Specific heat study in $U_{1-x}Th_xBe_{13}$: Enormous ΔC and strong coupling at $x=x_{c1}$ and x_{c2}; Correlation between γ and unusual superconductivity

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Specific heat measurements of samples of $U_{1-x}Th_xBe_{13}$ utilizing extremely fine gradations of x near x_{c1} and x_{c2}, where two superconducting phases are known to occur for $x_{c1}<x<x_{c2}$, were undertaken to study the genesis of the second transition. Surprisingly, this precise delineation of x in the critical regions of the phase diagram has revealed a strong peaking of the discontinuity in the specific heat ΔC at the superconducting transition that varies rapidly with x as the two transition concentration regime is approached from either side in the phase diagram. This was not seen in earlier pressure work. Correlated with the discovery of a sharp increase in ΔC at T_c at both x_{c1} and x_{c2}, the present work observes also a sharp increase in the normal state specific heat γ at both x_{c1} and x_{c2}, as well as peaks in $\Delta C/\gamma T_c$ at both critical concentrations. The implications for understanding the superconductivity in $U_{1-x}Th_xBe_{13}$ are discussed, including the possibility that the second transition for $x_{c1}<x<x_{c2}$ is caused by the anomalous behavior in $\gamma\propto N(0)(1+\lambda)$. [S0163-1829(98)03746-1]

INTRODUCTION

The discovery[1] by Ott *et al.* of two distinct transitions in the specific heat of $U_{1-x}Th_xBe_{13}$, $\sim 0.02<x\leqslant\sim 0.04$, remains a focus of considerable interest due to the as yet unknown type(s) of superconductivity involved. Several recent reviews[2–4] have quite thoroughly discussed the large body of experimental and theoretical work carried out in trying to determine the following. (1) Why does Th of all dopants produce a second, apparently superconducting, transition in $U_{1-x}Th_xBe_{13}$ beginning at $x\sim 0.02$? (2) What kind of superconductivity is involved at the two transitions? (3) Why does the second transition disappear with increasing Th content at about $x=0.04$?

Concerning the second question, current thinking[4,5] holds the superconducting transition for $x<x_{c1}$ (~ 0.02) and the upper transition for $x_{c1}<x<x_{c2}$ (see Fig. 1 below for a plot of T_c vs x) to be different in nature since the suppression of the two transitions with pressure differs[6] by more than a factor of 2; in contrast, the same measurements established that the superconducting transition for $x<x_{c1}$ has the same pressure dependence as the lower transition for $x_{c1}<x<x_{c2}$. Further differences exist between the two transitions for $x_{c1}<x<x_{c2}$. At the lower (but not the upper) transition a large peak in the ultrasound attenuation,[7] the onset of a small ($\sim 10^{-3}\mu_B$) magnetic moment measured[8] via μSR, an increase[9] in the slope of H_{c1} vs T (taken as an indication that the lower transition is, in addition to its coincidence with magnetic behavior, also superconducting), and a large anomaly[10] in the thermal expansion are observed. The magnetic field dependences of both transitions have been reported for $x=0.022$ (Ref. 11) and $x=0.03$ (Ref. 12) with the common result that the slope of the upper critical field with temperature near $T_c(H=0)$, H'_{c2}, is the same for both transitions. At higher fields, Ref. 11 found that the upper transition merges into the lower one. Consistent with the fact (see Fig. 1) that T_c grows with increasing $x>x_{c1}$ ($\Leftrightarrow$ increasing impurities) for the upper transition, while it falls for the lower transition, theorists generally[3,5] consider the upper transition to be s-wave superconductivity (BCS) while the lower transition has been variously[2–5] described, including d-wave superconductivity. A recent doping study,[14] where the response of the two transitions to magnetic and unmagnetic (La, Gd) doping of $U_{0.97}Th_{0.03}Be_{13}$ was studied, found evidence that indeed the upper transition behaves similarly to a conventional s-wave superconductor while the lower transition does not. A further study[15] of the temperature dependence of the specific heat below the upper transition also concluded that this transition was consistent with s-wave BCS superconductivity.

Experimental or theoretical insight into the other two extant questions for understanding $U_{1-x}Th_xBe_{13}$, i.e., concerning why Th produces these two transitions for $x_{c1}<x<x_{c2}$, is mostly lacking. It has been remarked[16,17] that the peak in the resistivity ρ of UBe_{13} at 2.5 K shifts downward with Th doping such that the peak in ρ at x_{c1} is just shifted to $T_c(x_{c1})$, ''allowing,'' not causing, other phase transitions to occur. The peak in ρ at 2.5 K in UBe_{13} corresponds to a peak in the specific heat C also at 2.5 K, whereby the peak in C can be more precisely followed as a function of

