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Low-temperature specific heat of $U_{1-x}Th_xBe_{13}$

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We present specific-heat C measurements of high-purity polycrystals of $U_{1-x}Th_xBe_{13}$ for $0 \le x \le 0.052$ down to 90 mK. The low-temperature data reveal extremely large residual linear contributions to the specific heat of these superconductors. In addition, we observe a change in $C(T)$ for $T<T_c$ where two transitions emerge with thorium doping x.

A compelling signature of the unconventional nature of the superconductivity in the heavy-fermion compounds is the existence of two transitions in the specific heat. For UPt_3, the recent transmission-electron microscopy of Midgley *et al.*[1] raises the question of whether an incommensurate lattice modulation might be at the source of the double superconducting transition. In a recent perspective on the heavy-fermion field, Fisk and Aeppli[2] point out that this leaves UBe_{13}-based superconductors as the only materials where the specifics of sample preparation and macroscopic sample homogeneity do not appear to be related intimately to the appearance of two reproducible transitions.

Accompanying the double transition in UPt_3 is a large residual linear term in the specific heat $C(T)$ below the superconducting transition, where the coefficient of the linear term γ_0 may have some sample dependence.[3] It is not clear whether this residual linear specific heat is intrinsic or indicative of sample problems. However, several theories have been proposed predicting an intrinsic linear specific heat which survives the superconducting state. For example, γ_0 has been attributed to nonunitary pairing,[4] odd-frequency pairing,[5] domain structure,[6] or resonant impurity scattering[7] in heavy-fermion superconductors. Less exotic explanations of a finite $T \to 0$ limit in C/T include gapless s-wave pairing in the presence of magnetic impurities and inhomogeneous materials with normal regions.

We report here the discovery of substantial γ_0's, of order 1 $J/mol\,K^2$, in $U_{1-x}Th_xBe_{13}$. Doping UBe_{13} with a few atomic percent of the nonmagnetic impurity thorium results in a nonmonotonic depression of T_c, with a second peak below the superconducting transition appearing in the specific heat for $0.02 \le x \le 0.045$.[8] This second peak has been interpreted as either a transition to a different superconducting phase or a transition to a magnetic state which co-exists with the superconductivity. We present a systematic study of $C(T)$ in the low-temperature limit which reveals that the T^3 behavior characteristic of pure UBe_{13} no longer applies for $x>0.02$ *when taking into account the existence of the* $\gamma_0 T$ *term.*

Power-law behavior of such quantities as the specific heat, the thermal conductivity, and the ultrasonic attenuation in heavy-fermion superconductors is evidence for exotic (non-BCS) superconductivity. A traditional BCS s-wave superconductor has an isotropic energy gap which leads to an exponential, $\exp(-\Delta/kT)$, probability of excitations at low temperatures; in contrast, a superconducting state with nodes in the gap at the Fermi surface will have a quasiparticle density of states that has a power-law dependence on T at low temperatures. For example, line nodes in the gap lead to a T^2 dependence of the specific heat C, as observed in UPt_3,[3] while point nodes lead to a T^3 dependence of C, as observed in UBe_{13}.[9] Experimentally, the determination of the power law depends on obtaining good data down to low temperatures.

We measured the specific heat $C(T)$ of $U_{1-x}Th_xBe_{13}$ for a series of extremely high-purity polycrystalline samples[10] with a wide range of thorium doping x. Two of the samples, $x=0.017$ and 0.052, were unannealed, while the other three, $x=0$, 0.022, and 0.030, were annealed at 1400 °C for 600, 950, and 1220 hours, respectively. These samples are superior to previous materials as judged by both the size of the jump in the specific heat at T_c and the narrow transition width.[10] We also studied for comparison a long-term annealed (six months at 1100 °C) single crystal of pure UBe_{13}. The experiments were performed using a transient heat pulse technique in a helium dilution refrigerator, with a flat ground Speer carbon chip for a thermometer, a Au-Cr film deposited on quartz for a heater, and a graphite pyramid as the thermal link. The background contribution from the apparatus was found to be less than one percent of the total specific heat even at the lowest temperatures, except for the pure UBe_{13} samples where a small (at most 5%) background contribution linear in T was subtracted from the data. We estimate the absolute accuracy of the data to be good to $\pm 5\%$. 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, typically 0.01 grams, this self-heating becomes non-negligible for $T<90$ mK. Given the unusual nature of the low-temperature specific heat results, we have verified the reproducibility of our data by repeating the measurements: (i) using a relaxation technique and (ii) using a completely different experimental configuration. In the latter case, the sample was mounted on a sapphire substrate and hung from the mixing chamber by cotton

