Two-Component Order-Parameter Model for Pure and Thorium-Doped Superconducting UBe_{13}

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We discuss a Ginzburg-Landau model of two even-parity superconducting order parameters (e.g., of s-wave and d-wave symmetry with transition temperatures T_0 and T_2, respectively) as a model for $U_xTh_{1-x}Be_{13}$. The critical temperatures for the pure system are assumed such that $T_2 > T_0$. We suggest that impurity scattering strongly suppresses T_2 but barely affects T_0 so that the above inequality is reversed for an impurity concentration $x > x_c$. For special choices of order parameters, the second component is switched on continuously in the pure system ($x < x_c$) but via a second-order phase transition in the impure system ($x > x_c$).

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Superconducting properties of a system with coexisting order parameters of different symmetry have been largely unexplored so far. This is because there are no material examples of such a system. The singular exception is the high-field phase[1] of ^{3}He-A near T_c whose up- and down-spin order parameters condense at different temperatures. In this paper, we study the behavior of a system whose pairing condensation is possible in both the s-wave and the d-wave states of relative angular momentum (here, s and d wave stands for any two order-parameter forms satisfying certain symmetry requirements as discussed below). We find that (a) the relative phase of the s-wave and d-wave pairs plays a critical role in determining the thermodynamic properties and (b) the temperature dependence of thermodynamic properties such as specific heat and the upper and lower critical fields resemble[2,3] those observed in $U_{1-x}Th_xBe_{13}$ for $0 < x < 0.03$. Finally, we argue that (c) there is a unique dynamic mode in this system, corresponding to the oscillations of the relative phase, which may give rise to an ultrasonic attenuation peak at relatively low frequency at lower temperatures.

The model is described below in terms of a Ginzburg-Landau (GL) free-energy functional, subject to the usual caveats regarding its applicability to low temperatures. Central to our analysis is the form of interactions between the two order parameters. Since the interaction terms are governed by symmetry, we expect the results reported here to be valid qualitatively even in regions where a GL functional is not expected to be applicable quantitatively. The analysis reported here is mean-field–like; we defer a discussion of fluctuation effects until later.

The GL free energy is written as

$$F=\alpha_0\Delta_0^2+\alpha_2\Delta_2^2+\beta_0\Delta_0^4+\beta_2\Delta_2^4+2\gamma_1\Delta_0\Delta_2^3\cos(\theta_0-\theta_2)+\gamma_2[1+\delta\cos^2(\theta_0-\theta_2)]\Delta_0^2\Delta_2^2, \quad (1)$$

where Δ_0 and Δ_2 are, respectively, the s-wave and d-wave order parameters. The first two terms in Eq. (1) are the quadratic terms with $\alpha_i=a_i(T-T_i)$, where T_0 and T_2 are the transition temperatures for the s and d pairs, respectively. The quartic terms satisfy the conditions of gauge invariance and also the orthogonality of the angular wave functions. Hence, terms of the form $\Delta_0^n\Delta_2\cos(\theta_0-\theta_2)$ with $n=1,3$ do not appear. The symmetry requirements allow, however, for a dependence on the relative-phase variable $\theta=\theta_0-\theta_2$. The most general order parameter involving s- and d-wave pairs can be written as

$$\Delta(\tau,\phi)=\Delta_0 e^{i\theta_0}+e^{i\theta_2}\sum_m \Delta_{2m}P_2^m(\tau)e^{im\phi}. \quad (2)$$

Anderson and Morel,[4] and Mermin and Stare[5] have identified the energetically preferred d-wave state in weak-coupling theory to be a linear combination of $m=0$ and $m=\pm 2$. Note, however, that the γ_1 term involves only the $m=0$ part of Δ_2^3. We further remark in passing that while $m=0$ only leads to lines of nodes in the gap at the Fermi surface, leading to a low-temperature specific heat $C(T)\propto T^2$, the presence of $m\neq 0$ leads to pointlike nodes[6] and $C(T)\propto T^3$.