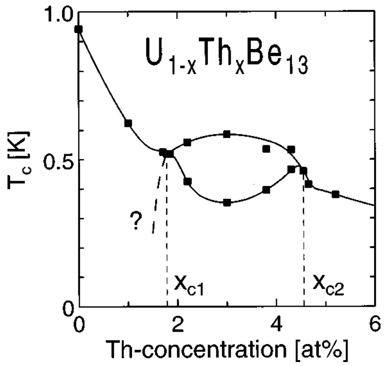

FIG. 1. T_c for $U_{1-x}Th_xBe_{13}$ is plotted vs x, whereby for $x_{c1} < x < x_{c2}$ two transitions in the specific heat are observed. In addition to the increased concentration of points near x_{c1} and x_{c2}, note two main features of this diagram that are different than the diagrams of Ott[13] and Heffner *et al.*[3] (1) As shown here for high quality, high purity samples, T_c of the lower transition (T_{c2}) decreases significantly for $x > x_{c1}$, before rising again as $x \rightarrow x_{c2}$ whereby in the literature (Refs. 3, 13) T_{c2} is approximately constant. (2) $T_c(x_{c1})$ appears to be constant over a range of composition in the single transition region as $x \rightarrow x_{c1}$ whereby for $x \rightarrow x_{c2}$, from above, T_c does not appear to have a region where it is constant. See also the text and Figs. 3 and 4. The dashed line marked by ''a question mark'' to the left of x_{c1} indicates a possible fourth transition, consistent with thermodynamics—choice (b) in the text.

Th doping. A study[18] of this peak in C in $U_{1-x}Th_xBe_{13}$ found a suppression of the peak in temperature and also in size with increasing x, with the peak still clearly present at $T \sim 1.5$ K for $x = 0.02$ and absent for $x = 0.03$. Another study[19] of the peak in C as a function of Th content found the peak still present (in size about 15% of ΔC in pure UBe_{13}) for $x = 0.0245$, contradicting the (less precise) resistivity data. The entropy $[S = \int (C/T) dT]$ under the peak in pure UBe_{13} (0.7 J/mol K) shifts downwards with increasing x and appears[18] in the low temperature γ ($\equiv C^{\text{normal}}_{\text{extrap}}/T$, hereafter C^n/T, as $T \rightarrow 0$). Thus γ for $U_{0.97}Th_{0.3}Be_{13} \cong 2300$ mJ/mol K^2 vs $\gamma = 1000$ mJ/mol K^2 for pure UBe_{13}.[12]

In order to investigate the role of Th in $U_{1-x}Th_xBe_{13}$, as well as to better understand the genesis of the double superconducting transitions, an investigation of the specific heat in the *close* neighborhood of x_{c1} (x_{c2}) where the second transition first appears (disappears) has the potential to reveal new information. Data to date[1,20] for $x = 0.019$, 0.0216, 0.0378, and 0.0433 reveal no trace of a separate transition at $x = 0.019$ and 0.0433, and quite sizable double transitions ($\Delta C_1 \sim \Delta C_2$) already existing at $x = 0.0216$ and 0.0378. Thermodynamic considerations[21] demand either that (a) one of the observed superconducting transitions at the critical points be first order,[22] (b) if the transitions are second order, a second, as yet unobserved,[23] superconducting transition must exist for x just near x_c, but outside of $x_{c1} \leqslant x \leqslant x_{c2}$, (c) as $x \rightarrow x_c$ from within $x_{c1} \leqslant x \leqslant x_{c2}$, $dT_{c1}/dx = dT_{c2}/dx$ where T_{c1} is the transition temperature of the higher temperature, upper transition and T_{c2} is the transition temperature of the lower transition (''tangential approach''), or (d) as $x \rightarrow x_c$ from within $x_{c1} < x < x_{c2}$, either ΔC_1 or $\Delta C_2 \rightarrow 0$.

Until now, the only careful specific heat investigation near x_c was a pressure experiment[6] for $U_{0.978}Th_{0.022}Be_{13}$ (i.e., near x_{c1}) up to 2.5 kbar where the two transitions were brought together around 2 kbar. In that study, pressure was equated to decreasing Th content (Th expands the UBe_{13} lattice), i.e., electronic effects (La and Pr also expand UBe_{13}, but generate no second transition) were outside the scope of the study. Thus, 0.1 kbar$\cong$0.0002 Th content, such that the double transition regime was suppressed around (an equivalent) $x = 0.018$. Additionally, the size of the jump in C at T_c, $\Delta C(T_c)$, was found[6] to decrease with increasing pressure.

In order to further investigate the region near x_{c1}, including electronic effects, as well as to perform a detailed specific heat study near x_{c2} the current work presents specific heat measurements of $U_{1-x}Th_xBe_{13}$ with very small steps ($\Delta x \geqslant 0.0007$) in x near x_{c1} and x_{c2}. Samples were made as the work progressed based on the unfolding results so that the very high purity U and Be could be used as efficiently as possible for the critical concentrations. Thus, we report here on high purity samples of $U_{1-x}Th_xBe_{13}$, $x = 0.01$, 0.017, 0.0178, 0.0185, 0.022, 0.043, 0.0455, 0.0465, 0.052.

