Influence of impurities and magnetic fields on the normal and superconducting states of UBe_{13}

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Small amounts of Th and Lu impurities considerably affect both the low-temperature normal and the superconducting states of UBe_{13}. Th enhances the electronic specific-heat parameter γ for $T \rightarrow 0$ K and leads to a second phase transition in the superconducting state. Lu substitution for U suppresses superconductivity quite effectively, and also γ is sizably reduced. Bulk measurements confirm the unusual $H_{c2}(T)$ curve of UBe_{13} that was previously obtained from electrical resistivity experiments.

I. INTRODUCTION

Soon after the discovery of bulk superconductivity of UBe_{13} involving electrons with extremely large effective masses[1] it was realized that impurities considerably affect the properties of both the superconducting and the normal state of this material.[2] Substituting U with various elements from different parts of the periodic system always leads to a reduction of the superconducting critical temperature T_c.[2,3] The same was found for impurities that were chosen to replace Be.[4] The most interesting features so far were found when U is replaced by Th. Few percent of Th not only change the temperature dependence of the electrical resistivity at low temperatures[2] but also dramatically alter the superconducting state. Previous measurements of the specific heat c_p of $U_{1-x}Th_xBe_{13}$ compounds revealed the occurrence of a second phase transition below the transition to the superconducting state for $0.01 < x < 0.06$.[5] In this range of impurity concentration, T_c is almost independent of x and about 0.6 K. At a lower temperature T_{c2} of approximately 0.4 K, a second phase transition, as indicated by a specific-heat anomaly[5] and subsequently confirmed by measurements of the thermal expansion (see below) and ultrasonic attenuation,[6] is observed.

According to resistivity measurements quite different changes are observed when U is replaced by Lu. Whereas additions of Th shift the resistivity peak of UBe_{13} at 2.5 K to lower temperatures and generally lower the resistivity below 10 K,[2] small amounts of Lu enforce the resistivity increase in UBe_{13} below 5 K and instead of the appearance of a maximum of $\rho(T)$, $\partial\rho/\partial T$ remains negative down to 20 mK.[3] It has also been found that a few percent of Lu impurities suppress T_c of UBe_{13} much more effectively than the same amount of Th.[3]

Concerning external influences on the low-temperature properties of UBe_{13}, it is not only the partial replacement of the constituents of the compounds that leads to surprising results but also the influence of external magnetic fields is quite spectacular. In a recent investigation[7] it was shown that the low-temperature electrical resistivity of UBe_{13} is drastically reduced by application of a magnetic field. Moreover, it was demonstrated that the superconducting state of UBe_{13} is extremely stable with respect to magnetic fields, leading to an unusual temperature dependence of the upper critical field H_{c2} with a very large value of $\partial H_{c2}/\partial T$ at T_c of -420 kOe/K and an extrapolated value of H_{c2} (0) at zero temperature of about 100 kOe depending somewhat on the chemical composition of the sample.[7,8]

In this work we examined the influence of Th, Lu, and Sc impurities on the normal-state specific heat of UBe_{13}. Furthermore we report on the influence of external magnetic fields on c_p of UBe_{13} and $U_{0.9669}Th_{0.0331}Be_{13}$ below 1 K and we measured the thermal expansion of $U_{0.9669}Th_{0.0331}Be_{13}$ below 1 K.