The relative-phase variable $\theta=\theta_0-\theta_2$ plays a crucial role in determining thermodynamic properties. With the minimization of Eq. (1) with respect to θ, assuming $\gamma_2\delta>0$, there are three minima. These are generated by the competition of the γ_1 term, which is minimum at $\theta=0,\pi$ for $\gamma_1 \lessgtr 0$, and the $\gamma_2\delta$ term, which attains a minimum value of zero at $\theta=\pi/2$. For $\Delta_2/\Delta_0>\delta\gamma_2/\gamma_1$, the free-energy minimum lies at $\theta=0$ or π, depending on whether $\gamma \lessgtr 0$. Otherwise the minimum lies at $\theta_0=\cos^{-1}(\gamma_1\Delta_2/\gamma_2\delta\Delta_0)$, referred to as region I in Fig. 1. The effective free energies for $\theta=\theta_0$ (region I) and $\theta=\pi$ (region II) are given as

$$F_{\rm I}=F_0+\gamma_2\Delta_0^2\Delta_2^2-\gamma_1^2\Delta_2^4/\delta\gamma_2, \quad \theta=\theta_0, \quad (3a)$$

$$F_{\rm II}=F_0+(\gamma_2+\delta\gamma_2)\Delta_0^2\Delta_2^2-2\gamma_1\Delta_0\Delta_2^3, \quad \theta=\pi, \quad (3b)$$

where $F_0=\alpha_0\Delta_0^2+\alpha_2\Delta_2^2+\beta_0\Delta_0^4+\beta_2\Delta_2^4$.

In the presence of a magnetic field, the gauge-

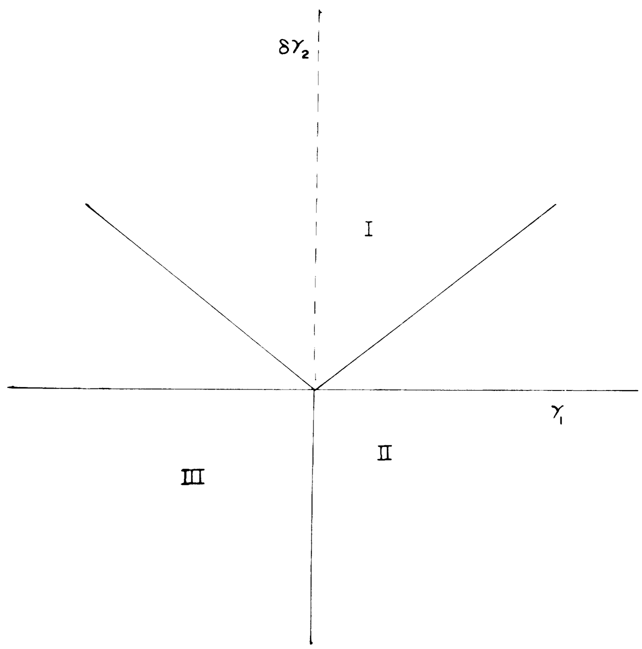

FIG. 1. Various regions of behavior in the $(\delta\gamma_2, \gamma_1)$ parameter space. The solid line for $\delta\gamma_2 > 0$ represents $\delta\gamma_2/\gamma_1 > \Delta_2/\Delta_0$, and defines region I with the relative phase $\theta = \theta_0 = \cos^{-1}[\gamma_1\Delta_2/\delta\gamma_2\Delta_0]$. The effective free energy in this region is given by Eq. (3a). The line separating regions II ($\theta = \pi$) and III ($\theta = 0$) is $\gamma_1 = 0$. In both cases, the free energy is Eq. (3b).

invariant derivative terms need to be added to Eqs. (3). These are

$$F_G = \xi_0^2 \left| \left(\nabla - i\frac{2\pi}{\phi_0}\mathbf{A} \right) \Delta_0 \right|^2 + \xi_2^2 \left| \left(\nabla - i\frac{2\pi}{\phi_0}\mathbf{A} \right) \Delta_2 \right|^2. \quad (4)$$