EXPERIMENT

As correctly stated in the specific heat under pressure experiment[6] by Zieve *et al.* on $U_{0.978}Th_{0.022}Be_{13}$, studying the vicinity of a critical point using composition of physical samples as a (extremely fine) control parameter is difficult. In order to avoid, as much as possible, sample variation, the highest available purity starting materials—electrotransport refined U from Ames Laboratory and 99.999% pure crystalline ''MBE quality'' Be from Atomergic (at \$800/g)—were used. Samples were melted in a dedicated-for-Be-use arc melter under a purified Ar atmosphere. In order to precisely monitor any possible Th loss (Th masses for a nominal U charge of 400 mg were as low as 3.9 mg) during the first melting of Th with other material, U and Th were first melted together. Since both have low vapor pressures at their melting temperatures (in contrast to Be), any loss could be controlled to 0.05 mg, or approximately $\Delta x_{\text{Th}} = 0.0001$. All meltings were done using the same procedures and performed by the same operator. After arc-melting the U and Th together three times, the resulting metal button was melted together with 1.06 times the correct stoichiometric amount of Be (to allow for Be weight loss) and then flipped and remelted two successive times. All samples were x rayed using a Siemens D5000 diffractometer; the powder was mixed with Si powder to provide an internal reference. The cubic $U_{1-x}Th_xBe_{13}$ lattice parameters so obtained, including also data for $x = 0.03$, 0.038, and 0.10 from our previous work, are shown in Fig. 2 and Table I. Near x_{c2}, for example, the deviations from the linear Vegard's law lattice parameter behavior shown in Fig. 2 would indicate that the $x = 0.043$ sample is really $x = 0.042$ and that the $x = 0.0465$ sample has the actual Th concentration $x = 0.487$. None of these possible deviations either bring the composition of one sample—as determined by lattice parameter—onto that of an adjacent composition or, as will be seen below, change any conclusions.

Specific heat measurements[24,25] were performed on 1–2 mg pieces of each sample taken from the top of the respective arc-melted buttons. As an indicator of homogeneity, a second sample of $x = 0.0455$ was also measured from the middle of the arc-melted button and gave a ΔC 11% smaller

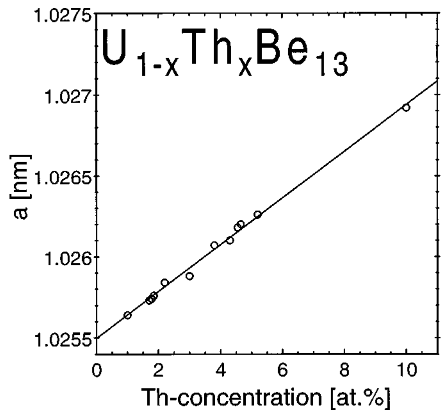

FIG. 2. Cubic lattice parameter vs Th concentration in $U_{1-x}Th_xBe_{13}$. These data show that the monotonic fine-tuning of the nominal composition near x_{c1} and x_{c2} in fact succeeds in producing monotonic variation in the actual resulting composition. Compositions used in the text are the nominal ones, due to the inherent scatter in the x-ray results.

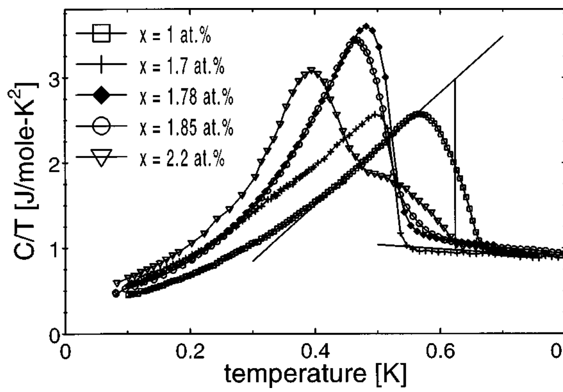

FIG. 3. Specific heat C divided by temperature T vs T for $U_{1-x}Th_xBe_{13}$ near x_{c1}. Note (1) the ''pinning'' of T_c at approximately the same value for $0.017 \leqslant x \leqslant 0.0185$ as remarked upon in Fig. 1, (2) the *increase* of ΔC for x decreasing from 0.022, in contradiction to pressure results (Ref. 6), and (3) the lack of any increase in C for $T < 0.4$ K with decreasing x below 0.022, again in contradiction to the pressure induced transition observed in Ref. 6. Also, note the increased normal state C/T for $x = 0.0178$ and 0.0185 vs that for $x = 0.017$, as well as the broadened superconducting transitions for the former vs the latter. The slight anomaly at 0.34 K in the C/T data for $x = 0.017$ may be the thermodynamically posited fourth phase transition shown as a dashed line to the left of x_{c1} in Fig. 1 and discussed in the text. Measurements on $x = 0.0174$ are planned. The equal area construction method (Ref. 26) for determining ΔC^{ideal} is shown here for $x = 0.01$.

and the same T_c. As will be seen below, such a variation also does not change any trends or conclusions.