II. EXPERIMENTS

So far the measurements of the specific heat, intended to reveal changes in the low-temperature properties of impurity-doped UBe_{13} in the range of a few percent of impurities, were restricted to the superconducting state of $U_{1-x}Th_xBe_{13}$.[5] Data of the specific heat of UBe_{13} in external magnetic fields have only been reported for the normal state between 1.5 and 11 K in a magnetic field of 110 kOe.[9] Here we report on measurements of the specific heat on $U_{1-x}M_xBe_{13}$ compounds where M = Th, Lu, or Sc. Measurements between 1.5 and 14 K were made for $U_{1-x}Th_xBe_{13}$ (x = 0.0331 and 0.06), for $U_{1-x}Lu_xBe_{13}$ (x = 0.016 and 0.034), and for $U_{1-x}Sc_xBe_{13}$ (x = 0.0152). Between 0.14 and 1 K, data were obtained for $U_{0.991}Th_{0.009}Be_{13}$ and for $U_{0.994}Lu_{0.006}Be_{13}$. The influence of external magnetic fields up to 52 kOe on the specific heat of UBe_{13} and $U_{0.9669}Th_{0.0331}Be_{13}$ was measured between 0.2 and 1 K. Finally we also give the result of measurements of the thermal expansion of $U_{0.9669}Th_{0.0331}Be_{13}$ between 0.1 and 0.9 K. Information on the preparation and characterization of the samples is given in Refs. 2, 3, and 5.

The specific heat was measured on polycrystalline specimens weighing about 100 mg using a thermal relaxation technique. Special attention was paid to the temperature measurements in magnetic fields. The sample thermometer was newly calibrated for each field setting using a field-independent capacitance thermometer as reference. The calibration of the capacitance thermometer was done in zero magnetic field using both a calibrated germanium- and a cerium-magnesium-nitrate (CMN) thermometer as primary standards. The thermal expansion was measured on a prism-shaped sample of about 5 mm in length using a capacitance dilatometer.

III. RESULTS

In Fig. 1 we show the varying influence of different impurities on the temperature dependence of the specific heat in the normal state of UBe_{13}, especially so in the temperature range where c_p/T varies considerably with temperature.[10] c_p/T is plotted versus T^2 for some $U_{1-x}Th_xBe_{13}$ and $U_{1-x}Lu_xBe_{13}$ compounds with $0<x<0.06$. For similar impurity concentrations it was shown that also the electrical resistivity ρ is affected quite differently in the same temperature range, depending on whether U is substituted by Th or by Lu.[3] This difference is made particularly clear when compounds with virtually the same impurity concentration of Th or Lu are compared with pure UBe_{13}. This is done in Fig. 2, where c_p/T is plotted versus T for UBe_{13}, $U_{0.9669}Th_{0.0331}Be_{13}$, and $U_{0.966}Lu_{0.034}Be_{13}$ in their normal state up to 14 K. Figures 1 and 2 together clearly indicate that, with respect to UBe_{13}, Th impurities shift the major increase of c_p/T with decreasing temperature to lower temperatures, while Lu impurities cause just the opposite. It is also quite obvious that Th-doped samples reach a higher c_p/T ratio in the normal state at their respective superconducting transition temperatures T_c which, for a certain range of concentrations, are almost not changing with x.[2,5] Lu impurities on the other hand provoke a much more effective suppression of superconductivity and, when superconductivity is no longer observed, a strong reduction of the

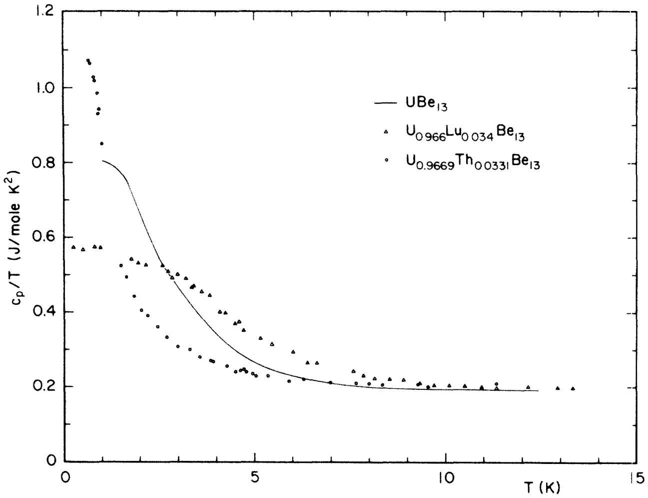

FIG. 2. Comparison of the influence of different impurities on the low-temperature normal-state specific heat of UBe_{13}.

