PHYSICAL REVIEW B VOLUME 53, NUMBER 13 1 APRIL 1996-I

H-*T* phase diagrams of the double transition in thoriated UBe_{13}

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(Received 28 July 1995)

We present magnetic field-temperature (H-T) phase diagrams of the double transitions of superconducting $U_{1-x}Th_xBe_{13}$ with $x=0.030$ and $x=0.022$. For both samples increasing the applied magnetic field moves the two transitions to lower temperature while decreasing their separation in temperature. For the $x=0.030$ sample, the transitions remain distinct for $T>100$ mK. For $x=0.022$, however, the two transitions appear to merge near $H=20$ kOe and $T=350$ mK, analogous to the situation in the related heavy fermion superconductor UPt_3.

Perhaps the most compelling manifestation of the exotic nature of the superconductivity in the heavy-fermion compounds is the occurrence of not one, but two transitions in the superconducting state. In addition to the normal-state–superconductor transition at T_c, a second phase transition occurs at a lower temperature, T_{c2}, which maintains the distinctive features of zero-resistance and inductive shielding. The most intensively studied double transition is that of UPt_3. With a relatively small temperature splitting $\Delta T=60$ mK, an explanation arises naturally in terms of two superconducting states with nearly degenerate energetics but different symmetries.[1–7] Detailed studies of the magnetic field-temperature[8–11] (H-T) and pressure-temperature[12–14] (P-T) phase diagrams of UPt_3 have revealed additional phases and have provided insight into the nature of the transitions between them.

Whereas the superconducting order in UPt_3 can be treated as a perturbation on the crystal symmetry, the situation in thoriated UBe_{13} is not so clear. $U_{1-x}Th_xBe_{13}$ exhibits a double transition in the superconducting state for $0.018<x<0.045$, but with ΔT's up to several hundred mK, a fair fraction of T_c. The material remains superconducting below T_{c2}, with the slope of the lower critical field actually increasing.[15,16] Muon-spin-relaxation (μSR) measurements have detected weak magnetic correlations below T_{c2},[16] suggesting that the lower transition may correspond to the onset of some weak magnetic ordering that then coexists with the superconductivity below T_{c2}. Alternatively, the second transition may correspond to a change in the symmetry of the superconducting state. In one such scenario,[17] buttressed by recent explorations of both the local magnetization in a torus of $U_{0.97}Th_{0.03}Be_{13}$ (Ref. 18) and the general P-T phase diagram,[19] the superconducting order parameter for the state below T_{c2} violates time reversal invariance. It thus gives rise to weak local magnetic fields consistent with the μSR result. Similarly, μSR measurements on UPt_3 have seen an increase in the internal magnetic field below the lower transition.[20]

For the comparatively neglected $U_{1-x}Th_xBe_{13}$ system, an understanding of the nature of the double transition and an explanation of their appearance in the unusual x-T phase diagram remain incomplete. Yet, the UBe_{13}-based superconductors are the only materials where the specifics of sample preparation and macroscopic sample homogeneity do not appear to be related to the appearance of two reproducible transitions.[21] We present here specific-heat measurements of the magnetic field-temperature phase diagrams of $U_{1-x}Th_xBe_{13}$. Previous experiments have looked at the H-T phase diagram for $x=0.03$ (Ref. 22) and $x=0.033$.[23] We also measure a high-quality polycrystal of $U_{0.970}Th_{0.030}Be_{13}$, and extend the phase diagram to significantly lower temperature. In addition, we present a determination of the H-T phase diagram for a double transition sample with a smaller thorium concentration, $U_{0.978}Th_{0.022}Be_{13}$, and therefore, a significantly smaller zero-field temperature splitting of the two transitions. We find that while the two transitions of the $x=0.030$ sample remain split for $T>0.1$ K, the transitions of the $x=0.022$ sample appear to merge near $T\approx0.35$ K, resulting in a H-T phase diagram for $U_{0.978}Th_{0.022}Be_{13}$ which closely resembles that of UPt_3.

