Pressure and linear heat capacity in the superconducting state of thoriated UBe_{13}

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Even well below T_c, the heavy-fermion superconductor (U,Th) Be_{13} has a large linear term in its specific heat. We show that under uniaxial pressure, the linear heat capacity increases in magnitude by more than a factor of two. The change is reversible and suggests that the linear term is an intrinsic property of the material. In addition, we find no evidence of hysteresis or of latent heat in the low-temperature and low-pressure portion of the phase diagram, showing that all transitions in this region are second order.

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For the past two decades, heavy-fermion superconductors have revealed a variety of unusual behaviors that hint at unconventional superconductivity.[1] Many low-temperature properties such as specific heat and NMR relaxation rates have power law rather than exponential temperature dependences. Two compounds, UPt_3 and $U_{1-x}Th_xBe_{13}$ for x between 0.02 and 0.04, each have two transitions leading to distinct superconducting phases. Further phase transitions appear with pressure or applied magnetic field. Yet no experiment has emerged that conclusively identifies the order parameters of the phases or even their symmetry.

One potential clue to heavy-fermion order parameters is the significant linear term in the thermal properties within the superconducting state. In theory linear heat capacity and thermal conductivity are normal-state phenomena, which should disappear once the superconducting energy gap alters the excitation spectrum. Yet specific heat $C(T)=\gamma_s T + C_{non-linear}(T)$ in the superconducting phase is a persistent feature in heavy-fermion superconductors. The coefficient γ_s can reach over 50% of γ_n, the normal-state value of $C(T)/T$ just above the transition. First seen in UPt_3,[2] a large γ_s and an analogous linear term in thermal conductivity are also found in $CeCoIn_5$,[3] URu_2Si_2,[4,5] and UPd_2Al_3,[6,7] among others.

The linear term is sometimes viewed as stemming entirely or in part from imperfect samples. One simple explanation would be that some fraction of the material remains normal. Another heavily discussed alternative, resonant impurity scattering, combines impurity effects with intrinsic features of the order parameter.[8–10] For a *d*-wave superconductor, a very small impurity concentration could create finite ungapped regions on the Fermi surface and a constant density of states. The strength, phase shift, and anisotropy of the impurity scattering and the impurity density all factor into the normallike behavior. Yet other scenarios treat the linear term as an intrinsic property. These include involvement of only part of the Fermi surface in superconductivity, and the more exotic odd-frequency pairing.[11]

In support of the importance of impurities, the magnitude of γ_s varies significantly from sample to sample, ranging from $0.12\gamma_n$ to $0.62\gamma_n$ in UPt_3. Furthermore, γ_s generally decreases as the superconducting transition temperature of the sample increases. Since a higher T_c often indicates a better-quality sample, the correlation does suggest that γ_s arises at least in part from sample problems.[2] Also, γ_s in pure UBe_{13} is small or zero, but doping with either thorium[12] or boron[13,14] increases both γ_s and the likelihood of sample inhomogeneities.

Any theory of the linear terms in the superconducting specific heat and thermal conductivity must also address the absence of a linear contribution to the NMR spin-lattice relaxation rate. If the large γ_s comes from either a normal portion of the sample or a finite region of the Fermi surface with no gap, that same source should lead to a linear Korringa relaxation, as in the normal state. However, NMR measurements on a variety of heavy-fermion superconductors find only a cubic temperature dependence down to temperatures well below where linear terms in heat capacity and thermal conductivity become significant.[15–17] The cubic dependence would be expected from line nodes in the gap. Reconciling the NMR and thermodynamic data would certainly be a step towards understanding heavy-fermion superconductivity.

Our present work shows a large and reversible change in γ_s with pressure in $U_{0.98}Th_{0.02}Be_{13}$. Explaining the pressure dependence, which occurs without a change in the impurity concentration, will further restrict theoretical treatments.

We use a pressure cell activated by a helium bellows. The setup is mounted at the mixing chamber of a KelvinOx 100 dilution refrigerator, and we can change pressure while keeping the sample temperature below 300 mK. Our cell, illustrated schematically in Fig. 1, is modeled after the cell described by Pfleiderer *et al.*[18] The expanding bellows presses on a column including the sample and a piezoelectric crystal to measure pressure changes. The small cross-sectional area of the sample amplifies the pressure within the bellows; by the time the helium solidifies at 25 bars we reach a uniaxial pressure of 7.8 kbar at the sample. The uniaxial technique is convenient for changing pressure at low temperature. Uniaxial pressure has also been used for an unrelated set of measurements on pure UBe_{13}, an attempt to split the single superconducting transition into two by breaking the cubic symmetry of the crystal.[19,20] We use a polycrystalline sample to avoid any such symmetry-breaking effects in this experiment.