c_p/T ratio for T approaching 0 K. Virtually no influence of the impurities on the specific heat is observed for temperatures above 10 K. One obvious difference between replacing U by Th or Lu is that the addition of Th expands the lattice while adding Lu reduces the lattice parameter. It is, however, quite unlikely that the atom size of the impurities is alone responsible for the mentioned observations because a replacement of Lu as the substitution of U by Sc, which reduces the lattice constant even further, has no obvious effect on the specific heat in the temperature range of interest. This may be seen in Fig. 3 on a similar plot as that of Fig. 2, where we compare c_p/T for similar concentrations of Lu and Sc in UBe_{13}. It may be that the tetravalent configuration of Th, as opposed to the trivalency of Lu or Sc, is of some importance.

With respect to the superconducting state of UBe_{13} it has recently been demonstrated that Th impurities induce surprising effects.[5] Here we want to point to the fact that

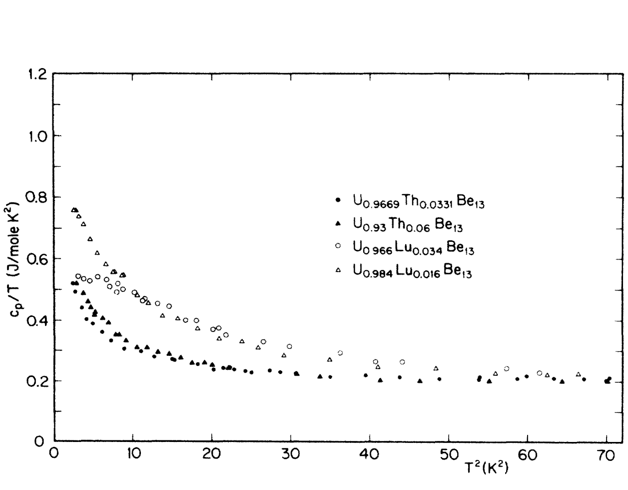

FIG. 1. $c_{p/T}$ versus T^2 for various $U_{1-x}M_xBe_{13}$ samples where $M=$ Th and Lu, between 1.5 and 8.5 K.

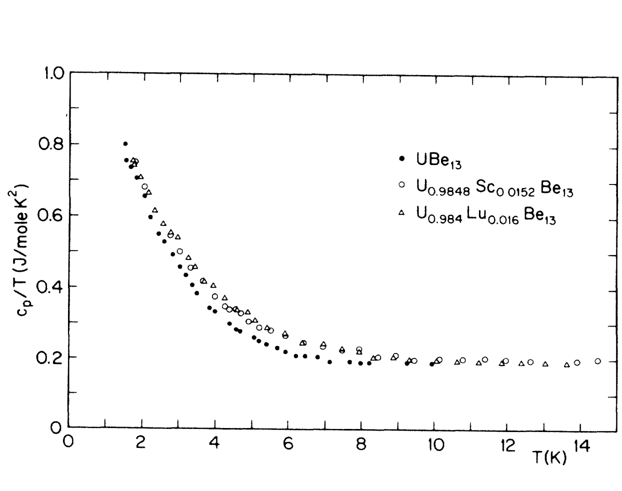

FIG. 3. Low-temperature normal-state specific heat of Lu- and Sc-doped UBe_{13}.

for even very small amounts of impurities, Th and Lu give sizably different results, as may be seen in Fig. 4. We note again, as pointed out above, the larger normal-state specific heat of the Th-doped material and the reduction when U is replaced by Lu. It is also confirmed that the initial decrease of T_c with increasing x is larger for Lu than for Th.