Our extremely high-purity polycrystals[24] were long-term annealed at 1400 °C for 1220 and 950 h for $x=0.030$ and $x=0.022$, respectively. These $U_{1-x}Th_xBe_{13}$ samples are superior to previous materials as judged by both the size of the specific-heat jump at T_c and the narrow transition widths.[24] The experiments were performed using a transient heat-pulse technique in a helium dilution refrigerator, with a Speer carbon chip for a thermometer, a Au-Cr film deposited on quartz for a heater, and either a graphite block or a silver wire as the thermal link. The lowest temperature at which we can accurately determine C is limited by radioactive self-heating from the depleted uranium. For our geometry and sample size (11 and 14 mg) this self-heating limits the measurements to $T\geqslant100$ mK. We performed both temperature sweeps $C(T)$ at constant H and magnetic-field sweeps $C(H)$ at constant T.[25] For the field sweeps, the magnetoresistance of the carbon chip made it necessary to recalibrate the thermometer at each magnetic-field point. The data obtained from $C(H)$ measurements agree well with the $C(T)$ data, but allow a better determination of the transition near our low temperature limit where the phase line is more nearly parallel to the temperature axis.

We show a representative sample of our $C(T)$ and $C(H)$ data for $U_{0.97}Th_{0.03}Be_{13}$ in Figs. 1 and 2. The two transitions are relatively sharp with the 10–90 % widths of the transi-

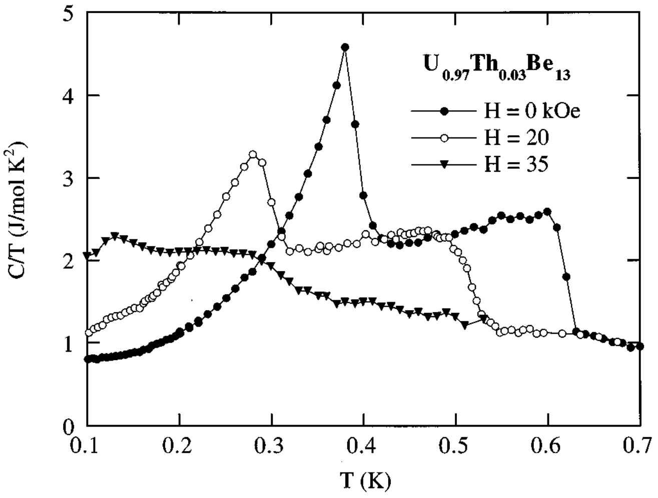

FIG. 1. Specific heat divided by temperature C/T vs T at representative magnetic fields $H=0$, 20, and 35 kOe. The nuclear contribution to the specific heat has been calculated and subtracted in this and the following figures.

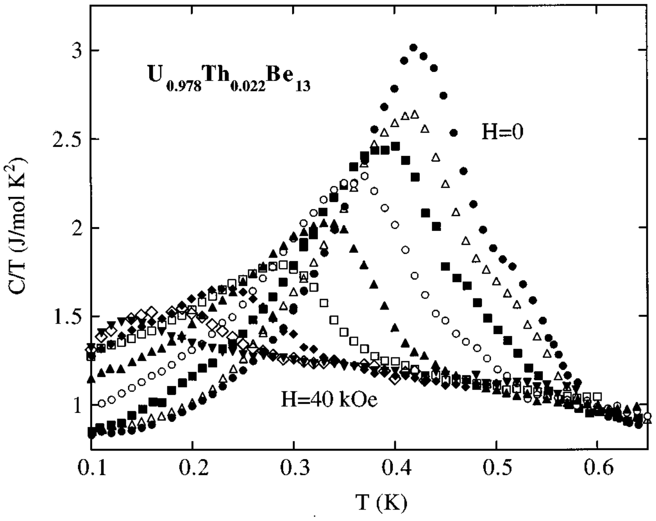

FIG. 3. Specific heat of $U_{0.978}Th_{0.022}Be_{13}$ divided by temperature C/T vs T at $H=0$, 5, 10, 15, 20, 25, 30, 35, and 40 kOe.

