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Phase transition in the superconducting state of $U_{1-x}Th_xBe_{13}$ ($x = 0$–0.06)

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We report results of specific-heat measurements and the observation of a new phase transition in the superconducting state of $U_{1-x}Th_xBe_{13}$ compounds for a narrow range of x values. Although the nature of this transition cannot be unambiguously established, its occurrence is important with regard to the characterization of the superconducting state in these compounds.

The occurrence of superconductivity in UBe_{13} out of a normal state which is characterized by a large electronic specific heat and a still very high electrical resistivity at T_c (Ref. 1) has led to various investigations and speculations as to whether this superconducting state, and eventually also those of other similar materials like $CeCu_2Si_2$ (Ref. 2) or UPt_3 (Ref. 3), are induced by interactions other than the normal electron-phonon coupling[4] and, as a consequence, might be characterized by an unconventional ($l \neq 0$) pairing of the electrons.[5–8]

The origin of these conjectures may be seen in the following facts. Considering UBe_{13}, the large discontinuity of the specific heat at T_c unambiguously demonstrates that the superconducting state is formed by those electrons whose effective mass is very large. The temperature dependence of the specific heat above T_c, however, clearly shows that this large mass only occurs below a certain temperature which, in principle, can be regarded as a renormalized Fermi temperature $\tilde{T}_F$ of the low-temperature electronic spectrum. A recent model calculation combined with available experimental data has set this temperature $\tilde{T}_F$ to about 20 K for UBe_{13}.[9] On the other hand, low-temperature specific-heat measurements indicate that the effective Debye temperature Θ_D for $T \rightarrow 0$ K is of the order of 650 K.[1,10] Considering these numbers and remembering that T_c is only about one order of magnitude lower than the relevant Fermi temperature $\tilde{T}_F$, any explanation for the occurrence of the observed superconducting state certainly calls for some unconventional ideas, irrespective of the chosen approach.

Recently the temperature dependence of the specific heat in the superconducting state of UBe_{13} was put forward as being compatible with an anisotropic p-wave superconducting state stabilized by strong local spin fluctuations.[6] Another attempt, mainly for the superconducting state of $CeCu_2Si_2$, favors an explanation based on Kondo-effect-induced changes of the electron-phonon interaction and conventional superconductivity.[11] More recently, the temperature dependence of the ultrasound absorption below the superconducting critical temperature of UPt_3 was interpreted as being due to a polar p-wave superconducting state in this material.[12] Further support for unconventional superconductivity in UBe_{13} was obtained from measurements of nuclear magnetic relaxation times.[13]

The possibility of p-wave superconductivity in these systems is often rejected by arguing that any impurity or imperfection would suppress such a state. It was therefore of some interest to study the influence of nonmagnetic impurities on the normal state and superconducting properties of UBe_{13} and an obvious choice was to replace U atoms by Th. Some of the results of this investigation have been published before,[14,15] showing that even small percentages (0–6%) of Th in UBe_{13} are sufficient to change both the normal state and the superconducting properties in a considerable and somewhat unexpected manner. As examples, we mention the nonsteady decrease of T_c with increasing Th content and the rather unexpected change in the $\rho(T)$ curves for $U_{1-x}Th_xBe_{13}$, indicating a decrease of the low-temperature resistivity with increasing x at constant temperature.[14] In this Rapid Communication we should like to put forward, in much more detail than before,[15] another very unexpected and surprising feature of these $U_{1-x}Th_xBe_{13}$ compounds, namely, the appearance of an additional phase transition in their superconducting state as revealed by measurements of the specific heat below 1 K.

The samples were prepared by arc melting the three constituents simultaneously in a zirconium-gettered argon atmosphere. The typical sample mass was about 1 g sustaining total weight losses averaging 0.070 g during seven or more melting and turning cycles. X-ray analysis of the residue in the furnace showed approximately equal proportions of the compound and of pure beryllium. To compensate for the beryllium loss a slight excess of beryllium was added during weighing. We assumed that the Th-U ratio remained unchanged during melting. Specific-heat samples were then spark cut from the center of the button, followed by mechanical polishing of the cut surfaces and etching in dilute HCl.

Some of these samples were checked by x-ray measurements, as well as metallographic and electron-microprobe examinations. The lattice parameter increases linearly with thorium content (see Fig. 1) and the linewidth does not vary among different samples. The result of the metallographic examination is consistent with highly oriented needlelike grains which are etched at different rates depending on the crystallographic orientation. Microprobe measurements did not detect any thorium but did show no variation in uranium levels over entire vertical sections of an arc-melted bead. However, x-ray fluorescence on the entire

