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Possible Coexisting Superconducting and Magnetic States

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(Received 20 October 1980)

The free energy is calculated for the various phases possible in a superconductor containing a periodic array of magnetic ions with ferromagnetic interactions. Suggestions are made for experimental observation of coexisting superconductivity and long-range magnetic order.

PACS numbers: 74.20.De, 75.10.Dg

Recent discoveries[1] of superconducting compounds that contain a lattice of magnetic rare-earth ions have raised anew the questions of interaction of superconductivity and magnetism.[2]

There are two principal interactions of the magnetization M with the superconducting order parameter ψ. One is the direct interaction of M with ψ due to spin-flip scattering of conduction electrons and the magnetic moments, giving rise to leading terms in the free-energy of the form

$$F_{\vec{M},\psi}=\eta_1|\vec{M}|^2|\psi|^2+\eta_2|\nabla\vec{M}|^2|\psi|^2. \qquad (1)$$

η_1 can be shown[3] to be $\approx J^2/T_cE_f\approx T_{\rm mag}/T_c$, and $\eta_2\approx\xi^2\eta_1$, where $T_{\rm mag}$ is the magnetic transition temperature, T_c is the superconducting transition temperature, J is the exchange energy of conduction electrons with the magnetic moments, and ξ is the superconducting coherence length. The other effect arises through the coupling of ψ to the electromagnetic field $\vec{B}$ and the coupling of $\vec{B}$ to $\vec{M}$. A dimensionless measure of the latter coupling is simply 4π. If $T_{\rm mag}/T_c\ll 4\pi$, the first effect is much less important than the second. The second effect does not occur for antiferromagnets. Experimentally, nothing very remarkable seems to happen in antiferromagnetic superconductors below the Néel temperature.

Ignoring the effects of spin-flip scattering, the free energy of an isotropic magnetic superconductor is[4]

$$F(\psi,\vec{M},\vec{A})=\int d^3r[\tfrac{1}{2}a|\psi|^2+\tfrac{1}{4}b|\psi|^4+p_0|(\nabla-ir_0\vec{A})\psi|^2+\vec{B}^2/8\pi+\tfrac{1}{2}\alpha|\vec{M}|^2+\tfrac{1}{4}\beta|\vec{M}|^4+\tfrac{1}{2}\gamma^2|\nabla\vec{M}|^2-\vec{B}\cdot\vec{M}], \qquad (2)$$

where $a=a_0(T-T_c)/T_c$, $\alpha=\alpha_0(T-T_m')/T_m'$, $p_0=\hbar^2/2m$, and $r_0=2e/\hbar c$. The free-energy density of the superconducting phase, $|\psi|\neq 0$ and $B=M=0$, is

$$F_s=-a^2/4b, \quad \text{for } T<T_c, \qquad (3)$$

while the free-energy density of the ferromagnetic phase with $|\psi|=0$ is

$$F_{\rm FM}=-(4\pi-\alpha)^2/4\beta, \quad \text{for } T<T_m^{\,0}=T_m'(1+4\pi/\alpha_0). \qquad (4)$$

We are interested in the situation where $T_m^{\,0}\ll T_c$. Also, for situations of experimental interest,

$$\zeta=[F_{\rm FM}/F_s]_{T=0} \qquad (5)$$

is about 5×10^2, as may be deduced from specific heat measurements[5] and/or the thermodynamic critical field[6] and considerations of spin entropy. Kuper, Revzen, and Ron[7] chose to estimate ζ from *ab initio* considerations and, in disagreement with the experimentally deduced value, found it to be about 10. This seriously affects the consideration of the relative stability of the various phases.