tions ($\approx$25 mK) much smaller than their separation ($\approx$225 mK). We define the transition temperature (or field) as the midpoint of the rise in $C(T)$ [or $C(H)$]. The contribution to the specific heat arising from the hyperfine splitting of the Be nuclear levels has been subtracted from the data shown in these and subsequent figures (less than 10% of C for $H=40$ kOe and $T>0.14$ K). The two transitions in $C(T)$ both move to lower temperature with increasing magnetic field (see Fig. 1). The upper transition moves somewhat faster, but the two transitions remain distinct for $T>0.1$ K. The agreement between the field-sweep and temperature-sweep results can be seen in Fig. 2, with the $C(T)$ data (filled triangles) lying on top of the $C(H)$ curve (open circles). Moreover, the jumps in $C(H)$ at $T=0.3$ K (Fig. 2) can be seen in the $C(T)$ curves of Fig. 1 for $H=20$ kOe and $H=35$ kOe; the arrows marking the two transitions in the magnetic field scan of Fig. 2 are derived from the temperature sweep data of Fig. 1.

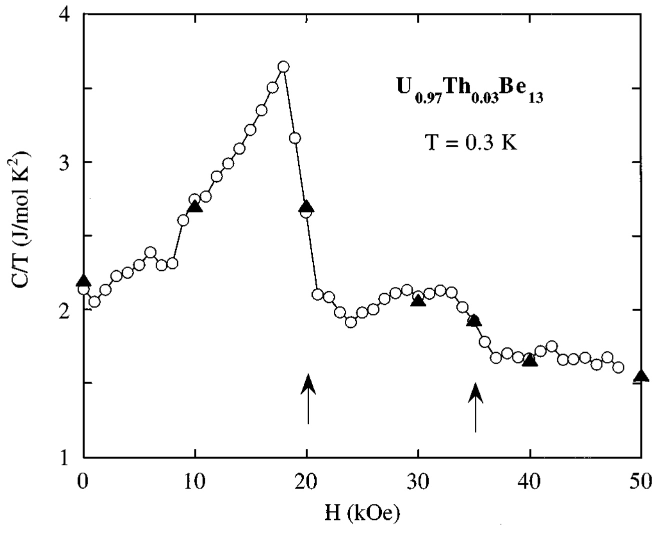

FIG. 2. Example of magnetic-field sweep data for $U_{0.97}Th_{0.03}Be_{13}$. The data obtained from temperature sweeps $C(T)$ at fixed field (filled triangles) lie on top of the field-sweep curve $C(H)$ at fixed temperature $T=0.3$ K (open circles). The expected fields of the transitions from the $C(T)$ data (see Fig. 1) are indicated by the arrows.

We plot in Fig. 3 a set of $C(T)$ curves of $U_{0.978}Th_{0.022}Be_{13}$ for $H=0$ to 50 kOe. For this thorium concentration, the zero-field temperature splitting of the two transitions has decreased to $\Delta T\approx100$ mK. The smaller temperature splitting, combined with the finite transition widths, make it more difficult to determine the transition temperatures as H increases. Hence, we fit the $C(T)$ data to a form consisting of two (or one) ideally sharp transitions plus smearing functions. The transition temperatures so obtained from the fit are not very sensitive to the exact form of the smearing function. Fits of this type to the $C(T)$ data for the previous sample, $U_{0.97}Th_{0.03}Be_{13}$, give transition temperatures within 1 mK of those determined from the midpoint of the rise. We show in Fig. 4 fits to the $C(T)$ data for $U_{0.978}Th_{0.022}Be_{13}$ at $H=15$ kOe. The fit to two transitions (solid line) agrees better with the data than the fit to one transition (broken line). The inset to Fig. 4 is a plot of the 10–90 % width of a one (smeared) transition fit to our $C(T)$ curves as a function of magnetic field. This width decreases with increasing H up to 20 kOe and then plateaus. We take this to be evidence that the two transitions are now one for $H>20$ kOe.