We use a transient pulse method for heat-capacity measurements. Our heater is a 50:50 AuCr thin film, our thermometer a RuO_2 film. Pieces of NbTi on each side of the

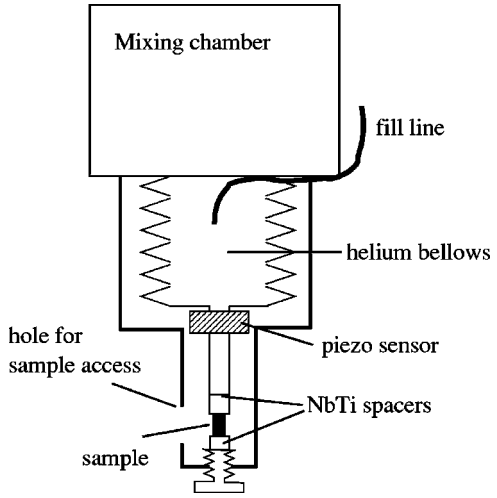

FIG. 1. Helium bellows setup for measuring specific heat under uniaxial pressure.

sample provide a thermal link, with a time constant of order 8 sec between the sample and the rest of the bellows. As a conventional superconductor well below T_c, the NbTi itself contributes negligibly to the measured heat capacity.

One difficulty with the measurements is a significant time constant between the helium bellows and the dilution refrigerator, of order 3 min near 500 mK and increasing to 10 min at 200 mK. Waiting for the bellows to equilibrate completely with the cryostat at each temperature takes prohibitively long. Instead, we measure the relaxation time of the bellows throughout our temperature range and verify that it is independent of pressure. We then account for a slowly changing bellows temperature in our fits of the temperature decays after each heat pulse.

In Fig. 2, we show C/T as a function of temperature for five different pressures. At the lowest pressure there are two

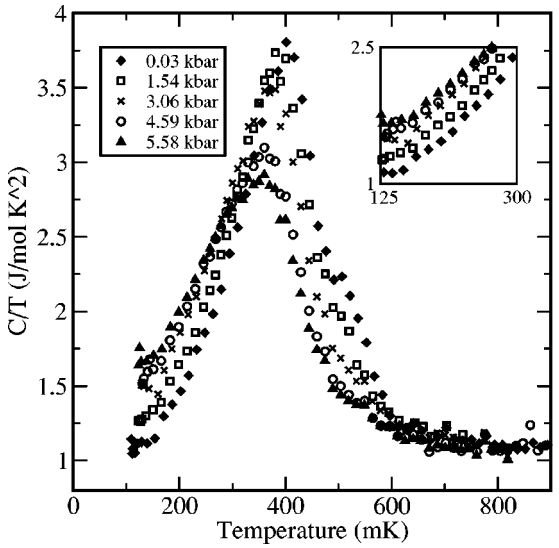

FIG. 2. Specific heat of $U_{0.98}Th_{0.02}Be_{13}$ as a function of temperature for several applied uniaxial pressures. Inset enlarges part of the low-temperature region, showing that the curves for different pressures are nearly parallel.

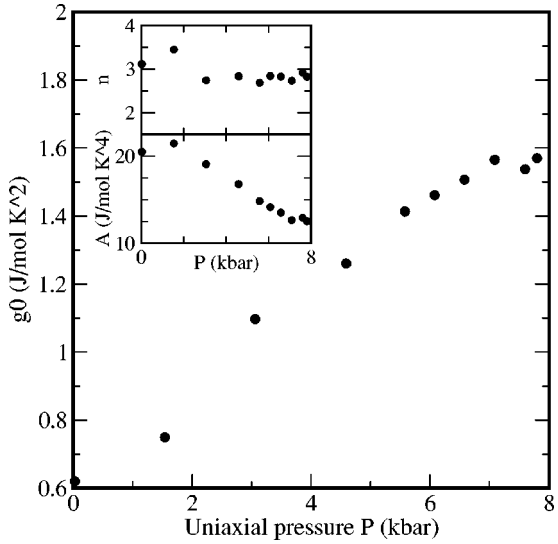

FIG. 3. Linear coefficient of specific heat in superconducting phase, γ_s, as a function of pressure. Inset: Best fit parameters for low-temperature tail: the exponent n from a three-parameter fit $C(T)=\gamma_s T+AT^n$ (top) and the prefactor A from a two-parameter fit $C(T)=\gamma_s T+AT^3$ (bottom).

transitions, centered at 450 and 550 mK, with a small shoulder between them. As pressure increases, the two transitions decrease in temperature and merge into one, the shoulder disappearing. The amplitude of the peak decreases, while that of the low-temperature tail increases. The normal-state heat capacity does not change with pressure. All this agrees with the previous uniaxial pressure experiment.[21]

