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SUPERCONDUCTIVITY IN THE PRESENCE OF MAGNETIC EXCHANGE FIELDS*

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The upper-critical-field behavior of type-II superconductors in the presence of strong magnetic exchange fields is reported. In regimes where the exchange fields are temperature dependent the critical-field displays a nonmonotonic dependence on temperature as predicted by de Gennes and Sarma.

Conduction-electron polarization is detrimental to superconductivity. It was first pointed out by Clogston[1] and by Chandrasekhar[2] that this effect can be important in high-kappa, type-II materials in which superconductivity extends to high magnetic fields. In a more quantitative treatment Maki[3] considered the effect of conduction-electron spin paramagnetism on the second-order transition at the upper critical field H_{c2} of a superconductor in the vortex state. Subsequent work[4,5] included the effect of spin-orbit scattering, which strongly mediates the spin susceptibility of the superconducting state. Numerous studies[6] have demonstrated the lowering of H_{c2} due to spin polarization in high-kappa bulk materials. The effect of spin polarization on the parallel critical field of thin Al films has been demonstrated by Strongin and Kammerer.[7]

In the work discussed above, the only case considered is that in which the electron spins are polarized by an externally applied field which penetrates the sample. A second method of obtaining electron polarization in superconductors is by utilizing the internal exchange fields which result from the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction[8] in superconductors with polarized magnetic impurities. Two cases may be considered. The first is the case in which the sample is magnetically ordered, wherein the exchange fields seen by the conduction electrons are independent of temperature and the applied magnetic field. This case was considered first by Gor'kov and Rusinov[9] and later by Fulde and Maki[10] and Bennemann.[11] Bennemann's extension of the existing theories qualitatively explained the anomalous dependence[12] of the superconducting-transition temperature on spin-impurity concentration in the $La_{3-x}Gd_xIn$ system, reported by Crow and Parks.[13] The second case is that in which the impurity spins are disordered in zero magnetic field but are polarized according to the Brillouin function in the presence of an externally applied field. This case has been considered by de Gennes and Sarma,[14] who demonstrated that in this regime it is possible to have a nonmonotonic temperature dependence of the upper critical field[15] because of the temperature dependence of the Brillouin function. We have made critical-field measurements on the $La_{3-x}Gd_xIn$ system both in the Gor'kov-Rusinov and de Gennes-Sarma regimes.

The samples of $La_{3-x}Gd_xIn$ were prepared by melting the constituents under argon in a conventional arc furnace. The disk-shaped ingots were turned over and remelted ten times to ensure spatial homogeneity of the Gd impurity. In addition to the previously mentioned x-ray measurements,[13] we have made electron-microprobe and metallographic studies on the $La_{3-x}Gd_xIn$ samples. The electron-microprobe study showed that for samples with Gd concentrations less than 2.5 at.% the Gd was dispersed uniformly. This was determined by scanning separate regions over distances of the order of 200 μ (approximately 5-7 times the average grain size[16]) with a 2-μ-diam probe. The noise level of the probe corresponded typically to

±0.03 times the Gd concentration. In addition to Gd and La scans, we also scanned for copper (the arc-furnace hearth material) to ascertain whether it was introduced during the melting process. We could detect no x-ray fluorescence due to Cu which is consistent with the extremely small weight change of the samples during melting (~0.02 %). All of our studies of the superconducting properties were made on samples with Gd concentrations smaller than 2.0 at.%.

The upper critical fields $H_{c2}^*(T)$ of the alloys were determined by measuring the resistive transitions of the samples. For these measurements the arc-melted buttons were remelted and then cast (in an argon atmosphere) into elongated cylindrical samples 4-5 mm in diameter and 30-40 mm long. We defined $H_{c2}^*(T)$ as that value of the externally applied field for which the sample resistance R was $\frac{1}{2}$ the normal-state resistance R_n. The critical fields defined in this way were found to be independent of the orientation of the magnetic field and the size of the measuring current (0.01-5 A). The breadth of the transitions in field [defined as $\Delta H = (H)_{R/R_n=0.9} - (H)_{R/R_n=0.1}$] was approximately 5-10% of the applied field; however, the nature of the temperature dependence of $H_{c2}^*(T)$ was essentially independent of the criterion used to define $H_{c2}(T)$ (e.g., $R/R_n = 0.5$, $R/R_n = 0.1$, etc.). The experimental results are shown in Figs. 1 and 2. The following qualitative features of the critical-field curves should be noted:

(1) The rapid depression of the critical field with Gd concentration. The ratio of $H_{c2}^*(0)$ for pure La_3In to that for a sample doped with 1.24 at.% Gd is greater than 10, whereas the ratio of the transition temperatures is approximately 2.

(2) The unusual temperature dependences as one goes from 0 to 1.83 at.% Gd. For low concentrations $H_{c2}^*(T)$ is monotonic with temperature, for intermediate concentrations $H_{c2}^*(T)$ is nonmonotonic, and for high concentrations it is again monotonic.

(3) The apparent saturation of the mechanism causing the depression of $H_{c2}^*(T)$ at low temperatures for the intermediate concentrations (as evidenced in the leveling off of the curves for the samples with 1.24 and 1.49% Gd. These features can be accounted for by including in the calculation of the upper critical field the effects of spin ordering on the conduction electrons.

To explain both the spin concentration and temperature dependence of the upper critical field, one must include in the Hamiltonian three separate depairing perturbations: (1) momen-

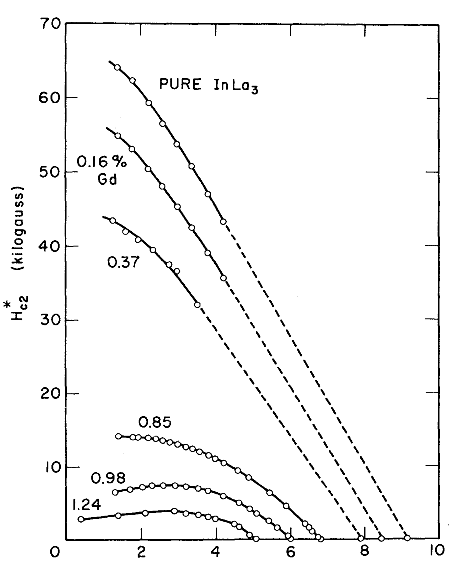

FIG. 1. Upper critical field H_{c2}^* versus temperature for six $La_{3-x}Gd_xIn$ samples with Gd concentrations ranging from 0 to 1.24 at.% (1 at.% corresponds to $x = 0.04$).

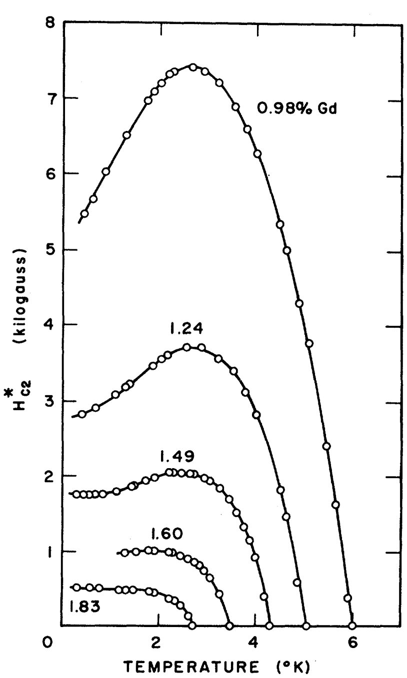

FIG. 2. H_{c2}^* vs T for five $La_{3-x}Gd_xIn$ samples with Gd concentrations ranging from 0.98 to 1.83 at.%.