The thermodynamic phase diagrams for $U_{1-x}Th_xBe_{13}$ with $x=0.030$ and $x=0.022$ are shown in Figs. 5(a) and 5(b), respectively. The filled circles are data from temperature sweeps $C(T)$ at fixed H; the open squares are from field sweeps $C(H)$ at fixed T. For $U_{0.97}Th_{0.03}Be_{13}$, the temperature splitting of the two transitions decreases with increasing H. While the two transitions do not merge for $T\geqslant0.1$ K, they appear to approach each other near $H\sim50$ kOe for $T\rightarrow0$ K. The solid lines in Fig. 5(a) are fits to the data using an empirical form, $H_{c2}(T)=H_{c2}(0)(1-T/T_c)^{\alpha}$. We find $\alpha=0.6$ ($\alpha=0.5$) for the higher (lower) temperature transition, and $H_c(0)=47\pm3$ kOe for both phase-transition lines. Our results agree qualitatively with the data taken by Mayer *et al.* on

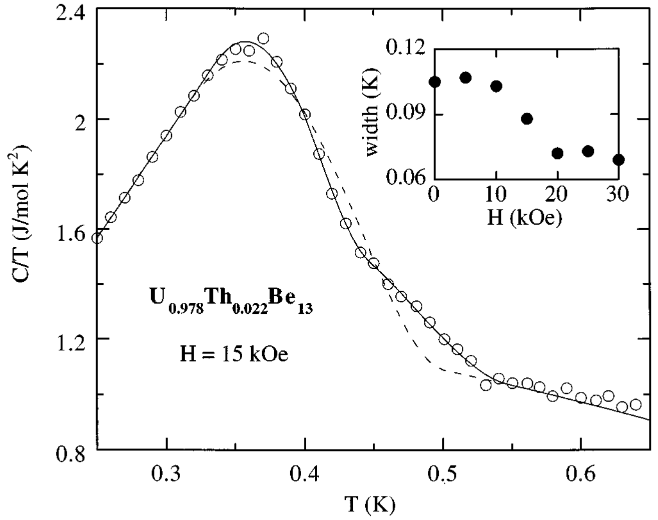

FIG. 4. Fits to C/T vs T for $H=15$ kOe. The fit to two smeared transitions (solid line) agrees better with the data than the fit to one smeared transition (broken line). Inset shows the 10–90 % widths of the fits to one transition vs magnetic field H. The double transition width decreases with H, flattening off for $H \geqslant 20$ kOe where the two transitions become one.

$U_{0.97}Th_{0.03}Be_{13}$ for $H \leqslant 20$ kOe.[22] However, their sample has significantly broader transitions with reduced peak heights and lower transition temperatures. The phase diagram reported by Ott *et al.* for $U_{0.967}Th_{0.033}Be_{13}$ with $H \leqslant 30$ kOe (Ref. 23) agrees well with our results. They also infer from their data, albeit extrapolating from higher temperature, that the $T=0$ limit of the critical fields is the same for both phases.[23]

For $U_{0.978}Th_{0.022}Be_{13}$ [see Fig. 5(b)], the smaller initial temperature separation again decreases with increasing H, and only a single transition can be resolved for $H \geqslant 20$ kOe (see Figs. 3 and 4). The solid lines in Fig. 5(b) are once more fits to the above form for $H_{c2}(T)$. We fit only the data for $H<20$ kOe, where two transitions can be discerned, and we fix the exponent α to the previously determined values: $\alpha=0.6$ ($\alpha=0.5$) for the higher (lower) temperature transition. As may be seen in Fig. 5(b), the points determined from the indicated single transition for $H>20$ kOe indeed lie on the continuation of fit to higher fields of the lower temperature phase line. The continuation of fit to the higher temperature line is shown by the broken line in Fig. 5(b). A study of polycritical points, where second-order phase-transition lines intersect, has shown that an additional phase line such as that suggested by the broken line in Fig. 5(b) is required by thermodynamics.[26] It can be difficult to discern because of the sum rule for specific-heat jumps around a tetracritical point.[26] In UPt_3, the analogous fourth phase line leaving the tetracritical point also is not seen in specific-heat experiments, but is evident in ultrasound and thermal expansion measurements. While specific-heat measurements provide a direct thermodynamic probe of the phase transitions, other types of measurements, such as thermal expansion,[23] may be better able to resolve the transitions and to extend these measurements below 100 mK.

