Pressure Tuning of the Double Transition in Thoriated UBe_{13}

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We measure the specific heat C under pressure of high purity polycrystals of the heavy fermion superconductor $U_{0.978}Th_{0.022}Be_{13}$ with a pressure resolution equivalent to 0.0002 in Th concentration. We discover a new low temperature phase boundary independent of temperature and close to the critical pressure required to merge the two transitions observed in $C(T)$.

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One of the earliest indications of the unconventional nature of the superconducting state in the heavy fermion compounds was the discovery that the heat capacity below the superconducting transition in UBe_{13} disappeared as a power law in temperature [1], as opposed to the expected exponential. It was soon found that substituting thorium for uranium leads to a highly irregular phase diagram, distinguished by a nonmonotonic depression of the superconducting transition temperature T_c, with a local minimum at 1.8 at.% Th [2]. Perhaps even more intriguing is the detection in specific heat [3] and ultrasound [4] measurements of a second transition at $T_{c2} < T_c$ for materials with 1.8% to 4.5% Th. The samples remain superconducting, with the lower critical field H_{c1} actually increasing [5,6]. Below T_{c2}, but only for concentrations where a double transition is observed, muon spin relaxation experiments find a small local magnetic moment [6]. These results yield the x-T phase diagram [6,7] for $U_{1-x}Th_xBe_{13}$ shown in the inset to Fig. 1, where the possible existence and character of the low temperature vertical boundaries presently remain a source for speculation.

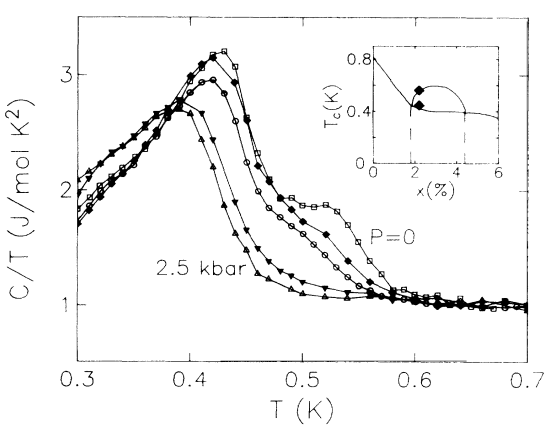

FIG. 1. Temperature T scans of the specific heat C at a series of pressures P (0, 0.9, 1.3, 2.2, and 2.5 kbar) for $U_{0.978}Th_{0.022}Be_{13}$. The two transitions merge into one with increasing P, accompanied by a distinct increase in C at low T. Inset: Generic x-T phase diagram for $U_{1-x}Th_xBe_{13}$ (Ref. [6]). Diamonds mark $x=0.022$ transitions at $P=0$.

The interpretations of the various phases and phase transitions fall into two major categories. The first suggests that the lower transition for $x=1.8\%$ to 4.5% involves either a spin-density wave [4,8] or (frozen) spin fluctuations [9] which coexist with a single superconducting state. The other approach assumes that the different regions of the phase diagram are distinct superconducting states, with the corollary that the $(U,Th)Be_{13}$ system exhibits non-s-wave superconductivity. In this scenario, the onset of local magnetic order is explained as a coexisting antiferromagnetic transition [10] or as a product of broken time-reversal symmetry [11]. Since any of these possibilities are rarely found in nature, the theoretical and experimental interest in the problem has been strong.

We report here a high resolution, low temperature investigation of the putative phase boundary at $x_0=0.018$, where two transitions emerge from one. Theoretical models with distinct superconducting states for $x<x_0$ and $x>x_0$ require a sharp phase transition. No previous thermodynamic measurement has revealed this boundary, the evidence for which is inferred from muon spin relaxation studies on samples widely spaced in x. Rather than study a series of different samples with varying Th concentration, we employ a superconducting stress cell to traverse the region of interest. This technique allows us to achieve an extremely fine step size while avoiding sample-to-sample variations, with only a modest background subtraction due to the cell.