RESULTS AND DISCUSSION

The specific heats divided by temperature of the samples near x_{c1} are shown in Fig. 3, while the data for the samples near x_{c2} are shown in Fig. 4. As may be seen, without recourse to any optimizing of the jumps in the specific heat using the equal area construction,[26] the size of $\Delta C/T$ grows significantly and quite rapidly as a function of x near both x_{c1} and x_{c2}. [For want of a more precise definition, let us for the following define x_{c1} (x_{c2}) as the concentration where $\Delta C/T$ is a maximum as x approaches (departs) the double transition regime, i.e., $x_{c1} \cong 0.0178$ and $x_{c2} \cong 0.0455$.]

x_{c1}. This peaking in $\Delta C/T$ effect was absent from the scanning[6] of x_{c1} using pressure, where a *decrease* in $\Delta C/T$ was seen scanning ''downward'' in composition from $x = 0.022$ using pressure, and no other previous experiments near x_{c1} combine to offer the fine scale on which Th concentration is varied here. Thus, previous data[20] for $x = 0.019$ show a peak in C/T within 3% in value of that measured[20] for $x = 0.0172$ vs a 74% difference in $\Delta C/T$ (see Table I) for the $x = 0.0178$ ($\cong x_{c1}$) data compared to the $x = 0.0170$ data shown in Fig. 3. Also, as has been remarked on[12] before, purity has been seen to play a role in ΔC, especially for the lower transition for $x_{c1} < x < x_{c2}$ where high purity $U_{0.97}Th_{0.03}Be_{13}$ showed[12] a $\Delta C_2 \sim 1.5$ that observed in samples with the purity in, e.g., Ref. 20. Thus, the fact that peaking in $\Delta C/T$ at x_{c1} has not been previously observed may also be partly due to the purity of the samples.

x_{c2}. Despite a much coarser delineation in x in the previous combined low-temperature specific heat studies of $U_{1-x}Th_xBe_{13}$ near x_{c2} [$x = 0.0378$,[1,12] 0.0433,[20] 0.052,[11] and 0.0603 (Ref. 1) have been measured] compared to that in the present work, the peaking observed in $\Delta C/T$ at x_{c2} in Fig. 4

TABLE I. $U_{1-x}Th_xBe_{13}$.

x [at. % Th]	0	1	1.7	1.78	1.85	2.2	3	3.8	4.3	4.55	4.65	5.2
T_c [mK]	941	624	525	519	519					460	415	380
T_{c1} [mK]						558	585	532	533			
T_{c2} (mK)						425	353	396	465			
ΔC (mJ/mol K)	1810	1250	940	1615	1635					2340	1425	895
ΔC_1 (mJ/mol K)[a]						510	840	765	115			
ΔC_2 (mJ/mol K)[a]						810	620	660	1890			
$\Delta C_{(1)}/\gamma_{C1}T_{C(1)}$[a]	2.65	2.06	1.8	2.73	2.90	0.84	1.24	1.34	0.20	4.38	2.72	1.88
$S(T_C)$ (mJ/mol K)	810	810	700	830	800	905	1105	1035	890	850	765	605
γ^* (mJ/mol K^2)	725	970	990	1140	1085	1085	1160	1075	1080	1160	1260	1255
γ (mJ/mol K^2)	995	1630	1700	2060	2000	2610	2615	2820	2230	2535	2415	1935
γ_{rest} (mJ/mol K^2)	100	350	450	415	365	400	600	700	430	300	715	650
a (Å)		10.2564	10.2573	10.2574	10.2576	10.2584	10.2588	10.2607	10.2610	10.2618	10.2620	10.2626

[a]All ΔC values are determined using the equal area construction method (Ref. 26).

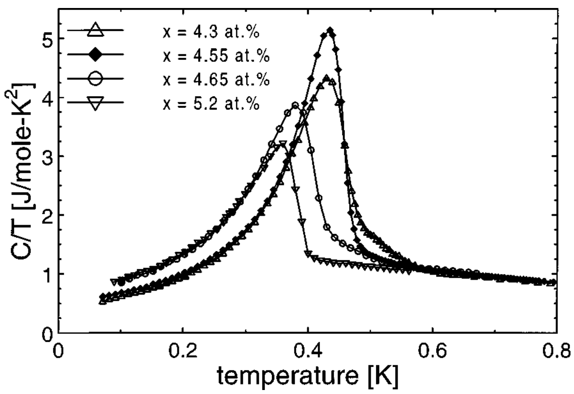

FIG. 4. Specific heat divided by temperature vs temperature for $U_{1-x}Th_xBe_{13}$, x near x_{c2}. Note the shoulder above the large ΔC for $x=0.043$ which corresponds to the beginning of the presence of ΔC_1 in the double transition region of the phase diagram. Ac susceptibility confirms T_c^{onset} for $x=0.043$ to be $\sim$0.56 K. This very small ΔC implies that, at least at x_{c2}, $\Delta C_1 \rightarrow 0$.