Th impurities of more than 1% induce a second phase transition in the superconducting state of $U_{1-x}Th_xBe_{13}$. In one of the attempts to demonstrate that one is not simply dealing with two consecutive superconducting transitions of two distinct phases with slightly different critical temperatures, we measured the thermal expansion of $U_{0.9669}Th_{0.0331}Be_{13}$, for which the two transitions are clearly discernible below 1 K. The result is shown in Fig. 5. At the superconducting transition temperature we observe the expected discontinuity in the temperature dependence of the linear thermal expansion coefficient α which, for a cubic polycrystal, is thermodynamically related to the electronic specific-heat parameter γ and the pressure dependence of T_c by

$$3(\alpha_n-\alpha_s)\,|_{T_c}=-2(\gamma/V)\frac{\partial T_c}{\partial p}\,, \tag{1}$$

where V is the volume and n and s denote the normal and superconducting state, respectively. In our case, however, Eq. (1) is only an approximation because its derivation is based on a temperature-independent value of γ which is not quite appropriate here, as will be shown below in Fig. 7. Nevertheless, the sign of the observed rapid change of α is in agreement with a depression of T_c under external pressure as observed for pure UBe_{13}.[11] The lower transition is obviously accompanied by a much larger volume effect thus giving further evidence that the above mentioned trivial explanation for the second transition can be ruled out. Further support for the obviously much larger pressure dependence of the second transition was recently obtained from measurements of the ultrasonic attenuation.[6]

The previously published, very unusual temperature dependence of the upper critical field H_{c2} of superconducting UBe_{13} resulted from measurements of the electrical resistivity.[7] It seemed of interest to check whether also the bulk transition as indicated, for example, by the anomaly of the specific heat in different external magnetic fields would lead to the same $H_{c2}(T)$ curve. In Fig. 6 we show the results of our specific-heat measurements on pure UBe_3 in various magnetic fields and at temperatures below 1 K. It is readily seen that the same large fields are necessary to shift the bulk transition, T_c still exceeding 0.5 K in a field of 52 kOe. For clarity we do not show the $c_p(T)$ curves obtained in fields between 0 and 20 kOe. We note, however, that they confirm the anomalous shape of the critical field curve that was presented in Ref. 7 and especially also the very large initial slope $\partial H_{c2}/\partial T$ at $T_c(H=0)$. From the present measurements this slope is

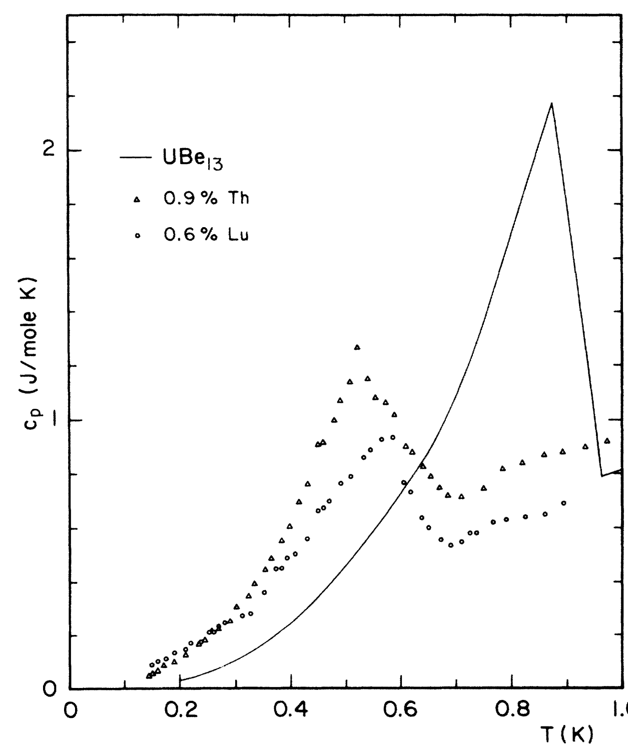

FIG. 4. Comparison of the influence of small amounts of Th and Lu impurities on the specific-heat anomaly at the superconducting transition of UBe_{13}.