Susceptibility measurements [12] show that the effect of increasing the pressure P mimics that of reducing the Th concentration, in particular implying a pressure dependence to x_0. Using the different values [12] of dT_c/dP for $x>x_0(P=0)$ and $x<x_0(P=0)$, combined with a model of two different superconducting states crossing at x_0, Sigrist and Rice deduce that [11]

$$x_0(P)=0.018+0.0017P \tag{1}$$

(with P in units of kbar). Hence, we start with a sample of $U_{0.978}Th_{0.022}Be_{13}$ and apply pressure up to 2.5 kbar for

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0.3 K $\leq T \leq$ 0.7 K. By measuring the specific heat C, we can observe the behavior of the lower as well as the higher temperature transition, and we do indeed find them merging with pressure. Furthermore, we are able to resolve a small but acute change in $C(P)$ at fixed T, proving the existence of a low temperature phase boundary at $x_0(P)$, as posited in the inset to Fig. 1.

We apply uniaxial stress at room temperature with a superconducting NbTi cell [13]. We apply uniaxial rather than hydrostatic pressure in order to avoid a large background heat capacity from the pressure cell and because we are able to make controlled adjustments in pressure at intervals an order of magnitude smaller than those reported in previous measurements on $(U,Th)Be_{13}$ [12, 14]. Our minimum step size of 0.1 kbar corresponds to a change in x of less than 0.0002 [Eq. (1)]. The sample, a high purity polycrystal, was prepared as in Ref. [15], with 950 h of annealing at 1400 °C, yielding material of unprecedented quality as judged by both the size of the jump in $C(T=T_c)$ and the narrow transition width [15]. The original sample weighed 11.6 mg; in order to achieve higher pressures we later spark cut the sample to $\frac{2}{3}$ the surface area and 7.5 mg. Once assembled, the cell is cooled in a ^{3}He cryostat and the specific heat measured by a transient pulse method. The thermal contraction of UBe_{13}, while not well known, is much greater than that of NbTi. An Invar spacer inserted in the stress cell with the sample compensates for this difference and reduces the pressure offset at low temperatures to 0.1 ± 0.1 kbar. The only appreciable background specific heat comes from the Invar spacer. As measured directly, this contribution is strictly linear in T and less than 30% of the peak height for the smaller sample.

We convert uniaxial stress on a polycrystal to proper pressure units by comparison to specific heat measurements in a standard BeCu hydrostatic pressure cell at a few calibration points over the range of interest. The sample and silicone oil, the pressure medium, are enclosed in a thick-walled hollow Teflon cylinder for thermal isolation, with a chip of single crystal $(V_{0.99}Ti_{0.01})_2O_3$ as the nanometer [16]. We match the uniaxial stress data to equivalent hydrostatic pressures by the peak position and width of the superconducting transition.

The $C(T)$ curves of Fig. 1 span our pressure range and capture the main features we observe. Two jumps indicating transitions are visible at zero stress. While both move to lower T as P increases, the upper transition moves faster. Hence, the features merge into a broad maximum, which later narrows. The low temperature tails ($T < 370$ mK) in $C(T)$ remain unchanged for low pressure, but between $P = 1.5$ and 2.1 kbar they rapidly increase, saturating at a new higher value of C.

We extract transition temperatures by fitting a smoothed curve to the zero-stress data, where we use a constant C/T in the normal state and a linear C/T below the second transition, as indicated by the data, and assuming constant C/T below the first transition. Keeping $\Delta C/T_c$ for the upper transition fixed [11], we then fit the pressure data. The T_c's so determined show little dependence on assumptions about the exact form of the smoothing function, and are plotted as the solid circles in the P-T phase diagram of Fig. 2. Above $P_c = 2.1$ kbar, the two transition temperatures are indistinguishable and agree with the T_c found from fitting the data with a single transition. We interpret this as the merging of the two transitions at P_c. The experimental value of $P_c = 2.1$ kbar, with absolute uncertainty ± 0.3 kbar and relative uncertainty ± 0.05 kbar, agrees well with Eq. (1), which gives $P_c = 2.3$ kbar for $x = 0.022$.

There has been considerable discussion about whether the lower temperature transition in the x-T phase diagram is a continuation of the single transition at Th concentrations below x_0 [4,7,17], and similar suggestions have been made about the P-T diagram [12]. We find that dT_c/dP varies from -29 ± 5 mK/kbar at low pressures ($P = 0.5$ kbar) to -100 ± 10 mK/kbar approaching $P_c = 2.1$ kbar. In contrast, $dT_{c2}/dP = -14 \pm 3$ mK/kbar, consistent with dT_c/dP for $P > P_c$. Our data, therefore, support the idea that the transitions at T_{c2} and $T_c(P > P_c)$ are related. In view of the possible pure magnetic nature of T_{c2}, we have checked at $P = 2.5$ kbar that the single heat capacity jump still coincides with a superconducting transition by simultaneously measuring the magnetic susceptibility in the stress cell.

