Pressure and linear heat capacity in the superconducting state of thoriated UBe$_{13}$

R.J. Zieve$^1$, R. Duke$^1$ and J.L. Smith$^2$

$^1$Physics Department, University of California at Davis
$^2$Los Alamos National Laboratory, Division of Materials Science and Technology

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$_x$Be$_{13}$ 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 $C(T) = \gamma_s T + C_{\text{non-linear}}(T)$ in the superconducting phase is a persistent feature in heavy-fermion superconductors. The coefficient $\gamma_s$ can reach over 50% of $\gamma_n$, the normal-state value of $C(T)/T$ just above the transition. First seen in UPt$_3$ [2], a large $\gamma_s$ and an analogous linear term in thermal conductivity are also found in CeCoIn$_5$ [3], URu$_2$Si$_2$ [4, 5], and UPd$_2$Al$_3$ [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, 9, 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 order parameter [8, 9, 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 order parameter [8, 9, 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 order parameter [8, 9, 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 order parameter [8, 9, 10].

In support of the importance of impurities, the magnitude of $\gamma_s$ varies significantly from sample to sample, ranging from 0.12$\gamma_n$ to 0.62$\gamma_n$ in UPt$_3$. Furthermore, $\gamma_s$ 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 $\gamma_s$ arises at least in part from sample problems [2]. Also, $\gamma_s$ in pure UBe$_{13}$ is small or zero, but doping with either thorium [12] or boron [13, 14] increases both $\gamma_s$ 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 $\gamma_s$ 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, 16, 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 $\gamma_s$ with pressure in U$_{0.98}$Th$_{0.02}$Be$_{13}$. Explaining the pressure

![Helium bellows setup for measuring specific heat under uniaxial pressure.](image)
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 Figure 1, is modelled 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 bar we reach a uniaxial pressure of 7.8 kbar at the sample. The uniaxial technique is necessary for changing pressure at low temperature. To avoid symmetry-breaking effects from the uniaxial pressure, we use a polycrystalline sample in the experiment.

We use a transient pulse method for heat capacity measurements. Our heater is a 50:50 AuCr thin film, our thermometer a RuO₂ film. Pieces of NbTi on each side of the sample provide a thermal link, with a time constant of order 8 seconds 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 minutes near 500 mK and increasing to 10 minutes 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 Figure 2, we show \( C/T \) as a function of temperature for five different pressures. At the lowest pressure there are two transitions, centered at 450 mK 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 [19].

The lowest-pressure data follows the power-law form previously observed for (U, Th)Be₁₃, \( C(T) = \gamma_s T + AT^n \) with \( \gamma_s = 0.64 \text{ J/mol K} \) at \( P = 0.03 \text{ kbar} \). 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 fits of \( C(T) \) to the form \( \gamma_s T + AT^n \) give an exponent \( n \approx 3 \) at all pressures, as shown in Figure 3. With this in mind, we fix \( n = 3 \) and carry out two-parameter fits. We find a steady increase in \( \gamma_s \) with pressure, while \( A \) decreases more slowly; these quantities are shown in Figure 4.

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 \( S(T) = \int_0^T dT \frac{C(T)}{T} \). Figure 4 compares the entropy for the lowest and highest pressure curves of Figure 2. By 700 mK, safely in the normal state, the total entropy varies

FIG. 2: Specific heat of \( \text{U}_{0.98}\text{Th}_{0.02}\text{Be}_{13} \) 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, \( \gamma_s \), as a function of pressure. Inset: Best fit parameters for low temperature tail: the exponent \( n \) from a 3-parameter fit \( C(T) = \gamma_s T + AT^n \) (top) and the prefactor \( A \) from a 2-parameter fit \( C(T) = \gamma_s T + AT^3 \) (bottom).
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.

With this confirmation, we return to the $\gamma_s$. 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 $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ includes boundaries within the superconducting regime as functions of concentration and pressure, as well as temperature. For Th concentrations with two transitions, $\mu$SR measurements find weak local magnetic order below the lower-temperature transition \cite{20, 21}. 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 \cite{22, 23}, pressure measurements can cross an analogous phase boundary and explore its thermodynamic properties.

The earlier heat capacity measurements under pressure \cite{19} 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 $^3\text{He}$ 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 $\gamma_s$ also demands, implausibly, that the defects anneal away at low temperature. The large reversible effect on $\gamma_s$ suggests that in fact the $\gamma_s$ is tied intimately to the mechanism of superconductivity itself.

Note that at our highest pressures $\gamma_s$ exceeds the normal-state $C/T$ just above $T_c$. This confirms other evidence of non-Fermi liquid behavior 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 \cite{24}.

The behavior of $\gamma_s$ 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, $\gamma_s$ generally decreases with decreasing Th concentration; it is more an order of magnitude smaller in pure UBe$_{13}$ than for 2% Th doping. Yet $\gamma_s$ increases with increasing pressure.

This suggests that changes in $\gamma_s$ come from quantitative rather than qualitative changes in the order parameter. For a BCS superconductor, the specific heat jump at the transition, $\Delta C$, 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 en-
tropy conserved between our data and the fit. The inset of Figure 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 $\gamma_s$ increases.