TABLE I. Specific heat parameters for $U_{1-x}Th_xBe_{13}$.

x	T_c (mK)	T_{c2} (mK)	S_n/S_{sc}	γ_0 (J/mol K^2)	n	$2\Delta_0/kT_c$
0[a]	860±24			0.19±0.02	3.2±0.1	
0	919±10			0.07±0.03	2.8±0.1	
0.017	519±21		0.76±0.03	0.59±0.04	3.1±0.1	
0.022	560±28	464±25	0.77±0.03	1.06±0.05	4.0±0.1	5.2±0.2
0.030	621±9	394±12	0.81±0.03	0.75±0.04	4.3±0.1	5.6±0.2
0.052	376±23		0.89±0.03	1.21±0.07	4.1±0.1	5.4±0.2

[a]Single crystal.

threads, with a silver wire serving as the heat leak.

We plot in Fig. 1 the specific heat $C(T)$ of $U_{1-x}Th_xBe_{13}$ for four different thorium concentrations. In agreement with previous observations,[8] the $x=0.022$ and 0.030 samples have two peaks in the specific heat while the bracketing concentrations, $x=0.017$ and 0.052, show only the one peak at the superconducting transition. The transition temperatures of these samples as well as those of the undoped materials, determined by the midpoint of the rises in $C(T)$, agree well with the known phase diagram.[11] The transition temperatures are listed in Table I, where the errors cited are equal to the 10–90 % half-widths.

At low temperatures we observe a large residual linear term in the specific heat for all the samples (see Table I and Fig. 2). This $T\rightarrow 0$ offset in C/T, γ_0, is smallest for pure UBe_{13}, where the value we measure is similar to that reported by Ravex *et al.*,[12] but somewhat larger than that reported by Ott *et al.*[13] The doped $U_{1-x}Th_xBe_{13}$ samples have γ_0's which are very large, comparable to or even exceeding the value of C/T in the normal state preceding the superconducting transition. Essentially all previous heat capacity measurements on samples of thoriated UBe_{13} do not go to sufficiently low temperature to see a flattening off in C/T, with the exception of Felder *et al.*[14] who mention as an aside the existence of a significant residual term in their study of the phase diagram of $U_{1-x}Th_xBe_{13}$.

Magnetic impurities or other localized moments could lead to a residual term in the specific heat. In such a case, one would expect a sharp Schottky upturn in a plot of C/T vs T in an applied field, as observed in a recent study of the high-temperature superconductor $La_{1.86}Sr_{0.14}CuO_4$.[15] We see *no* such Schottky signature at any thorium concentration x for magnetic fields up to 50 kOe (Fig. 2), which, when coupled with the unprecedented high quality of the samples, makes a magnetic impurity contribution to C unlikely. The gradual rise of C/T with decreasing T when the system is driven normal by $H=50$ kOe does allow, however, a more accurate means to estimate the entropy balance. The superconducting state entropy, $S_s=\int_0^{T_c}(C_s/T)dT$, for a second-order phase transition must be equal to the normal state entropy below the superconducting transition temperature T_c. If one assumes a temperature independent Sommerfeld "constant" $\gamma=C_n/T$, the normal state entropy $S_n=\gamma T_c$ is not sufficient to satisfy this entropy balance requirement. Nonetheless, even with γ continuing to increase below $T_c(H=0)$, we find that the entropy in the field-induced normal state (with a linear extrapolation of C/T below 150 mK) still falls 20% below the superconducting state entropy. The ratios of the normal and superconducting state entropies, S_n/S_{sc}, determined in this way