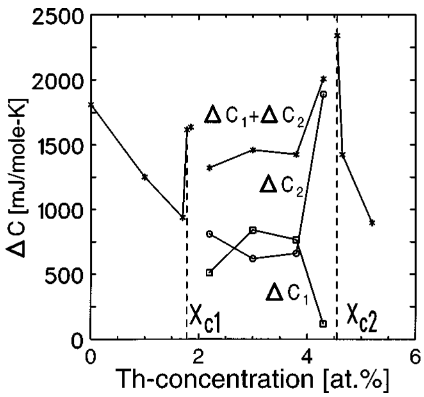

FIG. 5. The jump in the specific heat at T_c, ΔC, determined using the equal area construction (Ref. 26) vs Th concentration in $U_{1-x}Th_xBe_{13}$. In the region $x_{c1}<x<x_{c2}$ where there are two transitions, ΔC_1 (squares) and ΔC_2 (circles) as well as their sum (asterisks) are plotted separately. It is clear that ΔC for $x<x_{c1}$, as well as ΔC for $x>x_{c2}$, peaks as $x\rightarrow x_c$ from outside $x_{c1}<x<x_{c2}$, serving as a harbinger of the second transition. Note that $\Delta C_1 \rightarrow 0$ as $x\rightarrow x_{c2}$.

at $x=0.0455$ was already qualitatively evident in the discovery work[1] by Ott *et al.* In that work $C_{\max}/T$ for $x=0.0378$ for ΔC_2 (a weak upper transition was still observable) was 4.6 J/mol K^2, compared to 3.5 J/mol K^2 for $x=0.0331$ in the same work, 3.5 J/mol K^2 for $x=0.0433$ in Ref. 20 (vs 4.3 J/mol K^2 for $x=0.043$ and 5.1 J/mol K^2 for $x=0.0455$ reported here). The ability in the present work to see the precise point in the phase diagram (see Fig. 1) where the second transition first occurs (at $x=0.043$, see Fig. 4) shows how rapidly as a function of x the behavior of $U_{1-x}Th_xBe_{13}$ changes near x_{c2} (which would, given the proper composition, presumably also be the case for x near x_{c1}). What the present work also observes for x_{c2} which was not previously seen (also not in the present work at x_{c1}) and which may shed light on the nature of the superconducting critical point, is that the peak in $\Delta C/T$ occurs *just before* (see Fig. 4), as x approaches the region $x_{c1}<x<x_{c2}$ from above, the second transition occurs at $x=0.043$.

A question arises: is the peaking in $\Delta C/T$ at $x_{c1,2}$ due to an as of yet not understood physical phenomenon (possibly linked to the genesis of the second transition) or is it simply that the second transition seen for $x_{c1}<x<x_{c2}$ has the same T_c at x_{c1} (x_{c2}) as the transition observed for $x<x_{c1}$ ($x>x_{c2}$) and that the sum of the two ΔC's is large? In order to consider this question, consider the plot of ΔC vs Th concentration in Fig. 5. Away from $x_{c1,2}$, i.e., for $0.022\leqslant x\leqslant 0.038$, one cannot extrapolate the sum $\Delta C_1+\Delta C_2$ to come anywhere near $\Delta C(x_{c1,2})$. As one approaches an x_c from within (without) $x_{c1}<x<x_{c2}$, however, ΔC_2 (ΔC) grows enormously with a Δx of only at most 0.005 (0.0008), where the correct limiting value for Δx for ΔC_2 is likely smaller than 0.005 as would be revealed by further experiments for $x=0.0195$ and 0.041. Thus, something unusual, directly in the vicinity of $x_{c1,2}$, appears to occur.

Why the lower transition ΔC_2 grows so sharply—just as the upper transition is splitting off at $x=0.043$—in comparison with ΔC_2 at $x=0.038$ and why the single-transition region ΔC also jumps as the two transition region is approached from either side is the central question arising from this work and the focus of the further discussion. We treat, in advance of more data in the exact vicinity of x_{c1} (at, e.g., $x=0.0195$), x_{c1} as similar to x_{c2} as regards the behavior observed for $x=0.043$.[27] The early work of Ott *et al.* for $x=0.0378$, where a very large ΔC_2 had a small ΔC_1 shoulder, is—in terms of the results of the present work—seemingly equivalent to our $x=0.043$ or possibly to (as yet unmeasured) $x\cong 0.041$. This sample dependence, already commented on above for samples near x_{c1} and discussed also in Ref. 12, makes it clear that the intercomparison of high quality samples—all prepared using the same starting materials and preparation techniques—is absolutely necessary for exploring the critical behavior near x_{c1} and x_{c2}. The changes observed in the consistently made samples in the present work—although startingly rapid at x_{c1} and x_{c2}—all behave monotonically with x. Further, the peaking behavior in $\Delta C/T$ at x_{c1} is mirrored at x_{c2}, on the scale of things a great distance away in composition.