tum depairing associated with the penetration of the externally applied field into the superconductor (the vortex state), (2) spin-exchange depairing caused by the spin-dependent scattering of the conduction electrons by the localized magnetic moments, and (3) Pauli or exchange-field depairing caused by the conduction-band spin polarization due to the impurity-spin exchange field. Fulde and Maki,[10] in their extension of the Gor'kov-Rusinov theory[9] on the coexistence of ferromagnetism and superconductivity, derived the following expression which describes the behavior of a superconductor with spin-polarized impurities at the upper critical field:

$$\ln\frac{T}{T_{c0}}+\psi\left(\frac{1}{2}+0.140\frac{T_{c0}}{T}\left(\frac{\alpha_1}{\alpha_{\mathrm{cr}1}}+\frac{\alpha_2}{\alpha_{\mathrm{cr}2}}+\frac{\alpha_3}{\alpha_{\mathrm{cr}3}}\right)\right)-\psi\left(\frac{1}{2}\right)=0, \tag{1}$$

where the various symbols are explained below. This relation describes the second-order phase transition from the superconducting to the normal state in the limit that the transport mean free path l_{tr} and the spin-orbit mean free path l_{so} for the electrons are much smaller than the superconducting coherence length ξ_0. Here T_{c0} is the transition temperature of the pure superconductor in zero applied field, and ψ is the digamma function. The terms α_1, α_2, and α_3 are the parameters which characterize the three pair-breaking mechanisms discussed above, and $\alpha_{\mathrm{cr}i}$ is that value of any one of the parameters α_i required to suppress superconductivity completely in the absence of the other two depairing perturbations. The terms $\alpha_i/\alpha_{\mathrm{cr}i}$ are given by[17]

$$\sum_{i=1}^{3}\frac{\alpha_i}{\alpha_{\mathrm{cr}i}}=\frac{H_{c2}^*(T)}{H_{c2}(0)}+\frac{n}{n_{\mathrm{cr}}}+\frac{P}{P_{\mathrm{cr}}}, \tag{2}$$

where n is the concentration of magnetic impurities. The Pauli susceptibility term P is given by

$$P=\tau_{\mathrm{so}}I^2=\tau_{\mathrm{so}}[nJ(0)\langle \bar{S}_z\rangle]^2, \tag{3}$$

where τ_{so} is the spin-orbit scattering time, I is the spin exchange field, $J(0)$ the s-f exchange constant, and $\langle \bar{S}_z\rangle$ the average z component of the impurity spin vector. Solving Eq. (1) for the temperature dependence of the upper critical field, one obtains

$$H_{c2}^*(T)=H_{c2}(T)-H_{c2}(0)\left[\frac{n}{n_{\mathrm{cr}}}+\frac{P}{P_{\mathrm{cr}}}\right], \tag{4}$$

where $H_{c2}(T)$ is the upper critical field for the pure (viz. $n=0$) superconductor.[18]

Equation (4) has the following three limiting cases which are reflected in Figs. 1 and 2:

Case I. For very low concentrations the exchange-field term which depends quadratically on the concentration may be neglected in comparison with the first term in the brackets. Therefore, in this limit the upper critical field should be monotonic with temperature and $H_{c2}^*(0)$ should be depressed approximately linearly with concentration of magnetic impurities. This is essentially the behavior observed for the very dilute $\mathrm{La}_{3-x}\mathrm{Gd}_x\mathrm{In}$ samples.

Case II. For the intermediate range of concentration, where $\tau_{\mathrm{so}}n^2J^2(0)\langle \bar{S}_z\rangle^2/P_{\mathrm{cr}}$ is not negligible compared with n/n_{cr} and the magnetic-ordering temperature due to the RKKY interaction is much smaller than the superconducting transition temperature, the magnetic impurities are polarized by the externally applied field which penetrates the superconductor at fields greater than H_{c1}.[19] This gives rise to an average exchange field which is both temperature and field dependent because of the temperature and field dependence (viz. the Brillouin function) of $\langle \bar{S}_z\rangle$. Equation (4) takes the form

$$H_{c2}^*(T)=H_{c2}(T)-H_{c2}(0)\times\left[\frac{n}{n_{\mathrm{cr}}}+\frac{\tau_{\mathrm{so}}n^2J^2(0)S^2}{P_{\mathrm{cr}}}B_S^{\,2}\left(\frac{\mu H_{c2}^*}{kT}\right)\right], \tag{5}$$

where B_S is the Brillouin function. In this regime the depression of the upper critical field due to the exchange field, as the sample is cooled to lower temperatures, gives rise to nonmonotonic (re-entrant) critical-field curves such as those observed in Fig. 2.

