Specific-Heat Anomaly in Superconducting UPt_3 at 18 mK

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We have observed large specific-heat anomalies around 18 mK in two single-crystal samples of UPt_3 of different origin. These indicate additional forms of order which still take place in the electronic system of the heavy-fermion compound at these low temperatures. Since magnetic-susceptibility measurements showed that the samples remain superconducting, the new ordering coexists with superconductivity.

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Evidence is still mounting that the pairing in superconducting (SC) UPt_3 is nonconventional as indicated by the existence of multiple SC phases [1–9]. It is conjectured that the pairing is mediated through antiferromagnetic spin fluctuations leading to an anisotropic order parameter, i.e., to a gap function which can have zeros on points and lines of the Fermi surface [10–12]. Crucial experimental information can be derived from the specific heat which probes the spectrum of thermal excitations from the SC ground state, notably for temperatures much lower than T_c. Earlier measurements of the specific heat [3,4,6,7] of UPt_3 did not extend below 70 mK, in part because of the radioactive self-heating in the samples due to their U^{235} content. Previous measurements by us [13] in the normal state (in magnetic fields up to 7 T) reached down to just below 20 mK. In those studies we found, after subtracting the nuclear magnetic specific-heat contribution from the Pt nuclei, an increase in the electronic specific heat below 30 mK, the origin of which we could not clarify. Recently we extended the temperature range (in zero magnetic field) down to 6.5 mK by using short thermal relaxation times and a novel fast magnetic thermometer. We discovered, in the SC state, large maxima in the specific heat around 18 mK in two single crystals of UPt_3 of different sources. One of these crystals, which has been carefully annealed, shows the well-known double transition in the specific heat at T_c. The data indicate that the new peak is due to an electronic ordering phenomenon in the SC state of yet unknown origin.

Our experimental setup has been described in the previous publication [13]. In the work reported here we used the first stage ($PrNi_5$) of a double-stage nuclear demagnetization cryostat as the cooling reservoir with a minimum temperature of 600 μK monitored by pulsed NMR on Pt and Cu probes.

The samples were placed in a Ag clamp to which a short Cu wire, the thermal "weak link" to the nuclear stage, was screwed. Also attached was a Ag wire with a sample of Tl (4 mm diam, 12 mm long) soldered to it (see Fig. 1). The latter was placed into one side of an astatic pair of pickup coils which were part of a SC flux transformer leading to a Nb SQUID in the ^{4}He bath. All metals were of 99.999% purity except for the Tl which was of 99.99% purity. To suppress the SC phase of Tl, this probe had to be kept in a magnetic field above 18 mT. Its nuclear susceptibility had previously been checked to follow a Curie law at least down to 800 μK. Since Tl has an extremely small Korringa constant of 4.4 msK [14], the SQUID system provided a fast thermometer with an intrinsic response time at 6.5 mK (the lowest temperature of our samples) of 0.7 s and with a net response time of about 2 s with the probes connected to it [see Fig. 2(a)].

For temperature calibration, at first the thermal conductance of the weak link was measured over a wide temperature range (30–500 mK) and was observed to follow a T law as expected for pure metals ($\Lambda = 2.4\times10^{-4}T$ W/K^2). At the same time the radioactive heat leak (3.4 and 2.3 nW for both samples, respectively) was obtained. Then the deviation of the sample temperature from that

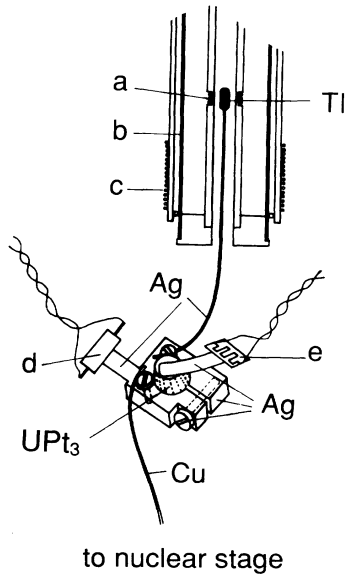

FIG. 1. Schematic drawing of the experimental setup. Ag clamp and probe are shown enlarged with respect to the magnetometer pickup system. (a) Pickup coil, (b) Pb cylinder, (c) magnetometer field coil, (d) carbon resistor used above 20 mK, and (e) PtW heater.