Earlier susceptibility [12] and thermal expansion [18] measurements have conflicting implications for dT_{c2}/dP. Our dT_c/dP values agree roughly with the susceptibility studies on samples with $x \sim 0.02$, taken over a larger pressure range but with a coarser grid [12] (dT_{c2}/dP is not, of course, directly accessible in a susceptibility measurement). On the other hand, the thermal expansion measurements on a 3% Th sample predict through the Ehrenfest relations that the lower transition should be far more sensitive to pressure than the upper one [18]. We

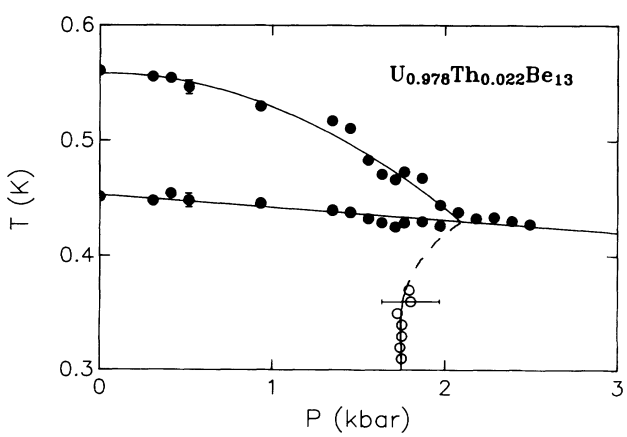

FIG. 2. Pressure-temperature phase diagram. Lines are guides to the eye.

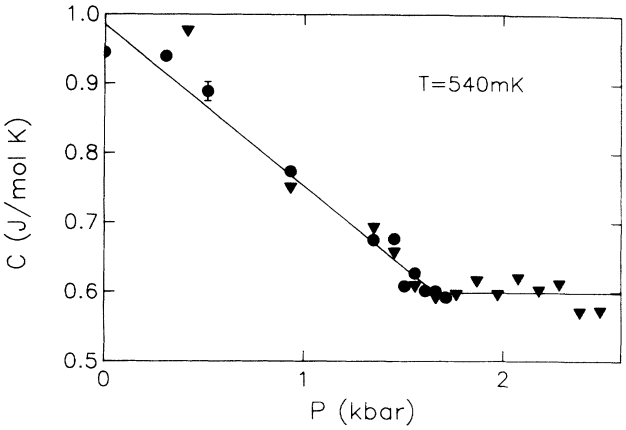

FIG. 3. Jump in the specific heat with pressure at the normal-superconducting transition for $T=540$ mK. Circles and triangles correspond to different pieces of the $x=0.022$ polycrystal.

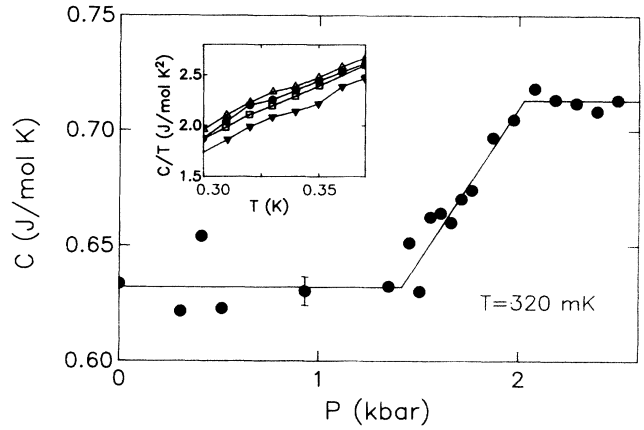

FIG. 4. Jump in the specific heat with pressure at $T=320$ mK, ending at the critical pressure to merge the two transitions, $P_c=2.1$ kbar. Inset shows the temperature independence of the step in $C(P)$ at low T, as reflected in the open circles in the phase diagram (Fig. 2). Pressures, in order of increasing C, are 1.3, 1.8, 2.0, and 2.2 kbar.

see the opposite for our 2.2% polycrystal, indicating a strong dependence on x of the pressure coefficients of T_c and T_{c2}.

