Se_{0.27}$. The critical temperature (measured inductively) was 4.04 K and the total width 0.6 K, with an onset at 4.4 K. The presence of the field-induced superconducting state in this sample was checked by ac-susceptibility measurements at several temperatures between T_c and 0.46 K.[10]

The magnetization measurements were carried out by use of an extraction method. The low-field data show the expected diamagnetic signal superposed on a Brillouin-type curve due to the nearly free Eu spins. The high-field magnetization observed at $T=1.2$ K is shown in Fig. 3. In addition to the Brillouin-type magnetization of the Eu atoms, the contribution of the field-induced superconducting state can be clearly seen. At about 7.5 T a positive magnetization due to this state is observed. At about 12.5 T the extra magnetization goes to zero and turns negative up to an upper critical field of 17.5 T. This result is consistent with the upper critical field determined by the ac susceptibility and confirms the paramagnetic behavior of the lower part of the field-induced state. Note also that the amplitude of the signal is of the expected size (i.e., a few gauss). We also measured the magnetization of a sample with a phase diagram like the one in Fig. 1(b). In this case the sample enters the paramagnetic region at low fields where the Brillouin curve varies very fast. It was then not possible to determine the sign of the small superconducting contribution to M. However, the change towards diamagnetism at higher fields was observed, similar to the results shown in Fig. 3. We also checked that these features disappear (the magnetization follows a smooth Brillouin-type curve with a deviation of less than one-fourth the error bars shown in Fig. 3), as the temperature is raised slightly ($T=1.6$ K). It should also be noted here that the results may be sample dependent since pinning might partly mask the paramagnetic state.

To conclude: The field-induced superconducting state has new and unusual properties in which the lower part of this state is an antivortex state. There will be one (or two) lines in the B-T phase diagram where the magnetization goes locally to zero, i.e., there is no flux variation associated with the spatially varying order parameter. We have observed for the first time the paramagnetic magnetization of the antivortex state.

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