The lowest-pressure data follows the power-law form previously observed for (U,Th) Be_{13}, $C(T)=\gamma_s T+AT^3$ with $\gamma_s=0.62$ J/mol K at $P=0.03$ kbar. Previous low-temperature heat-capacity measurements for different Th concentrations[12] found $C(T)=\gamma_s T+AT^n$ with a best-fit exponent n near 4, an unphysical value, for Th concentrations of 2.2% and above. Our sample, with a slightly lower Th concentration, retains the T^3 behavior. Indeed, this function proves to fit our data well for all pressures. Three-parameter least-squares fits of $C(T)$ to the form $\gamma_s T+AT^n$ give an exponent $n\approx 3$ at all pressures, as shown in Fig. 3. With this in mind, we fix $n=3$ and carry out two-parameter fits. For each pressure we fit $C(T)$ from the lowest temperature to within 50 mK of the peak. We find a steady increase in γ_s with pressure, while A decreases more slowly; these quantities are shown in Fig. 3. The earlier experiment[21] found essentially parallel curves for the low-temperature specific heat at different pressures, suggesting a constant A. The variation in A appears now because of the wider temperature and pressure ranges of the present work.

As a further check, we extrapolate the specific-heat curves to $T=0$ according to the above fits. We then integrate to find the entropy S by $S(T)=\int_0^T dT\, C(T)/T$. Figure 4 compares the entropy for the same data sets represented in Fig. 2. By 700 mK, safely in the normal state, the total entropy varies by only a few percent among pressures. The extra entropy under the C/T peak at low pressures offsets the extra entropy under the low-temperature tail at high pressures.

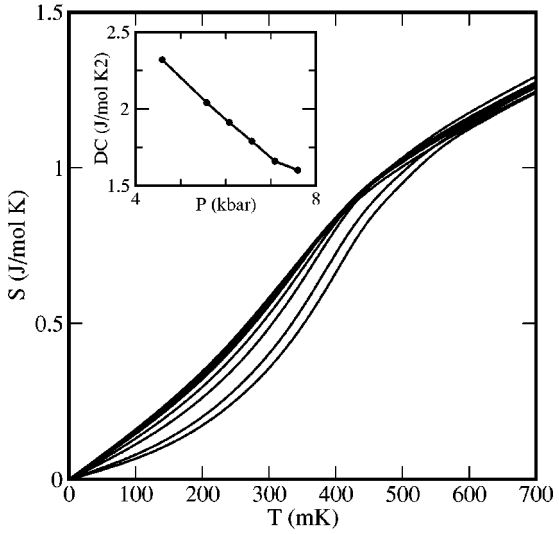

FIG. 4. Entropy from 0 to 700 mK for pressures in Fig. 2. Inset: Specific-heat jump at the transition, for single-transition regime.

With this confirmation, we return to the γ_s. The magnitude of the change with pressure is striking, more than a factor of two. Furthermore, the change is completely reversible, even without raising the temperature above 300 mK. In fact, exploring the reversibility of the low-temperature heat capacity originally motivated our measurements. The phase diagram of $U_{1-x}Th_xBe_{13}$ includes boundaries within the superconducting regime as functions of concentration and pressure, as well as temperature. For Th concentrations with two transitions, μSR measurements finds weak local magnetic order below the lower-temperature transition.[22,23] No local order appears for Th concentrations with a single transition, suggesting a phase boundary near $x=0.02$ between the single phase at $x<0.02$ and the lower-temperature phase for $x>0.02$. Since increasing pressure acts much like decreasing Th concentration,[24,25] pressure measurements can cross an analogous phase boundary and explore its thermodynamic properties.

The earlier heat-capacity measurements under pressure[21] drove the sample around rather than across the phase boundary: pressure was always changed at room temperature, with the sample then cooled into one phase or the other. Our bellows pressure cell allows us to change pressure while cold, thereby crossing the transition directly. We also use a sample with Th concentration closer to the transition and extend the measurements to lower temperatures by using a dilution refrigerator rather than the pumped ^{3}He cryostat of the earlier work.

We use several paths through the pressure-temperature space to search for hysteresis. In one case, we change pressure, keeping temperature below 300 mK. We then measure $C(T)$ from low temperature to above T_c. After the sample has warmed above T_c, we cool and repeat the specific-heat measurements from our lowest temperatures. The two specific-heat curves agree to better than 0.5% for both increasing and decreasing pressure, up to 5.5 kbar. Changing pressure at fixed temperature is less reliable, both because it is more difficult to return exactly to the original pressure and because the temperature always changes slightly during the pressure change, but again there is no evidence of hysteresis in the specific heat.