The superconducting state was found[4] to be unstable at a temperature

$$T_s \approx T_m^0[1-(4\pi)^{1/2}(\gamma/\lambda)/(\alpha_0+4\pi)] \tag{6}$$

to a phase with superconductivity preserved and transverse oscillatory magnetization and electromagnetic field. If the polarization is circular, we have a *spiral* magnetic structure of a wave vector q_0 given by[4,8]

$$q_0^2=(2\pi/\gamma^2\lambda^2)^{1/2}-\tfrac{1}{2}\lambda^{-2} \tag{7}$$

where $\lambda=(8\pi p_0 r_0^2|\psi|^2)^{-1/2}$ is the London penetration depth. In the spiral phase $|\psi|$ is uniform and the free-energy density is

$$F_{sp}(|\psi|)=-\chi^{-2}(q_0)/4\beta+\tfrac{1}{2}a|\psi|^2+\tfrac{1}{4}b|\psi|^4, \tag{8}$$

where

$$\chi^{-1}(q_0)=\alpha-4\pi[1-(1/8\pi)^{1/2}(\gamma/\lambda)]^2. \tag{9}$$

Equation (8) must further be minimized with respect to $|\psi|$; this is done numerically.

The circularly polarized state (spiral) will always be preferred over a linearly polarized state in an isotropic medium. At T_s, however, they are degenerate and magnetic anisotropy may prefer the linearly polarized state. The equations describing a state linearly polarized along the x axis may be obtained by minimizing Eq. (2) with respect to $|\psi(z)|$, the magnetization $M_x(z)$, and the vector potential $A_y(z)$:

$$2p_0 d^2|\psi|/dz^2=(a+2p_0 r_0^2|A_y|^2)|\psi|+b|\psi|^3, \tag{10}$$

$$d^2A_y/dz^2=8\pi p_0 r_0^2|\psi|^2 A_y-4\pi dM_x/dz, \tag{11}$$

$$\gamma^2 d^2M_x/dz^2=\alpha M+\beta M^3+dA_y/dz. \tag{12}$$

These nonlinear equations are solved numerically in the interval $(0,Z_{LP})$ with periodic boundary conditions. The resulting solutions are inserted back into Eq. (2) and the free energy is minimized with respect to the period Z_{LP}.

Another possible coexisting magnetic and superconducting state[3,7,9] is the *spontaneous vortex state*—an analog of the Abrikosov vortex state in ordinary type-II superconductors in the presence of an external field. No external field is required—the magnetization in the sample self-consistently generates the requisite magnetic field. The vortices are assumed to form a hexagonal, two-dimensional lattice. The hexagonal unit cell, containing one flux quantum, may be approximated with good accuracy by a cylinder of radius r_v. We then consider Eq. (2) in cylindrical coordinates (r,θ,z) inside this cylinder. The variational equations describing this vortex state are

$$r\frac{d}{dr}\left(r\frac{d|\psi|}{dr}\right)=+Q^2|\psi|+\frac{r^2}{2p_0}(a|\psi|+b|\psi|^3), \tag{13}$$

$$\frac{d}{dr}\left(r\frac{dQ}{dr}\right)=2\frac{dQ}{dr}+4\pi r_0 r\left(2r_0 p_0 Q|\psi|^2-r\frac{dM_z}{dr}\right), \tag{14}$$

$$\gamma^2\frac{d}{dr}\left(r\frac{dM}{dr}\right)=r(\alpha M+\beta M^3)+\frac{1}{r_0}\frac{dQ}{dr}, \tag{15}$$

where $Q(r)=1-r_0 rA(r)$. The boundary conditions at $r=0$ are $|\psi|=0$, $dM/dr=0$, and $Q(0)=1$; and at $r=r_v$, they are $d|\psi|/dr=0$, $dM/dr=0$, and $Q=0$. Interaction between the vortices is automatically included through the boundary conditions. The free energy is minimized as a function of r_v, which gives the equilibrium density of vortices.

Now we compare the free energy of the various possible phases.[10] We plot in Figs. 1–3 the free energies normalized to $|F_{FM}+F_s|$ as a function of temperature for various values of the parameters. In Fig. 4, we plot the periods of the coexisting magnetic-superconducting states as a function of temperature. The important parameters are ζ, λ/γ, and λ/ξ. For the last we take a value ≈ 10 as representative of the materials under discussion, which are strongly type II in the pure superconducting phase: $H_{c2}/H_{c1} \gg 1$.[6] The spiral, the linearly polarized, and the spontaneous vortex phases all preserve superconductivity—this is what favors them with respect to the ferromagnetic phase. What hurts them primarily are the gradients of M and ψ. The following physical points are evident in the numerical calculations:

(1) The spiral phase has the smaller M^4 term and the smaller gradient energy when compared with the linearly polarized phase and therefore has the lower free energy for all temperatures.