The H-T phase diagram of $U_{0.978}Th_{0.022}Be_{13}$ thus appears to include a critical point near $H=20$ kOe and $T=0.35$ K. The large temperature splitting of the double transition in thoriated UBe_{13} probably has been the most significant obstacle to an analysis of multiple superconducting states akin to that developed for UPt_3. The present data indicate, however, that the double transitions in superconducting $U_{0.978}Th_{0.022}Be_{13}$ and UPt_3 appear isomorphic in the H-T plane, making natural such comparisons.

In conclusion, we have determined the H-T phase diagrams for $U_{1-x}Th_xBe_{13}$ with thorium concentrations $x=0.030$ and $x=0.022$. We find that the two transitions for the $x=0.030$ sample do not merge for our temperature range, $T>0.1$ K, but approach each other near $H \approx 47$ kOe at zero temperature. The two transitions of the $x=0.022$ sample appear to merge near $H=20$ kOe, $T=0.35$ K, and the H-T phase diagram for this material mimics that of the double superconducting transition in UPt_3. The magnetic-field scales for thoriated UBe_{13} and UPt_3 differ greatly, but as expected from theory,[2] the value of the merging field to first order varies linearly with $dH_{c2}/dT|_{T_c} \equiv H'_{c2}$. For our sample of $U_{0.97}Th_{0.03}Be_{13}$, $H'_{c2} = -450 \pm 30$ kOe/K;[24] H'_{c2} for UPt_3 is of order 75 kOe/K for $H \| \hat{c}$.[8,11] This ratio of 6 in H'_{c2} compares well to the ratio for merging fields of order (47 kOe/8 kOe)$\approx$6.[8] Unfortunately, H'_{c2} is not known for $U_{0.978}Th_{0.022}Be_{13}$, but the pertinent crossover scale in $U_{1-x}Th_xBe_{13}$ appears to be set by $\Delta T(H=0)$; the ratio of the magnetic fields required to merge the double transitions

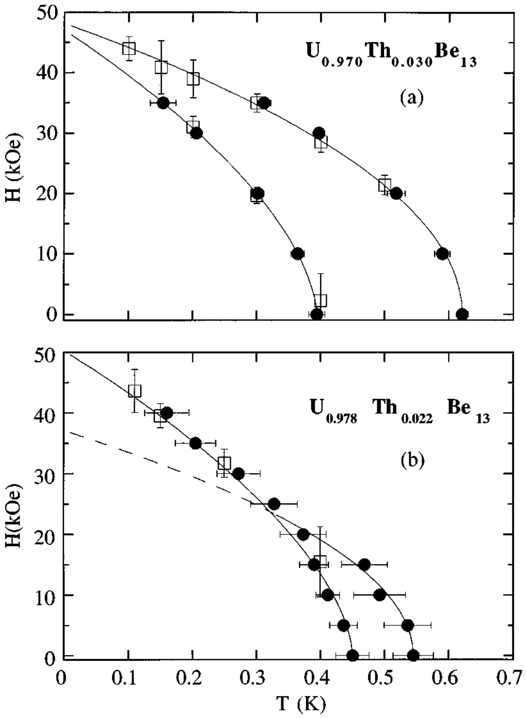

FIG. 5. H-T phase diagram for $U_{1-x}Th_xBe_{13}$ with (a) $x=0.03$ and (b) $x=0.022$. Filled circles are data from temperature sweeps $C(T)$ at fixed H; open squares are from field sweeps $C(H)$ at fixed T. The lines are empirical fits to the data, described in the text. For $x=0.022$, there appears to be a critical point near $H=20$ kOe, $T=0.35$ K.

($\sim$47 kOe for $x=0.03$ and $\sim$20 kOe for $x=0.022$) is equal within error bars to the ratio of the initial temperature splittings of the double transition (225 mK for $x=0.03$ and 100 mK for $x=0.022$).

We thank P. Kumar and J. Sauls for helpful conversations. The work at the University of Chicago was supported by NSF DMR95-07873. The work at the University of Florida was supported by DOE DE-FG05-86ER45268.

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