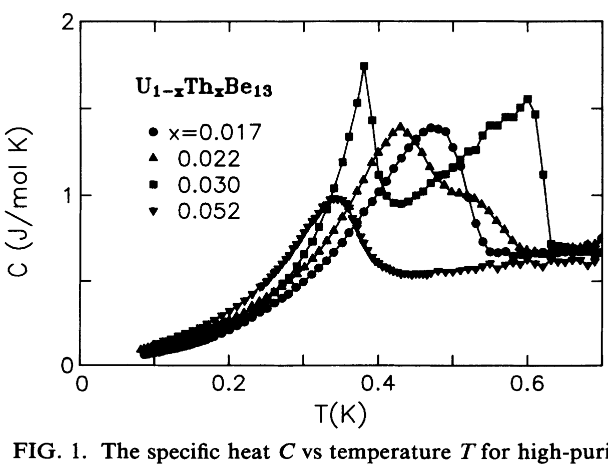

FIG. 1. The specific heat C vs temperature T for high-purity $U_{1-x}Th_xBe_{13}$ polycrystals.

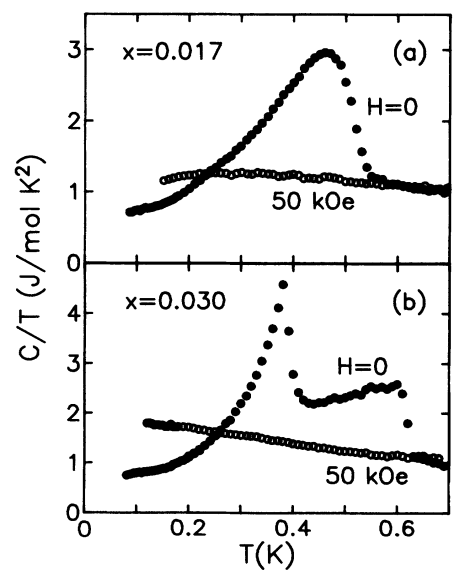

FIG. 2. Specific heat ratio C/T vs T for single peak and double peak samples in magnetic field $H=0$ and $H=50$ kOe. The nuclear Zeeman contribution to $C(T)$ from Be has been subtracted from the $H=50$ kOe data. Both samples exhibit surprisingly large values of $C/T(0)$, with no indication of a sharp Schottky upturn in field.

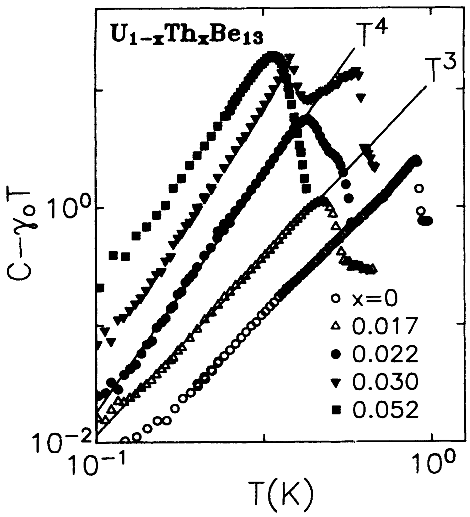

FIG. 3. Log-log plot of $C-\gamma_0 T$ vs temperature showing power-law behavior. Note that the power changes from three for $x<x_c$ to four for $x>x_c$, where x_c is the thorium doping at which the second specific heat peak initially appears.

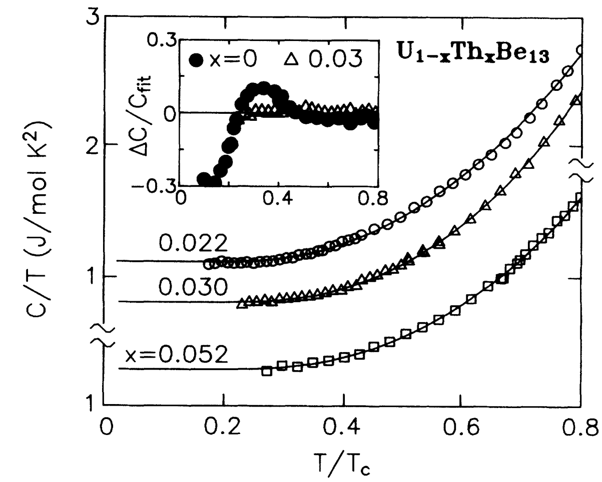

FIG. 4. Specific heat ratio C/T vs normalized temperature T/T_c for $U_{1-x}Th_xBe_{13}$ for $x>x_c$, showing fits to a BCS form plus a linear term. For comparison, the residuals for the same fit to pure UBe_{13} are shown in the inset.

are listed in Table I.

