Superconducting phases of UBe_{13} and $U_{1-x}Th_xBe_{13}$

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A hierarchical model of second-order phase transitions has been developed for the superconducting phases of $U_{1-x}Th_xBe_{13}$. Analysis of experimental data shows that at $x \gtrsim 1.75\%$ the following sequence of transitions occurs as the temperature is lowered: [normal metal] $\rightarrow$ [superconductor with symmetry $O(T) \times R$] $\rightarrow$ [superconductor with symmetry $D_3\ (C_3) \times R$]. At $x \lesssim 1.75\%$, the sequence is [normal metal] $\rightarrow$ [superconductor with symmetry $D_3\ (C_3) \times R$].

Among the experimental data characterizing the unusual behavior of heavy-fermion superconducting compounds, the nonmonotonic behavior of the superconducting transition temperature which is observed in UBe_{13} when the uranium atoms are replaced by thorium[1] has attracted particular interest (Fig. 1). The minimum in the dependence $T_c(x)$ at $x_m = 1.75\%$ shifts toward a higher concentration and becomes progressively deeper as the pressure is raised. At $P \sim 10$ kbar, the superconductivity near $x \approx 3\%$ disappears, even at $T = 0$. It remains only at lower or higher concentrations. In the anomalous region, $1.75\% < x < 6\%$ (at standard pressure), measurements of the heat capacity,[2] of the lower critical field,[3] and of ultrasound absorption[4,5] provide evidence of an additional second-order phase transition at a temperature below the superconducting transition temperature. Several explanations have been proposed for the nature of the transition.[4,6–11] The most plausible is the suggestion by Rauchschwalbe *et al.*,[10] that at concentrations $x > x_m$ a new superconducting phase appears at the phase transition temperature $T_{cb}(x)$ with an order parameter $\hat{\Delta}_b$. This new phase mixes with the existing superconducting phase (but does not replace it), with the order parameter $\hat{\Delta}_a$ and the transition temperature $T_{ca}(x) > T_{cb}(x)$. At $x < x_m$ where the relation $T_{cb}(x) > T_{ca}(x)$ is assumed[10] to hold, no second phase transition of any sort is observed, but near $T \sim 0.55$ K there is some increase in the heat capacity in comparison with its temperature dependence for an axial or isotropic phase in a strong-coupling superconductor.

The mixture of two superconducting states was interpreted by Rauchschwalbe *et al.*,[10] as a mixture of ordinary states corresponding to *s*-wave pairing for two independent groups of charge carriers. Actually, in the case of a mixture of this sort there would always be only a single phase transition, and in order to explain the experimental situation it would become necessary to invoke a mixture of superconducting states with different symmetries. This circumstance was taken into account by Kumar and Wölfle,[11] who considered an *s*-wave pairing phase $\hat{\Delta} = \Delta_0 \hat{\sigma}_y$ and a "polar" *d*-wave pairing phase $\hat{\Delta}_b = \Delta_2 (\hat{\mathbf{l}}\hat{\mathbf{k}})^2 \hat{\sigma}_y$ as the phases *a* and *b*. Here Δ_0 and Δ_2 are complex amplitudes, $\hat{\sigma}_y$ is a Pauli matrix, and $\hat{\mathbf{l}}$ is the direction of the quantization axis for the angular momentum. It was shown that when the parameter in the Ginzburg-Landau functional satisfies a certain relation, there will be a sequence of phase transitions at

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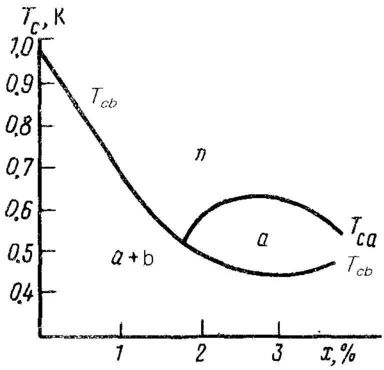

FIG. 1. Schematic (x, T_c) phase diagram of the phases of $U_{1-x}Th_xBe_{13}$.

$x > x_m$: [normal metal] → [s phase] → [($s + d$) phase]. In the region $x < x_m$, the s phase arises along with the d phase at the critical superconducting transition temperature $T_{cb}(x)$ but near it the relation $\Delta_0 \sim (\gamma\Delta_2^3/\alpha_0) \ll \Delta_2$ holds, and only in the region $T_{ca}(x) < T_{cb}(x)$ does its value increase substantially. This circumstance explains the anomaly in the heat capacity.

This behavior is completely natural from the standpoint of the overall hierarchical model of second-order phase transitions,[12] according to which a second-order phase transition should be accompanied by a spontaneous symmetry breaking. In the case at hand, the gauge symmetry is broken at the transition to the s phase at $x > x_m$ and then rotational symmetry is also broken at the transition to the d phase (a special direction for the vector $\hat{\mathbf{l}}$ appears). On the other hand, at $x < x_m$, where the transition to the d phase occurs, this transition is immediately accompanied by a mixing of the s phase to the former phase, since all of the existing symmetries have already been broken. It can be shown that in the case of a weak spin-orbit interaction and a mixing of "inert" phases of d-wave pairing with a phase of s-wave pairing, the mixture of an s phase and a "polar" d phase, which was analyzed by Kumar and Wölfle,[11] is the only possibility which has two phase transitions at $x > x_m$ and one at $x < x_m$. A mixing of phases of s-wave and p-wave pairing which has this property does not occur at all, because of the different spatial parity.