(2) The crossover from the spiral to the ferromagnetic state occurs at a temperature ΔT_m below T_m^0 calculated earlier[4] to be

$$\Delta T_m=\zeta^{-1/2}T_m^0.$$

(3) The free energy of the spiral and the linear-

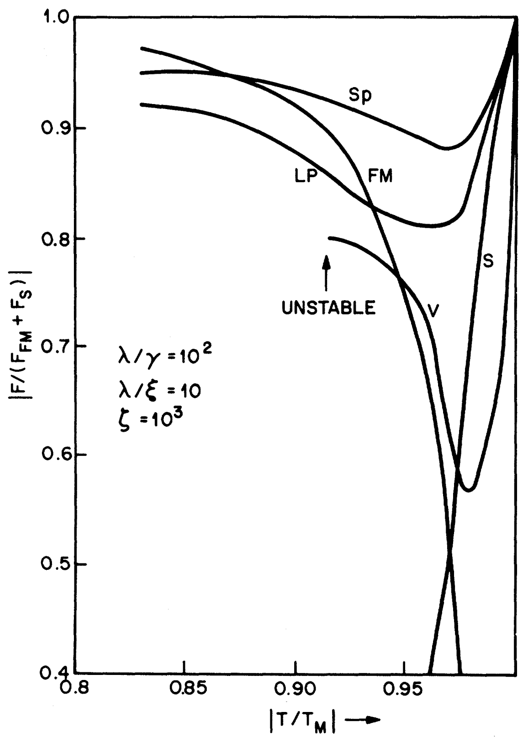

FIG. 1. Comparison of the calculated free energy of the various phases discussed in the text for a variety of physical parameters. FM denotes the pure ferromagnet, S the pure superconductor, SP the spiral phase, LP the linearly polarized phase, and V the spontaneous vortex phase. Note that the way the free energies are normalized, a curve lying higher denotes a phase with the lower free energy.

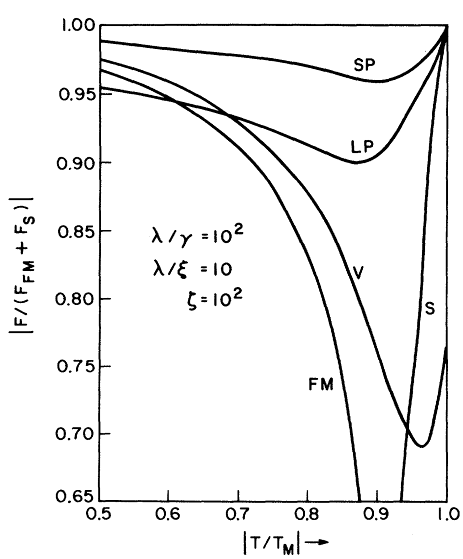

FIG. 2. As for Fig. 1, but with different ζ.

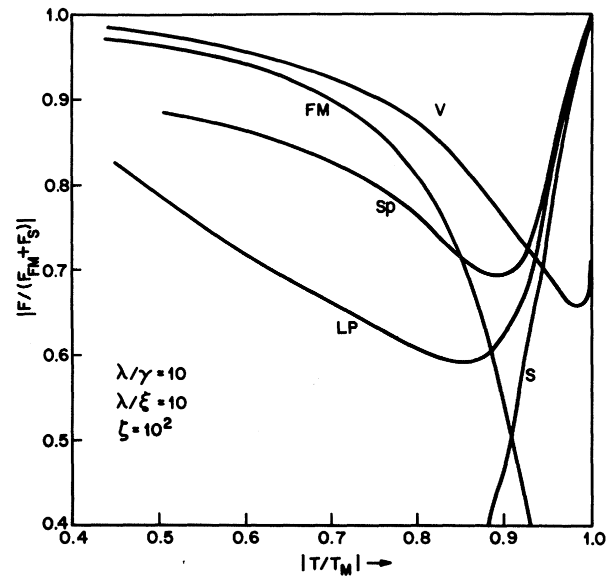

FIG. 3. As for Fig. 1, but with different λ/γ and ζ.

ly polarized states are adversely affected by a decreasing λ/γ. This is because (near T_s) their periods are of $O((\lambda\gamma)^{1/2})$.