Here ξ_0 and ξ_2 are the coherence lengths, ϕ_0 is the flux quantum, and A represents the vector potential. We identify the London penetration depth $\lambda(T)$ from Eq. (4) such that the magnetic field energy is given by $A^2/8\pi\lambda^2$,

$$\lambda^{-2}(T) = 8\pi(2\pi/\phi_0)^2[\xi_0^2\Delta_0^2 + \xi_2^2\Delta_2^2], \quad (5)$$

which leads[6] to the lower critical field

$$H_{c1}(T) = 4\pi(2\pi/\phi_0)[\xi_0^2\Delta_0^2 + \xi_2^2\Delta_2^2]. \quad (6)$$

We conclude this section with recalling that the upper critical field $H_{c2}(T)$ can be calculated by first looking at the shift in T_c with magnetic field. $H_{c2}(T)$ then is the field at which the shifted T_c goes to zero. The thermodynamic properties then become distinct in the various regions in Fig. 1. They also depend on whether $T_2 \gtrless T_0$.

We discuss the different regions of Fig. 1 separately.

Region I.—In region I, the coupling γ_1 has been renormalized away to an effective $\tilde{\beta}_2 = \beta_2 - \gamma_1^2/\delta\gamma_2$. This free energy is similar to that of ^{3}He-A_1 phase in that two second-order transitions take place. If $T_0 > T_2$, the upper transition takes place at T_0, but the lower one is shifted because of a finite γ_2 and Δ_0 to $\tilde{T}_2$, the zero of $\alpha_2 + \gamma_2\Delta_0^2$. Note that for negative γ_2, $\tilde{T}_2$ is shifted upward from T_2. The specific-heat discontinuity at $\tilde{T}_2$ is increased as the result of a smaller $\tilde{\beta}_2$ and a larger coefficient of the quadratic term. The lower critical field given by Eq. (6) resembles a sum of two critical fields in its temperature dependence. The upper critical field for $T_0 > T_2$ is given by

$$H_{c2}(T) = -\phi_0\alpha_0/2\pi\xi_0^2, \quad \tilde{T}_2 < T < T_0 \quad (7)$$

$$= -\frac{\phi_0}{2\pi}\frac{\alpha_2 + \gamma_2\Delta_0^2}{\xi_2^2 - \gamma_2\xi_0^2/2\beta_0}, \quad T < \tilde{T}_2. \quad (8)$$

Region II.—The phase angle $\theta = \pi$ and the condition for this region is $\Delta_2/\Delta_0 > \delta\gamma_2/\gamma_1$. Thus, when $T_2 > T_0$, we find the effective free energy described by Eq. (3b). There is no second phase transition in this case, but rather a continuous changeover into a mixed state. In particular, near $T \lesssim T_2$,

$$\Delta_2^2 = -\alpha_2/2\beta_2, \quad \Delta_0 = \gamma_1\Delta_2^3/\alpha_0. \quad (9)$$

The apparent divergence in Δ_0 at $T = T_0$ ($\alpha_0 \to 0$) is indicative of a (smooth) crossover behavior. Near $T = \tilde{T}_0$ (solution of $\alpha_0 + \tilde{\gamma}_2\Delta_2^2 = 0$), $\Delta_0 \simeq (\gamma_1/2\beta_0)^{1/3}\Delta_2$, i.e., Δ_0, initially small near T_2, rapidly rises in the vicinity of $\tilde{T}_0$. The specific heat has a broad peak located at $\tilde{T}_0$. There are, in fact, remnants of excess specific heat due to Δ_0 even near T_2. They are in the form of small $(T_2 - T)^3$ correction. The lower critical field given by Eq. (6), but with the Δ's now given by Eq. (9), shows some curvature near T_2 (as opposed to a linear GL behavior), rises rapidly near $\tilde{T}_0$, and is then linear in T. It should be noted, however, that the condition for region II, $\Delta_2/\Delta_0 > \delta\gamma_2/\gamma_1$ requires $\Delta_2^2 < \alpha_0/\delta\gamma_2$. Thus, near $\tilde{T}_0$, the crossover to region I also takes place.