Other heavy-fermion materials also show substantial changes in $\gamma_s$ with pressure. In UPd$_2$Al$_3$, with superconducting $T_c$ near 1.5 K and antiferromagnetic $T_N \approx 18$ K, $\gamma_s$ 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$_5$ [25] at the boundary between antiferromagnet and superconductor. In this case, the superconducting $\gamma_s$ vanishes at high pressures, but rises steadily as pressure decreases from 21 to 15 kbar. At 15 kbar, at the antiferromagnetic transition, $\gamma_s$ has reached its value within the antiferromagnet. The authors interpret the large linear term as a consequence of finite regions of ungapped Fermi surface that come from an increase in anisotropic impurity scattering near the antiferromagnetic transition [10].

Thus a large and changing $\gamma_s$ appears not only in our superconducting system but also in a superconducting antiferromagnet and at a superconductor/antiferromagnet transition. Whether or not 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 $\gamma_s$, 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 $\gamma_s$ 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 non-zero $\gamma_s$ 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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[1] R.H. Heffner and M.R. Norman, “Heavy fermion superconductivity,” Comments Cond. Mat. Phys. 17, 361 (1996) [arXiv:cond-mat/9506043].
[2] R.A. Fisher, S. Kim, B.F. Woodfield, N.E. Phillips, L. Taillefer, K. Hasselbach, J. Flouquet, A.L. Giorgi and J.L. Smith, “Specific heat of UPt$_3$: Evidence for unconventional superconductivity,” Phys. Rev. Lett. 62, 1411 (1989).
[3] R. Movshovich, M. Jaime, J.D. Thompson, C. Petrovic, Z. Fisk, P.G. Pagliuso and J.L. Sarrao, “Unconventional superconductivity in CeIrIn$_5$ and CeCoIn$_5$: Specific heat and thermal conductivity studies,” Phys. Rev. Lett. 86, 5152 (2001) [arXiv:cond-mat/0011365].
[4] R.A. Fisher, S. Kim, Y. Wu, N.E. Phillips, M.W. McElfresh, M.S. Torikachvili and M.B. Maple, “Specific heat of URu$_2$Si$_2$: Effect of pressure and magnetic field on the magnetic and superconducting transitions,” Physica B163, 419 (1990).
[5] K. Behnia, D. Jaccard, J. Sierro, P. Lejay and J. Flouquet, “Thermal conductivity of heavy-fermion superconductor URu$_2$Si$_2,” Physica C196, 57 (1992).
[6] R. Caspary, P. Hellmann, M. Keller, G. Sparn, C. Wassilew, R. Köhler, C. Geibel, C. Shank, F. Steglich and N.E. Phillips, “Unusual ground-state properties of UPd$_2$Al$_3$: Implications for the coexistence of heavy-fermion superconductivity and local-moment antiferromagnetism,” Phys.Rev. Lett. 71, 2146 (1993).
[7] M. Chiara, B. Lussier, B. Ellman and L. Taillefer, “Heat conduction in the heavy fermion superconductor UPd$_2$Al$_3,” Physica B230, 370 (1997) [arXiv:cond-mat/9609116].
[8] P.J. Hirschfeld, P. Wölfle and D. Einzel, “Consequences of resonant impurity scattering in anisotropic superconductors: Thermal and spin relaxation properties,” Phys. Rev. B37, 83 (1988).
[9] A.V. Balatsky, M.I. Salkola and A. Rosengren, “Impurity-induced virtual bound state in d-wave superconductors,” Phys. Rev. B51, 15547 (1995) [arXiv:cond-mat/9407102].
[10] S. Hass, A.V. Balatsky, M. Sigrist and T.M. Rice, “Extended gapless regions in disordered $d_{x^2-y^2}$ wave superconductors,” Phys. Rev. B56, 5108 (1997) [arXiv:cond-mat/9703082].
[11] P. Coleman, E. Miranda and A. Tsvelik, “Odd-frequency pairing in the Kondo lattice,” Phys. Rev. B49, 8955 (1994) [arXiv:cond-mat/9305017].
[21] R.H. Heffner, J.O. Willis, J.L. Smith, P. Birrer, C. Baines, F.N. Gygax, B. Hitti, E. Lippelt, H.R. Ott, A. Schenck and D.E. MacLaughlin, “Muon-spin relaxation studies of weak magnetic correlations in $U_{1-x}Th_xBe_{13}$,” *Phys. Rev. B* **40**, 806 (1989).

[22] S.E. Lambert, Y. Dalichaouch, M.B. Maple, J.L. Smith and Z. Fisk, “Superconductivity under pressure in $(U_{1-x}Th_x)Be_{13}$: Evidence for two superconducting states,” *Phys. Rev. Lett.* **57**, 1619 (1986).

[23] M. Sigrist and T.M. Rice, “Phenomenological theory of the superconductivity phase diagram of $U_{1-x}Th_xBe_{13}$,” *Phys. Rev. B* **39**, 2200 (1989).

[24] J.S. Kim, B. Andraka and G.R. Stewart, “Investigation of the second transition in $U_{1-x}Th_xBe_{13}$,” *Phys. Rev. B* **44**, 6921 (1991).

[25] R.A. Fisher, F. Bouquet, N.E. Phillips, M.F. Hundley, P.G. Pagliuso, J.L. Sarrao, Z. Fisk and J.D. Thompson, “Specific heat of $CeRhIn_5$: Pressure-driven transition from antiferromagnetism to heavy-fermion superconductivity,” *J. Supercond.* **15**, 433 (2002) [arXiv:cond-mat/0109221].