The sizable slope with respect to the T and P axes of the phase boundary for the normal to superconducting transition (Fig. 2) permits one to see the jump in $C(T_c,P)$ in either variable. By comparison to the temperature scans at fixed pressure of Fig. 1, we show in Fig. 3 a 540 mK cross section of the $C(T)$ data, cutting through the upper phase boundary of Fig. 2 in a horizontal rather than a vertical direction. Identifying the transition in $C(P)$ as the midpoint of the rise agrees with the phase boundary in Fig. 2, with the total change in specific heat as determined by either method, $\Delta C/T_c=0.60 \pm 0.06$ J/mol K^2. We note that any differences between the data from before (circles) and after (triangles) the sample was cut are smaller than the scatter in our data, reflecting the sample's high homogeneity.

The proposed additional low temperature phase boundary at $x_0(P)$ is expected to be essentially parallel to the T axis, and thus, can only be seen in a pressure scan at fixed temperature. We do indeed find its signature as illustrated by the jump in $C(P,T=320\text{ mK})$ in Fig. 4. The total change in heat capacity is small, $\Delta C/C=0.10\pm0.01$ on decreasing P, but well defined. We have averaged together data sets from the two samples at equal pressures to increase the signal-to-noise ratio. We have removed and reapplied pressure so as to cross this boundary several times and see the jump in the specific heat each time. The motion of the low temperature tail in $C(P,T)$ is also evident in the hydrostatic pressure measurements, although the large background makes it difficult to determine the magnitude of the change.

We identify the midpoint of the step in $C(P)$ as the transition pressure and plot the resulting phase boundary as the open circles in Fig. 2, where the error bar shows the 20%–80% width. The transition pressure of 1.8 kbar is essentially independent of T from 310 to 370 mK, as shown in the inset to Fig. 4. The dotted line in Fig. 2 is a possible continuation of the new phase boundary, although we have no evidence that the lines actually meet in a tetracritical point. In this context, we point out that the high-pressure end of the transition occurs at or very near $P_c=2.1$ kbar. Any location of the phase boundary between 1.5 and 2.1 kbar is consistent with the muon spin resonance results [6], since a pressure variation of 0.6 kbar corresponds to a concentration change of only 0.1% Th, much finer than the spacing used in any experiments as a function of concentration. Unfortunately, we cannot draw conclusions about the order [7] of the low temperature $C(P)$ transition by looking for hysteresis, because we are constrained to change the pressure at room temperature.

The change in $C(P)$ at fixed T varies smoothly from 8% to 11% as T decreases from 360 to 310 mK, and it is small compared to any other transition on the phase diagram. In particular, $\Delta C/C=(50\pm5)\%$ for the $P=0$ transition at T_{c2} into the same low temperature, low pressure state. Moreover, the relative symmetries of the three low T phases are such that $\Delta C/C$ is of opposite sign at the two transitions into the lower left hand portion of the P-T diagram of Fig. 2: The specific heat increases with decreasing T at fixed P, but decreases with decreasing P at fixed T. This opposing behavior restricts the possible representations allowed to describe the multiple phases. Although dissimilar to the transitions at T_c and T_{c2}, we note that the 10% change in $C(P)$ between the two low temperature phases is of comparable size to the 9% specific heat jump [19] at the A-B transition in superfluid ^{3}He. One theoretical treatment [11] of thoriated UBe_{13} actually involves a low temperature phase much like ^{3}He-A, in which the breaking of time-reversal symmetry

leads to magnetic effects.

In conclusion, our study of $C(T,P)$ of $U_{0.978}Th_{0.022}Be_{13}$ explicitly shows the merging of the two transitions at a critical pressure $P_c = 2.1$ kbar, delineating the pressure dependence of T_c for *both* transitions. The pressure coefficient of the lower transition, dT_{c2}/dP, is much smaller than that of the transition from normal state to superconductor, and continues through P_c. Furthermore, we find an additional phase boundary in $C(P)$ near P_c at fixed T. It is characterized by a small jump in $C(P)$ of opposite sign to the step in $C(T)$ at T_{c2} and $P=0$ into the same low temperature state. As a direct thermodynamic proof of the existence of this posited phase boundary, the data constrain the symmetry and entropy changes between multiple states in models of unconventional superconductivity in $(U,Th)Be_{13}$.

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