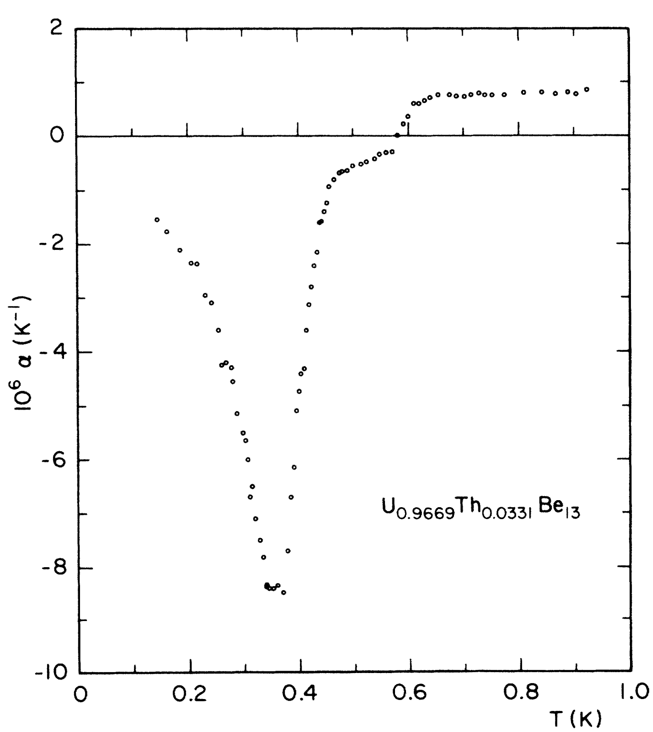

FIG. 5. Linear thermal-expansion coefficient of $U_{0.9669}Th_{0.0331}Be_{13}$ between 0.12 and 1 K.

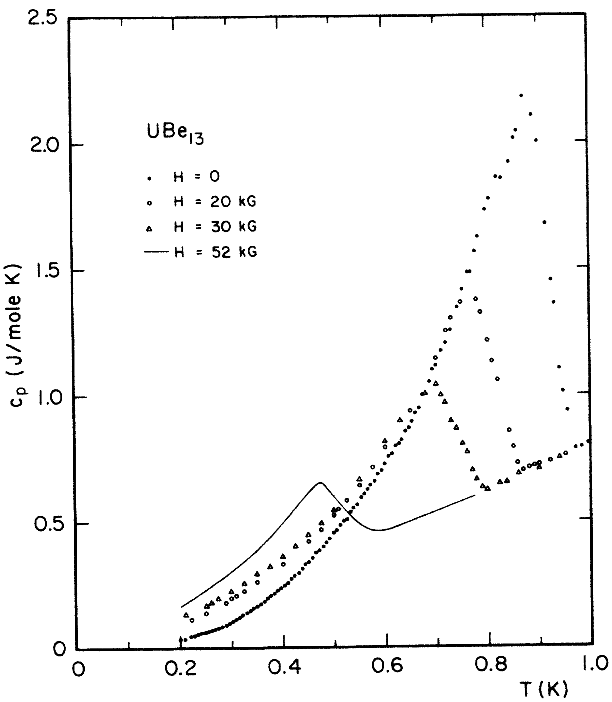

FIG. 6. Influence of external magnetic fields on the specific heat of UBe_{13} between 0.2 and 1 K.

at least -400 kOe/K, calculated from the difference of T_c in zero field and for $H=5$ kOe, respectively. The resulting $H_{c2}(T)$ curve is shown below in Fig. 8.

Of special interest was, of course, to investigate the influence of magnetic fields on the specific heat below 1 K of Th-doped UBe_{13}. Since previous NMR measurements[12] had shown only a very small shift of the resonance curves for $U_{0.9669}Th_{0.0331}Be_{13}$ below 0.2 K indicating an almost vanishing ordered moment in a hypothetical magnetically ordered state, it seemed necessary to check, whether the transition would still be observable in a field of 15 kOe that was also applied in the NMR measurements. In Fig. 7 we present the result of this experiment for $U_{0.9669}Th_{0.0331}Be_{13}$ which reveals a similar shift of the lower transition with increasing H as that observed for the superconducting transition. In 15 kOe, the peak of the lower transition is still present at 0.33 K but is shifted to below the investigated temperature range in fields exceeding 30 kOe. We also note that, in contrast to pure UBe_{13}, the normal-state specific heat varies considerably with increasing field, indicating fairly large c_p/T ratios exceeding 2 J/mole K^2 for T approaching 0 K. In Ref. 5 it was pointed out that a linear extrapolation of the normal-state specific heat was not sufficient to balance the entropy for the two transitions. The much stronger than anticipated increase of c_p/T in the magnetic-field-induced normal state with decreasing temperature, however, demonstrates that the requirement of entropy balance is approximately fulfilled. This suggests that both transitions involve the electrons that are responsible for the very high specific heat in the normal state at T_c.