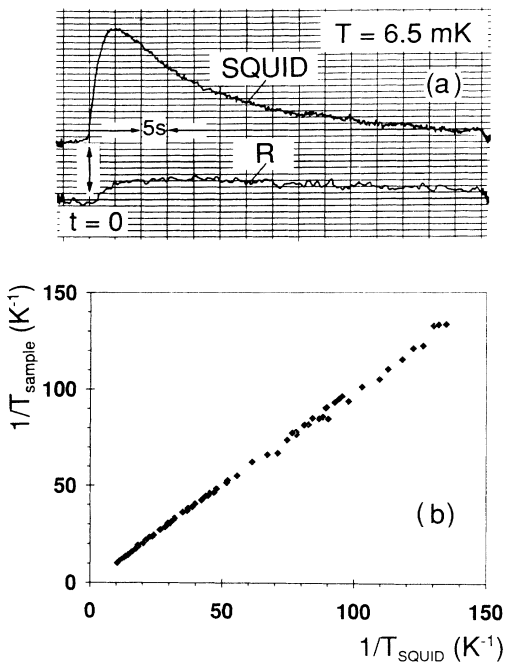

FIG. 2. (a) Time response of SQUID readout and of carbon-resistor bridge at low temperature. At $t=0$ a heat pulse of 0.25-s duration is applied to the sample. (b) Comparison of the calculated inverse probe temperature to the inverse Tl nuclear magnetic SQUID temperature.

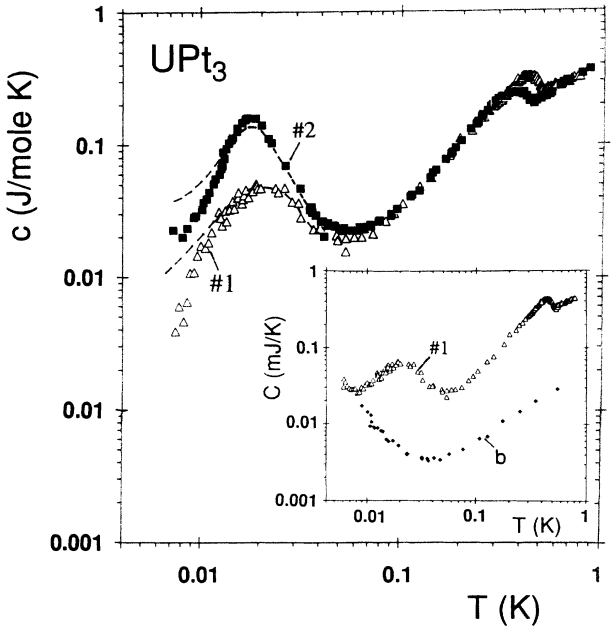

FIG. 3. Specific heat of sample 1 (Bucher, open triangles) and sample 2 (Menovsky, solid squares) after subtraction of the addendum contribution. The dashed lines represent the largest deviation consistent with a model of resistively coupled heat reservoirs [16]. Inset: The background b together with the raw data of sample 1 on an absolute scale.

of the nuclear stage (beginning below 25 mK) could be calculated. Sample temperatures obtained this way were compared to the SQUID signal which was calibrated against a carbon resistor at the nuclear stage which in turn had been calibrated against NBS fix-point standards and Pt NMR signals. Excellent matching of the two temperatures was found [see Fig. 2(b)].

The reliability of the SQUID thermometry for the heat-pulse technique was tested against the standard carbon-resistor technique in an overlapping temperature range and, at the lowest temperatures, against an ac heating method [15] which gave no significant deviation above 10 mK.