The dynamics of phase angle θ can be investigated with use of the Josephson equations $\hbar\dot{\theta}_i = -\mu_i$ and the quasiconservation laws $\dot{\mu}_i = (\partial\mu_i/\partial N_i)(\partial F/\partial\theta_i)$ where μ_i and N_i are the chemical potentials and particle numbers corresponding to the particles condensed with symmetry $i = 0$ or 2. Linearizing about the ground state, with $\partial F/\partial\theta_i = 0$, we find an oscillator equation for the relative phase angle $\theta = \theta_0 - \theta_2$. This is similar to the internal Josephson effect[7] found to exist in ^{3}He-A and predicted for spin-polarized hydrogen. The phase oscillation frequency ω_p is given by

$$\omega_p^2 = [4/\hbar^2\langle N(0)\rangle](d^2E/d\theta^2) \quad (10)$$

$$= [8/\hbar^2\langle N(0)\rangle]\delta\gamma_2\Delta_0^2\Delta_2^2[1 - (\gamma_1\Delta_2/\delta\gamma_2\Delta_0)^2] \quad \text{(region I)} \quad (11)$$

$$= [8/\hbar^2\langle N(0)\rangle]\delta\gamma_2\Delta_0^2\Delta_2^2[(\gamma_1\Delta_2/\delta\gamma_2\Delta_0) - 1] \quad \text{(region II)}.$$

Here $\langle N(0)\rangle^{-1}=N_0^{-1}(0)+N_2^{-1}(0)$, where $N_i(0) \equiv \partial N_i/\partial\mu_i$ and $N_0(0)$ and $N_2(0)$ are the Fermi-surface density of states of the corresponding-symmetry particles.

Note that the collective frequency ω_p given by Eq. (11) initially rises as a function of decreasing temperature below T_c (T_c meaning T_2 for $T_2 > T_0$ and $\tilde{T}_2$ for $T_2 < T_0$), goes through a maximum, and decreases until it vanishes at a temperature $T_{\rm coll}$, where $|\gamma_1|\Delta_2=\delta\gamma_2\Delta_0$ (with the assumption that $|\gamma_1| > \delta\gamma_2$ if $\Delta_2 < \Delta_0$ and vice versa). At this point ($\theta=0$) the two forces acting on the phase variable θ, deriving from the γ_1 and $\gamma_2\delta$ terms in the free energy Eq. (3) exactly cancel and large phase fluctuations are to be expected. At $T=T_{\rm coll}$, there is a weak phase transition from region I to region II (or vice versa, depending on the ratio $|\gamma_1|/\delta\gamma_2$) involving a discontinuity in the fourth derivative (with respect to temperature) of the free energy. The qualitative behavior of the collective frequency ω_p is shown in Fig. 2. Both the real and imaginary parts of the order-parameter fluctuation $\delta\Delta'$ and $\delta\Delta''$ associated with the relative phase are expected to couple to sound waves, but the coupling is much stronger for the imaginary part. Since we predict the collective frequency to become very small near $T_{\rm coll}$, even low-frequency sound (frequency $\hbar\omega \ll k_{\rm B}T_c$) will interact reasonably with the collective mode, causing a sharp peak in the sound attenuation α:

$$\alpha \simeq -q(\Delta C/C)\,{\rm Im}\{\omega^2/[(\omega^2-\omega_p^2)+i\omega\gamma]\}, \qquad (12)$$

where q is the wave number of the sound and $\Delta C/C$ is the relative change in sound velocity. The relaxation rate γ is small at low temperatures $\gamma \ll \Delta$. The attenuation peak height varies as ω^2, in contrast to the linear dependence found in the relaxation-dominated regime.