TOWARDS UNDERSTANDING THE LARGE $d\Delta C/dx|x_c$

If this large peaking in $\Delta C/T$ at x_c is due to an as of yet unobserved phenomenon (which would have implications for the genesis of the second transition), then unusual behavior at $x_{c1,2}$ should be observed in other superconducting *and* normal state observable quantities. Conversely, the simple melding together of two transitions at a common T_c at $x_{c1,2}$ to cause a large ΔC would not produce sharp changes at $x_{c1,2}$ in the other superconducting and normal state properties. Specific heat measurements lend themselves to a determination of an important normal state parameter γ proportional to the dressed density of states $N(0)(1+\lambda)$. In addition, specific heat data allow the determination of an important measure of the strength of the coupling of the superconducting electrons, namely, $\Delta C/\gamma T_c$, equal to 1.43 for a weak coupled BCS superconductor.

γ. The discussion of the specific heat γ ($\equiv C^n/T$ as $T\rightarrow 0$) in UBe_{13} and $U_{1-x}Th_xBe_{13}$ is complicated by the fact that these materials—unlike most ''nonheavy fermion'' systems—are not Fermi liquids by 1 K. This means that C/T, which is an indicator of the bare density of states at the

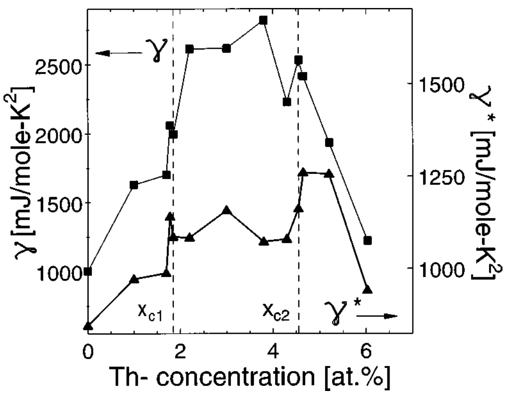

FIG. 6. $\gamma(\equiv C^n/T$ as $T\rightarrow 0)$ vs Th concentration (squares) as determined by linear extrapolation of C^{normal}/T below T_c to match the observed superconducting state entropy as discussed in the text. C^n/T at $T_c^+(\equiv\gamma^*)$ is also shown plotted as triangles. The large difference between the two values at a given x is proof of the continuing evolution at low temperature of the dressed density of states in these materials. Note the sharp rise in both γ and γ^* as $x\rightarrow x_{c1,2}$ from outside the double transition region. In the superconducting state for $U_{1-x}Th_xBe_{13}$, in contrast with other superconductors, C^{sc}/T does not approach zero as $T\rightarrow 0$, but rather has a remanent value γ_{rest}, see Table I and Ref. 11. This γ_{rest} varies between 20–30 % of γ and has also been seen in Ref. 11. If $\gamma-\gamma_{\text{rest}}$ is plotted (not shown), the data shown for γ are merely shifted downwards with no strong change in the observed structure at x_{c1} and x_{c2}.

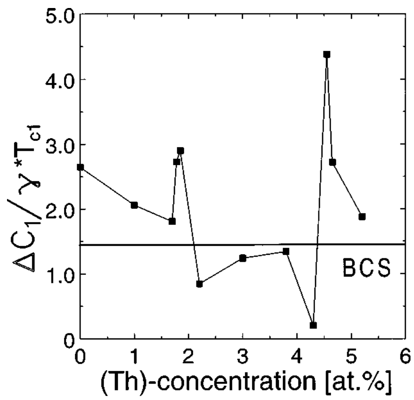

FIG. 7. The discontinuity in the specific at T_c, ΔC, (ΔC_1 for $x_{c1}<x<x_{c2}$) determined via the equal area construction (Ref. 26) divided by $\gamma^*\equiv C/T|_{T=T_c^+}$ multiplied by T_c (in the single transition regimes) or T_{c1} (in the double transition regime) vs Th concentration in $U_{1-x}Th_xBe_{13}$. The BCS value for weak coupling superconductors is 1.43. If $\Delta C_2/\gamma^? T_{c2}$ were plotted at $x=0.043$, or generally for $x_{c1}<x<x_{c2}$, the value for $\gamma^?$ used would be from C^n/T data above T_{c1} extrapolated down to T_{c2} using the entropy constraint. The resultant $\Delta C_2/\gamma^? T_{c2}$ at $x=0.043$ is about 3.2, i.e., the fact that $\Delta C_2/\gamma^? T_c$ rises as $x\rightarrow x_{c1}$ (from below) and $x\rightarrow x_{c2}$ (from above), and then falls for $x_{c1}<x<x_{c2}$ is independent of what is used in the two transition region for $\Delta C_2/\gamma T_c$.