(4) The free energy (and the density of vortices) of the spontaneous vortex phase is not noticeably affected by λ/γ. In this phase, there are net $\vec{M}$ and $\vec{B}$ fields in the sample, and the field $\vec{B}$ determines the density of the vortices. The decay length of B is of order λ just as in the Abrikosov solution. This is directly visible from Eqs. (14) and (15), where to first order M is a constant which leads to a length scale λ for B.

(5) For $T \ll T_m$, the magnetization in the spontaneous vortex phase is uniform and saturates at a value M_{sat}, which gives rise to a magnetic field $4\pi M_{\text{sat}}$. The full ferromagnetic energy is retained and therefore implies that, for $T\to 0$, the spontaneous vortex state has lower free energy than the ferromagnetic state for

$$H_{c2}/4\pi M_{\text{sat}} = (\alpha_0/4\pi\zeta)^{1/2}\lambda/\xi > 1.$$

(6) As a corollary to (3) and (4), the spontaneous vortex phase is unstable to the other oscillatory states for large λ/γ and for fixed λ/ξ. This is easy to understand. Consider the region inside the circle of radius r_v, away from the core, in which $|\psi|$ is almost a constant. An unconstrained minimization of B and M in this region would give oscillatory magnetizations of period $O((\lambda\gamma)^{1/2})$. The constrained variation of the spon-

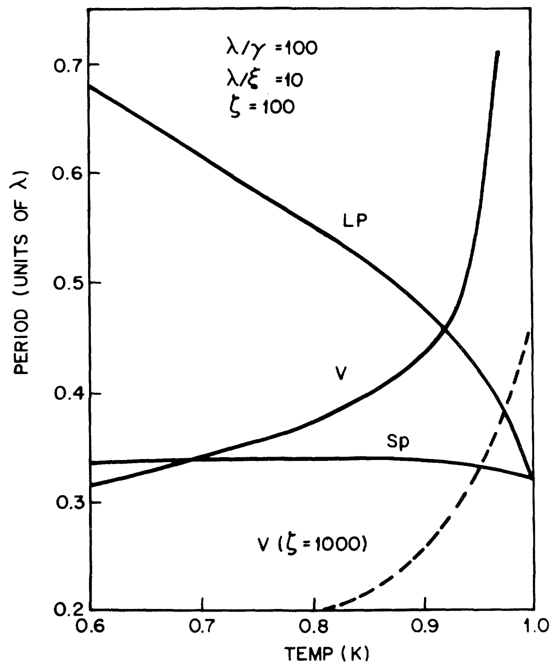

FIG. 4. The period of the spiral and the linearly polarized phase and the radius of the circle whose area is equal to that of the unit cell of the vortex lattice. Note that for the dashed line $\zeta = 1000$.

taneous vortex state necessarily increases the free energy. Another way of stating the above is to say that, because of the coupling of $\vec{B}$ and $\vec{M}$, the natural length scales of variation of $\vec{B}$ (and $\vec{M}$) are $(\lambda\gamma)^{1/2}$ and not λ. Thus, even for $\lambda/\xi \gg 1$, a magnetic superconductor behaves like a type-I superconductor for $(\lambda\gamma)^{1/2} \lesssim \xi$. Note that the linearly polarized state is the analog of the intermediate state of type-I superconductors.

(7) In Fig. 4 we show that the vortex spacing decreases strongly with decreasing temperature due to increased flux through the sample. When this period approaches ξ, the spontaneous vortex state becomes unstable relative to the ferromagnetic state. The rapid increase in period of the linearly polarized state as the temperature is decreased below T_m distinguishes this state from both the spiral and vortex states, and should be tested experimentally.