IV. DISCUSSION AND CONCLUSIONS

In previous work[13–16] it was pointed out that the peculiar low-temperature properties of UBe_{13} are most probably due to dominating many-body effects in the electronic system which are particularly borne out by the enhancement of the specific heat below about 7 K. Our results shown in Figs. 1–3 clearly indicate that small concentrations of impurities do not greatly affect the unrenormalized band structure of electronic states of UBe_{13}. This follows from the stability of the c_p/T ratio for different impurities between 9 and 14 K. In this temperature range, the specific heat is still essentially of electronic origin as was pointed out in Ref. 10 and has recently been confirmed by an estimate of the lattice specific heat from the phonon density of states that was extracted from neutron experiments.[17] The observed changes in the enhancement of c_p, however, suggest that adding impurities mainly influences the strength of the many-body interactions thus leading to a variation of the renormalized Fermi temperature and of the $T=0$ limit of the electronic specific heat.

So far it is absolutely not clear why the replacement of U by Th causes a second phase transition in the superconducting state but apparently disappears again when the Th content exceeds a concentration of about 5%. If this second transition is magnetic in character then the ordered moment definitely has to be very small because of the NMR results[12] and the failure of recent neutron diffraction experiments to reveal the appearance of magnetic Bragg peaks below T_{c2}.[18] If, on the other hand, the transition occurs between unconventional superconducting states, it would involve a rather strong coupling to the lattice. The data in Figs. 7 and 8 show that the shift of the

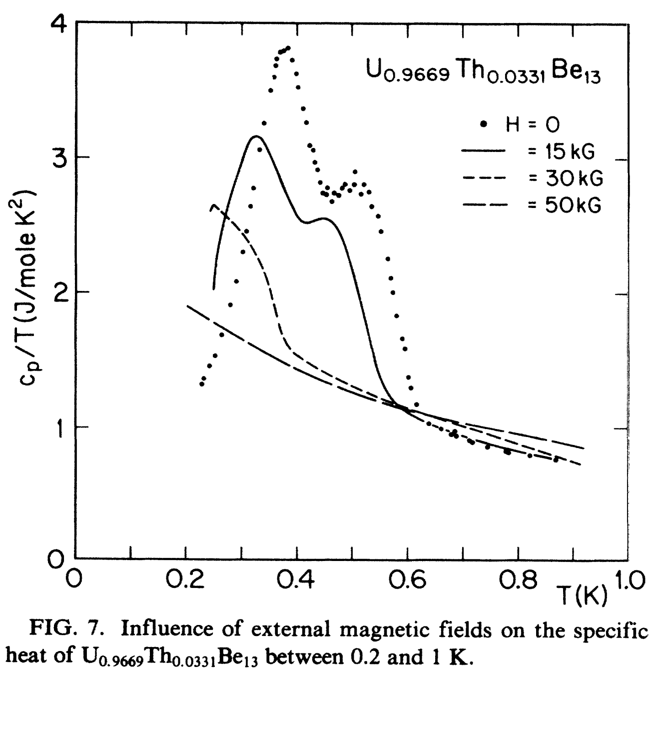

FIG. 7. Influence of external magnetic fields on the specific heat of $U_{0.9669}Th_{0.0331}Be_{13}$ between 0.2 and 1 K.