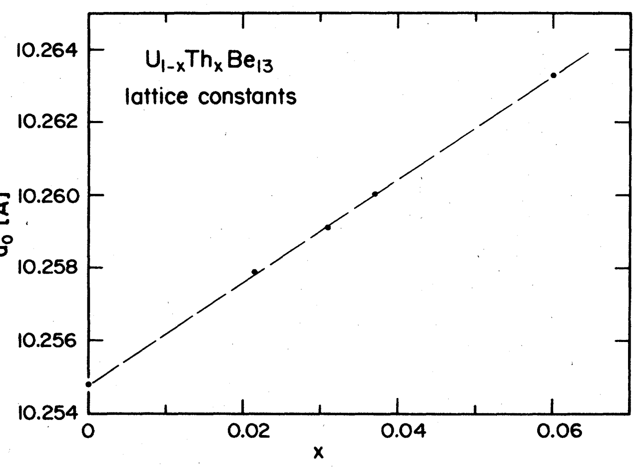

FIG. 1. Room-temperature lattice constants for $U_{1-x}Th_xBe_{13}$ compounds as a function of x.

face did identify thorium. Because of the obvious importance of demonstrating that the samples consist of one single phase, analysis is continuing. However, all of the current evidence taken together suggests that the samples are indeed homogeneous and single phase. Further evidence for this statement was recently obtained from nuclear magnetic resonance (NMR) spectra determined in the superconducting state of a $U_{1-x}Th_xBe_{13}$ sample with $x=0.033$.[13]

The specific heat c_p was measured on single pieces (~ 200 mg) of polycrystalline $U_{1-x}Th_xBe_{13}$ between 0.15 and 1 K using a thermal-relaxation technique. The lowest temperature is limited by the radioactive self-heating of the samples which, with our experimental arrangement, prohibits a reliable determination of c_p below 0.15 K. In Figs. 2(a) and 2(b) we show c_p/T for eight values of x between 0 and 0.06. As was shown in Ref. 14, the replacement of U by Th leads to a considerable decrease of the low-temperature electrical resistivity in the normal state. Here we note, however, that the electronic specific heat, given by the c_p/T ratio, instead increases above the value of pure UBe_{13} and obviously is still temperature dependent below 1 K.

As expected, for $x \simeq 0.009$ a sizable decrease of T_c and a broadening of the superconducting transition is observed. With increasing x, however, various surprising features develop. First we note a sharp and growing discontinuity of c_p/T at about 0.6 K which coincides in temperature with the magnetically observed transition to the superconducting state. For $x=0.026$, c_p/T adopts a very unusual temperature dependence. Below the distinct discontinuity at the superconducting transition the features might be interpreted as being due to a new and very narrow structure in the electronic density of states located in the gap induced by the superconducting transition at 0.6 K and disappearing below a second phase transition at about 0.3 K. A further increase of x at first leaves the discontinuity at $T_c=0.6$ K virtually unchanged. However, we observe a distinct second anomaly whose peak temperature is shifted to higher values with increasing x. For $x=0.038$, T_c is slightly depressed to about 0.56 K and the low-temperature anomaly clearly has grown at the expense of that at the superconducting transition.