Fermi energy $N(0)$ times a factor $1+\lambda$ which describes the electron interactions, is still changing as a function of temperature below 1 K. Thus, in $U_{0.97}Th_{0.03}Be_{13}$ $C/T \cong 1150\,\text{mJ/mol K}^2$ just above T_{c1}, and rises to $C^n/T\cong 2600\,\text{mJ/mol K}^2$ at $T\rightarrow 0$ (see Table I and Ref. 12). The determination of C^n/T below T_c can be carried out via measurements in magnetic field[12] to suppress the superconductivity or by matching the (measured) superconducting state entropy ($S_{\text{sc}}=\int_0^{T_c}C^{\text{sc}}/T dT$) with the extrapolated normal state entropy ($S_n=\int_0^{T_c}C^n_{\text{extrap}}/T dT$) under the assumption that the transition is second order, i.e., $S_{\text{sc}}=S_n$. Thus, *a priori* there are two γ's one can consider—the measured γ or more properly C/T, above T_{c1} (here called γ^*) and the linearly extrapolated, via entropy-matching determined $\gamma=C^n/T$ as $T\rightarrow 0$. These are listed in Table I and plotted in Fig. 6. As may be readily seen, the normal state γ ($\equiv C/T$ as $T\rightarrow 0$) as well as $C/T|_{T=T_{c1}^+}(=\gamma^*)$ both show structure as x approaches the double transition region $x_{c1}<x<x_{c2}$. Since γ is a normal state property, this sharp structure at x_{c1} and x_{c2} in γ is certainly consistent with the huge jumps in the specific heat at the superconducting transitions at x_{c1} and x_{c2} being indicative of some underlying physical phenomenon and not just simply the crossing of two superconducting $T_c(x)$ phase lines. Something is occurring in the *f*-electron density of states and/or with the electron interactions that is connected with the sharp peaking in ΔC at x_{c1} and x_{c2}, after which, as x enters the region $x_{c1}<x<x_{c2}$, two superconducting transitions appear. Obviously, a large γ implies a large entropy ($S=\int_0^{T_c}C^{\text{sc}}/T dT$)—shown in Table I. Thus, as γ peaks for $x_{c1}<x<x_{c2}$, so does the entropy ($\Leftrightarrow f$-electron degrees of freedom). This increase in entropy is of course necessary for (and probably connected to) the multiple large peaks in C^{sc}/T observed for $x_{c1}<x<x_{c2}$. That the entropy rises already at $x\sim 0.02$ is, as discussed above, connected with the suppression of the peak in C at 2.5 K in pure UBe_{13} with Th doping. The jump in γ at $x=0.0178$ (x_{c1}) occurs, however, before this 2.5 K peak is completely suppressed.[19] Thus, an exact correlation[16,17] is lacking at x_{c1}, and of course this peak suppression is long since complete before the behavior at x_{c2} occurs.

$\Delta C/\gamma T_c$. Figure 7 shows $\Delta C/\gamma^* T_c$ vs x for $U_{1-x}Th_xBe_{13}$, where $\gamma^*=C/T|_{T=T_c^+}$. This is the sensible choice, since the energy gap opens up in the dressed density of states present at T_c, not the eventual γ ($\equiv C^n/T$ as $T\rightarrow 0$) that is obtained well below the superconducting transition. (Measurements[12] of the normal state in a 2 T applied magnetic field—low enough not to affect C/T above $T_c(B=0)$—show indeed a continuing gradual increase in C/T with decreasing temperature, not a sudden jump in C/T.) If we compare the values shown in Fig. 7 with the weak-coupling BCS result of $\Delta C/\gamma T_c=1.43$, clearly the vicinity of x_{c1} and x_{c2} in $U_{1-x}Th_xBe_{13}$ sees very strong coupling. (Even without using an idealized[26] ΔC for an infinitely sharp transition, $\Delta C/\gamma^* T_c$ at $x=0.0455$ is 3.1, far in excess of the BCS value.) In fact, the value for $\Delta C/\gamma^* T_c$ observed at x_{c2} is larger than seen in any other superconductor with the exception of $UBe_{12.97}B_{0.03}$, where $\Delta C/\gamma^* T_c$ is also observed[28]—for an idealized transition—to be 4.4, although without any two transition region found in the phase diagram. The important implication to be drawn here from the data in Fig. 7 is, however, not the very strong coupling when compared to BCS but rather the sharp structure peaking at x_{c1} and x_{c2} just as for ΔC and γ discussed above. The large $\Delta C/\gamma^* T_c$ values themselves, if taking place[4,5] in a non-BCS superconductor, can first be quantitatively discussed only after the precise ground state is known.