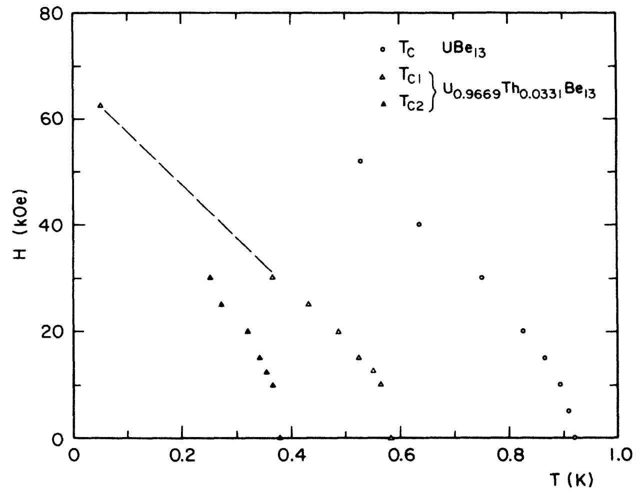

FIG. 8. Critical temperatures for the phase transitions of UBe_{13} and $U_{0.0669}Th_{0.0331}Be_{13}$ below 1 K as a function of external magnetic field.

second transition in the accessible range of external magnetic fields is somewhat smaller than that of the superconducting transition and by a very crude extrapolation it might be inferred that the $T=0$ K limit of the critical fields is the same for both phases. The lowest data point for the superconducting transition was obtained by resistivity measurements reported in Ref. 8. Finally the data in Fig. 8 suggest, that $(-\partial H_{c2}/\partial T)$ at T_c is even larger for the Th-doped material than for pure UBe_{13}.

Magnetic fields considerably enhance the normal-state specific heat of $U_{0.9669}Th_{0.0331}B_{13}$ below 1 K, quite in contrast to what is observed in pure UBe_{13}. In the latter case we note a slight decrease of c_p at 1 K in the highest available field but constant values of c_p/T_c with increasing fields. This indicates a very small shift of the enhancement of c_p to lower temperatures with increasing magnetic fields, at least below 1 K. This result seems to be in conflict with the trend reported in Ref. 9 where only data above 1.5 K were available, however. The present measurement of $c_p(T)$ on UBe_{13} in zero magnetic field confirms previously published data.[19] Again we find that the superconducting transition releases slightly more entropy than what is estimated from an extrapolation of the specific heat in the hypothetical zero-field normal state, assumed to be linear in T below T_c. The data shown in Fig. 6 give a ΔS of roughly 4%. Without an unambiguous knowledge of the normal-state specific heat—the relevant results in a magnetic field are only partly indicative—this entropy surplus seems to be too small to ascribe any significance to it, in the sense as to claim that another phase transition is hidden in the anomalous part of c_p below T_c. We further confirm the previously claimed non-exponential decay of c_p in the superconducting state of UBe_{13}.[18] The results shown in Fig. 6 for $H=0$ are fairly well described by a power-law dependence of c_p on T between 0.2 and 0.8 K, with an exponent $n=2.85$, close to 3. The rather sluggish decrease of c_p with decreasing temperature in fields exceeding 20 kOe (see Fig. 6) is due to the type-II character of superconductivity in UBe_{13} and the increasing density of normal state regions in the vortex lattice with increasing field.

In conclusion these experiments clearly demonstrate that small amounts of impurities considerably change the low-temperature properties of UBe_{13} in both its normal and superconducting state. There is good evidence that these changes are mainly caused by varying many-body effects rather than by alterations of the intrinsic band structure. The fact that Th or Lu impurities induce quite different changes in the normal-state concommitant with different influences on the superconducting state in our opinion implies that the same interactions that provide the enhancement of the specific heat, for example, are also in some way responsible for triggering the superconducting transition. It is then most likely that this superconducting state is of unconventional nature and may be described by some $l\neq 0$ pairing of the heavy-mass electrons. Finally we have shown, that bulk measurements confirm the anomalous $H_{c2}(T)$ curve established previously by measurements of the electrical resistivity.

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