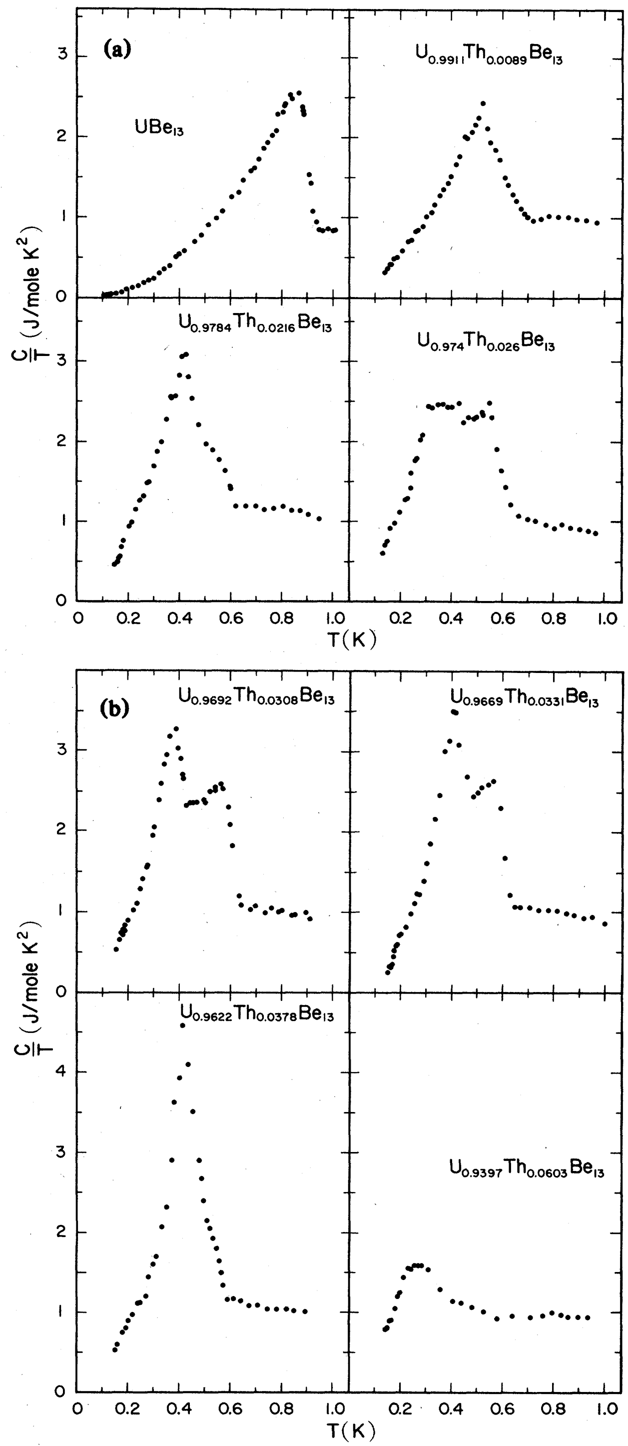

FIG. 2. (a),(b) Specific heat of various $U_{1-x}Th_xBe_{13}$ compounds, plotted as c_p/T vs T for temperatures between 0.15 and 1 K.

For $x \simeq 0.06$ finally, T_c has dropped to below 0.4 K and the specific-heat anomaly indicating the transition has collapsed to one structure and is reduced considerably in magnitude. Nevertheless it is of the same size as the c_p anomaly observed at the superconducting transition of pure UPt_3.[3]

The observation of two specific-heat anomalies, of course, immediately raises the question whether they are due to two phases contained in the samples. As we pointed out above, the present state of metallographic sample characterization rules this out. If the anomalies were due to two consecutive superconducting transitions of two separate phases with slightly different T_c's, they would have to occur in about equal amounts over a range of values of x, and that can absolutely be ruled out. Two separate superconducting transitions would also yield two steps in the temperature dependence of the ac magnetic susceptibility, a feature which we do not observe in small pieces taken from the respective batches. As mentioned before, recent NMR experiments[13] confirm the homogeneity and the occurrence of only one phase in at least one of the samples showing two transitions, on a scale as large as the microwave skin depth. Moreover, these same experiments indicate that if the lower transition was magnetic, the ordered moment per U site would be less than $0.01\mu_B$. A structural phase transition is also very unlikely because impurities or imperfections usually suppress cooperative transitions of that kind rather than provoke them.

Hence we are left with the very intriguing possibility that the second specific-heat anomaly observed in these $U_{1-x}Th_xBe_{13}$ compounds in a rather narrow range of x values indicates a continuous phase transition from one superconducting state below T_{c1} to another below T_{c2}. Such a phenomenon is very unlikely to occur in a conventional superconductor and thus our experimental results would support the earlier claim that superconductivity in UBe_{13} may be characterized by an $l \neq 0$ pairing of the heavy electrons.[6] We are, however, confronted with the following problem.

From the curves shown in Figs. 2(a) and 2(b), it is quite obvious that the entropy released by the two transitions considerably exceeds $[c_p^n(T_c)/T_c]T_c$, the entropy usually contained in a superconductor below T_c, if the corresponding normal state specific heat c_p^n may be described by a temperature-independent electronic specific-heat parameter γ below T_c. This latter assumption appears not to be valid in our case, because c_p/T clearly increases with decreasing temperature between 1 K and T_c. In principle, the entropy balance $\Delta S(T \leq T_c) = S_n - S_s$, where S_n and S_s are the entropies of the normal and superconducting state, respectively, could be made zero in our cases by assuming that γ has an appropriate temperature dependence in the hypothetical normal state below T_c. This assumption leads to quite large values of $\gamma(T=0)$ and we hesitate to adopt this simplest solution of the problem without further justification. For $x=0$, 0.0089, and 0.0603, the entropy requirement $\Delta S=0$ is fulfilled within a few percent. For the other x values an entropy surplus of between 10% and 50% is released by the transitions if we assume that c_p/T increases linearly with decreasing T down to $T=0$ K. At this point we can only speculate that an additional but not yet identified internal degree of freedom is responsible for the additional entropy release which, in absolute values, is only about 6% of $R \ln 2$ for the maximum excess-entropy case of $x=0.0308$.

The most trivial explanation for the second transition at T_{c2} could thus be given by assuming that a small percentage of ions undergo a magnetic phase transition without destroying the superconducting state. As outlined above, we have no other evidence to back up this idea, however. It may even be argued that in such a case, a spin-glass type of ordering would have to result but the shape of the specific-heat anomaly clearly gives no support for that either. Moreover, the collapse of the specific-heat anomaly for $x=0.06$ seems to rule out explanations of this sort.

It may be that this additional entropy is due to additional degrees of freedom that are related to the narrow resistivity peak observed at 2.5 K in pure UBe_{13} (Refs. 1 and 4) and which is gradually shifted to below T_{c1} for increasing x.[14] A first qualitative explanation for the occurrence of two phase transitions in $U_{1-x}Th_xBe_{13}$ in a restricted range of x values has recently been given by Volovik and Khmelnitskii,[16] emphasizing the complex behavior of the order parameter in the superconducting state of this unusual material. Although it is quite clear that further experimental *and* theoretical work remains to be done to settle all the questions regarding superconductivity in heavy-electron systems, our experimental results add an unexpected and novel aspect to this topic of high current interest.

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