The low-temperature specific heat can be fit to a power law plus a linear term, $C=\gamma_0 T+\alpha T^n$, for $T\leq 0.8T_c$, where T_c is the lower temperature transition for the samples with two peaks. We show in Fig. 3 the power-law behavior of the specific heat with the linear term subtracted. The extracted power is essentially three for the samples with $x<x_c$, where x_c is the doping level at which the second anomaly initially appears in the specific heat. This is expected if the energy gap vanishes at point nodes on the Fermi surface, and has been used as evidence for an axial superconducting state in pure UBe_{13},[9,14] with the caveat that no fits are truly in the low-temperature limit, $T\ll T_c$, where predictions of a pure power law are strictly valid. In contrast, fits to the specific heat of the samples with $x>x_c$ imply a power close to four. Given that a power of four is unphysical and can mimic a true gap near T_c, we also fit the data to an alternative form, $C=\gamma_0 T+\alpha C_{\rm BCS}$. Here, $C_{\rm BCS}$ is the specific heat of a weak-coupled BCS superconductor and we have evaluated the integrals numerically.[16] As a first-order means to take strong coupling into account, we float the size of the zero temperature energy gap Δ_0. This BCS form agrees well with the observed $C(T)$ of the samples with $x>x_c$, yielding best fit values $2\Delta_0 \sim(5.4\pm0.2)kT_c$ in all three cases. The coefficients of the linear term γ_0 determined from these fits are within 6% of the γ_0's of the power-law fits. We show in the main part of Fig. 4 the data fit to the BCS form less a $\gamma_0 T$ term. By comparison, we were unable to describe $C(T)$ for pure UBe_{13} by the same BCS function and plot the best fit residuals in the inset to Fig. 4. The fit to the $x=0.017$ data agrees somewhat better as compared to pure UBe_{13}, but misses at low T, giving a γ_0 that is 15% larger than that of the power-law fit. Finally, we have checked that the agreement of the data for $x>x_c$ with the form $C=\gamma T+\alpha C_{\rm BCS}$ is robust even when using a temperature-dependent γ taken from $C(T,H=50\ {\rm kOe})$ of Fig. 2. The fit parameters, γ_0 and n from the power-law form and $2\Delta_0/kT_c$ from the BCS form, are listed in Table I.

In summary, we find that the determination of the nodal structure of the energy gap from the temperature dependence of the specific heat of $U_{1-x}Th_xBe_{13}$ is complicated by a surprisingly large residual linear contribution to $C(T)$ present for a wide range of x. The large γ_0's are comparable to the normal state C/T and must be included in any theoretical understanding of these superconductors. If such large γ_0's are due to sample problems, then any conclusions drawn from low-temperature experiments on these materials become suspect. On the other hand, a large *intrinsic* linear term should provide clues as to the nature of the superconductivity. For example, a nonunitary pairing state has been proposed[4] for UPt_3 in part to account for the γ_0 puzzle, perhaps linking $U_{1-x}Th_xBe_{13}$ with the low-temperature β phase of UPt_3. Alternatively, as expected within a resonant impurity scattering approach,[7] we observe a general trend toward higher γ_0's for higher x,[17] except for one sample ($x=0.022$) which does not fit the pattern. Independent of any theory, we have established that the inclusion of a $\gamma_0 T$ term in power-law fits to the specific heat below T_c reveals a change with Th doping in the functional form of $C(T)$, coinciding with the change from one to two peaks in the specific heat. The previously claimed T^3 dependence in $C(T)$ for samples with $x<x_c$ does not change with the linear term subtracted and is consistent with an axial superconducting state with point nodes. However, power-law fits to $C(T)$ for the higher doped samples, $x>x_c$, give an unphysical power. This suggests a different superconducting state below the second transition, consistent (albeit over a limited temperature range) with a large $\gamma_0 T$ term coincident with a fully gapped Fermi surface.

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