

Influence of boron impurities on the superconducting phase transition of $U_{1-x}Th_xBe_{13}$

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It is demonstrated that weak boron doping of UBe_{13} drastically alters the temperature dependence of the specific heat just above and also below the superconducting transition. A strong enhancement of the anomaly at T_c and distinct deviations from mean-field behavior are the most significant features. The influence of small amounts of boron replacing Be in thorium-doped UBe_{13} is shown to depend on the concentration of Th impurities. Excessive specific heat well below T_c in these compounds indicates considerable variation of the electronic spectrum even at very low temperatures.

It has been shown previously¹ that most impurities introduced either on U or Be sites cause a strong depression of the superconducting transition temperature T_c of UBe_{13} . Apart from the decrease of T_c , specific-heat measurements^{2,3} revealed a considerable reduction of the specific-heat anomaly at T_c . In some cases it was observed that, although resistive and magnetic transitions to the superconducting state could still be identified, no visible anomaly in $C_p(T)$ gave a manifestation of the transition at the respective temperatures. Since these features occurred for both magnetic and nonmagnetic impurities at concentrations of less than 2 at.%, it was concluded that pair-breaking effects on an unconventional type of superconductivity are the reason for these observations.

At the same time it was also realized, that replacing U by Th with the same concentration level of a few at.% resulted in a distinctly different behavior.⁴ Although for small concentrations x of Th, T_c decreases on a scale similar to that for all other impurities on the U sites, the specific-heat anomaly, measured on the scale of the normal-state electronic specific heat at T_c , i.e., $C_n^e = \gamma T_c$, keeps its size which is slightly larger than the BCS value for pure UBe_{13} . For $x=0.018$, T_c reaches a minimum and increases again with a further increase of x , passing over a maximum in the range of x between 0.03 and 0.035. A second phase transition in the superconducting state as indicated by $C_p(T)$ data for $x > 0.02$ leads to a very unusual superconducting phase diagram which, again, gives evidence for unconventional superconductivity in this system. A recent microscopic study employing the μ SR technique⁵ and detailed specific-heat measurements⁶ established the boundaries of the phase diagram in some detail.

In further studies related to impurities in UBe_{13} it was found that boron doping on the Be sites again leads to extraordinary features concerning the superconducting phase transition.⁷ Small concentrations of B for Be in $UBe_{13-y}B_y$ ($0.01 < y < 0.045$) were found to lower T_c somewhat. More surprising was the concomitant in-

crease of the specific-heat anomaly at T_c which became considerably larger than that observed for pure UBe_{13} and surpasses the usual BCS value by a large margin. As will be shown below, extrapolations indicate that the usual balance of entropy can only be achieved if extreme enhancements of the C_p/T ratio in the hypothetical normal state at temperatures below T_c are postulated. In view of the results obtained for $U_{1-x}Th_xBe_{13}$, we conjectured that again two transitions of similar type occur in $UBe_{13-y}B_y$ which, however, cannot be resolved on the temperature scale. This explanation for the enhanced anomaly could not be substantiated in recent μ SR experiments.⁸

Before this microscopic study just mentioned was made, we investigated the influence of B doping on pure UBe_{13} and some $U_{1-x}Th_xBe_{13}$ compounds. Of course, it was of interest to coarsely study the effect of B doping on the superconducting phase diagram mentioned above and therefore we report here on measurements of the specific heat of $U_{1-x}Th_xBe_{13-y}B_y$ compounds below 1 K. Since previous measurements on $UBe_{13-y}B_y$ gave essentially the same results for either polycrystalline or single-crystalline samples with the same B concentration y ,⁹ we continued to do the experiments, whose results are presented here, on polycrystalline specimens. Our material was obtained by arc-melting the constituents in inert atmosphere, taking the usual necessary precautions to ensure homogeneity. The specific heat was determined using a relaxation technique with samples of approximately 100 mg weight. For all samples, the superconducting transition was checked by ac susceptibility measurements.