For an isotropic medium and with ξ of the order deduced from experiment and λ/γ of order 10^2–10^3 as expected, the spiral state is favored below T_s, giving way eventually to a ferromagnetic state via a first-order transition. For smaller ξ, the range of coexistence of superconductivity and states of long-range magnetic order increases and can persist down to $T = 0$. We would highly recommend that experiments be performed on materials with the density of magnetic moments reduced by substitution to achieve this goal.

Magnetic anisotropy is expected to play a crucial role in determining the state of lowest energy. Anisotropy has similar effects on the ferromagnetic, linearly polarized, and the spontaneous vortex states. A uniaxial anisotropy favors these over the spiral phase. Easy-basal-plane anisotropy affects all the phases equally, but if there is anisotropy within the basal plane, it again hurts the spiral phase most. We have calculated the effect of an easy axis anisotropy, replacing $\alpha|\vec{M}|^2$ in Eq. (2) by $\alpha_\parallel M_z^2 + \alpha_\perp(M_x^2 + M_y^2)$. The spiral phase then acquires an elliptic polarization. For $\xi = 10^2$ and $\lambda/\gamma = 10^2$, we find that at $T/T_M = 0.91$, the linearly polarized phase is favored over the spiral phase when $\alpha_\parallel/\alpha_\perp \gtrsim 1.8$. For cubic crystals,[11] the important anisotropy to consider is in the M^4 terms. It again hurts the spiral phase while affecting the others equally. Taking into account our calculated free energies, it seems likely that the spiral state is the preferred coexisting magnetic-superconducting state if anisotropy is small. For significant magnetic anisotropies, the linearly polarized state is the preferred state for T not too far below T_m and the vortex state is the preferred state at the lowest temperatures. The preference for the vortex state increases for smaller λ/γ. Experimentally, the prediction of oscillatory magnetization critical fluctuations[4] and possibly coexisting phases appears to be fulfilled.[12,13]

We would like to thank N. L. Schryer for several useful explanations on how to use his POST computer program for numerically integrating nonlinear differential equations.

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Resonant Electronic Raman Scattering in Semiconductors

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(Received 11 August 1980)

Electronic Raman scattering on shallow donors in semiconductors is enormously enhanced when the incident photon energy approaches the fundamental exciton region. This excitonic resonance was observed for the first time and it was found that $\sigma_{\text{peak}} \approx 5\times 10^{-14}$ cm^2 for CdTe and GaAs in the $n=2$ free-exciton resonance. The enhancement of $\gtrsim 10^{10}$ over off-resonance excitation and the peculiar $n=2$ exciton predominance are well described in a model of exciton-polariton–mediated light scattering.

PACS numbers: 71.36.+c, 71.55.Fr, 78.30.Gt

The inelastic scattering of light by low-lying electronic excitations in solids—electronic Raman scattering (ERS)—has been thoroughly investigated in various configurations since its proposal by Elliott and Loudon.[1] Donor and acceptor excitations in GaP and Si have been studied[2] with fixed incident-light frequencies ω_i off resonance, i.e., far below the fundamental band gap E_g, and extremely small scattering cross sections σ of $\sim 10^{-25}$ cm^2 were found. The scattering was described in a *second-order-perturbation* treatment involving interband transitions between one-electron states in valence and conduction bands and reasonable qualitative agreement between theoretical cross sections and experiment was found. Later, Burstein, Pinczuk, and Buchner[3] discussed the relative importance of *third-order processes* for ERS in the context of resonant light scattering by collective carrier excitations. More recently, Yu studied ERS in relatively highly doped CdS ($N_D \approx 10^{16}$ cm^{-3}) with ω_i below the fundamental exciton.[4] A weak resonant enhancement of <10 in efficiency was found below the I_2 bound-exciton level and was attributed to resonant interband terms in a perturbation scheme. To our knowledge, the effects of electron-hole correlation and exciton-polariton–mediated resonances on ERS have been neither observed nor discussed up to now.

We report in this Letter the first experimental observation of an enormous resonance enhancement of ERS on shallow donors in semiconductors by a factor of $\sim 10^{10}$ in σ, when ω_i is tuned into the fundamental exciton region. We give an