CONCLUSIONS AND FUTURE WORK

It seems that the two phase region in $U_{1-x}Th_xBe_{13}$ for $\sim 0.0178 < x < 0.0455$ is preceded on both the Th-richer and -poorer sides by enormous increases in the size of the specific heat jumps at the superconducting transition, in the size of γ (defined either as C/T at $T = T_c^+$ or at $T \to 0$), and in the size of $\Delta C/\gamma^* T_c$ ($\Leftrightarrow$ superconducting coupling strength). These facts taken together argue that such peaking at $x_{c1,2}$ is not simply a crossing of $T_c(x)$ phase lines of two transitions, but rather is more fundamental in nature. Considering now the central questions (type of superconductivity and why Th produces two transitions for $x_{c1} < x < x_{c2}$) which this work was undertaken to try to answer, the extremely large ΔC and $\Delta C/\gamma^* T_c$ for x approaching the two phase regime, where according to, e.g., pressure work[6] the lower transition for $x_{c1} < x < x_{c2}$ corresponds to the large single transition for $x < x_{c1}$, do not appear consistent with BCS theory. The strong increase in γ and also γ^* at $x_{c1,2}$ (see Fig. 6) is consistent with some double resonance structure, with a shallow minimum between, in the dressed density of states moving through the Fermi energy as a function of increasing Th concentration such that the Fermi energy is between the two sharp peaks for $x_{c1} < x < x_{c2}$. As we have discussed before,[12] one important difference between Th, which creates two separate transitions and, e.g., La, which does not, is the size of the peaks in $N(0)(1+\lambda)$ caused by Th. For $U_{1-x}Th_xBe_{13}$, $\gamma (= C^n/T$ as $T \to 0)$ exceeds 2.6 J/mol K^2(see Table I) while for $U_{1-x}La_xBe_{13}$, values of ''only'' 1.5 J/mol K^2 are reached.[18]

Why and whether the genesis of the two transition region in $U_{1-x}Th_xBe_{13}$ is linked to a non-BCS superconducting mechanism caused by large values of γ in $\gamma[\propto N(0)(1+\lambda)]$ as a function of x as x moves through $x_{c1,2}$ provides an incentive for further experimental and theoretical work. Certainly the clues revealed here, that ΔC and $\Delta C/\gamma^* T_c$ peak sharply at $x_{c1,2}$, *before* the two transition region occurs, should provide a helpful initial direction. Electron tunneling measurements on $U_{1-x_{c1,2}}Th_{x_{c1,2}}Be_{13}$ are planned to directly determine the energy gap, another indicator—in addition to $\Delta C/\gamma^* T_c$—for the coupling strength.

Concerning the search[23] for a second transition for $x < x_{c1}$ and $x > x_{c2}$ [so that the thermodynamic structure of Yip, Li, and Kumar[21] (YLK) that three second order phase transition lines cannot meet at a point is obeyed as discussed above in the Introduction], the present work with all its fine gradations in Th concentration can offer only hints for further work. As seen in Fig. 3, there *may* be a small second transition at 0.34 K below the large transition at 0.5 K in $U_{0.983}Th_{0.017}Be_{13}$. (Whether this small anomaly is related to the very large anomaly in the ultrasonic attenuation observed[7] at 0.36 K for $x = 0.0175$ is a question of how intercomparable the differing preparations are, as discussed above when comparing Ott's $x = 0.0378$ results with our $x = 0.043$ data.) This implies an almost vertical $T_c(x)$ for this second transition—work at $x = 0.0174$ is planned. As discussed above, the YLK stricture can also be fulfilled in the special case that, in the two phase region, $dT_{c1}/dx = dT_{c2}/dx$ as $x \to x_c$. This, based on the present work, remains an open question at both x_{c1} and x_{c2}. However, the last way to fulfill the YLK stricture (barring a first order phase transition), i.e., $\Delta C_1 \to 0$ before x_c is reached so that there are not three phase lines, seems to be consistent with the data (see Fig. 4 and 5) at $x = 0.043$ near x_{c2}. Thus, to decide the thermodynamic behavior near x_{c1} requires further data on ΔC, for $0.0185 < x < 0.022$, as well as the continuing search for the almost vertical phase line at $x = 0.0174$.

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[27] Note, however, that (see Figs. 3 and 4 and Table I) the behavior of T_c vs x as measured is different at the two x_c's since T_c is pinned to around the same value for $x=0.017$, 0.0178, and 0.0185 while T_c for $x=0.043$ (0.0465) is higher (lower) than that of $x=0.0455$ by $\sim$0.05 K. It is possible that data for $x=0.0445$ would show the same T_c as for $x=0.0455$.
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