In Fig. 1 we show the variation of $C_p(T)$ below 1 K upon changing the B content in $UBe_{13-y}B_y$ in the form of C_p/T versus T plots. It should be realized that the small boron concentrations introduced here are very difficult to control and determine on an absolute scale in the resulting material. The most clear distinction with respect to pure UBe_{13} is actually achieved by these very measurements. No clear trend of $T_c(y)$ can be estab-

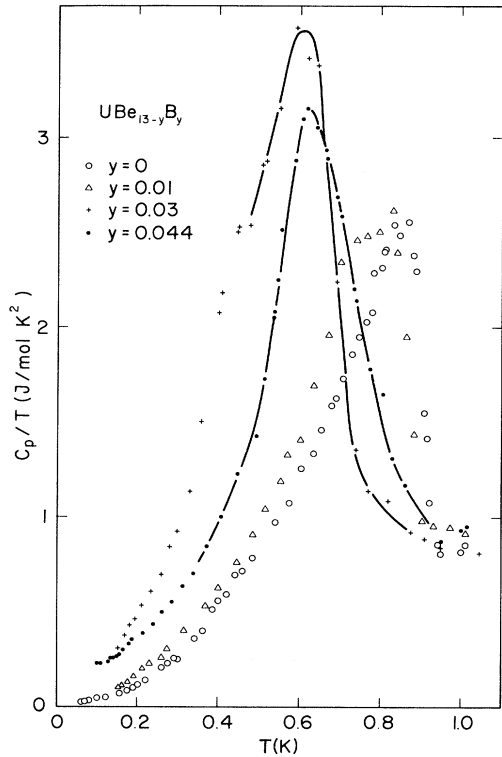


FIG. 1. C_p/T vs T for superconducting $UBe_{13-y}B_y$ between 0.05 and 1 K. The solid lines are meant to guide the eye.

lished and also the shape of $C_p(T)$ does not change systematically and seems to depend on the sample quality. Nevertheless, it appears that the largest enhancement of the C_p anomaly at T_c is obtained for $y \sim 0.03$ and therefore we concentrated on using material with this B content in subsequent experiments. The normal-state C_p/T ratio at T_c is distinctly larger than for pure UBe_{13} , a feature that has been studied in more detail in Ref. 8. It may be seen from Fig. 1 that the entropy balance dictated by a superconducting transition can only be achieved if a large enhancement of the C_p/T ratio in the normal state toward $T=0$ K is assumed.

In Fig. 2 we show analogous data that were obtained from investigating a small piece that was cut from the sample used in the above mentioned μ SR study. We recall that no difference in the temperature dependence of the muon-spin relaxation rate between this material and pure UBe_{13} was observed below 1 K. Although the nominal concentration y is also 0.03 here, the curve in Fig. 2 is distinguishable from the corresponding curve in Fig. 1. The reason for this discrepancy is not really known, but it may be sought in a slight difference of the actual boron concentrations in both materials which, according to Fig. 1, may well account for the different behavior. In any case, also the data in Fig. 2 are far from being compatible with simple BCS behavior at T_c , which is indicated by the broken line in Fig. 2, and also quite at variance with the data for pure UBe_{13} shown in Fig. 1. Since the microscopic probe (μ SR), which is sensitive to both structural

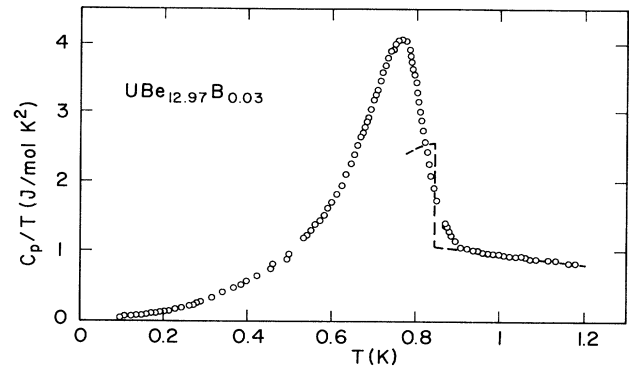


FIG. 2. C_p/T of superconducting boron-doped UBe_{13} , previously used in a μ SR study (Ref. 5), between 0.1 and 1.2 K. The broken line indicates the discontinuity at T_c as expected from the BCS theory in the weak-coupling limit.