We suggest that superconductivity in $U_{1-x}Th_xBe_{13}$ closely resembles the model discussed above. Rauchschwalbe *et al.*[2,3] have analyzed their experiments in terms of two coexisting order parameters where the detailed nature of the order parameters has been left undetermined, except insofar as they come from different parts of the Fermi surface. We submit that for $x < x_c = 0.007$, $T_2 > T_0$, and the first transition takes place with pairs in a d-wave state, with small amplitude in s wave which is followed by a specific-heat peak at T_0 at which Δ_0 reaches substantial magnitude. The features correspond to those of region II with relative phase $\theta=\pi$. We imagine impurity scattering to affect the two order parameters in different ways, in particular if the scattering rates are very anisotropic. A gap (Δ_0) having the full symmetry of the lattice will be less sensitive to the averaging effect of impurities than a gap structure (Δ_2) with lower symmetry, where the principal effect of the scattering will be to restore the lattice symmetry for the gap. The effect of Th impurities then is to substantially suppress T_2 while hardly affecting T_0 so that, for $x > x_c$, the system is described by the relative phase in region I and two second-order transitions at T_0 and $\tilde{T}_2$, respectively. The qualitative features of the upper and lower critical fields are in accord with the results reported above.

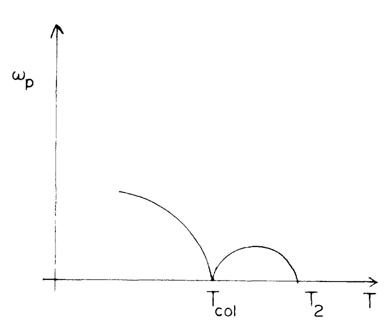

FIG. 2. Schematic behavior of the gap frequency (for the motion of the relative phase $\theta=\theta_0-\theta_2$) as a function of temperature. Near $T_{\rm coll}$, the gap frequency goes to zero because of the cancellation of the restoring force.

Because of the complex band-structure properties of the heavy-fermion systems, the coexistence of two or more types of pairs seems highly likely. Indeed, Wolfle,[8] analyzing the normal-state properties of a number of heavy-fermion superconductors in terms of Landau's Fermi-liquid theory, has already noted the possibility of coexistence of s and d pairs in UBe_{13} (and p-d pairs in UPt_3). Klemm and Scharnberg[9] have explored the transition in UPt_3 between different p-wave states in their effect on the upper critical field. Their analysis did not take into account the interaction terms in the GL energy functional. We believe, however, that angular orthogonality precludes the existence of a γ_1 term between different p-wave states (or between p-d coexisting pairs), the principal source of anomalous results reported here.

We would have liked to identify the collective mode discussed above with the large sound absorption peak observed at the lower transition in Th-doped UBe_{13}. However, in the temperature regime close to the transition, the relative phase mode is overdamped as are all other order-parameter modes and its contribution to the sound attenuation may be estimated to be of the same order of magnitude as the one from amplitude fluctuation of the order parameter, which is two orders of magnitude smaller than experimentally observed. We are inclined to believe that the superconductivity transition at $\tilde{T}_2$ is accompanied by an antiferromagnetic transition and that the attenuation peak is due to antiferromagnetic fluctuations, as originally suggested by Batlogg *et al.*[10,11] A coupling of superconducting and antiferromagnetic orders in a two-dimensional model system has recently been discussed by Machida and Kato.[12] These authors find that the suppression of itinerant antiferromagnetism by a superconducting state depends entirely on the nature of the superconducting order parameters. This suggests the possibility that antiferromagnetism may appear simultaneously with a favorable change in superconducting order. A closer investigation of this intriguing possibility will be the subject of future work.

On the other hand, we predict a collective-mode contribution to the sound attenuation from coupling to the relative phase mode for frequencies $\omega \ll \Delta$ near $T \simeq T_{\text{coll}}$. A feature in the absorption and velocity of 50-MHz sound in $U_{1-x}Th_xBe_{13}$ ($x=0.9\%$, 1.7%, and 3%) has indeed been seen at temperatures $T \simeq 0.1$ K, well below the transition.[13]

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