Case III. At higher concentrations the magnetic impurities will be ordered by the indirect exchange interaction even in zero applied field. This gives rise to a nearly temperature-independent exchange field. Thus for higher concentrations the critical field should again be monotonic with temperature as is observed. The onset of magnetic order[20] due to the RKKY interaction is also manifested in the leveling off of the $H_{c2}^*(T)$ curves at low temperatures in the intermediate range of concentrations.

One can show, using the values of $J(0)$ and τ_{so} employed by Bennemann in his analysis of the zero-field results,[13] that the perturbation due to the conduction-band polarization by exchange fields is more than strong enough to give rise to the nonmonotonic critical-field curves observed. Attempts to fit the data for the sample with 0.98 at.% Gd with Eq. (5) have not been too successful, especially at temperatures below the maximum in $H_{c2}^*(T)$. If one lets $H_{c2}(0) = 67\,000$ G (the measured critical field for the pure sample) and determines τ_{so} by fitting Eq. (5) to the data near T_c,[21] the computed values of the field near the maximum are too large by about 20-30 % and the computed values decrease too rapidly at lower temperatures. Inclusion of a molecular field, which reflects the indirect exchange interaction, does not significantly improve the fit at lower temperatures. It should be noted that there are serious limitations to a quantitative comparison of Eqs. (1), (4), and (5) to the experimental data. The most serious of these is that the constraint $l_{so}/\xi_0 \ll 1$ in the Fulde-Maki theory is not valid in the $La_{3-x}Gd_xIn$ system; in fact $l_{so} \sim \xi_0$.[22] In addition, a question which should be answered experimentally is whether the transition is second order or first order. If the transition is first order over any portion of the $H_{c2}^*(T)$ curve, then the situation is complicated and one cannot utilize the generalized pair-breaking theory to analyze quantitatively the results. In spite of these objections the Fulde-Maki theory provides an informative basis for discussing the present results and yields at least a qualitative understanding of the results.

The critical-field measurements in the field range 15 000-70 000 G were carried out at Brookhaven National Laboratory and the National Magnet Laboratory. We are grateful to both laboratories for their hospitality. We thank A. Cendrowski, O. F. Kammerer, and J. Sadofsky of Brookhaven National Laboratory for their assistance with the electron-microprobe studies. We have enjoyed discussing the present work with K. H. Bennemann and M. Strongin.

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[17]For low temperatures and large spin impurity concentrations, it is important to generalize the second pair-breaking term in Eq. (2) to include the effects of internal exchange fields on the RKKY scattering cross section. According to Bennemann (Ref. 11) this would require multiplying the term n/n_{cr} by the factor $[1-f/(S+1)]$, where f is a temperature-dependent function relating to the alignment of the impurity spin in the internal magnetic field ($0 \le f \le 1$) and S is the total spin of the impurity ion. For Gd impurities ($S=\frac{7}{2}$), the greatest effect that this correction could have would be to decrease the n/n_{cr} term by 22%. Since a quantitative comparison between Eq. (2) and the experimental results will not be sought, we shall ignore the correction in the following discussion.

[18]The temperature dependence of $H_{c2}(T)/H_{c2}$ is given by

$$\ln\frac{T}{T_{c0}}+\psi\left(\frac{1}{2}+0.140\frac{T_{c0}}{T}\frac{H_{c2}(T)}{H_{c2}(0)}\right)-\psi\left(\frac{1}{2}\right)=0.$$

[19]Since $k \gg 1$ for the $La_{3-x}Gd_xIn$ system as is indicated by the large value of $H_{c2}(0)$ for La_3In, H_{c1} is small

compared with H_{c2}^*, except perhaps for the samples with high spin concentrations.