and magnetic phenomena, gives no evidence for an additional phase transition, the reason for this unprecedented large anomaly at the superconducting phase transition of B-doped UBe_{13} is a puzzle. It is also of interest to compare $C_p(T)$ data of this material with those of pure UBe_{13} at temperatures well below T_c . To this end we have plotted the data of Fig. 2 on a graph with logarithmic scales, which is shown in Fig. 3. At the lowest temperatures, $C_p(T)$ tends to vanish proportional to T^2 . Analogous results for pure UBe_{13} to even lower temperatures indicate a T^3 dependence there.¹⁰

The specific-heat features at the superconducting transition of boron-doped UBe_{13} imply a dramatic increase of the strong-coupling character of this phase transition. The data in Fig. 2 further indicate distinct deviations from the usual mean-field behavior of superconductors, especially when taking into account the increase of the C_p/T ratio at lower temperatures which we need to postulate for obtaining the necessary entropy balance.

As mentioned above, it also seemed of interest to investigate the influence of B doping on material of the type $U_{1-x}Th_xBe_{13}$ with different values of concentration x .

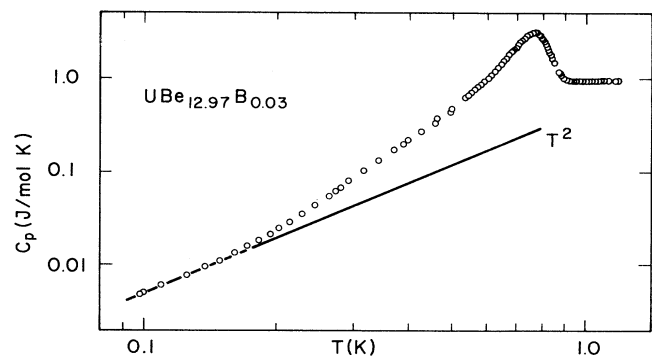


FIG. 3. The same data as shown in Fig. 2 but plotted as C_p vs T on logarithmic scales.

Keeping in mind the features of the $T_c(x)$ phase diagram of $U_{1-x}Th_xBe_{13}$,⁶ at least three different regions of interest may be identified. In a first experiment we checked whether the enhancement of the C_p anomaly persists in Th-doped material with values of x less than 0.018, i.e., the concentration for which a relative minimum of T_c has been established. In Fig. 4, it may be seen that this is definitely the case and we also note, taking into account the slightly different Th concentrations in the two samples, that addition of B does not result in a large decrease of T_c , if any. Again, the requirement of entropy balance is obviously a problem.

Particularly intriguing is the behavior for x values slightly exceeding 0.018. Our results of previous measurements on thorium-doped UBe_{13} indicate, that for $x \approx 0.019$, while T_c is higher than the minimum value for $x \approx 0.018$, no second-phase transition is indicated by specific heat measurements above 0.1 K (see Fig. 5). Boron doping of such material leads to the observation of two distinct and well-resolved transitions, as demonstrated in Fig. 5. Some caution in connection with their interpretation is necessary here, however. It is not yet quite clear, whether the appearance of the second peak in $C_p(T)$ is due to B doping or whether it has to be traced back to a slightly higher Th concentration in the sample also containing Boron. Combined $C_p(T)$ and μ SR measurements indicate that the phase boundary for the second transition is almost vertical in this range of x (Refs. 5 and 6) and very small shifts in concentrations of Th are obviously very difficult to control. In any case, it is clear that the two-phase transitions in Th-doped UBe_{13} survive small amounts of B impurities on Be sites. This is definitely not so, if similar amounts of Cu atoms are introduced to replace Be. Both transitions are completely wiped out in this latter case.⁹

At higher Th concentrations, also boron seems to be a harmful ingredient, as may be seen from Fig. 6. Apart from a distinct decrease of T_c , a considerable quenching and broadening of the C_p anomaly is observed.

This investigation on which we briefly reported here allows for at least four conclusions.