The first sample, a 1.01-g cylindrical piece, was from the same batch as the crystals used in our previous work and was prepared from highly depleted uranium ($U^{235}/U^{238} < 10^{-4}$) in a zone-refining furnace by Hufnagl and Bucher at Konstanz. The high quality of these crystals has been established previously [4,13], although they do not show a clear double transition at 500 mK. The second crystal was much smaller (343 mg) and was grown by the Czochralski method by Menovsky and de Visser at the Natuurkundig Laboratorium, Amsterdam. It had been annealed after growth and exhibits a double transition at T_c as already determined by the Amsterdam group [7].

Because the addendum was large (30 mmoles of Tl in 26 mT and 20 mmoles of Ag), its contribution to the specific heat had to be measured separately. This "background" consisted of a term linear in T (due to the electronic specific heat of the two metals involved) dominating above 40 mK and a term $\propto T^{-2}$ significant below 20 mK but structureless around 18 mK (see inset in Fig. 3). This second term was an order of magnitude larger than the calculated nuclear specific heat of Tl. It is presumably of magnetic origin and due to impurities (e.g., in the carbon resistor and the GE varnish with which the heater was glued on), but it could not be clearly identified.

For size reasons it was not possible to attach the thermometer separately onto the sample. The heater on the other hand was connected directly to the probe to ensure that the whole heat pulse is traveled through the sample and heated it homogeneously. In this configuration, a finite thermal resistance between sample and Ag clamp combined with the finite specific heat of the addendum can cause systematic errors, especially at low temperatures. However, since we know the contribution of the addendum from an independent measurement, we can calculate the time dependence of the probe temperature after the heat pulse using a theory introduced by Turrell *et al.* [16] for coupled heat baths with thermal resistances. The dashed lines in Fig. 3 show the maximum possible deviation arising from a finite sample-holder resistance, which can be seen to become large only below 10 mK.

The specific heat of the two samples (i.e., the total

TABLE I. Parameters derived from Figs. 3 and 4 for our two samples of UPt_3 in zero magnetic field.

Sample	T_c (mK) (idealized)	γ_n (mJ/mole K)	β (J/mole K^3)	$\Delta C/\gamma_n T_c$ (idealized)
1	470	430	1.75	1.1
2	420/335	420	1.8	1.0[a]

[a]Both transitions combined into an equivalent single one.

measured specific heat with the addendum contribution subtracted) is shown in Fig. 3 in a double logarithmic plot. Most notable are the surprising new maxima at low temperatures, which are of different height but are both centered at 18 mK. The observed γ_n values (for $T > T_c$) as well as the magnitudes of the βT^2 term (for $T < T_c$) are summarized in Table I.

The appearance of these new maxima immediately raises questions about the entropy balance, both between the two samples in the SC state as well as between their normal and SC states. We therefore plot, in Figs. 4 and 5, c/T vs T and the entropy change Δs vs T counted from a lowest temperature of 10 mK. From Fig. 5, two important conclusions can be drawn: (i) The total entropy change from 10 mK to T_c is approximately equal for both samples, although the low-temperature anomaly in c is much larger for sample 2. The entropy change is just distributed differently over the temperature range. (ii) When extrapolating the normal-state entropy $\gamma_n T$ from above T_c towards $T=0$, the amount $\gamma_n T_c$ is substantially smaller (by about 120 mJ/mole K) than the observed change Δs in the SC state between 10 mK and T_c.

In addition to the specific-heat measurements we investigated a piece of sample 1 in the SQUID magnetometer, in order to search for eventual changes around 18 mK. No anomalous behavior, apart from the well-known constant flux creep from flux-line motions, was observed. The sample was still superconducting far below 10 mK.

Attempts to fit the low-temperature specific-heat anomalies with a Schottky-type law were unsuccessful. Its high-temperature side (especially for sample 2) rises faster than T^{-2} (see Fig. 4). In addition, the value of the gap (50 mK) would be unreasonably high for nuclear two-level systems.