We also find no evidence of latent heat when we monitor the sample temperature while increasing or decreasing pressure. The temperature rises during any pressure change. The effect is more noticeable upon increasing pressure, but the difference is completely explained by the heat load to the cryostat from adding additional room-temperature helium and by the work done in compressing the sample. We never find a temperature reduction on changing pressure. We conclude that any transition with pressure in this region is second order.

Although pressure might introduce additional defects into a sample, perhaps even defects that could substantially alter the heat capacity, such an explanation for the change in γ_s also demands, implausibly, that the defects anneal away at low temperature. Pressure can also alter the scattering properties of an existing defect by producing strain near the defect. For our sample, the strong influence of pressure on γ_s would require a scattering mechanism unusually sensitive to strain. Whether or not the strain near existing defects causes the change in γ_s, the large reversible effect suggests that γ_s is tied intimately to the mechanism of superconductivity itself.

Note that at our highest pressures γ_s exceeds the normal-state C/T just above T_c. This confirms other evidence of temperature-dependent γ_n in UBe_{13}. An entropy deficit in normal UBe_{13} relative to the superconducting phase has long been known, suggesting that $\gamma_n(T)$ increases substantially below T_c. Suppressing T_c with a magnetic field bears this out, with C/T increasing steadily toward lower temperatures. The same effect, with an even stronger increase in $\gamma_n(T)$, appears for Th-doped UBe_{13}. Heat capacity in a 3 T field shows $\gamma_n(T)$ of 1400 mJ/mole K^2 at 0.42 K. To match the measured superconducting entropy it must rise to 2300 mJ/mole K^2 at $T=0$, a faster than linear increase in $\gamma_n(T)$ itself.[26]

The behavior of γ_s emphasizes that increasing pressure and decreasing Th concentration have analogous but not identical effects. As shown previously, the topology of the phase diagram appears to be similar for the two variables, but the temperature dependence of the transitions is not. On decreasing Th concentration below 2%, T_c rises. While pressure also merges the transitions, T_c decreases monotonically. Similarly, γ_s generally *decreases* with decreasing Th concentration; it is more an order of magnitude smaller in pure UBe_{13} than for 2% Th doping. Yet γ_s *increases* with increasing pressure.

This suggests that changes in γ_s come from quantitative rather than qualitative changes in the order parameter. For a BCS superconductor, the specific-heat jump at the transition, ΔC, and the magnitude of the energy gap, $\Delta(0)$, satisfy $\Delta C=1.43\gamma_n T_c$ and $\Delta(0)=1.76kT_c$. Although these simple proportionalities fail for a non-s-wave order parameter or strong coupling, the discontinuity is still related to $\Delta(0)$. We fit our specific-heat data with a single sharp transition, with entropy conserved between our data and the fit. The inset of Fig. 4 shows the size of the jump, at pressures high enough

that a single transition provides a good fit to the data. The jump decreases with increasing pressure, although not as rapidly as γ_s increases.

Other heavy-fermion materials also show substantial changes in γ_s with pressure. In UPd_2Al_3, with superconducting T_c near 1.5 K and antiferromagnetic $T_N \approx 18$ K, γ_s increases over 50% at 10.8 kbar of hydrostatic pressure.[6] In this case the heat capacity just above T_c, deep in the antiferromagnetic phase, increases by a comparable amount. A possible explanation is that separate electron subsystems are responsible for the magnetic and superconducting behaviors, with the pressure dependence arising only from the electrons responsible for the magnetism.

Another example is $CeRhIn_5$ (Ref. 27) at the boundary between antiferromagnet and superconductor. In this case, the superconducting γ_s vanishes at high pressures, but rises steadily as pressure decreases from 21 to 15 kbar. At 15 kbar, at the antiferromagnetic transition, γ_s has reached its value within the antiferromagnet. The authors interpret the large linear term as a consequence of finite regions of ungapped Fermi surface[27] that come from an increase in anisotropic impurity scattering near the antiferromagnetic transition.[10]

Thus a large and changing γ_s appears not only in our superconducting system but also in a superconducting antiferromagnet and at a superconductor/antiferromagnet transition. Whether there is any further connection among these systems, such as proximity to an unrealized antiferromagnetic transition in (U,Th) Be_{13}, remains to be seen.

In summary, we observe a large increase with pressure in γ_s, the linear coefficient of the superconducting specific heat. We also find that all pressure-dependent behavior is reversible, indicating that all phase transitions in the region are second order. The change in γ_s with no change in the impurity density appears inconsistent with some proposed explanations for the origin of the linear term, including resonant impurity scattering. Whether or not a nonzero γ_s is itself an intrinsic property of (U,Th) Be_{13}, its strong variation within a single sample is likely intrinsic and may prove a useful signature of the nature of superconductivity in the material.

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