If we wish to analyze a mixture of two superconducting states in the spirit of Kumar and Wölfle's approach in the case of $U_{1-x}Th_xBe_{13}$, however we need to incorporate effects of strong spin-orbit coupling, which alters the classification of the types of superconducting pairing in a cubic crystal. The transition to a superconducting state is known[13] to mean a spontaneous breaking of the symmetry specified by the group $G = O \times R \times U(1)$. Here O is the group of symmetry axes of a cube (SO_3 in the case of a weak spin-orbit coupling), R is time reversal, and $U(1)$ is the gauge-transformation group. During the transition, the order parameter $\hat{\Delta}(\hat{\mathbf{k}})$ remains symmetric with respect to any subgroup H of group G, and the list of allowed phases (superconducting classes) reduces to the list of all subgroups of group G which consist (see Ref. 13 regarding nontrivial phases) of combined elements $O \times R$ and $U(1)$. Let us assume that the order parameter $\hat{\Delta}_a$ is invariant under subgroup H_a, and $\hat{\Delta}_b$ is invariant under H_b. In the region $x > x_m$ the a and b phases should have different transition temperatures, $T_{ca}(x) > T_{cb}(x)$. In other words, they should correspond to different representations $\hat{T}_a$ and $\hat{T}_b$ of group O. Furthermore, if a phase with $\hat{\Delta}_a$ is to appear at the same time as $\hat{\Delta}_b$ at $x < x_m$, rather than through an additional phase transition at $T_{ca}(x) < T_{cb}(x)$, there must be no further symmetry breaking when $\hat{\Delta}_a$ is mixed with $\hat{\Delta}_b$. In other words, we must have $H_b \subset H_a \subset G$. The order parameters $\hat{\Delta}_a$ and $\hat{\Delta}_b$ must of course both have even spatial parity (the spin of a Cooper pair is $S = 0$), or both must have odd spatial parity ($S = 1$).

Using the results of Ref. 13, we find that there are only four possibilities (in the notation of the present paper):

N°	H_a	H_b	$\hat{T}_a$	$\hat{T}_b$
1	$O(T) \times R$	$D_3(C_3) \times R$	A_2	F_1
2	$O(D_2)$	$D_3(E)$	E	F_1, F_2
3	$O \times R$	$D_3 \times R$	A_1	F_2
4	$O \times R$	$D_4 \times R$	A_1	E

The third and fourth of these possibilities are of no interest, since they correspond to an activation behavior of the heat capacity in the limit $T \to 0$. With regard to the first two cases, we note that the corresponding phases are experimentally distinguishable. Specifically, only the transition to the b phase (Refs. 4 and 5) is accompanied by a pronounced increase in the ultrasonic absorption at a temperature slightly below $T_{cb}(x)$. Rodriguez[14] has derived a hydrodynamic theory for the absorption of sound on the basis of the excitation of spin-orbit waves near T_c. That theory agrees well with observations in the case of UBe_{13} (Ref. 15). This attenuation mechanism operates only for phases corresponding to multidimensional representations of group O. Since no absorption peak is observed near $T_c(x)$ at $x > x_m$, we must deal with case 1 alone. In other words, we must identify the a phase as corresponding to a one-dimensional representation A_2. We then unambiguously find that pure UBe_{13} corresponds to a three-dimensional representation F_1, for which the solution of the Ginzburg-Landau equation [with symmetry $O_3(C_3) \times R$], i.e., $\eta = (1, 1, 1)$ (Ref. 13), does in fact correspond to the equilibrium value of the order parameter which was used by Rodriguez.[14]

We thus find that **in the region** $x < x_m$ in $U_{1-x}Th_xBe_{13}$ a phase transition occurs to the phase $\hat{\Delta}_b$ [with the symmetry $D_3(C_3) \times R$, which corresponds to representation F_1], to which a phase Δ_a with symmetry $O(T) \times R$ (corresponding to representation A_2) has been mixed. Near T_c, the admixture is $\Delta_a \sim (\gamma \Delta_b^3 / \alpha_0)$. This superconducting state must be characterized by a power-law behavior of the heat capacity in the limit $T \to 0$, a pronounced absorption of ultrasound at $T \lesssim T_c$ and an anisotropy[16] of H_{c2} in the limit $T \to T_c$. Just why this anisotropy has not been seen experimentally[17] requires further research (see also the discussion in Ref. 18).

In the region $x > x_m$ there is first, at $T_{ca}(x)$, a transition to an a phase with a symmetry $O(T) \times R$, which corresponds to representation A_2. Accordingly, the upper critical field in $U_{1-x}Th_xBe_{13}$ at $x > 1.75\%$ must be isotropic,[16] and there must be no peak in the ultrasonic absorption near T_{ca}. The superconductivity of $\hat{\Delta}_a$ is more nearly isotropic than that of $\hat{\Delta}_b$, and it should be suppressed to a lesser extent by impurities: this is indeed what we see experimentally.[19] As the temperature is lowered further, a second-order phase transition occurs ($T = T_{cb}$), accompanied by the formation of a mixture of phases with symmetries $O(T) \times R$ and $D_3(C_3) \times R$. This phase transition is accompanied by a pronounced absorption of ultrasound at $T \lesssim T_{cb}$. We intend to publish calculations on this effect. We thus see that we can explain the peak in the ultrasonic absorption at $T \lesssim T_{cb}$ without invoking an additional phase transition to a state with a spin density wave,[6] as was done in Ref. 11. On the other hand, even in a mixture of these phases we will observe an additional absorption of sound due to the excitation of collective oscillations with respect to the phase of the complex order parameters $\hat{\Delta}_a$ and $\hat{\Delta}_b$, as was pointed out in Ref. 11. At low temperatures, we should also observe a power-law behavior of the thermodynamic and kinetic properties.

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