- (i) Small amounts of boron replacing Be in UBe_{13} and

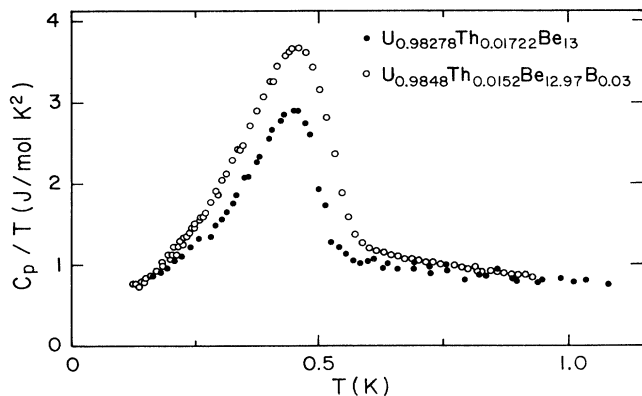


FIG. 4. Comparison of C_p/T vs T for $U_{0.983}Th_{0.017}Be_{13}$ and $U_{0.985}Th_{0.015}Be_{12.97}B_{0.03}$ below 1.1 K.

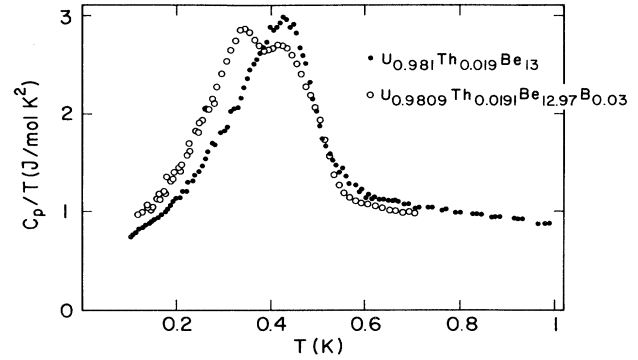


FIG. 5. Influence of B doping on the specific-heat anomaly of superconducting $U_{1-x}Th_xBe_{13}$ for $x \approx 0.019$, i.e., in the vicinity of the T_c minimum observed at $x = 0.018$.

$U_{1-x}Th_xBe_{13}$ with $x < 0.018$, lead to unexpected enhancements of the specific-heat anomaly at the superconducting transition of these compounds. Especially in UBe_{13} , this enhancement is, to our knowledge, of unprecedented size and indicates a considerable tendency toward strong coupling in the subsystem providing superconductivity.

- (ii) It may be recognized, that B doping influences the $T_c(x)$ phase diagram of superconducting $U_{1-x}Th_xBe_{13}$. Of course, more experiments to establish the details have to be made.

- (iii) The requirement of entropy balance for a superconductor at temperatures between 0 K and T_c can only be fulfilled in these compounds, if their hypothetical normal-state C_n^e/T ratio below T_c is strongly enhanced, as we postulate (C_n^e = specific heat of the charge carriers that provide superconductivity). This implies that some unknown degree of freedom needs to be considered.

- (iv) The temperature dependence of the specific heat is distinctly different from BCS behavior. For boron-doped UBe_{13} the loss of mean-field character is the most intriguing

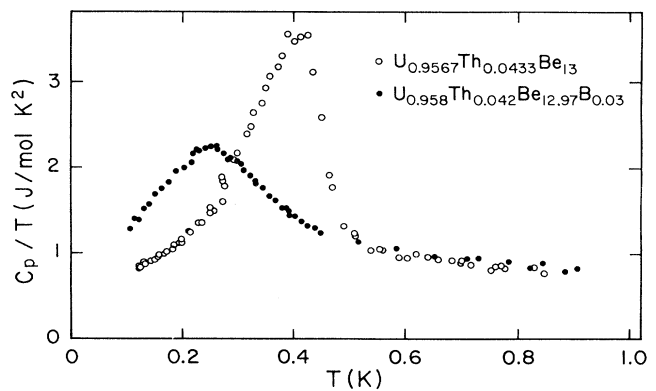


FIG. 6. Influence of B doping on the specific-heat anomaly at the superconducting transition of $U_{1-x}Th_xBe_{13}$ for $x \approx 0.043$.

ing new feature. At the lowest temperatures, the experimental results may have to do with anomalous background features of $C_p(T)$ as mentioned in (iii), but they may also be caused by properties of an unconventional superconducting state. With this in mind, we plan to study $C_p(T)$ of these compounds to still lower temperatures.

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