What is the nature of the new low-temperature peak in the specific heat of UPt_3? It cannot be of (noncooperative) nuclear magnetic origin, because it has the wrong form (no Schottky anomaly), would require much too large internal fields (of the order of 200 T) if it came from the Pt nuclei, and is much too large for a contribution from the nuclear quadrupolar splitting of the remaining small concentration of U^{235} or from other impurities (a 3.5% U^{235} content would be necessary for sample 2). An attempt to ascribe the peak to normal fractions [3] of the Fermi surface immediately leads to contradictions regarding the relative sizes of the entropy drops (see Fig. 5). Therefore, the new phase transition must take place in the superconducting electronic system.

Group theory would indeed allow for a third transition in the conjectured anisotropic SC state [10,12]. However, the associated entropy change is unreasonably large to be explained as arising from an order-parameter change only. Rather, we believe that the normal state must have a similar transition at a lower temperature. This is in agreement with our previous measurements in the normal state in fields of 1.7–7 T, which showed an increase in the specific heat over the $\gamma_n T$ value at temperatures below 70 mK (without, however, going through a maximum down to 15 mK) [13] and with a similar increase in zero field in a sample where superconductivity was suppressed by heat treatment [17].

Such a transition in the normal state of UPt_3, which gets modified in the SC state, would mean that the heavy-fermion state in this material is not stable down to

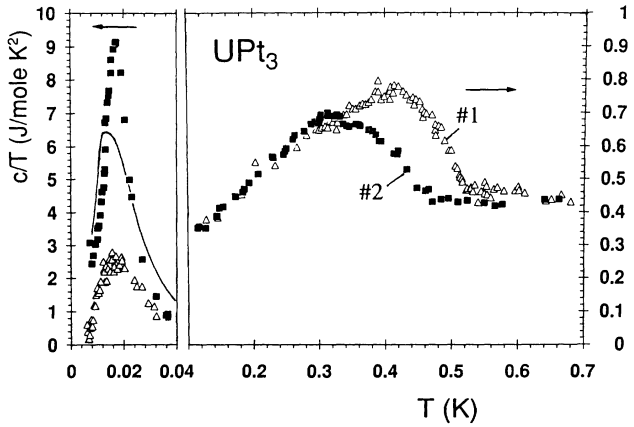

FIG. 4. Specific heat of UPt_3 divided by T. The double transition in sample 2 is clearly visible. Note the different scales for the two parts of the figure. The solid line shows the failure of a Schottky-law fit to the low-temperature peak of sample 2.

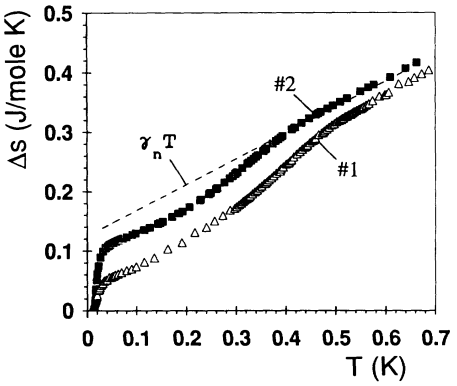

FIG. 5. Entropy difference from 10 mK to T for both samples. The integral is numerically evaluated after subtraction of the addendum contribution. The dashed line is $\gamma_n T$ extrapolated from above T_c.

zero degrees, but that some form of order, presumably among the uranium ions, occurs which partly (or completely) destroys it. It is known that UPt_3 undergoes a transition to a short-range (fluctuating) type of antiferromagnetic state at 5 K, without, however, a noticeable drop in entropy [18]. Possibly, our observed transition at 18 mK manifests the development of long-range static order.

This is the first time that such a low-temperature instability is observed in a heavy-fermion material. Clearly, it would be desirable to have normal-state data down to lower temperatures in order to corroborate the above scenario. This is difficult to do in the uranium compounds because of the radioactivity, but might be more feasible in other heavy-fermion compounds such as $CeAl_3$ or $CeCu_6$.

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