[20]The nature of the magnetically ordered state cannot be determined from the $H_{c2}^*(T)$ results in Fig. 2 alone; however, the zero-field studies (Ref. 13), in view of Bennemann's theory (Ref. 11), indicate that the magnetically ordered state in $La_{3-x}Gd_xIn$ is ferromagnetic and that the range of order is at least over distances comparable with the coherence length.

[21]The value of τ_{so} determined in this way is in good agreement with Bennemann's value (Ref. 11).

[22]According to the BCS theory, $l_{so}/\xi_0 \simeq kT_{c0}\tau_{so}/0.18\hbar$. For $T_{c0} = 9.1°K$ (Ref. 13) and $\tau_{so} \sim 2\times10^{-13}$ sec (for $La_{3-x}Gd_xIn$ with 1 at.% Gd (Ref. 11), $l_{so}/\xi_0 \sim 1$.

ELECTROMAGNETIC SHEAR-WAVE INTERACTION IN A SUPERCONDUCTOR*

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The purpose of this paper is twofold:

(1) Expressions for the electromagnetic part of the interaction between electrons and shear waves in a superconductor have been developed in the case where the electronic mean free path l is long compared with the wavelength λ. We believe these expressions have a wide range of validity in both frequency and temperature. The lower end of the frequency range corresponding to the extreme anomalous limit is discussed as a special example.

(2) It presents accurate measurements[1] on the turn-off of electromagnetic interaction between electrons and transverse phonons near the superconducting transition temperature of a metal. To our knowledge, these are the first measurements performed with sufficient accuracy to provide a quantitative test of experiment against theory. We believe this also to be the first experiment to measure the penetration depth [in this case the London penetration depth at 0°, $\lambda_L(0)$] of a superconductor at a single wave vector[2] q; because the wave propagates through the sample it probes the penetration depth in the bulk, contrary to the usual methods employed in penetration-depth studies.

It has been known for many years that the shear-wave attenuation in superconductors at low frequencies shows a sharp decrease in a millidegree range below the superconducting-transition temperature T_c when the sample is cooled through this region; cf. Morse[3] and Morse and Bohm.[4] It has been shown by several authors (see below) that this decrease could be explained at least qualitatively as due to screening of the induced fields by the sharply increasing number of "super" electrons in this region. However, the absence of sufficiently accurate measurements and a quantitative theory valid over the entire temperature and frequency range of electromagnetic interaction in the superconductor has prevented resolution of the interesting questions this problem poses.

The theoretical treatment given by Cullen and Ferrell[2] was for high frequencies (typically 1 Gc/sec). It should be noted that the expression for the electromagnetic attenuation takes a different form at lower frequencies owing to the frequency dependence of the terms involved. We find that a straightforward derivation of the electromagnetic part of the electronic attenuation in the superconducting state, α_S, relative to that in the normal state, α_N, leads to the following formula, valid at all temperatures below T_c and at all frequencies, assuming $ql \gg 1$:

$$\left.\frac{\alpha_S}{\alpha_N}\right|_E = \frac{\sigma_{1S}|E_S|^2}{\sigma_{1N}|E_N|^2} = \frac{\sigma_{1S}/\sigma_{1N}[(q^2c^2/4\pi\omega\sigma_{1N})^2+1]}{(q^2c^2/4\pi\omega\sigma_{1N}+\sigma_{2S}/\sigma_{1N})^2+(\sigma_{1S}/\sigma_{1N})^2}. \quad (1)$$

In Eq. (1) $\sigma_{1S}+i\sigma_{2S}=\sigma_S$ is the transverse conductivity in the superconducting state, and $\sigma_{1N}+i\sigma_{2N}=\sigma_N$ the transverse conductivity in the normal state. E_S and E_N are the induced self-consistent electronic fields in the superconducting and normal state, respectively; ω is the angular frequency of the shear wave, and c is the velocity of light. The frequency variation of (1) is slow at frequencies up to a few hundred megacycles per second.

In the extreme anomalous limit,[5] σ_N has negligible imaginary part, and σ_{1N} can be rewritten[5] as

$$\sigma_{1N} = \frac{e^2}{4\pi^2\hbar q}\oint R_e \cos^2\varphi d\varphi. \quad (1a)$$